

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, $Z=4$.

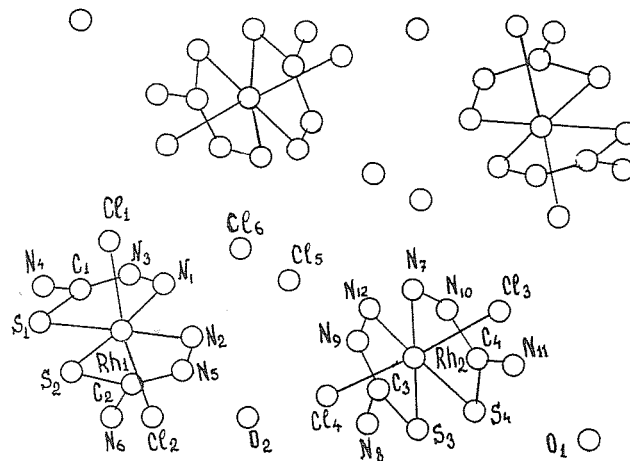
Unlike thiosemicarbazide which behaves as a bidentate NS-ligand (Campbell, 1975), S-alkylthiosemicarbazide is bonded to Ni (in $\bar{1}$) as a chelate through the nitrogen atoms from both NH_2 and hydrazone groups. The centrosymmetric complexes of $[\text{Ni}(\text{L-R})]^{2+}$ are well separated mutually 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.

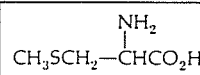
09.4-35 SUPERSYMMETRY IN THE COORDINATION COMPOUND OF RHODIUM (III) WITH THIOSEMICARBAZIDE. By I.D.Samus, M.E.Rusanovsky and N.J. Chernikova, Kishinev-Moscow, USSR.

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

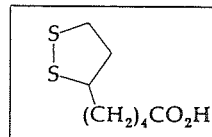
By E.Dubler, G.B.Jameson, N.Cathomas, M.Baumgartner and A.Reller. Institute of Inorganic Chemistry, University of Zürich, 8057 Zürich, Switzerland.

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

spectroscopic evidence, that the thioether sulfur is not coordinated to copper(II), even though there is a potentially favorable chelate ring size with sulfur and nitrogen as coordinating atoms. Bridging of the copper centers by carboxylate groups leads to a two-dimensional polymeric structure approximately isostructural with its cadmium analogue (P.deMeester, D.J.Hodgson, J.Am. Chem.Soc. 99, 6884 (1977)). The copper(II) atom exhibits a (4+2) tetragonally elongated CuN_2O_4 coordination octahedron with Cu-O 1.936(6), 1.951(6) Cu-N 2.001(8), 1.995(8); Cu-O axial 2.728(7), 2.703(7) Å. The metrical details for the S-methyl-L-cysteine ligand show no unusual features.

Crystal and refinement data for $ZnC_{16}H_{30}O_6S_4$, $Zn(LIP^-)_2 \cdot 2H_2O$: $a=39.916(13)$, $b=5.344(1)$, $c=10.772(3)$ Å, $\beta=95.76(2)^\circ$, space group $C2/c$, $Z=4$, $R=0.068$ and $R_w=0.084$ for 1215 observed reflections. As suggested (H.Sigel, Angew.Chem.Int.Ed. 21, 389 (1982)) there is no interaction of the disulfide moiety of α -lipoic acid with the metal atom. The structure consists of isolated molecules $[Zn(LIP^-)_2(H_2O)_2]$ with the carboxylate groups acting as bidentate ligands. The coordination geometry for the zinc(II) atom is a ZnO_6 octahedron with pronounced distortion: Zn-O 2.163(4) (2x), 2.228(5) (2x) and Zn-O(H₂O) 2.021(4) (2x) Å, bonding angles from 59.2(1) to 106.4(2)°. Some disorder of the atoms within the non-coordinating part of the α -lipoic acid molecule is evidenced by high thermal parameters of the corresponding atoms. The S-S distance is 2.025(4) Å, close to the S-S distance of 2.053(4) Å in the free ligand (R.M.Stroud, C.H.Carlisle, Acta Cryst. B28, 304 (1972)).

This is the first crystal structure reported of a metal complex of lipoic acid.

