

an Mo₂Co-triangle bridged by two μ₃-sulfur ligands and a new structural unit, an η²-AsS ligand as bridge between two Mo atoms. The AsS-ligand, the two S-bridges and the Co-atom lie in a plane bisecting the molecule. The carbonyl groups are located in the plane of the three-membered ring of metal atoms (Fig. 1). Hence, **3** constitutes the first example of a molecule containing complex-stabilized arsenic monosulfide, which, in the free state, is unstable. With the proviso that there is a 50% statistical distribution of arsenic and sulfur at the As and S1 sites, the As–S1 distance in **3** can be said to be 2.237(3) Å, a value which corresponds to the average length of the As–S single bond in α-As₄S₄^[4]. We conclude, therefore, that the new ligand has a bond order of 1 and functions as a 5e-donor. Furthermore, if we consider the μ₃-S atoms as 4e-donors and the remaining ligands as 5e-donors (C₅Me₅-moieties) and 2e-donors (CO groups), then each metal atom acquires noble-gas configuration by formation of M–M single bonds. The experimentally determined metal-metal distances lend support to this conclusion.

Remarkably, the Co(CO)₂-fragment is incorporated exclusively in the η²-S₂-group of **1** and **2**, even though there are several sites open to attack in the ligand sphere of the starting complex. The S₂-bridge over the Mo atoms is thereby enlarged to an SCoS unit, while elimination of X from the XSX-bridge leads to formation of the bridging XS-ligand. This apparent lability of an Mo–X bond is confirmed by the sensitivity of **1** towards oxidation: Only the previously reported arsenic-free complexes [(C₅Me₅)₂Mo₂O₂S₂] and [(C₅Me₅)₂Mo₂OS₃] can be isolated from toluene solutions of **1** in presence of air.

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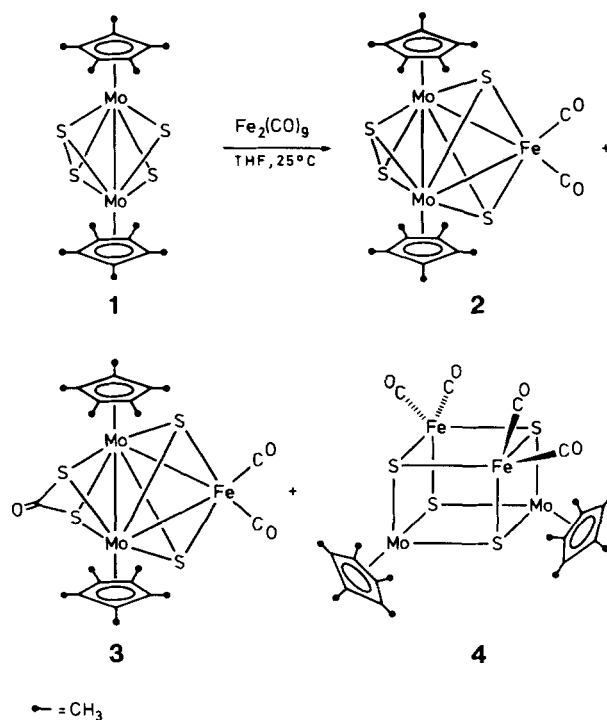
CAS Registry numbers:

1, 90790-24-2; **2**, 94570-20-4; **3**, 94570-21-5; **4**, 94570-22-6;
[(C₅Me₅)₂Mo₂OS₃], 94570-23-7; [(C₅Me₅)₂Mo₂O₂S₂], 94570-24-8; [Co₂(CO)₈],
10210-68-1.

Novel MoFeS Clusters from [(C₅Me₅)₂Mo₂S₄] and Fe(CO)₅ or Fe₂(CO)₉

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Thio-transition-metal clusters containing various metal atoms serve as model compounds, both in the catalysis of industrially important desulfurization reactions as well as in the deciphering of bioinorganic reactions. Of particular importance is the coupling of Mo and Fe with sulfur to give "heterocubanes", among which, compounds with a Mo₂Fe₂S₄ core are still very poorly represented in the literature. The first such cluster to be prepared and spectroscopically characterized was [(C₅Me₅)₂Mo₂Fe₂(NO)₂S₄]^[1]. But "mixed" trinuclear clusters with a trigonal pyramidal M₂M'S₂ core and a μ₂,η²-di-(main group element) ligand are also still relatively rare^[2].



