Ring-size and Substituent Effects in Relatively Rigid Macrocyclic Quinquedentate Ligands. Structure Determinations of $[ZnL^4(H_2O)_2][ClO_4]_2\cdot MeCN$ and $[ZnL^3(ClO_4)_2]$ ‡

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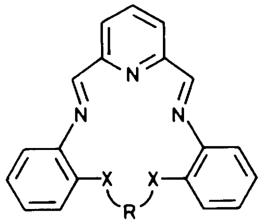
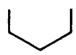
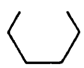
Twenty one metal complexes of macrocyclic quinquedentate ligands with N_5-, N_3O_2-, and N_3S_2-donor sets have been isolated from cyclocondensation reactions between pyridine-2,6-dicarbaldehyde and α,ω-dianilines [*e.g.* 1,2-di(*o*-aminophenylthio)ethane] carried out in the presence of salts of bivalent transition metals. *X*-Ray structure analyses of $[ZnL^3(ClO_4)_2]$ and $[ZnL^4(H_2O)][ClO_4]_2\cdot MeCN$ (L^3 = 6,7-dihydro-15,19-nitrilodibenzo[*e,p*][1,4,7,15]-dithiadiazacycloheptadecine and L^4 = 7,8-dihydro-6*H*-16,20-nitrilodibenzo[*f,q*]-[1,5,8,16]dithiadiazacyclo-octadecine), together with spectroscopic evidence show that the 15- and 16-membered ring ligands form seven-co-ordinate complexes in which the macrocycle defines the equatorial plane of an approximate pentagonal bipyramid and the axial sites are occupied by water molecules or co-ordinated anions. The geometry of the N_3X_2-donor set (X = O or S) and hence the goodness of fit for different metal ions depends crucially on the nature of the bridge between the benzene rings in the macrocycle.

In the last decade a large number of complexes of macrocyclic quinquedentate ligands which contain imine donors have been isolated from cyclocondensation reactions performed in the presence of metal-ion 'templates.' The majority of the ligand systems prepared in this way have either been extremely rigid,[1] based on 1,10-phenanthroline, 2,2′-bipyridyl, or 2,2′:6′,2″-terpyridyl precursors, or have been fairly flexible, containing linear alkane linkages between several of the donor atoms.[2] In this paper we describe the preparation of a range of ligands with intermediate rigidity which contain two benzo linkages. The ligands studied are listed below.

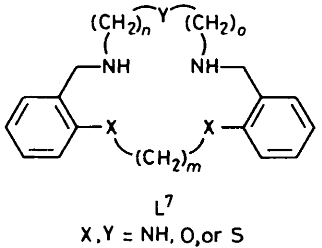
X-Ray structures of two zinc complexes, $[ZnL^4(H_2O)_2][ClO_4]_2\cdot MeCN$ (**1**) and $[ZnL^3(ClO_4)_2]$ (**2**), have been determined and allow the effect of ring-size expansion and donor-atom substitution to be assessed by comparison with the previously published structures[3,4] of $[ZnL^5I_2]$ (**3**) and $[MnL^1(ClO_4)_2]$ (**4**). Recent work,[5,6] in these and our collaborators' laboratories, has demonstrated that dibenzo-substituted quinquedentate ligands of another class, L^7, but also of intermediate rigidity, are particularly effective in showing metal-ion discrimination effects.



