CRYSTAL AND MOLECULAR STRUCTURE OF THE NICKEL(II) CHELATE OF SALICYLIDENETHIOSEMICARBAZONE AMMINE — $C_8H_7N_3OSNi.NH_3$

Eduard GYEPES[a], František PAVELČÍK[b] and Anton BEŇO[a]

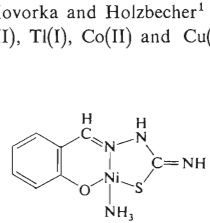
[a] *Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, 816 50 Bratislava and*
[b] *Department of Analytical Chemistry, Pharmaceutical Faculty, Comenius University, 880 34 Bratislava*

Received December 18th, 1979

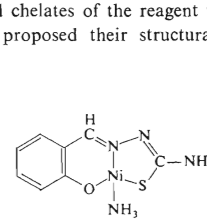
The nickel(II) chelate of salicylidenethiosemicarbazone ammine — $C_8H_7N_3OSNi.NH_3$ crystallizes in a monoclinic system. The lattice parameters are: $a = 6{\cdot}857(2)$, $b = 9{\cdot}763(2)$, $c = 15{\cdot}340(4) . 10^{-10}$ m, $\beta = 90{\cdot}34(2)°$ and the volume of the unit cell $V = 1027(1) . 10^{-30}$ m^3; the specific weight was measured as $d_m = 1{\cdot}76$ Mg m^{-3} and calculated as $d_c = 1{\cdot}74$ Mg m^{-3}. The number of formula units in the unit cell, $Z = 4$, and the symmetry space group is $P\,2_1/c$.

In basic medium, salicylidenethiosemicarbazone behaves as a tridentate ligand with coordination on the central nickel atom through the atoms of oxygen, the nitrogen of the azomethine group and sulphur. The interatomic distances are Ni—O = 1·851 (4), Ni—N = 1·853 (5), Ni—S = 2·146 (2) . 10^{-10} m. The ammonia molecule also acts as a ligand in the coordination sphere of the central atom (Ni—N = 1·941 (5) . 10^{-10} m).

Salicylidenethiosemicarbazone reacts with some metal ions yielding coloured products. Hovorka and Holzbecher[1] prepared chelates of the reagent with Ni(II), Pb(II), Cd(II), Tl(I), Co(II) and Cu(II) and proposed their structural formulae, *e.g. I*:



I



II

On the basis of spectroscopic measurements, the authors[2] proposed structural formula *II* for the nickel(II) chelate. This work was carried out in order to confirm the validity of the proposed formula using X-ray structure analysis of this chelate.

EXPERIMENTAL

Chelate Preparation

0·406 g of salicylidenethiosemicarbazone is dissolved in 50 ml of methanol and heated in a flask under reflux and a solution of 0·605 g of nickel(II) nitrate hexahydrate in 50 ml of 5% methanolic ammonia solution is added to the hot solution. The brown-red solution produced is refluxed for 5 min and poured into a Dewar vessel while hot. After six days the crystals are filtered off, washed with a 2% ammonia solution and dried in a dessicator. The brown-red needle-shaped crystals* decompose at a temperature of 221°C.

For $C_8H_{10}N_4NiOS$ (269·0) calculated: 35·72% C, 3·75% H, 20·83% N, 21·82% Ni; found: 35·37% C, 3·76% H, 20·92% N, 21·70% Ni.

Basic Crystallographic Data

The lattice parameters and symmetry space group of the chelate were obtained from rotation, weissenberg and precession photographs using CuK_α radiation ($\lambda = 1{\cdot}5418 \cdot 10^{-10}$ m). The lattice parameters were refined on a Syntex $P2_1$ automatic four circle diffractiometer using monochromatized MoK_α radiation ($\lambda = 0{\cdot}7107 \cdot 10^{-10}$ m): $a = 6{\cdot}857(2)$, $b = 9{\cdot}763(2)$, $c = 15{\cdot}340(4) \cdot 10^{-10}$ m, $\beta = 90{\cdot}34(2)°$. The volume of the unit cell was $V = 1027(1) \cdot 10^{-30}$ m^3, and the specific weight found $d_m = 1{\cdot}76$ Mg m^{-3} and calculated $d_c = 1{\cdot}74$ Mg m^{-3}. The number of formula units in the unit cell $Z = 4$ and the symmetry space group is $P2_1/c$.