- [1] I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter, M. L. Ziegler, *Angew. Chem.* 96 (1984) 428; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 438.
- [2] a) A mixture of 0.60 mmol **1** or **2** and 0.64 mmol Co₂(CO)₈ in 50 mL toluene is stirred for 1 h (**1**) or 2.5 h (**2**) at room temperature. Chromatographic purification on SiO₂ with toluene/petroleum ether (1:1) afforded the red-brown complexes **3** and **4** in 60 and 28% yield, respectively. The complexes can be recrystallized from toluene/pentane (5:2).—b) IR (KBr, [cm⁻¹]): **3**: ν(CO)=1975 (vs), 1927 (s); **4**: ν(CO)=1982 (vs), 1932 (s). ¹H-NMR (δ(CH₃), CDCl₃): **3**: 1.88; **4**: 1.90.
- [3] P2₁/n, a=11.529(7), b=15.348(9), c=15.588(5) Å, β=107.28(3)°, V=2633.75 Å³, Z=4, Syntex P3 diffractometer (MoKα), 3° ≤ 2θ ≤ 55°, 2490 observed reflections with I ≥ 2.5σ(I), Patterson (Co, Mo, As, S) and Fourier methods, anisotropic refinement to R_w=0.04. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51104, the names of the authors, and the full citation of the journal.
- [4] D. J. E. Mullen, W. Nowacki, Z. *Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* 136 (1972) 48.
- [5] If a solution of **1** in toluene is stirred for 48 h in presence of air, subsequent chromatographic work-up enables isolation of [(C₅Me₅)₂Mo₂OS₃] (green, 46% yield; IR (KBr, [cm⁻¹]): ν(Mo=O)=900 (vs), ν(Mo=S)=482 (s); ¹H-NMR (δ(CH₃), CDCl₃): 2.03, 1.96) and [(C₅Me₅)₂Mo₂O₂S₂] (orange, 39% yield; IR (KBr, [cm⁻¹]): ν(Mo=O)=898 (vs), ν(Mo=S)=451 (w); ¹H-NMR (δ(CH₃), CDCl₃): 2.00.
- [6] H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn, M. L. Ziegler, *Organometallics* 1 (1982) 1107; M. Rakowski DuBois, D. L. DuBois, M. C. VanDerveer, R. C. Haltiwanger, *Inorg. Chem.* 20 (1981) 3064.

The three new diamagnetic MoFeS clusters **2–4** are formed on reaction of the complex **1** with Fe₂(CO)₉ in tetrahydrofuran (THF) (molar ratio 1:1.3). **2** and **4** are also formed in the photochemical reaction of **1** with Fe(CO)₅ (in the molar ratio 1:2) in THF^[3a]. The composition of each product has been confirmed by elemental analysis and mass spectra. The ¹H-NMR and IR spectra^[3b] are consistent with the results of the X-ray structure analysis.

Characteristic of the structures of **2** and **3**^[4] (Figs. 1 and 2) is a trigonal-bipyramidal Mo₂FeS₂ core; the Mo₂Fe(CO)₂ moiety is perpendicular to the plane of the sulfur ligands. As 48e-clusters, **2** and **3** each contain three metal-metal single bonds, consistent with the observed

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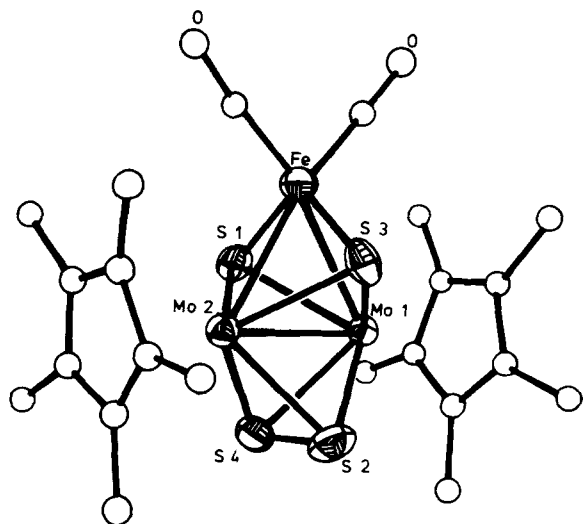


