As mentioned above the Ni–S distances are equal, within experimental error, in Ni(dtpi)$_2\cdot$2py and Ni(dtp)$_2\cdot$2py, while a significant difference has been observed on the two adducts from both optical spectra and calculations. This leads to the conclusion that the position in the spectrochemical series is a more sensitive indication of variations in the electronic structures of sulfur-containing ligands than differences in the metal–sulfur bond lengths. In our opinion, the similarity of Ni–S distances in the two structures may be ascribed to the smallness of the variation of the electronic effects with respect to the experimental standard deviations.

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The Crystal and Molecular Structure of the Tetrahedrally Coordinated Complex Dibromo[*cis-endo-N,N'*-di(4-methylbenzylidene)-*meso*-2,3-butanediamine]nickel(II)

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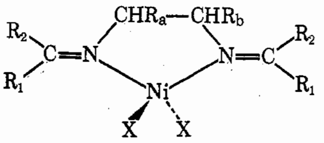
The crystal structure of Ni[$C_{20}H_{24}N_2$]Br_2 where $C_{20}H_{24}N_2$ is the bidentate imine ligand formed in the Schiff base reaction of 4-methylbenzaldehyde with *meso*-2,3-butanediamine has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods. The structure has been refined by full-matrix least-squares method to a conventional R factor of 0.065 and a weighted R factor of 0.059 based on 1273 reflections for which $I_{\text{obsd}} > \sigma(I)$. The compound crystallized in the monoclinic space group Cc with cell constants a = 15.584 (3) Å, b = 11.325 (3) Å, c = 14.135 (4) Å, and β = 122.53 (1)°. The density calculated for z = 4 is 1.6132 g/cm^3 while the observed density is 1.60 (2) g/cm^3. The structure consists of discrete molecules in which the coordination polyhedron about the nickel is a highly distorted tetrahedron with Br–Ni–Br and N–Ni–N angles of 138.8 (1) and 85.0 (7)°, respectively. The average Ni–Br distance is 2.359 (4) Å and the average Ni–N distance is 1.96 (2) Å. The tolyl groups are cis-endo with respect to the nickel atom and the aliphatic chain is puckered in the *gauche* configuration with one axial and one equatorial methyl substituent.

Introduction

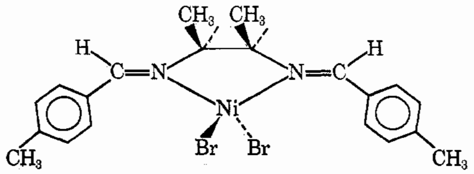
A recent series of pmr investigations[2-4] in these laboratories of paramagnetic Schiff base complexes of type **1** sought to establish, among other things, a criterion of stereochemistry based on the observed aryl proton isotropic nmr shift behavior. For complexes synthesized from benzaldehyde derivatives (B; R_1 = aryl, R_2 = H) the aryl proton resonances exhibit the ortho, meta, para alternation of shifts generally ascribed to the π-spin delocalization, while those derived from acetophenones (Ap; R_1 = CH_3, R_2 = aryl) show a shift behavior ascribable to σ-spin delocalization in the aryl moiety. The complexes prepared from benzophenone derivatives (Bp; R_1 = R_2 = aryl) exhibit aryl proton nmr spectra corresponding to a superposition of those of the B and Ap complexes, indicating magnetic inequivalence of the aryl groups with one showing σ- and the other π-type delocalization.



1, R_1, R_2 = H, CH_3, aryl
R_a, R_b = H, CH_3
X = halogen

It was argued at the time[3] that a steric interaction between the endo aryl groups (R_1 in **1**) and the coordinated halogen atoms would probably prevent their becoming coplanar with the Ni—N=C moiety and hence that σ-spin delocalization behavior would occur for such endo aryl groups. On the other hand, it was thought that an exo-situated aryl group (R_2) might be reasonably free of steric restraint and could conjugate with the imino π system, resulting in a predominant π-delocalization pattern. The present structural investigation on a B derivative, R_1 = tolyl, R_2 = H, was carried out to test this hypothesis and to put the pmr assignments on a firm basis.

Another structural feature of interest in the complex chosen for study, dibromo[*cis-endo-N,N'*-di(4-methylbenzylidene)-*meso*-2,3-butanediamine]nickel(II), **2**, lies in the geometry of the 2,3-butanediamine (bn) chelate ring. Fairly large differences in isotropic shifts were observed for the bn ring methyl resonances between meso and racemic forms of this complex.[2] For a puck-



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[1] Petroleum Research Fund predoctoral fellow, 1969–1970.

