Acta Cryst. (1993). C**49**, 1703–1706

Structures of the Nitroimidazole Platinum Group Metal Complexes *cis*-Amminedibromo[1-({[(2-hydroxyethyl)amino]carbonyl}methyl)-2-nitroimidazole]-platinum(II) and *trans*-Dichlorobis(1-hydroxyethyl-2-methyl-5-nitroimidazole)-palladium(II)

BY FERNANDE D. ROCHON AND ROBERT MELANSON

Department of Chemistry, Université du Québec à Montréal, CP 8888, *succ. A, Montréal, Canada H3C 3P8*

AND NICHOLAS FARRELL

Department of Chemistry and Vermont Cancer Research Center, University of Vermont, Burlington, VT 05404, *USA*

(*Received* 20 *August* 1992; *accepted* 16 *June* 1993)

Abstract. *cis*-Amminedibromo[*N*-(2-hydroxyethyl)-2-nitro-1-imidazole-$\kappa N'$-acetamide]platinum, $[PtBr_2(C_7H_{10}N_4O_4)(NH_3)]$, (I), $M_r = 586.11$, orthorhombic, *Pnca*, $a = 15.214\ (6)$, $b = 19.077\ (8)$, $c = 9.991\ (4)$ Å, $V = 2900\ (2)$ Å^3, $Z = 8$, $D_x = 2.684$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 15.25$ mm^{-1}, $F(000) = 2160$, $T = 295$, $R = 0.062$ and $wR = 0.059$ for 1521 unique observed reflections. Pt has a square-planar coordination. The Pt—Br bond *trans* to the nitroimidazole ligand is slightly shorter [2.375 (3) Å] than the Pt—Br bond *trans* to NH_3 [2.397 (3) Å]. The dihedral angle between the Pt coordination plane and the imidazole ring is 69.1 (8)°, while the nitro group makes an angle of 32 (1)° with the imidazole ring plane. The structure is stabilized by the hydrogen bonding of the NH_3 ligands and the hydroxyl groups. *trans*-Dichlorobis(2-methyl-5-nitro-1-imidazole-$\kappa N'$-ethanol)palladium, $[PdCl_2(C_6H_9N_3O_3)_2]$, (II), $M_r = 519.62$, monoclinic, $P2_1/c$, $a = 7.155\ (4)$, $b = 20.989\ (9)$, $c = 7.148\ (4)$ Å, $\beta = 115.37\ (4)°$, $V = 970.0\ (9)$ Å^3, $Z = 2$, $D_x = 1.779$ Mg m^{-3}, λ(Mo$K\alpha$) = 0.71069 Å, $\mu = 1.26$ mm^{-1}, $F(000) = 520$, $T = 295$, $R = 0.027$ and $wR = 0.028$ for 2260 unique observed reflections. The bond distances Pd—Cl = 2.297 (1) and Pt—N = 2.007 (2) Å. The dihedral angle between the Pd coordination plane and the imidazole ring is 88.6 (1)°, while the nitro groups make an angle of 3.9 (3)° with the imidazole plane. The structure is stabilized by hydrogen bonding between the hydroxyl groups and the chloro ligands.

Introduction. Nitroimidazole–platinum(II) complexes are of interest both as radiosensitizers and hypoxic cytotoxins (Skov, Adomat, Chaplin & Farrell, 1990). The biological properties of mixed ammine–nitroimidazole–Pt^{II} complexes have intermediate properties between the well known antitumor complex, cisplatin [*cis*-$Pt(NH_3)_2Cl_2$] and the bis(nitroimidazole) compounds. Various derivatives of 2- and 5-nitroimidazoles have clinical interest and the two most studied species are misonidazole [2-methoxy-3-(2-nitro-1-imidazolyl)-2-propanol] and metronidazole [1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole]. Etanidazole, [*N*-(2-hydroxyethyl)]-2-nitro-1-imidazoleacetamide (also known as SR2508), which seems less toxic, is currently in clinical trial as a possible radiosensitizer (Coleman, Noll, Howes, Harris, Zakar & Kramer, 1989). We have synthesized several nitroimidazole Pt complexes and studied the crystal structure of the mixed-ligand complex *cis*-$Pt(NH_3)$(etanidazole)Br_2, which is reported below. We also report the structure of *trans*-Pd(metronidazole)$_2Cl_2$.

