O(4) = 110 (2)°. There might also be a weak interaction between N(5) and the Br ligands with distances from 3.24 (4) to 3.61 (3) Å and reasonable angles.

The Pd atom of the *trans*-Pd(metronidazole)$_2$Cl$_2$ molecule is located on an inversion center, as similarly observed for the Pt analogue (Bales *et al.*, 1983). The Pd—Cl and Pd—N bonds are normal [2.297 (1) and 2.007 (2) Å, respectively]. The dihedral angle between the Pd coordination plane and the imidazole rings is 88.6 (1)°. For the analogous Pt compound, the dihedral angle between the planes of the imidazole rings and the square Pt plane is significantly smaller (75.3°; Bales *et al.*, 1983). The nitro group forms an angle of 3.9 (3)° with the imidazole ring. The angle for the Pt analogue was not reported, but seems also close to 0°. These results are in agreement with those obtained with another 5-nitroimidazole complex (Bales *et al.*, 1985).

The bond distances and angles of the organic ligands are normal and agree with published values and those reported for the structure described above in this publication. The temperature factors of all the atoms, including the side-chain atoms, are normal.

The structure is stabilized by hydrogen bonding involving the hydroxyl groups with the chloro ligands. The short distances, O(3)···Cl = 3.187 (3) Å, indicate fairly strong intermolecular hydrogen bonds.

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A Comparison of the Inner Coordination Spheres of a Series of Nickel(II) Macrocyclic Imine Ethers

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Abstract. Six nickel(II) macrocyclic imine ether structures are compared with regard to their inner geometries and configurations around the central atom. The X-ray structures of three of these are presented. (2,13-Dioxa-5,16-diazatricyclo[16.4.0.0^{7,12}]docosa-1(18),5,7(12),8,10,16,19,21-octaene-κ^2N,N',κ^2O,O')bis(thiocyanato-κN)nickel, [$Ni(C_{18}H_{18}N_2O_2)(NCS)_2$] (1), M_r = 469.23, orthorhombic, *Pbca*, a = 8.775 (2), b = 18.848 (9), c = 25.185 (8) Å, V =

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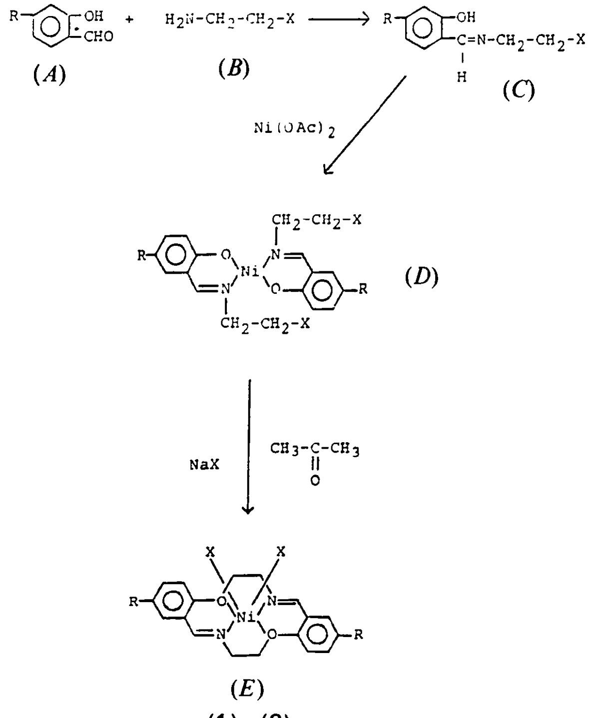
4165 (3) Å^3, $Z = 8$, $D_m = 1.49$ (1), $D_x = 1.49$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 11.50$ cm^{-1}, $F(000) = 1936$, $T = 295$ (1) K, $R = 0.065$ for 1653 ($I \geq 3\sigma$) reflections. The structure consists of discrete molecules; the two isothiocyanate groups lie in a *cis* configuration to each other, the two N atoms of the ligands lie *cis* to one another and the two O atoms are *trans* to each other in the inner coordination sphere. Dibromo(9,20-dimethyl-2,13-dioxa-5,16-diazatricyclo[16.4.0.0^{7,12}]docosa-1(18),5,7(12),8,10,16,19,21-octaene-$\kappa^2N,N',\kappa^2O,O'$)nickel, [Ni($C_{20}H_{22}N_2O_2$)$Br_2$] (2), $M_r = 540.94$, orthorhombic, $P2_12_12_1$, $a = 10.593$ (3), $b = 18.366$ (4), $c = 10.420$ (3) Å, $V = 2027.2$ (9) Å^3, $Z = 4$, $D_m = 1.77$ (2), $D_x = 1.78$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 51.4$ cm^{-1}, $F(000) = 1080$, $T = 295$ (1) K, $R = 0.054$ for 1643 ($I \geq 3\sigma$) reflections. The structure consists of discrete molecules; the inner coordination sphere shows the two Br atoms, the two N atoms and the two O atoms of the ligands all in *trans* configurations around the central metal atom. (2-(*tert*-Butyl)-6-{2-[(2-butylimino-κN-methyl)phenoxy-κO]ethylimino-κN-methyl}phenolato-κO)iodonickel, [Ni($C_{24}H_{31}N_2O_2$)I] (3), $M_r = 565.1$, triclinic, $P\bar{1}$, $a = 8.358$ (2), $b = 13.259$ (3), $c = 12.870$ (4) Å, $\alpha = 106.74$ (2), $\beta = 73.51$ (2), $\gamma = 110.54$ (1)°, $V = 1252.1$ (6) Å^3, $Z = 2$, $D_m = 1.49$ (2), $D_x = 1.50$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 20.2$ cm^{-1}, $F(000) = 572$, $T = 295$ (1) K, $R = 0.054$ for 2018 ($I \geq 3\sigma$) reflections. The structure consists of monomer units; the geometry of the coordination sphere is a highly distorted trigonal bipyramid with the I atom and the two N atoms of the ligands in the equatorial plane, and the two O atoms of the ligands in axial positions.