L	Donor atoms	X	R	Ring size
L^1	N_5	NH		15
L^2	N_3O_2	O		15
L^3	N_3S_2	S		15
L^4	N_3S_2	S		16
L^5	N_3S_2	S		17
L^6	N_5	N		15

Results and Discussion

The metal complexes listed in Table 1 were readily prepared from the condensation of pyridine-2,6-dicarbaldehyde and the appropriate diamine in the presence of various metal(II) salts. When the reactions were carried out in methanol complexes were formed as amorphous precipitates, but similar reactions in acetonitrile generally produced crystals or crystalline precipitates. In the majority of cases the complexes separate as hydrates. The three most feasible formulations for such hydrates are: (*i*) with one or two co-ordinated water molecules, as in $[ZnL^4(H_2O)_2][ClO_4]_2\cdot MeCN$ which has been characterised by *X*-ray crystallography (see later), (*ii*) with lattice water of crystallisation, as in $[MnL^2(ClO_4)_2]\cdot H_2O$ which has bands in its i.r. spectrum (see SUP 56657) which are consistent with strongly co-ordinated ClO_4^- and 'free' H_2O, or (*iii*) with the



L^7
X,Y = NH, O,or S
m,n,o, = 2 or 3

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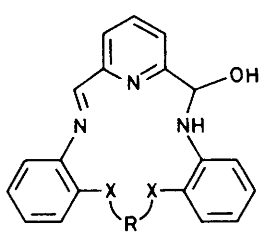
‡ Diaqua{7,8-dihydro-6*H*-16,20-nitrilodibenzo[*f,q*][1,5,8,16]dithiadiazacyclo-octadecine-*N,N′,N″,S,S′*}zinc(II) perchlorate–acetonitrile (1/1) and {6,7-dihydro-15,19-nitrilodibenzo[*e,p*][1,4,7,15]dithiadiazacycloheptadecine-*N,N′,N″,S,S′*}diperchloratozinc(II).

Supplementary data available (No. SUP 56657, 4 pp.): i.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

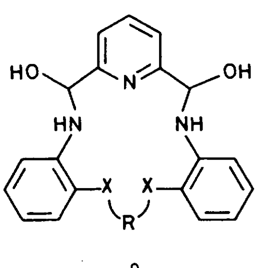
Table 1. Complexes of the potentially quinquedentate macrocyclic ligands

			Analysis/%					
			C		H		N	
Complex	Reaction solvent	Typical yield/%	Calc.	Found	Calc.	Found	Calc.	Found
$[MnL^1Cl_2]$	MeOH	81	54.0	53.8	4.1	4.3	15.0	14.8
	MeCN	68	54.0	54.2	4.1	4.4	15.0	14.9
$[MnL^1(NO_3)_2]$	MeOH	72	48.5	47.9	3.7	4.1	18.8	18.7
$[MnL^1(H_2O)_2][ClO_4]_2$	MeOH	65	40.0	40.5	3.4	3.2	11.1	11.3
$[MnL^1(ClO_4)_2]$	MeCN	60	42.4	42.2	3.2	3.1	11.8	11.4
$[ZnL^1(ClO_4)_2]$	MeCN	63	41.6	42.1	3.2	3.0	11.7	11.9
$[FeL^1(H_2O)_2][ClO_4]_3$	MeOH	52	34.5	34.1	2.9	3.4	9.6	9.9
	MeCN	50	34.5	34.0	2.9	3.3	9.6	9.3
$[NiL^1(H_2O)_2][ClO_4]_2$	MeCN	54	39.7	39.1	3.7	4.2	11.0	10.7
$[MnL^2(NO_3)_2]$	MeCN	70	48.3	47.8	3.3	3.3	13.4	14.0
$[MnL^2(H_2O)_2][NO_3]_2$	MeCN	62	45.2	44.8	3.8	3.9	12.5	12.3
$[MnL^2(ClO_4)_2]\cdot H_2O$	MeCN	67	41.0	40.7	3.1	3.2	6.8	6.6
$[MnL^3(H_2O)_2][ClO_4]_2$	MeCN	65	37.9	38.4	3.2	3.0	6.3	6.4
$[ZnL^3(NO_3)_2]$	MeCN	74	44.7	45.3	3.0	3.3	12.4	12.7
$[ZnL^3(H_2O)_2][ClO_4]_2$	MeOH	70	37.3	36.8	3.1	3.5	6.2	5.9
$[ZnL^3(ClO_4)_2]$	MeCN	62	39.4	38.8	2.7	2.8	6.6	6.9
$[NiL^3(H_2O)_2][ClO_4]_2$	MeCN	58	37.7	37.2	3.2	3.4	6.3	6.2
$[ZnL^4(H_2O)_2][ClO_4]_2\cdot MeCN$	MeCN	60	39.4	39.7	3.2	3.2	7.7	7.5
$[ZnL^5Cl_2]\cdot 2H_2O$	MeOH	54	48.0	48.5	4.4	4.2	7.3	7.5
$[ZnL^5(H_2O)_2][ClO_4]_2$	MeOH	63	39.2	38.9	3.6	3.8	6.0	6.3
	MeCN	58	39.2	38.7	3.6	3.7	6.0	6.3
$[MnL^6Cl_2]\cdot H_2O$	MeCN	79	54.0	53.6	4.5	4.5	13.7	13.5
$[MnL^6(NCS)_2]\cdot H_2O$[a]	MeCN	62	53.9	54.0	4.2	4.4	17.6	17.5
b	MeCN	59	53.9	54.2	4.2	4.0	17.6	17.3
$[MnL^6(ClO_4)_2]\cdot 2H_2O$	MeCN	58	42.0	41.7	3.8	4.0	10.6	10.5

