

Chemistry of crown thioether complexes of low-valent second-row transition metals

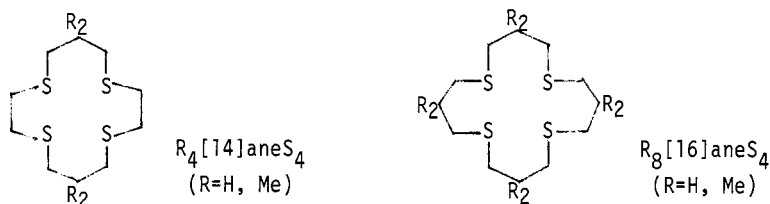
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Abstract - Preparation, structures, and reactions of 14- and 16-membered quadridentate crown thioethers complexes, trans-Mo(N₂)₂Me₈[16]aneS₄, cis- and trans-RuCl₂L, and RhL⁺ (L=R₄[14]aneS₄, R₈[16]aneS₄; R=H, Me) are described emphasizing the novel features of crown thioethers vs. phosphines. The most prominent electronic property of the crown thioethers is π donor ability. The factors determining the reactivities of these complexes such as ring size and conformational effects of the macrocycles and geometrical effect of the complexes are discussed.

INTRODUCTION

In contrast to the vast coordination chemistry of phosphines, thioethers have been ignored long as a principal ligand in low-valent transition metal complexes probably due to poor π-acceptor ability (ref. 1). This inherent property may be modified for polydentate crown thioethers by macrocyclic effect. In fact, the enormously high reduction potentials found for the Cu(II), Co(III), and Mo(II) complexes (ref. 2-4) suggest that crown thioethers exhibit a strong preference for the lower oxidation states of metal ion. In addition, crown thioethers are unique ligand capable of stabilizing rather unusual oxidation states of metals and/or structures of the complexes, e.g., RhL₂²⁺ and PdL₂³⁺ (L=[9]aneS₃) (ref. 5,6). These salient features may promise the rich chemistry of crown thioether complexes of transition metals, particularly in low-oxidation states. Here we present preparation, structures, and reactions of Mo(0), Rh(I), and Ru(II) complexes of quadridentate crown thioethers shown below. Our work has been focused on elucidating the possible analogy and difference between the coordination chemistry of crown thioethers and phosphines.



PREPARATION AND STRUCTURES OF Mo(0), Rh(I), AND Ru(II) COMPLEXES

Despite involvement of sulfur ligands in the nitrogenase cofactor, molybdenum dinitrogen complexes containing S ligand only are completely unknown. We have prepared the first example of such Mo(0) dinitrogen complex, trans-Mo(N₂)₂Me₈[16]aneS₄ (**1**), by reducing the corresponding dibromide with Na/Hg under N₂ (ref. 7). The choice of 16-membered crown thioether is crucial for the preparation of N₂ complex since attempts to prepare the Me₄[14]aneS₄ and Me₆[15]aneS₄ analogues were fruitless. Molecular structure of **1** is shown in Fig. 1. Comparison of Mo-N distances (1.991(5), 2.002(5) Å), ν(N=N) (1995m, 1890s cm⁻¹), and Mo(0/I) oxidation potential (-0.52 V vs. SCE) of **1** with the respective values (2.015(5) Å; 2020, 1970 cm⁻¹; -0.16 V vs. SCE) of trans-Mo(N₂)₂(dppe)₂ (ref. 8,9) indicates that **1** is more electron rich than the diphosphine analogue.

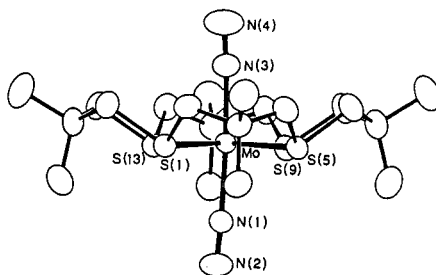


Fig. 1. Molecular structure of **1**.

