Crystal Structures of Tris(1,8-naphthyridine)(perchlorato)mercury(II) Perchlorate and Tetrakis(1,8-naphthyridine)cadmium(II) Bis(perchlorate)

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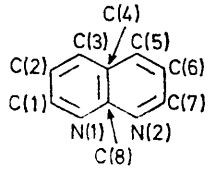
The crystal structures of the title compounds, (I) $[Hg(N_2C_8H_6)_3(ClO_4)][ClO_4]$ and (II) $[Cd(N_2C_8H_6)_4][ClO_4]_2$, have been determined from single-crystal diffractometer data and refined to R 0·08 [(I) 2595 reflections] and 0·07 [(II) 1147 reflections].

Crystals of (I) are triclinic, space group $P\bar{1}$, a = 11·786(3), b = 13·480(3), c = 9·820(1) Å, α = 103·98(1), β = 111·81(1), γ = 77·44(2)°, Z = 2. Crystals of (II) are triclinic, space group $P\bar{1}$, a = 9·273(1), b = 9·496(1), c = 20·001(3) Å, α = 99·01(1), β = 79·49(1), γ = 90·95(1)°, Z = 2.

In (I), the mercury atom is involved in an irregular seven-co-ordination with the three asymmetrically co-ordinated bidentate ligands and one of the perchlorate oxygen atoms. [Hg–N: 2·64, 2·30; 2·84, 2·14; 2·87, 2·20(2); Hg–O, 2·93(4) Å.]

(II) Is isostructural with the corresponding iron(II) derivative, the metal atom being eight-co-ordinate [Cd–N: 2·44, 2·47; 2·44, 2·57; 2·59, 2·42; 2·39, 2·73(2) Å]. The thermal motion of the perchlorate atoms in both structures is high but there appears to be no disorder.

NAPHTHYRIDINE, (III), is a bidentate ligand of unusually small 'bite'; mercury(II) and cadmium(II) are habitually unpredictable in their stereochemistry. The structures of the two complexes reported in this paper were determined as a continuation of our efforts



(III) Showing atom numbering system for a typical ligand

to rationalise the stereochemistry of mercury and of complexes of high co-ordination number with ligands of different 'bite'.

EXPERIMENTAL

The complexes were prepared as described previously [1,2] from suitable molar ratios of ligand and metal perchlorate dissolved in methanol; a small amount of triethyl orthoformate was added to remove any moisture and the complexes precipitated by the addition of dry ether, and slowly recrystallised from methanol–ether. Crystals of (I) were substantial; those of (II) were much smaller. The crystals chosen for the X-ray work were respectively a 0·20 mm cuboid (I) and a prism 0·08 × 0·09 × 0·12 mm (II). Unit-cell dimensions were obtained in each case by a least-squares fit of 15 reflections (2θ *ca.* 20—30°) centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer. Unique data sets in the range $2\theta < 100°$ were collected by a conventional 2θ—θ scan, yielding, for (I), 2770 reflections of which 2595 having $I > \sigma(I)$ were regarded as 'observed' and for (II), 3454 reflections of which 1147 having $I > 3\sigma(I)$ were regarded as 'observed'. Only these 'observed' reflections were used in the structure solutions and refinement, and were allocated unit weights.

Crystal Data.†—(I), $HgN_6C_{24}H_{18}Cl_2O_8$, M = 789·9, Triclinic, a = 11·786(3), b = 13·480(3), c = 9·820(1) Å, α = 103·98(1), β = 111·81(1), γ = 77·44(2)°, U = 1391·5(5) Å^3, D_m = 1·93(2), Z = 2, D_c = 1·89 g cm^{-3}, $F(000)$ = 764. Cu-K_α radiation, λ = 1·5418; μ(Cu-K_α) = 129·5 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

(II), $CdN_8C_{32}H_{24}Cl_2O_8$, M = 831·9, Triclinic, a = 9·273(1), b = 9·496(1), c = 20·001(3) Å, α = 99·01(1), β = 79·49(1), γ = 90·95(1)°, U = 1710·8(4) Å^3, D_m = 1·60, Z = 2, D_c = 1·61 g cm^{-3}, $F(000)$ = 836. μ(Cu-K_α) = 72·9 cm^{-1}. Space group $P\bar{1}$.

Scattering factors employed were for the neutral atoms, those for the metals and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[3,4] Data were corrected for absorption.

