

## *Original Investigations*

# Calculation of Transition Metal Compounds Using an Extension of the CNDO-Formalism

## II. Metal to Metal Bonding in Binuclear Transition Metal Compounds

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A recently developed extension of the CNDO-method is used to study the electronic structure of a number of binuclear transition metal carbonyls and carboxylates with fourfold or quasi-fourfold symmetry. The results are compared to those available from nonempirical calculations. Special attention is paid to the nature of the metal–metal bond. Connections with qualitative MO-considerations allow a fairly general discussion of metal–metal bonding in binuclear transition metal complexes with basic fourfold symmetry. A few, up to now unknown, but possibly existing, complexes are considered.

**Key words:** Transition metal compounds – Multiple metal–metal bonds – Extended CNDO

### 1. Introduction

Binuclear transition metal complexes with direct metal–metal bonding have been the pivot subject of a wide recent research. Extensive synthetic effort has lead to a great variety of  $d^n-d^n$ -complexes with metals from the third, fourth and fifth row of the periodic table and with  $n = 3, 4, 5, 7$  and  $9$ . All different types of M–M-linkages up to quadrupel bonds [1] have been proposed from detailed spectroscopic studies of these systems. Most of the information has been deduced from bond-length [2] and force-constant [3] considerations but also the investigation of electronic [4], photoelectron [5] and EPR [6] spectra has contributed much to the better understanding of multiple M–M-bonds in this type of complexes.

The theory of the electronic structure of binuclear transition metal complexes is, however, not as developed as e.g. for small and medium size organic molecules. The discussion of bonding capabilities is mostly based on qualitative MO-considerations and on the results of Extended-Hückel calculations [7]. Not till recently a number of more advanced theoretical studies dealing with the problem of multiple M–M-bonding have appeared. Most of them make use of the  $X_\alpha$ -SW-method [4a, 8] but a few nonempirical HF-LCAO-SCF-calculations [5a, b, 9, 10] are now available, too. These studies usually deal with the bonding in a special type of complex. Generalizations and, particularly, connections to qualitative MO-considerations – easily possible in the case of the simple EH-calculations – are difficult to extract from these calculations. Due to the structure of the method this is particularly true for the  $X_\alpha$ -results. The situation becomes even more complicated by discrepancies which appear between the results of different theoretical methods: EH-[7] and  $X_\alpha$ -[4a, 8] calculations, e.g. confirm Cotton's proposal [2] of a quadruple bond for the Cr–Cr-linkage in  $\text{Cr}_2(\text{O}_2\text{CH})_4$  whereas *ab-initio* LCAO-results do not predict such a bond at the HF-level [5a, b, 9, 10].

Advanced semiempirical LCAO-SCF-methods like CNDO or INDO, which in organic chemistry successfully fill the gap between elaborate, but system specific nonempirical methods, and crude but widely applicable qualitative MO-considerations have not been applied to the above mentioned problem so far. This seems at least partly to be due to some discouraging opinions on the applicability of these methods to transition metal complexes which can be found in the literature [11]. It is the main purpose of this paper to show that these opinions are misleading and that a well structured and properly parameterized extension of the basic CNDO-formalism – as proposed in Part I of this series [12] – is highly suitable to fill the above mentioned gap also in the case of transition metal complexes. To demonstrate this, we have studied a number of binuclear carbonyl and carboxylate complexes of third row transition elements. Most of the examples are either  $d^4$ – $d^4$  or  $d^7$ – $d^7$  systems, which preferably have been investigated experimentally and by the other theoretical methods. As we follow the above outlined strategy to use an advanced semiempirical method like CNDO as a link between nonempirical calculations (besides all the problems involved we refer to the  $X_\alpha$ -SW method as a “nonempirical” one in this context) and simple MO-considerations we compare our results on one side with available nonempirical studies and on the other, with qualitative MO-schemes. From the information obtained in this way we then deduce a few generalizations which allow to include higher transition elements and to discuss several unknown but possibly existing compounds.

In the course of such a comparison it turns out, that we have to distinguish between two main classes of compounds with respect to their basic symmetry: Class A, which is subject of this paper, consists of molecules with a fourfold axis (like e.g.  $\text{M}_2\text{Cl}_8$  or  $\text{M}_2(\text{CO})_{10}$ ) or of molecules for which the fourfold symmetry is not too much disturbed (like in  $\text{M}_2(\text{O}_2\text{CCH}_3)_2\text{L}_2$  with a nonlinear ligand L). For the latter we use the notation “systems with quasi fourfold symmetry”. Class B, for which some examples will be discussed in a forthcoming paper of this series,

consists of molecules of threefold (e.g.  $\text{Fe}_2(\text{NO})_6^{++}$  or  $\text{Fe}_2(\text{CO})_9$ ) or quasi threefold (e.g.  $\text{Co}_2(\text{CO})_8$ ) symmetry. The main heuristic difference between these two classes is, that most of the Class B compounds contain bridging ligands forming three-center-bonds whereas no such structures are known for molecules which belong to Class A.

## 2. Computational Section

In their fundamental paper on the CNDO-formalism Pople and co-workers [13] have introduced the condition that the results have to be invariant under an arbitrary unitary transformation within the basis functions centered at a given atom. This requirement leads to the well known restriction that the basic parameters depend only on the nature of the atom and not on the nature of the special atomic orbital. The resulting parametrization scheme is rather unflexible and does not allow transition metal elements to be handled properly, where the orbital electronegativity and especially its dependence on occupation is quite different for *s*-, *p*- and *d*-orbitals.

Such difficulties can be overcome if one remembers that for a semiempirical method in which parametrization is based on a well specified set of atomic functions (usually *s*, *p*, *d* . . .), hybridization invariance turns out to be an oversatisfaction of invariance conditions. A Slater-exponent decoupled basis set for example fulfils the remaining requirement of invariance against rotation of the local coordinate systems and allows to obtain a much more flexible parametrization. The first step in this direction was introduced by Baetzold [14] and Blyholder [15] in connection with application to problems from surface chemistry. However, these authors went only half the way. They use decoupled *d*-functions but retain a common set of *s*- and *p*-functions which is treated as in standard CNDO. In addition, there are some difficulties concerning the Hamiltonian which has been used by these authors. In Part I of this series [12] we therefore introduced an extended version of the CNDO formalism, by treating the *s*-, *p*-, *d*- and if necessary, *f*-functions separately. Up to now this method has been successfully applied to the study of bonding properties [12, 16] and intramolecular insertion reactions [17] of mononuclear transition metal complexes, to the description of surface cluster models [16], to the discussion of many body effects in PE-spectra [18], and to the theoretical investigation of electronic spectra and photo-chemical reactivity [19].

In spite of these very promising applications we have to point out that at present we have not completely dealt with all the possibilities inherent in the decoupled scheme. Up to now we have only parametrized the third row transition elements in the fully decoupled scheme. For the ligands we still use the standard CNDO/2 parametrization [20]. To compensate this inconsequence we only deal with ligands reasonably well described by standard CNDO especially with respect to the ordering and relative spacing of the one electron levels. We therefore, restrict our calculations at present mainly to carbonyl and carboxylate complexes, thereby

omitting the highly interesting  $M_2Cl_8$  compounds for which quadruple bonds have been claimed to exist [1].

The main consequence of the use of the standard CNDO parametrization for the ligands is the following: Since the spacing of the occupied orbitals of the free ligands is somewhat overestimated, a similar overestimation is found in the complexes for orbitals with predominant ligand character. Compared to PE-spectra, a good overall correlation is found between "experimental" and theoretical one particle energies but the slope is about 2 (compare Part I and Fig. 5). From comparison with *ab initio* results and from our own studies on many body effects [18] we know however, that a major portion of this too steep slope results from the neglect of relaxation.

The parameters for the transition metal atoms Cr to Ni are collected in Table 1. The same nomenclature is used as in Part I [12] where all the necessary formulas are given. The values for Co and Ni are slightly different from those published in Part I. As far as possible the geometries of the calculated systems have been taken from X-ray data. The corresponding references are given in the captions to the tables. For systems for which bond lengths are not known experimentally and for hypothetic structures, bond lengths have been estimated from closely related compounds. Test calculations showed, however, that the basic results are not changed if bond lengths and bond angles are varied within reasonable limits.

Besides of the most important part of the one particle spectra (orbital diagrams), we mainly report charge densities and bond orders. For the bond orders we follow Wiberg's definition [21].

$$K_{AB} = \sum_{\substack{\nu \in A \\ \mu \in B}} P_{\mu\nu}^2$$

However, to obtain better insight in the nature of a given bond the Wiberg index is split into  $\sigma$ -,  $\pi$ - and  $\delta$ -contributions.

$$K_{AB} = K_{AB}^{\sigma} + K_{AB}^{\pi} + K_{AB}^{\delta}$$

with

$$K_{AB}^{\lambda} = \sum_{\substack{\nu^{\lambda} \in A \\ \mu^{\lambda} \in B}} P_{\mu^{\lambda}\nu^{\lambda}}^2 \quad \lambda = \sigma, \pi, \delta.$$

In the above formula  $\nu^{\lambda}$  and  $\mu^{\lambda}$  denote those components of the atomic orbitals  $\mu$  and  $\nu$  which have local symmetry  $\lambda$  with respect to the AB-bond.