Homoleptic thioether complexes of Rh(I), {RhR₄[14]aneS₄}Cl (**2**, R=H; **3**, R=Me), {RhR₈[16]aneS₄}Cl (**4**, R=H; **5**, R=Me), and {Rh(Me₂-2,3,2-S₄)Cl} (**6**)

were obtained by treating $\{\text{RhCl}(\text{C}_6\text{H}_4)_2\}_2$ or $\{\text{RhCl}(\text{cod})\}_2$ with the corresponding thioethers. (ref. 10). Due to the small cavity, an attempt to prepare the $[\text{12}]_{\text{aneS}_4}$ analogue failed. The complex 2 was originally prepared by D.H. Busch et al. through reduction of $\text{cis-}\{\text{RhCl}_2[\text{14}]_{\text{aneS}_4}\text{Cl}\}$ with NaBH_4 (ref. 11). 2 crystallizes as a mixture of reddish brown dimer (2a) and a trace of yellow monomer (2b) (Fig. 2). The dimer is composed from two monomer units joined through a $\text{Rh}\cdots\text{Rh}$ (3.313(1) Å) and four $\text{Rh}\cdots\text{S}$ (3.69(1)-3.82(1) Å) non-bonded interactions. The structures of 2b and the monomer units in 2a are essentially similar except the deviation of the Mo atom from the 4S plane (0.1332(2) Å for 2a and 0.083(2) for 2b). When the all-up conformer 3 was treated with NaBPh_4 in MeCN at room temperature, a facile isomerization took place to give an up-up-down-down conformer, $\text{trans-}\{\text{RhMe}_4[\text{14}]_{\text{aneS}_4}\text{BPh}_4\}$ (7). Both conformers are stable up to 100° C in DMSO, while the conformation of $\text{Rg}[\text{16}]_{\text{aneS}_4}$ in 4 and 5 is non-rigid at 30° C and rapid equilibria exist between four possible conformers.

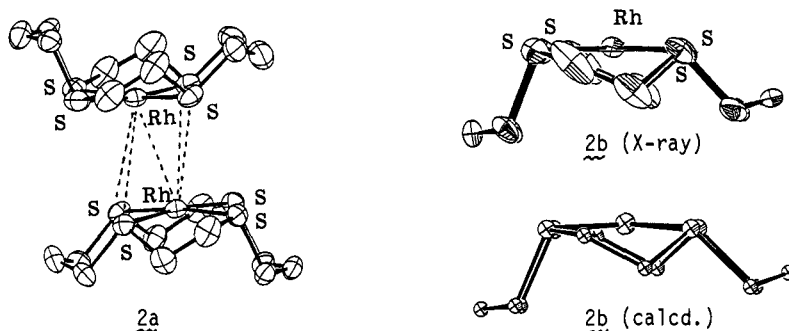


Fig. 2. Molecular structures of the cation of 2.

Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{R}_4[\text{14}]_{\text{aneS}_4}$ and $\text{Me}_8[\text{16}]_{\text{aneS}_4}$ in toluene (60° C) gave $\text{cis-RuCl}_2\text{-R}_4[\text{14}]_{\text{aneS}_4}$ (8, R=H; 9, R=Me) and $\text{cis-RuCl}_2\text{Me}_8[\text{16}]_{\text{aneS}_4}$ (10), respectively (ref. 12). cis- stereochemistry of 8 has been confirmed (ref. 13). On heating in PhCl 9 isomerized into the trans- isomer (11) with the all-up conformation. A similar reaction of $\text{Me}_4[\text{14}]_{\text{aneS}_4}$ with $\text{RuH}(\text{Cl})(\text{PPh}_3)_3$ gave $\text{RuH}(\text{Cl})(\text{PPh}_3)_2\text{Me}_4[\text{14}]_{\text{aneS}_4}$ (12) where the thioether coordinates as a bidentate ligand forming a $\text{RuSCH}_2\text{CH}_2\text{S}$ five-membered ring. The phosphine ligands in 12 show no tendency to dissociate in toluene (80° C). In MeOH, however, both PPh_3 and Cl^- ligands dissociated readily at room temperature affording $\{\text{RuH}(\text{PPh}_3)\text{Me}_4[\text{14}]_{\text{aneS}_4}\text{Cl}\}$ (13) in which $\text{Me}_4[\text{14}]_{\text{aneS}_4}$ adopts a folded conformation. Under similar conditions, $\text{Me}_8[\text{16}]_{\text{aneS}_4}$ failed to react with $\text{RuH}(\text{Cl})(\text{PPh}_3)_3$ (ref. 14).

