CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS,
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The Crystal and Molecular Structure of a Five-Coordinate Nickel(II) Complex

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The crystal and molecular structure of bis(salicylidene-γ-iminopropyl)aminenickel(II) [$NiC_{20}H_{23}N_3O_2$] has been determined using three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares methods to a conventional R factor of 0.046 (based on isotropic temperature factors). This complex crystallizes in the monoclinic system in space group $P2_1/c$ with 4 molecules in a unit cell of dimensions $a = 12.09 \pm 0.02$, $b = 14.05 \pm 0.01$, $c = 11.48 \pm 0.02$ Å, and $\beta = 101.3 \pm 0.1°$. The geometry about the nickel is pentacoordinate and is best approximated in terms of a trigonal-bipyramidal arrangement. The molecular geometry is compared with the effective geometry as determined by optical measurements.

Introduction

In the past 15 years a large research effort has been directed toward the preparation and characterization of five-coordinate complexes of transition metals. This work has shown that such compounds are indeed not rare but are easily produced if one selects his reaction system astutely. There has, however, been a lack of experimental work which would lead to more than a very rudimentary understanding of the electronic structure of five-coordinate species. Indeed, although Ciampolini,[1] Norgett, *et al.*,[2] and Wood[3] have produced energy level diagrams, based on crystal field calculations, which have subsequently been extensively used, there has been no experimental confirmation of the validity of these schemes. Certainly there have been many measurements of the reflectance, mull, and solution spectra of five-coordinate compounds, but as has been shown,[4,5] these techniques are of little use when one wishes an accurate description of the electronic structure.

In an effort to provide sound experimental data for an investigation of the electronic structure of five-coordinate complexes, we have begun the structural investigation of several compounds whose room-temperature polarized absorption spectra indicate they are well suited for a detailed optical analysis.

Preparation of Crystals and Collection and Reduction of the X-Ray Data

Bis(salicylidene-γ-iminopropyl)aminenickel(II), Ni(Saldipa), was prepared as described by Sacconi and Bertini.[6]

Crystals, in the form of green rods with their largest dimension parallel to the c axis, were grown from CH_2Cl_2. A sample measuring 0.10 × 0.20 × 0.40 mm was selected for data collection about the c axis. On the basis of zero and first-layer Weissenberg and precession photographs, taken with Ni-filtered Cu Kα radiation (λ 1.5418 Å), the material was assigned to the monoclinic system. Reflections of the type $0k0$ with k odd and $h0l$ with l odd were found to be systematically absent. The unit cell dimensions, determined by least-squares fitting of data obtained from a Guinier powder photograph using Cu Kα radiation and KCl as an internal standard, are $a = 12.09 \pm 0.02$, $b = 14.05 \pm 0.01$, $c = 11.48 \pm 0.02$ Å, and $\beta = 101.3 \pm 0.1°$. The density obtained by flotation in carbon tetrachloride–hexane is 1.38 g/cm^3 while the calculated density, assuming 4 molecules/unit cell, is 1.40 g/cm^3. These data indicate that the space group is $P2_1/c$.

Intensity data were collected with a PAILRED automatic diffractometer using Mo Kα radiation and an ω-scan routine. The incident beam was monochromatized by means of a graphite single crystal. The diameter of the beam collimator was 0.5 mm and the receiving collimator had a 3.5° aperture. The takeoff angle was 3.0°. Data were collected using Weissenberg geometry with the crystal mounted along c. Intensities on layers $hk0$–$hk7$ were recorded giving a total of 1742 independent reflections. Of these, 168 were nonsystematically absent. Peaks of all 1742 reflections were scanned $\pm 1.6°$ (2θ) on each side of the Bragg angles. The scanning rate was 1°/min. Background counts at each end of the scan were taken for 24 sec. The intensities of four standard reflections, measured after completing data collection for each Weissenberg layer, remained essentially constant throughout, showing deviations from the mean attributable only to counting statistics.