### 3. Qualitative MO-considerations

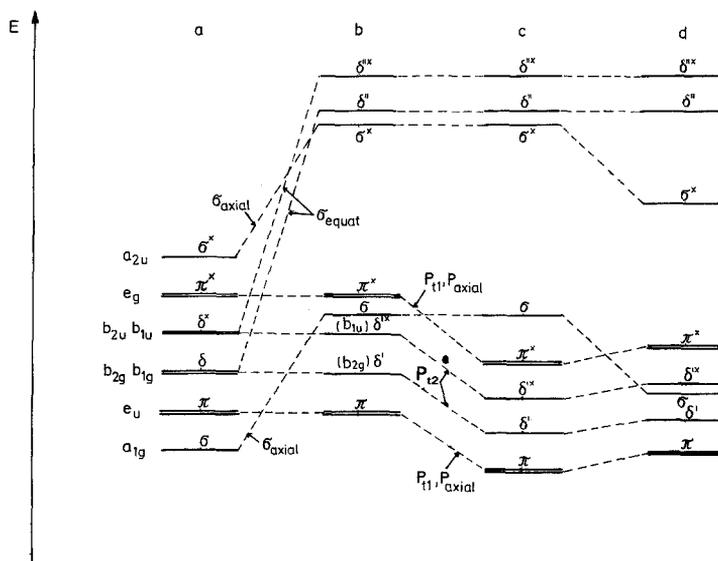
Before we start to discuss the results of our different calculations, it is useful to establish a qualitative MO-scheme, since such a scheme is very helpful to rationalize bonding capabilities in binuclear transition metal complexes.

**Table 1.** Parameter values for transition metal atoms Cr to Ni used in our extended version of the CNDO-method

	$\frac{1}{2}(I_{\mu} + A_{\mu})$ (eV)			$\beta$ (eV)			$\zeta_{\mu}$		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
Cr	3.909	0.876	4.822	-3.0	-3.0	-7.0	1.225	0.150	1.355
Mn	3.983	0.975	5.157	-4.0	-4.0	-8.0	1.325	0.388	1.499
Fe	4.120	1.062	5.504	-6.0	-6.0	-9.0	1.375	0.413	1.780
Co	4.170	1.160	5.839	-5.0	-5.0	-10.0	1.475	0.438	1.930
Ni	4.306	1.260	6.184	-5.0	-5.0	-10.0	1.530	0.400	2.180

If we only consider the *d*-orbitals of the binuclear metal cluster, we have to distinguish three types of overlap (*z* denotes the internuclear axis): A  $\sigma$ -type overlap between the  $d_{z^2}$ -orbitals, a  $\pi$ -type overlap between  $d_{xz}$  and  $d_{yz}$ , respectively, and a  $\delta$ -type overlap between  $d_{x^2-y^2}$  and  $d_{xy}$ , respectively. For experimentally verified distances the different overlaps decrease in the order  $\sigma > \pi > \delta$ . This leads to the orbital sequence shown in Fig. 1a. As the orbitals found in most of the complexes are either of predominant metal or of predominant ligand character it is convenient to use the same symbols as in Fig. 1a to denote those orbitals in a complex which contain large contributions from the metal *d*-orbitals.

We now introduce a ligand sphere of the  $D_{4h}$ -symmetry consisting of 8 (without axial) or 10 (with axial) ligands. For this qualitative consideration we further



**Fig. 1.** Qualitative MO-scheme for binuclear transition metal carbonyls of quasifourfold symmetry; **a** unsubstituted; **b** coupling of scheme (a) to  $\sigma$ -donor levels of CO; **c** coupling of scheme (b) to  $\pi$ -acceptor levels of CO; **d** scheme (c) without axial ligands

assume that the ligands themselves have axial symmetry and that the bonding capabilities of the ligands result from an occupied  $\sigma$ -orbital which acts as donor and an empty- $\pi$ -orbital which is suitable for backbonding. This assumption implies that the occupied orbitals of the ligands lie below and the unoccupied ones above the  $d$ -orbitals of the metal atom. The well known prototype of such a ligand is CO.

To study the interaction between the binuclear metal cluster and the ligand sphere, we first construct symmetry adapted linear combinations of the ligand orbitals. The group theoretical assignment for these combinations is given in the Appendix. In  $D_{4h}$ -symmetry the orbitals  $\delta$  and  $\delta^*$  of the metal cluster split into  $b_{2g}(\delta')$  and  $b_{1g}(\delta'')$  and into  $b_{1u}(\delta'^*)$  and  $b_{2u}(\delta''^*)$ , respectively, due to the fact that the lobes of the constituting atomic  $d$ -orbitals lie either in the direction of the axis  $x$  and  $y$  ( $d_{x^2-y^2}$ ) or in the direction of the angle bisector ( $d_{xy}$ ). The  $\sigma$ -donating ligand orbitals which transform like the radial  $p$ -orbitals  $p_{rad}$ , yield symmetry adapted combinations which belong to the irreducible representations  $a_{1g}$ ,  $a_{2u}$ ,  $b_{1g}$ ,  $e_g$  and  $e_u$ . To evaluate the symmetry of the accepting  $\pi$ -orbitals it is convenient for further discussion to distinguish between two different types of tangential atomic  $p$ -orbitals ( $p_{t1}$  and  $p_{t2}$ ) and the  $p$ -orbitals of the axial ligands ( $p_{ax}$ ). The resulting linear combinations belong to the representations  $a_{1g}$ ,  $a_{1u}$ ,  $a_{2g}$ ,  $b_{1g}$ ,  $b_{1u}$ ,  $b_{2g}$ ,  $b_{2u}$ ,  $e_g$  and  $e_u$ .

At a first glance the situation seems to be discouraging. All orbitals of the binuclear metal cluster which evolve from  $d$ -orbitals can interact with the accepting  $\pi$ -orbitals and all except  $b_{1u}$  and  $b_{2g}$  with the donating  $\sigma$ -orbitals of the ligand sphere. Even a qualitative treatment of such an interaction would depend on a detailed knowledge of the relative magnitude of  $\sigma$ - and  $\pi$ -type overlaps between ligands and metal atoms. As this overlap depends on the special nature of both constituents, very little systematization should be possible in such a case. The situation is, however, not as bad. For the evaluation of the metal-ligand interaction, we have not only to take into account the global symmetry of the interacting orbitals but also the local symmetry which determines the interaction between a given pair of atoms. If we include the constraints which are imposed by local symmetry, we find that in first order only the orbitals  $\sigma$ ,  $\delta''$ ,  $\delta''^*$  and  $\sigma^*$  interact with the  $\sigma$ -donor orbitals of the ligand system. The interaction of the  $\delta''$ -orbitals is restricted to the equatorial ligands. For the orbitals  $\sigma$  and  $\sigma^*$  no such restriction exists but the main interaction takes place with the axial ligands. Thus, as a whole, we have to assume that these orbitals are less destabilized by interaction with the ligand donor orbitals than the  $\delta''$  orbitals which can interact with 8 ligands. As the orbitals  $\pi$ ,  $\delta'$ ,  $\delta'^*$  and  $\pi^*$  do not interact with the  $\sigma$ -donating ligand orbitals, we obtain a level scheme as depicted in Fig. 1b. It should be mentioned that it is the strong destabilization of the  $\delta''$ -orbitals, which itself is a consequence of the  $C_4$ -axis, which discerns the Class A and Class B compounds mentioned in the introduction. Apart from the pronounced shift of the orbitals  $\sigma$  and  $\sigma^*$ , caused by the axial ligands, an orbital diagram similar to Fig. 1b, was recently shown by Christoph and Koh [22].

A second comment seems to be necessary at this point. From the above discussion, it becomes obvious that the  $\sigma$ -donating orbitals  $e_g$  and  $e_u$  of the ligand system cannot interact with  $d$ -orbitals of the binuclear metal cluster, due to local symmetry constrains. To obtain a bonding interaction with these ligand orbitals we have to take into account the empty  $p$ -orbitals of the transition metal atoms. These orbitals yield linear combinations of  $e_g$  and  $e_u$  symmetry (compare appendix), too, and these combinations can interact with the  $\sigma$ -donating ligand orbitals under local symmetry. As a consequence, it becomes very likely that any method which does not include the empty  $p$ -orbitals of the transition metal atoms is not adequate to describe the ligand-metal bonding properly.

We now take into account the empty ligand orbitals which by interaction stabilize the  $d$ -orbitals of the metal cluster. In spite of the fact that all molecular orbitals which result from the atomic  $d$ -orbitals of the binuclear cluster seem to be able to interact with the empty ligand orbitals under global symmetry, the inclusion of local symmetry constrains shows that only the orbitals  $\pi$  and  $\pi^*$  interact with the tangential  $p$ -orbitals  $p_{t1}$  and the axial  $p$ -orbitals  $p_{ax}$ . Correspondingly the  $\delta'$  orbitals only interact with the tangent  $p$ -orbitals  $p_{t2}$ . Thus only those  $d$ -orbitals which do not interact with the donor orbitals of the ligands interact with the acceptor orbitals and vice versa. From the possible number of interactions, we have to assume that the stabilization of  $\pi$  and  $\pi^*$  and of  $\delta'$  and  $\delta'^*$ , respectively, is comparable in a complex with equal ligands. The resulting level scheme is shown in Fig. 1c. For ligands with the assumed bonding capabilities, we have to expect four lower lying orbitals ( $\pi$ ,  $\delta'$ ,  $\delta'^*$  and  $\pi^*$ ) well separated from three higher lying ones ( $\sigma^*$ ,  $\delta''$ ,  $\delta''^*$ ). This result should be independent from the relative strengths of the  $\sigma$ -donor and  $\pi$ -acceptor abilities. The only question which cannot be answered from such a qualitative discussion is the location of the  $M$ - $M$ -bonding orbital  $\sigma$ . For strong  $\sigma$ -donating and strong  $\pi$ -accepting ligands, this orbital should be located between  $\pi$  and  $\sigma^*$ . For less strong  $\sigma$ -donors or less strong  $\pi$ -acceptors, however, it is probably embedded among the above mentioned four lower lying levels. Removal of the axial ligands should lead to a small destabilization of the orbitals  $\pi$  and  $\pi^*$  and to a strong stabilization of the orbitals  $\sigma$  and  $\sigma^*$ , as indicated in Fig. 1d.

