A Potentially Seven-Co-ordinate Complex that is only Five-Co-ordinate; Crystal and Molecular Structure of Di-iodo(6,7,8,9-tetrahydro-16,22-dimethyl-5,10-dithia-15,23,24-triaza-17,21-methenodibenzo[*a*,*i*]cyclononadecene-*NN'N''*)zinc(II)

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A crystal structure determination of the title complex has been carried out. Cell dimensions are a = 19.523(11), b = 8.491(7), c = 18.792(11) Å, α = 79.6(1), β = 115.6(1), and γ = 96.4(1)°. The crystals are triclinic, space group $P\bar{1}$, with Z = 4. The two molecules in the asymmetric unit have similar geometries. The zinc atoms have five-co-ordinate square-pyramidal environments, being bonded to an axial [2.628(4), 2.620(3) Å] and an equatorial [2.540(4), 2.558(4) Å] iodine atom and to three equatorial nitrogen atoms [Zn–N(pyridine) 2.103(17), 2.101(19) Å; Zn–N 2.235(15)—2.280(15) Å]. The sulphur atoms of the macrocycle are not bonded to the metal primarily because the four carbon atoms between them cannot fit into an approximately planar girdle.

IT is well established that seven-co-ordinate complexes of the type $[MX_2L]$ ($L =$ macrocycle) can be prepared for magnesium and the majority of the first-row transition metals.[1-3] There are two basic requirements for the formation of such complexes. The metal atom must be of the appropriate size to fit into the macrocycle hole, and the macrocycle must remain approximately planar thus ensuring that the sterically favourable pentagonal-bipyramidal geometry is viable. These conditions are satisfied with macrocycles L[1], L[2], and L[3] ($m,n = 2,2$;

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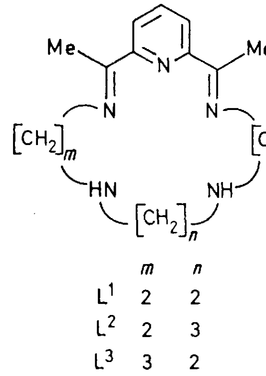
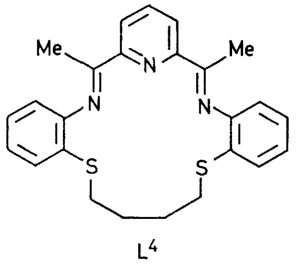
[1] M. G. B. Drew, A. H. Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507.

[2] M. G. B. Drew, A. H. Othman, and S. M. Nelson, *J.C.S. Dalton*, 1976, 1394.

[3] M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 438.

2,3; or 3,2 respectively) as shown by the many seven-co-ordinate molecules that have been prepared and characterised. In particular, crystal structures of complexes of Mg^{II}, Fe^{II}, Fe^{III}, Mn^{III}, and Zn^{II} with these macrocycles have been reported and shown to have relatively undistorted pentagonal-bipyramidal environments around the metal. We wished to investigate whether analogous seven-co-ordinate complexes could be prepared with macrocycles of a slightly different type and so have prepared the complex $[ZnI_2L^4]$ and report here its crystal and molecular structure.





EXPERIMENTAL

The complex $[ZnI_2L^4]$ was prepared using the published method.[4]

Crystal Data.—$C_{25}H_{25}I_2N_3S_2Zn$, $M = 750.8$, Triclinic, $a = 19.523(11)$, $b = 8.491(7)$, $c = 18.792(11)$ Å, $\alpha = 79.6(1)$, $\beta = 115.6(1)$, $\gamma = 96.4(1)°$, $U = 2\,761.9$ Å^3, $D_m = 1.77$, $Z = 4$, $D_c = 1.80$ g cm^{-3}, $F(000) = 1\,356$, μ(Mo-K_α) = 33.3 cm^{-1}; space group confirmed as $P1$ from the successful structure determination.

A crystal with dimensions 0.2 × 0.4 × 0.6 mm was mounted with its c^* axis parallel to the instrument axis of a G.E. XRD5 diffractometer which was used to measure cell dimensions (*via* least-squares refinement of high-angle reflections) and intensity data. The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered Mo-K_α radiation was used with the stationary-crystal–stationary-counter method, a 4° take-off angle, and a counting time of 10 s. Individual backgrounds were recorded for reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background against 2θ. Several standard reflections monitored during the course of the experiment showed no significant changes in intensity. No absorption or extinction corrections were applied. Of 5 174 independent reflections measured with $2\theta < 40°$, 3 262 having $I > \sigma(I)$ were used in the final stages of refinement.