The structure of the mercury derivative was solved by the usual Patterson–Fourier methods; that of the cadmium was found to be isomorphous and isostructural with the already determined iron(II) derivative and refinement was initiated from the iron(II) parameters.[5] Both structures were refined to convergence by use of block-diagonal (9 × 9) least-squares methods, the cationic core in each case being 'fudged' as a full-matrix by refining the parameters of the metal and the associated nitrogen atoms jointly. In the latter stages of refinement, hydrogen atom positions were estimated assuming C–H 0·95 Å, and C–C–H *ca.* 120°, and included in the calculation. At convergence, no parameter shift in either structure was >0·1 σ; final difference maps showed no significant features. The final R was 0·079 (I) and 0·072 (II), and R' $\{=[\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$ 0·092 (I) and 0·082 (II). Anisotropic thermal parameters of the form $\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$ were employed for all non-hydrogen atoms in (I) and for all non-hydrogen and non-carbon atoms in (II); carbon atoms in (II) were refined with isotropic parameters.

† The reduced cell for (I) is: a = 9·820(1), b = 11·786(3), c = 13·480(3) Å, α = 77·44(2), β = 76·02(1), γ = 68·19(1)°. That for (II) is: a = 9·273(1), b = 9·496(1), c = 20·001(3)Å, α = 80·99(1), β = 79·49(1), γ = 89·05(1)°.

[1] R. L. Bodner and D. G. Hendricker, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 421.
[2] R. L. Bodner, *Diss. Abs. Int. B.*, 1971, **32**, 136.
[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
[5] P. Singh, A. Clearfield, and I. Bernal, *J. Co-ordination Chem.*, 1971, **1**, 29.

Computation was carried out using a local adaptation of the ' *X*-Ray '72 ' system on the CDC 6200 machine at this University.[6] Atom co-ordinates and bond distances and angles are listed in Tables 1 and 2. Structure-factors and Tables of ligand geometries and of hydrogen-atom positions are deposited as Supplementary Publication No. SUP 21048 (17 pp., 1 microfiche).*

DISCUSSION

The structures of all the ligands determined in this work did not deviate significantly from that of the free parent ligand;[7] the structures were inaccurate, in respect of the light atoms, on account of dominance of the scattering by the heavy atoms, and a limited data set in the case of (II). Accordingly, they are not discussed further. The perchlorate geometries are likewise poorly determined, owing to very high thermal motion, contributing further to the inaccuracy, and are not discussed, except in so far as they affect the metal co-ordination; they are not disordered.

* For details see Notice to Authors No. 7, in *J.C.S. Dalton*, Index issue, 1973.

[6] ' *X*-Ray System of Programs, version of June 1972, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

[7] A. Clearfield, M. J. Sims, and P. Singh, *Acta Cryst.*, 1972, **B28**, 350.

TABLE 1

Final non-hydrogen atomic fractional cell and thermal parameters, with least-squares estimated standard deviations in parentheses. A decimal point is implied before (*x*, *y*, *z*)

(*a*) Compound (I)