Corrections were made for Lorentz and polarization factors, including those introduced by the monochromator. Absorption correction was considered superfluous because of the relatively small size of the crystal combined with the low value of the linear absorption coefficient ($\mu = 10.34$ cm^{-1} for λ(Mo Kα)).

Solution of the Structure

The structure was solved by heavy-atom techniques. The x and z parameters of the nickel atom were determined from the Harker section $P(u,{}^1/_2,w)$ and the y parameters from the Harker line $P({}^1/_2, y, {}^1/_2)$. Positional and thermal parameters for all nonhydrogen atoms were determined by difference Fourier methods and refinement using full-matrix least squares.[7] The atomic scattering factors used are those given by Hanson, *et al.*[8] The nickel scattering factors were corrected for the real part of the anomalous dispersion

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10)

correction.[9] Calculated H coordinates assuming normal bond angles and C–H and N–H distances of 1.0 and 0.9 Å were initially used.

A subsequent difference synthesis confirmed the correctness of these positions. The R value (where $R = \Sigma||F_o| - |F_c||/\Sigma F_o$) was then 0.047 when all reflections with $|F_o| < 11.67$ (20.0 unscaled) were omitted from the refinement and the rest given unit weight. A refinement using anisotropic temperature factors for all nonhydrogen atoms has also been made. This gave an R value of 0.026. Since it was considered desirable to keep the reflection/parameter ratio as high as possible, the final refinements were made with isotropic temperature factors and with only the weakest reflections ($F <$ 5.92) omitted from the refinement. The final weights applied to the F_o values were chosen to keep the quantity $\Sigma w(F_o - F_c)^2$ reasonably near unity over the entire range of data and were $w = (0.09F_o)^{-1}$ for $5.92 < F_o < 12.0$, $w = (1.20 - 0.01F_o)^{-1}$ for $12.0 < F_o < 44.0$, and $w = (0.10 + 0.015F_o)^{-1}$ for $44.0 < F_o$.

Observed and final calculated structure amplitudes, multiplied by 10, are given in Table I.

The refined positional and thermal parameters are listed in Table II. The higher values of the temperature factors for the carbon atoms at the outer ends of the molecule indicate the expected flapping motion of the phenyl groups. After the last refinements, all of the shifts in parameters for nonhydrogen atoms and most of the shifts in parameters for hydrogen atoms were well below 10% of the standard deviations. The

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(9) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.20.