[a] From preparations using $MnCl_2$ + Li(NCS). [b] From preparations using $[Mn(py)_4(NCS)_2]$.



L^8



L^9

elements of water added across one or both of the imine linkages to yield a mono- or di-α-hydroxylamine form of the ligands, L^8 or L^9. Such addition would greatly increase the flexibility of the chelate rings containing the pyridine donor and would allow the macrocycle to provide a more three-dimensional donor set. Examples of this type of addition have been found[7] in particularly rigid macrocyclic imines in which the increased flexibility provided by the α-hydroxylamine groups presumably allows the ligand to adapt more readily to the stereoelectronic requirements of the complexed metal ions. A ring contraction[8] in a rigid sexidentate ligand, which involves a similar addition across an imine bond, also has this driving force.

The formulations of the hydrates listed in Table 1 as type (*i*) or (*ii*) are based mainly on C, H, and N analyses and on the interpretation of i.r. spectra (see SUP 56657). A clear distinction between formulations as aqua complexes or as type (*iii*), complexes of the α-hydroxylamine form of the ligands, cannot be made with certainty on this basis because the imine stretching band in the i.r. spectra cannot be unambiguously assigned. Following a preliminary report on the isolation of complexes of the 15-membered ring ligands (L^2 and L^3) it has been shown[9] that on treatment with aliphatic alcohols both manganese(II)

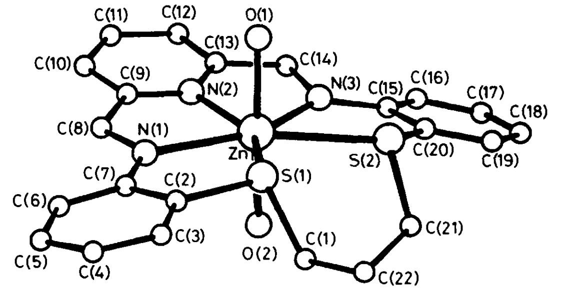


Figure 1. The structure of the dication $[ZnL^4(H_2O)_2]^{2+}$ in (**1**)