Atom	*x*	*y*	*z*	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Hg	10563(9)	18585(9)	1761(1)	60(1)	81(1)	93(1)	−6(1)	26(1)	33(1)
	x	*y*	*z*	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
(i) Ligand (a)									
N(1)	341(2)	182(1)	222(2)	5(1)	9(1)	10(2)	0(1)	2(1)	4(1)
N(2)	242(2)	282(1)	368(2)	7(1)	7(1)	11(2)	0(1)	6(1)	2(1)
C(1)	436(3)	156(2)	174(3)	9(2)	12(2)	11(2)	1(2)	3(2)	5(2)
C(2)	542(2)	207(3)	234(3)	4(1)	16(3)	12(2)	1(2)	4(2)	7(2)
C(3)	551(2)	282(2)	351(3)	6(2)	16(3)	13(3)	−2(2)	2(2)	9(2)
C(4)	448(2)	311(2)	403(3)	7(2)	8(2)	9(2)	−2(1)	0(1)	5(2)
C(5)	445(2)	391(2)	525(4)	7(2)	11(2)	14(3)	−4(2)	0(2)	6(2)
C(6)	344(3)	411(2)	564(3)	10(2)	9(2)	12(2)	0(2)	3(2)	2(2)
C(7)	246(2)	355(2)	479(3)	5(2)	10(2)	12(2)	0(1)	3(2)	4(2)
C(8)	347(2)	259(2)	334(3)	6(2)	7(2)	10(2)	−1(1)	2(1)	5(1)
(ii) Ligand (b)									
N(1)	−054(2)	045(2)	143(2)	8(2)	9(2)	9(2)	−1(1)	5(1)	0(1)
N(2)	136(2)	050(1)	267(2)	7(1)	6(1)	11(2)	−1(1)	4(1)	2(1)
C(1)	−160(2)	007(2)	122(3)	8(2)	12(2)	11(2)	−2(2)	4(2)	−1(2)
C(2)	−161(3)	−071(2)	201(4)	13(2)	9(2)	15(3)	−7(2)	10(2)	−3(2)
C(3)	−056(3)	−106(2)	300(3)	15(3)	9(2)	10(2)	−2(2)	5(2)	1(2)
C(4)	040(2)	−068(2)	320(3)	9(2)	7(2)	11(2)	−2(1)	5(2)	2(1)
C(5)	154(3)	−099(2)	429(3)	13(2)	9(2)	10(2)	−2(2)	6(2)	3(2)
C(6)	256(3)	−058(2)	451(4)	10(2)	10(2)	15(3)	2(2)	5(2)	7(2)
C(7)	244(2)	019(2)	372(3)	9(2)	8(2)	13(2)	−1(2)	7(2)	4(2)
C(8)	040(2)	005(2)	245(2)	7(2)	5(1)	7(2)	−1(1)	3(1)	1(1)
(iii) Ligand (c)									
N(1)	146(2)	322(2)	020(2)	5(1)	7(1)	9(1)	−1(1)	3(1)	1(1)
N(2)	−029(2)	266(1)	−002(2)	7(1)	8(1)	6(1)	−1(1)	3(1)	2(1)
C(1)	198(2)	378(2)	−028(3)	6(2)	8(2)	14(3)	−2(1)	4(2)	1(2)
C(2)	128(3)	437(2)	−145(3)	16(3)	7(2)	10(2)	−3(2)	6(2)	2(2)
C(3)	007(2)	439(2)	−199(3)	6(2)	9(2)	10(2)	0(1)	2(2)	2(2)
C(4)	−052(2)	381(2)	−159(3)	8(2)	9(2)	7(2)	−3(1)	4(1)	0(1)
C(5)	−176(2)	378(2)	−212(3)	7(2)	14(2)	7(2)	−2(2)	2(1)	4(2)
C(6)	−225(2)	318(2)	−168(3)	4(1)	18(3)	7(2)	1(2)	2(1)	2(2)
C(7)	−147(2)	259(2)	−057(3)	5(2)	10(2)	10(2)	−2(1)	3(1)	1(2)
C(8)	023(2)	322(2)	−047(2)	5(1)	7(1)	7(2)	0(1)	3(1)	2(1)
(iv) Perchlorate (a)									
Cl	5125(6)	8439(6)	2192(8)	9·1(5)	11·3(5)	11·0(6)	−2·1(4)	3·9(4)	3·7(4)
O(1)	514(3)	853(3)	359(3)	17(3)	40(5)	15(3)	7(3)	9(2)	11(3)
O(2)	399(3)	827(4)	128(4)	15(3)	53(7)	16(3)	−18(4)	3(2)	−4(4)
O(3)	593(5)	766(3)	181(5)	47(7)	34(5)	29(5)	27(5)	23(5)	15(4)
O(4)	541(4)	922(3)	191(5)	28(4)	19(3)	42(6)	−2(3)	21(4)	12(4)
(v) Perchlorate (b)									
Cl	8831(6)	3247(5)	3670(7)	7·7(4)	9·1(4)	9·6(5)	−0·9(3)	5·2(4)	2·6(4)
O(1)	791(2)	290(3)	239(3)	9(2)	50(6)	10(2)	−5(3)	3(1)	−6(3)
O(2)	981(3)	249(2)	398(4)	19(3)	13(2)	31(4)	7(2)	13(3)	7(2)
O(3)	837(2)	347(2)	479(3)	9(2)	26(3)	12(2)	0(2)	6(1)	2(2)
O(4)	934(2)	404(2)	365(4)	12(2)	25(3)	35(4)	−4(2)	6(2)	21(3)