Fig. 1. Molecular structure of **2** (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Mo1–Mo2 2.592(0), Mo1–Fe 2.778(1), Mo1–S1 2.432(1), Mo1–S2 2.437(1), Mo1–S3 2.436(1), Mo1–S4 2.440(1), Mo2–Fe 2.776(1), Fe–S1 2.153(1), S2–S4 2.071(1); Mo2–Mo1–Fe 62.1(0), Fe–Mo1–S1 48.3(0), S1–Mo1–S4 76.5(0), S2–Mo1–S4 50.3(0), S1–Mo1–S3 89.1(0), Mo1–Fe–S1 57.4(0).

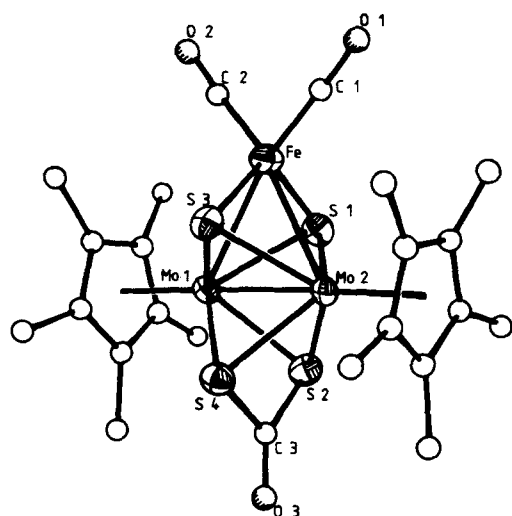


Fig. 2. Molecular structure of **3** (ORTEP diagram). Most important bond lengths [Å] and angles [°]: Mo1–Mo2 2.574(0), Mo1–Fe 2.830(1), Mo1–S1 2.467(1), Mo1–S2 2.470(1), Mo1–S3 2.448(1), Mo1–S4 2.467(1), Mo2–Fe 2.819(1), Fe–S1 2.130(1), S2–C3 1.800(4), S4–C3 1.817(4), C3–O3 1.196(5); Mo2–Mo1–Fe 62.7(0), Mo2–Mo1–S1 58.1(0), S1–Mo1–S2 69.8(0), S1–Mo1–S3 87.1(0), S2–Mo1–S4 68.2(0), Mo1–S4–C3 89.2(1), S2–C3–O3 130.7(3).

M–M distances. Thus, in both cases the relatively short Mo–Mo distance is ascribable to a “bracketing effect” of the bridge ligands. **2** can be regarded as an Fe(CO)₂-adduct of **1**^[5], whereas **3** unexpectedly contains a dithiocarbonyl-ligand as structural element bridging the two Mo atoms.

The X-ray structure analysis of **4**^[4] confirms the presence of a Mo₂Fe₂S₄-cubane with relatively small differences (up to 0.09 Å) between the Mo–S and Fe–S bond lengths. In **2** and **3**, however, these differences are up to 0.44 Å. There are five metal-metal bonds of equal length (on average 2.803 Å) as opposed to one Fe–Fe distance of 3.334 Å (Fig. 3). A qualitative confirmation of this finding is obtained from the distribution of the 62 valence electrons over the cluster. A similar situation is found in the

