

**[s11.m1.p19.la]** A New Commensurate Structure of Co-åkermanite. K. Hagiya, K. Kusaka<sup>a</sup>, M. Ohmasa and K. Iishi<sup>b</sup>. *Dept. of Life Science, Himeji Inst. of Tech., Kohto 3-2-1, Kamigori, Akogun, Hyogo 678-1297, Japan.* <sup>a</sup>*Dept of Material Science, Himeji Inst. of Tech.* <sup>b</sup>*Dept of Mineralogical Science and Geology, Yamaguchi Univ., Yoshida, Yamaguchi 753-0841, Japan.*  
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The incommensurate structure of Co-åkermanite, with the two modulation wave vectors  $\mathbf{k}_1=q(\mathbf{a}^*+\mathbf{b}^*)$ ,  $\mathbf{k}_2=q(-\mathbf{a}^*+\mathbf{b}^*)$  where  $\mathbf{a}^*$  and  $\mathbf{b}^*$  are the reciprocal lattice vectors of the basic structure and  $q=0.2913$ , was determined at room temperature by a five-dimensional refinement based on the superspace group  $P(P4_2/m / p4mg)^1$ . Recently, Riester and Böhm<sup>2</sup> found a lock-in phase transition of the incommensurate phase into an approximately commensurate phase with  $q=0.324(6)$  in the temperature range  $155\text{K} \leq T \leq 270\text{K}$ . They observed reflections violating the extinction rule for  $P_21_1$  and gave a structure model of twinned micro-domains of the space group  $P\bar{4}$ <sup>3</sup>. In the present study we could hardly observe the violation of the extinction rule. Thus another model was tried for the commensurate structure determination.

A fragment of Co-åkermanite was mounted in a N<sub>2</sub> gas-flow cooling system (Rigaku Co., Ltd.) installed on an Enraf-Nonius CAD-4 diffractometer. Temperature dependence of the modulation wave vectors was examined *in situ* to determine the transition temperature between the incommensurate and commensurate phases. The temperature of the sample was varied from 493K to 96K with arbitrary intervals. The profile of the satellite reflection 34001 splits into two peaks at 242K. The  $q$ -values of the two peaks are 0.333(1) i.e. 1/3 and 0.303(1) respectively. Thus the  $q$ -value jumps discontinuously at the IC-C transition. Below 242K the  $q$ -value shows no change with temperature variations. In heating cycle, the  $q$ -value jumps almost discontinuously from 0.332(1) to 0.310(1) in the temperature range between 279K and 283K. The intensities of the main and satellite reflections of the  $3 \times 3 \times 1$  commensurate phase were determined at 170K. The cell parameters  $a=23.51(4)\text{Å}$ ,  $c=5.025(1)\text{Å}$  with diffraction symmetry  $4/mmm$  were determined. Several models were tried for structure determination and a model of twinned micro-domains with the space group  $P2_12_12$  gives good agreement between the observed and calculated intensities. The structure determined by Riester *et al.*<sup>3</sup> is considered to be derived from a part of the incommensurate structure and the structure determined in this study is similar to another part. The latter contains more bundles (which are called clusters by them) of 6-fold coordination of Ca than the former.

[1] Hagiya K., Ohmasa M. and Iishi K. "The modulated structure of synthetic Co-åkermanite, Ca<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>," *Acta Cryst.*, (1993), **B49**: 172-179.

[2] Riester M. and Böhm H. "Phase transition of modulated Co-åkermanite, Ca<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>," *Z. Krist.*, (1997), **212**: 506-509.

[3] Riester M., Böhm H. and Petricek V. "The commensurately modulated structure of the lock-in phase of synthetic Co-åkermanite, Ca<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>," *Z. Krist.*, (2000), **215**: 102-109.

**[o.m12.p21.la]** Crystal and molecular structure of cobalt 2-methylthio-8-mercaptoquinolate. L. Pechl, Yu. Bankovsky<sup>1</sup>, A. Kemme<sup>2</sup>, E. Silina<sup>1</sup>, J. Lejejs<sup>1</sup>. *Institute of Inorganic Chemistry of the Riga Technical University, Latvian Institute of Organic Synthesis.*

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The present study is a part of systematic research of internal complexes of 8-mercaptoquinoline and its derivatives.

The title compound was prepared from CoCl<sub>2</sub>·6H<sub>2</sub>O and 2-methylthio-8-mercaptoquinoline in ethanol solution. Crystals suitable for X-ray analysis were obtained by recrystallization from CHCl<sub>3</sub> / C<sub>2</sub>H<sub>5</sub>OH.

A black crystal of cobalt 2-methylthio-8-mercaptoquinolate Co[C<sub>9</sub>H<sub>5</sub>(SCH<sub>3</sub>)NS]<sub>2</sub> was chosen for X-ray diffractometric measurements (Syntex P2<sub>1</sub>, λMoKα). R=0.0779 for 2138 reflections with I>2σ(I).

The crystals are triclinic, the unit cell parameters: a= 8.379(2); b= 9.794(2); c= 12.888(3) Å; α= 97.02(2); β= 91.71(2); γ= 109.43(2)°; V= 987.1(4) Å<sup>3</sup>; Z= 2; space group P-1.

The complex is formed by the discrete molecules Co[C<sub>9</sub>H<sub>5</sub>(SCH<sub>3</sub>)NS]<sub>2</sub>. The sulfur and nitrogen atoms act as bidentate ligands forming two five-membered metal-containing cycles. The cobalt atom forms a distorted coordination tetrahedron with two sulfur and two nitrogen atoms. The Co-S and Co-N bond lengths are 2.255(3); 2.265(3) and 2.064(8); 2.061(8)Å respectively. The chelate angles at the cobalt atom are 87.8(3) and 88.2(2)° whereas all inter-ligand angles at Co atom are in the range of 119.3(2) - 124.3(3)°. The dihedral angle between the coordination planes S1CoN1 / S2CoN2 is 88.0°. Each of two quinoline ring is approximately planar and dihedral angle between those least-square planes is 89.7°. The Co atoms are displaced by 0.34 and -0.13Å, but sulfur atoms by -0.11 and -0.05Å from the quinoline ring planes 1 and 2 respectively, therefore the break of the five-membered metal-containing cycles is formed along the lines S1...N1 and S2...N2 by dihedral angles of 15.5 and 3.5° respectively. Methylthio group in position "2" of the quinoline ring is situated in the ligand plane but exerts the considerable influence of the complex formation.

The complex Co[C<sub>9</sub>H<sub>5</sub>(SCH<sub>3</sub>)NS]<sub>2</sub> (I) is compared with the previously studied ones Co[C<sub>9</sub>H<sub>5</sub>(CH<sub>3</sub>)NS]<sub>2</sub> (II), Co(C<sub>9</sub>H<sub>6</sub>NS)<sub>3</sub>·CHCl<sub>3</sub> (III) and Co(C<sub>9</sub>H<sub>6</sub>NO)<sub>3</sub>·CH<sub>3</sub>OH (IV). The monomeric complexes III and IV is cocrystallized with a chloroform and ethanol molecules which does not contact the metal atom. The coordination polyhedron of Co(III) ion is a slightly distorted octahedron, but that of Co(II) ion- a tetrahedron. The average length of the Co-S bond in the octahedral complex Co(C<sub>9</sub>H<sub>6</sub>NS)<sub>3</sub> amounts to 2.247Å; this bond is a bit shorter than the Co-S bond in the complex I and is less than the sum of covalent radii of Co and S atoms. Such a bond length gives evidence on the possible additional π-bonding in the complex.