[2] I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Chem. Commun.*, 1471 (1969).

[3] I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 693, 698 (1970).

[4] D. L. Johnston, I. Bertini, and W. DeW. Horrocks, Jr., *ibid.*, in press.

ered chelate chain one methyl must be axial and one equatorial for the meso complex while in a racemic form both methyl groups can occupy identical stereochemical configurations. In the absence of a planar–tetrahedral equilibrium[5] the meso–racemic shift difference must be due to a difference in the effective electron–nuclear hyperfine interaction constants for the two molecules. This can arise through differences in dipolar and/or Fermi contact interactions. In either case, a significant difference in the geometric position of the methyl groups (axial or equatorial) is required to explain the results. For dipolar shifts, differences in methyl group geometric factors[6] are needed to account for shift differences. Furthermore it has recently been shown[7] that Fermi contact shifts in chelate ring substituents depend on stereochemical disposition. Since the nitrogen donor atoms in the present complex are formally sp^2 hybridized, the degree of puckering of the chelate ring was of some interest.

Finally, while a number of X-ray structure determinations have been reported for complexes derived from 1,2-diaminoethane (en) and 1,2-diaminopropane (pn), the present structure represents the first determination involving a bn derivative.

Experimental Section

Preliminary Crystal Data.—The preparation and elemental analysis of $Ni(C_{20}H_{24}N_2)Br_2$ have been previously reported.[3] Violet crystals of the compound were grown by slow evaporation of a chloroform solution under a controlled stream of dry nitrogen. Preliminary Weissenberg photographs on the $hk0$, $hk1$, and $hk2$ layers (Cu $K\alpha$ radiation) showed systematic extinctions: hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, indicating space group Cc or $C2/c$. A crystal having irregular shape but roughly approximating an ellipsoid of dimensions 0.15 × 0.25 × 0.37 mm was chosen for cell dimension and intensity measurements. The crystal was mounted on a glass fiber with the [−2, 0, 4] direction in the monoclinic cell parallel to the spindle axis (φ) of the four-circle Syntex computer-controlled automatic diffractometer equipped with a scintillation counter and pulse-height analyzer. Unit cell dimensions were determined from a least-squares analysis[8] of 11 carefully centered, high 2θ reflections measured at 20° using nickel-filtered (at the X-ray source) copper radiation (Cu $K\alpha_1$, λ 1.54051 Å). The results, with standard deviations of the least significant figure given in parentheses, are a = 15.584 (3) Å, b = 11.325 (3) Å, c = 14.135 (4) Å, β = 122.53 (1)°, and V = 2103.5 (4) Å^3. The density calculated for four molecules per unit cell (Z = 4) is 1.613 (2) g/cm^3. The density found by flotation in a mixture of carbon tetrachloride and methyl iodide was 1.60 (2) g/cm^3. With Z = 4, in space group $C2/c$ the nickel atom would be required to lie at a special position of either 2 or 1 symmetry, both of which are rejected on chemical grounds (the coordination sphere can have at best C_{2v} symmetry and *meso*-bn cannot possess a C_2 axis). Space group Cc (C_s^4, no. 9) was therefore chosen; this choice is supported by the statistical distribution of unitary structure factors (E's)[8] and the successful refinement of the structure.

Collection and Reduction of Intensity Data.—The intensity data were collected at 20° by the θ–2θ scan technique using zirconium-filtered (at the source) Mo $K\bar{\alpha}$ (λ 0.71069 Å) radiation at a scan rate (2θ) of 1°/min. The scans covered a range of 1.25° on each side of the calculated peak position and 15-sec stationary background counts were taken at each end of the scan range. The net intensity, I, was calculated as $I = S - \alpha(B_1 + B_2)$ and the square of the standard deviation of the intensity was taken as $\sigma(I)^2 = S + \alpha^2(B_1 + B_2) + (dS)^2$ where S is the total accumulated scan count, α is the ratio of the scan time to total background time, B_1 and B_2 are the initial and final background counts, and d is the empirical constant here taken as 0.04. Three check reflections were recorded every 105 measurements throughout the data collection. These remained reasonably constant except for a decrease on restarting about halfway through the data set. A scaling factor of 1.083 was applied to (955) and all subsequently measured reflections (the data were collected in the order indicated by Table I). This brought the check reflections into agreement with random variations in I of ±1.3% at I = 194,000, ±1.9% at I = 80,000, and ±6.0% at I = 8000 counts.