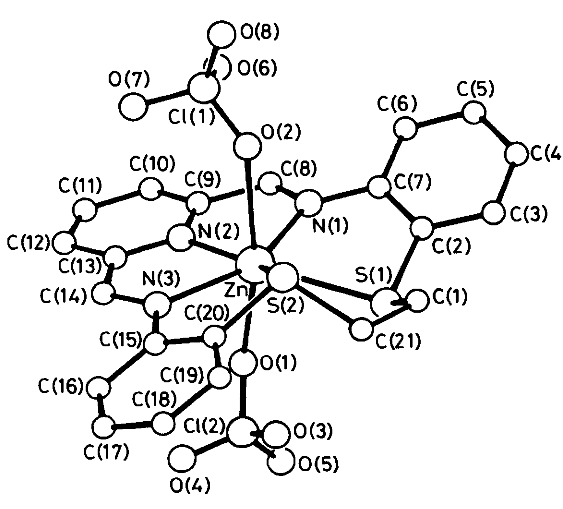


Figure 2. The structure of $[ZnL^3(ClO_4)_2]$ (**2**)

Table 2. Bond lengths, selected interatomic contact * distances (Å) and interbond angles (°) for $[ZnL^4(H_2O)_2][ClO_4]_2 \cdot MeCN$ (**1**)

Zn–S(1)	2.752(5)	N(2)–C(13)	1.32(2)	C(12)–C(13)	1.40(2)	Cl(1)–O(15)	1.33(5)
Zn–S(2)	2.667(5)	N(3)–C(14)	1.29(2)	C(13)–C(14)	1.49(2)	Cl(1)–O(6)	1.37(4)
Zn–O(1)	2.132(10)	N(3)–C(15)	1.44(2)	C(15)–C(16)	1.41(2)	Cl(1)–O(16)	1.38(5)
Zn–O(2)	2.061(10)	C(1)–C(21)	1.57(2)	C(15)–C(20)	1.39(2)	Cl(2)–O(7)	1.42(3)
Zn–N(1)	2.332(11)	C(2)–C(3)	1.42(2)	C(16)–C(17)	1.43(2)	Cl(2)–O(17)	1.33(4)
Zn–N(2)	2.108(12)	C(2)–C(7)	1.38(2)	C(17)–C(18)	1.40(3)	Cl(2)–O(8)	1.34(4)
Zn–N(3)	2.344(12)	C(3)–C(4)	1.39(2)	C(18)–C(19)	1.37(2)	Cl(2)–O(18)	1.26(6)
S(1)–C(1)	1.86(2)	C(4)–C(5)	1.39(3)	C(19)–C(20)	1.45(2)	Cl(2)–O(9)	1.55(3)
S(1)–C(2)	1.79(1)	C(5)–C(6)	1.40(2)	C(20)–C(21)	1.53(2)	Cl(2)–O(19)	1.50(4)
S(2)–C(20)	1.77(2)	C(6)–C(7)	1.41(2)	Cl(1)–O(3)	1.41(1)	Cl(2)–O(10)	1.38(4)
S(2)–C(21)	1.86(2)	C(8)–C(9)	1.45(2)	Cl(1)–O(4)	1.35(5)	Cl(2)–O(20)	1.33(4)
N(1)–C(7)	1.42(2)	C(9)–C(10)	1.41(2)	Cl(1)–O(14)	1.37(6)	N(4)–C(23)	1.13(2)
N(1)–C(8)	1.27(2)	C(10)–C(11)	1.42(2)	Cl(1)–O(5)	1.43(5)	C(23)–C(24)	1.44(3)
N(2)–C(9)	1.33(2)	C(11)–C(12)	1.36(2)				

O(1) ··· O(3^{I})	2.79(2)	O(1) ··· O(14^{II})	2.79(7)	O(2) ··· O(8^{I})	2.78(3)
O(1) ··· O(4^{II})	2.81(5)	O(2) ··· N(4^{I})	2.82(2)	O(2) ··· O(18^{I})	2.82(4)