TABLE 1 (*Continued*)

(b) Compound (II)

Atom	*x*	*y*	*z*	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cd	0580(3)	1162(3)	2455(2)	63(2)	50(2)	95(3)	−3(1)	−12(1)	11(1)
(i) Ligand (a)									
	x	*y*	*z*	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
N(1)	−187(3)	025(2)	237(1)	14(3)	5(2)	5(2)	3(2)	−3(2)	−2(1)
N(2)	−120(3)	043(3)	341(1)	7(2)	9(2)	11(3)	1(1)	0(2)	2(2)
C(1)	−285(4)	−008(4)	200(2)	10·5(12) †					
C(2)	−427(4)	−062(3)	223(2)	10·1(12)					
C(3)	−458(3)	−086(3)	288(2)	7·8(10)					
C(4)	−367(3)	−043(3)	339(2)	7·9(10)					
C(5)	−382(4)	−060(3)	403(2)	10·0(2)					
C(6)	−274(4)	−024(4)	439(2)	11·7(13)					
C(7)	−149(4)	026(4)	405(2)	10·7(12)					
C(8)	−223(3)	011(2)	304(1)	4·5(8)					
(ii) Ligand (b)									
N(1)	153(3)	−128(2)	221(1)	6(2)	3(1)	10(2)	0(1)	−4(2)	1(1)
N(2)	136(3)	−032(2)	126(1)	12(2)	7(2)	11(3)	−1(2)	−2(2)	3(2)
C(1)	187(3)	−224(3)	257(2)	7·6(10) †					
C(2)	258(3)	−353(3)	219(2)	8·1(10)					
C(3)	286(4)	−374(3)	150(2)	9·5(11)					
C(4)	248(3)	−271(3)	113(1)	6·6(9)					
C(5)	268(4)	−272(3)	042(2)	10·4(12)					
C(6)	222(4)	−166(4)	012(2)	13·2(15)					
C(7)	158(4)	−045(4)	061(2)	12·1(14)					
C(8)	179(3)	−143(3)	153(2)	8·4(10)					
(iii) Ligand (c)									
N(1)	−010(2)	312(3)	179(2)	4(2)	9(2)	15(3)	0(1)	−1(2)	7(2)
N(2)	−036(3)	351(3)	299(1)	9(2)	11(2)	6(2)	2(2)	0(2)	4(2)
C(1)	−021(4)	355(4)	121(1)	11·6(13) †					
C(2)	−079(4)	491(4)	118(2)	12·8(14)					
C(3)	−116(4)	573(4)	178(2)	11·3(13)					
C(4)	−115(3)	556(3)	244(2)	8·0(10)					
C(5)	−151(4)	619(3)	312(2)	10·0(12)					
C(6)	−130(4)	568(4)	361(2)	11·2(13)					
C(7)	−078(4)	427(4)	358(2)	11·2(13)					
C(8)	−058(3)	406(3)	242(2)	7·1(9)					
(iv) Ligand (d)									
N(1)	298(2)	215(2)	234(1)	6(2)	5(2)	8(2)	0(1)	3(1)	3(1)
N(2)	226(3)	190(3)	345(2)	9(2)	7(2)	16(3)	0(2)	−2(2)	3(2)
C(1)	386(3)	250(3)	180(2)	8·7(10)					
C(2)	517(4)	325(3)	186(2)	12·7(14)					
C(3)	546(4)	344(3)	253(2)	9·9(12)					
C(4)	467(4)	307(3)	307(2)	9·6(12)					
C(5)	481(4)	318(4)	376(2)	13·2(15)					
C(6)	391(5)	281(4)	426(2)	14·6(16)					
C(7)	256(5)	212(4)	407(2)	14·7(16)					
C(8)	326(3)	238(3)	299(2)	8·0(10)					
(v) Perchlorate (a)									
Cl	314(1)	272(1)	9659(4)	12·6(9)	13·0(8)	8·3(8)	0·4(6)	−4·4(6)	0·8(6)
O(1)	171(3)	235(3)	957(2)	12(2)	21(3)	19(3)	−1(2)	−9(2)	4(2)
O(2)	403(4)	145(4)	947(2)	14(3)	22(4)	27(4)	0(3)	0(3)	5(3)
O(3)	374(3)	362(3)	917(2)	14(3)	25(4)	17(3)	2(2)	0(2)	13(3)
O(4)	330(4)	313(3)	032(1) *	22(3)	23(3)	7(2)	−3(2)	−4(2)	−4(2)
(vi) Perchlorate (b)									
Cl	770(1)	312(1)	5607(6)	21·1(13)	13·6(9)	11·1(9)	−4·7(9)	−5·9(9)	1·9(7)
O(1)	657(5)	313(3)	528(3)	34(6)	14(3)	60(9)	−4(3)	−36(6)	3(4)
O(2)	785(5)	179(3)	577(2)	45(7)	13(3)	23(4)	1(3)	−12(4)	6(3)
O(3)	757(5)	403(3)	620(2)	38(5)	15(3)	17(3)	11(3)	−11(3)	−5(2)
O(4)	866(8)	345(6)	516(2)	69(11)	42(7)	17(4)	−36(7)	11(5)	0(4)