Experimental. *cis*-$Pt(NH_3)$(etanidazole)Br_2 was prepared as follows: $K[Pt(NH_3)Cl_3]$ (0.5 mmol), dissolved in 3 ml of water, was added to an aqueous solution (3 ml) of 0.5 mmol of etanidazole; an excess of KBr was added to the mixture, which was left to crystallize slowly at room temperature. *trans*-Pd(metronidazole)$_2Cl_2$ was prepared as reported in the literature (Farrell, Carneiro, Einstein, Jones & Skov, 1984).

The experimental details of the two crystal structure determinations are shown in Table 1. Syntex $P\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from refined angles of 15 centered reflections (2θ range 14–25°); absorption correction based on equations of crystal faces; data corrected for Lorentz and polarization effects; atomic scattering factors from *International Tables*

Table 1. *Experimental details for the two crystal structures cis-*$Pt(NH_3)$*(etanidazole)*Br_2 (I) *and trans-*Pd*(metronidazole)*$_2Cl_2$ (II)

	(I)	(II)
Max. 2θ (°)	50	60
Quadrants	h,k,l	$h,k,\pm l$
Scan technique	$2\theta/\theta$	$2\theta/\theta$
Scan speed (° min^{-1})	1.5–24.0	1.0–24.0
Standard reflections	622, 10,4,$\bar{2}$, 333	0,10,0, 500, 004
Variations (%)	<2.0	<2.0
No. of independent reflections	2594	3124
Observed reflections	1521 ($I_{net} > 2.5\sigma$)	2260 ($I_{net} > 2.5\sigma$)
h,k,l	0 to 18, 0 to 22, 0 to 11	0 to 10, 0 to 29, −10 to 9
Crystal faces and dimensions (mm)	011–0$\bar{1}\bar{1}$ (0.28)	010–0$\bar{1}$0 (0.048)
	100–$\bar{1}$00 (0.44)	100–$\bar{1}$00 (0.365)
	0$\bar{1}$1–01$\bar{1}$ (0.40)	001–00$\bar{1}$ (0.356)
		10$\bar{1}$–$\bar{1}$01 (0.346)
Transmission factors	0.0116–0.0748	0.460–0.885
Max. shift/e.s.d.	0.024	0.044
$\Delta\rho_{max}$ (e Å^{-3})	1.02 (close to Pt)	0.39 (close to Pd)
No. of parameters varied	200	125
R	0.062	0.027
wR	0.059	0.028
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Standard deviation (unit weight)	1.9	2.2

for X-ray Crystallography (1974, Vol. IV); anomalous-dispersion terms of Pt, Pd, Br, Cl and O included.

Patterson maps showed the positions of Pt or Pd; other non-H atoms located by structure factor and Fourier map calculations; N(5), C(6) and C(7) of structure (I) disordered on two positions, *A* (occupancy 0.66) and *B* (occupancy 0.34); refinement for (I) by block diagonal and for (II) by full-matrix least-squares calculations minimizing $\sum w(|F_o| - |F_c|)^2$, isotropic secondary-extinction correction varied; several H atoms located from a difference Fourier synthesis map, others calculated with C—H and N—H = 0.98 [for (I)] and 0.96 Å [for (II)] and fixed at their calculated positions with $U_{eq} = 1.1$ (I) and 1.2 (II) × U_{eq} of the C to which they are bonded; the refinement of the scale factor, coordinates and anisotropic temperature factors of all non-H atoms converged to $R = 0.062$ and $wR = 0.059$ for (I) and $R = 0.027$ and $wR = 0.028$ for (II); calculations on a MIPS1 with programs of the *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) system for crystal (I) and with a *SHELXTL* (Sheldrick, 1984) system for crystal (II).

Discussion. Labelled diagrams of the two compounds are shown in Figs. 1 and 2. Positional parameters are given in Table 2* and bond angles and distances are listed in Table 3. The coordination around the Pt and Pd atoms is square planar as expected. The angles around the Pt and Pd atoms are close to the expected 90 and 180°.

The mixed-ligand Pt^{II} compound is the *cis* isomer. It was synthesized from the reaction of $K[Pt(NH_3)Cl_3]$ with the 2-nitroimidazole derivative in water in the presence of KBr. Under these conditions *cis* isomers are expected since the *trans* effect of chloride is larger than the *trans* effect of NH_3. The crystal structure of the complex is very similar to that of the chloro analogue whose structure has been published recently (Rochon, Kong, Melanson, Skov & Farrell, 1991).

