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Crystal and Molecular Structure of the Nickel(II) Complex with the Pentadentate Ligand Bis(salicylidene-γ-iminopropyl)methylamine

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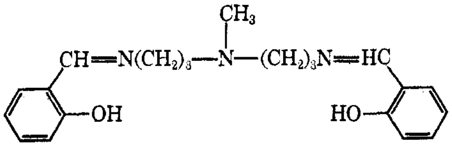
The crystal structure of bis(salicylidene-γ-iminopropyl)methylaminenickel(II) has been determined by X-ray photographic techniques and refined by full-matrix least-squares methods to an R factor of 7.1%, over 1540 observed reflections. The cell dimensions are $a = 6.913\ (4)$ Å, $b = 13.975\ (11)$ Å, $c = 19.893\ (13)$ Å, and $\beta = 91°\ 49'\ (3')$; $Z = 4$, $d_c = 1.42$ g cm^{-3}, $d_m = 1.39$ g cm^{-3}, space group $P2_1/c$. The structure consists of discrete molecules in which the nickel atom is coordinated by the five donor atoms of the ligand molecule. The coordination polyhedron can be described as a distorted trigonal bipyramid, with a large equatorial angle (O(1)–Ni–O(2) = 140.6°). Two geometrical isomers are present in the crystal, differing in the orientation of the N–C bonds about N(3). The structure appears mainly determined by the geometric constraints of the ligand molecule.

Introduction

The pentadentate ligand bis(salicylidene-γ-iminopropyl)methylamine (SalMedpt)



forms with 3d transition metals a series of high-spin complexes with general formula (SalMedpt)M^{II}, where M^{II} = Mn, Co, Ni, Cu, and Zn.[1] On the basis of magnetic and spectral measurements a five-coordinate structure was proposed for these complexes and a preliminary X-ray investigation confirmed this assignment.[2] Early work on some of these complexes had been done by Calvin,[3] who studied the oxygen-carrier properties of the cobalt(II) complex. A proton magnetic resonance study on the nickel(II) complex has been reported more recently.[4] We report here the detailed results of the X-ray analysis on the nickel(II) complex.

Experimental Section

Data Collection.—Preparation and physicochemical properties of (SalMedpt)Ni^{II} have been reported elsewhere.[1] Monoclinic green plates elongated along a were grown from benzene and cyclohexane solutions. Cell constants were determined by a least-squares refinement of 24 2θ values from $0kl$ and $h0l$ Weissenberg photographs calibrated with NaCl (a = 5.6273 Å; λ(Cu Kα) 1.5418 Å). Their values with estimated standard deviations are $a = 6.913 \pm 0.004$ Å, $b = 13.975 \pm 0.011$ Å, $c = 19.893 \pm 0.013$ Å, $\beta = 91°\ 49' \pm 3'$, $V = 1930.3$ Å^3, $Z = 4$, $d_c = 1.42$ g cm^{-3}, $d_m = 1.39$ g cm^{-3}, and $\mu = 15.7$ cm^{-1} for Cu Kα. Systematic extinctions of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/c$.

The crystal used for the collection of the intensities had approximate dimensions 0.10 × 0.20 × 0.35 mm, coincident with the [001], [010], and [100] directions, respectively.

Reciprocal lattice levels $0kl$ through $5kl$ were collected on a double-integrating Weissenberg camera, by the equiinclination multiple-film technique with Cu Kα radiation. The intensities of 1540 independent reflections above background were measured on a Nonius microdensitometer. The various levels were put on a common scale by recording on the same film 30° samples from each level, taken with the equiinclination technique.

Intensities were corrected for Lorentz and polarization effects. The real part of the anomalous dispersion correction for nickel(II) was subtracted from f_{Ni} ($\Delta f'_{\mathrm{Ni}} = -3.2$ e$^-$ for Cu Kα radiation). The reflections 020, $11\bar{3}$, $12\bar{2}$, $30\bar{4}$, $32\bar{2}$, $40\bar{2}$, and $40\bar{4}$ were later considered affected by secondary extinction and were omitted from the least-squares calculations. The effect of the Kα_1–Kα_2 splitting was corrected, but no corrections were made for absorption effects. However, with a calculated μ value of 15.7 cm^{-1} the transmission factors ranged only between 0.73 and 0.85. Atomic scattering factors were taken from Cromer and Waber[5] for Ni, O, N, and C and from ref 6 for H.