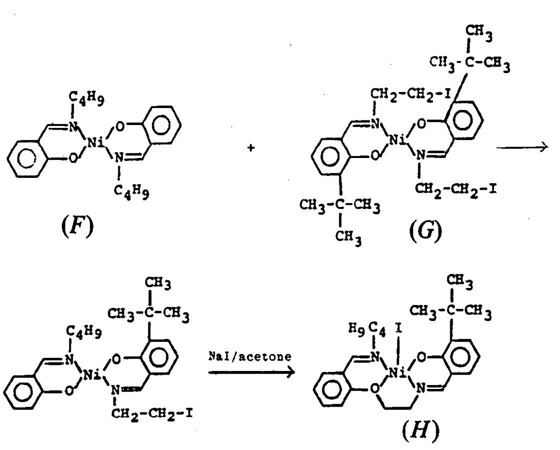
Introduction. Charles (1957) prepared a series of nickel and copper salicylaldimine chelates. These complexes had been reported previously in the literature by Martell & Calvin (1952) and were primarily green crystalline materials which had the general structure shown in the scheme below (Cotton & Wilkinson, 1962). Frasson, Panattoni & Sacconi (1959) published the structure of the bis(*N*-methylsalicylideneaminato)nickel(II) complex. Lingafelter & Braun (1966) summarized X-ray data and theoretically calculated bond distances for a number of these salicylideneamine metal complexes. Kluiber & Sasso (1970) reported an interesting and new example of a template reaction involving an ether linkage. In their study, bis(*N*-2-bromoethylsalicylideneaminato)nickel(II) was reacted with sodium iodide in acetone to yield a paramagnetic ($\mu_{\text{eff}} = 3.12\ \mu_B = 2.879 \times 10^{-23}$ JT^{-1}) complex of empirical formula [Ni($C_{18}H_{18}N_2O_2$)I_2]. Johnston & Horrocks (1971) reported the structure of this octahedral complex with the nickel at a center of symmetry and the inner coordination sphere containing the I, N and O atoms all in *trans* configurations. We present three additional structures of cyclized nickel(II) salicylideneamine chelates which have been investigated to elucidate the bonding in the inner coordination sphere. This series of nickel complexes contains different *R* groups on the phenyl rings and different counter ions (N=C=S and Br), and includes a five-coordinate complex which was formed by a semi-cyclization process. Comparison with other similar structures in the literature provides a more complete picture of the coordination scheme surrounding the central Ni atom.

Experimental. A typical synthesis (Kluiber & Sasso, 1970) for the octahedral nickel(II) complexes is shown below. The reaction of an *R*-substituted salicylaldehyde (*A*) with an *N*-haloethylamine (*B*) yields the salicylidenamine halide (*C*). Reaction of this product with nickel acetate yields a four-coordinate nickel complex (*D*) with the salicylidenanine halides non-cyclized. When this product is refluxed in acetone in the presence of sodium halide, the octahedral nickel(II) species (*E*) with two halogens on the nickel(II) is isolated.



(1), (2)

The five-coordinate species with only one iodine can be prepared in the following manner (see scheme below): a four-coordinate bis(*N*-alkylsalicylideneamine)nickel(II) complex (*F*) is mixed with a four-coordinate bis(*N*-iodoethylsalicylideneamine)nickel(II) complex (*G*) to form, after refluxing in acetone and sodium iodide, the five-coordinate semi-cyclized complex (*H*).



(3)

A blue crystal (0.20 × 0.15 × 0.20 mm) of (1) was mounted on a glass fiber; density was measured by flotation in carbon tetrachloride and ethyl benzene. Data ($2\theta_{\max} = 60^\circ$; $0 \le h \le 9$, $0 \le k \le 25$, $0 \le l \le 35$) were collected on a Syntex $P2_1$ diffractometer with graphite monochromator using Mo $K\alpha$ radiation; 15 reflections (θ range 7–15°) used to calculate orientation matrix and best cell dimensions. Space group chosen on the basis of cell dimensions and extinctions (in $0kl$, $k = 2n + 1$; in $hk0$, $h = 2n + 1$; in $h0l$, $l = 2n + 1$). Three standards (022, 204, 200) every 27 reflections (±3.0%), 4363 reflections measured in θ–2θ scan mode; 2710 unobserved with $I < 3\sigma(I)$, 1653 had $I > 3\sigma(I)$; the low percentage of reflections observed was due to the low power at which the X-ray generator was run during these data measurements. Absorption corrections based on Howell's analytical expression for polyhedra [$1.182 \le A \le 1.245$ (Alcock, 1970)]. The structure was solved by the Patterson method (Ni atom); all non-H atoms found in difference Fourier maps; H-atom positions (except for those in methyl groups) calculated. H-atom positional parameters were not refined, and their isotropic B values were set at ($B + 1$) Å², where B is the value for the atom to which H is bound; all non-H atoms refined with anisotropic thermal parameters by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized; $R = 0.065$, $wR = 0.083$, $S = 1.25$, $w = 1/\sigma^2$ with $\sigma = -0.0067|F_o| + 2.033$ for $0 < F_o \le 30.0$, $\sigma = 0.0184|F_o| + 1.44$ for $F_o > 30.0$, last cycle max. $\Delta/\sigma = 0.0018$; final $\Delta\rho$, max. = 0.6 e Å^{-3} at Ni site, min. = -0.05 e Å^{-3}. Atomic scattering factors taken from Cromer & Waber (1965) and the real and imaginary parts of the anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs used: data reduction with local adaptation of Glick's (1975) Lp correction *SYNCOR* and Hollander's (1975) *ABSOR* (*AGNOST*; Templeton & Templeton, 1973); direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement and Fourier synthesis analysis with *FLINUS* (Andrews, 1974) from *ORFLS* (Busing, Martin & Levy, 1962); Fourier analysis and difference maps with *FORDAP* (Zalkin, 1962); geometric atom-position calculation with *GEOM* (Shiono, 1971); analysis of variance with *NANOVA* (Lalancette, Cefola, Hamilton & LaPlaca, 1967); bond-distance and bond-angle error analysis with *ORFFE* (Busing, Martin & Levy, 1964); graphics with *ORTEP*II (Johnson, 1970).

An orange crystal (0.60 × 0.18 × 0.15 mm) of (2) was mounted and its density measured as for (1). Space group chosen by cell and extinctions (in $h00$, $h = 2n + 1$; in $0k0$, $k = 2n + 1$; in $00l$, $l = 2n + 1$). Data ($2\theta_{\max} = 60^\circ$; $0 \le h \le 15$, $0 \le k \le 25$, $0 \le l \le 14$) as for compound (1). Three standards (432, 371, 331) every 37 reflections (±4.3%), 3370 reflections measured, 1727 unobserved with $I < 3\sigma(I)$, 1643 had $I \ge 3\sigma(I)$. Absorption corrections as above ($1.189 \le A \le 1.543$). Structure solved by *MULTAN*80 yielding Ni and two Br atoms. All non-H atoms were found in subsequent Fourier maps. H-atom positions calculated and held fixed as above. $R = 0.054$, $wR = 0.067$, $S = 1.46$, $w = 1/\sigma^2$ with $\sigma = -0.020|F_o| + 2.68$ for $0 < F_o \le 30.0$, $\sigma = 0.0013|F_o| + 2.08$ for $30.0 < F_o \le 60.5$, $\sigma = 0.028|F_o| + 0.64$ for $60.5 < F_o \le 229.0$, last cycle max. $\Delta/\sigma = 0.061$; final $\Delta\rho$, max. = 1.56 e Å^{-3} at Ni site, min. = -0.10 e Å^{-3}.