The intensity data were measured in the range $0° < 2\Theta_{MoK} < 55°$ using the $\Theta - 2\Theta$ scan technique. A total of 2366 independent diffractions were recorded in the given range, of which 1547 (65·4%) were considered as observed. A diffraction was considered observed when $I_{hkl} > 1{\cdot}96\sigma(I_{hkl})$. The intensity data were corrected for Lorentz and polarization factors. Absorption was not considered for the crystal dimensions employed, $0{\cdot}015 \times 0{\cdot}026$ cm^2 ($\mu\bar{R} = 0{\cdot}42$).

Structure Analysis and Refinement of the Structure Model

The chelate structure was solved by the heavy atom method and Fourier syntheses. The position of the heavy atom — nickel — was found from the three-dimensional Patterson map. Calculation of the structure factors from the contribution of the nickel atoms yielded the approximate signs of the structural amplitudes, which were used as coefficients in the Fourier series for calculation of the three-dimensional electron density map. It was thus possible, to a first approximation, to localize the positions of the sulphur and oxygen atoms, the nitrogen atom of the azomethine group and the nitrogen atom of the NH_3 group, which form the coordination sphere of the central atom. Further calculation yielded the positions of the remaining 10 atoms (two nitrogen and eight carbon atoms). The positions of the hydrogen atoms were found from the difference Fourier map. During the structure analysis and after rescaling of the F_0 values, the value of $R = \Sigma \Delta F / \Sigma F_0$ decreased to 0·145.

The structural model obtained was refined by the full-matrix least-squares method. After three isotropic and three anisotropic refining cycles was $R = 0{\cdot}09$ for 2366 diffractions and

* Under different crystallization conditions, crystals are formed with lattice parameters: $a \approx 4{\cdot}79$, $b \approx 18{\cdot}39$, $c \approx 12{\cdot}08 \cdot 10^{-10}$ m, $\beta \approx 105{\cdot}7°$, $V \approx 1023 \cdot 10^{-30}$ m^3, $d_m = 1{\cdot}78$ Mg m^{-3}, $d_c = 1{\cdot}75$ Mg m^{-3}, $Z = 4$ and symmetry of $P2_1/c$. The results of chemical analysis and IR spectrometry indicate that this modification is chemically identical with the studied chelate.

$R = 0{\cdot}07$ for 1787 diffractions, including in the weight analysis. The weight coefficients were $w_F^{-1} = \sigma_F^2 + (0{\cdot}03|F_0|)^2$. The shifts of the positional and temperature parameters of the atoms in the last refining cycle were negligible compared with their standard deviations. The value of the residual electron density in the final difference map was $0{\cdot}7e/10^{-30}$ m^3.

TABLE I

Refined Positional and Thermal Parameters of the Atoms (standard deviations) . 10^5

Atom	x	y	z	β_{11}/β_{12}	β_{22}/β_{13}	β_{33}/β_{23}
Ni	08 181 (11)	24 635 (7)	03 889 (5)	1 554 (17) —133 (20)	544 (7) 9 (11)	249 (3) 14 (8)
S	—12 192 (26)	28 580 (16)	—06 482 (11)	2 193 (42) —198 (41)	724 (17) —176 (26)	298 (7) 129 (16)
O	26 816 (63)	22 131 (39)	12 526 (26)	1 931 (105) —471 (114)	789 (49) —270 (76)	361 (21) 245 (49)
N_A	26 384 (77)	38 073 (51)	—00 616 (33)	1 954 (134) —592 (146)	807 (58) 146 (97)	389 (25) 161 (62)
N_N	—09 025 (67)	11 499 (46)	07 956 (30)	1 488 (117) 12 (124)	630 (50) 31 (82)	293 (21) —26 (53)
N_T	—26 721 (73)	08 867 (49)	03 688 (31)	1 557 (119) —141 (135)	816 (57) —147 (87)	339 (23) 49 (59)
N_K	—45 989 (75)	15 169 (54)	—08 030 (33)	1 670 (122) 140 (150)	1 016 (64) —284 (97)	368 (25) 25 (66)
C1	11 010 (105)	03 585 (68)	19 980 (42)	1 841 (182) 211 (185)	645 (72) 35 (119)	238 (28) 2 (72)
C2	26 931 (104)	12 622 (67)	18 559 (43)	1 668 (168) 169 (181)	645 (72) —43 (118)	276 (30) 82 (74)
C3	44 386 (114)	11 117 (80)	23 604 (47)	2 173 (213) 111 (221)	960 (89) —123 (134)	296 (32) —83 (88)
C4	45 371 (125)	00 697 (80)	29 889 (47)	2 259 (216) —11 (223)	973 (93) —208 (141)	291 (34) —124 (89)
C5	29 384 (126)	—07 963 (77)	31 591 (44)	2 750 (225) 166 (230)	874 (86) —207 (134)	221 (30) —157 (82)
C6	12 402 (119)	—06 446 (74)	26 745 (45)	2 480 (212) 259 (207)	701 (76) —49 (133)	273 (31) —56 (80)
C7	—06 302 (105)	03 696 (70)	14 870 (45)	1 623 (175) 98 (186)	736 (77) 50 (121)	297 (31) 110 (78)
C8	—29 256 (108)	16 389 (72)	—03 213 (45)	1 746 (175) 174 (194)	788 (78) 72 (123)	298 (31) —28 (82)