Structure Determination.—The positions of the nickel atoms were easily found from a three-dimensional Patterson synthesis. Owing to the value of the y coordinate of the nickel atom (0.0007), the three-dimensional Fourier synthesis, phased with the heavy-atom positions, showed two images of the molecule related by a pseudosymmetry plane at $y = 0$. An arbitrary choice was made between the two sets of peaks and two more electron density syntheses were calculated. All the nonhydrogen atoms were clearly evident in the last synthesis, with the exception of C(17), C(20), and C(21), which appeared as low and diffuse electron density peaks. At this point the R factor was 18.5%, with $B_{\mathrm{Ni}} = 2.5$ Å^2 and $B_{\mathrm{O}} = B_{\mathrm{N}} = B_{\mathrm{C}} = 3.0$ Å^2. R is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, where the sums are over the independent observed reflections.

Four cycles of block-diagonal least-squares refinement with isotropic temperature factors for the individual atoms reduced the R factor to 11.8%. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights calculated according to the expression[7] $w = 1/(a + F_o + cF_o^2)$, where a and c were 10.0 and 0.02, respectively.

At this point a difference synthesis, calculated without the contribution of C(17), C(20), and C(21), showed clearly the presence of six peaks near N(3), about half as high as a carbon atom. This was attributed to the existence of twofold orientational disorder of the N(3)–C(17), N(3)–C(20), and N(3)–C(21) bonds about an axis collinear with the Ni–N(3) bond direction. In the following calculations C(17), C(20), and C(21) were introduced in the two positions with a weight of 0.5.

Two more block-diagonal least-squares cycles, varying the positional and the thermal parameters of the atoms, reduced the R factor to 9.8%.

All the above calculations were performed on an IBM 1620

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(1) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

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TABLE I

FINAL ATOMIC POSITIONAL[a] AND THERMAL[b] PARAMETERS ($\times 10^4$)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	537 (2)	7 (1)	2952 (1)	125 (4)	33 (1)	15 (1)	−3 (1)	−1 (1)	−1 (1)
O(1)	2830 (9)	364 (5)	2461 (3)	179 (19)	82 (5)	17 (2)	−32 (7)	−3 (4)	6 (2)
O(2)	−1844 (9)	565 (5)	3282 (3)	174 (18)	58 (5)	31 (2)	28 (7)	0 (4)	−20 (2)
N(1)	−856 (11)	−320 (5)	2080 (4)	106 (21)	43 (4)	26 (2)	−14 (6)	1 (5)	−3 (2)
N(2)	1929 (11)	403 (6)	3801 (4)	149 (22)	52 (4)	19 (2)	8 (8)	−4 (5)	3 (2)
N(3)	520 (11)	−1424 (5)	3247 (4)	185 (23)	39 (4)	25 (2)	7 (8)	10 (5)	5 (3)
C(1)	1430 (13)	405 (6)	1356 (4)	167 (26)	34 (4)	15 (2)	−3 (8)	5 (5)	1 (2)
C(2)	2984 (13)	572 (5)	1834 (4)	136 (25)	41 (5)	13 (2)	0 (8)	8 (5)	0 (2)
C(3)	4678 (15)	993 (7)	1621 (4)	223 (31)	42 (5)	20 (3)	−20 (9)	13 (6)	3 (3)
C(4)	4875 (17)	1221 (8)	944 (6)	276 (37)	51 (7)	34 (4)	−17 (11)	32 (9)	5 (4)
C(5)	3391 (19)	1062 (8)	472 (5)	336 (41)	67 (8)	21 (3)	−15 (13)	23 (8)	8 (4)
C(6)	1774 (17)	668 (8)	687 (5)	351 (39)	54 (7)	16 (3)	−6 (12)	8 (7)	4 (3)
C(7)	−326 (14)	−91 (7)	1498 (4)	210 (28)	37 (5)	17 (2)	−14 (9)	−5 (5)	−5 (3)
C(8)	−333 (14)	1624 (7)	4083 (4)	220 (30)	37 (5)	16 (2)	−12 (9)	21 (6)	−4 (3)
C(9)	−1913 (13)	1340 (6)	3660 (4)	161 (26)	39 (5)	18 (2)	10 (9)	10 (6)	−2 (3)
C(10)	−3586 (16)	1889 (8)	3643 (5)	243 (34)	60 (7)	25 (3)	42 (11)	23 (7)	5 (4)
C(11)	−3724 (19)	2712 (8)	4023 (5)	370 (41)	52 (7)	26 (3)	68 (13)	35 (9)	8 (4)
C(12)	−2169 (22)	3016 (8)	4428 (6)	476 (49)	43 (7)	27 (3)	22 (14)	39 (10)	−1 (4)
C(13)	−544 (17)	2467 (8)	4463 (5)	333 (37)	47 (6)	20 (3)	−21 (11)	29 (7)	−5 (3)
C(14)	1406 (13)	1088 (7)	4180 (4)	115 (27)	54 (6)	20 (2)	−22 (9)	0 (5)	−1 (3)
C(15)	−2631 (14)	−865 (7)	2157 (5)	155 (28)	41 (6)	29 (3)	−31 (9)	−4 (6)	1 (3)
C(16)	−2132 (17)	−1889 (8)	2386 (6)	296 (35)	49 (7)	37 (4)	−50 (11)	−19 (8)	0 (4)
C(17)′	−1367 (31)	−1842 (13)	3178 (12)	211 (66)	27 (10)	53 (8)	−25 (18)	−23 (17)	13 (7)
C(17)″	−63 (30)	−2071 (13)	2659 (11)	243 (62)	20 (9)	44 (8)	9 (17)	7 (16)	−15 (7)
C(18)	3693 (14)	−158 (7)	3979 (5)	127 (27)	56 (8)	26 (3)	−1 (9)	−13 (6)	4 (3)
C(19)	3192 (17)	−1170 (9)	4151 (6)	274 (37)	71 (8)	37 (4)	−18 (13)	−24 (9)	21 (5)
C(20)′	1207 (32)	−1483 (15)	3972 (10)	309 (65)	59 (13)	19 (5)	1 (22)	−9 (13)	−5 (6)
C(20)″	2271 (34)	−1715 (17)	3516 (12)	298 (77)	52 (14)	47 (8)	37 (24)	−64 (19)	−4 (8)
C(21)′	2099 (34)	−1923 (17)	2838 (12)	203 (68)	65 (16)	43 (8)	26 (23)	18 (18)	−2 (9)
C(21)″	−1047 (32)	−1580 (17)	3794 (11)	249 (64)	70 (16)	24 (7)	6 (24)	8 (15)	11 (8)