## 4. Results and Discussion

### 4.1. Binuclear Carbonyl Complexes

$Mn_2(CO)_{10}$ , the first binuclear carbonyl complex [23] ever synthesized, can still be regarded as the prototype of a whole family of  $MM'(CO)_{10}$  complexes, where  $M$  and  $M'$  are elements of group VIIb. Today all possible compounds with  $M = M'$  and most of the combinations  $M \neq M'$  are known. All existing members of this family have  $D_{4d}$ -symmetry (ligands staggered). Similar to most other  $d^7$ - $d^7$ -dimers it is usually assumed that the metals are connected by a single bond.

As we have not parametrized transition elements higher than third row up to now, we concentrate on the prototype molecule  $Mn_2(CO)_{10}$ . The full eigenvalue



the reason for its high energy. The contributions from the  $\pi$ -orbitals of the equatorial ligands are non-bonding in this case.

If compared to the experimental photoelectron spectrum [24] the gap between  $\sigma$  and  $\pi^*$  is overestimated in our calculation. This may be partly due to shortcomings in our computational scheme, but partly it is also due to the differences in relaxation. Such effects have been found to be very important in the case of mononuclear carbonyl complexes (see Part VI [18] of this series for further discussion).

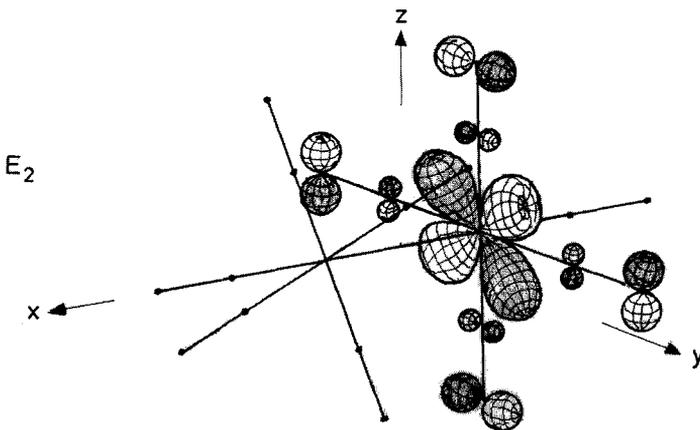
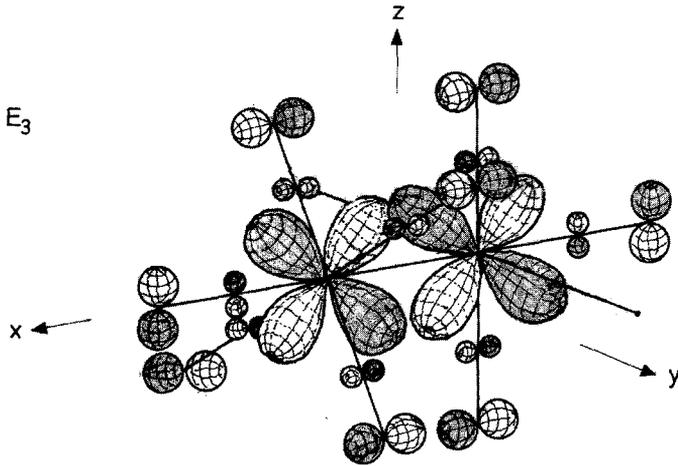
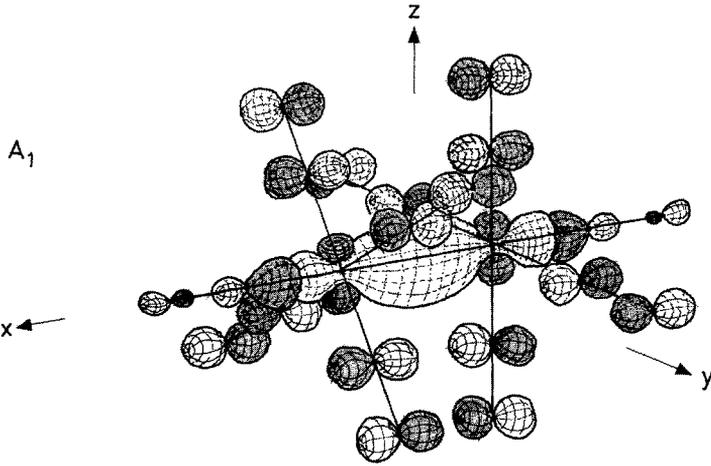
The lowest empty orbital which has larger metal  $d$ -character is a  $\sigma$ -antibonding orbital of  $a_2$  symmetry. The  $\delta''$ -orbitals are found at very high energies in full agreement with the qualitative scheme shown in Fig. 1. The two empty orbitals which appear between  $\sigma$  and  $\sigma^*$  are orbitals with large contributions from metal  $p$ -orbitals.

With respect to metal-metal-bonding we face the following situation: The  $\pi$ -interactions nearly cancel each other due to the occupation of  $\pi$  as well as  $\pi^*$ .  $\delta'$  is a non-bonding orbital. Thus the main contribution comes from the uppermost occupied orbital  $a_1$ , which is  $\sigma$ -bonding. As this result is exclusively based on the bonding or antibonding nature of the four uppermost occupied orbitals, it only leads to a formal bond order. It is, however, confirmed by the calculated Wiberg-indices (Table 3). The index for the Mn-Mn-bond is 0.32 which is rather small compared to the indices found for metal-carbon or carbon-oxygen bonds. If decomposed into  $\sigma$ - and  $\pi$ -contributions the  $\pi$ -index turns out to be only 6.6% of the  $\sigma$ -index. Thus in accordance with the experimental findings [23] the metal-metal-bond in  $\text{Mn}_2(\text{CO})_{10}$  is best described as a single  $\sigma$ -bond. A further confirmation of this result is achieved by localization of the occupied orbitals by the Foster-Boys criterion [25]. Within the subset of the occupied localized orbitals one finds only one orbital, which can be assigned to a metal-metal bond and this is of  $\sigma$ -type.

The Wiberg indices for the Mn-C-bonds are nearly the same for axial and equatorial ligands. If there is any difference at all, the equatorial ligands should have a slightly greater force constant than the axial ones. This also is in agreement with the available experimental data (compare Table 2). The charge distribution is as expected: The metal cluster is somewhat positive which has to be attributed to the  $\pi$ -acceptor qualities of the CO-ligands.

If we now look at the other member of the  $\text{M}(\text{VIIb})\text{M}'(\text{VIIb})(\text{CO})_{10}$  family, it seems unlikely that the overall picture is changed very much. Because of the well known similarity of transition elements which belong to the same group of the periodic table and due to the clear separation of occupied ligand, occupied metal and unoccupied levels we expect only changes in the actual position, but not in the order of the main groups of levels. We therefore assume the binding in all members of the  $\text{M}(\text{VIIb})\text{M}'(\text{VIIb})(\text{CO})_{10}$  family to be the same as in  $\text{Mn}_2(\text{CO})_{10}$ .

To extend the discussion of possible similarities in the binding scheme to the whole class of binuclear decacarbonyls it is of special interest to include charged



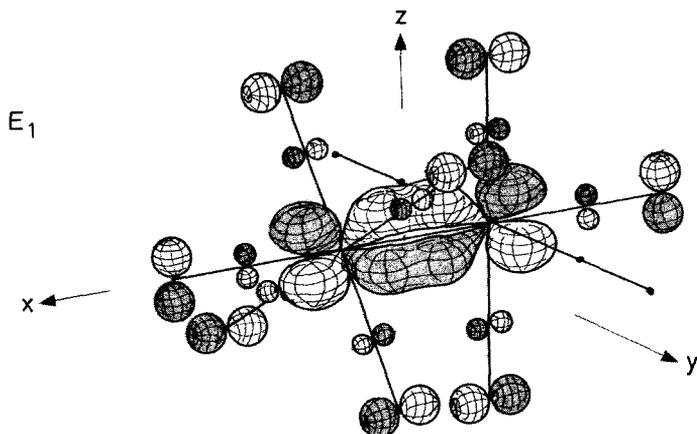


Fig. 3. Main atomic contributions to the four uppermost occupied orbitals in  $\text{Mn}_2(\text{CO})_{10}(\text{D}_{4d})$

Table 2. Orbital energies (in eV) for several neutral and charged binuclear transition metal carbonyls.