TABLE II
POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	x	*y*	*z*	*B*, Å^2
Ni	0.17615 (7)	0.38196 (6)	0.90705 (9)	2.87 (3)
O(1)	0.3196 (4)	0.3660 (3)	0.8502 (4)	4.23 (10)
O(2)	0.0080 (4)	0.3647 (3)	0.8681 (5)	4.24 (10)
N(1)	0.1995 (5)	0.4586 (4)	0.0630 (5)	3.50 (12)
N(2)	0.1556 (4)	0.5050 (4)	0.8121 (6)	3.43 (11)
N(3)	0.2023 (4)	0.2575 (4)	−0.0028 (6)	3.59 (12)
C(1)	0.2869 (5)	0.2011 (5)	−0.0026 (7)	3.56 (14)
C(2)	0.3700 (5)	0.2094 (4)	0.9245 (7)	3.34 (14)
C(3)	0.4411 (6)	0.1298 (6)	0.9220 (8)	4.69 (17)
C(4)	0.5220 (7)	0.1293 (7)	0.8498 (9)	5.80 (20)
C(5)	0.5353 (8)	0.2077 (7)	0.7838 (11)	6.14 (23)
C(6)	0.4692 (6)	0.2902 (5)	0.7850 (8)	4.71 (17)
C(7)	0.3828 (6)	0.2896 (5)	0.8552 (7)	3.92 (15)
C(8)	0.0720 (5)	0.5237 (5)	0.7321 (7)	3.60 (15)
C(9)	0.9730 (5)	0.4664 (4)	0.6936 (7)	3.25 (14)
C(10)	0.8965 (6)	0.4879 (6)	0.5885 (8)	4.25 (17)
C(11)	0.7995 (8)	0.4375 (6)	0.5455 (10)	5.40 (21)
C(12)	0.7727 (7)	0.3629 (6)	0.6148 (8)	5.03 (17)
C(13)	0.8434 (6)	0.3403 (6)	0.7210 (9)	4.52 (18)
C(14)	0.9464 (5)	0.3901 (5)	0.7648 (6)	3.43 (14)
C(15)	0.2495 (7)	0.5738 (6)	0.8457 (8)	4.17 (16)
C(16)	0.2663 (7)	0.6057 (6)	0.9737 (8)	4.80 (18)
C(17)	0.2923 (7)	0.5289 (6)	0.0703 (9)	4.53 (18)
C(18)	0.2143 (6)	0.3975 (5)	0.1714 (7)	3.90 (15)
C(19)	0.1175 (6)	0.3282 (5)	0.1610 (9)	4.15 (16)
C(20)	0.1290 (7)	0.2384 (5)	0.0836 (8)	4.07 (16)
H(N1)	0.142 (5)	0.492 (4)	0.062 (5)	−0.3 (12)
H(C1)	0.293 (4)	0.148 (4)	0.064 (6)	0.4 (13)
H(C3)	0.423 (5)	0.070 (5)	0.975 (6)	2.1 (15)
H(C4)	0.542 (10)	0.068 (9)	0.843 (12)	10.9 (40)
H(C5)	0.564 (7)	0.228 (6)	0.729 (9)	4.1 (25)
H(C6)	0.470 (4)	0.350 (3)	0.723 (5)	−0.8 (11)
H(C8)	0.073 (5)	0.578 (4)	0.675 (6)	1.3 (15)
H(C10)	0.922 (4)	0.536 (4)	0.560 (6)	0.1 (13)
H(C11)	0.762 (8)	0.457 (7)	0.483 (10)	6.4 (29)
H(C12)	0.685 (7)	0.326 (6)	0.576 (8)	5.4 (23)
H(C13)	0.825 (6)	0.307 (6)	0.783 (8)	3.9 (20)
H(C15)*A*	0.308 (5)	0.540 (4)	0.832 (5)	0.0 (12)
H(C15)*B*	0.229 (6)	0.625 (5)	0.776 (7)	3.4 (17)
H(C16)*A*	0.208 (4)	0.635 (4)	−0.008 (5)	−0.7 (11)
H(C16)*B*	0.342 (9)	0.657 (7)	0.996 (10)	8.4 (31)
H(C17)*A*	0.321 (6)	0.554 (6)	0.164 (9)	4.7 (21)
H(C17)*B*	0.353 (4)	0.498 (3)	0.057 (4)	−2.3 (9)
H(C18)*A*	0.294 (5)	0.366 (4)	0.192 (6)	1.9 (15)
H(C18)*B*	0.220 (4)	0.439 (4)	0.258 (6)	0.6 (13)
H(C19)*A*	0.110 (6)	0.305 (6)	0.248 (9)	4.5 (21)
H(C19)*B*	0.039 (5)	0.354 (4)	0.114 (6)	1.0 (14)
H(C20)*A*	0.158 (6)	0.183 (6)	0.137 (8)	4.3 (20)
H(C20)*B*	0.058 (4)	0.224 (3)	0.040 (5)	−1.6 (10)

[a] See Figure 1 for the identities of the atoms. The esd, in parentheses, is in the units of the least significant digit given for the corresponding parameter.

R value was then 0.046 for the 1198 reflections used in the refinement. Including zero-weight data, the *R* value was 0.059.