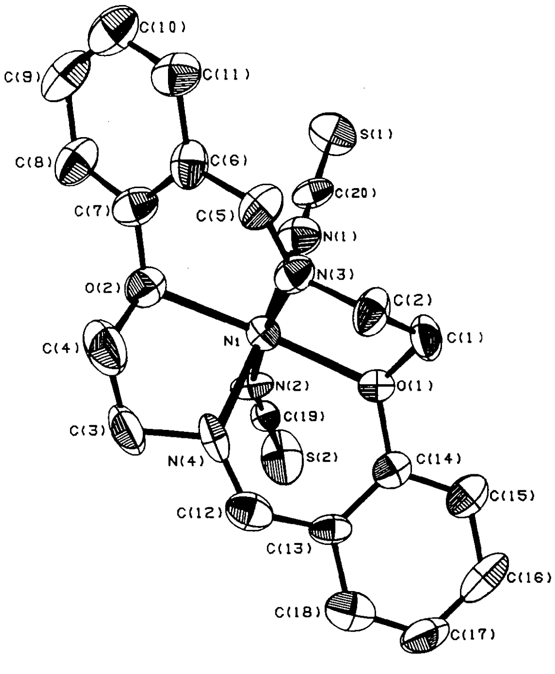


Fig. 1. The atom-numbering scheme for compound (1), $[Ni(C_{18}H_{18}N_2O_2)(NCS)_2]$.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for* $[Ni(C_{18}H_{18}N_2O_2)(NCS)_2]$ (1)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Ni	0.7114 (2)	0.6033 (1)	0.1294 (1)	2.68 (1)
S(1)	0.3670 (4)	0.7928 (2)	0.0982 (2)	5.71 (3)
S(2)	0.2423 (5)	0.4798 (3)	0.1436 (2)	6.14 (3)
O(1)	0.7135 (9)	0.5571 (4)	0.0528 (3)	3.07 (2)
O(2)	0.8015 (10)	0.6446 (4)	0.2028 (3)	3.77 (4)
N(1)	0.5911 (13)	0.6909 (6)	0.1114 (5)	4.06 (4)
N(2)	0.5147 (13)	0.5546 (5)	0.1497 (4)	3.51 (3)
N(3)	0.9044 (11)	0.6518 (5)	0.0975 (4)	3.18 (2)
N(4)	0.8235 (11)	0.5150 (6)	0.1550 (4)	3.45 (3)
C(1)	0.8042 (16)	0.5981 (8)	0.0173 (4)	3.76 (3)
C(2)	0.9491 (16)	0.6195 (7)	0.0463 (5)	3.83 (2)
C(3)	0.8747 (19)	0.5233 (8)	0.2093 (6)	4.97 (3)
C(4)	0.9279 (18)	0.5931 (9)	0.2188 (6)	3.06 (2)
C(5)	0.9715 (14)	0.7059 (7)	0.1147 (5)	3.46 (3)
C(6)	0.9313 (14)	0.7430 (7)	0.1630 (5)	3.58 (3)
C(7)	0.8492 (15)	0.7125 (7)	0.2054 (6)	3.69 (3)
C(8)	0.8108 (16)	0.7535 (8)	0.2488 (6)	4.50 (3)
C(9)	0.8560 (21)	0.8244 (8)	0.2513 (6)	5.68 (4)
C(10)	0.9411 (18)	0.8545 (8)	0.2118 (7)	5.00 (3)
C(11)	0.9813 (15)	0.8140 (7)	0.1676 (6)	4.07 (3)
C(12)	0.8280 (14)	0.4525 (7)	0.1318 (6)	3.84 (3)
C(13)	0.7669 (14)	0.4348 (6)	0.0817 (5)	2.90 (2)
C(14)	0.7154 (14)	0.4839 (6)	0.0428 (5)	2.81 (3)
C(15)	0.6628 (14)	0.4596 (7)	−0.0054 (6)	3.65 (3)
C(16)	0.6563 (16)	0.3869 (8)	−0.0159 (6)	4.73 (3)
C(17)	0.7022 (19)	0.3388 (7)	0.0224 (6)	4.60 (4)
C(18)	0.7567 (16)	0.3627 (7)	0.0695 (6)	4.08 (3)
C(19)	0.4015 (14)	0.5243 (6)	0.1468 (4)	2.69 (3)
C(20)	0.4957 (14)	0.7325 (6)	0.1065 (5)	3.15 (3)

A crystal of (3), ground into a sphere of diameter 0.15 mm was mounted; density as above. Space group by cell dimensions and no extinctions. Data ($2\theta_{max} = 50°$; $0 \le h \le 9$, $-15 \le k \le 15$, $-15 \le l \le 15$) as above for compound (1). Three standards (135, $\bar{2}21$, 313) every 27 reflections (±4.2%), 4698 reflections measured, 2680 unobserved with $I < 3\sigma(I)$, 2018 had $I \ge 3\sigma(I)$; no absorption corrections applied since crystal was spherical ($\mu = 20.2$ cm^{-1}). Structure solved by Patterson method (Ni and I atoms); all non-H atoms found in difference Fourier maps. H-atom positions calculated and held fixed as above. $R = 0.054$, $wR = 0.073$, $S = 1.35$, $w = 1/\sigma^2$ with $\sigma = -0.060|F_o| + 3.84$ for $0 < F_o \le 27.5$, $\sigma = 0.004|F_o| + 2.00$ for $27.6 \le F_o \le 54.0$, $\sigma = 0.027|F_o| + 0.80$ for $54.1 \le F_o \le 217.0$, last cycle max. $\Delta/\sigma = 0.055$; final $\Delta\rho$, max. = 1.5 e Å^{-3} at Ni site, min. = −0.07 e Å^{-3}.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $[Ni(C_{18}H_{18}N_2O_2)(NCS)_2]$ (1) *with e.s.d.'s in parentheses*