	$\text{Mn}_2(\text{CO})_{10}^{\text{a}}$	$\text{Cr}_2(\text{CO})_{10}^{2-\text{b}}$	$\text{Fe}_2(\text{CO})_{10}^{2+}$	$\text{FeCr}(\text{CO})_{10}(\text{C}_{2v})$
$a_1$	-6.66	-2.20	-16.10	-7.53 ( $a_1$ )
$e_3$	-11.08	-7.48	-21.66	-10.02 ( $e$ )
$e_2$	-11.92	-8.84	-22.03	-10.52 ( $b_1$ )
				-12.51 ( $b_2$ )
$e_1$	-12.74	-9.33	-22.57	-12.76 ( $e$ )

<sup>a</sup> Geometry from Ref. [23]

<sup>b</sup> Geometry from Ref. [26b]

Table 3. Calculated Wiberg-indices and charge densities for several transition metal carbonyls.

	$\text{Mn}_2(\text{CO})_{10}$	$\text{Cr}_2(\text{CO})_{10}^{2-}$	$\text{Fe}_2(\text{CO})_{10}^{2+}$	$\text{FeCr}(\text{CO})_{10}$	$\text{Co}_2(\text{CO})_8$
$K_{\text{M-M}}$	0.32	0.39	0.36	0.17	0.28
$K_{\text{M-Cax}}$	0.78	0.95	0.59	0.48 1.07	0.74
$K_{\text{M-Ceq}}$	0.80	0.92	0.66	0.75 0.80	0.73
$K_{\text{C-Oax}}$	2.17(16.31 <sup>a</sup> )	2.09	2.38	2.27 2.10	2.23
$K_{\text{C-Oeq}}$	2.20(16.50 <sup>a</sup> )	2.11	2.37	2.28 2.18	2.22
$q_{\text{M}}$	6.66	6.71	7.46	7.59 5.76	8.86
$q_{\text{Cax}}$	3.87	3.81	3.86	3.95 3.82	3.88
$q_{\text{Ceq}}$	3.92	3.88	3.91	3.92 3.89	3.90
$q_{\text{Oax}}$	6.18	6.23	6.01	6.14 6.24	6.13
$q_{\text{Oeq}}$	6.16	6.17	6.01	6.12 6.20	6.13

<sup>a</sup> Bor, G.: Chem. Comm. 641 (1969)

systems like e.g.  $\text{Cr}_2(\text{CO})_{10}^{2-}$ . Due to its charge this is also a  $d^7-d^7$ -dimer. The question is, however, whether the same qualitative argument can be applied as in the case of neutral  $\text{MM}'(\text{CO})_{10}$ -compounds or whether the charge changes the level scheme in a more fundamental way.

To answer this question we have calculated  $\text{Cr}_2(\text{CO})_{10}^{2-}$  and the – up to now – unknown dication  $\text{Fe}_2(\text{CO})_{10}^{2+}$ . The results are collected in Tables 2 and 3.

The orbital sequence is found to be the same as in  $\text{Mn}_2(\text{CO})_{10}$  for both systems. In each case the orbitals with large metal  $d$ -character have lower binding energies than the orbitals with dominant ligand character. The highest occupied  $\sigma$ -level ( $a_1$ ) is also well separated from the three lower lying  $e$ -levels in both cases. The main difference is a shift of all orbitals to higher binding energies for the positive and to lower binding energies for the negative charged complex. The calculated orbital energies of the charged species are not directly comparable to experimental ionization potentials since these measurements can only be made in solid state, where one has to take into account the influence of the counter ions.

The Wiberg indices for the dianion (Table 3) are similar to those of the neutral system. If there is any effect at all, we would expect a somewhat stronger metal–ligand bond and some weakening in the CO-linkage. As far as experimental data are available, the IR-shifts of the carbonyl band are in accordance with this result [26]. For the dication the differences are somewhat greater: The metal–carbon index is reduced if compared to the neutral system and the carbon–oxygen index has nearly the same value as in free CO. These results may be taken as a hint that  $\text{Fe}_2(\text{CO})_{10}^{2+}$  is not very stable against dissociation into metal and carbon monoxide and that this is the reason why it has not been synthesized until now. The charge is more or less equally distributed to the metal cluster and to the ligand sphere in both complexes. Within the ligands the charge is mainly added to or subtracted from the oxygen atoms.

If the results of the last two calculations can be extended to higher transition elements, it is very likely that other dianions of the type  $\text{M}(\text{VIb})\text{M}'(\text{VIb})(\text{CO})_{10}^{2-}$  can be obtained. As in the case of the neutral decacarbonyls of VIIb-elements, it should be possible to prepare not only systems with  $\text{M} = \text{M}'$  but also mixed systems with  $\text{M} \neq \text{M}'$ . The existence of dications with general structure  $\text{MM}'(\text{CO})_{10}^{2+}$  ( $\text{M}, \text{M}' \in \{\text{Fe}, \text{Ru}, \text{Os}\}$ ) is somewhat more doubtful if the results obtained for  $\text{Fe}_2(\text{CO})_{10}^{2+}$  can be used as a guideline. However, if they can be prepared, all these ions should exhibit a closed shell ground state and a single metal–metal bond.

The above given generalization leads to the closely connected question, to what extent the underlying ideas can be transferred to unsymmetric binuclear metal clusters. To study this problem we calculated the hypothetic molecule  $\text{FeCr}(\text{CO})_{10}$ . The bond lengths had to be estimated from related compounds, but, as mentioned earlier, the important results are not very sensitive against small variations in the internuclear distances. The results for  $\text{FeCr}(\text{CO})_{10}$  are also given in Tables 2 and 3. The orbital energies of the highest occupied orbitals are similar to those of  $\text{Mn}_2(\text{CO})_{10}$ . Only the distance between  $\pi^*$  and  $\sigma$  is somewhat reduced

and  $\delta'$  is again split to  $\delta'$  and  $\delta'^*$  due to the reduced symmetry. As the order of the levels is retained, one might suggest the same bonding capabilities as in  $\text{Mn}_2(\text{CO})_{10}$ . If we study the Wiberg indices given in Table 3, we clearly notice, however, that this is not true. The index for the M–M-bond has dropped to 0.16, indicating very weak M–M-bonding. Contrary to the nearly equal M–C-indices for the equatorial ligands the corresponding indices for the axial ligands are quite different. The low Fe–C- and the high Cr–C-value fit well into the trend observed for the other compounds shown in Table 3. Correspondingly the C–O-indices are higher and more similar to free CO on the iron than on the chromium side.

From the results obtained for  $\text{FeCr}(\text{CO})_{10}$  it seems to be very unlikely that compounds of the general formula  $\text{M}(\text{VIb})\text{M}'(\text{CO})_{10}$  ( $\text{M}' \in \{\text{Fe}, \text{Ru}, \text{Os}\}$ ) are stable enough to be prepared. If our calculations predict the correct qualitative trends, the M–M' as well as the M'–C<sub>ax</sub>-bond is weakened to such an extent that these bonds are probably not stable against dissociation. The chances may be somewhat better for the less unsymmetric systems  $\text{M}(\text{VIIb})\text{M}'(\text{CO})_{10}^+$  ( $\text{M}' \in \{\text{Fe}, \text{Ru}, \text{Os}\}$ ) and if the trends seen in Table 3 hold for these compounds, too, even more for the corresponding anions  $\text{M}(\text{VIb})\text{M}(\text{VIIb})(\text{CO})_{10}^-$ . However, if any of these systems really exist they should follow the bonding scheme of  $\text{Mn}_2(\text{CO})_{10}$  with a closed shell ground state and a single metal–metal bond.

We now turn to another example, namely  $\text{Co}_2(\text{CO})_8$ . The stable form of this  $d^9$ – $d^9$ -system is a Class B compound with bridging ligands and quasi threefold symmetry. However, according to Noack et al. [27] there exists also an isomeric form without bridging ligands. A  $\text{C}_{2v}$ -structure with eclipsed equatorial ligands and two adjacent lone-pair orbitals has been deduced from the IR-spectrum. The Co–Co-bond was claimed to be single. To our knowledge this isomeric form of  $\text{Co}_2(\text{CO})_8$  is the only known neutral binuclear carbonyl complex without bridging ligands besides  $\text{Mn}_2(\text{CO})_{10}$  and its analogs.

To study whether such a system, with only three equatorial ligands present at each metal atom, can still be treated as a Class A compound with quasi fourfold symmetry or not, we performed calculations not only for  $\text{Co}_2(\text{CO})_8$  itself but also for two configurations of a hypothetical molecule  $\text{Mn}_2(\text{CO})_8$ . In one of these two configurations we have removed the two axial and in the other two adjacent equatorial ligands from the  $\text{D}_{4h}$ -structure of  $\text{Mn}_2(\text{CO})_{10}$ . The relevant parts of the eigenvalue spectra are included in Fig. 2.

If the two axial ligands are removed from  $\text{Mn}_2(\text{CO})_{10}$  the remaining system still has  $\text{D}_{4h}$ -symmetry. As the strong metal–ligand antibonding interaction of the axial ligands which destabilizes the metal–metal bonding orbital  $\sigma$  is no longer present, the  $\sigma$ -level comes down in energy and is embedded into the lower lying group of orbitals which originate from the metal atom  $d$ -orbitals.  $\sigma^*$  is stabilized in a similar manner but the  $\delta''$ -orbitals remain at very high energies.