[a] Estimated standard deviations for the last significant digit are given within parentheses. [b] Anisotropic thermal factors are of the form $\exp(-\Sigma_{i=1}^{3} \Sigma_{j=1}^{3} h_i h_j \beta_{ij})$.

computer with programs written by Albano, Bellon, Pompa, and Scatturin.[8]

Further refinement was continued with the full-matrix least-squares program of Busing and Levy, adapted for the IBM 7090 by Stewart.[9] The weighting scheme was $w = 1$ for reflections with $F_o \leq 25$ and $\sqrt{w} = 25/F_o$ for reflections with $F_o > 25$.

After two cycles of refinement with isotropic temperature factors, hydrogen atoms were introduced in calculated positions, assuming a C–H distance of 1.05 Å and $B_H = 5.0$ Å^2. Two distinct sets of positions were considered for the hydrogen atoms attached to C(16), C(17), C(19), C(20), and C(21), a weighting factor of 0.5 being applied to these hydrogen atoms. Two cycles of least squares on positional and thermal parameters of the nonhydrogen atoms with anisotropic temperature factors and one cycle on the level scale factors reduced the discrepancy index to 7.2%.

At this point a difference Fourier synthesis was calculated without the contribution of the hydrogen atoms, using reflections with $(\sin \theta)/\lambda \leqslant 0.45$. With the exception of the hydrogen atoms attached to C(7), C(16), C(17), C(19), and C(20), all the hydrogen atoms were clearly visible close to the calculated positions, with peak heights varying from 0.2 to 0.5 e$^-$/Å^3. The difference synthesis did not show any higher peaks. It was then decided to introduce the hydrogen atoms in the observed positions, except those attached to C(7), C(16), C(17), C(19), and C(20), which were still introduced in the calculated positions.

The relative probability of the two sets of positions for the atoms C(17), C(20), and C(21) was then tested by refining the occupancy factors for these atoms together with an overall scale factor for the F_o's. After three cycles of refinement the occupancy factors did not differ significantly from 0.5 showing that both orientations are equally probable.

A final least-squares cycle on the positional and thermal parameters of the nonhydrogen atoms gave no shift greater than the standard deviations on the parameters, the average shift-to-error ratio being 0.2. The R factor was 7.1% and the weighted R 9.7%, where weighted R is defined as $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} \times 100$. The final value for the estimated standard deviation of an observation of unit weight was 2.12.

