Some New Aspects of the Coordination Chemistry of Thiometalato Ligands

ACHIM MULLER, WINFRIED HELLMANN, JENS SCHNEIDER, UWE SCHIMANSKI, UDO DEMMER, ALFRED TRAUTWEIN and USCHI BENDER

Fakultat fur Chemie, Universitat Bielefeld, F.R.G. and Universitat des Saarlandes, Fachbereich 12.1, Werkstoffphysik and Werkstofftechnologie, 6600 Saarbrücken 11, F.R G.

Received March 17, 1982

Transition metal thiometalates, first introduced as ligands in coordination chemistry, can be used to produce heterometal complexes which are either interesting from the structural point of view, or which have unusual electronic properties [1]. No other general preparation route is known for complexes with heterometal aggregates, some of which are also of interest in bioinorganic chemistry.

The reaction of various divalent transition metal cations with thiometalates in solution (*e.g.* in H_2O) takes place as follows:

$$2\,XR_4^+ + 2\,MO_{4-n}S_n^{2-} + M'^{2+} \rightarrow (XR_4)_2[M'(MO_{4-n}S_n)_2] \qquad (1)$$

(M' = Fe, Co, Ni, Pd, Pt, Zn, Cd, Hg; M = Mo, W; n = 2, 3, 4; X = P, As; R = C_6H_5)

whereby bis(thiometalato) complexes, which can be isolated *e.g.* as quaternary phosphonium salts, are formed. In this note we will refer to the fact that in some cases species other than the bis(thiometalato) complexes can also be obtained from thiometalates and M'^{2+} ions.

The reactions in the system $Fe^{2+}/MS_4^{2-}/H_2O$ (M = Mo, W) are more complicated and were not understood until now. Whereas $[Fe(WS_4)_2]^{2-}$ can be isolated from aqueous media [1], the corresponding reaction between Fe^{2+} and MoS_4^{2-} according to eqn. (1) generally gives variable products with the above mentioned cation. But the ^{57}Fe Mössbauer spectrum of a frozen solution of Fe^{2+} and MoS_4^{2-} in oxygen free H_2O (1.2 mmol $(NH_4)_2MoS_4$, 0.5 mmol $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, 10 ml H_2O, 77 K; IS = 0.423 ± 0.035 [mm/s] (α-Fe); QS = 1.060 + 0.070 [mm/s]) shows surprisingly that the complex $[Fe(MoS_4)_2]^{3-}$ is formed (which until now could only be obtained from Fe complexes with S-containing ligands and MoS_4^{2-} [3]). This indicates the high stability of $[Fe(MoS_4)_2]^{3-}$, and demonstrates that sulfur containing organic ligands are not necessary for the reduction.

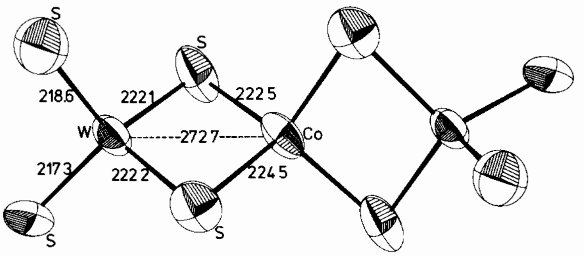


Fig. 1. Structure of $[Co(WS_4)_2]^{3-}$ in crystals of $(NEt_4)(PNP)_2[Co(WS_4)_2]\cdot 2CH_3CN$ (standard deviations for M–S bonds 0.9 ± 0.2 pm).

Therefore it was also possible to isolate directly the $(NMe_4)_3[Fe(MoS_4)_2]$ in high yield from a solution of $(NH_4)_2MoS_4$ and $FeSO_4\cdot 7H_2O$ in CH_3CN/H_2O (1:1).

The different formation tendency and stability of the complexes $[Fe(WS_4)_2]^{n-}$ (M = Mo, W) and $[Co(WS_4)_2]^{n-}$ and the instability of $[Fe(MoS_4)_2]^{2-}$ can be explained as follows: the low-energy MO's of the 3d(M′) type [1] in the Co complexes (these are occupied here, in contrast to those of the Fe complexes with n = 2) and in $[Fe(MoS_4)_2]^{2-}$ are located at lower energy, and in the case of $[Fe(WS_4)_2]^{2-}$ at about the same energy, as the nonbonding ligand orbitals [1]. Thus the unstable, discrete $[Fe(MoS_4)_2]^{2-}$ is stabilized by taking up one electron to form $[Fe(MoS_4)_2]^{3-}$, $[Fe(WS_4)_2]^{n-}$ exists with n = 2 and 3, and the reduction of the Co di-anion takes place in a d level having a higher energy than the ligand orbitals.

Also trianions of Cu^I like the orange $(NEt_4)(PNP)_2[Cu(WS_4)_2]\cdot 2CH_3CN$ (IR: ν(WS) = 476, 466, 446/438 [cm^{-1}]) can be obtained directly (the above mentioned one from $CuSO_4\cdot 5H_2O$ and $(NH_4)_2WS_4$ in CH_3CN (PNP = $[(C_6H_5)_3\ P{=}N{=}P(C_6H_5)_3]^+$)). The (bis)thiometalato complex, the first discrete one of Cu, has practically the same unit cell dimensions as the corresponding Co complex mentioned below.