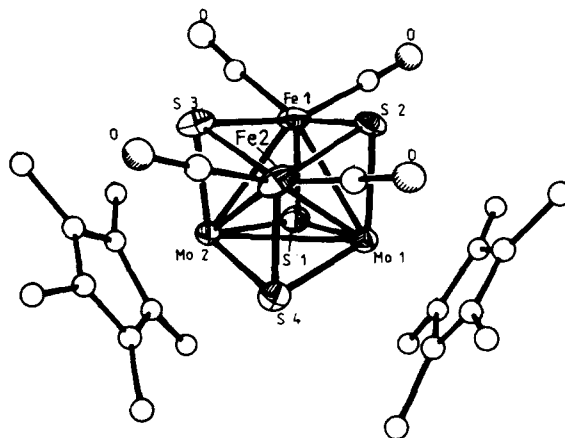


Fig. 3. Molecular structure of **4** (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Mo1–Mo2 2.761(1), Mo1–Fe1 2.832(4), Mo1–Fe2 2.792(3), Mo1–S1 2.357(2), Mo1–S2 2.333(2), Mo1–S4 2.320(2), Mo2–Fe1 2.813(3), Mo2–Fe2 2.815(4), Mo2–S1 2.342(2), Mo2–S3 2.282(2), Mo2–S4 2.303(2), Fe1–S1 2.214(3), Fe1–S2 2.271(5), Fe1–S3 2.330(4), Fe1...Fe2 3.334; Mo2–Mo1–Fe1 60.4(1), Mo2–Mo1–Fe2 60.9(1), Fe1–Mo1–Fe2 72.7(1).

complex **5**, which is isoelectronic with **4** and is accessible from **6** and Ni(CO)₄^[6]. However, in contrast to **1**, **5** is only able to incorporate Fe(CO)₅ or Fe₂(CO)₉ in a 66e-cluster **7** with planar metal framework^[7]. The 62e-complex **8** obtainable from **1** and Mo(CO)₆ in boiling toluene should, on the other hand, be isostructural with **4**.

$[(C_5H_5)_2Mo_2Ni_2(CO)_2S_4]$	$[(MeC_5H_4)_2Mo_2(SH)_2S_2]$
5	6
$[(MeC_5H_4)_2Mo_2Fe_2(CO)_6S_4]$	$[(C_5Me_5)_2Mo_4(CO)_6S_4]$
7	8
$[(MeC_5H_4)_2V_2S_4]$	$Hg[Fe(NO)(CO)_3]_2$
9	10

The clusters **2**–**4** are formed in different ways: **2** and **3** can be synthesized by stepwise substitution of CO in the carbonyliron complexes by the two μ -S bridges in **1**, whereas transformation of the η^2 -S₂-ligand into two μ -S-bridges requires a redox reaction with participation of the carbonyliron compounds. This reaction behavior essentially conforms with that of the vanadium complex **9**, which gives a similar reaction sequence with the iron complex **10**, resulting in a 58e-cluster with a V₂Fe₂S₄ core^[2b]. However, the extraordinarily mild carbonyl transfer from Fe₂(CO)₉ to the η^2 -S₂-ligand warrants further investigation.

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1, 82167-40-6; **2**, 94598-08-0; **3**, 94598-09-1; **4**, 94619-63-3; Fe₂(CO)₉, 15321-51-4; Fe(CO)₅, 13463-40-6; Mo, 7439-98-7; Fe, 7439-89-6.

[1] H. Brunner, H. Kauermann, J. Wachter, *Angew. Chem.* 95 (1983) 567; *Angew. Chem. Int. Ed. Engl.* 22 (1983) 549.

[2] Examples known to us are a) $[(MeC_5H_4)_2V_2Fe(CO)_3S_4]$ (C. M. Bolinger, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* 104 (1982) 7313); b) $[(MeC_5H_4)_2V_2Fe(NO)_2S_4]$ (T. B. Rauchfuss, T. D. Weatherhill, S. R. Wilson, J. P. Zebrowski, *ibid.* 105 (1983) 6508); c) $[(C_5Me_5)_2Mo_2Co(CO)_2AsS_3]$

(H. Brunner, H. Kauermann, U. Klement, J. Wachter, T. Zahn, M. L. Ziegler, *Angew. Chem.* 97 (1985) 122; *Angew. Chem. Int. Ed. Engl.* 24 (1985) 132.