The final values of the parameters and their estimated standard deviations are reported in Table I. Standard deviations are calculated from the inverse least-squares matrix according to the expression $\sigma_j = ((\Sigma w \Delta F^2)a^{jj}/(m - n))^{1/2}$, where m is the number of reflections, n the number of parameters, and a^{jj} is the jjth element of the inverse matrix. Table II reports the coordinates of the hydrogen atoms and Table III the root-mean-square components of the thermal displacements along the principal axes. The observed and calculated structure factors are reported in Table IV.

Discussion

The structure of the compound consists of discrete molecules in which the nickel atom is five-coordinated by the three nitrogen and the two oxygen atoms of the ligand molecule (Figure 1). The coordination polyhedron can be described in terms of a distorted trigonal bipyramid, with O(1), O(2), and N(3) in the equatorial plane and N(1) and N(2) in the axial positions. The metal atom lies exactly in the equatorial plane. Bond lengths and angles about the metal atom are reported in Table V. The main deviations from the regular trigonal bipyramid are in the equatorial angles O(1)–Ni–

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(8) (a) V. Albano, P. L. Bellon, and F. Pompa, *Ric. Sci., Suppl.*, **33**, 285 (1963); (b) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, **33**, 1067 (1963).

(9) J. M. Stewart, Technical Report TR-64-6, University of Maryland Computer Science Center, 1964.

TABLE II

POSITIONAL PARAMETERS OF THE HYDROGEN ATOMS[a,b] ($\times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
H(3)	596	104	194	H(171)′	−138	−250	340
H(4)	628	122	70	H(172)′	−235	−137	344
H(5)	316	130	−10	H(171)″	88	−197	227
H(6)	56	56	35	H(172)″	15	−279	283
H(7)	−123	−30	108	H(191)′	417	−162	390
H(10)	−496	170	335	H(192)′	344	−125	468
H(11)	−504	292	396	H(191)″	448	−153	433
H(12)	−252	374	464	H(192)″	218	−118	454
H(13)	68	270	475	H(201)′	24	−109	427
H(14)	264	142	455	H(202)′	109	−223	412
H(151)	−360	−68	264	H(201)″	221	−244	363
H(152)	−384	−92	175	H(202)″	333	−163	312
H(181)	468	0	360	H(211)′	90	−260	295
H(182)	460	26	435	H(212)′	360	−174	300
H(161)′	−339	−234	235	H(213)′	180	−180	235
H(162)′	−105	−218	209	H(211)″	−100	−90	405
H(161)″	−311	−208	277	H(212)″	−152	−216	410
H(162)″	−239	−235	197	H(213)″	−200	−134	355

[a] The hydrogen atoms are labeled as follows: the last entry in parentheses, in the symbol H(*abc*), refers to the hydrogen atom attached to carbon atom C(*ab*). See Figures 1 and 2 for labeling of the carbon atoms. [b] Calculated positions are reported for the hydrogen atoms attached to C(7), C(16), C(17), C(19), and C(20).

TABLE III

ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS (Å) ALONG PRINCIPAL AXES[a]

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Ni	0.166	0.177	0.183	C(10)	0.188	0.217	0.293
O(1)	0.182	0.194	0.297	C(11)	0.179	0.207	0.343
O(2)	0.161	0.214	0.303	C(12)	0.195	0.222	0.352
N(1)	0.153	0.209	0.234	C(13)	0.180	0.209	0.301
N(2)	0.179	0.203	0.231	C(14)	0.154	0.203	0.239
N(3)	0.188	0.202	0.238	C(15)	0.154	0.228	0.246
C(1)	0.171	0.184	0.203	C(16)	0.178	0.261	0.311
C(2)	0.153	0.187	0.202	C(17)′	0.143	0.218	0.346
C(3)	0.171	0.213	0.245	C(17)″	0.116	0.243	0.309
C(4)	0.195	0.245	0.297	C(18)	0.164	0.226	0.249
C(5)	0.179	0.267	0.294	C(19)	0.202	0.244	0.336
C(6)	0.177	0.234	0.292	C(20)′	0.188	0.246	0.277
C(7)	0.161	0.204	0.232	C(20)″	0.173	0.233	0.370
C(8)	0.157	0.187	0.248	C(21)′	0.198	0.268	0.298
C(9)	0.170	0.203	0.211	C(21)″	0.201	0.244	0.280

[a] Estimated standard deviations, occurring on the last significant digit, are less than 3 for Ni, 30 for O, N, and C, and 60 for C′ and C″.