* Add 1. † Isotropic.

The stereochemistry of both mercury-(I) and -(II) is remarkable for the variety of structural types observed; in spite of this variety, the present mercury(II) co-ordination geometry is unprecedented (Figure 1), being a highly irregular seven-co-ordinate array, comprised of the six nitrogen atoms of the three asymmetrical non-equivalent bidentate naphthyridine ligands and O(b2) of perchlorate (b) [Hg–N, 2·64, 2·30; 2·84, 2·14; 2·87, 2·20(2) Å; Hg–O(b2) (*x* −1, *y*, *z*) 2·93(2) Å].

The stereochemistry remaining if the perchlorate oxygen atom is disregarded is a distorted pentagonal pyramid, the pentagonal plane being formed from

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

	Complex (I)			Complex (II)			
Ligand (i):	(a)	(b)	(c)	(a)	(b)	(c)	(d)
(*a*) The metal environment							
M–N(i1)	2·64(2)	2·84(2)	2·87(2)	2·44(3)	2·44(2)	2·59(3)	2·39(2)
M–N(i2)	2·30(2)	2·14(2)	2·20(2)	2·47(3)	2·57(2)	2·42(2)	2·73(3)
N(a1)–M–N(i1)		137·9(6)	67·1(6)		89·4(8)	85·1(8)	170·2(9)
N(a1)–M–N(i2)	52·3(7)	94·0(7)	117·1(8)	54·8(9)	85·1(8)	92·6(8)	138·4(8)
N(a2)–M–N(i1)		137·5(7)	78·9(7)		87·6(8)	120·7(8)	134·9(9)
N(a2)–M–N(i2)		100·3(7)	117·1(8)		125·6(8)	82·1(8)	83·7(9)
N(b1)–M–N(i1)			142·0(5)			138·8(8)	92·6(7)
N(b1)–M–N(i2)		48·0(6)	93·9(7)		53·6(9)	165·8(9)	92·0(8)
N(b2)–M–N(i1)			157·0(7)			85·2(8)	88·3(8)
N(b2)–M–N(i2)			140·9(7)			140·7(9)	127·7(8)
N(c1)–M–N(i1)							87·0(8)
N(c1)–M–N(i2)			51·2(7)			55·5(9)	118·5(8)
N(c2)–M–N(i1)							87·8(8)
N(c2)–M–N(i2)							77·2(9)
N(d1)–M–N(i1)							
N(d1)–M–N(i2)							51·2(8)
M–N(i1)–C(i1)	150(2)	160(2)	164(1)	148(2)	136(2)	150(1)	131(2)
M–N(i1)–C(i8)	90(2)	84(2)	80(2)	95(2)	99(2)	91(2)	104(2)
M–N(i2)–C(i7)	141(2)	124(2)	125(2)	148(2)	151(2)	142(2)	157(2)
M–N(i2)–C(i8)	105(1)	119(1)	112(1)	95(2)	92(2)	100(2)	90(2)
(*b*) The perchlorates							
Cl(i)–O(i1)	1·35(4)	1·37(2)		1·40(3)	1·33(6)		
Cl(i)–O(i2)	1·34(3)	1·36(3)		1·42(3)	1·37(4)		
Cl(i)–O(i3)	1·34(5)	1·35(3)		1·43(3)	1·34(3)		
Cl(i)–O(i4)	1·28(5)	1·34(4)		1·35(3)	1·22(6)		
O(i1)–Cl(i)–O(i2)	107(2)	110(2)		108(2)	108(3)		
O(i1)–Cl(i)–O(i3)	114(3)	107(2)		109(2)	115(3)		
O(i1)–Cl(i)–O(i4)	116(3)	117(2)		115(2)	99(4)		
O(i2)–Cl(i)–O(i3)	108(3)	108(2)		105(2)	106(2)		
O(i2)–Cl(i)–O(i4)	110(3)	104(2)		102(2)	115(3)		
O(i3)–Cl(i)–O(i4)	102(3)	111(2)		117(2)	113(3)		