[3] a) The blue solution of **1** (290 mg, 0.50 mmol) and $\text{Fe}_2(\text{CO})_9$ (240 mg, 0.66 mmol) in THF (100 mL) was stirred for 17 h at room temperature. Column chromatographic separation of the greenish-brown mixture (SiO_2 , toluene/pentane 2:1) afforded green **4**, then brown **3**, followed by brown **2** (in yields of 33, 11 and 21%, respectively). The photolytic reaction with $\text{Fe}(\text{CO})_5$ (THF, 125W Hg-lamp) afforded **4** in 10% yield and **3** in 38% yield. All the compounds can be recrystallized from CH_2Cl_2 .—b) IR (KBr, $[\text{cm}^{-1}]$): **2**: $\nu(\text{CO})=1918, 1855$; **3**: $\nu(\text{CO})=1937$ (vs), 1883 (s), 1872 (s) (CH_2Cl_2 1943, 1879), $\nu(\text{S}_2\text{C}=\text{O})=1734$ (s); **4**: 1995 (s), 1962 (vs), 1934 (s), $^1\text{H-NMR}$ ($\delta(\text{CH}_3)$, CDCl_3): **2**: 1.89; **3**: 1.80; **4**: 1.80.

[4] The structures of **2–4** were determined on a Syntex diffractometer ($\text{MoK}\alpha$), $3^\circ \leq 2\theta \leq 60^\circ$, Patterson (Mo, Fe, S) and Fourier methods. **2**: $P2_1/n$, $a=11.476(3)$, $b=15.259(4)$, $c=15.589(4)$ Å, $\beta=107.39(2)^\circ$, $V=2605.05$ Å³, $Z=4$. 4854 observed reflections, anisotropic refinement to $R_w=0.026$. **3**: $P2_1/c$, $a=11.540(5)$, $b=15.235(5)$, $c=15.303(7)$ Å, $\beta=99.14(4)^\circ$, $V=2656.29$ Å³, $Z=4$. 5877 reflections, anisotropic refinement to $R_w=0.028$. **4**: Cc , $a=21.338(5)$, $b=8.795(2)$, $c=20.431(4)$ Å, $\beta=130.75(1)^\circ$, $V=2904.68$ Å³, $Z=4$. 3319 observed reflections, anisotropic refinement to $R_w=0.025$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51103, the names of the authors, and full citation of the journal.

[5] H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn, M. L. Ziegler, *Organometallics* 1 (1982) 1107.

[6] M. D. Curtis, P. D. Williams, *Inorg. Chem.* 22 (1983) 2661.

[7] B. Cowans, J. Noordik, M. Rakowski DuBois, *Organometallics* 2 (1983) 931.

[8] IR (KBr, $[\text{cm}^{-1}]$): $\nu(\text{CO})=2000, 1975, 1932, 1883, 1870$; $^1\text{H-NMR}$ ($\delta(\text{CH}_3)$, CDCl_3): 1.88.

Diamminebis(1,5-cyclooctadiene)(μ -1,4,10,13-tetraoxa-7,16-diazacyclooctadecane- N^7, N^{16})dirhodiumbis(hexafluorophosphate): An Example of Simultaneous First and Second Sphere Coordination**

By Howard M. Colquhoun, Simon M. Doughty, Alexandra M. Z. Slawin, J. Fraser Stoddart*, and David J. Williams

Previously, we have observed several examples^[1] of second sphere coordination^[2] of transition-metal complexes by crown ethers. Although numerous cases of first sphere coordination of transition metals to macrocyclic polyether ligands containing nitrogen atoms have been described^[3], we now report a remarkable example of simultaneous first and second sphere coordination of rhodium by 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane **1**^[4].

cyclo-[(O-CH₂CH₂)₂NH-CH₂CH₂]₂ **1**

[Rh(cod)(NH₃)₂][PF₆]₂ **2**

[[Rh(cod)(NH₃)₂]₂·**1**][PF₆]₂ **3**

The fortuitous discovery^[5] of [[Rh(cod)(NH₃)₂]₂·**1**][PF₆]₂ (cod=1,5-cyclooctadiene) **3** followed an unsuccessful attempt to isolate a crystalline adduct between

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[Rh(cod)(NH₃)₂][PF₆]₂ **2**^[6] and **1**. Elemental analysis^[5] indicated the formation of a 2:1 covalent complex with loss of 2 NH₃^[7]. X-Ray analysis^[8] not only confirmed the constitution of the complex **3** but also revealed several interesting conformational features (Fig. 1). The complex contains a