The Pt—Br(1) bond, located in *trans* position to the imidazole-derivative ligand, is shorter [2.375 (3) Å] than normal bonds, while the Pt—Br(2) distance [2.397 (3) Å] is close to the reported values (2.40–2.43 Å) for Pt^{II}–amine complexes (Melanson, Rochon & Hubert, 1979; Lock & Pilon, 1981; Melanson, Hubert & Rochon, 1975). The difference is probably significant, especially since similar results were observed for the chloro analogue [2.269 (3) and 2.304 (3) Å]. The shorter Pt—Br bond might be caused by the presence, in its *trans* position, of π bonds between the Pt atom and the organic ligand. The imidazole ring has some empty π^* orbitals which are capable of accepting electron density from the Pt atom. Similar short Pt—Cl distances [2.264 (4) and 2.263 (3) Å] were observed in the structure of *cis*-$[Pt(CH_3CN)_2Cl_2]$ (Rochon, Melanson, Howard-Lock, Lock & Turner, 1984). Acetonitrile is also

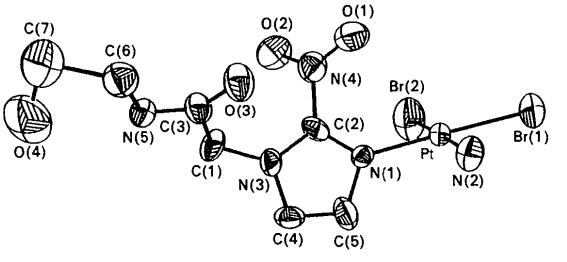

Fig. 1. Labelled diagram of *cis*-$Pt(NH_3)$(etanidazole)Br_2 (I) (only the major component; ellipsoids correspond to 50% probability).

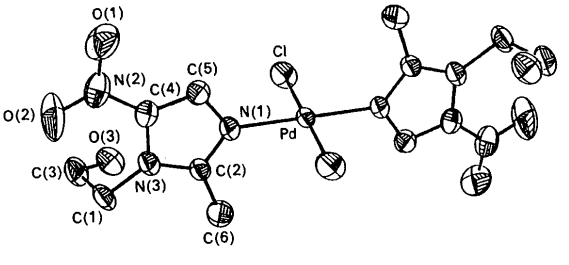

Fig. 2. Labelled diagram of *trans*-Pd(metronidazole)$_2Cl_2$ (II) (ellipsoids correspond to 50% probability).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data, and stereoscopic views of the packing in the crystal for both molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71189 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1020]

Table 2. *Positional parameters* ($\times 10^4$) *with their e.s.d.'s and temperature factors* ($Å^2 \times 10^3$)