09.4-37 STEREOCHEMISTRY OF Cu(II) AND ITS PECULIARITY IN PSEUDOHALOGENIDE COMPLEXES WITH PHENANTHROLINE AND BIPYRIDINE LIGANDS. By M. Dunaĵ-Jurĉo, M. Kabešová, A. Sedov, J. Garaĵ and J. Gažo. Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia.

In connection with mutual influence of ligands in Cu(II) complexes (Kabešová, Gažo, Chem. Zvesti (1980) 34 800) the properties of the following complexes were investigated:

$[Cu(phen)_2(NCS)_2]$ (I), $[Cu(phen)_2(NCSe)_2]$ (II)
 $[Cu(bipy)_2(NCS)]NCS$ (III), α - $[Cu(bipy)_2(NCSe)]$
 NCSe (IV), and β - $[Cu(bipy)_2(NCSe)_2]$ (V) where

phen = phenanthroline and bipy = bipyridine. For complexes I - IV, their crystal structures were solved (Sedov et al., Koord. Khim., (1982) 8 1062 (I, II); Sedov et al. Inorg. Chim. Acta (1983) 75 73 (III); Sedov et al. Chem. Zvesti (1983) 37 43 (IV)).

Complexes with phen are isostructural and Cu(II) is pseudo-octahedrally coordinated. An exchange of pseudohalogenide ligands causes the axial distortion of coordination polyhedra. Complexes with bipy in both compounds have a quasi-trigonal bipyramidal coordination of Cu(II) and in the case of (III) two symmetrically independent coordination polyhedra of Cu(II) were found. Also here, the exchange of pseudohalogenide ligands causes the differences in the distortion degree of coordination polyhedra. The cations

$[Cu(bipy)_2NCX]^+$ where X = S, Se, differ

mainly in bonding angles in equatorial plane while differences in interatomic distances are negligible.

In studying the properties of bipyridine complexes we have found that the cation distortion isomerism (Harrison et al. J. Chem. Soc. Dalton (1981) 1556) can also be registered under other experimental conditions as described. Two isomeric forms were prepared for $Cu(bipy)_2(NCSe)_2$ (IV and V) which differ in their EPR and IR spectra. We expect that α - and β -isomers will also differ in the distortion degree of their coordination polyhedra which should be intermediates between trigonal bipyramid and tetragonal pyramid. The comparison of X-ray results shows that the exchange of neutral ligand causes changes in the configuration of Cu(II) coordination polyhedra and the exchange of pseudohalogenide ligands in this type of complexes causes a different deformation degree at given type of coordination polyhedra.

09.4-38 Conformational Trends in the Metalloporphyrin Series Ni(TMP), Ni(TMC), and Ni(TMIBC). By Paul N. Swebston and James A. Ibers, Department of Chemistry, Northwestern University, Evanston, IL 60201, U.S.A.

(5,10,15,20-tetramethylisobacteriochlorinato)nickel(II), Ni(TMIBC), has been structurally characterized by X-ray diffraction. Ni(TMIBC) is unique in that the structures of the porphyrin (Ni(TMP)) and chlorin (Ni(TMC)) analogues with exactly the same metal and ring substituents are already known (Acta Cryst. (1982). B38, 2134-2139). Thus the structure of Ni(TMIBC) provides an opportunity to assess the metrical changes that occur as a porphyrin ring is progressively reduced with other molecular parameters being constant.

Ni(TMIBC) crystallizes in space group $P2_1/n$ with $Z=8$ in a unit cell of dimensions $a=23.656(2)$, $b=7.644(1)$, $c=24.014(2)$ Å, and $\beta=118.94(1)^\circ$. $R(F^2)=0.086$ based on 5307 unique data collected at $-69^\circ C$. The two independent molecules possess different packing environments and small but significant differences in the bond length patterns and macrocycle distortions.

The isobacteriochlorin macrocycle exhibits an S_4 -ruffled conformation and a bond length pattern indicative of a reduction in aromaticity, both of which are more pronounced than those found in the corresponding porphyrin (Ni(TMP)) and chlorin (Ni(TMC)). A comparative conformational analysis involving pyramidalization and bond twist angles indicates a significant increase in conformational distortion going from the porphyrin to the chlorin, but only a slight increase in going from the chlorin to the isobacteriochlorin.