Discussion

The structure of Ni(Saldipa) consists of discrete molecules in which the nickel atom is pentacoordinated by three nitrogen and two oxygen atoms. As can be seen from Figure 1, the molecular geometry, while not truely trigonal bipyramidal, approximates distorted trigonal-bipyramidal symmetry if one defines the equatorial plane as containing O_1, O_2, N_1. The molecular symmetry as determined by X-ray methods is C_1, even if only the first coordination sphere is considered; however, room-temperature polarized optical measurements indicate that the effective symmetry of the molecule is at least C_2.[10]

It is possible to compare this structure with that of bis(salicylidene-γ-iminopropyl)methylaminenickel(II), Ni(SalMeDPT), as determined by Orioli, *et al.*[11] These two compounds differ in that on the ligand SalMeDPT

TABLE III
BOND DISTANCES WITH THEIR STANDARD DEVIATIONS

Bond	Distance, Å	Bond	Distance, Å
Ni–O(1)	1.981 (5)	C(5)–C(6)	1.40 (1)
Ni–O(2)	2.008 (5)	C(6)–C(7)	1.43 (1)
Ni–N(1)	2.060 (6)	N(1)–C(17)	1.48 (1)
Ni–N(2)	2.032 (6)	C(17)–C(16)	1.53 (1)
Ni–N(3)	2.024 (6)	C(16)–C(15)	1.51 (1)
N(1)–C(18)	1.49 (1)	C(15)–N(2)	1.48 (1)
C(18)–C(19)	1.50 (1)	N(2)–C(8)	1.25 (1)
C(19)–C(20)	1.56 (1)	C(8)–C(9)	1.43 (1)
C(20)–N(3)	1.47 (1)	O(2)–C(14)	1.32 (1)
N(3)–C(1)	1.29 (1)	C(14)–C(9)	1.42 (1)
C(1)–C(2)	1.43 (1)	C(9)–C(10)	1.40 (1)
O(1)–C(7)	1.31 (1)	C(10)–C(11)	1.37 (1)
C(7)–C(2)	1.40 (1)	C(11)–C(12)	1.39 (1)
C(2)–C(3)	1.41 (1)	C(12)–C(13)	1.38 (1)
C(3)–C(4)	1.40 (1)	C(13)–C(14)	1.43 (1)
C(4)–C(5)	1.36 (1)		

TABLE IV
BOND DISTANCES INVOLVING HYDROGEN ATOMS[a]

Bond	Distance, Å	Bond	Distance, Å
N(1)–H(Ni)	0.84	C(17)–H(17)A	1.13
C(18)–H(C18)A	1.04	C(17)–H(C17)B	0.89
C(18)–H(C18)B	1.15	C(16)–H(C16)A	0.87
C(19)–H(C19)A	1.08	C(16)–H(C16)B	1.15
C(19)–H(C19)B	1.05	C(15)–H(C15)A	0.89
C(20)–H(C20)A	1.01	C(15)–H(C15)B	1.07
C(20)–H(C20)B	0.92	C(8)–H(C8)	1.01
C(1)–H(C1)	1.06	C(10)–H(C10)	0.83
C(3)–H(C3)	1.08	C(11)–H(C11)	0.81
C(4)–H(C4)	0.90	C(12)–H(C12)	1.19
C(5)–H(C5)	0.83	C(13)–H(C13)	0.91
C(6)–H(C6)	1.10		

[a] Average esd is 0.07 Å.

TABLE V
ANGLES IN THE MOLECULE (DEG)