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}
cis-Pt(NH_3)(etanidazole)Br_2 (I)				
Pt	1743.1 (5)	2016.1 (4)	1536.1 (9)	30.9 (4)
Br(1)	3008 (1)	2394 (1)	2727 (3)	56.6 (14)
Br(2)	1751 (2)	897 (1)	2628 (4)	75.3 (19)
O(1)	1925 (10)	1040 (9)	−1009 (19)	59 (9)
O(2)	985 (11)	182 (8)	−1134 (22)	63 (11)
O(3)	196 (9)	1305 (8)	−3189 (17)	45 (8)
O(4)	−2159 (12)	699 (11)	−6022 (26)	94 (14)
N(1)	665 (9)	1728 (8)	531 (17)	24 (7)
N(2)	1692 (11)	2997 (9)	625 (19)	40 (9)
N(3)	−347 (10)	1163 (9)	−621 (18)	30 (8)
N(4)	1188 (11)	783 (9)	−899 (20)	41 (10)
N(5*A*)	−1056 (15)	839 (13)	−4000 (26)	32 (13)
N(5*B*)	−732 (30)	440 (25)	−3887 (54)	32 (26)
C(1)	−752 (13)	742 (11)	−1657 (24)	36 (11)
C(2)	501 (12)	1243 (10)	−334 (23)	30 (10)
C(3)	−473 (13)	942 (11)	−3034 (25)	39 (12)
C(4)	−775 (13)	1641 (12)	113 (26)	40 (11)
C(5)	−156 (13)	1988 (13)	800 (26)	45 (12)
C(6*A*)	−894 (21)	1088 (19)	−5388 (39)	45 (21)
C(6*B*)	−622 (35)	505 (30)	−5303 (76)	50 (40)
C(7*A*)	−1450 (27)	603 (24)	−6531 (52)	75 (28)
C(7*B*)	−1179 (31)	896 (28)	−6133 (57)	22 (25)
trans-Pd(metronidazole)$_2Cl_2$ (II)				
Pd	0	0	0	27.4 (1)
Cl	15 (1)	665 (1)	2558 (1)	52.7 (2)
O(1)	−2542 (3)	−2077 (1)	3538 (3)	71.8 (3)
O(2)	498 (3)	−2475 (1)	5460 (3)	88.5 (3)
O(3)	4682 (3)	−930 (1)	8346 (3)	55.5 (3)
N(1)	684 (2)	−739 (1)	1963 (2)	32.3 (3)
N(2)	−632 (3)	−2073 (1)	4261 (3)	53.2 (3)
N(3)	2376 (3)	−1474 (1)	4250 (2)	35.7 (3)
C(1)	4137 (3)	−1804 (1)	5923 (3)	47.2 (3)
C(2)	2562 (3)	−963 (1)	3194 (3)	33.4 (3)
C(3)	4363 (3)	−1602 (1)	8041 (3)	50.4 (3)
C(4)	276 (3)	−1566 (1)	3622 (3)	35.9 (3)
C(5)	−741 (3)	−1107 (1)	2211 (3)	35.9 (3)
C(6)	4516 (3)	−703 (2)	3292 (3)	53.2 (3)

Table 3. *Bond distances* (Å) *and angles* (°)

cis-Pt(NH_3)(etanidazole)Br_2 (I)

Pt—Br(1)	2.375 (3)	Pt—Br(2)	2.397 (3)
Pt—N(1)	2.000 (15)	Pt—N(2)	2.083 (18)
N(1)—C(2)	1.30 (3)	N(1)—C(5)	1.37 (3)
N(3)—C(1)	1.45 (3)	N(3)—C(2)	1.33 (2)
N(3)—C(4)	1.34 (3)	N(4)—C(2)	1.47 (3)
N(4)—O(1)	1.23 (2)	N(4)—O(2)	1.21 (2)
C(3)—O(3)	1.24 (2)	C(1)—C(3)	1.49 (3)
C(4)—C(5)	1.34 (3)	N(5*A*)—C(3)	1.33 (3)
N(5*B*)—C(3)	1.34 (5)	N(5*A*)—C(6*A*)	1.49 (5)
N(5*B*)—C(6*B*)	1.43 (9)	C(6*A*)—C(7*A*)	1.69 (6)
C(6*B*)—C(7*B*)	1.40 (9)	C(7*A*)—O(4)	1.21 (5)
C(7*B*)—O(4)	1.54 (5)		

Br(1)—Pt—Br(2)	92.2 (1)	O(2)—N(4)—C(2)	117 (2)
Br(1)—Pt—N(1)	178.3 (4)	N(1)—C(5)—C(4)	111 (2)
Br(1)—Pt—N(2)	88.7 (5)	N(3)—C(1)—C(3)	113 (2)
Br(2)—Pt—N(1)	89.3 (5)	O(3)—C(3)—C(1)	120 (2)
Br(2)—Pt—N(2)	117.8 (5)	N(1)—C(2)—C(3)	114 (2)
N(1)—Pt—N(2)	89.8 (7)	N(1)—C(2)—N(4)	123 (2)
Pt—N(1)—C(5)	123 (1)	N(3)—C(2)—N(4)	123 (2)
Pt—N(1)—C(2)	133 (1)	N(3)—C(4)—C(5)	106 (2)
C(5)—N(1)—C(2)	103 (2)	O(3)—C(3)—N(5*A*)	123 (2)
C(1)—N(3)—C(2)	129 (2)	O(3)—C(3)—N(5*B*)	124 (2)
C(1)—N(3)—C(4)	124 (2)	C(1)—C(3)—N(5*A*)	116 (2)
C(2)—N(3)—C(4)	107 (2)	C(1)—C(3)—N(5*B*)	108 (2)
O(1)—N(4)—C(2)	117 (2)	C(3)—N(5*A*)—C(6*A*)	121 (2)
O(1)—N(4)—O(2)	127 (2)	C(3)—N(5*B*)—C(6*B*)	122 (5)
O(4)—C(7*A*)—C(6*A*)	94 (3)	N(5*A*)—C(6*A*)—C(7*A*)	111 (3)
O(4)—C(7*B*)—C(6*B*)	114 (5)	N(5*B*)—C(6*B*)—C(7*B*)	124 (5)

trans-Pd(metronidazole)$_2Cl_2$ (II)