A total of 1876 independent reflections were measured (not including space group extinctions $h0l$, $l \neq 2n$, all of which had $I < \sigma(I)$ and were deleted from the data set). A strip chart record and preliminary copper radiation data indicated that seven of the most intense reflections had exceeded the counter capacity. These were remeasured along with twelve other reflections of lower intensity using lower kilovolt and milliampere levels and were entered in the data set with a scaling factor so obtained. The 1, 1, −1 reflection apparently suffers from beam stop interference $2\theta < 6°$ (see Table I) as did −1, 1, 0, and 1, 1, 0, but these latter two were entered with a scaling from preliminary copper radiation data. A total of 1273 reflections had $I \geq \sigma(I)$ and were used in the final refinement.

Observed structure factors, on an arbitrary scale, were obtained by applying Lorentz (L), polarization (p), and absorption (A) corrections to the measured intensities: $F_{\text{obsd}} = [I/ALp]^{1/2}$. The standard deviation of an observed structure factor was computed by $\sigma(F) = 0.5\sigma(I)[IALp]^{-1/2}$ for reflections with $I \geq 3\sigma(I)$ and $\sigma(F) = 0.5\sigma(I)[3\sigma(I)ALp]^{-1/2}$ for reflections with $I < 3\sigma(I)$. Rotation of φ at χ = 90° for the reflection (−6, 0, 12) showed a variation of $I^{1/2}$ between 80 and 100 an a relative scale. Application of an absorption correction (μ_{Mo} = 49.4 cm^{-1}) reduced this variation to between 90 and 100. Transmission factors A varied between 0.43 and 0.59 for the entire data set.

Solution and Refinement of the Structure.—A three-dimensional Patterson synthesis[8] based on preliminary copper radiation data located the positions of the nickel and the two bromine atoms. The x and z nickel atom coordinates were arbitrarily specified as 0.0 and 0.25, respectively, to fix the origin. Three cycles of least-squares refinement of these three atoms[9] yielded residuals[10] R_1 = 0.276 and R_2 = 0.344. Of the highest 50 peaks from a three-dimensional Fourier synthesis phased on the above result, 22 appropriately spaced ones were subjected to two cycles of least-squares refinement with isotropic temperature factors under the assumption that they were all carbon atoms. The nickel and bromine parameters were held fixed during this process. Of the 22 "carbon atoms," 12 appeared to be refining satisfactorily as judged by the magnitudes of their temperature factors ($B \leq 6$). These were retained and were refined for an

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(5) In systems involving a planar ⇄ tetrahedral equilibrium isotropic shift differences have been attributed largely to the difference in the free energy changes $\Delta\Delta G$ for the meso and racemic species involved in this equilibrium: *cf.* R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969), and references therein.

(6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); G. N. La Mar, *ibid.*, **43**, 1085 (1965).

(7) K. I. Zamaraev, Yu. N. Molin, and G. I. Skubevskaya, *J. Struct. Chem.*, **7**, 740 (1966); F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969); F. F.-L. Ho and C. N. Reilley, *ibid.*, **42**, 600 (1970); L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970); L. E. Erickson, F. F.-L. Ho, and C. N. Reilley, *ibid.*, **9**, 1148 (1970).

(8) Programs used for computations on an IBM 360-67: refinement of cell dimensions—Hope's CELDIM; conversion of papertape output to IBM cards—Stanko's PTAPE; absorption and Lp corrections—Prewitt's ACAC; Patterson function and Fourier synthesis—Zalkin's FORDAP; least-squares refinement—the Brown University version of ORFLS; interatomic distance and angle computation—Zalkin's DISTAN; position of hydrogen atoms—Zalkin's HFINDR; unitary structure factors (E's)—Dewar's FAME; calculation of least-squares planes—Chu's LSPLAN; preparation of Table I—Zalkin's List.

(9) Scattering factors for neutral nickel, bromine, carbon, and nitrogen were taken from the "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 201 ff.