ELECTRONIC FEATURES OF CROWN THIOETHERS

Molecular structures of 1, 2a, and 2b reveal several features; 1) all-up conformation of the crown thioethers, 2) very short Mo(O)-S (2.418(2)-2.427(2) Å) and Rh-S distances (2.247(3)-2.285(4) Å) compared to the corresponding lengths (2.48-2.56 and 2.29-2.50 Å) found for monodentate thiolato and thioether complexes so far, and 3) a displacement of the metal ion from the 4S plane by ca. 0.1 Å. How these structural features do affect the electronic structure of the metal ion. At first, a rationale for the electron richness of 1 compared to the phosphine analogue has been sought by EHMO calculations on the models, $\text{Mo}(\text{SH}_2)_4$ and $\text{trans-Mo}(\text{N}_2)_2(\text{SH}_2)_4$ (D_{4h}) and the corresponding PH_3 analogues (C_{4v}) (ref. 7). The coordinated thioethers differ from the phosphines in exhibiting p_π donor ability. An antibonding $p_\pi(\text{S})\text{-}d_{xz}(d_{yz})(\text{Mo})$ interaction destabilizes the e_g orbitals (HOMO) of $\text{Mo}(\text{SH}_2)_4$, which are 0.78 eV higher in energy than the corresponding e orbitals of $\text{Mo}(\text{PH}_3)_4$. Consequently, a stronger $d_\pi(\text{Mo})\text{-}p_\pi^*(\text{N}_2)$ back-bonding is expected for $\text{trans-Mo}(\text{N}_2)_2(\text{SH}_2)_4$. Indeed, the overlap population of Mo-N π -bonding (0.160) assessed for the SH_2 complex is larger than that (0.133) of the PH_3 analogue, while the populations of σ -bonding for the former (0.444) and the latter (0.437) are comparable. On distortion of $\text{trans-Mo}(\text{N}_2)_2(\text{SH}_2)_4$ from D_{4h} symmetry to the observed structure of 1 (C_{4v}), the σ - (0.454) and π -overlap populations (0.169) of the N_2 ligand located on the same side to the Mo atom with respect to the 4S plane increase, while the respective values (0.432 and 0.129) on the opposite side decrease. This stereoelectronic effect due to the Mo atom deviation is most clearly demonstrated by the molecular structure of $\text{trans-Mo}(\text{PhNC})_2\text{Me}_8[\text{16}]_{\text{aneS}_4}$ (14) prepared from 1 and PhNC (Fig. 3) (ref. 14).

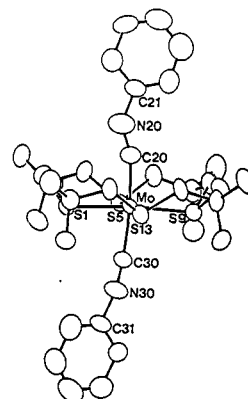


Fig. 3. Molecular structure of 14

The PhNC molecule coordinated on the same side to the ring C atoms of the macrocycle with respect to the 4S plane bends extensively, while that on the opposite side is essentially linear; the angles at the N(20) and N(30) atoms are 139 and 167°, respectively and the deviation of the Mo atom from the 4S plane towards the ring C atoms is 0.11 Å.

Next, the ring size effect upon the nucleophilicity of the Rh(I) complexes was examined by molecular mechanics and EHMO calculations (ref. 14). The calculated molecular structure of **2b** agrees well with the observed one (Fig. 2). The strain-free Rh-S distance (2.305 Å) thus assessed is much longer than that found for **2b** (average 2.264 Å). The e (d_{xz} , d_{yz}) orbitals of the model $\text{Rh}(\text{SH}_2)_4^+$ (C_{4v}) are again 0.34 eV unstable compared to those of $\text{Rh}(\text{PH}_3)_4^+$ (C_{4v}). The e orbitals are further destabilized by the shrinkage of Rh-S bond and by the increment of pyramidal angle between C_4 axis and Rh-S vector (Table 1). By contrast, the a_1 (d_{z^2}) orbital is stabilized by such deformations. Thus, π -basicity of the Rh(I) ion is expected to be enhanced on decreasing the ring size as the result of compression of the Rh-S bond and concomitant out-of-plane deviation of the Rh atom.

