

09.4-30 THE CRYSTAL AND MOLECULAR STRUCTURE OF "SERIES G" MODEL COMPOUNDS FOR THE ACTIVE CENTER OF NITROGENASE. By Huang Liangren and Lu Jiayi (C.S. Lu), Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China.

In an attempted synthesis of model compounds of the Fuzhou "string-bag" structural type by vigorous reduction of $(\text{NH}_4)_2\text{MoS}_4$ and FeCl_3 by means of EtMgBr , three groups of dark-colored crystals, designated respectively as GA, GB and GC, were isolated upon extraction of the reaction products with N,N -dimethylformamide (DMF). X-ray diffraction studies were carried out for two typical crystals of GA: G-4 with a bulk elemental composition $(\text{Mg}, 6\text{DMF})_6(\text{Mo}_6\text{Fe}_3\text{S}_{25}\text{Cl}_{22})$ and G-4' recrystallized from dimethylsulfoxide (and thus containing Mg.6DMSO instead) and one typical crystal of GB: G-2 with a bulk elemental composition $(\text{Mg}, 6\text{DMF})_4(\text{MoFe}_{10}\text{S}_7\text{Cl}_8\text{Br}_{10})$. A noteworthy feature of the diffraction patterns of G-4 and G-4' is that they look very similar to each other; in particular, these crystals have practically identical triclinic unit cells of the following dimensions: $a_0 = 11.27$, $b_0 = 9.47$, $c_0 = 9.25 \text{ \AA}$; $\alpha = 87.2$, $\beta = 71.2$, $\gamma = 74.90^\circ$; $Z = 1$ (referred to Mg); space group $C_1 - P1$, as long as they are recrystallized from DMF. With G-4' a somewhat different unit cell is obtained belonging to space group $C_1 - P1$. The possibility exists that the compounds crystallize in a clathrate structure, with different cluster dianions statistically imbedded in a six-sided cage of $(\text{Mg}, 6\text{L})^{2+}$. No structural investigation was made for GC, one typical example of which is G-806 with the bulk elemental composition $(\text{Mg}, 6\text{DMF})(\text{Mo}_3\text{Fe}_2\text{S}_2\text{X}_4)$. Careful analysis of the diffraction data for both G-4 and G-4' shows that the cluster dianions are mainly composed of $K_A: (\text{MoFe}_4\text{X}_2)^{2-}$, with dianions of at least another type $K_D: (\text{Fe}_2\text{X}_6)^{2-}$. Similarly, the cluster dianions for G-2 are composed of at least three different types: $K_B: (\text{MoFeS}_2\text{X}_4)^{2-}$; $K_C: (\text{Fe}_2\text{S}_2\text{X}_4)^{2-}$; $K_D: (\text{Fe}_2\text{X}_6)^{2-}$. The relevant bond distances and bond angles for G-4, G-4' and G-2 are listed in the following table. The origin of the reduction activity of GB compounds under pseudo-enzyme-catalyzed conditions is now under investigation. Finally, it is likely that the anions in the GC series are mainly composed of the cluster dianions K_C .

Structure of the Dianions $(\text{M}_2\text{B}_2\text{X}_2\text{T}_2)^{2-}$

Atomic Compositions in $(\text{M}_2\text{B}_2\text{X}_2\text{T}_2)^{2-}$

	G-4	G-4'	G-2
M_1	Fe	0.5Mo	Fe
M_2	0.89Mo+0.11Fe	0.5Fe	0.21Mo+0.79Fe
B	0.89 S+0.11Cl	S	0.73 S+0.27Cl
X_1	Cl	0.5 S	0.74Cl+0.26Br
X_2			0.47Br+0.53Cl
T_1	0.89 S+0.11Cl	0.5Cl	0.74Cl+0.26Br
T_2			

Table. Structural Parameters of the Dianions $(\text{M}_2\text{B}_2\text{X}_2\text{T}_2)^{2-}$