S(1)–Zn–S(2)	71.9(1)	S(2)–Zn–O(2)	94.7(3)	O(1)–Zn–N(3)	92.7(4)
S(1)–Zn–O(1)	84.5(3)	S(2)–Zn–N(1)	142.9(3)	O(2)–Zn–N(1)	88.2(4)
S(1)–Zn–O(2)	92.2(3)	S(2)–Zn–N(2)	142.3(3)	O(2)–Zn–N(2)	97.2(4)
S(1)–Zn–N(1)	71.0(3)	S(2)–Zn–N(3)	72.2(3)	O(2)–Zn–N(3)	90.1(4)
S(1)–Zn–N(2)	142.7(3)	O(1)–Zn–O(2)	176.7(4)	N(1)–Zn–N(2)	73.3(4)
S(1)–Zn–N(3)	144.1(3)	O(1)–Zn–N(1)	90.5(4)	N(1)–Zn–N(3)	144.9(4)
S(2)–Zn–O(1)	84.5(3)	O(1)–Zn–N(2)	85.3(4)	N(2)–Zn–N(3)	72.2(4)

* First named atom at *x*,*y*,*z*, second atom in equivalent position: I *x*,*y*,*z*; II $\bar{x},\bar{y},\bar{z}$.

Table 3. Bond lengths (Å) and selected interbond angles (°) for $[ZnL^3(ClO_4)_2]$ (**2**)

Zn–S(1)	2.635(3)	Cl(2)–O(2)	1.445(8)	N(2)–C(13)	1.33(1)	C(9)–C(10)	1.41(1)
Zn–S(2)	2.513(4)	Cl(2)–O(6)	1.41(1)	N(3)–C(14)	1.28(1)	C(10)–C(11)	1.38(1)
Zn–O(1)	2.39(2)	Cl(2)–O(7)	1.380(8)	N(3)–C(15)	1.42(1)	C(11)–C(12)	1.39(1)
Zn–O(2)	2.53(1)	Cl(2)–O(8)	1.40(1)	C(1)–C(21)	1.49(2)	C(12)–C(13)	1.40(1)
Zn–N(1)	2.212(8)	S(1)–C(1)	1.81(1)	C(2)–C(3)	1.43(1)	C(13)–C(14)	1.45(1)
Zn–N(2)	2.057(6)	S(1)–C(2)	1.75(1)	C(2)–C(7)	1.38(1)	C(15)–C(16)	1.40(1)
Zn–N(3)	2.210(8)	S(2)–C(20)	1.76(1)	C(3)–C(4)	1.38(2)	C(15)–C(20)	1.37(1)
Cl(1)–O(1)	1.44(1)	S(2)–C(21)	1.83(1)	C(4)–C(5)	1.36(1)	C(16)–C(17)	1.37(1)
Cl(1)–O(3)	1.44(1)	N(1)–C(7)	1.42(1)	C(5)–C(6)	1.39(1)	C(17)–C(18)	1.38(2)
Cl(1)–O(4)	1.27(1)	N(1)–C(8)	1.29(1)	C(6)–C(7)	1.41(1)	C(18)–C(19)	1.38(2)
Cl(1)–O(5)	1.38(2)	N(2)–C(9)	1.33(1)	C(8)–C(9)	1.45(1)	C(19)–C(20)	1.41(1)

S(1)–Zn–S(2)	80.4(1)	S(2)–Zn–O(2)	74.7(2)	O(1)–Zn–N(3)	80.1(4)
S(1)–Zn–O(1)	79.2(2)	S(2)–Zn–N(1)	130.0(2)	O(2)–Zn–N(1)	77.4(4)
S(1)–Zn–O(2)	111.6(2)	S(2)–Zn–N(2)	142.4(3)	O(2)–Zn–N(2)	86.4(3)
S(1)–Zn–N(1)	72.5(2)	S(2)–Zn–N(3)	75.7(2)	O(2)–Zn–N(3)	96.9(3)
S(1)–Zn–N(2)	137.2(3)	O(1)–Zn–O(2)	165.6(3)	N(1)–Zn–N(2)	74.4(3)
S(1)–Zn–N(3)	136.1(2)	O(1)–Zn–N(1)	97.8	N(1)–Zn–N(3)	148.9(2)
S(2)–Zn–O(1)	117.2(2)	O(1)–Zn–N(2)	79.2(4)	N(2)–Zn–N(3)	74.8(3)