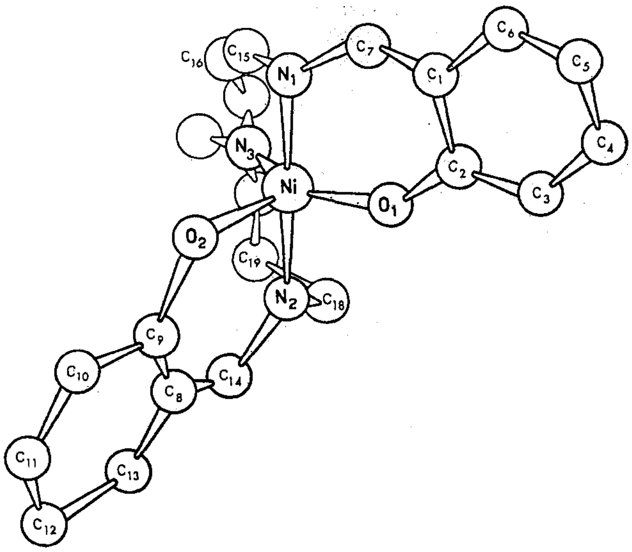

Figure 1.—A perspective view of the molecule (SalMedpt)-Ni^{II}, with the labeling of the atoms. Only one conformation of the chain is shown. Labeling of disordered atoms is shown in Figure 2.

TABLE V

DISTANCES (Å) AND ANGLES (DEG) IN THE MOLECULE OF (SalMedpt)Ni^{II}

(a) Coordination Polyhedron

Ni–O(1)	1.956 (7)	O(1)–Ni–N(1)	89.8 (3)
Ni–O(2)	1.954 (7)	O(1)–Ni–N(2)	88.8 (3)
Ni–N(1)	2.017 (8)	O(2)–Ni–N(1)	89.9 (3)
Ni–N(2)	2.001 (7)	O(2)–Ni–N(2)	89.5 (3)
Ni–N(3)	2.086 (8)	N(3)–Ni–O(1)	113.5 (3)
		N(3)–Ni–O(2)	105.9 (3)
O(1)–Ni–O(2)	140.6 (3)	N(3)–Ni–N(1)	91.1 (3)
N(1)–Ni–N(2)	177.0 (3)	N(3)–Ni–N(2)	91.8 (3)