Ni—O(1)	2.154 (8)	Ni—O(2)	2.117 (7)
Ni—N(1)	2.01 (1)	Ni—N(2)	2.02 (1)
Ni—N(3)	2.09 (1)	Ni—N(4)	2.038 (9)
O(1)—C(14)	1.40 (1)	O(2)—C(7)	1.35 (1)
O(1)—C(1)	1.42 (1)	O(2)—C(4)	1.53 (2)
S(1)—C(20)	1.62 (1)	S(2)—C(19)	1.63 (1)
N(1)—C(20)	1.16 (1)	N(2)—C(19)	1.15 (1)
N(3)—C(5)	1.25 (1)	N(3)—C(2)	1.48 (2)
N(4)—C(3)	1.45 (2)	N(4)—C(12)	1.31 (2)
C(1)—C(2)	1.52 (2)	C(3)—C(4)	1.42 (2)
C(5)—C(6)	1.45 (2)	C(6)—C(7)	1.41 (2)
C(7)—C(8)	1.38 (2)	C(8)—C(9)	1.40 (2)
C(9)—C(10)	1.37 (2)	C(10)—C(11)	1.40 (2)
C(6)—C(11)	1.41 (2)	C(12)—C(13)	1.41 (2)
C(13)—C(14)	1.42 (2)	C(14)—C(15)	1.38 (2)
C(15)—C(16)	1.40 (2)	C(16)—C(17)	1.38 (2)
C(17)—C(18)	1.36 (2)	C(13)—C(18)	1.40 (2)
N(1)—Ni—N(2)	89.0 (4)	N(1)—Ni—N(3)	88.9 (4)
N(1)—Ni—N(4)	174.3 (4)	N(1)—Ni—O(1)	97.8 (4)
N(1)—Ni—O(2)	95.1 (4)	N(2)—Ni—N(3)	171.9 (4)
N(2)—Ni—N(4)	87.8 (4)	N(2)—Ni—O(1)	92.9 (4)
N(2)—Ni—O(2)	105.1 (4)	N(3)—Ni—N(4)	95.1 (4)
N(3)—Ni—O(1)	79.7 (4)	N(3)—Ni—O(2)	82.8 (3)
N(4)—Ni—O(1)	87.0 (4)	N(4)—Ni—O(2)	81.2 (4)
O(1)—Ni—O(2)	157.9 (3)	Ni—N(1)—C(20)	164 (1)
Ni—N(2)—C(19)	162 (1)	N(2)—C(19)—S(2)	179 (1)
N(1)—C(20)—S(1)	177 (1)	Ni—O(1)—C(1)	110.7 (7)
Ni—O(1)—C(14)	124.6 (6)	Ni—O(2)—C(7)	119.9 (8)
Ni—O(2)—C(4)	105.3 (7)	Ni—N(3)—C(2)	112.0 (7)
Ni—N(3)—C(5)	127.1 (9)	Ni—N(3)—C(2)	111.8 (7)
Ni—N(4)—C(3)	111.0 (9)	Ni—N(4)—C(12)	127.3 (9)
O(1)—C(1)—C(2)	108.0 (9)	C(1)—C(2)—N(3)	108 (1)
C(2)—N(3)—C(5)	120 (1)	N(3)—C(5)—C(6)	125 (1)
C(5)—C(6)—C(7)	124 (1)	C(6)—C(7)—O(2)	120.6 (1)
C(4)—O(2)—C(7)	111.2 (9)	C(3)—C(4)—O(2)	108 (1)
C(4)—C(3)—N(4)	111 (1)	C(3)—N(4)—C(12)	120 (1)
N(4)—C(12)—C(13)	126.7 (1)	C(12)—C(13)—C(14)	126 (1)
O(1)—C(14)—C(13)	121.3 (1)	C(1)—O(1)—C(14)	114.5 (9)
C(5)—C(6)—C(11)	117 (1)	C(7)—C(6)—C(11)	117 (1)
C(6)—C(7)—C(8)	120 (1)	C(8)—C(9)—C(10)	121 (1)
C(9)—C(10)—C(11)	119 (1)	C(6)—C(11)—C(10)	119 (1)
O(2)—C(7)—C(8)	120 (1)	O(1)—C(14)—C(15)	119 (1)
C(12)—C(13)—C(18)	117 (1)	C(13)—C(14)—C(15)	120 (1)
C(14)—C(15)—C(16)	120 (1)	C(15)—C(16)—C(17)	120 (7)
C(16)—C(17)—C(18)	120 (1)	C(14)—C(13)—C(18)	117 (1)

Discussion. The structure of (1) consists of discrete molecules of $[Ni(C_{18}H_{18}N_2O_2)(NCS)_2]$. Fig. 1 is an *ORTEP*II representation of the molecule and shows the labeling scheme. Table 1* lists positional and equivalent isotropic thermal parameters and Table 2 lists interatomic distances and angles. The configuration around the central Ni atom is as follows: the two isothiocyanate groups are *cis* to one another, the two N atoms of the ligand lie *cis* to one another and the two O of the salicylaldimine ligand lie *trans* to one another. Since the O atoms occupy the *trans* positions in this crystal, the ether Ni—O bond is weakened, and thus long Ni—O bond lengths are encountered. Consequently, Ni—O distances of 2.154 (8) and 2.117 (7) Å are much longer than the sum of the covalent radii, 2.05 Å [octahedral Ni^{II} 1.39, O 0.66 Å (Pauling, 1960)]. The Ni—N distances of 2.09 (1) and 2.038 (9) Å are in good agreement with that found in the high-spin octahedral bis(*N*-γ-dimethylaminopropylsalicylideneaminato)-nickel(II) complex (2.05 Å; Hawkinson & Fleisher, 1969). The Ni—N bond distances in the two isothio-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71167 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1041]

cyanate groups are 2.01 (1) and 2.02 (1) Å. The isothiocyanate groups deviate slightly from linearity, having bond angles of 177 (1) and 179 (1)°; these groups have N—C distances of 1.15 (1) and 1.16 (1) Å and C—S distances of 1.63 (1) and 1.62 (1) Å and these are similar to N—C distances of 1.18 Å and C—S distances of 1.65 Å found in cobalt(II) dithiocyanate dipyridine, a four-coordinate square-planar structure, by Porai & Tischenko (1960). The present structure is much more precise and accurate.

The structure of (2) consists of discrete molecules of [$Ni(C_{20}H_{22}N_2O_2)Br_2$]. Table 3 lists positional and isotropic thermal parameters and Table 4 lists interatomic distances and angles. Fig. 2 is a representation of the molecule and shows the labeling scheme. The configuration of the N, O and Br atoms around the Ni atom is *trans*, *trans*, *trans*. The Ni—Br, Ni—O and Ni—N bond distances should be noted. Ni—Br distances of 2.698 (3) and 2.603 (2) Å are longer than Ni—Br distances of 2.54 (1) Å found by Koda, Ooi, Kuroya, Isobe, Nakamura & Kawaguchi (1971) in their tetragonally-distorted octahedral dibromobis(acetylacetone)nickel(II) structure where the Br atoms occupy apical positions as in (2). Bombieri, Forsellini, Bandoli, Sindellari, Graziani & Panattoni (1968) found Ni—Br distances of 2.603 (3) Å in their distorted octahedral structure of the dibromodiaqua(*N*,*N*,*N*′,*N*′-tetramethyl-*o*-phenylenediamine)-nickel(II) complex, where the Br atoms occupy *cis* positions. Orioli & DiVaira (1968) found Ni—Br distances of 2.416 (4) and 2.398 (4) Å in their five-coordinate nickel complex dibromo[1-(*o*-methoxyphenyl)-2,6-diazaoctane]nickel(II). DiVaira & Orioli (1968) also reported longer Ni—Br distances in the five-coordinate trigonal bipyramidal [Ni(Me_6tren)-Br]$^+$, where this distance was found to be 2.47 (2) Å.