Table 4. Deviations (Å) of atoms from the least-squares planes through the macrocyclic MN_3X_3 unit

	$[MnL^1(ClO_4)_2]$	$[ZnL^3(ClO_4)_2]$	$[ZnL^4(H_2O)_2]^{2+}$
	(**4**)	(**2**)	(**1**)
	X = NH	X = S	X = S
Metal	0.00	−0.02	0.09
N^2(pyridino)	0.00	−0.05	−0.20
N^3(imino)	0.20	0.57	0.10
X^1	−0.30	−0.73	−0.04
X^2	0.30	0.70	−0.08
N^1(imino)	−0.20	−0.48	0.13

and magnesium(II) complexes of L^2 readily add alcohol across the imine bonds to yield α-aminoethers analogous to the α,α′-dihydroxylamines L^9.

The *X*-ray structure analyses have shown that the cation, $[ZnL^4(H_2O)_2]^{2+}$ in (**1**) and the complex $[ZnL^3(ClO_4)_2]$ (**2**) are seven-co-ordinate with the slightly distorted pentagonal-bipyramidal structures shown in Figures 1 and 2 respectively. Selected bond lengths and angles for (**1**) and (**2**) are listed in Tables 2 and 3 respectively. In both species the five donor atoms of the ligands define the equatorial planes and the deviations of these atoms from their 'planes of best fit' are given in Table 4, together with those for the related compound $[MnL^1(ClO_4)_2]$ (**4**). In the cationic complex (**1**) the axial co-ordination sites are occupied by donor water molecules with Zn–O(1) 2.132(10) and Zn–O(2) 2.061(10) Å. In the neutral compound (**2**) the axial sites are occupied by co-ordinated perchlorate ions with bond distances Zn–O(1) 2.39(2) and Zn–O(2) 2.53(1) Å.

On the basis of the observed structures of $[ZnL^3(ClO_4)_2]$ (**2**), $[ZnL^4(H_2O)_2]^{2+}$ in (**1**), and the third member of the series to have been fully characterised by *X*-ray structure determination $[MnL^1(ClO_4)_2]$ (**4**), it is assumed that the 15-membered (*i.e.* L^1, L^2, and L^3) and 16-membered (*i.e.* L^4) ring ligands present all five of their donor atoms to the complexed metal ion in an

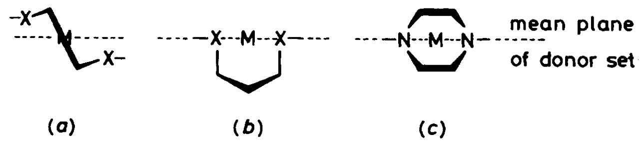


Figure 3. Conformations of the linkages between the benzene rings: (*a*) in the ligands L^2 and L^3, (*b*) in L^4, and (*c*) in L^6

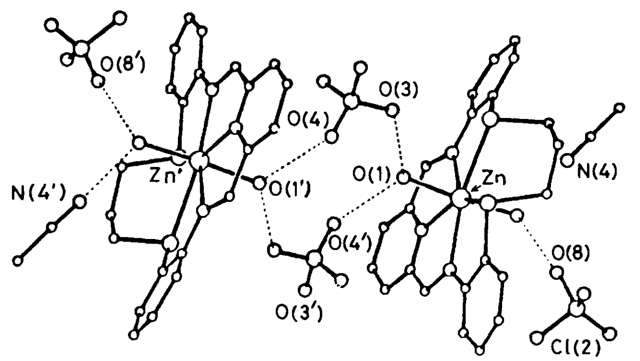
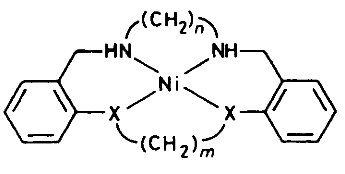