TABLE II

Interatomic Distances (10^{-10} m) and Bond Angles (°) in the Chelate (standard deviations)

$A_i - A_j$	d	$A_i - A_j - A_k$	Angle
Ni—O	1·851 (4)	S—Ni—N_A	91·82 (16)
Ni—N_N	1·853 (5)	S—Ni—N_N	87·76 (15)
Ni—N_A	1·941 (5)	O—Ni—N_A	84·35 (20)
Ni—S	2·146 (2)	O—Ni—N_N	96·07 (19)
S—C8	1·745 (7)	Ni—S—C8	95·69 (24)
O—C2	1·311 (8)	Ni—O—C2	126·87 (41)
N_N—C7	1·318 (8)	Ni—N_N—N_T	121·44 (35)
N_N—N_T	1·399 (7)	Ni—N_N—C7	125·69 (44)
N_T—C8	1·299 (8)	N_T—N_N—C7	112·87 (49)
N_K—C8	1·366 (9)	N_N—N_T—C8	112·89 (51)
C1—C7	1·419 (10)	C2—C1—C6	119·25 (64)
C1—C2	1·421 (10)	C2—C1—C7	123·46 (60)
C2—C3	1·429 (10)	C6—C1—C7	117·28 (64)
C3—C4	1·403 (11)	O—C2—C1	123·13 (61)
C4—C5	1·410 (12)	O—C2—C3	117·17 (16)
C5—C6	1·386 (11)	C1—C2—C3	119·65 (61)
C6—C1	1·430 (10)	C2—C3—C4	118·91 (70)
		C3—C4—C5	121·86 (73)
		C4—C5—C6	119·22 (67)
		C5—C6—C1	120·99 (70)
		N_N—C7—C1	124·26 (62)
		S—C8—N_T	122·22 (54)
		S—C8—N_K	117·80 (50)
		N_T—C8—N_K	119·95 (62)

TABLE III

Deviations of the Atoms (10^{-10} m) from the Mean Plane of the Ni Chelate $0{\cdot}427x - 0{\cdot}669y - 0{\cdot}609z = -1{\cdot}690$

Atom	d	Atom	d	Atom	d
Ni	—0·043	N_T	—0·018	C4	0·173
S	0·075	N_K	0·105	C5	0·110
O	—0·143	C1	—0·094	C6	—0·033
N_A	0·036	C2	—0·084	C7	—0·130
N_N	—0·071	C3	0·053	C8	0·064

All the calculations were carried out on a Siemens 4004/150 computer system with the programs written by Gantzel, Sparks, and Trueblood and modified by Zalkin (all from the University of California) and by Lindgren (Uppsala). The atomic scattering factors were taken from International Tables[3].

RESULTS AND DISCUSSION

The refined positional and thermal parameters of the atoms are listed in Table I, the interatomic distances and bond angles are given in Table II. The arrangement of the chelate molecules in the unit cell is depicted in Fig. 1.

