

09.4-27 STRUCTURAL INVESTIGATIONS ON α -BIS-(N-METHYLSALICYLALDIMINATO)-ME(II), ME = Ni, Cu, Pd. By W. Steurer and W. Adlhart, Institut für Kristallographie und Mineralogie der Universität München, München, Federal Republic of Germany.

The title compounds with Me = Ni, Cu show a first order phase transition from a monoclinic to an incommensurate phase with orthorhombic average structure. The one dimensional displacively modulated structure ($\bar{q} = 0.3 \cdot a^*$) changes by a second order transformation into a commensurate orthorhombic modification. The transition temperatures are for the Ni(II)-complex 155(2) K and 205(5) K, for the Cu(II)-chelate 257(2) K (W. Adlhart and V.K. Syal, Z. Krist. (1981) 154, 227-255) and 505(5) K. The isotopic Pd(II)-compound exists only in the monoclinic modification.

The crystal structures of all phases have been determined by single-crystal X-ray methods. The low temperature modification has the space group Ic , $Z = 4$. The monoclinic angle increases with decreasing temperature and is equivalent to the tilt of the molecules which are stacked like columns.

The orthorhombic phase crystallizes in the space group $Iba2$, $Z = 4$, not $Ibam$ (E.C. Lingafelter, G.L. Simmons, B. Morosin, C. Scheringer and C. Freiburg, Acta Cryst. (1961) 14, 1222). The mirror symmetry is violated by high anisotropic temperature factors U_{15} , U_{25} and slight out-of-plane distortions of the molecules. The lattice constants of the isotopic compounds are quite similar in spite of different distances Me(II)-N, respectively Me(II)-O for the various ions.

A model for the mechanism of the phase transition is discussed.

09.4-28 THE CRYSTAL STRUCTURE OF INCLUSION COMPOUND $(Mo(S_2CN(Et)_2)_4)^+(FeCl_4)^-(PhCH_2SSCH_2Ph)$. By Mei-Cheng Shao, Gen-Pei Li, You-Chi Tang, Institute of Physical Chemistry, Peking University, Beijing; Dung-Yao Guo, Pin-Zhe Lu, Yu-Guo Fan, Institute of Theoretical Chemistry, Jilin University, Jilin, The People's Republic of China.

Very recently we have identified an intermediate product obtained during the course of studies on fixation of nitrogen as

$(Mo(S_2CN(Et)_2)_4)^+(FeCl_4)^-(PhCH_2SSCH_2Ph)$. The starting materials were $MoCl_5$, $FeCl_3$, sodium dithiocarbamate ($NaS_2C_5H_{10}$) and benzylthioalcohol. The reaction takes place in methanol solution.

The compound crystallizes in space group Cc with unit cell constants $a=17.900(5)$ Å, $b=18.466(7)$ Å, $c=15.483(4)$ Å, $\beta=92.78(2)^\circ$, $d=1.47$ g.cm $^{-3}$ and $Z=4$.

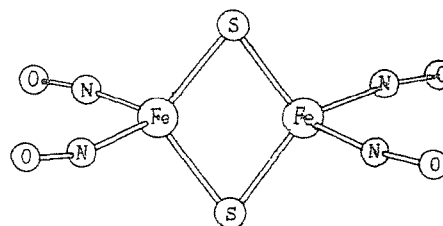
Intensities of 3499 independent reflections were collected with a diffractometer using $MoK\alpha$ radiation. The coordinates of Mo were derived from a Patterson function. The remaining non-hydrogen atoms were found from successive Fourier and difference syntheses. The block-diagonal least-square refinement for coordinates and temperature factors of all atoms gave a final discrepancy factor $R=0.054$.

The result of the structure analysis shows that the inclusion compound consists of three kinds of species: the oppositely charged complex ions $Mo(S_2CN(Et)_2)_4^+$ and $(FeCl_4)^-$ form a very interesting host framework with channels extending along the c -axis and including guest disulfide molecules $C_6H_5CH_2SSCH_2C_6H_5$.

09.4-29 THE CRYSTAL AND MOLECULAR STRUCTURE OF A TYPICAL RED ROUSSIN SALT $(Me_4N)_2[Fe_2S_2(NO)_4]$. By Lin Xianti, Huang Jinling (Huang Chinling) and Lu Jiayi (C. S. Lu), Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China.

The title compound was prepared by addition of $(Me_4N)OH$ to an aqueous solution of potassium red Roussinate $K_2[Fe_2S_2(NO)_4]$. The dark brown crystals so obtained are stable under a dinitrogen atmosphere.

The crystals are monoclinic belonging to the space group $P2_1/a$ with $a = 14.804$, $b = 14.086$, $c = 9.382$ Å, $\beta = 92.2^\circ$ and $Z = 4$. The intensities were collected on a Philips PW1100 four-circle diffractometer with $MoK\alpha$ radiation. The structure was solved by the heavy atom technique and refined by block-diagonal least-squares with anisotropic temperature factors for 2681 independent reflections ($R = 0.066$). The results of our structure investigation show that there are two independent sets of centrosymmetrical anions in the unit cell with center of symmetry located respectively at the special positions (a): $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and (d): $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, while the nitrogen atoms of the tetramethylammonium cations are located in two sets of general positions (e) with $X_1 = Z_1 = 0$, $Y_1 = 1/3$ and $X_2 = 1/3$, $Y_2 = Z_2 = 1/2$. The important bond lengths and angles of the two non-equivalent anions follow.



Bond lengths (Å) and angles (°)		
	Set I	Set II
Fe-S	2.245, 2.242	2.247, 2.250
Fe-N	1.664, 1.659	1.677, 1.660
N-O	1.200, 1.202	1.165, 1.178
Fe...Fe	2.715	2.713
S...S	3.575	3.565
Fe-S-Fe	74.5	74.2
S-Fe-S	105.5	105.8
S-Fe-N	109.6, 109.2	108.2, 108.9
N-Fe-N	113.0	113.6