THE CRYSTAL STRUCTURE OF NICKEL(II) DIMETHYLDITHIOCARBAMATE

Ján Lokaj[a], Ján Garaj[a], Viktor Kettmann[b] and Viktor Vrábel[a]

[a] *Department of Analytical Chemistry,*
Faculty of Chemical Technology, 880 37 Bratislava and
[b] *Department of Analytical Chemistry,*
Comenius University, 880 34 Bratislava

Crystal and molecular structure of nickel(II) dimethyldithiocarbamate, $Ni[S_2CN(CH_3)_2]_2$, was solved by X-ray structural analysis and refined by the least squares method to $R = 0.06$ for 1065 reflections. The compound crystallizes in a space group $P\bar{1}$ and the triclinic unit cell has the dimensions: $a = 6.521$ (7), $b = 6.798$ (9), $c = 7.633$ (4), $\alpha = 67.21$ (8)°, $\beta = 67.34$ (6)° $\gamma = 85.59$ (9)°. The experimentally observed density is 1.75 g cm^{-3} and the calculated value for $Z = 1$ is 1.73 g cm^{-3}. In the structure, the Ni atom occupies a special position in the centre of symmetry and is coordinated by four sulphur atoms in a plane: Ni—S 0.2218 (4) and 0.2198 nm S1—Ni—S2 angle 79.62 (8)°. The ligand S_2CNC_2 is nearly planar.

Among dithiocarbamate chelates of the transition metals with oxidation state $+2$ the best known and studied are compounds of Ni(II) with stoichiometric formula $Ni[S_2CNR^1R^2]_2$, in which the Ni atom is coordinated by four sulphur atoms with almost equivalent Ni—S bonds (R^1 = alkyl, aryl or methylene ring)[1]. Neutral diamagnetic Ni(II) complexes with formula $Ni(R_2dtc)_2$ were described[2]. Structural studies of a great variety of R groups[3-8] showed a square planar coordination geometry as is expected for a four-coordinated metal in a d^8 configuration. This work deals with structural study of $Ni[S_2CN(CH_3)]_2$.

EXPERIMENTAL AND RESULTS

Crystals of the compound $Ni[S_2CN(CH_3)_2]_2$ (molecular mass 299.2 g mol^{-1}) with following elemental analysis were prepared:

	C	H	N	S
calc., %	24.1	4.1	9.4	42.9
found, %	24.3	4.3	9.1	42.7

The crystals are needle-shaped with triclinic symmetry. The approximate dimensions of the unit cell found from the rotation and Weissenberg patterns were refined by the least squares fit on the $P2_1$ Syntex diffractometer. The 15 precisely centred reflections yielded the following values: $a = 6.521$ (7), $b = 6.798$ (9), $c = 7.633$ (4), $\alpha = 67.21$ (8)°, $\beta = 67.34$ (6)°, $\gamma = 85.51$ (9)°.

The experimentally observed density $D_0 = 1.75 \text{ g cm}^{-3}$ (measured by the flotation in the bromoform–ethanol mixture) agrees well with the value calculated assuming one formula unit per unit cell ($D_c = 1.73 \text{ g cm}^{-3}$).

Diffraction data were obtained on the automatic diffractometer Syntex $P2_1$ using crystal of dimensions $0.25 \times 0.15 \times 0.10$ mm and MoK_α radiation. The 1065 independent reflections were used to solve the crystal structure. The absorption was neglected ($\mu R = 0.6$).

The statistical average values of $\langle |E_h|^2 \rangle$, $\langle |E_h^2| - 1 \rangle$, $\langle E_h \rangle$ and distribution of $|E_h|$'s didn't decide unambiguously in favour of $P1$ or $P\bar{1}$ probably as a consequence of a small amount of observed reflections (57.5%) of the studied difraction sphere ($0 < 2\theta < 55°$). The choice of $P\bar{1}$ was confirmed as correct by successful refinement of the structure.

TABLE I

Refined Atomic Coordinates in the Crystal Structure of $\text{Ni}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ (standard deviations are given in parentheses)

Atom	x/a	y/b	z/c
Ni	0	0	0
S1	0.3094 (3)	0.1891 (2)	0.9182 (2)
S2	−0.0665 (3)	0.3209 (2)	0.8198 (2)
C	0.1947 (11)	0.4021 (10)	0.7951 (10)
N	0.2832 (9)	0.6071 (8)	0.6921 (8)
C1	0.4950 (11)	0.6628 (11)	0.6901 (11)
C2	0.1621 (11)	0.7811 (10)	0.5983 (10)

TABLE II

Anisotropic Coefficients ($. 10^4$) of Thermal Vibrations in the Equation $\exp[-(B_{11} . h^2 + B_{22} . k^2 + B_{33} . l^2 + 2B_{12} . hk + 2B_{13} . hl + 2B_{23} . kl)]$ and the Corresponding Isotropic Coefficients ($. 10^2$) of Thermal Vibration from the Equation $\exp(-B_j \sin^2 \theta/\lambda^2)$ (standard deviations are given in parentheses)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_j
Ni	227 (4)	207 (4)	217 (3)	5 (6)	179 (6)	140 (6)	3.28
S1	240 (6)	230 (5)	243 (5)	1 (9)	229 (9)	136 (9)	3.53
S2	223 (1)	221 (4)	249 (5)	5 (9)	207 (9)	148 (9)	3.41
C	292 (26)	246 (23)	203 (22)	66 (40)	214 (40)	116 (37)	3.55
N	274 (21)	205 (19)	237 (19)	108 (32)	197 (34)	37 (31)	3.83
C1	205 (26)	280 (25)	296 (25)	74 (41)	144 (42)	179 (42)	4.06
C2	319 (30)	265 (26)	275 (26)	37 (45)	262 (47)	146 (447)	4.35