If two adjacent equatorial ligands are removed instead of the axial ones, the fourfold symmetry is disturbed. Within the occupied orbitals the situation is, however, much the same as in  $\text{Mn}_2(\text{CO})_{10}$ . The orbitals  $\pi$  and  $\pi^*$  are no longer

degenerate but the splitting is comparatively small. Due to the presence of axial ligands the orbital  $\sigma$  is still well separated from the lower lying group. Greater changes are observed within the unoccupied levels. The reduced symmetry leads to a somewhat larger mixing of metal  $s$ -,  $p$ - and  $d$ -orbitals in this energy range, but we still find three orbitals, which due to their atomic contributions can be assigned  $\sigma^*$ ,  $\delta''$  and  $\delta''^*$ . The removal of two equatorial ligands strongly stabilized the  $\delta''$ -orbitals so that they are located below  $\sigma^*$ .

We now compare these results to the one obtained for the  $d^9-d^9$ -system  $\text{Co}_2(\text{CO})_8$ . As no X-ray data are available for the less stable isomer, we took the necessary data from the stable isomer [28]. For the metal ligand distance we used the value of the terminal ligands.

Compared to  $\text{Mn}_2(\text{CO})_8$  the four additional electrons occupy the levels  $\delta''$  and  $\delta''^*$  as one would have expected from a  $d$ -only scheme. The orbitals originating from the  $p$ -orbitals of the metal atoms remain unoccupied. The other occupied orbitals with high metal  $d$ -character are similar to those of the corresponding form of  $\text{Mn}_2(\text{CO})_8$ . They are somewhat stabilized due to the increase in atomic number but the spacing between them is not changed very much.

As far as metal to metal bonding is concerned, the situation has to be described again by single  $\sigma$ -bond. The four new electrons occupy one bonding and one antibonding orbital, thus we do not have to expect a large net effect. This is confirmed by the Wiberg indices (Table 3): The index for the metal-metal bond (0.28) is even smaller than in  $\text{Mn}_2(\text{CO})_{10}$  but to some extent this may be due to the overestimated bond distance, which we have taken from the isomer with bridging ligands. Decomposition into  $\sigma$ ,  $\pi$  and  $\delta$  contributions yields 96%  $\sigma$ -character. The other indices compare quite well with those found for  $\text{Mn}_2(\text{CO})_{10}$ .

The above results clearly show that the concept of quasi fourfold symmetry is still applicable if one equatorial ligand is missing at each metal atom or if it is replaced by a lone pair. This opens the opportunity to discuss the basic facts of bonding in such compounds by using an MO-diagram deduced for a system of higher symmetry.

For comparison we have also calculated the stable isomer of  $\text{Co}_2(\text{CO})_8$  although this is a Class B compound. In this case the geometric data are known from an X-ray analysis [28]. Again: the nine uppermost occupied orbitals contain large contributions from the metal  $d$ -orbitals. Due to the different basic symmetry, however, the bonding capabilities of these orbitals are not directly related to those of the less stable isomer. We therefore compare only the Wiberg indices. The index for the metal-metal bond is 0.35. In comparison to the other molecules which we have discussed up to now, this corresponds to a direct metal-metal interaction also in the bridged system. This confirms Braterman's [29] qualitative interpretation of the bonding situation in the stable form of  $\text{Co}_2(\text{CO})_8$ . The ligand metal indices are somewhat reduced if compared to the isomer without bridging ligands but the most dramatic effect is the strong decrease of the CO index of the bridging ligands. Such a reduction is also found for other cluster compounds with

bridging ligands like  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$ . This is in full accordance with the experimental results obtained from IR-spectroscopy where the observation of CO stretching vibrations with unusually low frequencies has been established as an indicator for bridging CO-ligands [26]. The same trend is found for surface cluster models where it also seems to be in accordance with IR-spectroscopic measurements [16, 30].

#### 4.2. Binuclear Carboxylate Complexes

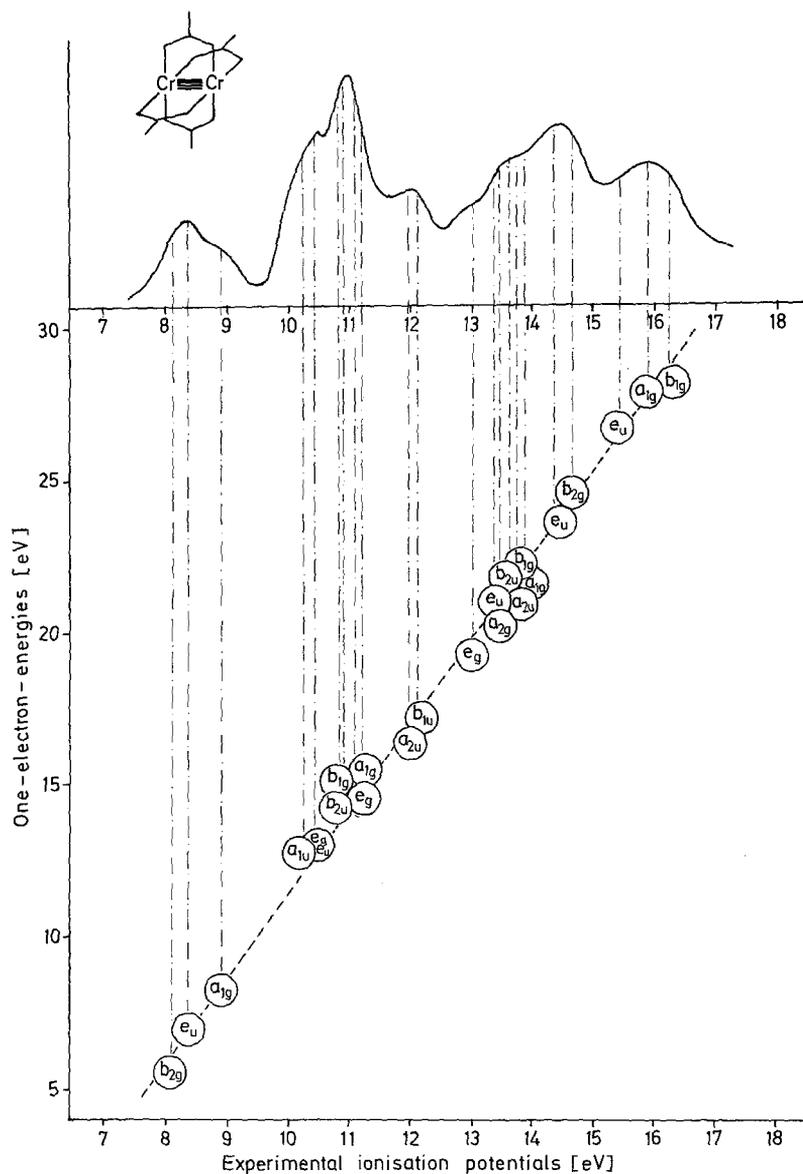
As mentioned in the introduction,  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$  is one of the first molecules where bond length considerations lead to the proposal of a quadruple bond [2]. Other examples are  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  or the corresponding  $\text{M}_2(\text{Cl})_8$  complexes. The unusual quadruple bond in these  $d^4-d^4$ -systems has caused a lot of theoretical effort to explain the bonding capabilities of the above mentioned systems. The theoretical analysis is, however, complicated by the fact that the axial positions are often occupied by other ligands (e.g.  $\text{H}_2\text{O}$ ) and that these ligands have pronounced influence on the metal-metal bond (compare Table 4): Usually the M-M-bond is shortened if the M-ligand distance becomes longer. This influence led Cotton to suggest in a recent review [2] that the presence and the nature of axial ligands partly determine the nature of the M-M-bond in complexes of this type.

As stated earlier nonempirical LCAO-SCF- as well as  $X_\alpha$ -SW-calculations have been performed for  $\text{Cr}_2(\text{O}_2\text{CH})_4$  [5, 8, 9, 10],  $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$  [5, 9, 10] and  $\text{Mo}_2(\text{O}_2\text{CH})_4$  [9, 10]. Whereas in the case of the molybdenum compound a quadruple bond is found in all calculations, the results of LCAO- and  $X_\alpha$ -SW-treatments are contradictory for the chromium complexes. However, before we compare the results of our own calculations to those of the nonempirical ones, we have to reconsider the qualitative MO-scheme shown in Fig. 1. This is due to the fact the carboxylates are ligands which do not possess  $\pi$ -acceptor abilities like CO. A carboxylate ligand is best described as a ligand consisting of one  $\sigma$ -donor orbital at each oxygen atom and a  $\pi$ -system with two occupied and one empty orbitals. Due to the lack of local symmetry the interaction of the  $\sigma$ -donor orbitals of the ligand system with the empty  $d$ -orbitals of the metal cluster are not as easy to estimate as in the case of the CO ligands. The donor orbitals can interact with the cluster orbitals  $\sigma$ ,  $\pi$ ,  $\delta''$ ,  $\delta''^*$ ,  $\pi^*$  and  $\sigma^*$  (compare Fig. 4) resulting in a destabilization of these levels. As in the case of  $\text{Mn}_2(\text{CO})_{10}$  this destabilization is expected to be most pronounced for the levels  $\delta''$  and  $\delta''^*$ . As long as no axial

**Table 4.** Examples of chromium-chromium and chromium-water distances in different chromium complexes (from Ref. [31])

Compound $\text{Cr}_2(\text{CRO}_2)_4(\text{H}_2\text{O})_2$	R	$d_{\text{Cr-Cr}}$	$d_{\text{Cr-OH}_2}$
$[\text{Cr}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]^{4-}$	$\text{O}^-$	2.22	2.317
$\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$	$\text{CH}_3$	2.362	2.272
$\text{Cr}_3(\text{O}_2\text{CH})_6(\text{H}_2\text{O})$	H	2.415	2.224