TABLE 1. Energy Levels of a_1 and e orbitals in RhL_4^+

L	Rh-L (Å)	pyramidal angle (deg.)	energy level (eV) a_1	energy level (eV) e
SH ₂	2.305	90.0	-12.512	-12.585
	2.264	90.0	-12.514	-12.555
	2.264	92.1	-12.531	-12.526
PH ₃	2.306	90.0	-12.590	-12.922

REACTIONS OF Mo(0), Rh(I), AND Ru(II) COMPLEXES

Electron richness of **1** was manifested by the ready N,N-dimethylation with MeBr under ambient conditions to give trans- $\{\text{MoBr}(\text{N}_2\text{Me}_2)\text{Meg}[\text{16}] \text{aneS}_4\} \text{Br}$ (**15**) (ref. 7). A similar dimethylation of trans- $\text{Mo}(\text{N}_2)_2(\text{depe})_2$ with MeBr has been shown to require photo-irradiation (ref. 15a). Unprecedented N-arylation and -benzylation of the coordinated N_2 molecule of **1** with the corresponding organic halides also proceed readily under ambient conditions to give trans- $\text{MoX}(\text{N}_2\text{Ar})\text{Meg}[\text{16}] \text{aneS}_4$ (**16**, Ar=Ph, X=Br; **17**, Ar=Ph, X=I; **18**, Ar=p-C₆H₄C(O)Me, X=I) and trans- $\{\text{MoBr}[\text{N}_2(\text{CH}_2\text{Ph})_2]\text{Meg}[\text{16}] \text{aneS}_4\} \text{Br}$ (**19**), respectively (ref. 16). Formation of the aryldiazenido complexes was confirmed by transforming into trans- $\{\text{MoI}(\text{N}_2\text{MePh})\text{Meg}[\text{16}] \text{aneS}_4\} \text{I}$ (**20**) for **17** and by a single crystal X-ray structural study for **18** (Fig. 4). Surprisingly, a reaction of **1** with MeI in toluene under ambient conditions gave trans- $\{\text{MoI}[\text{N}_2\text{Me}(\text{CH}_2\text{Ph})]\text{Meg}[\text{16}] \text{aneS}_4\} \text{I}$ (**21**) together with an expected trans- $\{\text{MoI}(\text{N}_2\text{Me}_2)\text{Meg}[\text{16}] \text{aneS}_4\} \text{I}$ (**22**) in a 1:3 ratio. This suggests that N-benylation proceeds through a radical process similar to that confirmed for N-alkylation of trans- $\text{M}(\text{N}_2)_2(\text{dppe})_2$ (M=Mo, W) by alkyl halides (ref. 15b). The enhanced reactivity of the coordinated N_2 molecule in **1** toward such a stable radical $\text{PhCH}_2\cdot$ is rather remarkable since a reaction of the dppe analogue with PhCH_2Br gave trans- $\text{MoBr}_2(\text{dppe})_2$ and dibenzyl (ref. 15b).

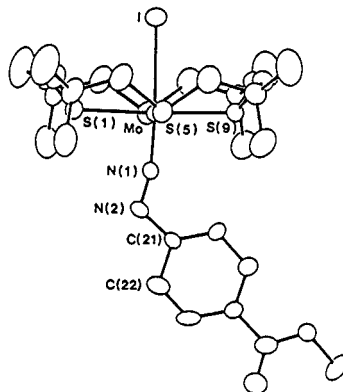


Fig. 4. Molecular structure of **18**.