The Ni—Br distances in compound (2) are longer than the sum of the covalent radii, 2.50 Å [octahedral Ni^{II} 1.39, Br 1.11 Å (Pauling, 1960)]. This same elongation of the nickel–halogen bond was found by Johnston & Horrocks (1971), where I atoms occupy *trans* positions and have longer bonds to Ni than expected [2.880 (3) Å, as compared to the calculated value of 2.67 Å from the sum of the covalent radii]. The Ni—O distances of 2.043 (8) Å agree with the Johnston & Horrocks (1971) value of 2.07 (1) Å, and also with the sum of the covalent radii (2.05 Å). The ring systems in this molecule are essentially planar, except for some puckering in the two five-membered rings.

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters for* [$Ni(C_{20}H_{22}N_2O_2)Br_2$] (2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq} (Å^2)
Ni	0.9177 (2)	0.6399 (1)	0.8334 (2)	2.55 (1)
Br(1)	0.6788 (1)	0.6183 (1)	0.9145 (2)	3.57 (3)
Br(2)	1.1476 (1)	0.6562 (1)	0.7500 (2)	3.74 (3)
O(1)	0.9213 (10)	0.5330 (4)	0.7793 (8)	2.77 (2)
O(2)	0.9055 (10)	0.7457 (4)	0.8922 (9)	2.95 (3)
N(1)	0.8527 (10)	0.6579 (5)	0.6657 (10)	2.42 (3)
N(2)	0.9738 (10)	0.6211 (5)	1.0034 (11)	2.78 (3)
C(1)	0.8429 (16)	0.5244 (8)	0.6634 (14)	3.29 (4)
C(2)	0.8626 (15)	0.5931 (7)	0.5839 (14)	2.98 (3)
C(3)	0.8059 (14)	0.7176 (7)	0.6234 (13)	2.62 (3)
C(4)	0.8000 (13)	0.7854 (7)	0.6972 (13)	2.42 (3)
C(5)	0.8422 (14)	0.8002 (7)	0.8242 (13)	2.57 (3)
C(6)	0.8316 (16)	0.8694 (8)	0.8747 (13)	3.24 (4)
C(7)	0.7765 (16)	0.9243 (8)	0.8021 (15)	3.23 (4)
C(8)	0.7351 (14)	0.9146 (7)	0.6775 (15)	2.79 (3)
C(9)	0.7459 (14)	0.8442 (8)	0.6289 (13)	2.95 (3)
C(10)	0.9110 (17)	0.7483 (8)	1.0317 (12)	3.21 (3)
C(11)	1.0000 (18)	0.6886 (8)	1.0744 (17)	3.99 (5)
C(12)	0.9325 (12)	0.4753 (6)	0.8661 (13)	2.11 (2)
C(13)	0.9084 (14)	0.4037 (7)	0.8242 (15)	2.75 (3)
C(14)	0.9329 (12)	0.3458 (7)	0.9083 (15)	2.78 (3)
C(15)	0.9744 (13)	0.3578 (7)	1.0318 (15)	2.99 (3)
C(16)	0.9902 (13)	0.4285 (7)	1.0713 (15)	2.78 (3)
C(17)	0.9684 (13)	0.4883 (7)	0.9949 (15)	2.73 (3)
C(18)	0.9875 (15)	0.5596 (8)	1.0568 (15)	3.14 (2)
C(19)	0.6793 (18)	0.9765 (8)	0.6005 (18)	4.35 (4)
C(20)	1.0041 (15)	0.2944 (8)	1.1234 (17)	3.49 (3)

In (3), the one molecule per asymmetric unit exists as a discrete monomeric unit as can be seen in Fig. 3. Table 5 lists positional and isotropic thermal parameters and Table 6 lists interatomic distances and angles. In this molecule, the inner coordination sphere around the Ni atom is a distorted trigonal bipyramid with the I atom and the two N atoms in equatorial positions, and the two O atoms in axial positions. The Ni—I distance of 2.646 (2) Å is longer than the average value of 2.616 Å found in carbonyl-[ferrocene-1,1′-bis(dimethylarsine)]diiodonickel(II) (Pierpont & Eisenberg, 1972) where the two I atoms are equatorial and much longer than the basal Ni—I distances of 2.514 (5) and 2.567 (5) Å found in the low-spin square-pyramidal complex [Ni(DSP)I_2] [DSP = bis(*o*-methylthiophenyl)-phenylphosphine] (Meek & Ibers, 1969). This distance is smaller than the 2.657 (1) and 2.664 (1) Å found by Vande Griend, Clardy & Verkade (1975) in their five-coordinate diiodotris(trimethylphosphite)nickel(II) complex where both of the I atoms were in equatorial positions. The Ni—I distance found in our structure is very close to the sum of the octahedral radii of Ni^{II} (1.39 Å) and I (1.28 Å), which is 2.67 Å (Pauling, 1960). The Ni—N distances of 2.02 (1) Å agree well with those found in previous cyclized Ni^{II} salicylidenamine complexes (Lalancette, Macchia & Furey, 1976; Johnston & Horrocks, 1971). Also, these values are in good agreement with the value of 2.05 Å found in high-spin octahedral bis(*N*-γ-dimethylaminopropylsalicylideneaminato)nickel(II) (Hawkinson & Fleisher, 1969). The Ni—O distances show much greater variation in this structure than has been found in Ni^{II} six-coordinate complexes, where the O atoms are always found in *trans* positions. In our structure, O(1) is similar to the atoms in

Table 4. *Interatomic distances* (Å) *and angles* (°) *for* [Ni($C_{20}H_{22}N_2O_2$)Br_2] (2) *with e.s.d.'s in parentheses*

Ni—Br(1)	2.698 (3)	Ni—Br(2)	2.603 (2)
Ni—O(1)	2.043 (8)	Ni—O(2)	2.043 (8)
Ni—N(1)	1.91 (1)	Ni—N(2)	1.90 (1)
O(1)—C(1)	1.47 (2)	O(2)—C(10)	1.46 (2)
O(1)—C(12)	1.40 (1)	O(2)—C(5)	1.40 (2)
N(1)—C(2)	1.47 (2)	N(2)—C(11)	1.47 (2)
N(1)—C(3)	1.28 (2)	N(2)—C(18)	1.27 (2)
C(1)—C(2)	1.52 (2)	C(3)—C(4)	1.47 (2)
C(4)—C(5)	1.42 (2)	C(4)—C(9)	1.41 (2)
C(5)—C(6)	1.38 (2)	C(6)—C(7)	1.39 (2)
C(7)—C(8)	1.38 (2)	C(8)—C(9)	1.39 (2)
C(8)—C(19)	1.51 (2)	C(10)—C(11)	1.51 (2)
C(12)—C(13)	1.41 (2)	C(12)—C(17)	1.42 (2)
C(13)—C(14)	1.40 (2)	C(14)—C(15)	1.38 (2)
C(15)—C(16)	1.37 (2)	C(15)—C(20)	1.54 (2)
C(16)—C(17)	1.38 (2)	C(17)—C(18)	1.47 (2)