(b) Rest of the Molecule

O(1)–C(2)	1.29 (1)	O(2)–C(9)	1.32 (1)
N(1)–C(7)	1.27 (1)	N(2)–C(14)	1.28 (1)
N(1)–C(15)	1.46 (1)	N(2)–C(18)	1.48 (1)
N(3)–C(17)′	1.43 (2)	N(3)–C(17)″	1.53 (2)
N(3)–C(20)′	1.51 (2)	N(3)–C(20)″	1.37 (3)
N(3)–C(21)′	1.55 (3)	N(3)–C(21)″	1.58 (2)
C(1)–C(2)	1.43 (2)	C(8)–C(9)	1.42 (1)
C(1)–C(6)	1.41 (1)	C(8)–C(13)	1.41 (2)
C(1)–C(7)	1.44 (1)	C(8)–C(14)	1.43 (1)
C(2)–C(3)	1.39 (1)	C(9)–C(10)	1.39 (2)
C(3)–C(4)	1.40 (2)	C(10)–C(11)	1.38 (2)
C(4)–C(5)	1.39 (2)	C(11)–C(12)	1.39 (2)
C(5)–C(6)	1.33 (2)	C(12)–C(13)	1.36 (2)
C(15)–C(16)	1.54 (2)	C(18)–C(19)	1.50 (2)
C(16)–C(17)′	1.65 (3)	C(19)–C(20)′	1.47 (3)
C(16)–C(17)″	1.53 (2)	C(19)–C(20)″	1.59 (3)
Ni–O(1)–C(2)	129.6 (0.6)	Ni–O(2)–C(9)	124.4 (0.6)
Ni–N(1)–C(7)	126.2 (0.6)	Ni–N(2)–C(14)	124.8 (0.6)
Ni–N(1)–C(15)	114.1 (0.6)	Ni–N(2)–C(18)	115.3 (0.6)
C(7)–N(1)–C(15)	119.7 (0.8)	C(14)–N(2)–C(18)	119.9 (0.8)
Ni–N(3)–C(17)′	112.1 (0.9)	Ni–N(3)–C(17)″	110.7 (0.8)
Ni–N(3)–C(20)′	108.6 (0.9)	Ni–N(3)–C(20)″	112.5 (1.1)
Ni–N(3)–C(21)′	105.8 (1.0)	Ni–N(3)–C(21)″	109.8 (0.9)
C(17)′–N(3)–C(20)′	109.2 (1.3)	C(17)″–N(3)–C(20)″	109.6 (1.3)
C(17)′–N(3)–C(21)′	114.8 (1.3)	C(17)″–N(3)–C(21)″	106.3 (1.2)
C(20)′–N(3)–C(21)′	106.0 (1.3)	C(20)″–N(3)–C(21)″	107.8 (1.4)
C(2)–C(1)–C(6)	116.4 (0.8)	C(9)–C(8)–C(13)	117.6 (0.9)
C(2)–C(1)–C(7)	124.5 (0.7)	C(9)–C(8)–C(14)	124.4 (0.8)
C(6)–C(1)–C(7)	118.8 (0.8)	C(13)–C(8)–C(14)	117.8 (0.9)
O(1)–C(2)–C(1)	121.7 (0.8)	O(2)–C(9)–C(8)	121.9 (0.8)
O(1)–C(2)–C(3)	119.3 (0.8)	O(2)–C(9)–C(10)	118.9 (0.8)
C(1)–C(2)–C(3)	118.9 (0.7)	C(8)–C(9)–C(10)	119.1 (0.8)
C(2)–C(3)–C(4)	120.1 (0.9)	C(9)–C(10)–C(11)	121.2 (1.0)
C(3)–C(4)–C(5)	121.8 (1.0)	C(10)–C(11)–C(12)	120.5 (1.1)
C(4)–C(5)–C(6)	117.3 (1.0)	C(11)–C(12)–C(13)	118.7 (1.0)
C(1)–C(6)–C(5)	125.5 (1.0)	C(8)–C(13)–C(12)	122.8 (1.0)
N(1)–C(7)–C(1)	125.0 (0.8)	N(2)–C(14)–C(8)	124.5 (0.8)
N(1)–C(15)–C(16)	109.6 (0.8)	N(2)–C(18)–C(19)	111.1 (0.8)
C(15)–C(16)–C(17)′	108.1 (1.0)	N(3)–C(20)′–C(19)	118.5 (1.5)
C(15)–C(16)–C(17)″	117.2 (1.0)	N(3)–C(20)″–C(19)	119.7 (1.7)
N(3)–C(17)′–C(16)	111.8 (1.5)	C(18)–C(19)–C(20)′	116.4 (1.2)
N(3)–C(17)″–C(16)	113.3 (1.3)	C(18)–C(19)–C(20)″	111.0 (1.2)

N(3), N(3)–Ni–O(2), and O(1)–Ni–O(2) which are, respectively, 113.5, 105.9, and 140.6°.

The large value of the O(1)–Ni–O(2) angle, which is attained at the expense of some strains (see below) in the aliphatic chains of the ligand, can be interpreted as a distortion of the complex toward a square-pyramidal structure. This distortion does not originate from ligand–ligand repulsions, which favor the trigonal-bipyramidal arrangement for five identical ligands.[10] The contribution to the energy due to the repulsions, however, does not depend critically on the values of the angles in the equatorial plane of the bipyramid.[11] Therefore, distortions such as those found in the present structure may be easily attained if some additional factor favoring a square-pyramidal arrangement exists. CFSE, indeed, decidedly favors the latter arrangement for a d^8 high-spin configuration.[11] Considering in addi-

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TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

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[a] Columns are l, $10F_o$, and $10F_c$. Reflections considered affected by extinction are marked with an E.

tion that, from the viewpoint of repulsions, a square pyramid with L_{ap}–M–L_{bas} angles of 104° is only slightly less stable than the trigonal bipyramid,[10] CFSE may be expected to represent the structure-determining factor for high-spin five-coordinate nickel(II) complexes, at least in the absence of particularly strict steric requirements imposed on the molecule.

