09.4-27 STRUCTURAL INVESTIGATIONS ON α-BIS- (N-METHYLGLUTATHIOLIMINATO)-NE(II), NE = Ni, Co, Pd. By K. Hayner and W. Adlhart, Institut für Kristallographie und Mineralogie der Universität München, München, Federal Republic of Germany.

The title compounds with Me = Ni, Co show a first order phase transition from a monoclinic to an incommensurate phase with orthorhombic average structure. The one dimensional displaceably modulated structure \( (2 = 0.3 \times 5^\circ) \) changes by a second order transformation into a commensurate orthorhombic modification. The transition temperatures are for the Ni(II)-complex 153(2) K and 205(5) K, for the Co(II)-chelate 237(2) K (W. Adlhart and W.K. Syal, Z. Kristal. (1981) 152, 227-233) and 205(3) K. The isotypic 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 \( \text{Pcm} \), \( Z = \frac{4}{3} \). 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 \( \text{Pcab} \), \( Z = 4 \), with \( a=17.900(5) \), \( b=18.466(7) \), \( c=15.463(4) \) Å, \( \alpha=92.78(2)^\circ \), \( \beta=149.2(2)^\circ \), and \( \gamma=120(30)^\circ \). The lattice constants of the isotypic compounds are quite similar in spite of different distances \( \text{Ni(II)}-\text{Ni} \), respectively \( \text{Pd(II)}-\text{Pd} \), for all four phases.

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

09.4-28 THE CRYSTAL STRUCTURE OF INCLUSION COMPOUND \((\text{Mo}(\text{S}_2 \text{CN(Et)}_2)_4)^+\text{(FeCl}_4^-)(\text{PhCH}_2\text{SSCH}_2\text{Ph})\). By Mei-Cheng Shao², Gen-Fei Li, You-Chi Tang, Institute of Physical Chemistry, Peking University, Beijing; Dung-Yao Guo, Pin-Zhe Lu, Yuan-Guo Pan, 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 \((\text{Mo}(\text{S}_2 \text{CN(Et)}_2)_4)^+\text{(FeCl}_4^-)(\text{PhCH}_2\text{SSCH}_2\text{Ph})\). The starting materials were \text{MoCl}_4^2-, \text{FeCl}_4^-, sodium dithiocarbamate (NaS\text{C(H}_2\text{)}_2\text{S}), and benzylthioalcohol. The reaction takes place in methanol solution.

The compound crystallizes in space group \( \text{Cm} \) with unit cell constants \( a=17.900(5) \) Å, \( b=18.466(7) \) Å, \( c=15.463(4) \) Å, \( \alpha=92.78(2)^\circ \), \( \beta=149.2(2)^\circ \), \( \gamma=120(30)^\circ \). Intensities of 3499 independent reflections were collected with a four-circle diffractometer using \( \text{MoK}_\alpha \) radiation. The coordinates of \( \text{Mo} \) 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 \((\text{Mo}(\text{S}_2 \text{CN(Et)}_2)_4)^+ \) and \((\text{FeCl}_4^-)\) form a very interesting host framework with channels extending along the \( c \)-axis and including guest disulfide molecules \( \text{C}_5\text{H}_3\text{CH}_2\text{SSCH}_2\text{C}_6\text{H}_5 \).