(10) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w = \sigma(F_o)^{-2}$. The function minimized in all least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Ni($C_{20}H_{24}N_2$)Br_2[a]

```
FCA(0,0,0) =    464

   H FOR FCA     1  33  32     10   5   9*  -11  29  30
K,L=  0,   0     3  35  33     12  10   5*   -9  12  12
   2  77  70     5  11  12     14   4  10*   -7   5   5*
   4 199 177     7  24  29   K,L=   7,  1    -5  41  41
   6  66  65     9   6   4*   -13  25  23    -3  40  38
   8 102 101    11  14  15   -11  15  13    -1  21  21
  10  22  25   K,L= 10,  0    -9  28  27     1  45  49
  12  14  14   -10  12  11*   -7  36  35     3  60  59
  14  30  32    -8  14  14    -5  35  35     5  35  35
  16   9  11*   -6  13  12    -3  48  49     7  22  24
K,L=  1,   0    -4  23  25    -1  21  25     9  21  22
 -15  14  16    -2   0   7*    1  64  66    11   9   5*
 -13  21  20     0  26  24     3  24  22    13   6   6*
 -11   0  10*    2   8   8*    5  34  34   K,L=  4,  2
  -9   9   9*    4  25  22     7  30  30   -16   9   4*
  -7  57  57     6  15  14     9  28  27   -14  11  12*
  -5  24  25     8   4  13*   11  20  19   -12  36  37
  -3  38  34    10  15  13    13   0  10*  -10  12   9
  -1 120 121   K,L= 11,  0   K,L=  8,  1    -8  23  24
   1 121 121    -9   0   8*  -14   8   8*   -6  51  51
   3  34  28    -7  13   9   -12  14  12    -4  42  44
   5  29  25    -5  10   5*  -10  20  15    -2  43  45
   7  56  55    -3  18  16    -8  19  21     0  38  39
   9  12   9    -1   9  10*   -6  36  36     2  98  95
  11   7   6*    1   8  10*   -4  22  21     4  18  18
  13  20  20     3  18  17    -2  37  35     6  32  32
  15  16  14     5  10   4*    0  55  58     8  34  36
K,L=  2,   0     7  13  11     2  34  32    10  20  24
 -16   4   2*    9   4   7*    4  34  33    12  15  12
```

[a] The asterisks indicate data not used in the refinement.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS[a]

Atoms	x	y	z	$10^4\beta_{11}$[b]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ni	0[c]	0.0259 (2)	1/4[c]	49 (2)	69 (2)	56 (2)	11 (2)	30 (2)	7(2)
Br(1)	0.1428 (3)	0.0998 (2)	0.4174 (3)	52 (2)	100 (3)	55 (2)	1 (2)	27 (2)	−4 (2)
Br(2)	−0.1395 (3)	−0.1001 (2)	0.1943 (3)	63 (2)	84 (3)	109 (3)	−13 (2)	44 (2)	−13 (3)
N(1)	0.0547 (12)	−0.0139 (15)	0.1581 (14)	44 (11)	49 (15)	66 (16)	2 (11)	29 (11)	1 (14)
N(2)	−0.0605 (12)	0.1637 (14)	0.1492 (16)	34 (11)	40 (15)	104 (19)	−4 (11)	20 (13)	−14 (14)
C(1)	0.0940 (15)	−0.1146 (20)	0.1496 (18)	36 (14)	71 (23)	66 (21)	−7 (15)	12 (14)	6 (19)
C(2)	0.1126 (16)	−0.2222 (20)	0.2113 (24)	18 (14)	50 (23)	123 (30)	−8 (15)	25 (18)	−8 (22)
C(3)	0.1124 (18)	−0.2282 (23)	0.3135 (23)	42 (17)	94 (28)	78 (25)	33 (17)	23 (17)	26 (21)
C(4)	0.1265 (17)	−0.3384 (22)	0.3646 (22)	35 (16)	79 (25)	107 (27)	30 (18)	13 (18)	−5 (23)
C(5)	0.1444 (16)	−0.4386 (21)	0.3180 (25)	23 (15)	59 (25)	135 (32)	0 (14)	27 (19)	−3 (22)
C(6)	0.1470 (17)	−0.4366 (23)	0.2196 (26)	31 (15)	109 (29)	122 (30)	−21 (16)	40 (19)	−55 (24)
C(7)	0.1295 (18)	−0.3205 (22)	0.1646 (26)	37 (18)	46 (24)	188 (38)	−14 (16)	24 (21)	−58 (26)
C(8)	0.1600 (19)	−0.5616 (22)	0.3739 (29)	70 (21)	70 (26)	242 (46)	5 (18)	42 (27)	22 (27)
C(9)	−0.0973 (16)	0.2615 (18)	0.1624 (21)	36 (14)	37 (19)	99 (24)	−29 (13)	18 (15)	−13 (18)
C(10)	−0.1091 (18)	0.2886 (22)	0.2578 (21)	52 (18)	59 (24)	68 (24)	3 (16)	22 (17)	2 (19)
C(11)	−0.1089 (17)	0.2031 (21)	0.3264 (21)	41 (17)	72 (23)	75 (23)	−25 (15)	34 (16)	−17 (19)
C(12)	−0.1192 (17)	0.2346 (23)	0.4167 (19)	50 (19)	93 (28)	38 (20)	20 (18)	21 (16)	11 (19)
C(13)	−0.1281 (17)	0.3546 (25)	0.4373 (19)	50 (18)	102 (29)	34 (19)	31 (19)	−1 (15)	12 (19)
C(14)	−0.1296 (18)	0.4367 (22)	0.3601 (22)	57 (20)	92 (28)	70 (24)	14 (17)	13 (19)	−23 (21)
C(15)	−0.1230 (19)	0.4079 (21)	0.2704 (24)	67 (19)	78 (26)	113 (27)	11 (18)	72 (20)	−15 (21)
C(16)	−0.1349 (18)	0.3873 (20)	0.5344 (19)	87 (19)	97 (26)	56 (20)	2 (19)	38 (16)	−11 (19)
C(17)	0.0434 (19)	0.0789 (20)	0.0856 (23)	68 (21)	62 (24)	95 (27)	9 (17)	30 (20)	14 (21)
C(18)	−0.0583 (16)	0.1374 (19)	0.0444 (19)	45 (16)	73 (23)	65 (20)	−2 (15)	44 (16)	−4 (18)
C(19)	0.1366 (17)	0.1635 (21)	0.1502 (22)	47 (17)	84 (25)	113 (27)	25 (17)	38 (19)	12 (22)
C(20)	−0.0790 (22)	0.2503 (23)	−0.0259 (21)	101 (22)	120 (31)	63 (21)	53 (20)	47 (19)	65 (20)

