Inorganica Chimica Acta, 83 (1984) L75–L77

New Homo- and Heteronuclear Tetrathiometalato Complexes, Specific to the Fe^{II}/WS_4^{2-} System: The Novel Tetranuclear $[S_2WS_2FeS_2FeS_2WS_2]^{4-}$ Complex with Linear Metal Atom Array

ACHIM MÜLLER*, WINFRIED HELLMANN, CHRISTIAN RÖMER, MICHAEL RÖMER, HARTMUT BÖGGE, RAINER JOSTES and UWE SCHIMANSKI

Faculty of Chemistry, University of Bielefeld, F.R.G.

Received November 7, 1983

By heating or acidifying solutions of MoS_4^{2-} and WS_4^{2-} isopolythioanions (for instance $[WS(WS_4)_2]^{2-}$ [1, 2] see below) can be obtained [1–5]. I the presence of other cations heterometal complexes are formed which can exist with different electron poluations and the structural chemistry of which is very versatile [6]. The object of this paper is to report some new results on the chemistry of thiometalato complexes (species existing with different electron populations, novel complexes isolated from the remarkably versatile Fe^{II}/WS_4^{2-} system, and new isopolythioanions).

Results and Discussion

Species with Different Electron Populations

We were able to isolate black $(PNP)_2(NEt_4)[Co(MoS_4)_2]\cdot 2CH_3CN$ (*1*)[a] (for details of the crystal structure determination of this and the other new compounds see Table I; the structure of the complex anion is shown in Fig. 1a) and could identify $[Co(MoS_4)_2]^{2-}$ formed by reaction of $CoCl_2$ and $(NH_4)_2MoS_4$ in dimethylformamide[b].

The electronic absorption spectrum of $[Co(MoS_4)_2]^{2-}$ is similar to that of $[Co(WS_4)_2]^{2-}$, except for the shift of all bands to lower energy ($\nu_{C.T.}$ (L → Co) = 10.7, $\nu_{C.T.}$ (L → L*) = 22.3 × 10^3 cm^{-1}; for assignments *cf.* [6])[b]. The addition of a strong reducing agent is required to synthesize the $[Co(MS_4)_2]^{3-}$ (M = Mo, W) complexes (*e.g., 1* was obtained from $(NH_4)_2MoS_4$ and $CoCl_2\cdot 6H_2O$ in $CH_3CN/EtOH$ by reduction with $Na(BH_4)$; for $[Co(WS_4)_2]^{3-}$ see [7]) whereas the $[Fe(MS_4)_2]^{3-}$ complexes [6, 8–11] can be obtained directly *without* reducing agents (see the following section).

---

*Author to whom correspondence should be addressed.

[a] PNP ≙ $Ph_3P{=}N{=}PPh_3$.

[b] In a similar way $[Co(MoOS_3)_2]^{2-}$ is formed in a DMSO solution of $CoCl_2$ and Cs_2MoOS_3 ($\nu_{C.T.}$ (L → Co) = 12.2 × 10^3 cm^{-1}); both $[Co(MoS_4)_2]^{2-}$ and $[Co(MoOS_3)_2]^{2-}$ complexes can be reversibly reduced to the corresponding trianions, as shown by cyclic voltammetry. Attempted isolation as PPh_4^+ salts, however, did not give pure samples.

TABLE I. Results of the Crystal Structure Analyses.[a]

Compound	*1*	*2*	*3*	*4*	*5*
Space group	$P2_12_12$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [pm]	1261.0(9)	704.5(5)	1087.5(5)	1239.4(4)	993.0(3)
b [pm]	3393.2(28)	983.2(8)	1279.9(6)	1450.8(4)	1464.1(3)
c [pm]	1084.4(7)	1147.5(10)	3723.4(37)	2988.8(8)	2010.4(6)
α [°]		101.62(6)			
β [°]		94.69(6)	97.43(6)	91.83(2)	111.48(2)
γ [°]		92.16(6)			
V [10^6 pm^3]	4640.0	774.7	5139.1	5371.5	2719.7
Z	2	1	2	4	2
Number of independent reflections ($F_o > 3.92\sigma(F_o)$)	763[b]	3085	6426	6441	5122
Number of variables	23[b]	142	212	223	128
$R = \Sigma \lVert F_o\rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.130	0.041	0.094	0.080	0.107