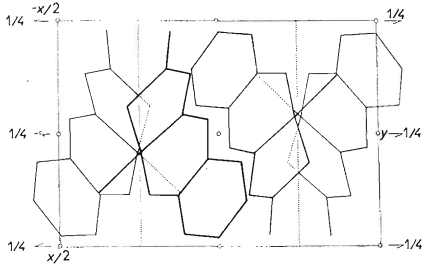


FIG. 1
Arrangement of the Chelate Molecules in the Unit Cell Projected onto the (001) Plane

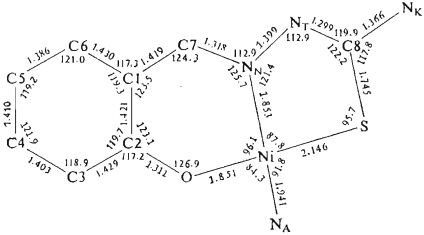


FIG. 2
Interatomic Distances (10^{-10} m) and Bond Angles (°) in the Chelate

The crystal structure of the chelate is composed of discrete molecules, with van der Waals interactions between them. The minimum intermolecular distances of the atoms are $N_K(1)-C4(2) = 3{\cdot}68 \cdot 10^{-10}$ m, $N_K(1')-O(1) = 3{\cdot}72 \cdot 10^{-10}$ m. The sum of the van der Waals radii for these interactions are 3·2 and $2{\cdot}9 \cdot 10^{-10}$ m (ref.[4]).

The chelate molecule is planar. The results of the structure analysis confirm the results of magnetic measurements according to which the chelate is diamagnetic[5]. Deviations of the atoms from the mean plane of the chelate molecule $0{\cdot}427x - 0{\cdot}669y - 0{\cdot}609z = -1{\cdot}690$ are given in Table III.

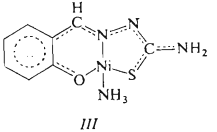
The coordination sphere of the central nickel atom is formed by the sulphur and oxygen atoms, by the nitrogen atom of the azomethine group, N_N, and by the nitrogen atom of the NH_3-group, N_A. The interatomic distances are: Ni—S = 2·146 (2), Ni—O = 1·851 (4), Ni—N_N = 1·853 (5), Ni—N_A = $1{\cdot}941\,(5) \cdot 10^{-10}$ m. Because of the different character of the atoms forming the coordination sphere of the central atom, the coordination square is distorted, as is confirmed by the given interatomic distance values and by the bond angles: S—Ni—N_A = 91·82 (16°), S—Ni—N_N = 87·76 (15°), O=Ni—N_A = 84·35 (20°), O—Ni—N_N = 96·07 (19°). The chelate molecule is depicted. schematically in Fig. 2, with designated interatomic distances and bond angles.

The average value of interatomic distances in the benzene ring is equal to $1{\cdot}413 \cdot 10^{-10}$ m, while the tabulated value is $1{\cdot}395 \cdot 10^{-10}$ m. The lengthening is probably connected with partial dearomatization of the benzene ring, produced by its incorporation into the conjugated system of the chelate molecule. In this connection, it is interesting to compare some of the interatomic distances found with the tabulated values[3,4], given in brackets (both in units of 10^{-10} m):

C1—C7	1·419	(1·541[a])	N_K—C_8	1·366	(1·472[a])
N_N=C7	1·318	(1·322–1·352[b])	S—C8	1·745	(1·812[a], 1·73[b])
N_N—N_T	1·399	(1·480[a])	O—C2	1·311	(1·432[a], 1·36[b])
N_T=C8	1·299	(1·322–1·352[b])			

([a] for single bonds, [b] for partial double bonds)

It follows from the comparison that all the values for the single bonds are shorter than those given in the tables, while the double bonds exhibit values comparable with the tabulated values for partial double bonds. Thus the structure of the nickel II chelate can be depicted by formula *III*:



III

REFERENCES

1. Hovorka V., Holzbecher Z.: Chem. Listy *45*, 2 (1951).
2. Gyepes E., Beňo A., Maro M.: Proc. 6th Conf. Coord., Chem., Smolenice/Bratislava (1976), p. 83.
3. *International Tables for* X-Ray *Crystallography* III, p. 202—276. The Kynoch Press, Birmingham 1968.
4. Pauling L.: *The Chemical Bond*, p. 135, 150. Cornell University Press, Ithaca N. Y. 1967.
5. Gyepes E., Španková M.: Acta F.R.N. Univ. Comen. — Chimia *29*, 81 (1981).

Translated by M. Štuliková.