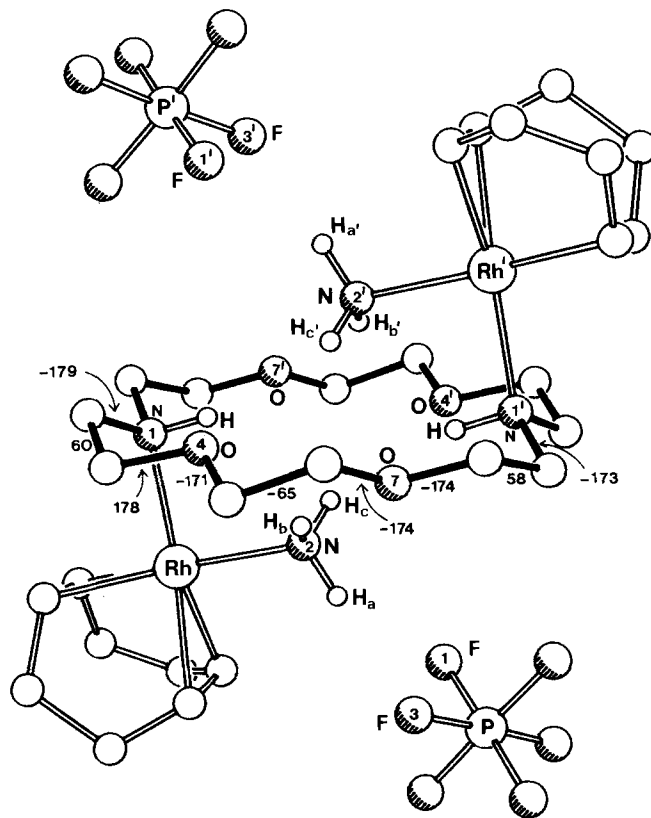


Fig. 1. Structure of **3** in the crystal. **3** is monoclinic, $a=11.445(3)$, $b=11.329(3)$, $c=15.192(5)$ Å, $\beta=90.45(2)^\circ$, $V=1970$ Å³, space group $P2_1/n$, $Z=2$, $\rho=1.71$ g cm⁻³, $\mu_{\text{CuK}\alpha}=86$ cm⁻¹, 2213 independent reflections with $[|F_o| > 3\sigma(|F_o|)]$, $\theta \leq 55^\circ$, $R=0.101$. Torsional angles [$^\circ$] associated with the 18-membered ring are shown beside the relevant bonds. Selected bond lengths [Å]: Rh-N(1) 2.17(1); Rh-N(2) 2.14(1). Selected bond angles [$^\circ$]: Rh-N(1)-C(2) 117(1); Rh-N(1)-C(9') 116(1); C(2)-N(1)-C(9') 111(1). Intramolecular contact distances from N(2) to O(4), O(4'), O(7), O(7'), F(1), F(3): 3.22, 3.50, 3.45, 3.45, 3.22, 3.13 Å. Distance of N(2) from the mean plane of the ring heteroatoms: 1.92 Å. N(2)···N(2') distance: 3.97 Å. The PF₆⁻ ions have two orientations of estimated occupancies 0.65 and 0.35. Only the orientation of the major occupancy is illustrated.

crystallographic center of symmetry at the center of the 18-membered ring^[9]. Despite the torsional freedom around the N(1)-Rh bonds, the ammine ligands [N(2)] are oriented directly over the faces of the macrocycle. There is also an appreciable flattening of the expected tetrahedral geometry at N(1), which is confined to the Rh-N-C angles (117 and 116°), enabling a closer approach of the ammine ligands to the faces of the macrocycle. However, the resulting N(2)···O distances are still rather long with only N(2)···O(4) (3.22 Å) lying within what would conventionally be considered a hydrogen bonding distance. In this instance, the contact is to an oxygen atom [O(4)] on the opposite face of the macrocycle, i.e., a nesting arrangement^[10] analogous to that observed in [(Ph₃PMe)₂·[18]crown-6][PF₆]₂^[11]. The associated H_b···O(4) distance and N(2)-H_b···O(4) angle are 2.41 Å and 142°, respectively. The other H···O distances are 2.60 Å for H_b···O(7) and 2.59 Å for H_c···O(4'). The associated N(2)···O distances are given in the Figure caption^[12].