[a] *1*: $(PNP)_2(NEt_4)[Co(MoS_4)_2]\cdot 2CH_3CN$; *2*: $(NEt_4)_2[Fe(H_2O)_2(WS_4)_2]$; *3*: $(PNP)_2(NEt_4)_2[Fe_2S_2(WS_4)_2]\cdot 3CH_3CN$; *4*: $(PPh_4)_2[MoO(MoS_4)_2]$; *5*: $(PPh_4)_2[WO(WS_4)_2(dmf)]$. [b] Due to the small number of reflections obtained, only the atoms of the anion were refined (isotropically). The parameters of the cations (for the calculation of the F_c's) were taken from the isostructural tungsten compound [7].

0020-1693/84/$3.00

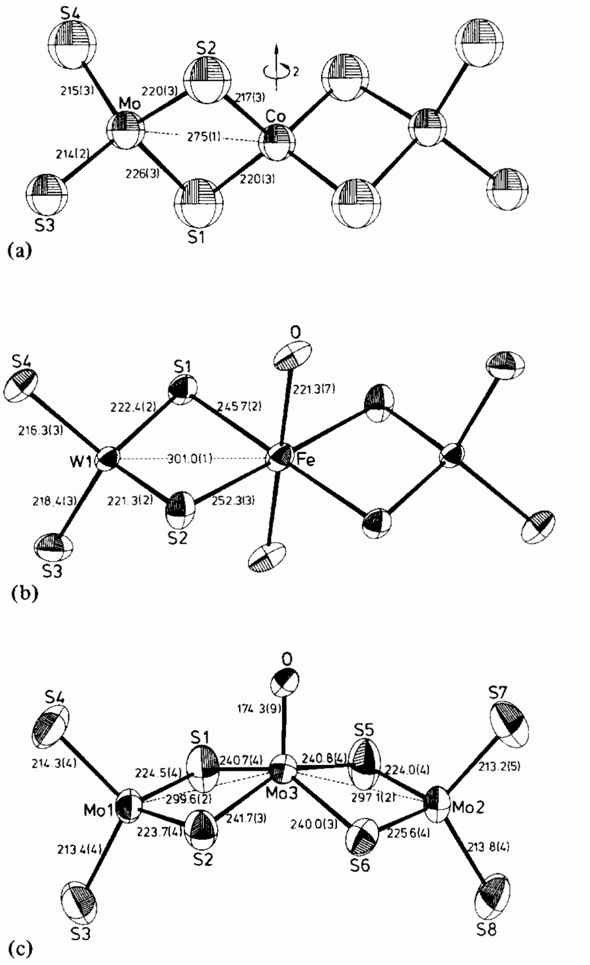


Fig. 1. ORTEP plots of trinuclear MS_4^{2-} complexes (bond lengths in [pm], selected bond angles in [°]). (a): $[Co(MoS_4)_2]^{3-}$ in crystals of *1*. The Co atom lies on a twofold axis. (Mo–Co–Mo 169.6(8); S1–Mo–S2 101.3(11); S3–Mo–S4 111.2(11); S1–Co–S2 104.3(10); Co–S_{br}–Mo 77.0). (b) $[Fe(H_2O)_2(WS_4)_2]^{2-}$ in crystals of *2*. The Fe atom occupies a centre of inversion. (S1–W–S2 107.9(1); S3–W–S4 110.1(1); S1–Fe–S2 92.2(1); O–Fe–S1 90.3(2); O–Fe–S2 90.2(2); O–Fe–W 96.2(2); Fe–S1–W 79.9(1); Fe–S2–W 78.6(1)). (c): $[MoO(MoS_4)_2]^{2-}$ in crystals of *4*. (Mo1–Mo3–Mo2 151.9(1); S1–Mo1–S2 103.9(1); S3–Mo1–S4 111.1(2); S5–Mo2–S6 103.7(1); S7–Mo2–S8 111.1(2); S1–Mo3–O 106.1(3); S2–Mo3–O 104.3(3); S5–Mo3–O 102.6(3); S6–Mo3–O 106.8(3); S1–Mo3–S2 94.1(1); S2–Mo3–S6 77.9(1); S5–Mo3–S6 94.7(1); S1–Mo3–S5 78.1(1); Mo1–S_{br}–Mo3 80.1; Mo2–S_{br}–Mo3 79.3).