Structure Determination.—The structure was determined using statistical methods[5] which provided the positions of the four independent iodine and two independent zinc atoms. Fourier methods led to the positions of the remaining atoms, which were refined by least-squares using two large block matrices. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $(\sin\theta)/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 160$ and $w^{\frac{1}{2}} = 160/F_o$ for $F_o > 160$. Calculations were made on a C.D.C. computer at the University of London Com-

TABLE 1

Positional co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
Zn(A)	4 515(1)	1 893(3)	1 964(1)
I(1A)	4 527(1)	0 316(2)	0 888(1)
I(2A)	3 882(1)	0 229(2)	2 797(1)
N(3A)	5 711(10)	1 909(20)	2 897(10)
N(6A)	5 051(9)	4 010(19)	1 643(10)
N(9A)	3 606(9)	3 621(20)	1 137(10)
S(12A)	2 848(5)	5 909(11)	1 709(6)
S(17A)	5 865(5)	3 920(9)	4 158(5)
C(1A)	5 984(13)	1 825(28)	4 281(14)
C(2A)	5 937(11)	1 015(24)	3 700(12)
C(4A)	6 210(12)	2 901(25)	2 728(12)
C(5A)	5 816(13)	4 015(27)	1 968(14)
C(7A)	4 671(12)	5 065(24)	1 024(12)
C(8A)	3 806(12)	4 882(25)	0 768(12)
C(10A)	2 840(12)	3 299(25)	1 002(13)
C(11A)	2 423(13)	4 181(28)	1 253(14)
C(13A)	3 217(31)	4 961(63)	2 799(36)
C(14A)	3 716(39)	5 344(72)	3 451(39)
C(15A)	4 484(25)	5 297(49)	3 499(25)
C(16A)	4 889(17)	3 935(38)	4 040(19)
C(18A)	6 147(14)	0 852(30)	5 045(15)
C(19A)	6 224(15)	−0 743(32)	5 146(16)
C(20A)	6 175(15)	−1 500(31)	4 560(16)
C(21A)	5 997(13)	−0 634(28)	3 806(15)
C(22A)	7 053(15)	3 025(30)	3 197(16)
C(23A)	6 234(13)	5 162(26)	1 629(13)
C(24A)	5 809(14)	6 186(29)	0 985(15)
C(25A)	5 037(13)	6 235(25)	0 688(13)
C(26A)	3 321(13)	6 058(28)	0 145(14)
C(27A)	2 477(13)	1 881(25)	0 667(13)
C(28A)	1 760(15)	1 447(31)	0 548(15)
C(29A)	1 375(15)	2 262(32)	0 774(16)
C(30A)	1 666(15)	3 651(32)	1 137(16)
Zn(B)	0 452(1)	−0 915(3)	7 830(1)
I(1B)	0 812(1)	−2 508(2)	9 267(1)
I(2B)	0 850(1)	−2 354(2)	6 991(1)
N(3B)	−0 832(10)	−1 196(20)	7 208(10)
N(6B)	−0 007(9)	1 054(18)	7 983(9)
N(9B)	1 349(9)	1 125(18)	8 102(9)
S(12B)	1 520(4)	3 423(8)	6 704(4)
S(17B)	−1 706(5)	0 367(11)	5 469(5)
C(1B)	−1 595(14)	−1 747(29)	5 817(15)
C(2B)	−1 208(12)	−2 241(25)	6 651(13)
C(4B)	−1 195(13)	−0 354(26)	7 402(13)
C(5B)	−0 760(12)	0 889(25)	7 892(13)
C(7B)	0 436(12)	2 193(26)	8 369(13)
C(8B)	1 203(12)	2 253(24)	8 375(12)
C(10B)	2 041(12)	1 025(25)	8 023(13)
C(11B)	2 141(12)	1 924(24)	7 377(12)
C(13B)	0 792(21)	2 405(41)	6 035(21)
C(14B)	0 085(42)	2 969(73)	5 733(39)
C(15B)	−0 611(27)	2 606(53)	5 259(27)
C(16B)	−0 789(21)	0 772(47)	5 320(22)
C(18B)	−1 930(16)	−2 806(35)	5 306(17)
C(19B)	−1 896(17)	−4 352(38)	5 548(19)
C(20B)	−1 531(18)	−5 026(36)	6 339(20)
C(21B)	−1 155(15)	−3 924(31)	6 884(16)
C(22B)	−2 077(14)	−0 430(29)	7 111(15)
C(23B)	−0 989(13)	1 784(26)	8 279(14)
C(24B)	−0 498(15)	2 949(31)	8 696(16)
C(25B)	0 246(13)	3 146(27)	8 759(14)
C(26B)	1 724(13)	3 704(28)	8 651(14)
C(27B)	2 562(13)	0 005(27)	8 570(14)
C(28B)	3 236(14)	−0 197(28)	8 498(15)
C(29B)	3 366(14)	0 667(30)	7 861(15)
C(30B)	2 796(14)	1 711(28)	7 303(14)