Pd—Cl	2.297 (1)	Pd—N(1)	2.007 (2)
N(1)—C(2)	1.337 (2)	N(1)—C(5)	1.349 (3)
N(3)—C(2)	1.350 (3)	N(3)—C(4)	1.385 (3)
N(3)—C(1)	1.485 (2)	C(4)—C(5)	1.358 (3)
N(2)—C(4)	1.422 (3)	C(2)—C(6)	1.475 (3)
C(3)—O(3)	1.431 (4)	C(1)—C(3)	1.513 (3)
O(1)—N(2)	1.237 (3)	O(2)—N(2)	1.227 (3)

Cl—Pd—N(1)	89.8 (1)	Cl—Pd—N(1*a*)	90.2 (1)
Pd—N(1)—C(5)	124.2 (1)	Pd—N(1)—C(2)	127.4 (2)
C(2)—N(1)—C(5)	108.4 (2)	C(2)—N(3)—C(4)	106.4 (2)
C(1)—N(3)—C(2)	124.6 (2)	C(1)—N(3)—C(4)	128.7 (2)
N(1)—C(2)—N(3)	109.6 (2)	N(1)—C(2)—C(6)	124.4 (2)
N(3)—C(2)—C(6)	125.9 (2)	N(1)—C(5)—C(4)	108.0 (2)
N(3)—C(4)—C(5)	107.7 (2)	N(3)—C(4)—N(2)	125.5 (2)
C(5)—C(4)—N(2)	126.6 (2)	N(3)—C(1)—C(3)	111.4 (2)
C(4)—N(2)—O(1)	116.5 (2)	C(4)—N(2)—O(2)	119.0 (2)
O(1)—N(2)—O(2)	124.6 (3)	C(1)—C(3)—O(3)	111.8 (2)

expected to accept electron density from the metal into its empty π^* orbitals. The Pt—N(imidazole) distance is 2.000 (15) Å, as observed for the chloro analogue [2.000 (8) Å; Rochon, *et al.*, 1991]. These values agree well with the values observed in other Pt–imidazole-derivative complexes (Farrell *et al.*, 1984; Bales, Coulson, Gilmour, Mazid, Neidle, Kuroda, Peart, Ramsden & Sadler, 1983; Graves, Hodgson, van Kralingen & Reedijk, 1978; Carmichael, Chan, Cordes, Fair & Johnson, 1972). The Pt—NH_3 distance is 2.083 (18) Å [chloro analogue, 2.084 (9) Å], which is slightly longer than normal Pt—NH_2R bonds (2.03–2.06 Å; Lock & Pilon, 1981; Rochon, Melanson & Doyon, 1987; Howard-Lock, Lock, Turner & Zvagulis, 1981; Rochon, Melanson & Doyon, 1989) as usually observed for Pt—NH_3 complexes. The longer Pt—NH_3 bond (relative to Pt—NH_2R) might be attributed to the fact that NH_3 is involved in extensive hydrogen bonding.

The imidazole ring is planar and its dihedral angle with the Pt coordination plane is 69.1 (8)°, close to the reported values for several Pt–nitroimidazole complexes (Bales *et al.*, 1983; Bales, Mazid, Sadler, Aggarwal, Kuroda, Neidle, Gilmour, Peart & Ramsden, 1985; Rochon *et al.*, 1991). The nitro group makes a 32 (1)° angle with the imidazole ring plane. The N—O distances [1.23 (2) and 1.21 (2) Å] are close to the published values for nitroimidazole compounds (Farrell *et al.*, 1984; Bales *et al.*, 1983; Rochon *et al.*, 1991). The bond lengths and angles in the imidazole ring are normal, but the last four atoms on the side chain, N(4), C(6), C(7) and O(4), have high standard deviations resulting from the observed disorder. For the chloro analogue (Rochon *et al.*, 1991) and other published structures (Bales *et al.*, 1985; Farrell *et al.*, 1984), the thermal factors are high, resulting also in high standard deviations on these bonds and angles.