The homoleptic thioether complexes of Rh(I) described here added CH_2Cl_2 at room temperature to give trans- $\{\text{RhCl}(\text{CH}_2\text{Cl})\text{L}\}^+$ (**23**) (ref. 10). The high reactivity of these thioether complexes contrasts to the inertness of $\text{RhCl}(\text{PPh}_3)_3$ and $[\text{Rh}(\text{t-BuNC})_4]^+$ toward CH_2Cl_2 . The rate of oxidative addition of CH_2Cl_2 increases in the order **2** > **4** > **6**, the relative rate being 5.4, 2.6, and 1.0, respectively. The order is consistent with that of increasing π -basicity of the Rh(I) ion (vide supra). The rate is also affected by the conformation of crown thioether; the second order rate constants for the all-up (**3**) and up-up-down-down conformers (**7**) are 7.4×10^{-3} and $1.1 \times 10^{-3} \text{ M}^{-1}\text{min}^{-1}$ (DMSO, 25° C), respectively. For the up-up-down-down conformer with inversion symmetry, the Rh atom should be exactly in the 4S plane and then, π -basicity of the Rh(I) ion is expected to be lower than that of the all-up conformer.

A remarkable difference was observed for the reaction of two geometrical isomers of octahedral Ru(II) complexes of $\text{R}_4[\text{14}] \text{aneS}_4$ with alkylating reagents in aromatic hydrocarbons (ref. 12). Treatment of cis-isomer **9** with Al_2Me_6 or MeMgBr in toluene (-20° C) gave trans- $\text{RuCl}(\text{C}_6\text{H}_4\text{Me})\text{Me}_4[\text{14}] \text{aneS}_4$ (**24**) as the all-up conformer. This is rather unexpected since a reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with Al_2Me_6 in benzene afforded $\text{RuCl}(\text{Me})(\text{PPh}_3)_3$ (ref. 17). The generality of extremely facile intermolecular $\text{C}(\text{sp}^2)\text{-H}$ bond activation was confirmed by the formation of trans- $\text{RuCl}(\text{Ar})[\text{14}] \text{aneS}_4$ (**25**, Ar=C₆H₄Me; **26**, Ar=Ph) from the reaction of **9** with Al_2Me_6 in the

respective aromatic hydrocarbons. By contrast, a similar reaction of trans-isomer **11** with Al_2Me_6 in toluene gave trans-RuCl(Me) $\text{Me}_4[14]\text{aneS}_4$ (**27**) as the sole isolable product.

Reaction of cis-RuCl $_2$ L **9** and **10** with NaBH_4 is severely affected by the ring size of crown thioethers (ref. 14). Treatment of **9** with an excess of NaBH_4 gave trans-RuH(Cl) $\text{Me}_4[14]\text{aneS}_4$ (**28**) and a bridging hydrido binuclear complex {Ru $_2$ H(Cl)(μ -H)[$\text{Me}_4[14]\text{aneS}_4$] $_2$ }Cl (**29**). The molecular structures of both complexes were elucidated by a single crystal X-ray structural study (Fig. 5). The positions of hydrido ligands in **29** were deduced from the ^1H NMR datum (δ -20.8(d), -33.3(d); J(H-H)=14.9 Hz). The complex **29** may be produced through a nucleophilic attack of the hydrido ligand of **28** to a five coordinate intermediate {RuHMe $_4[14]\text{aneS}_4$ } $^+$ formed by a dissociation of Cl $^-$ in **28**. A similar reaction of **10** with an equi-molar amount of NaBH_4 gave trans-RuH(Cl)Me $_8[16]\text{aneS}_4$ (**30**), which further reacts with BH_4^- affording trans-RuH(η^1 - BH_4)Me $_8[16]\text{aneS}_4$ (**31**). A rather rare monodentate coordination of BH_4^- ligand (Fig. 5) was confirmed by a longer B \cdots Ru non-bonded distance (2.89(2) Å) than that (2.3 Å) estimated for RuH(η^2 - BH_4)(PMe $_3$) $_3$ (ref. 18). Due to a weak trans-influence of the hydrido ligand ($\nu_{\text{Ru-H}}$ 1860 cm^{-1}) of **30** compared to that ($\nu_{\text{Ru-H}}$ 1958 cm^{-1}) of **28**, **30** shows no tendency to dissociate the coordinated Cl $^-$ ligand and does not afford the Me $_8[16]\text{aneS}_4$ analogue of **29**.