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[4] L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2494.

[5] 'Shel-X' system of programs, G. M. Sheldrick, personal communication, 1975.

puter Centre using for the most part the 'X-ray' system.[6] Atomic-scattering factors were taken from ref. 7 as were the anomalous- dispersion corrections for Zn, I, and S.

TABLE 2

Bond distances (Å) and angles (°)

	Molecule A	Molecule B
Zn–I(1)	2.628(4)	2.620(3)
Zn–I(2)	2.540(4)	2.558(4)
Zn–N(3)	2.235(15)	2.269(17)
Zn–N(6)	2.103(17)	2.101(19)
Zn–N(9)	2.256(15)	2.280(15)
I(1)–Zn–I(2)	111.4(1)	111.7(1)
I(1)–Zn–N(3)	105.5(6)	104.7(5)
I(1)–Zn–N(6)	96.3(6)	97.0(5)
I(1)–Zn–N(9)	98.0(5)	100.4(4)
I(2)–Zn–N(3)	98.9(5)	101.1(6)
I(2)–Zn–N(6)	152.3(6)	151.2(5)
I(2)–Zn–N(9)	102.2(5)	100.4(5)
N(3)–Zn–N(6)	73.6(6)	72.3(6)
N(3)–Zn–N(9)	139.9(6)	137.7(6)
N(6)–Zn–N(9)	71.9(6)	71.2(6)
C(1)–S(17)	1.780(26)	1.797(26)
C(1)–C(2)	1.36(4)	1.42(3)
C(1)–C(18)	1.44(3)	1.34(4)
C(2)–N(3)	1.46(3)	1.40(3)
C(2)–C(21)	1.39(3)	1.42(3)
N(3)–C(4)	1.32(3)	1.26(4)
C(4)–C(5)	1.50(3)	1.47(3)
C(4)–C(22)	1.50(3)	1.56(4)
C(5)–N(6)	1.35(3)	1.40(3)
C(5)–C(23)	1.44(4)	1.37(4)
N(6)–C(7)	1.32(2)	1.32(3)
C(7)–C(8)	1.54(3)	1.49(4)
C(7)–C(25)	1.38(3)	1.36(4)
C(8)–N(9)	1.28(3)	1.28(3)
C(8)–C(26)	1.45(3)	1.52(3)
N(9)–C(10)	1.41(3)	1.44(3)
C(10)–C(11)	1.43(4)	1.39(3)
C(10)–C(27)	1.43(3)	1.35(3)
C(11)–S(12)	1.773(25)	1.769(24)
C(11)–C(30)	1.43(4)	1.38(4)
S(12)–C(13)	1.90(6)	1.71(3)
C(13)–C(14)	1.26(8)	1.35(9)
C(14)–C(15)	1.47(10)	1.30(8)
C(15)–C(16)	1.44(5)	1.55(6)
C(16)–S(17)	1.82(4)	1.91(5)
C(18)–C(19)	1.35(4)	1.31(4)
C(19)–C(20)	1.33(5)	1.39(4)
C(20)–C(21)	1.39(4)	1.42(4)
C(23)–C(24)	1.35(3)	1.39(3)
C(24)–C(25)	1.37(4)	1.40(4)
C(27)–C(28)	1.34(4)	1.41(4)
C(28)–C(29)	1.31(5)	1.39(4)
C(29)–C(30)	1.41(4)	1.41(3)
C(18)–C(1)–S(17)	120(2)	120(2)
C(18)–C(1)–C(2)	115(3)	122(2)
C(2)–C(1)–S(17)	125(2)	118(2)
C(1)–C(2)–N(3)	117(2)	124(2)
C(1)–C(2)–C(21)	124(2)	115(2)
N(3)–C(2)–C(21)	118(2)	121(2)
Zn–N(3)–C(2)	123(1)	123(2)
Zn–N(3)–C(4)	117(1)	116(1)
C(2)–N(3)–C(4)	119(1)	121(2)
N(3)–C(4)–C(5)	110(2)	117(2)
N(3)–C(4)–C(22)	129(3)	125(2)
C(5)–C(4)–C(22)	121(2)	117(2)
C(4)–C(5)–N(6)	118(2)	112(2)
C(4)–C(5)–C(23)	122(2)	128(2)
N(6)–C(5)–C(23)	120(2)	119(2)
Zn–N(6)–C(5)	115(1)	117(1)
Zn–N(6)–C(7)	121(1)	121(1)
C(5)–N(6)–C(7)	121(2)	119(2)
N(6)–C(7)–C(8)	113(2)	112(2)
N(6)–C(7)–C(25)	121(2)	125(2)
C(8)–C(7)–C(25)	126(2)	123(2)
C(7)–C(8)–N(9)	113(2)	117(2)
C(7)–C(8)–C(26)	119(2)	118(2)
N(9)–C(8)–C(26)	128(2)	126(2)
Zn–N(9)–C(8)	118(1)	115(1)
Zn–N(9)–C(10)	121(1)	120(1)