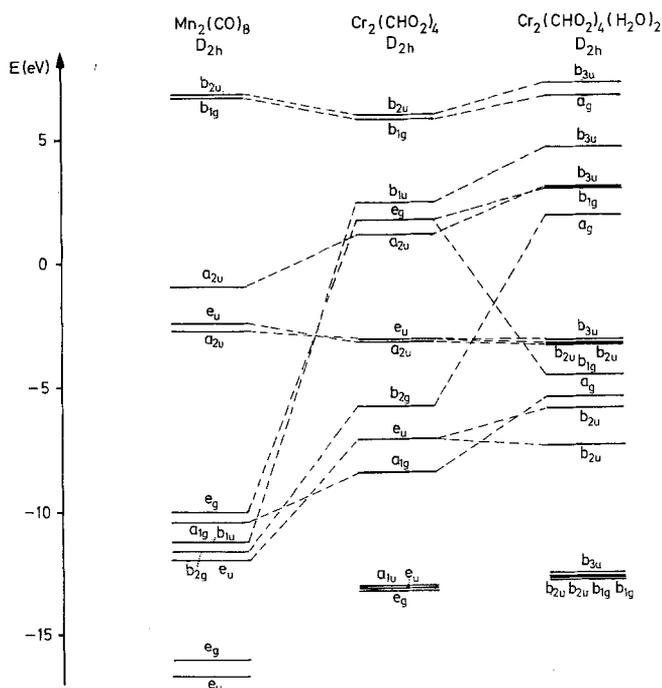
**Fig. 5.** Correlation of the experimental photoelectron spectrum of  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$  with calculated orbital energies

In Fig. 5 the orbital energies obtained from our CNDO-calculation on  $\text{Cr}_2(\text{O}_2\text{CH})_4$  are compared to the experimental photoelectron spectrum of  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$  [5a]. It is assumed that no axial ligands are present in the gasphase. An excellent linear relation is found between theoretical and experimental results. The slope of the correlation line is close to 2.0. As mentioned in the computational section, a similar value was found for mono-nuclear carbonyl

complexes and for  $\text{Mn}_2(\text{CO})_{10}$ . It should be mentioned that some additional density has to be expected around 25 eV in the theoretical spectrum if the calculation would have been performed for the acetate instead of the formate complex due to the larger number of CH-bonds.

The important portions of the level diagrams of  $\text{Cr}_2(\text{O}_2\text{CH})_4$  and  $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$  are reproduced in Fig. 6. For comparison we also included the corresponding part of the eigenvalue spectrum of the  $D_{4h}$  form of  $\text{Mn}_2(\text{CO})_8$ .

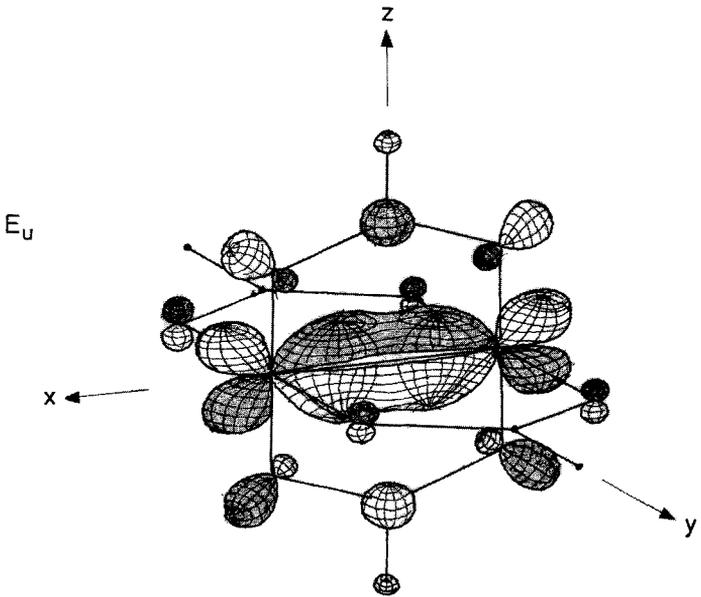
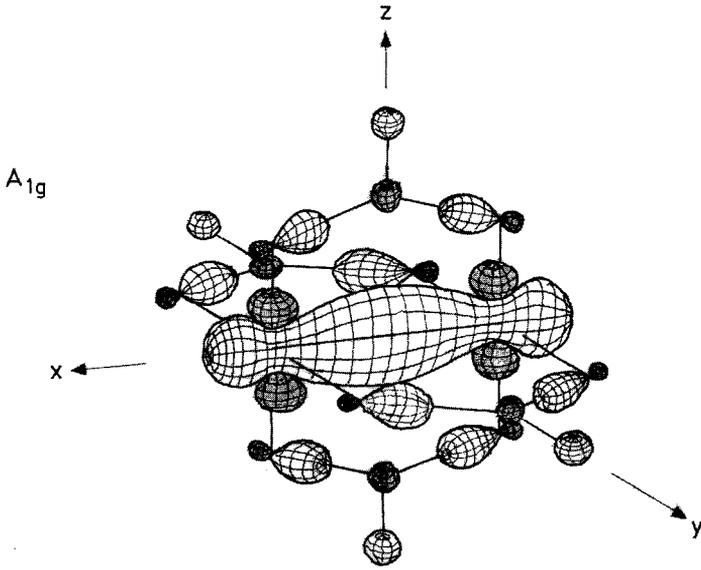
For  $\text{Cr}_2(\text{O}_2\text{CH})_4$  the three occupied orbitals with large metal  $d$ -contributions ( $\sigma$ ,  $\pi$ ,  $\delta'$ ) are well separated from the occupied orbitals with predominant ligand character.  $\sigma$  is found below  $\pi$  and  $\delta'$ , thus confirming the above discussed qualitative scheme. The important atomic contributions to the orbitals  $\sigma$ ,  $\pi$  and  $\delta'$  are shown in Fig. 7. The unoccupied orbitals with strong metal  $d$ -character are found in the order  $\sigma^* < \pi^* < \delta'^*$  and at much higher energies  $\delta''^*$  and  $\delta''$ . This is not in full accordance with the qualitative scheme of Fig. 4c but the detailed order of the levels  $\sigma^*$ ,  $\pi^*$  and  $\delta'^*$  depends on the relative magnitude of the different types of interactions with the donor orbitals of the ligand system and these are hard to estimate from qualitative considerations. Similar to the carbonyl compounds the lowest unoccupied orbitals mainly evolve from  $s$ - and  $p$ -functions of the metal atoms.



**Fig. 6.** Orbital diagram as calculated by CNDO. The geometries of the chromium complexes have been taken from the X-ray structure of the hydrated complex [31c]. For comparison  $\text{Mn}_2(\text{CO})_8(D_{4h})$  is included (see Fig. 2)

As the orbitals  $\sigma$ ,  $\pi$  and  $\delta'$  are all M–M-bonding the level scheme resulting from our calculation is in agreement with the assumption of a quadruple bond. This is further confirmed by an extremely large Wiberg index for the Cr–Cr-bond (Table 5). The index is about 8 times larger than the corresponding value found for  $\text{Mn}_2(\text{CO})_{10}$ . If the index is split into  $\sigma$ ,  $\pi$  and  $\delta$  contributions, the  $\sigma$ -part is found to be about twice as large as in the manganese compound. This underlines how weak the metal–metal interaction in  $\text{Mn}_2(\text{CO})_{10}$  really is. The Wiberg indices further indicate that the carbon oxygen bonds of the formiate ligand are weakened only little by complexation. The formal electron counting rule is correct in predicting the number of electrons ( $12 - 4 = 8$ ) which occupy the orbitals mainly responsible for M–M-bonding. This does, however, not imply that the metal charge is necessarily +2. To some extent the  $d$ -orbitals of the metal atoms also participate in orbitals which are mainly concentrated at the ligands. Instead of a formal charge +2 the calculated net charge (Table 6) is close to +1. Most of the charge comes from the oxygen atoms of the formiate ligands which are found to be less negative ( $-0.480$ ) as in the free ion ( $-0.579$ ). This is in accordance with the strong  $\sigma$ - and weak  $\pi$ -donating character of the formiate ion.