[a] Numbers in parentheses in all tables are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] Coordinates chosen to fix the unit cell origin.

additional cycle along with the nickel and bromine atoms yielding $R_1 = 0.203$ and $R_2 = 0.264$. A difference Fourier computed at this point revealed likely positions for the remaining 10 nonhydrogen atoms. The total of 25 atoms were refined for two cycles at which point two of the carbon atoms were discarded owing to their rapidly increasing temperature factors. One additional cycle ($R_1 = 0.100$, $R_2 = 0.137$), followed by a difference Fourier disclosed the positions of the two remaining carbon atoms (bn ring methyl groups). At this point molybdenum radiation data became available and two cycles of isotropic refinement of all 25 nonhydrogen atoms using real and imaginary dispersion corrections[11] for nickel and bromine atoms gave $R_1 = 0.101$ and $R_2 = 0.101$. The absorption correction was then applied and one cycle of refinement resulted in $R_1 = 0.079$ and $R_2 = 0.072$. Hydrogen atoms were inserted at their calculated positions, but as they produced a negligible effect on the residuals ($R_1 = 0.078$, $R_2 = 0.068$) without refinement, they were omitted from the final refinement. Anisotropic temperature factors[12] were applied to all atoms and three cycles of refinement converged to final residuals $R_1 = 0.065$ and $R_2 = 0.059$. The standard deviation of an observation of unit weight is 1.05. The maximum shift of any positional parameter during the final cycle was 0.25 of its standard deviation and that of any thermal parameter was 0.38 of its standard deviation. A final difference Fourier showed residual density of 0.38 e$^-$/Å^3 near the nickel atom, but all other peaks were less than 0.3 e$^-$/Å^3, on a scale where a carbon atom has a peak density of 1.04 e$^-$/Å^3.

The observed and calculated structure factors are given in Table I. The fractional atomic positional coordinates and the components of the anisotropic thermal tensors are set out in Table II.

Description and Discussion of the Structure

The structure consists of discrete molecules of the four-coordinate complex Ni[$C_{20}H_{24}N_2$]Br$_2$ containing the bidentate Schiff base ligand and two coordinated bromine atoms. The shortest intermolecular Ni–Br distance is 6.35 Å and the nearest intermolecular Ni–Ni approach is 7.09 Å. The atoms in the first coordination sphere correspond roughly to C_{2v} symmetry. The dihedral angle between the planes defined by N(1), Ni, N(2) and Br(1), Ni, Br(2) is 88.1°. Deviations from idealized tetrahedral symmetry are large (*vide infra*). A view of the molecule projected on the (100) plane is given in Figure 1, where the atom-labeling scheme is also indicated. Table III gives selected bond distances and angles.