Br(1)—Ni—Br(2)	177.8 (1)	Br(1)—Ni—O(1)	87.8 (3)
Br(1)—Ni—O(2)	89.2 (3)	Br(1)—Ni—N(1)	88.5 (3)
Br(1)—Ni—N(2)	88.5 (3)	Br(2)—Ni—O(1)	90.3 (3)
Br(2)—Ni—O(2)	92.9 (3)	Br(2)—Ni—N(1)	90.7 (3)
Br(2)—Ni—N(2)	92.3 (3)	O(1)—Ni—O(2)	177.0 (4)
N(1)—Ni—N(2)	177.0 (5)	O(1)—Ni—N(1)	85.4 (4)
O(1)—Ni—N(2)	94.5 (4)	O(2)—Ni—N(1)	95.0 (4)
O(2)—Ni—N(2)	84.9 (4)	Ni—O(1)—C(1)	108.6 (7)
Ni—O(1)—C(12)	123.4 (7)	Ni—O(2)—C(5)	124 (8)
Ni—O(2)—C(10)	109.2 (7)	Ni—N(1)—C(2)	111.4 (8)
Ni—N(1)—C(3)	127.1 (8)	Ni—N(2)—C(11)	112.1 (8)
Ni—N(2)—C(18)	127.3 (9)	O(1)—C(1)—C(2)	106 (1)
N(1)—C(2)—C(1)	110 (1)	O(2)—C(10)—C(11)	107 (1)
N(2)—C(11)—C(10)	110 (1)	C(1)—O(1)—C(12)	120 (1)
C(2)—N(1)—C(3)	121 (1)	C(5)—O(2)—C(10)	120 (1)
C(11)—N(2)—C(18)	121 (1)	N(1)—C(3)—C(4)	124 (1)
C(3)—C(4)—C(5)	130 (1)	C(3)—C(4)—C(9)	114 (1)
O(2)—C(5)—C(4)	119 (1)	O(2)—C(5)—C(6)	120 (1)
C(4)—C(5;—C(6)	120 (1)	C(5)—C(6)—C(7)	120 (1)
C(5)—C(4)—C(9)	117 (1)	C(6)—C(7)—C(8)	123 (1)
C(7)—C(8)—C(9)	116 (1)	C(4)—C(9)—C(8)	124 (1)
C(7)—C(8)—C(19)	122 (1)	C(9)—C(8)—C(19)	123 (1)
O(1)—C(12)—C(13)	119 (1)	O(1)—C(12)—C(17)	121 (1)
N(2)—C(18)—C(17)	126 (1)	C(12)—C(17)—C(16)	117 (1)
C(12)—C(17)—C(18)	127 (1)	C(12)—C(13)—C(14)	119 (1)
C(13)—C(14)—C(15)	121 (1)	C(14)—C(15)—C(16)	118 (1)
C(14)—C(15)—C(20)	121 (1)	C(16)—C(15)—C(20)	120 (1)
C(15)—C(16)—C(17)	124 (1)	C(13)—C(12)—C(17)	120 (1)
C(16)—C(17)—C(18)	116 (1)		

the six-coordinate structures because it is part of a six-membered ring (the salicylideneamine bidentate ligand complexing the metal) as well as a five-membered cyclized ring. The Ni—O(1) distance of 2.163 (9) Å can be compared to values of 2.154 (8) and 2.117 (7) (compound 1), 2.043 (8) (compound 2) and 2.042 (9) Å (Johnston & Horrocks, 1971), and 2.186 (8) and 2.248 (6) Å (Lalancette, Macchia & Furey, 1976) in other octahedral cyclized nickel salicylideneaminato complexes. O(2), on the other hand, only belongs to a six-membered chelate ring; therefore, the Ni—O(2) distance of 1.937 (9) Å is substantially shorter and must be compared to Ni—O distances in similar environments. A very short Ni—O distance of 1.80 Å has been reported (Frasson, Panattoni & Sacconi, 1959), but leads one to question its accuracy. The distance we found agrees well with the distance of 1.92 Å calculated from the sum of the covalent radii when one assumes

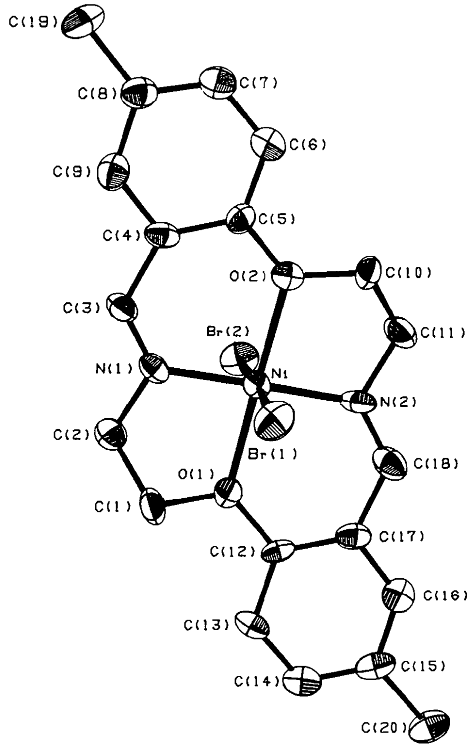

Fig. 2. The atom-numbering scheme for compound (2), [Ni($C_{20}H_{22}N_2O_2$)Br_2].

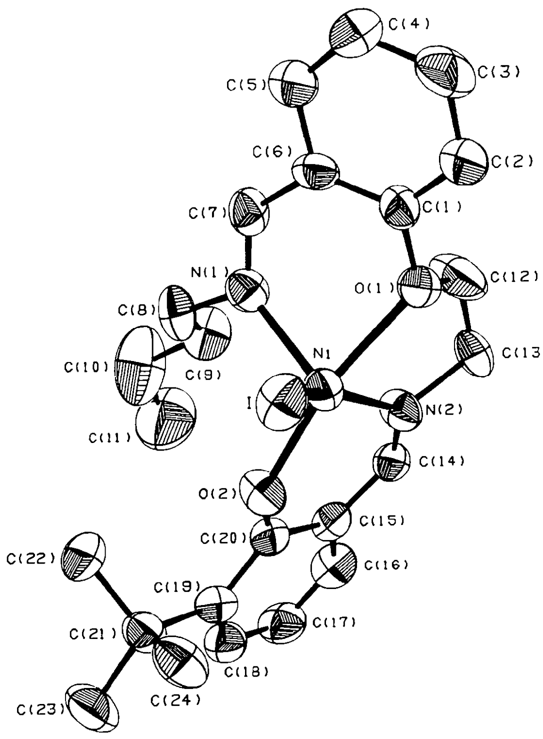

Fig. 3. The atom-numbering scheme for compound (3), [Ni($C_{24}H_{31}N_2O_2$)I].