Dist (\AA) or Angle ($^\circ$)	G-4	G-4'	G-2
M_1-M_2	2.762	2.763	2.694
B_1-B_2	3.580	3.577	3.485
M_1-B_1, M_2-B_2	2.267, 2.248	2.262	2.216, 2.184
M_1-B_2, M_2-B_1	2.273, 2.256	2.258	2.243, 2.177
M_1-X_1, M_2-T_2	2.268, 2.161	2.185	2.223, 2.320
M_1-X_2, M_2-T_1	2.213, 2.232	2.190	2.298, 2.280
$X_1-M_1-X_2, T_1-M_2-T_2$	110.5, 109.8	109.5	105.9, 109.1
$X_1-M_1-B_1, T_2-M_2-B_2$	106.0, 113.8	110.4	117.1, 104.2
$X_1-M_1-B_2, T_2-M_2-B_1$	112.4, 106.8	110.0	111.2, 108.9
$X_2-M_1-B_1, T_1-M_2-B_2$	107.8, 111.8	109.8	109.6, 113.0
$X_2-M_1-B_2, T_1-M_2-B_1$	115.2, 109.1	112.4	110.2, 115.0
$B_1-M_1-B_2, B_1-M_2-B_2$	104.1, 105.3	104.6	102.8, 106.1
$M_1-B_1-M_2, M_1-B_2-M_2$	75.3, 75.3	75.4	75.6, 75.0
R	0.050	0.066	0.068

09.4-31 THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPYRIDINE (S-METHYLTHIOSEMICARBAZONE SALICYL-ALDEHYDATO)COBALT(II)TRICHLOROPYRIDINE COBALTAT (II). By Vladimir Divjaković and Vukadin Leovac, Institute of Physics and Institute of Chemistry, Faculty of Natural Sciences, University of Novi Sad, 21000 Novi Sad, Dr. I. Djuričića 4, Jugoslavija.

The crystal structure of the title compound, empirical formula and asymmetric unit $\text{Co}_2\text{C}_{25}\text{H}_{30}\text{N}_7\text{O}_5\text{SCL}_3$ has been solved and refined to $R = 0.068$. The space group was $P1$ with $a = 9.005$, $b = 11.832$, $c = 16.864 \text{ \AA}$; $\alpha = 100.34$, $\beta = 92.38$, $\gamma = 94.27^\circ$; $\rho = 1.42 \text{ g/cm}^3$ (meas.).

The unit cell contains asymmetric complex cations $[\text{Co}(\text{HL})\text{Py}_3]^+$ and $[\text{CoCl}_3\text{Py}]^-$ as anions, where HL is the residuum of the tridentate NNO salicylaldehyde S-methylthiosemicarbazone. The cobalt atom belonging to the complex cation is octahedrally coordinated through the five nitrogens both from the chelate ligand and pyridines and one oxygen of the chelate ligand. Unlike this, the cobalt atom from the anion is tetrahedrally coordinated through the three chlorine atoms and one pyridine nitrogen. The conformation of the chelate ligand shows a nearly planar arrangement.

09.4-32 SECONDARY EXPLOSIVES OF SUBSTITUTED TETRAZOLATOAMMINE COBALT COMPLEXES*. E. J. Graeber and B. Morosin, Sandia National Laboratories,** Albuquerque, New Mexico, 87185.

Various inorganic coordination compounds with substituted tetrazolatoammine ligands are being evaluated for their explosive properties. The electron withdrawing characteristics of substituents on the five member ring of the ligand alter the bonding capabilities and hence the nature of these energetic compounds.

Substituents thus far studied (Graeber and Morosin, Oklahoma ACA meeting, 1978; *ibid*, Eufaula ACA meeting, 1980; Ortega, Campana and Morosin, Calgary ACA meeting, 1980) have included cyano, methyl, phenyl, and 3,5-dinitrophenyl groups on the tetrazole ring as well as the related amidino chelate. Typically cobalt is octahedrally coordinated to ammine groups with $\langle \text{Co-N} \rangle = 1.97 \text{ \AA}$, with the ammine opposite the tetrazole ligand being a bit longer (2.00 \AA), and a shorter average tetrazole ring nitrogen at $\sim 1.91 \text{ \AA}$ (in the amidino chelate, the additional ring nitrogen is at 1.94 \AA).

The 5-cyano and 5-methyl perchlorate analogs show a striking similarity of crystal packing in projection even though the symmetry elements are along different directions. This points to the importance of molecular configuration in the two compounds. The perchlorate analogs also tend to exhibit some radiation induced damage; for these materials the perchlorate ions generally are disordered. Our most radiation sensitive analog, the 3,5-dinitrophenyl compound, also has linear channels occupied with water molecules.

The bonding of the tetrazole ring to cobalt, the hydrogen bonding to the perchlorate ions and the relationship of structure to stability for all the materials will be discussed.

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