N(1)–Ni–O(1)	111.4 (2)	C(7)–C(6)–C(5)	118.4 (8)
O(1)–Ni–O(2)	145.7 (2)	C(6)–C(5)–C(4)	122.0 (9)
O(2)–Ni–Ni(1)	102.5 (2)	C(5)–C(4)–C(3)	119.8 (9)
N(1)–Ni–N(2)	90.1 (3)	C(4)–C(3)–C(2)	120.9 (8)
N(1)–Ni–N(3)	91.5 (3)	C(3)–C(2)–C(7)	119.2 (6)
O(1)–Ni–N(2)	86.7 (2)	N(1)–C(17)–C(16)	112.4 (7)
O(1)–Ni–N(3)	90.7 (2)	C(17)–C(16)–C(15)	117.7 (7)
O(2)–Ni–N(2)	88.3 (2)	C(16)–C(15)–N(2)	113.3 (7)
O(2)–Ni–N(3)	93.4 (2)	C(15)–N(2)–Ni	114.0 (5)
N(2)–Ni–N(3)	177.2 (2)	Ni–N(2)–C(8)	124.6 (5)
N(1)–C(18)–C(19)	109.9 (6)	C(15)–N(2)–C(8)	121.3 (6)
C(18)–C(19)–C(20)	114.2 (7)	N(2)–C(8)–C(9)	127.7 (7)
C(19)–C(20)–N(3)	111.5 (6)	Ni–O(2)–C(14)	122.3 (4)
C(20)–N(3)–Ni	116.5 (4)	O(2)–C(14)–C(9)	124.7 (6)
Ni–N(3)–C(1)	125.0 (5)	O(2)–C(14)–C(13)	118.8 (6)
C(20)–N(3)–C(1)	117.7 (6)	C(9)–C(14)–C(13)	116.4 (7)
N(3)–C(1)–C(2)	126.4 (7)	C(14)–C(13)–C(12)	122.9 (8)
Ni–O(1)–C(7)	128.2 (4)	C(13)–C(12)–C(11)	120.2 (8)
O(1)–C(7)–C(2)	123.5 (6)	C(12)–C(11)–C(10)	117.4 (9)
O(1)–C(7)–C(6)	116.8 (6)	C(11)–C(10)–C(9)	124.7 (8)
C(2)–C(7)–C(6)	119.6 (6)	C(10)–C(9)–C(14)	118.2 (6)

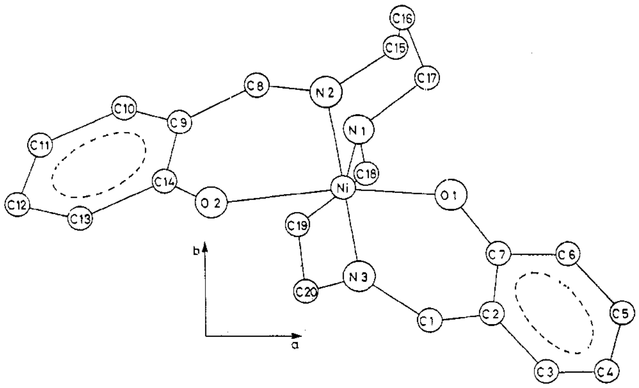

Figure 1.—The molecular structure of Ni(Saldipa).

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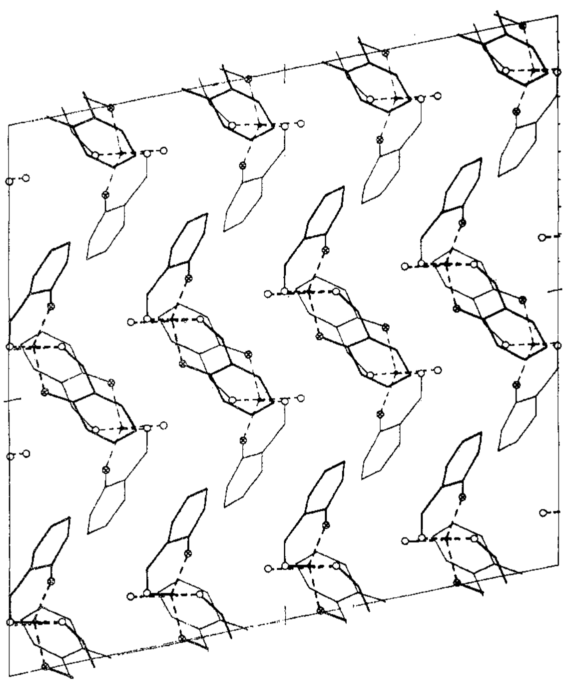