Figure 4. The hydrogen bonding to form a dimer across the centre of symmetry in the solid-state structure of $[ZnL^4(H_2O)_2][ClO_4]_2\cdot MeCN$ (**1**)

approximately planar equatorial arrangement, as shown in Figures 1 and 2. The planarity of the N_3X_2-donor sets in these macrocycles depends crucially on the nature of the chelate ring linking the benzene rings. An ethane linkage as in (**2**) and (**4**) produces a relatively symmetrical ruffling of the donor set (see Table 4) to allow the preferred configuration of the ethane bridge to be adopted [Figure 3(*a*)]. The propane bridge of $[ZnL^4(H_2O)_2]^{2+}$ in (**1**) allows a more planar (Table 4) geometry by adopting a chair-type chelate ring [Figure 3(*b*)]. It is assumed that the geometrical requirements of the piperazinediyl unit in the complexes of L^6 will force the macrocycle to present a very nearly planar N_5-donor set to a complexed metal ion [see Figure 3(*c*)].

The influence of ring size on co-ordination geometry can be examined by considering the series of N_3S_2 ligands. The hole size of the donor sets in zinc complexes of these ligands can be estimated by defining the centroid of the five donors and then taking the radius, R_H, of the hole defined by the donors to be the mean distance of the donor atoms from their centroid.[10,11] Incorporation of an additional methylene group is found to increase R_H from a value of 2.33 Å in the 15-membered ring ligand in $[ZnL^3(ClO_4)_2]$ to 2.44 Å in the related 16-membered ring complex $[ZnL^4(H_2O)_2]^{2+}$. The larger hole in L^4 is a consequence of the increase in the circumference of the ring, caused by the additional atom, and of the flattening of the donor set created by the chair form of the sulphur-containing chelate ring (see above). The increase in R_H of 0.11 Å is, therefore, greater than the values observed (0.04—0.05 Å) in quadridentate complexes of nickel(II) (**5**) in which the planarity of the N_2X_2-donor set is maintained in all the ring sizes examined.[10]

As the ring size in macrocyclic ligands is systematically increased a point will usually be reached at which a 'structural dislocation'[5] occurs for complexes with a given type of metal ion. For the zinc(II) complexes of the N_3S_2 ligands the 'structural dislocation' occurs between the 16-membered (L^4) and 17-membered ring (L^5) ligands. In $[ZnL^4(H_2O)_2]^{2+}$ the zinc maintains a seven-co-ordinate geometry (Figure 4), albeit with rather long Zn–S bonds (Table 2). However, in the reported structure[3] of the 17-membered ring complex $[ZnL^5I_2]$ (**3**) the two sulphur atoms are no longer co-ordinated and the ligand adopts a conformation which allows the approach of one iodide approximately in the plane of the three nitrogen atoms of the macrocycle, with the other iodide in an apical co-ordination site, giving an approximately square-pyramidal geometry about about the zinc(II) ion. Structural dislocations of this type have an important influence[5] on metal-ion discrimination shown by macrocyclic ligands. Unfortunately, the hydrolytic instability of imine ligands of the type described in this paper precludes measurements of metal complex stability constants. The ligands, therefore, cannot be used in a systematic study of ring-size and substituent effects and of variation of donor-atom type on selectivity of metal-ion complex formation as is underway[5,6] with the quinquedentate ligands of type L^7.



(**5**)

$m = 2, n = 2$ or 3
$m = 3, n = 3$ or 4

Experimental

Preparation of the α,ω-*Dianilines*.—The compounds 1,2-bis(*o*-aminophenylthio)ethane and 1,3-bis(*o*-aminophenylthio)propane were prepared by literature[12–14] methods and 1,4-bis(*o*-aminophenylthio)butane by a closely related procedure. The compound 1,2-bis(*o*-aminophenoxy)ethane was obtained[15] *via* the corresponding dinitro compound[12] on reduction with hydrazine hydrate in the presence of Pd/C. The compound *N*,*N*′-bis(*o*-aminophenyl)-1,2-diaminoethane was prepared by a previously reported method,[15] and *N*,*N*′-bis(*o*-aminophenyl)piperazine by a closely related procedure.