C(8)–N(9)–C(10)	121(2)	125(1)
N(9)–C(10)–C(11)	125(2)	119(2)
N(9)–C(10)–C(27)	118(2)	118(2)
C(11)–C(10)–C(27)	117(2)	122(3)
C(10)–C(11)–S(12)	120(2)	124(2)
C(10)–C(11)–C(30)	119(2)	117(2)
S(12)–C(11)–C(30)	121(2)	119(2)
C(11)–S(12)–C(13)	99(2)	105(1)
S(12)–C(13)–C(14)	135(5)	118(4)
C(13)–C(14)–C(15)	111(7)	140(6)
C(14)–C(15)–C(16)	112(4)	113(4)
C(15)–C(16)–S(17)	113(3)	108(3)
C(1)–S(17)–C(16)	101(1)	97(2)
C(1)–C(18)–C(19)	121(3)	122(3)
C(18)–C(19)–C(20)	123(3)	124(3)
C(19)–C(20)–C(21)	119(2)	115(3)
C(2)–C(21)–C(20)	119(3)	123(2)
C(5)–C(23)–C(24)	115(2)	120(3)
C(23)–C(24)–C(25)	124(3)	120(3)
C(7)–C(25)–C(24)	117(2)	116(2)
C(10)–C(27)–C(28)	122(3)	120(2)
C(27)–C(28)–C(29)	121(3)	120(2)
C(28)–C(29)–C(30)	124(3)	117(3)
C(11)–C(30)–C(29)	117(3)	123(2)

The anisotropic thermal parameters are defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}b_ib_jh_ih_j)$ where $i,j = 1$—3 and b_i is the ith reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2\sin^2\theta/\lambda^2)$. A difference-Fourier map based on the heavy atoms gave the positions of most hydrogen atoms. These were idealised in trigonal or tetrahedral positions, given the thermal parameter of the atoms to which they were bonded, and included in the structure-factor calculation but not refined. The final R value was 0.065. A subsequent difference-Fourier map showed no significant peaks and the zero-weighted reflections gave no serious discrepancies. In the final cycle no shift was greater than 0.1σ. Final positional coordinates are given in Table 1, bond lengths and angles in Table 2. Anisotropic thermal parameters and observed and calculated structure factors are given in Supplementary Publication No. SUP 22191 (14 pp.).*

DISCUSSION

The asymmetric unit of $[ZnI_2L^4]$ contains two molecules A (Figure 1) and B. Atoms in the two molecules are numbered in an equivalent manner. The two independent molecules have generally similar geometries with just a few differences in the relative orientations of the benzene rings and in the torsion angles for the four carbon atoms between the sulphur atoms. The metal atoms have almost identical co-ordination spheres being bonded to two iodine atoms and three nitrogens but not to the sulphur atoms (Zn–S >4.3 Å). The two sulphur atoms are twisted out of the bonding range of the metal by a rotation of the benzene rings so that they are

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[6] 'X-Ray' system of programs, ed. J. M. Stewart, University of Maryland Technical Report, TR 192, 1972.