Table 5. *Fractional atomic coordinates and equivalent isotropic thermal parameters for* [Ni($C_{24}H_{31}N_2O_2$)I] (3)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Ni	0.1437 (2)	0.2077 (1)	0.0390 (1)	3.87 (2)
I	0.4749 (1)	0.2246 (1)	0.0213 (1)	5.05 (3)
O(1)	0.1740 (12)	0.1877 (7)	−0.1377 (7)	4.61 (3)
O(2)	0.0783 (12)	0.1932 (8)	0.1921 (7)	4.57 (3)
N(1)	0.1711 (15)	0.3668 (9)	0.0439 (9)	4.46 (3)
N(2)	−0.0989 (14)	0.1166 (9)	0.0183 (9)	4.14 (4)
C(1)	0.3005 (19)	0.2626 (11)	−0.1943 (11)	4.19 (3)
C(2)	0.3845 (22)	0.2272 (12)	−0.2995 (12)	5.25 (5)
C(3)	0.5132 (23)	0.3026 (15)	−0.3580 (12)	6.14 (3)
C(4)	0.5544 (23)	0.4160 (13)	−0.3069 (14)	5.88 (4)
C(5)	0.4720 (22)	0.4505 (12)	−0.2021 (13)	5.35 (4)
C(6)	0.3414 (19)	0.3737 (11)	−0.1429 (11)	4.27 (3)
C(7)	0.2592 (19)	0.4205 (11)	−0.0318 (12)	4.34 (3)
C(8)	0.1013 (21)	0.4316 (12)	0.1516 (12)	5.33 (4)
C(9)	−0.0953 (22)	0.3983 (14)	0.1775 (14)	6.20 (5)
C(10)	−0.1684 (28)	0.4552 (18)	0.2967 (19)	9.30 (5)
C(11)	−0.3311 (34)	0.3912 (19)	0.3476 (20)	10.40 (6)
C(12)	0.0030 (25)	0.1597 (17)	−0.1600 (14)	7.68 (5)
C(13)	−0.1243 (22)	0.0830 (13)	−0.0997 (12)	5.63 (4)
C(14)	−0.2267 (18)	0.0855 (10)	0.0922 (12)	3.77 (3)
C(15)	−0.2281 (18)	0.1020 (10)	0.2059 (12)	4.00 (3)
C(16)	−0.3886 (20)	0.0634 (12)	0.2737 (14)	5.36 (4)
C(17)	−0.4081 (20)	0.0727 (13)	0.3852 (14)	5.41 (4)
C(18)	−0.2545 (21)	0.1194 (12)	0.4281 (12)	4.78 (4)
C(19)	−0.0918 (20)	0.1578 (11)	0.3667 (12)	4.44 (3)
C(20)	−0.0737 (19)	0.1546 (10)	0.2520 (11)	4.15 (3)
C(21)	0.0690 (20)	0.2072 (12)	0.4217 (12)	4.98 (4)
C(22)	0.1598 (24)	0.3294 (12)	0.4120 (15)	6.61 (5)
C(23)	0.0215 (26)	0.2052 (15)	0.5478 (14)	7.64 (6)
C(24)	0.2048 (22)	0.1422 (15)	0.3633 (13)	6.15 (6)

Table 6. *Interatomic distances* (Å) *and angles* (°) *for* [Ni($C_{24}H_{31}N_2O_2$)I] (3) *with e.s.d.'s in parentheses*

Ni—I	2.646 (2)	Ni—O(1)	2.163 (9)
Ni—O(2)	1.937 (9)	Ni—N(1)	2.02 (1)
Ni—N(2)	2.02 (1)	O(1)—C(1)	1.37 (1)
O(2)—C(20)	1.30 (2)	O(1)—C(12)	1.44 (1)
N(1)—C(7)	1.28 (2)	N(1)—C(8)	1.49 (2)
N(2)—C(13)	1.51 (2)	N(2)—C(14)	1.25 (2)
C(1)—C(2)	1.37 (2)	C(2)—C(3)	1.40 (2)
C(3)—C(4)	1.42 (2)	C(4)—C(5)	1.36 (2)
C(5)—C(6)	1.42 (2)	C(1)—C(6)	1.39 (2)
C(6)—C(7)	1.46 (2)	C(8)—C(9)	1.51 (2)
C(9)—C(10)	1.56 (2)	C(10)—C(11)	1.42 (2)
C(12)—C(13)	1.41 (2)	C(14)—C(15)	1.41 (2)
C(15)—C(16)	1.39 (2)	C(16)—C(17)	1.37 (2)
C(17)—C(18)	1.41 (2)	C(18)—C(19)	1.37 (2)
C(15)—C(20)	1.44 (2)	C(19)—C(21)	1.55 (2)
C(21)—C(22)	1.56 (2)	C(21)—C(23)	1.56 (2)
C(21)—C(24)	1.56 (2)		