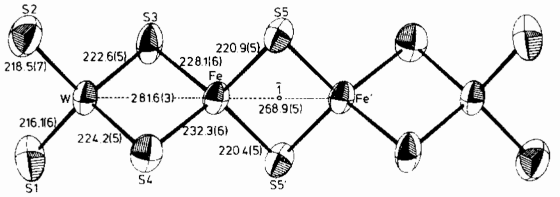


Fig. 2. ORTEP plot of the tetranuclear $[Fe_2S_2(WS_4)_2]^{4-}$ in crystals of *3* (bond lengths in [pm], selected bond angles in [°]). The two halves of the anion are connected by a centre of inversion (S1–W–S2 110.8(2); S3–W–S4 105.4(2); S3–Fe–S4 101.1(2); S5–Fe–S5' 105.0(2); Fe–S3–W 77.3(2); Fe–S4–W 76.2(2); Fe–S5–Fe' 75.1(2)).

Complexes from the Fe^{II}/WS_4^{2-}/(solvent) System

The Fe^{II}/WS_4^{2-}/solvent system is especially interesting. While $[Fe(WS_4)_2]^{2-}$ and $[Fe(WS_4)_2]^{3-}$ can be precipitated directly (and immediately) from an aqueous solution[c] [6, 8, 11], $[Fe_3S_2(WS_4)_3]^{4-}$ [13] is formed in organic solvents after several hours (in high yield only if a small amount of water (yielding S^{2-}) and traces of oxygen (preventing the formation of $[Fe(WS_4)_2]^{3-}$) are present). We have now obtained the remarkable black compound $(NEt_4)_2[Fe(H_2O)_2(WS_4)_2]$ (*2*) from $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2WS_4$, and $(NEt_4)I$ *in aqueous solution* in the presence of saccharoses (structure of the complex anion shown in Fig. 1b). This illustrates that central atoms in bis(thiometalato) complexes may be coordinatively unsaturated [6].

Our recent synthesis has concentrated on novel types of thiometalato complexes with central Fe_xS_y units. We are now able to show that $[Cl_2Fe(WS_4)]^{2-}$ (in O_2 free CH_3CN solution containing ~1% H_2O) reacts witn NaHS to form $[Fe_2S_2(WS_4)_2]^{4-}$. The structure of the 'linear' complex anion in violet crystals of $(PNP)_2(NEt_4)_2[Fe_2S_2(WS_4)_2] \cdot 3CH_3CN$[a] (*3*) is shown in Fig. 2.

Polythiometalates

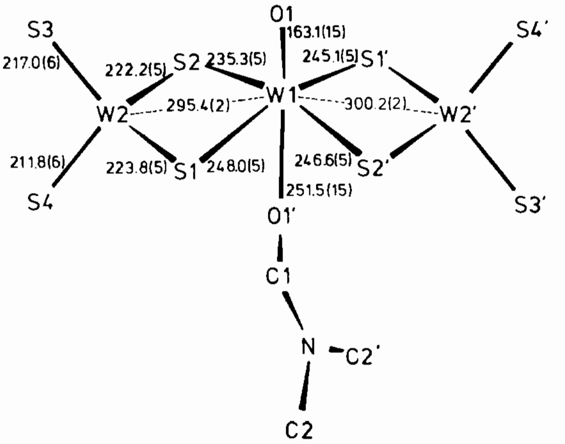
Polythioanions of the type $[MX(MS_4)_2]^{2-}$ (M = Mo, W; X = O, S) [1–3, 5] (except $[MoO(MoS_4)_2]^{2-}$) can be generated in solution directly from the corresponding tetrathioanions. We were also able to get black $(PPh_4)_2[MoO(MoS_4)_2]$ (*4*) in pure form by heating $(NH_4)_2(MoS_4)$ in CH_3CN/EtOH in the presence of $Na(BH_4)$. It contains the first trinuclear isopolythioanion showing no disorder of the MX unit in the crystal lattice [2, 5] (see Fig. 1c). Also the central Mo atom does not coordinate to a sixth ligand as in the corresponding $[WO(WS_4)_2(H_2O)]^{2-}$ [2].