The sequence  $\sigma < \pi < \delta'$  for the highest occupied orbitals was first obtained from  $X_\alpha$ -calculations [8]. The close resemblance between the results of our CNDO-calculations and those of the  $X_\alpha$ -treatment is, however, not restricted to the three uppermost levels: Also the lower lying ligand type orbitals compare quite well in sequence and in the energies of the main blocks of one electron levels. On the contrary, an *ab initio* LCAO-SCF-HF calculation reported by Benard and Veillard [9, 10] leads to the sequence  $\sigma < \delta < \delta^* < \sigma^*$  for the occupied orbitals with predominant metal  $d$ -character. The same result was obtained by Garner et al. [5a] for the hydrated complex which we will discuss below. With eight electrons occupying the levels  $\sigma$ ,  $\delta$ ,  $\delta^*$  and  $\sigma^*$  the bonding and antibonding metal–metal interactions roughly cancel and no net bonding between the metal atoms is therefore predicted from these calculations. If, however the HF-treatment is followed by a limited CI-calculation, a quadruple bond is found [9, 10] in accordance with the  $X_\alpha$ -result. This has led to the idea that the existence of a quadruple bond in dichromiumtetracarboxylate complexes is mainly due to correlation effects and that the correct result of the  $X_\alpha$ -calculation is gained by partially incorporating these effects in this method. The same may be true for our semiempirical LCAO-scheme, which predicts a quadruple bond even at the HF-level. We do, however, not believe that this is the real reason: From the qualitative MO-scheme (Fig. 4) it is very difficult to understand what type of interaction could lead to a sequence  $\sigma < \delta < \delta^* < \sigma^*$ . Such a sequence can only be obtained if a strong and very specific interaction with the donor orbitals of the ligand system destabilizes the level  $\pi$  in such a way that it lies above  $\sigma^*$ . The sequence  $\sigma < \delta < \delta^* < \sigma^*$  is even more difficult to understand if one takes into account that the same authors find a sequence  $\sigma < \pi < \delta'$  for the corresponding binuclear molybdenum complex [31] in accordance with  $X_\alpha$ -results [8]. One would not expect the differences between Cr and Mo to be so strong that they lead to a completely different level diagram.



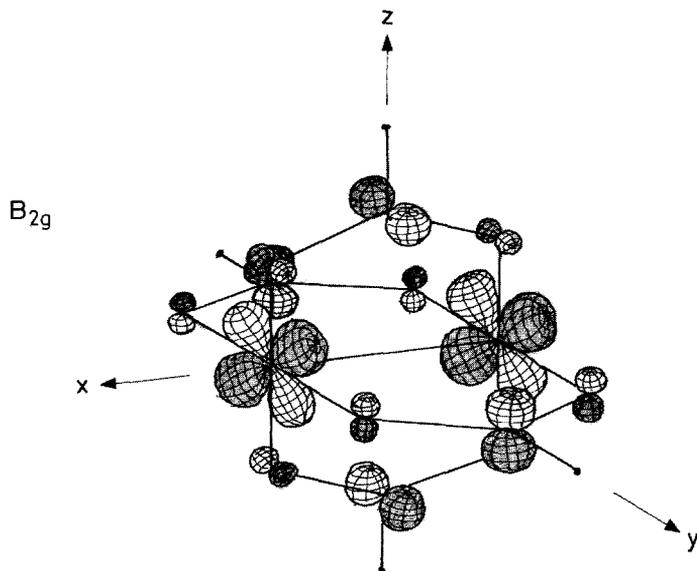


Fig. 7. Main atomic contributions to the three uppermost occupied orbitals in  $\text{Cr}_2(\text{CHO}_2)_4$

We now turn to the water coordinated complex. Due to the X-ray data [31a] the two water molecules lie in a common plane which is diagonal to the planes of the ligands. This reduces the symmetry from  $D_{4h}$  to  $D_{2h}$ . As a consequence the orbitals  $\pi$  and  $\pi^*$  are no longer degenerate.

As expected from the results obtained for the carbonyl complexes the orbital  $\sigma$  is strongly destabilized by the occupation of the axial positions. It now lies above the two levels which originate from the orbital  $\pi$  of the non-hydrated complex (Compare Fig. 6). What, however, is not expected, is an interchange of  $\delta'$  with one of the components originating from  $\pi^*$ . This interchange is caused by a strong

**Table 5.** Wiberg indices for the pure and for the water coordinated dichromiumtetraformate complex. The geometry was adopted from the X-ray analysis of  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$  [31c]

	$\text{Cr}_2(\text{O}_2\text{CH})_4$	$\text{Cr}_2(\text{O}_2\text{CH})(\text{H}_2\text{O})_2$	$[\text{O}_2\text{C}_\text{H}]^-$	$\text{H}_2\text{O}$
$k_{\text{Cr-Cr}}$				
$\sigma$	0.78	0.77		
$\pi$	1.76	0.88		
$\delta$	0.56	0.00		
tot	3.10	1.65		
$k_{\text{Cr-OFor}}$	0.43	0.42		
$k_{\text{Cr-OH}_2\text{O}}$		0.05		
$k_{\text{C-O}}$	1.45	1.43	1.52	
$k_{\text{C-H}}$	0.93	0.93	0.87	
$k_{\text{O-H}}$		0.86		0.96

**Table 6.** Population analysis for  $\text{Cr}_2(\text{O}_2\text{CH})_4$  and  $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$  as obtained from our CNDO-calculations

		$\text{Cr}_2(\text{O}_2\text{CH})_4$	$\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$
Cr	4s	0.4230	0.4264
	4p	0.0005	0.0006
	3d( $\sigma$ )	1.4303	1.4180
	3d( $\pi$ )	2.0920	3.0274
	3d( $\delta$ )	1.1255	0.3078
	Density	5.714	5.1803
$\text{O}_{\text{For}}$	2s	1.6505	1.6570
	2p	4.7297	4.7348
	Density	6.3802	6.3918
$\text{C}_{\text{For}}$	2s	1.0531	1.0699
	2p	2.5935	2.5107
	Density	3.6466	3.5806
$\text{H}_{\text{For}}$	1s	1.0572	1.0681
$\text{O}_{\text{H}_2\text{O}}$	2s		1.4906
	2p		4.8689
	Density		6.3585
$\text{H}_{\text{H}_2\text{O}}$	1s		0.7984

interaction with the  $p_\pi$ -orbital of the oxygen atoms of the water molecules, resulting in a pronounced metal–ligand  $\pi$ -bonding character of the now occupied  $b_{2g}$ -level. It is, however, doubtful whether this  $\pi$ -type interaction is overestimated in our calculation or not. The use of equal Slater exponents for O2s and O2p might well favour the  $\pi$ - with respect to the  $\sigma$ -interaction. In any case, from this we learn that in spite of weak bonding indicated by the very small Wilberg-index (Table 5), we have to be very cautious to treat axial ligands e.g.  $\text{H}_2\text{O}$  as small perturbations.

As the newly occupied  $b_{2g}$ -level has a node between the two metal atoms, we now have three M–M-bonding and one M–M-antibonding orbitals which hold the eight electrons of the  $\text{Cr}_2^{4+}$ -cluster. This leads to a formal double bond. Correspondingly, we find a Wiberg-index (Table 5) for the Cr–Cr-bond of 1.65, a value just about one half of the one obtained for the complex without axial ligands. In accordance with the above given orbital description the  $\delta$ -contribution has vanished and the  $\pi$ -part is reduced by a factor of about two. Contrary to bond orders the charge distributions of the water coordinated and the pure complex (Tables 6 and 7) are quite similar. Even the chromium atoms gain only little electron density by  $\sigma$ - and/or  $\pi$ -donation from the water molecules.

In spite of the pronounced influence of water molecules as axial ligands, we do not obtain a sequence  $\sigma < \delta < \delta^* < \sigma^*$  as found by Garner et al. [5a] in their *ab initio* calculation. From the qualitative information gathered in the course of this investigation such a sequence is even less understandable for  $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$  than it is for the complex with missing axial ligands. Occupation of the axial

**Table 7.** Separation of the charge density at the ligand atoms into  $\sigma$ - and  $\pi$ -contributions

	O			C			H
	$\sigma$	$\pi$	total	$\sigma$	$\pi$	total	$\sigma$
$\text{Cr}_2(\text{O}_2\text{CH})_4$	4.8138	1.5664	6.3802	2.8436	0.8030	3.6466	1.0572
$\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$	4.8051	1.5867	6.3918	2.9073	0.6733	3.5806	1.0681
	4.7527	1.6058	6.3585				0.7984
$\text{O}_2\text{CH}^-$	4.9547	1.6246	6.5793	2.8779	0.7508	3.6287	1.2132
$\text{H}_2\text{O}$	4.2881	2.0000	6.2881				0.8559

positions certainly destabilizes the levels  $\sigma$  and  $\sigma^*$ . It is therefore very unlikely that the level  $\pi$ , or else, its components in the reduced symmetry, remain unoccupied.

Since our results are neither in accordance with the *ab initio* LCAO-HF (predicting no bond) nor with the  $X_\alpha$ -calculation (predicting a quadruple bond) and since we have learned from the example  $\text{Cr}_2(\text{O}_2\text{CH})_4$  how sensitive results can be against correlation effects, we have recalculated both systems at the CI-level. The scheme, used for these calculations has been reported elsewhere [32]. Contrary to Bernard and Veillard [9, 10], who took into account only closed shell determinants up to octaexcited ones, we have included up to 4800 single and double excited open and closed shell singlet and triplet spin adapted configurations.

For  $\text{Cr}_2(\text{O}_2\text{H})_4$  the SCF-result is found to be stable. The CI ground state consists mainly of the SCF ground state determinant with 11.8% double excited configurations mixed in. The first excited state is described by a nearly pure single excited determinant corresponding to a  $\delta' \rightarrow \delta'^*$  excitation. Accordingly, the Wiberg-index of the Cr–Cr-bond is reduced by 0.9 but all other indices and most of the charge densities remain unchanged. The electron density on the chromium atoms rises only little from 5.07 to 5.18.