In (I) there is a close Hg · · · O(b2′) contact [2·93(4) Å]; O(b2′)–Hg–N(a1, a2, b1, b2, c1, c2) 127·4(7), 78·4(8), 67·9(7), 76·1(8), 125·4(7), 99·7(8), Hg–O(b2′)–Cl(b′), 114(2)°; O(b2′) is derived from O(b2) by the transformation: $x-1, y, z$.

(*c*) The ligands							
N(i1)–C(i1)	1·32(4)	1·38(4)	1·31(4)	1·28(5)	1·33(4)	1·32(5)	1·31(4)
C(i1)–C(i2)	1·41(4)	1·45(5)	1·45(4)	1·43(5)	1·44(4)	1·42(5)	1·41(5)
C(i2)–C(i3)	1·31(4)	1·33(4)	1·32(4)	1·33(5)	1·34(5)	1·31(5)	1·39(6)
C(i3)–C(i4)	1·43(4)	1·28(5)	1·35(5)	1·30(4)	1·40(5)	1·35(5)	1·28(5)
C(i4)–C(i5)	1·40(4)	1·43(3)	1·37(4)	1·44(5)	1·39(5)	1·38(4)	1·41(6)
C(i4)–C(i8)	1·38(3)	1·36(4)	1·41(1)	1·50(4)	1·43(3)	1·53(4)	1·47(5)
C(i5)–C(i6)	1·34(5)	1·36(5)	1·32(5)	1·34(5)	1·36(6)	1·21(6)	1·26(6)
C(i6)–C(i7)	1·40(4)	1·38(5)	1·42(4)	1·34(5)	1·44(5)	1·42(5)	1·49(6)
C(i7)–N(i2)	1·28(3)	1·36(3)	1·31(3)	1·29(4)	1·26(5)	1·28(4)	1·32(6)
N(i2)–C(i8)	1·35(4)	1·32(3)	1·31(4)	1·32(4)	1·35(4)	1·37(4)	1·31(4)
N(i1)–C(i8)	1·30(3)	1·30(3)	1·35(3)	1·35(4)	1·33(4)	1·43(4)	1·35(4)
C(i8)–N(i1)–C(i1)	118(2)	111(3)	116(2)	117(3)	125(2)	119(3)	125(2)
N(i1)–C(i1)–C(i2)	124(2)	122(2)	123(2)	125(3)	116(3)	122(3)	122(3)
C(i1)–C(i2)–C(i3)	119(3)	119(3)	118(3)	117(3)	121(3)	115(4)	113(3)
C(i2)–C(i3)–C(i4)	117(3)	117(3)	123(3)	124(3)	121(3)	135(4)	128(3)
C(i3)–C(i4)–C(i5)	123(2)	119(3)	126(2)	131(3)	130(3)	145(3)	135(3)
C(i3)–C(i4)–C(i8)	119(2)	123(2)	116(2)	110(3)	117(3)	107(3)	118(3)
C(i4)–C(i8)–N(i1)	123(3)	127(3)	124(3)	126(3)	120(3)	122(3)	115(3)
C(i4)–C(i8)–N(i2)	125(2)	125(2)	119(2)	118(3)	125(3)	125(2)	131(3)
C(i4)–C(i5)–C(i6)	118(3)	119(6)	121(2)	120(3)	125(3)	126(3)	128(4)
C(i5)–C(i6)–C(i7)	119(3)	118(3)	120(2)	118(4)	113(4)	124(3)	116(4)
C(i6)–C(i7)–N(i2)	127(3)	123(3)	119(3)	128(4)	128(4)	119(3)	125(4)
C(i7)–N(i2)–C(i8)	113(2)	117(2)	123(2)	117(3)	116(3)	118(3)	113(3)
N(i1)–C(i8)–N(i2)	112(2)	108(2)	117(2)	116(2)	115(2)	114(2)	114(3)

