

A 1,2-Dithiolenenickel Complex with Different Substituents—a Novel Type of Mixed-Valence Compounds**

By Arnd Vogler* and Horst Kunkely

Mixed-valence (intervalence (IT)) compounds^[1] are distinguished, among other characteristics, by unusual bands in their absorption spectra. If the metal-metal interaction is weak, definite oxidation states can be assigned to the metals, and charge transfer (CT) electronic transitions from reduced to oxidized metal occur at relatively low energies. The associated IT absorption bands lie in the long wavelength spectral region, frequently in the near IR, and their position is solvent dependent.

Mononuclear metal complexes, in which a ligand occurs in different oxidation states ($L_{red}ML_{ox}$), can also be viewed as IT compounds. In this case too, CT electronic transitions from the reduced to the oxidized ligands should be possible. No IT absorption bands can be detected in complexes having catecholates and *o*-semiquinone as IT-ligands^[2]. Mixed valence ligands are also present in the 1,2-dithiolene complexes of Ni^{II}, Pd^{II}, and Pt^{II}.



When $R = R'$ the ground state is described by the two resonance forms **A** and **B**^[3]; both the highest occupied ($2b_{1u}$) and the lowest unoccupied ($3b_{2g}$) ligand orbitals—both are not degenerate—are delocalized over both ligands^[3]. In consequence, the $3b_{2g} \leftarrow 2b_{1u}$ electronic transition has no CT contribution and the position of the associated absorption band is not dependent on the solvent. The complexes are not mixed-valence compounds.

The resonance form **B** ($R = CN$, $R' = C_6H_5$) contributes strongly to the ground state of the complex



This assumption is consistent with the observation that homogeneous complexes with $R = R' = CN$ are considerably more difficult to oxidize than those with $R = R' = C_6H_5$ ^[4]. The donor orbital $2b_{1u}$ is more strongly localized on the ligand with $R = CN$, and the acceptor orbital $3b_{2g}$ more strongly localized on the ligand with $R' = C_6H_5$. The electronic transition between both orbitals, therefore, possesses more CT character and the position of the associated absorption band should depend on the solvent.

I is not stable, however, the anion **1**^[4] is; in the latter compound the acceptor orbital $3b_{2g}$ is singly occupied, but the electronic transition $3b_{2g} \leftarrow 2b_{1u}$ is still possible. The typical, intense longwave absorption band (Fig. 1) is dependent upon the solvent. For the solvents chlorobenzene, chloroform, pyridine, dimethyl sulfoxide, and acetonitrile a linear plot of the wavenumber of the maximum *vs.* $1/n^2 - 1/D$ ^[1] (n^2 and D are, respectively, the optical and static dielectric constants of the solvent) is obtained with a slope of 440 cm^{-1} . The solvent dependence is certainly much smaller than that of the "mixed" 1,2-dithiolatediim-

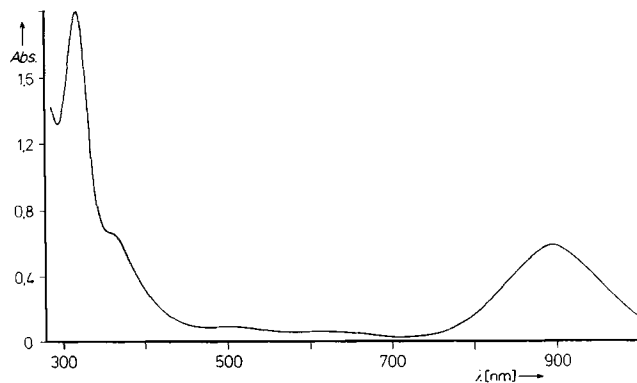


Fig. 1. Absorption spectrum of **1**⁻ ($c = 6.75 \cdot 10^{-5} \text{ mol/L}$, CH_3CN , 1 cm cuvette).

ine complexes of Ni^{III}^[5] and Pt^{III}^[6], in whose ground state the resonance form with dithiolate and diimine as ligands almost exclusively occurs.

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Intervalence Transfer between Hexaamminecobalt(III) and Hexacyanoruthenate(II)**

By Arnd Vogler* and Josef Kisslinger

A distinction is made between outer-sphere and inner-sphere redox reactions in thermal electron transfer between transition-metal complexes^[1]; optical charge-transfer transitions (CT) between a reducing and an oxidizing metal center can be observed (intervalence transfer, IT)^[2], either if both metals are bonded *via* bridging ligands in a dinuclear complex (inner-sphere) or are in close contact in separated metal complexes (outer-sphere), *e.g.* as ion-pairs^[3]. Until now, inner- and outer-sphere IT-transitions in *one* system have never been observed. We have previously investigated the dinuclear complex $[(NH_3)_5Co^{III}(\mu-NH_2)Ru^{II}(CN)_5]^-$ ^[4] and now describe the ion-pair $[Co(NH_3)_6]^{3+}/[Ru(CN)_6]^{4-}$, the mononuclear components of **1**.

Earlier attempts to study $[Co(NH_3)_6]^{3+}/[Ru(CN)_6]^{4-}$ in solution were thwarted by the fact that $[Co(NH_3)_6]_4[Ru(CN)_6]_3$, which is insoluble in all the usual solvents, immediately precipitates out. We have now found that supersaturated solutions, from which the difficultly soluble precipitate is first formed after several hours, are formed from mixtures of not too concentrated solutions ($c < 5 \times 10^{-3} \text{ mol/L}$) of $[N(C_2H_5)_4]_4[Ru(CN)_6]$ and $[Co(NH_3)_6]^{3+}(CH_3CO_2^-)_3$ in dimethyl sulfoxide (DMSO).

[*] Prof. Dr. A. Vogler, Dr. H. Kunkely
Institut für Anorganische Chemie der Universität
Universitätsstrasse 31, D-8400 Regensburg (Germany)

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[*] Prof. Dr. A. Vogler, J. Kisslinger
Institut für Anorganische Chemie der Universität
Universitätsstrasse 31, D-8400 Regensburg (Germany)

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