In the case of  $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$  the correlated ground state is no longer identical to the SCF ground state with the occupation  $\pi^2\pi^2\sigma^2\pi^{*2}$ . The new ground state is dominated (83%) by a double excited configuration  $\pi^{*0}\delta'^2$  (1Ag). This means that we now find a quadruple bond even in the case of the water coordinated complex. This is in accordance with the  $X_\alpha$ -results [8]. The lowest excited singlet state  $1B_{2g}$  is mainly (94%) described by the single excited determinant  $\pi^{*1}\delta'^1$ . While no major changes occur in the charge distribution and in the other Wiberg-indices the index for the Cr–Cr bond is raised to 1.80 in the  $1B_{2g}$ - and to 2.85 in the  $1A_g$ -state. The latter value is still smaller than the value 3.1 found for the ground state of  $\text{Cr}_2(\text{O}_2\text{CH})_4$  without axial ligands. This fits perfectly to the trend of the experimental data shown in Table 4. In spite of the fact that both, the water coordinated and the pure complex are now formally described by a quadruple bond, occupation of the axial positions leads to some weakening of the M–M-bond. The influence of the  $p_\pi$ -orbitals of the water molecules further shows that this weakening cannot only be related to differences in the  $\sigma$ -donor strength.

The  $\sigma$ -interaction merely influences the level  $\sigma$  which is occupied in any case. The  $\pi$ -interaction, however, determines the actual position of the M–M-bonding level  $\delta'$  and the M–M-antibonding level  $\pi^*$ .

As our calculations on the water coordinated chromium compound exhibit the same remarkable sensitivity against correlation effects as the cited *ab initio* LCAO-treatment – in spite of the completely different HF-result – the idea of a “weak” chromium–chromium and “strong” molybdenum–molybdenum bond, as introduced by Benard and Veillard [9, 10], becomes quite attractive. If one adopts this kind of argumentation it is reasonable that the Mo–Mo-distance is only little sensitive to different ligand surroundings while the Cr–Cr-bond length is strongly influenced by changes in the ligand sphere.

After having discussed mainly  $d^7$ – $d^7$ -carbonyls and  $d^4$ – $d^4$ -carboxylates, we finally look at a complex which can be considered as a link between these two types of compounds, namely  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ . This  $d^7$ – $d^7$  tetracarboxylate has recently been the subject of detailed experimental [33] and theoretical [22, 34] studies. Thus these complexes can be taken to prove some of the qualitative results which we have extracted from our calculations: As carboxylate ligands do not act as  $\pi$ -acceptors a level diagram as shown in Fig. 4c is adequate instead of the scheme of Fig. 1d. The main difference is that  $\sigma$  is now the deepest of the levels with predominant metal  $d$ -character. The expected sequence for a  $d^7$ – $d^7$ -tetracarboxylate without axial ligands is therefore  $\sigma < \pi < \delta' < \delta'^* < \pi^*$ , leading to the prediction of a single  $\sigma$ -bond. Due to the experience gained from the carbonyl complexes, especially from  $\text{Co}_2(\text{CO})_8$  (where even the  $\delta''$ -orbitals become occupied), it is very unlikely that levels with large metal  $p$ -character will be occupied according to Cotton's original proposal of a triple bond in  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$  [34]. The more recent spectroscopic investigations [2–4], as well as the  $X_\alpha$ -results [34] are in agreement with the assumption of a single bond, in spite of the unusually short Rh–Rh-distance. The basic orbitals configuration obtained from the  $X_\alpha$ -calculation is  $\sigma^2 \pi^4 \delta'^2 \pi^{*4} \delta'^{*2}$ . With exception of the order of the two highest occupied orbitals, which is difficult to estimate qualitatively, this is the expected sequence. The  $X_\alpha$ -results also confirm the strong destabilization of the levels  $\sigma$  and  $\sigma^*$  in connection with an occupation of the axial positions by two molecules of water. It is, however, very difficult to think of an interaction that shifts the M–M-bonding orbital  $\pi$  to higher energies than  $\pi^*$  as it has been claimed recently to explain the influence of axial ligands on the Rh–Rh-bond [22].

## 5. Concluding Remarks

The examples investigated in this paper clearly show that the extended CNDO-formalism introduced in Part I of this series can be successfully applied to study the bonding problems in binuclear transition metal complexes. As far as  $X_\alpha$ -calculations are available, the important details of the orbital diagrams of the studied compounds are in accordance with the results of these calculations. The obtained bonding properties also compare quite well with the information derived from different spectroscopic investigations. This is not only true for the metal–

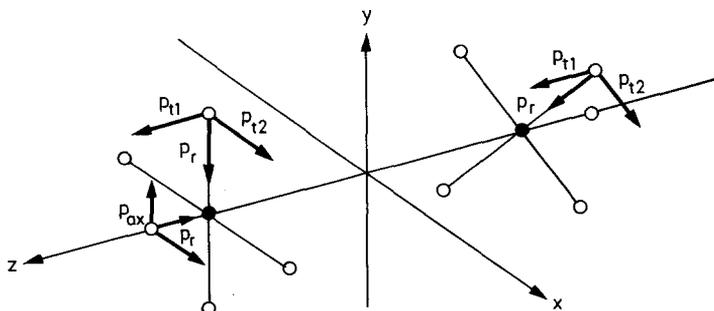
metal bond but also for the metal–ligand and ligand internal bonds. From this we conclude, that the general results which can be extracted from the quantitative calculations will hold for a great variety of compounds. For the Class A molecules with fourfold or quasifourfold symmetry the most important facts are as follows:

- (i) Two of the  $\delta$ -orbitals (which we call  $\delta''$  and  $\delta''^*$ ) are strongly destabilized due to an antibonding interaction with  $\sigma$ -donor orbitals of the equatorial ligands. These orbitals will not be occupied until we come to  $d^8-d^8$  or  $d^9-d^9$  systems. The existence of a fivefold bond is therefore impossible.
- (ii) Axial ligands strongly destabilize the orbitals  $\sigma$  and  $\sigma^*$  due to an antibonding interaction of these orbitals with the  $\sigma$ -donor orbitals of the axial ligands.
- (iii) Axial symmetric ligands with  $\pi$ -acceptor qualities in the axial positions lead to a stabilization of the levels  $\pi$ ,  $\delta'$ ,  $\delta'^*$  and  $\pi^*$ .
- (iv) For bracketing ligands like acetate and formiate the phase correlations within the ligand  $\pi$ -system has to be taken into account. For three center, four electron allylanion-type ligands the  $\pi$ -interaction should always lead to a pronounced destabilization of  $\delta'^*$ .
- (v) Orbitals with large contributions from the metal  $p$ -orbitals are very unlikely to be occupied in binuclear transition metal complexes in spite of the fact that these are usually the lowest unoccupied levels.

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## Appendix

Transformation properties of atomic orbitals for the binuclear metal cluster and for the pure ligand sphere in  $D_{4d}$  and  $D_{4h}$ .  $s$ - and  $p$ -orbitals are taken into account for the ligands and  $s$ -,  $p$ - and  $d$ -orbitals for the metal atoms. The following notation is used for the  $p$ -orbitals of the ligand atoms:



**D<sub>4d</sub>**  
**Metal-Orbitals**

D <sub>4d</sub>	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>
<i>s</i>	1	0	0	1	0	0	0
$\sigma$	1	0	0	1	0	0	0
$\pi$	0	0	0	0	1	0	1
$\sigma$	1	0	0	1	0	0	0
$\pi$	0	0	0	0	1	0	1
$\delta$	0	0	0	0	0	2	0

**Ligand-Orbitals:**

	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>
<i>s</i>	2	0	0	2	1	1	1
<i>p<sub>rad</sub></i>	2	0	0	2	1	1	1
<i>p<sub>t1</sub></i>	1	0	0	1	1	1	1
<i>p<sub>t2</sub></i>	0	1	1	0	1	1	1
<i>p<sub>ax</sub></i>	0	0	0	0	1	0	1

If axial ligands are not present there is one A<sub>1</sub> and one B<sub>2</sub> representation less for *s* and *p<sub>rad</sub>*.

**Symmetry D<sub>4h</sub>**  
**Metal-Orbitals**

	A <sub>1g</sub>	A <sub>1u</sub>	A <sub>2g</sub>	A <sub>2u</sub>	B <sub>1g</sub>	B <sub>1u</sub>	B <sub>2g</sub>	B <sub>2u</sub>	E <sub>g</sub>	E <sub>u</sub>
<i>s</i>	1	0	0	1	0	0	0	0	0	0
$\sigma$	1	0	0	1	0	0	0	0	0	0
$\pi$	0	0	0	0	0	0	0	0	1	1
$\sigma$	1	0	0	1	0	0	0	0	0	0
$\pi$	0	0	0	0	0	0	0	0	1	1
$\delta$	0	0	0	0	1	1	1	1	0	0

**Ligand-Orbitals:**

	A <sub>1g</sub>	A <sub>1u</sub>	A <sub>2g</sub>	A <sub>2u</sub>	B <sub>1g</sub>	B <sub>1u</sub>	B <sub>2g</sub>	B <sub>2u</sub>	E <sub>g</sub>	E <sub>u</sub>
<i>s</i>	2	0	0	2	1	0	0	1	1	1
<i>p<sub>rad</sub></i>	2	0	0	2	1	0	0	1	1	1
<i>p<sub>t1</sub></i>	1	0	0	1	1	0	0	1	1	1
<i>p<sub>t2</sub></i>	0	1	1	0	0	1	1	0	1	1
<i>p<sub>ax</sub></i>	0	0	0	0	0	0	0	0	1	1

If axial ligands are not present there is one A<sub>1g</sub> and one A<sub>2u</sub> representation less for *s* and *p<sub>rad</sub>*.

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