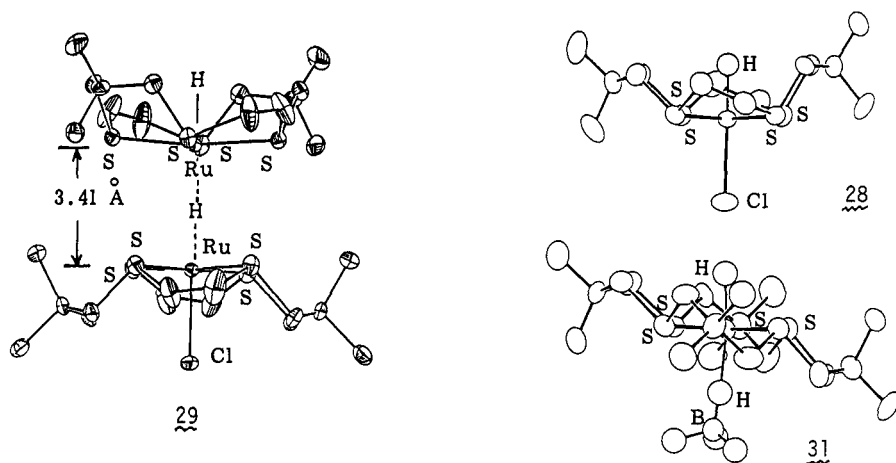


Fig. 5. Molecular structures of Ru(II) hydrido complexes.

REFERENCES

1. S.M. Murray and F.R. Hartley, *Chem. Rev.*, **81**, 365(1981).
2. T.E. Johns, D.B. Rorabacher, and L.A. Ochrymowycz, *J. Am. Chem. Soc.*, **98**, 4322(1976).
3. J.R. Hartman, E.J. Hinst, and S.R. Cooper, *J. Am. Chem. Soc.*, **108**, 1208(1986). H.-J. Kupper, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, **25**, 2400(1986).
4. T. Yoshida, T. Adachi, T. Ueda, M. Watanabe, M. Kaminaka, and T. Higuchi, *Angew. Chem. Int. Ed. Engl.*, **26**, 1182(1987).
5. S.C. Rawle, R. Yagbasa, K. Prout, S.R. Cooper, *J. Am. Chem. Soc.*, **109**, 6181(1987).
6. A.J. Blake, A.J. Holder, T.I. Hyde, and M. Schroder, *J. Chem. Soc. Chem. Commun.*, 987(1987).
7. T. Yoshida, T. Adachi, M. Kaminaka, T. Ueda, and T. Higuchi, *J. Am. Chem. Soc.*, **110**, 4872(1988).
8. T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Acta. Cryst.*, **B31**, 1179(1975).
9. T.I. Al-Salih and C.J. Pickett, *J. Chem. Soc. Dalton Trans.*, 1255(1985).
10. T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto, and T. Higuchi, *J. Chem. Soc. Chem. Commun.*, 1137(1985).
11. W.D. Lemke, K.E. Travis, N.E. Takvovyan, and D.H. Busch, *Adv. Chem. Ser.*, **150**, 358(1976).
12. T. Ueda, H. Yamanaka, T. Adachi, and T. Yoshida, *Chem. Lett.*, 525(1988).
13. T.H. Lai and C-K. Poon, *J. Chem. Soc. Dalton Trans.*, 1465(1982).
14. T. Yoshida et al., to be published.
15. a) W. Hussain, G.J. Leigh, H.M. Ali, and C.J. Pickett, *J. Chem. Soc. Dalton Trans.* 553(1988). b) J. Chatt, A.A. Diamantis, G.A. Heath, N.E. Hooper, and G.J. Leigh, *J. Chem. Soc. Dalton Trans.*, 688(1977).
16. T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka, N. Sasaki, T. Higuchi, T. Aoshima, I. Mega, Y. Mizobe, and M. Hidai, *Angew. Chem.*, in press.
17. R.A. Porter and D.F. Shriver, *J. Organometal. Chem.*, **90**, 41(1975).
18. J.A. Statler, G. Wilkinson, M.T.-Pett, and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, 1731(1984).