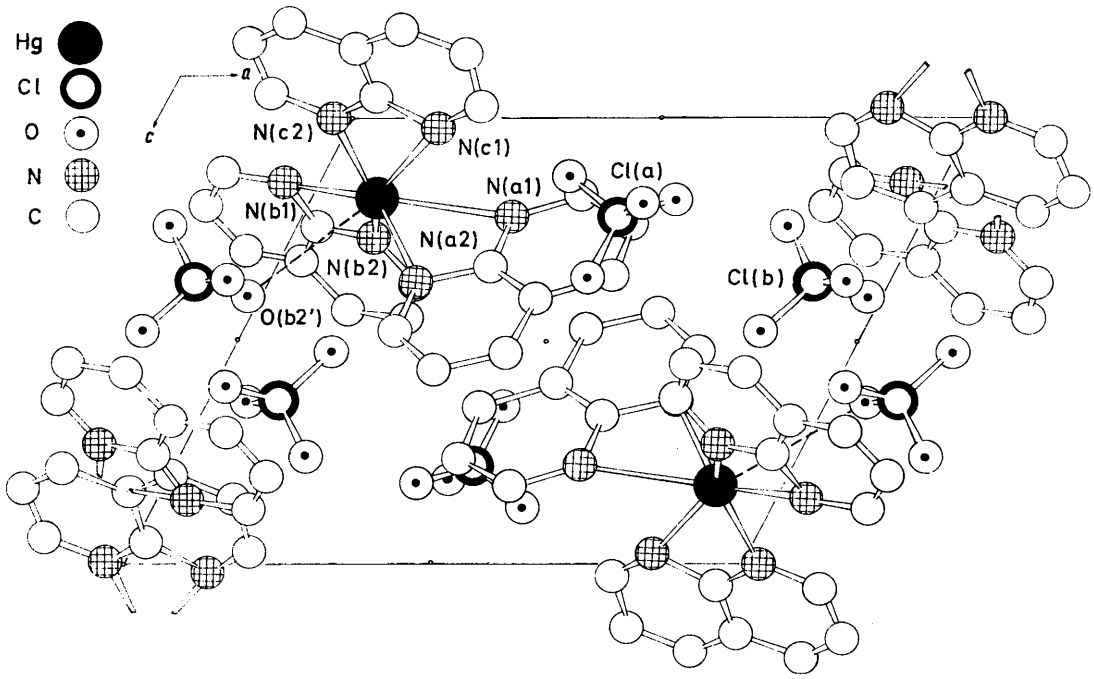


FIGURE 1 Unit-cell contents and ligand labels for complex (I), a projection down b^*

N(a1), N(b2), N(b1), N(c2), and N(c1). The mercury atom and N(a2) lie on the same side of this plane. An approximate mirror plane is formed by Hg, N(a1), N(a2). The mercury atom is not symmetrically bonded to the naphthyridine ligands [Hg–N(i1), 2·64, 2·84, 2·87; Hg–N(i2), 2·30, 2·14, 2·20 Å]. If the ligands were simply unidentate, the angles Hg–N(i2)–C(8) should be *ca.* 120; whereas if they were bidentate the same angles [together with Hg–N(i1)–C(8)] should be equal. The present situation is clearly intermediate between these two extreme possibilities [Hg–N(i1)–C(8), 90, 84, 80; Hg–N(i2)–C(8), 105, 119, 112°]. The bonding of two of the naphthyridine molecules [(b) and (c)] is considerably more asymmetric than the third and the structure could alternatively be considered to be a distorted tetrahedron, formed from N(a1), N(a2), N(b2), and N(c2).

Attempts to rationalise this stereochemistry in terms of ligand–ligand repulsion calculations have not been successful.