[7] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

almost perpendicular to the pyridine part of the macrocycle. Calculation of the least-squares planes (Tables 3) shows that the angle between the benzene rings and plane (1) (consisting of the two unsaturated five-membered rings and the pyridine ring) is 79.4, 89.2° in molecule A and 89.4, 84.1° in molecule B. The sulphur atoms are thus positioned *ca.* 2.5 Å below this plane.

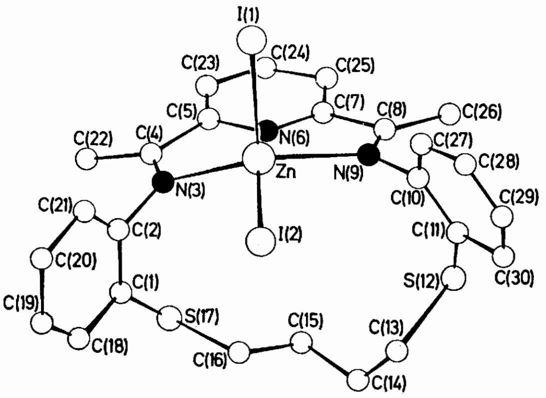


FIGURE 1 Molecule A

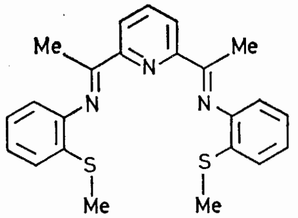
TABLE 3

Least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets. Atoms marked with an asterisk were not used to calculate the plane

		A	B	C	D	
Plane (1)	Molecule A	−6.31	6.70	14.03	1.89	[C(2) 0.23, N(3) −0.16, C(4) −0.05, C(5) −0.12, N(6) −0.09, C(7) −0.01, C(8) 0.05, N(9) −0.15, C(10) −0.07, C(22) 0.16, C(23) −0.09, C(24) −0.03, C(25) 0.07, C(26) 0.27, Zn * −0.72, I(2) * −0.27, I(1) * −3.29]
	Molecule B	−0.27	−4.64	12.70	9.59	[C(2) 0.07, N(3) −0.14, C(4) −0.01, C(5) −0.04, N(6) −0.06, C(7) −0.01, C(8) 0.03, N(9) −0.14, C(10) −0.07, C(22) 0.30, C(23) −0.12, C(24) −0.09, C(25) −0.07, C(26) 0.37, Zn* −0.77, I(2) * −0.36, I(1) * −3.32]
Plane (2)	Molecule A	0.32	−3.62	13.94	0.30	[C(10) −0.02, C(11) 0.00, C(27) 0.02, C(28) −0.01, C(29) −0.00, C(30) 0.01, S(12) * 0.02, N(9) * 0.08]
	Molecule B	3.10	6.83	9.82	9.21	[C(10) −0.00, C(11) 0.01, C(27) −0.00, C(28) −0.00, C(29) 0.01, C(30) −0.01, S(12) * 0.18, N(9) * −0.07]
Plane (3)	Molecule A	18.49	0.74	−2.94	9.95	[C(1) −0.01, C(2) 0.02, C(18) −0.00, C(19) −0.01, C(20) 0.02, C(21) −0.02, S(17) * −0.03, N(3) −0.10]
	Molecule B	19.37	−1.15	−10.13	−8.80	[C(1) 0.01, C(2) −0.03, C(18) 0.00, C(19) 0.00, C(20) −0.02, C(21) 0.03, S(17) * −0.09, N(3) 0.02]