I—Ni—O(1)	92.8 (3)	I—Ni—O(2)	93.7 (3)
I—Ni—N(1)	98.6 (3)	I—Ni—N(2)	150.5 (3)
O(1)—Ni—O(2)	167.0 (4)	N(1)—Ni—N(2)	108.6 (5)
O(1)—Ni—N(1)	84.3 (4)	O(1)—Ni—N(2)	79.3 (4)
O(2)—Ni—N(1)	105.7 (4)	O(2)—Ni—N(2)	89.6 (4)
Ni—O(1)—C(1)	121.0 (7)	Ni—O(1)—C(12)	107.3 (4)
Ni—O(2)—C(20)	130.4 (8)	Ni—N(1)—C(7)	126.5 (9)
Ni—N(1)—C(8)	116.7 (9)	Ni—N(2)—C(13)	115.3 (9)
Ni—N(2)—C(14)	126.8 (9)	O(1)—C(1)—C(2)	120 (1)
O(1)—C(1)—C(6)	119 (1)	O(1)—C(12)—C(13)	113 (1)
N(2)—C(13)—C(12)	108 (1)	N(1)—C(7)—C(6)	125 (1)
C(1)—O(1)—C(12)	115 (1)	N(2)—C(14)—C(15)	127 (1)
C(1)—C(6)—C(7)	126 (1)	C(1)—C(2)—C(3)	120 (1)
C(1)—C(6)—C(5)	119 (1)	C(2)—C(1)—C(6)	121 (1)
C(2)—C(3)—C(4)	119 (1)	C(3)—C(4)—C(5)	120 (1)
C(4)—C(5)—C(6)	120 (1)	C(5)—C(6)—C(7)	116 (1)
C(7)—N(1)—C(8)	116 (1)	N(1)—C(8)—C(9)	112 (1)
C(8)—C(9)—C(10)	112 (1)	C(9)—C(10)—C(11)	114 (1)
C(13)—N(2)—C(14)	118 (1)	O(2)—C(20)—C(15)	122 (1)
O(2)—C(20)—C(19)	120 (1)	C(14)—C(15)—C(20)	123 (1)
C(14)—C(15)—C(16)	117 (1)	C(16)—C(15)—C(20)	120 (1)
C(15)—C(16)—C(17)	123 (1)	C(16)—C(17)—C(18)	116 (1)
C(17)—C(18)—C(19)	124 (1)	C(18)—C(19)—C(20)	119 (1)
C(15)—C(20)—C(19)	117 (1)	C(18)—C(19)—C(21)	120 (1)
C(20)—C(19)—C(21)	121 (1)	C(19)—C(21)—C(22)	111 (1)
C(19)—C(21)—C(23)	113 (1)	C(19)—C(21)—C(24)	108 (1)
C(22)—C(21)—C(23)	107 (1)	C(22)—C(21)—C(24)	108 (1)
C(23)—C(21)—C(24)	108 (1)		

the value of 1.15 Å for the covalent radius of nickel (Moeller, 1952).

Table 7 displays the inner geometry and configuration around the central Ni atoms, the substituents on the phenyl groups, and the counter ions in the pertinent structures. Bond distances are compared for all of these structures. As can be seen, all of the octahedral structures have O atoms in *trans* positions. A systematic comparison of these bond distances indicates important trends. The Ni—O bond distances for all the octahedral structures should be similar because the O atoms are always *trans* in the pertinent structures. However, much longer Ni—O bond distances result when the N atoms are *cis* rather than *trans* to each other. In the *trans*, *cis*, *cis* structures, the Ni—O bond distances are longer than those in the *trans*, *trans*, *trans* structures by 0.101 Å (in *trans*, *cis*, *cis*, the average distance is 2.158 Å; in *trans*, *trans*, *trans*, the average distance is 2.057 Å). The same trend is found for the Ni—N distances. The average Ni—N distances are longer in the *trans*, *cis*, *cis* configuration by 0.134 Å than in the *trans*, *trans*, *trans* configuration (2.042 *versus* 1.913 Å). Where comparisons can be made [structures (4), (5) and (6)], the Ni—I bond distances elongate on average by 0.139 Å for the *trans*, *trans*, *trans* structure *versus* the *trans*, *cis*, *cis* structure (in *trans*, *trans*, *trans*, the average distance is 2.880 Å; in *trans*, *cis*, *cis*, the average distance is 2.741 Å). These distortions can be explained by the following: the ligands in the apical z direction are elongated away from the central Ni atom, while the ligands in the x and y directions are moved in closer to the central atom. To view it somewhat differently, the electronegativity or attraction of the metal ion for the electrons of the ligand will be less in the z direction than in the x and y directions. This anisotropic electronegativity will result in stronger bonds to the x and y ligands and weaker bonds to the z ligands; the former will be shorter and the latter will be longer.

In the five-coordinate structure, the Ni—N distances of 2.02 (1) Å are very close to the average value of 2.042 Å for the *trans*, *cis*, *cis* octahedral structures. One of the Ni—O bond distances [2.163 (9) Å] is very close to the average Ni—O bond distance for the *trans*, *cis*, *cis* configuration (2.158 Å). Since this structure is a highly distorted trigonal

Table 7. *Comparison of inner geometries, substituents and bond distances* (Å) *for all structures*

	$(1)^a$	$(2)^a$	$(3)^a$	$(4)^b$	$(5)^c$	$(6)^d$
Phenyl group substituent	None	CH_3—	*tert*-Butyl^e	None	CH_3O—	CH_3O—
Counterion	—N=C=S	—Br	—I	—I	—I	—I
Inner coordination^f	*t*, *c*, *c*	*t*, *t*, *t*	5-coord.	*t*, *t*, *t*	*t*, *c*, *c*	*t*, *c*, *c*
Ni—I			2.646 (2)	2.880 (3)	2.757 (1)	2.747 (1)
Ni—I′				2.880 (3)	2.711 (1)	2.747 (1)
Ni—Br		2.698 (3)				
Ni—Br′		2.603 (2)				
Ni—(NCS)	2.01 (1)					
Ni—(NCS)′	2.02 (1)					
Ni—O	2.154 (8)	2.043 (8)	2.163 (9)	2.07 (1)	2.186 (8)	2.122 (6)
Ni—O	2.117 (7)	2.043 (8)	1.937 (9)	2.07 (1)	2.248 (6)	2.122 (6)
Ni—N	2.09 (1)	1.91 (1)	2.02 (1)	1.92 (1)	2.063 (6)	2.030 (8)
Ni—N	2.038 (9)	1.90 (1)	2.02 (1)	1.92 (1)	2.029 (7)	2.030 (8)
C—O	1.40 (1)	1.40 (1)	1.37 (1)	1.36 (2)	1.40 (1)	1.40 (1)
C—O	1.35 (1)	1.40 (2)	1.30 (2)	1.36 (2)	1.39 (1)	1.40 (1)
C=N	1.25 (1)	1.28 (2)	1.28 (2)	1.19 (2)	1.27 (1)	1.27 (1)
C=N	1.31 (2)	1.27 (2)	1.25 (2)	1.19 (2)	1.27 (1)	1.27 (1)

Notes: (*a*) this work; (*b*) Johnston & Horrocks (1971); (*c*) Lalancette, Macchia & Furey (1976); (*d*) R. A. Lalancette, J. Potenza & D. Mastropaolo (unpublished), hexagonal form of compound (5): $P6_2$, $a = b = 15.60$ (1), $c = 7.778$ (8) Å; (*e*) only one side cyclized; (*f*) inner coordination: *t*, *c*, *c* = *trans*, *cis*, *cis*; *t*, *t*, *t* = *trans*, *trans*, *trans*.

bipyramid, it can be thought of as being between the extremes of a perfect trigonal bipyramid and a perfect square pyramid. If it had been a perfect square pyramid, the configuration would have been *trans*-O atoms, *cis*-N atoms, with the iodine in the basal plane. This approaches the configuration of the *trans*, *cis*, *cis* octahedral arrangement in structures (5) and (6), with one apical I atom missing.

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