

07-Crystallography of Organometallic and Coordination Compounds

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PS-07.03.03 THE DESIGNED SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF TWO NOVEL HETEROTRIMETALLIC LINEAR COMPLEXES OF $[\text{Et}_4\text{N}][(\text{Ph}_3\text{P})_2(\text{AgS}_2\text{MS}_2\text{Fe})\text{Cl}_2]$ ($\text{M}=\text{Mo}, \text{W}$). By Xintao Wu*, Tianlu Sheng and Shaowu Du, State Key Laboratory of Structure Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002 China

The complex of $[\text{S}_2\text{MoS}_2\text{FeCl}_2]^{2-}$ (R. H. Tieckelmann, H. C. Silvis, T. A. Kent, B. H. Huynh, J. V. Waszczak, Boon-Keng Teo, and B. A. Ayerill. *J. Am. Chem. Soc.*, 1980, 102, 5550-5559) has served as a model compound for the active center of the FeMo cofactor (FeMo-co). The MoS_4^{2-} anion has been claimed to be the most effective antagonist of copper metabolism. The extensive research that has been performed on MoS_4^{2-} -Cu(I) complexes shows rich structural varieties. A number of MoS_4^{2-} -Ag(I) complexes have now been obtained. Recently, heterotrimetallic compounds $[(\text{PPh}_3)_2\text{AgS}_2\text{MS}_2\text{Cu}(\text{CN})]^-$ ($\text{M}=\text{Mo}, \text{W}$) (S.-W. Du, N.-Y. Zhu, P.-C. Chen, X.-T. Wu and J.-X. Lu. *Polyhedron*, 1992, 11, 109-113) and $[(\text{PPh}_3)_2\text{AgS}_3\text{MOCu}(\text{CN})]^-$ ($\text{M}=\text{Mo}, \text{W}$) (a) S.-W. Du, N.-Y. Zhu, P.-C. Chen, X.-T. Wu and J.-X. Lu. *J. Chem. Soc. Dalton. Trans.*, 1992, 339-344. b) N.-Y. Zhu, S.-W. Du, P.-C. Chen, X.-T. Wu, J.-X. Lu. *J. Coord. Chem.*, 1992, 26, 35-43) have been synthesized in our laboratory. The anionic fragment $[\text{MS}_4\text{FeCl}_2]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) may be expected to combine with another metal complex to form a heterobimetallic complex, for example the type $[\text{Cl}_2\text{FeS}_2\text{MS}_2\text{FeCl}_2]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) cluster, but no heterotrimetallic complexes of this series are reported yet. In this paper, the designed synthesis of two novel heterotrimetallic complexes is reported.

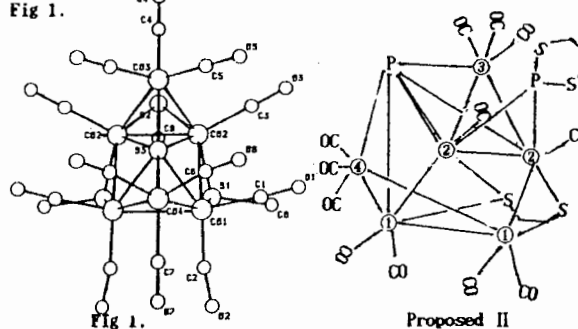
The complexes $[\text{Et}_4\text{N}][(\text{Ph}_3\text{P})_2(\text{AgS}_2\text{MoS}_2\text{Fe})\text{Cl}_2]$ (I) and $[\text{Et}_4\text{N}][(\text{Ph}_3\text{P})_2(\text{AgS}_2\text{WS}_2\text{Fe})\text{Cl}_2]$ (II), have been obtained by reaction of $[\text{Et}_4\text{N}][\text{S}_2\text{MS}_2\text{FeCl}_2]$ ($\text{M}=\text{Mo}, \text{W}$) with $\text{Ag}(\text{PPh}_3)_3\text{NO}_3$ in $\text{MeCN}/\text{CH}_2\text{Cl}_2$. Complex I crystallizes in the triclinic space group $\text{P}\bar{1}$ (No. 2) with $Z=2$ and unit cell parameters $a=13.41(1)\text{\AA}$, $b=15.54(1)\text{\AA}$, $c=12.30(1)\text{\AA}$, $\alpha=105.24(6)^\circ$, $\beta=94.63(7)^\circ$, $\gamma=101.38(6)^\circ$, and $V=2399(4)\text{\AA}^3$. Complex II is isomorphous with I and has unit cell parameters $a=13.457(5)\text{\AA}$, $b=15.601(6)\text{\AA}$, $c=12.338(4)\text{\AA}$, $\alpha=105.20(3)^\circ$, $\beta=94.61(4)^\circ$, $\gamma=101.43(4)^\circ$, and $V=2426(2)\text{\AA}^3$. The lengths of the Mo-Fe bond in complex I and the W-Fe bond in complex II are $2.756(2)\text{\AA}$ and $2.786(2)\text{\AA}$, respectively; while the distances Mo-Ag in complex I and W-Ag in complex II are $3.033(2)\text{\AA}$ and $3.076(1)\text{\AA}$, respectively.