---

[c] The precipitated compound depends on the cation. $(PPh_4)_2[Fe(WS_4)_2]$ can be obtained directly from the components under the conditions described in [12] (addition of a very small amount of hydrazine prevents oxidation of Fe^{II} by air, but is not necessary) and $[(C_6H_5)CH_2N(CH_3)_3]_3[Fe(WS_4)_2]$ *also from an aqueous solution* of WS_4^{2-} and Fe^{2+} after addition of $[(C_6H_5)CH_2N(CH_3)_3]Cl$ (washing of the precipitate with CH_3CN is necessary) [8]. On standing a solution of $(PPh_4)_2[Fe(WS_4)_2]$ in CH_3CN, the brown compound $(PPh_4)Fe(WS_4)$ (probably with a chain structure of the anion [11]) precipitates.

Crystals of red $(PPh_4)_2[WO(WS_4)_2(dmf)]$ (*5*) could be obtained as a minor by-product in the synthesis of $(PPh_4)_2[WS(WS_4)_2]$ (*6*) [2] by heating $(NH_4)_2WS_4$ in dimethylformamide. After adding nitromethane and $(PPh_4)Cl$ (to the filtrated solution at room temperature), filtration of *6* and addition of ether to the mother liquor *5* precipitates slowly besides $(PPh_4)_2[W_2S_4(S_4)(S_2)]$ (*7*) (for details of *7* see [14]).

As the $[WO(WS_4)_2(dmf)]^{2-}$ anion is disordered, no ORTEP plot is given. The structure of the $\{WO(WS_4)_2\}$ fragment is comparable to the corresponding one in $[WO(WS_4)_2(H_2O)]^{2-}$ [2]. The bond distances are given in the following schematic diagram:



Details of all crystal structure determinations have been summarized in Table I. The intensity data were collected on a Syntex $P2_1$ diffractometer with MoKα radiation.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung NRW.

References

1 E. Königer-Ahlborn and A. Müller, *Angew. Chem., 87,* 598 (1975); *Int. Ed. Engl., 14,* 573 (1975).
2 A. Müller, H. Bögge, E. Krickemeyer, G. Henkel and B. Krebs, *Z. Naturforsch., 37b,* 1014 (1982).
3 A. Müller, R. G. Bhattacharyya, E. Königer-Ahlborn, R. C. Sharma, W. Rittner, A. Neumann, G. Henkel and B. Krebs, *Inorg. Chim. Acta, 37,* L493 (1979).
4 F. Sécheresse, J. Lefebvre, J. C. Daran and Y. Jeannin, *Inorg. Chem., 21,* 1311 (1982).
5 W.-H. Pan, M. E. Leonowicz and E. I. Stiefel, *Inorg. Chem., 22,* 672 (1983).
6 A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., 93,* 957 (1981);
Int. Ed. Engl., 20, 934 (1981).
7 A. Müller, W. Hellmann, U. Schimanski, R. Jostes and W. E. Newton, *Z. Naturforsch., 38b,* 528 (1983).
8 J. W. McDonald, G. D. Friesen, W. E. Newton, A. Müller, W. Hellmann, U. Schimanski, A. Trautwein and U. Bender, *Inorg. Chim. Acta, 76,* L297 (1983);
A. Müller and W. Hellmann, unpublished results.
9 D. Coucouvanis, E. D. Simhon and N. C. Baenziger, *J. Am. Chem. Soc., 102,* 6644 (1980).
10 J. W. McDonald, G. D. Friesen and W. E. Newton, *Inorg. Chim. Acta, 46,* L79 (1980).
11 A. Müller, W. Hellmann, J. Schneider, U. Schimanski, U. Demmer, A. Trautwein and U. Bender, *Inorg. Chim. Acta, 65,* L41 (1982).
12 A. Müller and S. Sarkar, *Angew. Chem., 89,* 748 (1977); *Int. Ed. Engl., 16,* 705 (1977).
13 A. Müller, W. Hellmann, H. Bögge, R. Jostes, M. Römer and U. Schimanski, *Angew. Chem., 94,* 863 (1982);
Int. Ed. Engl., 21, 860 (1982);
Angew. Chem. Suppl., 1757–1776 (1982).
14 A. Müller, M. Römer, C. Römer, U. Reinsch-Vogell, H. Bögge and U. Schimanski, *Monatshefte für Chemie* (to be published).