The stereochemistry of (II) is approximately the D_{2d} dodecahedron (Figure 2). The donor atoms N(b1), N(b2), N(c1), and N(c2) define one trapezoid, and N(a1), N(a2), N(d1), and N(d2) the other. The angle between the least-squares planes of those two trapezoids is 88·1°. The average normalised bite of the bidentate ligands [defined as N(i1)–N(i2)/Cd–N(i)] is 0·90. It has previously been predicted [8] that the only eight-co-ordinate isomer for $[M(\text{bidentate})_4]^{x\pm}$ which will occur for such small normalised bites is the D_{2d} dodecahedron. The detailed geometry of (II) also agrees very well with that predicted. The two angular parameters previously used to define the dodecahedron are, in this case, ψ_A(av) 47·8°, ψ_B(av) 6·0°, which may be compared

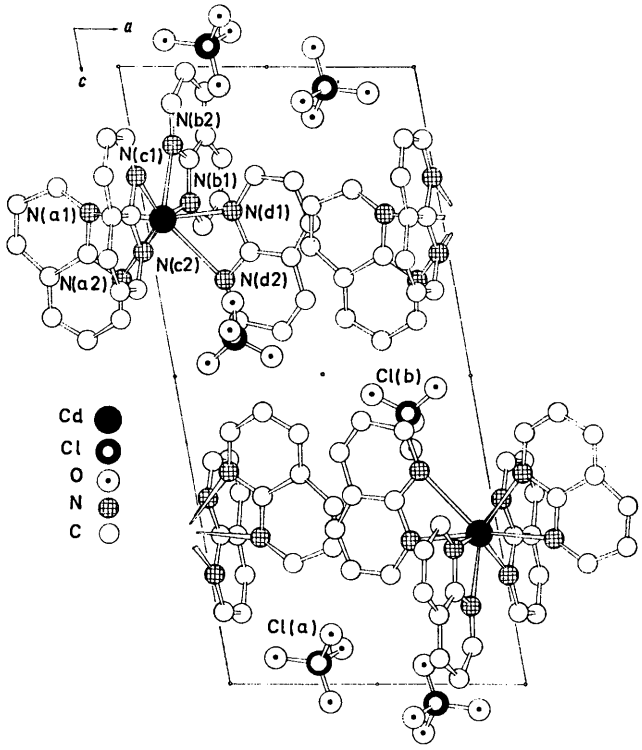


FIGURE 2 Unit-cell contents and ligand labels for complex (II), a projection down b^*

with values of ψ_A 48·5, 47·9°, ψ_B 5·0, 5·6°, for the repulsion exponent n of 6 and 12 respectively. Similarly,

[8] D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1556.

TABLE 3

Equations of least-squares planes through the ligands in the form: $pX + qY + rZ = s$ where X, Y, and Z are orthogonal co-ordinates, with X parallel to a, and Z in the ac plane

	Complex (I)			Complex (II)			
Ligand (i):	(a)	(b)	(c)	(a)	(b)	(c)	(d)
10^4p	−0391	−3678	−2676	3507	9064	9217	−4568
10^4q	6549	7186	7705	9311	4188	3665	8885
10^4r	−7547	5902	5786	1001	−0563	1274	0440
10^4s	2290	15359	21618	9994	12823	11483	3444
σ	3	3	2	3	1	2	2
Deviations (Å × 10^{-2})							
N(i1)	−3	−3	3	−1	0	0	0
N(i2)	3	1	0	−1	1	3	1
C(i1)	−2	3	0	0	−1	1	−4
C(i2)	4	3	−4	1	0	−2	3
C(i3)	0	0	1	−5	0	1	1
C(i4)	0	−2	0	6	1	1	−1
C(i5)	−2	0	3	0	1	−2	−3
C(i6)	−3	−1	−1	−1	−3	3	0
C(i7)	3	4	−2	−1	0	−2	1
C(i8)	−2	−3	0	3	1	−2	2
Metal dev.	42	46	6	−2	19	−4	18

Angles (°) between planes

(I): (a)–(b) 87·7, (a)–(c) 85·5, (b)–(c) 6·5
(II): (a)–(b) 86·2, (a)–(c) 89·7, (a)–(d) 7·3, (b)–(c) 5·1, (b)–(d) 87·5, (c)–(d) 84·2.

the dihedral angles between the two bidentate ligands of each trapezoid, α 2·7° [for the dihedral angle between N(b1), N(b2) and N(c1), N(c2)] and α 3·2° [for the dihedral angle between N(a1), N(a2), and N(d1), N(d2) closely agree with that predicted of 2·4°. The ratio of the mean bond lengths of the two different types of ligand sites $Cd–N_A/Cd–N_B$ is 1·07, reflecting the greater repulsion energy experienced by the atoms at the A sites of the dodecahedron.

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