In agreement with the above considerations, of the 15 five-coordinate structures of high-spin nickel(II) complexes so far determined by X-ray analysis,[12–26] three show a trigonal-bipyramidal geometry,[12–14] four show a geometry intermediate between the two idealized models,[15–18] and eight show a square-pyramidal geometry.[19–26] Moreover, in the complexes with trigonal-bipyramidal structure, the geometry of the coordination polyhedron is clearly influenced by the shape of the ligand molecule. Also in the complexes with intermediate structure it appears that the formation of a dimeric structure[15] or the steric requirements of the ligand molecule[16,17] would not allow a square-pyramidal structure to be attained.

Of course it would be interesting to know how many square-pyramidal stereochemistries are influenced by the shape of the ligand molecule, but this is not so obvious as in the case of ligands having trigonal symmetry. In this connection it should be pointed out that the complex $[((CH_3)_3AsO)_5Ni](ClO_4)_2$ with five identical unidentate ligands[24] has a square-pyramidal stereochemistry.

In (SalMedpt)Ni^{II} the square pyramidal structure with the metal atom above the basal plane cannot be attained presumably because the N–Ni–N angles are bound to be close to 90°. Some evidence in support of this interpretation is given by the strains present in the trimethylene chains, where the angles at the carbon atoms are larger than the expected tetrahedral value. The same steric factors would prevent the O(1)–Ni–O(2) angle from attaining higher values through a rotation of the Sal rings around the Ni–N(1) and Ni–N(2) bonds.

Bond lengths in the coordination polyhedron are in agreement with values from analogous structures. The Ni–O (average 1.95 Å) and the salicylaldimine Ni–N (average 2.01 Å) distances are in good agreement with the corresponding Ni–O (average 1.94 Å) and Ni–N (average 1.99 Å) distances found in the high-spin five-coordinate complex bis(*N*-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II).[19] The Ni–N(3) distance is in agreement with analogous distances between nickel(II) and tertiary nitrogen atoms in five-coordinate complexes.[21,23]

One of the most interesting features of this structure is the presence of two geometrical isomers, differing for the orientation of the N–C bonds about N(3) (Figure 2). The complex molecule possesses, at least to a first approximation, twofold symmetry about the Ni–N(3) bond direction, save for the presence of *three* N–C bonds originating from N(3). Therefore, the existence of the two geometrical isomers in the lattice may be interpreted as approximately restoring statistical twofold symmetry for the whole molecule. The entropy increase, due to the disorder, should contribute to stabilize

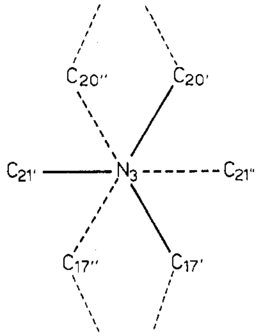

Figure 2.—Schematic view along the N(3)–Ni bond direction, showing the disorder about N(3).

TABLE VI

LEAST-SQUARES PLANES WITH DEVIATIONS OF ATOMS FROM THE PLANES

Equations of the Planes[a]

Plane	Atoms	A	B	C	D
1	O(1), N(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7), Ni,[b] C(15)[b]	−2.724	12.616	3.698	0.586
2	O(2), C(8), C(9), C(10), C(11), C(12), C(13), C(14), C(18), Ni,[b] N(2)[b]	−2.806	−7.409	15.125	5.091
3	Ni, O(1), O(2), N(3)	3.113	3.406	16.871	5.155

Plane 1

Atoms	Dev, Å	Atoms	Dev, Å	Atoms	Dev, Å
O(1)	−0.01	C(3)	0.01	C(7)	0.06
N(1)	−0.01	C(4)	0.03	Ni[b]	−0.37
C(1)	−0.04	C(5)	0.00	C(15)[b]	0.16
C(2)	0.00	C(6)	−0.03		

Plane 2

Atoms	Dev, Å	Atoms	Dev, Å	Atoms	Dev, Å
O(2)	0.03	C(11)	−0.03	C(18)	−0.01
C(8)	0.03	C(12)	0.02	Ni[b]	0.78
C(9)	0.01	C(13)	0.02	N(2)[b]	0.18
C(10)	−0.03	C(14)	−0.03		

Plane 3

Atoms	Dev, Å	Atoms	Dev, Å	Atoms	Dev, Å
Ni	0.004	O(1)	−0.002	O(2)	−0.001
N(3)	−0.001				

[a] The equations of the planes are $Ax + By + Cz = D$ in monoclinic fractional coordinates. [b] Atoms not included in the calculation of the planes (weight zero).