Figure 2.—Molecular packing in Ni(Saldipa).

a methyl group has replaced the proton on the secondary amine. While this is a small perturbation with respect to the entire molecule, it appears that the introduction of this methyl group has a significant effect on the geometry of the first coordination sphere, as evidenced by a somewhat more regular arrangement of the nitrogen and oxygen atoms around the nickel atom in Ni(SalMeDPT) than in Ni(Saldipa). For Ni(SalMeDPT) the angles in the equatorial plane are O–Ni–O′ = 142°, O′–Ni–N = 105°, and N–Ni–O = 113°,[11] while in Ni(Saldipa) the corresponding angles are $\mathrm{O_1}$–Ni–$\mathrm{O_2}$ = 145.7 (2)°, $\mathrm{O_2}$–Ni–$\mathrm{N_1}$ = 102.5 (2)°, and $\mathrm{N_1}$–Ni–$\mathrm{O_1}$ = 111.4 (2)°. Analogous bond distances in the two structures agree quite well.

The geometry of Ni(Saldipa) is in clear contrast to the structure of the Schiff's base complex $\mathrm{Ni[O(5\text{-}Cl\text{-}C_6H_3)CH{=}NC_2H_4N(C_2H_5)_2]_2}$. This complex has been shown to have a distinctly square-pyramidal configuration.[12] Here two nitrogen and two oxygen atoms form a square plane and the Ni atom is somewhat out of the plane. An apical nitrogen then completes the coordination polyhedron.

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The Crystal and Molecular Structure of the Mixed Sandwich Complex π-Cyclopentadienyl-π-triphenylcyclopropenylnickel, (π-$\mathrm{C_5H_5}$)Ni(π-$\mathrm{C_3(C_6H_5)_3}$)

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The crystal and molecular structure of π-cyclopentadienyl-π-triphenylcyclopropenylnickel, (π-$\mathrm{C_5H_5}$)Ni(π-$\mathrm{C_3(C_6H_5)_3}$), has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecular units in the orthorhombic space group $Pna2_1$ with four molecules per unit cell of dimensions a = 21.003 (1), b = 12.3596 (7), and c = 7.4959 (5) Å. The measured and calculated densities are 1.32 (1) and 1.328 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.056 for the 1751 intensities above background. The nickel atom is complexed in a sandwich fashion between the parallel cyclopentadienyl and triphenylcyclopropenyl rings, the averages of the nickel–carbon distances being 2.100 (6) and 1.961 (4) Å, respectively, for the two rings. Average C–C distances were 1.405 (9) Å for the cyclopentadienyl ring and 1.428 (5) Å for the cyclopropenyl ring. The phenyl groups are bent and twisted out of the plane of the cyclopropenyl ring in "propeller" fashion. Disorder was found in the cyclopentadienyl ring.

Introduction

An area of continuing interest in the field of organometallic chemistry is that of π-bonded "sandwich" complexes of the transition elements. The vast majority of complexes of this nature obey the well-known noble gas formalism. This rule suggests that an isoelectronic series of mixed sandwich compounds[1] containing a cyclopentadienyl ring and carbocyclic rings of varying sizes should exist—namely, (π-$\mathrm{C_5H_5}$)Cr(π-$\mathrm{C_7H_7}$),[2] (π-$\mathrm{C_5H_5}$)Mn(π-$\mathrm{C_6H_6}$),[3] (π-$\mathrm{C_5H_5}$)Fe(π-$\mathrm{C_5H_5}$),[4,5] (π-$\mathrm{C_5H_5}$)Co(π-$\mathrm{C_4R_4}$) where R = H[6,7] and $\mathrm{C_6H_5}$,[8,9] and (π-$\mathrm{C_5H_5}$)Ni(π-$\mathrm{C_3R_3}$) where R = H[10] and $\mathrm{C_6H_5}$.[11,12] With the exception of ferrocene, no crystallographic data

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