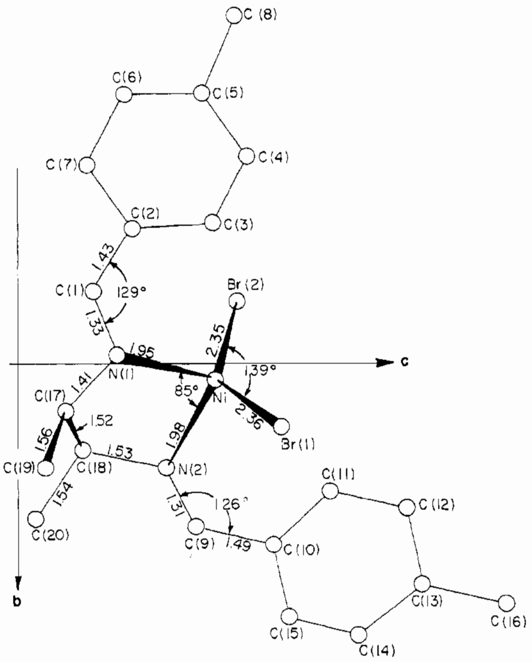

Figure 1.—Projection of Ni($C_{20}H_{24}N_2$)Br$_2$ onto the (100) plane. C(19) has been moved 0.5 Å to negative *c* to clarify the bonding.

A major finding of the present work is that the chelating Schiff base ligand is in the cis-endo configuration as indicated in structure **2**. This is contrary to our previous arguments.[3] A steric interaction between

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[11] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[12] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)

Ni–Br(1)	2.364 (3)	C(2)–C(3)	1.45 (4)
Ni–Br(2)	2.354 (4)	C(2)–C(7)	1.39 (4)
Ni–N(1)	1.95 (2)	C(3)–C(4)	1.40 (4)
Ni–N(2)	1.98 (2)	C(4)–C(5)	1.41 (4)
Ni–C(3)	3.24 (3)	C(5)–C(6)	1.41 (4)
Ni–C(11)	3.17 (2)	C(6)–C(7)	1.48 (4)
Br(1)–Br(2)	4.416 (5)	C(5)–C(8)	1.55 (4)
Br(1)–C(3)	3.93 (3)	C(9)–C(10)	1.49 (4)
Br(1)–C(11)	3.60 (2)	C(10)–C(11)	1.37 (4)
Br(2)–C(3)	3.64 (2)	C(10)–C(15)	1.40 (3)
Br(2)–C(11)	3.82 (2)	C(11)–C(12)	1.42 (4)
N(1)–C(1)	1.33 (3)	C(12)–C(13)	1.41 (4)
N(1)–C(17)	1.41 (3)	C(13)–C(14)	1.43 (4)
N(2)–C(9)	1.31 (3)	C(14)–C(15)	1.37 (4)
N(2)–C(18)	1.53 (3)	C(13)–C(16)	1.48 (3)
N(1)–N(2)	2.65 (2)	C(17)–C(18)	1.52 (3)
N(1)–C(20)	3.77 (3)	C(17)–C(19)	1.56 (3)
N(2)–C(19)	3.07 (3)	C(18)–C(20)	1.54 (3)
C(1)–C(2)	1.43 (3)	C(19)–C(20)	3.08 (4)
Br(1)–Ni–(Br(2)	138.8 (1)	Ni–N(1)–C(1)	130 (1)
Br(1)–Ni–N(1)	103.6 (5)	Ni–N(1)–C(17)	112 (1)
Br(1)–Ni–N(2)	105.6 (5)	C(1)–N(1)–C(17)	117 (2)
Br(2)–Ni–N(1)	107.0 (5)	Ni–N(2)–C(9)	130 (2)
Br(2)–Ni–N(2)	103.9 (5)	Ni–N(2)–C(18)	107 (1)
N(1)–Ni–N(2)	85.0 (7)	C(9)–N(2)–C(18)	123 (2)
N(1)–C(1)–C(2)	129 (2)	N(2)–C(9)–C(10)	126 (2)
C(1)–C(2)–C(3)	123 (2)	C(9)–C(10)–C(11)	123 (2)
C(1)–C(2)–C(7)	115 (3)	C(9)–C(10)–C(15)	115 (2)
C(3)–C(2)–C(7)	123 (2)	C(11)–C(10)–C(15)	123 (2)
C(2)–C(3)–C(4)	118 (2)	C(10)–C(11)–C(12)	120 (2)
C(3)–C(4)–C(5)	119 (2)	C(11)–C(12)–C(13)	120 (2)
C(4)–C(5)–C(6)	124 (2)	C(12)–C(13)–C(14)	116 (2)
C(4)–C(5)–C(8)	120 (3)	C(12)–C(13)–C(16)	120 (2)
C(6)–C(5)–C(8)	116 (2)	C(14)–C(13)–C(16)	125 (2)
C(5)–C(6)–C(7)	116 (2)	C(13)–C(14)–C(15)	125 (2)
C(2)–C(7)–C(6)	120 (3)	C(14)–C(15)–C(10)	116 (2)
N(1)–C(17)–C(18)	108 (2)	N(2)–C(18)–C(17)	106 (2)
N(1)–C(17)–C(19)	108 (2)	N(2)–C(18)–C(20)	111 (2)
C(18)–C(17)–C(19)	114 (2)	C(17)–C(18)–C(20)	115 (2)