Other trianions can be obtained by reduction of the dianions. We were now able to isolate violet $(NEt_4)(PNP)_2[Co(WS_4)_2]\cdot 2CH_3CN$, the crystal structure of which could be determined (Fig. 1), by reduction of $(PNP)_2[Co(WS_4)_2]$ with BH_4^- in CH_3CN (space group $P2_12_12$, a = 1252.6(4), b = 3385.2(7), c = 1077.6(3) [pm], Z = 2; R = 0.082 for 3094 observed reflections; IR ν(WS) = 467, 438 [cm^{-1}]; UV/VIS (in CH_3CN): 650, 555, 460 sh, 385 sh, 355 [nm]; $\mu_{eff} = 3.0\ \mu_B$ at 293 K).

Particularly the tetrathiomolybdate – due to the high electron density on the S atom – should form a species in which it acts as a doubly bridging ligand,

0020-1693/82/0000-0000/$02.75

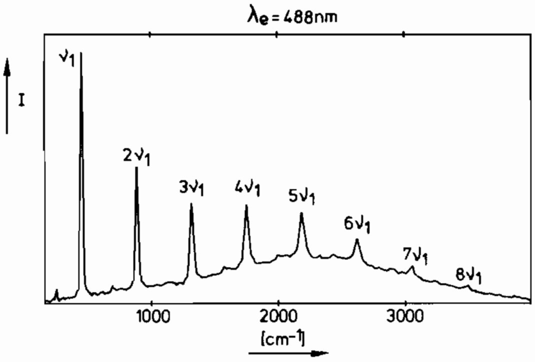
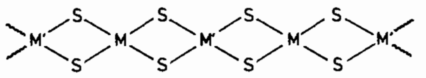


Fig. 2. Resonance Raman spectrum of $(PPh_4)Ag(MoS_4)$ (λ_e = 488 nm).

instead of a bidentate one (in some cases non-homogeneous and X-ray amorphous products with polymeric anions are therefore obtained in the reaction system of eqn. (1) [1]). We could now show for the first time that the above mentioned reaction (1) can also lead to the formation of the following isostructural compounds $(PPh_4)M'(MoS_4)$ (M' = Fe, Co) and $(PPh_4)M'(MS_4)$ (M' = Cu, Ag; M = Mo, W).

$(PPh_4)Cu(MoS_4)$ (red-black), $(PPh_4)Cu(WS_4)$ (orange), $(PPh_4)Ag(MoS_4)$ (dark red) and (PPh_4)-$Ag(WS_4)$ (yellow) are obtained by reaction of $CuSO_4 \cdot 5H_2O$ or $AgNO_3$ with $(PPh_4)_2MS_4$ in CH_3CN and green $(PPh_4)Fe(MoS_4)$ (^{57}Fe-Mossbauer (290 K): IS = 0.41, QS = 0.79 [mm/sec]) by solving the corresponding amorphous product of reaction (1) in DMF (O_2-free and precipitation with diethylether (the thiomolybdato complexes of Cu and Ag cannot yet be obtained in analytically pure form).

The compounds according to their well defined and nearly identical powder diffraction patterns are isostructural, and have practically the same unit cell dimensions [(d values in [Å] and relative intensities for the 8 most intense peaks of $(PPh_4)Cu(WS_4)$: 10.91(25), 9.51(15), 7.25(100), 5.57(25), 5.15(15), 4.82(85), 4.37(40), 4.04(25)]. According to the vibrational spectra and especially to the resonance Raman spectrum of $(PPh_4)M'(MoS_4)$ (M' = Cu, Ag) they contain doubly bridging MS_4^{2-} ligands, and probably chains of $M'S_4$ and MS_4 tetrahedra connected via edges (as in $(NH_4)Cu(MoS_4)$ [1])



Thiometalates like $MoOS_3^{2-}$, MoS_4^{2-} or ReS_4^-, and especially tetrathiomolybdato complexes, give very well defined resonance Raman spectra using the 488 nm exciting line of an Ar laser (Fig. 6 of ref. [1]). In the spectra of the complexes only the lines due to the totally symmetric stretching vibrations of the MoS_4^{2-} chromophore show a strong enhancement of intensity. This offers a unique and very sensitive probe for doubly bridging ligands, as the effect is pronounced if the ligand is symmetrically coordinated. Figure 2 shows the spectrum of $(PPh_4)Ag(MoS_4)$ with only *one* ν_s(MoS) band and 8 overtones, proving that MoS_4^{2-} acts as a doubly bridging ligand [1].

Acknowledgement

We thank the 'Deutsche Forschungsgemeinschaft', the 'Fonds der Chemischen Industrie' and the 'Minister fur Wissenschaft und Forschung (NRW)' for financial support.

References

1 See A. Müller, E. Diemann, R. Jostes and H. Bogge, Angew. Chem. 93, 967 (1981); *ibid., 20,* 934 (1981).
2 See A. Müller and E. Diemann (Ed.), 'Transition Metal Chemistry – Current Problems of General, Biological and Catalytical Relevance', Verlag Chemie, Weinheim, 1981; A. Müller and W. E. Newton (Ed.), 'Nitrogen Fixation Chemical, Biochemical, Genetics Interface', Plenum Press, New York, 1982.
3 D. Coucouvanis, *Acc. Chem. Res., 14,* 201 (1981).