There are two possible explanations for the present structure being only five-co-ordinate while similar complexes of the L^2 and L^3 macrocycles are seven-co-ordinate. First there is the steric effect of the four carbon atoms between the sulphur atoms. If both sulphur atoms were bonded to the metal a seven-membered ring would be formed which would cause considerable distortion in the girdle. Indeed, the geometry of $[MnL^3(NCS)_2]$[3] is much distorted from a pentagonal-bipyramidal structure (maximum deviation of a contributing atom from the MnN_5 plane, 0.46 Å) because of the steric requirements of the two six-membered rings. The distortion caused by a seven-membered ring would be greater than that from a six-membered ring and the resulting buckled macrocycle might well contain atoms positioned too close to the iodine atoms. With such bulky axial atoms a closely planar macrocycle is clearly necessary for a seven-co-ordinate structure to be viable. More flexibility might be possible in the analogous dichloro-complex and this is being investigated.*

The second explanation is that zinc is well known for its weak affinity towards sulphur atoms,[8] and that the macrocycle therefore adopts a conformation in which the sulphur atoms are not bonded rather than one in which they are bonded (assuming for the moment that both conformations are equally possible). It is difficult to assess the validity of this argument particularly as no structures of analogous complexes of sulphur-containing macrocycles have been determined. However, the structures of two manganese complexes containing macrocycles of the N_3O_2 (m,n = 2,2) type have been determined,[9,10] but the sulphur analogues though prepared have not been characterised by X-ray diffraction. The N_3S_2 (m,n = 2,2) macrocycles would be expected to form seven-co-ordinate complexes since they are too rigid for the sulphur atoms not to be bonded to the metal. An interesting comparison can be made with the analogous (but not macrocyclic) complex $[CdI_2L^5]$ in which the sulphur atoms are bonded to terminal methyl groups and not linked to each other. This complex is also five-co-ordinate and the sulphur atoms are not bonded to the metal.[11]



L^5

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* *Note added in proof:* Powder patterns show that the dichloro- and dibromo-complexes are isomorphous with the di-iodo-complex.

[8] M. G. B. Drew, D. A. Rice, and C. W. Timewell, *J.C.S. Dalton*, 1975, 144.

[9] M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 1173.

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Clearly there are no steric reasons why this complex is not seven-co-ordinate and the low affinity of the metal for sulphur is the most likely explanation for the unexpected structure.

For [ZnI$_2$L^4] both explanations therefore complement each other. This work demonstrates that it is of paramount importance to use relatively rigid, planar, quinquedentate macrocycles L in the preparation of seven-co-ordinate [MX$_2$L] complexes particularly with the smaller metals. Previous examples of seven-co-ordinate zinc(II) complexes use such planar macrocycles [12,13] or a related non-macrocyclic quinquedentate ligand.[14]

In [ZnI$_2$L^4] the metal atoms have square-pyramidal environments with I(1) in an axial site [2.628(4), 2.620(3) Å] and I(2) [2.540(4), 2.558(4) Å] together with three nitrogen atoms in equatorial sites. The I(1)–Zn–N angles range from 96.3(6) to 105.5(6)° in the two molecules, considerably less than the I(1)–Zn–I(2) angles of 111.4(1) and 111.7(1)°. The four equatorial atoms I(2), N(3), N(6), and N(9) are planar within experimental error and the metal atoms are 0.55, 0.58 Å above the plane in the direction of I(1). The main distortions from the regular C_{4v} symmetry found in the square pyramid are caused by the macrocycle, with the angle N(3)–Zn–N(9) necessarily being much smaller [139.9(6), 137.7(6)°] than the *ca.* 160° expected. It is apparent from models, and possibly from Figure 1, that the structure could not be the more popular trigonal bipyramid with the iodines equatorial because the –C–C–C–C– linkage between the sulphur atoms would obstruct one of the iodines. It is interesting to note that in [CdI$_2$L^5], where there is no such linkage, the geometry of the co-ordination sphere is trigonal bipyramidal.[11]

As shown in Table 3, the unsaturated part of the macrocycle associated with the pyridine ring is closely planar [plane (1)] and equivalent in the two molecules. The two benzene rings are twisted out of this plane by similar amounts such that the molecule maintains approximate C_s symmetry. The chain of four carbon atoms between the sulphur atoms has much higher thermal parameters (0.131—0.255 Å^2) than the rest of the molecules, but there was no sign of disorder in the difference-Fourier map. The torsion angles which describe the conformations of these linkages are shown in Table 4. There are some major differences between the conformations of the two linkages in the molecules, for instance the C(16)–C(15)–C(14)–C(13) angles are −106.2 and 35.1° in molecules A and B.