The molecules are held together by hydrogen bonds. The NH_3 ligand forms hydrogen bonds with O(3) [N(2)···O(3) = 2.89 (2) Å, Pt—N(2)···O(3) = 105.3 (8)°], O(4) [N(2)···O(4) = 3.07 (3) Å, Pt—N(2)···O(4) = 130.6 (9)°] and maybe Br(1) [N(2)···Br(1) = 3.60 (2) Å, Pt—N(2)···Br(1) = 98.3 (6)°]. The hydroxyl groups are hydrogen bonded to each other. The O(4)···O(4) distance is 2.86 (4) Å and the angles C(7*A*)—O(4)···O(4) = 101 (3) and C(7*B*)—O(4)···

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.

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (FDR), to MRC and NCI (Canada) (NF) for financial support.

References

BALES, J. R., COULSON, C. J., GILMOUR, D. W., MAZID, M. A., NEIDLE, S., KURODA, R., PEART, B. J., RAMSDEN, C. A. & SADLER, P. J. (1983). *J. Chem. Soc. Chem. Commun.* pp. 432–434.

BALES, J. R., MAZID, M. A., SADLER, P. J., AGGARWAL, A., KURODA, R., NEIDLE, S., GILMOUR, D. W., PEART, B. J. & RAMSDEN, G. A. (1985). *J. Chem. Soc. Dalton Trans.* pp. 795–802.

CARMICHAEL, J. W., CHAN, N., CORDES, A. W., FAIR, C. K. & JOHNSON, D. A. (1972). *Inorg. Chem.* **11**, 1117–1120.

COLEMAN, C. N., NOLL, L., HOWES, A. E., HARRIS, J. R., ZAKAR, J. & KRAMER, R. (1989). *Int. J. Radiat. Oncol. Biol. Phys.* **16**, 1085.

FARRELL, N., CARNEIRO, T. M. G., EINSTEIN, F. W. B., JONES, T. & SKOV, K. A. (1984). *Inorg. Chim. Acta*, **92**, 61–66.

GABE, E. J., LE PAGE, Y., CHARLAND, J. P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

GRAVES, B. J., HODGSON, D. J., VAN KRALINGEN, C. G. & REEDIJK, J. (1978). *Inorg. Chem.* **17**, 3007–3011.

HOWARD-LOCK, H. E., LOCK, C. J. L., TURNER, G. & ZVAGULIS, M. (1981). *Can. J. Chem.* **59**, 2737–2745.

LOCK, C. J. L. & PILON, P. (1981). *Acta Cryst.* B**37**, 45–49.

MELANSON, R., HUBERT, J. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.

MELANSON, R., ROCHON, F. D. & HUBERT, J. (1979). *Acta Cryst.* B**35**, 736–738.

ROCHON, F. D., KONG, P. C., MELANSON, R., SKOV, K. A. & FARRELL, N. (1991). *Inorg. Chem.* **30**, 4531–4535.

ROCHON, F. D., MELANSON, R. & DOYON, M. (1987). *Inorg. Chem.* **26**, 3065–3068.

ROCHON, F. D., MELANSON, R. & DOYON, M. (1989). *Can. J. Chem.* **67**, 2209–2212.

ROCHON, F. D., MELANSON, R., HOWARD-LOCK, H. E., LOCK, C. J. L. & TURNER, G. (1984). *Can. J. Chem.* **62**, 860–869.

SKOV, K. A., ADOMAT, H., CHAPLIN, D. J. & FARRELL, N. (1990). *Anti-Cancer Drug Des.* **5**, 121.

SHELDRICK, G. M. (1984). *SHELXTL User's Manual.* Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1993). C**49**, 1706–1713

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

BY DOMINIC J. MACCHIA,* WILLIAM F. FUREY JR† AND ROGER A. LALANCETTE‡

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA

(*Received* 6 *July* 1992; *accepted* 6 *May* 1993)

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 =

* Present address: Department of Chemistry, Middlesex County College, Edison, NJ 08817, USA.

† Present address: Veterans Administration Hospital, University of Pittsburgh, Pittsburgh, PA 15240, USA.

‡ To whom correspondence should be addressed.