

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-34 THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO BIS(S-ALKYLTHIOSEMICARBAZIDE)Ni(II) COMPLEXES

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Crystal data of $[\text{Ni}(\text{L-R})_2] \cdot \text{X}_2$

{where $\text{L-R} \equiv \text{S-alkylthiosemicarbazide: H}_2\text{N-N=C} \begin{matrix} \text{NH}_2 \\ \text{S-R} \end{matrix}$ }
are for $\text{R}=\text{Et}$, $\text{X}=\text{J}$: triclinic $\bar{1}$, $a=4.878(3)$, $b=10.826(3)$, $c=9.064(3)$ Å; $\alpha=103.39(2)^\circ$, $\beta=113.28(2)^\circ$, $\gamma=100.50(2)^\circ$, $V=407.2$ Å³, $M=548.9$, $D_o=2.26$ gcm⁻³, $D_c=2.24$ gcm⁻³, $Z=1$, and for $\text{R}=\text{Me}$, $\text{X}=\text{Br}$: orthorhombic P_{b21} , $a=4.399(3)$, $b=19.663(4)$, $c=15.293(3)$ Å; $V=1322.8$ Å³, $M=428.8$, $D_o=2.23$ gcm⁻³, $D_c=2.25$ gcm⁻³, $Z=4$.

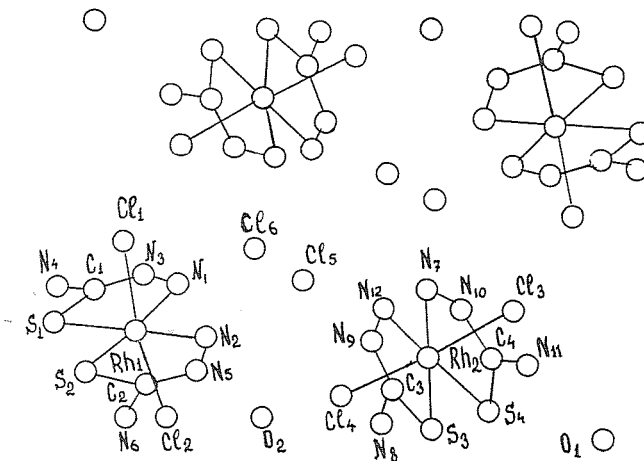
Unlike thiosemicarbazide which behaves as a bidentate NS-ligand (Campbell, 1975), S-alkylthiosemicarbazide is bonded to Ni (in $\bar{1}$) as a chelate through the nitrogen atoms from both NH_2 and hydrazone groups. The centrosymmetric complexes of $[\text{Ni}(\text{L-R})]^{2+}$ are well separated mutually and from X anions. Each complex ion is formed by two S-alkylthiosemicarbazide molecules in a *trans*-planar coordination about a Ni atom. This could also be inferred from the diamagnetic behaviour and crystal data.

The Ni-N bond distances are similar to those found in other square planar complexes with sp^3 hybridized nitrogen (Campbell, 1975). Neither Ni-Ni bonding interaction is observed, nor does the Ni atom show any tendency to assume an octahedral coordination.

REFERENCES:

Campbell, M.J.M. (1975) *Coord. Chem. Rev.* 15, 279.

The space $\text{O}_i^1 = \bar{1}$; $R=0.072$ under 1250 reflexes $J \geq 3\sigma(J)$.



The projection of structure on XY plane.

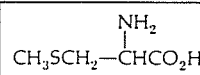
09.4-35 SUPERSYMMETRY IN THE COORDINATION COMPOUND OF RHODIUM (III) WITH THIOSEMICARBAZIDE. By I.D.Samus, M.E.Rusanovsky and N.J. Chernikova, Kishinev-Moscow, USSR.

The crystal structure of a monohydrate of dichloromethylenedithiosemicarbaziderhodium(III) chloride was determined by X-ray technique. In the unit cell of the compound there were two independent crystal complexes having related structures. Rhodium atom coordinates over the octahedron both two sulphur and two nitrogen atoms of hydrazone remainder of thiosemicarbazide molecules in *cis*-position, as well as two chlorine atoms in *trans*-position along the distorted line Cl-Rh-Cl with the angle equal to 176.4 and 172.4° for A and B cations respectively. The average distances are found to be 2.30 , 2.14 and 2.25 Å for Rh-S, Rh-N and Rh-Cl complexes respectively. Cl anions and water molecules are inside the "wells" created by complexes and take part in forming intermolecular contacts. A and B cations are independent in Fedorov group and are transformed into each other by an operation of supersymmetry consisting of a rotation by 180° and of a shift along the rotation axis, the components of the shift being $0.15a$, $0.27b$ and $0.09c$. The supersymmetry operation is carried out within the accuracy of 0.11 Å. The symmetry of both cations is $\text{mm}2$ and is done within the accuracy of 0.14 and 0.18 Å respectively. The supersymmetry operation is not extended to the chlorine anions and water molecules. The figure shows the projection of the structure on xy plane. The X-ray characteristics of the crystal are as follows: $a=12.456(4)$, $b=13.792(3)$, $c=8.098(6)$ Å; $\alpha=94.75(3)^\circ$, $\beta=107.21(4)^\circ$, $\gamma=96.82(2)^\circ$; $\rho_{\text{exp}}=2.09$, $\rho_{\text{calc}}=2.19$ g/mm³;

09.4-36 METAL COMPLEXES OF SULFUR-CONTAINING BIO-LIGANDS: THE CRYSTAL STRUCTURES OF BIS(S-METHYL-L-CYSTEINATO)-COPPER(II) AND OF BIS(α -LIPONATO)-ZINC(II) DIHYDRATE

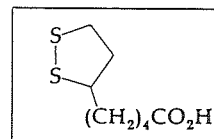
By E.Dubler, G.B.Jameson, N.Cathomas, M.Baumgartner and A.Reller. Institute of Inorganic Chemistry, University of Zürich, 8057 Zürich, Switzerland.

The naturally occurring S-methyl-L-cysteine (SMC) offers three possible binding sites for metal atoms:



The carboxylate group, the amino nitrogen atom and the thioether linkage. Since sulfur atoms are soft bases, they are expected to interact most favorable with soft acids such as Hg(II), Pt(II), Ag(I) or Cu(I), but to a less extent with borderline acids as e.g. Cu(II), Zn(II) or Cd(II).

α -Lipoic acid (LIP, DL-6,8-thioctic acid) is an important biomolecule widely distributed in animals and plants. Obviously, there are two binding sites for metal atoms: The disulfide moiety and the carboxylate group.



Crystals of the two title compounds have been grown from solution on the surface of solid hydroxy-salts of the corresponding metals.

Crystal and refinement data for $\text{CuC}_8\text{H}_{16}\text{N}_2\text{O}_4\text{S}_2$, $\text{Cu}(\text{SMC})_2$: $a=13.250(8)$, $b=5.033(3)$, $c=9.562(6)$ Å, $\beta=97.54(2)^\circ$, space group $P2_1$, $Z=2$, $R=0.045$ and $R_w=0.052$ for 921 observed reflections with $I \geq 3\sigma(I)$. The structure determination confirms