The Zn–I bond lengths are significantly different, the axial bonds (mean 2.624 Å) being longer than the equatorial (mean 2.549 Å); Zn–I$_{ax.}$ is 2.58 Å in square-pyramidal [(3,6-diazaoctane-1,8-diamine)iodozinc(II)]$^+$ [15] and 2.53—2.60 Å in a number of tetrahedral complexes.[16-18] The differences within the present complex are presumably due to a steric effect, with the equatorial I(2) being far from the adjacent equatorial nitrogens because of the shape of the macrocycle and therefore able to approach closer to the metal than the axial I(1). A survey of axial and equatorial bond lengths in square-pyramidal zinc(II) complexes found that neither type was consistently shorter than the other.[15]

TABLE 4

Torsion angles (°)

	Molecule A	Molecule B
C(2)–C(1)–S(17)–C(16)	100.1	90.7
C(1)–S(17)–C(16)–C(15)	−145.8	−163.2
S(17)–C(16)–C(15)–C(14)	−176.3	129.5
C(16)–C(15)–C(14)–C(13)	−106.2	35.1
C(15)–C(14)–C(13)–S(12)	−68.5	−177.1
C(14)–C(13)–S(12)–C(11)	160.0	145.6
C(13)–S(12)–C(11)–C(10)	−95.2	−83.1
C(1)–C(2)–N(3)–C(4)	76.5	74.3
C(11)–C(10)–N(9)–C(8)	−70.4	−98.3
N(3)–C(2)–C(1)–S(17)	−5.2	−7.9
N(9)–C(10)–C(11)–S(12)	4.9	9.4

The Zn–N(pyridine) bond in [ZnI$_2$L^4] is, as usual in such complexes, by far the shortest [2.103(17), 2.101(19) Å compared to 2.235(15)—2.280(15) Å] of the Zn–N bonds. These bond lengths can be compared to Zn–N of 2.283 and 2.292 [for Zn–N(pyridine)], 2.318, 2.045, and 2.041 Å in [ZnL(OH$_2$)$_2$]$^{2+}$,[13] and 2.251(4)—2.305(4) Å in a related [ZnL(OH$_2$)$_2$]$^{2+}$ complex [14] (L = N$_5$ macrocycle). In [ZnL(OH$_2$)$_2$]$^{2+}$ the rigidity of the macrocycle causes the inequality of the bond lengths. This cannot

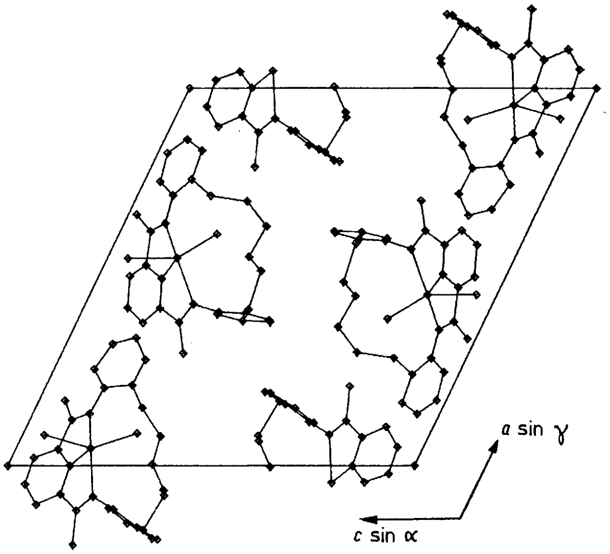

FIGURE 2 The unit cell in the *b* projection

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be the case in our complex, and presumably the strength of the Zn–N(pyridine) bond is due to an electronic effect. In a five-co-ordinate zinc complex in which the S^- of the N_3S_2 ($m,n = 2,0$) macrocycle are directly bonded to the metal,[19] the Zn–N(pyridine) distance [2.117(6) Å] is also shorter than the other Zn–N bonds [2.170(7), 2.122(7) Å]. In this molecule the two benzene rings are twisted out of the plane of the pyridine ring in opposite directions [torsion angles of the type C(8)–N(9)–C(10)–C(11) being 56 and 57°] so that the sulphur atoms are above and below the plane. The comparable angles in $[ZnI_2L^4]$ are 75.4 and −84.3° (mean).

In the present complex there are no excessively short intermolecular contacts. The packing diagram in the *b* projection is shown in Figure 2.

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