PS-07.03.04 SEMI-INTERSTITIAL AND BRIDGING S- OR P-CONTAINING HEXANUCLEAR COBALT CARBYNOL CLUSTERS. By H. Xiang*, L. Qiwang, L. Shutang, Z. Liping and W. Baoshan, Department of Chemistry, Inner Mongolia University, China.

The reactions of CH_3SPCl_2 and $\text{Cl}_2\text{PSCH}_2\text{CH}_2\text{SPCl}_2$ with $\text{Co}(\text{CO})_8$ give $\text{Co}_6(\mu_6\text{-S})(\mu\text{-SCH}_3)_3(\text{CO})_{12}$ I and $\text{Co}_6(\mu_6\text{-P})(\mu_4\text{-SCH}_2\text{CH}_2\text{S})(\mu\text{-PSCH}_2\text{CH}_2\text{S})(\text{CO})_{12}$ II, respectively. The Co_6 metal cores of I and II, which are not compact, have eight metal-metal bonds and occupy six vertexes of a cube-octahedron. They have two octahedral triangular faces and a cubic square face.

The fragmentation of the ligand precursors RSPCl_2 and $\text{Cl}_2\text{PSR}'\text{SPCl}_2$ yield five kinds of bridging ligands: $\mu_6\text{-S}$, $\mu_6\text{-P}$, $\mu_4\text{-SR}'\text{S}$, $\mu\text{-PSR}'\text{S}$, and $\mu\text{-SR}$ in I and II. The semi-interstitial bridging $\mu_6\text{-S}$ or $\mu_6\text{-P}$ atom is in the center of the cube-octahedron are linked to the Co_6 core by six M-E (S or P) interactions. The bridging $\mu_4\text{-SCH}_2\text{CH}_2\text{S}$ or two bridging $\mu\text{-SCH}_3$ are linked to the square face of the Co_6 core by four M-S bonds and are on the opposite side of the interstitial S or P atom. Another bridging $\mu\text{-SCH}_3$ or $\mu\text{-PSCH}_2\text{CH}_2\text{S}$ is linked to the $\text{Co}(2)\text{-Co}(2)'$ edge of the cubic square face. All these bridging interactions are important factors in stabilizing these two unusual half-cube-octahedron geometries, which also showed unusual bonding modes (six M-E bonds and interstitial $\mu_6\text{-S}$ or $\mu_6\text{-P}$, etc.).

The analytical data, IR (vac), ^1H NMR and MS spectra are consistent with the proposed structures and the molecular structure of I determined by x-ray diffraction is shown in Fig 1.



- (1. Liu, S.T., H.X., Liu, Q.W., & Zhang, W.T. (1991). *Chin. Chem. Lett.* 2, 335-338.
2. Gervasio, G., Rossetti, R., & Stanghellini, P.L. (1984). *Inorg. Chem.* 23, 2073.

PS-07.03.05 Experimental and Theoretical Charge Density Study for the Rh-Rh Metal-Metal Bond By Kuan-Jiuh Lin* and Yu Wang, Department of Chemistry, National Taiwan University, Taipei, Taiwan

Single crystal of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{py})_2$ was reinvestigated by X-ray diffraction at 133K in the aim of understanding the metal-metal bond of a 4d-transition metal, rhodium. The space group of the crystal is monoclinic $\text{C}2/c$ and the cell parameters are $a=9.897(2)$, $b=16.157(2)$, $c=12.504(3)\text{\AA}$, $\beta=96.709(2)^\circ$ and $Z=4$. Each rhodium(II) ion is coordinated to four oxygen atoms of the acetate ligand in D_{4h} symmetry within the standard deviation. The asphericity in electron density around each rhodium is quite apparent in the deformation density distribution and is in accordance with the phenomena prediction by the simple crystal field theory. The Rh-Rh distance is $2.4017(2)\text{\AA}$ and there are some positive deformation electron density distribution along the Rh-Rh bond. The detail chemical bond characters are going to be presented in terms of experimental X-X deformation density