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the structure. Although the geometrical isomers are not bound to be of identical energy, the refinement of the occupancy factors of C(17), C(20), and C(21) (see above) showed that both isomers are equally distributed throughout the crystal.

Bond lengths and angles in the ligand molecule (Table V) are in agreement within their standard deviations with values from other salicylaldimine complexes.[27] It appears however that standard deviations on distances and angles including atoms involved in the disorder are somewhat optimistic. The equations of some significant least-squares planes and the deviations of the atoms from these planes are reported in Table VI. It can be noted that the nickel atom is not symmetrically displaced from the salicylaldimine planes, the two distances being 0.37 and 0.78 Å. The angle between the two planes passing through the salicylaldimine moieties is 101.0°.

Inspection of the intermolecular distances below 3.6 Å shows that there are no unusually short contacts between molecules (Table VII).

TABLE VII

INTERMOLECULAR CONTACTS BELOW 3.6 Å

Atom 1	Atom 2	Dist, Å
C(3)	C(15) $(x + 1, y, z)$	3.35
C(18)	O(2) $(x + 1, y, z)$	3.57
C(18)	C(10) $(x + 1, y, z)$	3.50
C(13)	C(20)' $(\bar{x}, \bar{y}, \bar{z} + 1)$	3.46
C(10)	C(21)' $(\bar{x}, y + {}^1/_2, \bar{z} + {}^1/_2)$	3.57

Finally it should be mentioned that this structure represents an unusual case of a pentacoordinated complex formed by a pentadentate ligand. Only recently another similar case has been reported,[26] in which the pentadentate ligand tpen (*N,N,N'*-tris(2-(2'-pyridyl)-ethyl)ethylenediamine) forms a square-pyramidal stereochemistry around the nickel atom.

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The Crystal Structure, Absolute Configuration, and Circular Dichroism of a Cobalt(III) Complex of an Optically Active Triethylenetetramine Homolog, $(+)_{589}$-*trans*-($(-)_{589}$-*N,N'*-Bis((*S*)-2-amino-3-phenylpropyl)-*trans*-(*R*)-1,2-cyclohexanediamine-δλδ)dichlorocobalt(III) Perchlorate

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This complex $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$ crystallizes in space group $P2_1$ with unit cell dimensions of $a = 13.237 \pm 0.007$ Å, $b = 16.671 \pm 0.009$ Å, $c = 12.988 \pm 0.006$ Å, $\beta = 94.81 \pm 0.02°$, $Z = 4$, and $\rho_{calcd} = 1.416 \pm 0.003$ g cm^{-3} at 23°. The structure was solved by the heavy-atom method with 2277 observed reflections collected on an automatic diffractometer. Refinement proceeded anisotropically for Co and Cl and isotropically for the remaining light atoms to a final reliability index $R_1 = 0.096$. The Cl atoms show trans coordination, and the absolute configuration has been verified from anomalous dispersion data. Both molecules in the asymmetric unit have the same conformation in the coordination sphere, but pendant groups show differences in orientation caused by crystal packing requirements. Average bond lengths in the coordination octahedra are Co–N = 1.96 ± 0.01 Å and Co–Cl = 2.260 ± 0.008 Å. Optical rotatory dispersion, circular dichroism, and absorption spectra for this complex are shown and compared with spectra for similar complexes in the literature. The correlation of these spectra with absolute configuration and the conformation of the chelate rings is discussed.

Introduction

The assignment of absolute configuration and chelate ring conformation on the basis of optical rotatory dispersion (ORD) and circular dichroism (CD) data has too often been incorrect. Robinson, *et al.*, pointed out the need for care in making such assignments "even for complexes which have similar visible absorption spectra and chromophores which have effectively D_{4h} symmetry."[1] Reference molecules are needed for which both crystal and molecular structure and the circular dichroism data are known in detail. Preferably, these should have high conformational and configurational stability to minimize the possibility of alteration during phase changes from solution to solid. Recently a new tetradentate ligand with four optical centers of different relative configurations has been reported.[2] In a Co(III) complex, the ligand is strongly stereoselective for the trans isomer (Figure 1), and the only other isomer observed, the L-cis-β, readily isomerizes to the trans geometry. Initially, a D-cis-α isomer was predicted by analogy with (*S,S*)-α,α'-$(CH_3)_2$trien which complexes with Co(III) to give 95% D-cis-α, 4% L-cis-β, and 1% trans isomers.[3] As in the new ligand, the backbone of this trien molecule has a configuration

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