the endo tolyl groups and the coordinated bromine atoms may account for the extremely large observed Br(1)–Ni–Br(2) angle of 139°, which may be compared with 126° for the corresponding angle in Ni[$(C_6H_5)_2$P]$_2$-Br_2.[13] The tolyl planes roughly bisect the Br–Ni–Br angle and two of the ortho hydrogen atoms approach the nickel atom quite closely (to within 2.51 and 2.43 Å for hydrogen atoms placed 1.0 Å from carbon atoms C(3) and C(11), respectively). Close approach of an ortho phenyl hydrogen atom to the metal has been found in other complexes[14] and may be indicative of a positive Ni–H interaction. The Ni–Br average bond length of 2.36 Å agrees with the same distances in other tetrahedral nickel complexes: Ni[$(C_6H_5)_3$P]$_2$$Br_2$, 2.34 Å;[13] [$(n\text{-}C_4H_9)_4$N][Ni($C_9H_7$N)$Br_3$], 2.38 Å.[15]

The average Ni–N distance of 1.96 Å agrees well with the 1.97 Å average for tetrahedral bis(*N*-isopropylsalicyladiminato)nickel(II).[16] The N–Ni–N angle of 85°, fixed by the bite size of the ligand (2.65 Å), is in the range of 82–89° found for ethylenediamine chelate compounds.[17,18] Except for the N–Ni–N and Br–Ni–Br angles, the bond angles formed at the nickel atom are all within 6° of the idealized tetrahedral angle (see Table III).

Chelating Schiff Base Ligand.—Since the present complex is synthesized from a preformed Schiff base and nickel bromide, the finding that it exists in the cis-endo configuration suggests that the Schiff base itself is formed with the *N*-alkyl substituent trans to the aryl moiety. Despite the steric interaction with the coordinated bromine atoms, the planes of the tolyl group and the imine moiety are roughly parallel (the tolyl group planes make angles of 15 and 18°, respectively, with the planes defined by C(2), C(1), N(1) and C(10), C(9), N(2)). This degree of coplanarity is consistent with the observed π-spin delocalization as evident from nmr isotropic shifts of the aryl protons in this and analogous complexes derived from benzaldehyde. This result places the pmr assignments on a firm basis and demonstrates that π delocalization in an aryl moiety is diagnostic of an endo configuration with respect to the metal center in complexes of this type. Contrary conclusions[19] based on steric arguments for spin delocalization in monodentate imines octahedrally coordinated to nickel(II) may also require modification.

Since the present determination is the first for a complex containing a ligand derived from 2,3-diaminobutane, bn, this portion of the structure is of some interest. Despite the fact that the donor nitrogen atoms are formally sp^2 hybridized, the chelate ring is significantly puckered. Linking carbon atom C(17) is 0.25 Å above the NiN_2 plane defined by N(1), Ni, N(2) while C(18) is 0.43 Å below this plane. As is required for the *meso* form, one ring methyl, C(19), is axial, 1.80 Å above the NiN_2 plane while the other ring methyl, C(20), is equatorial, 0.13 Å below the same plane. These results may be compared with those for *l*-[Co((*R*)-pn)$_3$]Br_3[20] wherein the linking carbon atoms are 0.31 Å above and 0.39 Å below the CoN_2 plane, while the ring methyl substituent (equatorial) is 0.02 Å below this plane. In terms of dihedral angles the ring conformation is clearly seen to be gauche with one axial and one equatorial methyl group as shown in Figure 2. The dihedral angles between planes defined by the linking carbon atoms C(17) and C(18) and each of the four neighboring atoms are indicated (the planes are labeled according to the unique atom). The dihedral angle of 50.5° between the N(1) and N(2) planes is fairly typical for diamine chelates (51° for *l*-[Co((*R*)-pn)$_3$]Br_3,[20] 46 and 63° for [Co(*l*-pn)$_2$$Cl_2$]-[Cl·HCl·2$H_2O$],[21] 53–55° for Pt(en)$_2$$Cl_2$,[22] and 62.4° for dichloro(*N*,*N*-ethylenedimorpholine)cobalt(II)[18]).