From the number of the formula unit and the space group it follows that the Ni atom occupies a special position in the centre of symmetry. Three-dimensional Patterson synthesis using all the data available is in accordance with this position and enabled the localization of the sulphur atoms. The nickel atom was located at $(0,0,0)$ and other atoms to the general positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$. The successive three dimensional Fourier synthesis gave the positions of all nonhydrogen atoms, the isotropic thermal coefficient being assumed to be 0.025 nm^2. The structure parameters were refined by the least squares method using the full matrix, the minimization function $w(|F_0| - |F_c|)^2$ and the weighting scheme according to Cruickshank[1,2], $w = (a + |F_0| + b(|F_0|)^{-1/2}$, where $a = 4.5$ and $b = 0.013$. After three refinement cycles using the isotropic

TABLE III

Bond Lengths (nm) and Valence Angles (°) in Symmetrically Independent Parts of the Molecule (standard deviations are given in parentheses)

Bond	Bond length	Bond	Bond length
Ni—S1	0·2217 (2)	C1—C2	0·2514 (11)
Ni—S2	0·2198 (2)	N—C	0·1349 (9)
S1—C	0·1691 (8)	N—C1	0·1453 (10)
S2—C	0·1750 (8)	N—C2	0·1473 (10)

Atom	Angle	Atom	Angle
S1—Ni—S2	79·29 (7)	S1—C—S2	109·9 (4)
Ni—S1—C	85·03 (2)	S1—C—N	122·8 (5)
Ni—S2—C	85·70 (2)	S2—C—N	127·2 (5)
C—N—C1	119·2 (6)	C—N—C2	122·1 (6)
C1—N—C2	118·4 (5)		

TABLE IV

Values of the Coefficients in the Equation of Planes in the Form $AX + BY + CZ = D$ and Designation of Atoms Through Which the Plane Was Constructed by the Least Squares Method

Plane	Atoms defining the plane	A	B	C	D
1	Ni, S1, S2	0·1136	—0·5391	—0·8344	—6·7002
2	Ni, S1, S2, N, C, C1, C2	0·1235	—0·5201	—0·8450	—6·6562
3	S1, S2, C, N	0·1167	—0·5287	—0·8407	—6·6794
4	S1, S2, C, N, C1, C2	0·1259	—0·5123	—0·8494	—6·6198

TABLE V

Deviations of Some Atoms From the Plane (nm . 10^4)

The atomic designation is as in Fig. 1.

Plane	Ni	S1	S2	C	N	C1	C2
1				—9	29	120	95
2	—29	16	4	24	35	32	18
3	—21	—0·6	—0·6	2	—0·8	—83	—57
4	—65			13	37	—23	— 9

thermal parameters, factor R converged to the value of 0·15. Introduction of the anisotropic thermal parameters for all nonhydrogen atoms in the structure decreased R after two cycles to 0·06. In the last cycle all the shifts in the positional parameters were $<0·1\sigma$ and the thermal parameters $<0·2\sigma$.

The final coordinates of the Ni, S, C, N atoms are given in Table I. The coefficients of anisotropic thermal vibration of the atoms are given in Table II and interatomic bond lengths and valence angles in Table III. Projection of the structure into the (001) plane and designation of the atoms in the molecule are given in Fig. 1. The values of the observed and calculated structure factors are filled with the autors. All the calculations were carried out on a Siemens 4004/150 computer.
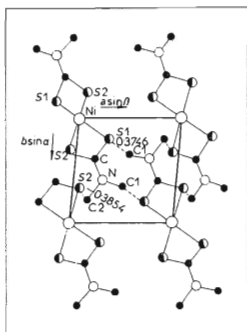

FIG. 1

Projection of the Structure of Ni[S$_2$CN. .(CH$_3$)$_2$]$_2$ into the (001) Plane and Designation of the Atoms in the Molecule

DISCUSSION

The crystal structure of the compound $Ni[S_2CN(CH_3)_2]_2$ is composed of discrete monomeric units, which are centrosymmetric and the Ni atom lies in the centre of symmetry $(0, 0, 0)$. The Ni atom is coordinated by two pairs of sulphur atoms from two ligands; the geometry of the NiS_4 coordination sphere is thus perfectly planar and the two pairs of Ni—S bond lengths have similar values (0·2218 and 0·2198 nm) and are in good agreement with those published in many papers[1–11]. The interatomic distances and valence angles in the dithiocarbamate ligand are comparable with the values which so far have been found in the structure of other dithiocarbamates[13–15]. The lengths of C—N and C—S bonds lie in an interval betwen the sum of Pauling covalent radii corresponding to single and double bonds indicating considerable delocalization of π-bonds in the ligand fragment. According to our previous work[1] ligand fragment S_2CNC_2 should be planar, as was observed.

It follows from the Table IV and V that the maximum deviation of the atoms from the plane calculated by the least squares method through the S_2CNC_2 system is 0·0037 nm (Plane 4 in Table V). According to the work[1] ligand geometry is practically insensitive to a change of substituent, in contrast to the geometry of the NiS_4 coordination sphere.

The considerably distorted S—C—S bond angles (with respect to the value of 90°) result from the strain in the four-membered ring. The average value of the S—C—S bond angle is approximately 110°, irrespective of the nature of the central metal ion, its charge, number of ligands bonded to the central atom, and the monomer or dimer nature of the complex[16].

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