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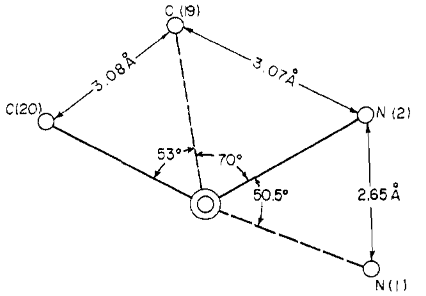


Figure 2.—Projection of the bn moiety perpendicular to the C(18) to C(17) bond. Dashed line indicates bonds to C(17) which is below C(18). Angles indicated are dihedral angles between planes through C(17), C(18), and each of the other atoms.

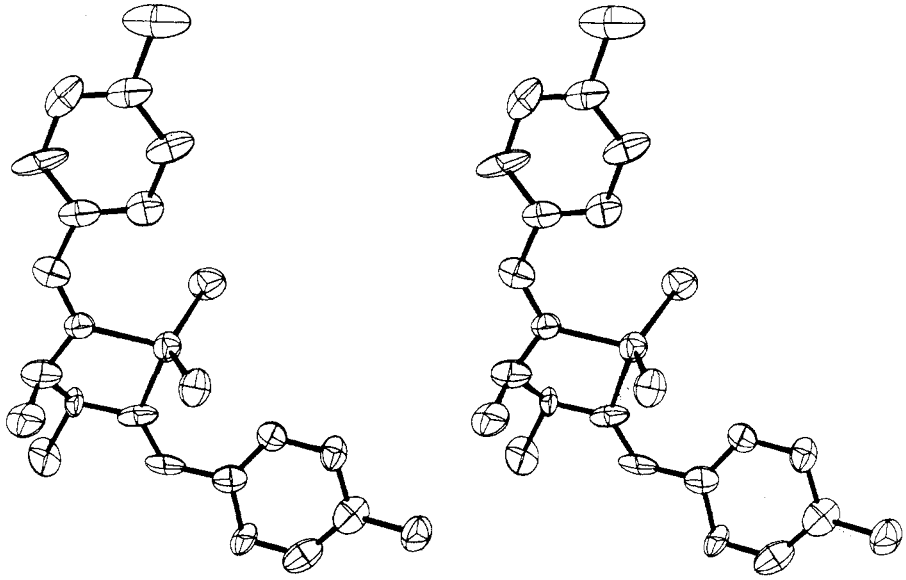
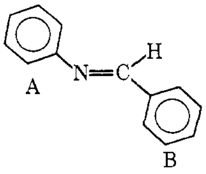


Figure 3.—A stereoscopic view of the Ni[$C_{20}H_{24}N_2$]Br_2 molecule prepared by C. K. Johnson's program ORTEP. Hydrogen atoms are not shown. The ellipsoids are drawn to include 50% of the probability distribution.

The axial methyl group C(19) is only 3.07 Å from N(2) and it is possible that the resulting interaction is repulsive and might account for the N(2)–C(18) bond distance (1.53 Å) being longer than the corresponding N(1)–C(17) distance (1.41 Å) where this interaction is absent. It should be noted, however, that the two values differ from the average (1.47 Å) by only two standard deviations and the discrepancy may result from inaccuracies in the data. The small but significant differences in isotropic shift magnitudes between the racemic and meso forms of the present complex and between nonequivalent aryl groups in complexes derived from the unsymmetrical diamine, pn, may be related to these structural effects. In the present meso complex a rapid axial equatorial equilibrium would average any differences between aryl groups.

The N(1)–C(1) and N(2)–C(9) bond distances of 1.33 and 1.31 Å, respectively, compare closely with the corresponding bond length (1.30 Å) in tetrahedral bis(*N*-isopropylsalicylaldiminato)nickel(II),[16] both being somewhat longer than reported for uncomplexed benzylideneanilines,[23] **3**. Of interest in this latter study was the fact that the plane of aniline phenyl ring (A) exhibited a large twist out of the C—N═C—C plane while the benzylidene (B) twist angle was smaller (8–14°) and quite comparable to those found for the present study (15 and 18°). Conjugation is apparently more important with the B ring in such molecules.



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For a stereoscopic view of the Ni[$C_{20}H_{24}N_2$]Br_2 molecule see Figure 3.

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