Preparation of the Macrocyclic Complexes.—Pyridine-2,6-dicarbaldehyde (0.135 g, 1 mmol), the required dianiline (1 mmol), and a slight excess (1.1—1.3 mmol) of the required metal salt were dissolved separately in methanol or acetonitrile. The solutions were mixed (total volume 100 cm^3) and set aside at room temperature for 24 h. Reactions in methanol yielded precipitates (usually orange or orange-red amorphous powders) which were collected, washed with a little cold methanol, and dried under reduced pressure to give the materials listed in Table 1. Reactions in acetonitrile generally resulted in orange solutions from which crystals or crystalline precipitates were obtained by slow evaporation under nitrogen. An exception to this procedure was used for the thiocyanato complex $[MnL^6(NCS)_2]\cdot H_2O$ which was obtained by addition of Li(NCS) to the solution obtained when the cyclocondensation had been performed in the presence of manganese(II) chloride. Alternatively, this complex can be obtained by performing the condensation in the presence of $[Mn(py)_4(NCS)_2]$ (py = pyridine).

X-*Ray Structure Determination*.—*Crystal data*. (**1**), $C_{24}H_{26}Cl_2N_4O_{10}S_2Zn$, $M = 730.90$, monoclinic, space group $P2_1/c$, $a = 8.068(2)$, $b = 30.985(6)$, $c = 12.259(3)$ Å, $\beta = 99.03(3)°$, $U = 3\,027$ Å^3, $D_m = 1.58$, $Z = 4$, $D_c = 1.60$ kg dm^{-3}, $F(000) = 1\,396$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo}K_\alpha) = 12.1$ cm^{-1}.

(**2**), $C_{21}H_{17}Cl_2N_3O_8S_2Zn$, $M = 639.79$, monoclinic, space group $P2_1/c$, $a = 11.385(2)$, $b = 29.509(5)$, $c = 8.922(2)$ Å, $\beta = 126.62(2)°$, $U = 2\,406$ Å^3, $D_m = 1.75$, $Z = 4$, $D_c = 1.77$ kg dm^{-3}, $F(000) = 1\,296$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 14.6$ cm^{-1}.

Table 5. Fractional atomic co-ordinates for complex (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	0.286 0(2)	0.111 12(6)	0.196 7(1)	C(18)	−0.306(2)	0.215 3(5)	0.031(1)
S(1)	0.241 6(5)	0.078 3(1)	0.398 7(4)	C(19)	−0.253(2)	0.188 7(5)	0.120(1)
S(2)	−0.022 4(5)	0.131 9(1)	0.231 3(3)	C(20)	−0.092(2)	0.167 6(5)	0.121(1)
O(1)	0.172 2(14)	0.052 3(3)	0.133 2(9)	C(21)	0.001(2)	0.169 0(6)	0.351(1)
O(2)	0.395 6(12)	0.166 6(3)	0.267 2(8)	C(22)	0.034(2)	0.144 1(5)	0.460(1)
N(1)	0.527 8(14)	0.073 9(4)	0.273 0(10)	Cl(1)	−0.103 2(6)	−0.040 4(1)	0.179 9(4)
N(2)	0.435 0(13)	0.105 0(4)	0.070 8(9)	O(3)	−0.030(2)	−0.003 2(4)	0.234(1)
N(3)	0.157 9(14)	0.151 0(3)	0.044 0(10)	O(4)	−0.206(6)	−0.031(2)	0.085(3)
C(1)	0.213(2)	0.124 2(5)	0.491(1)	O(14)	−0.259(8)	−0.034(2)	0.120(7)
C(2)	0.452(2)	0.063 6(5)	0.453(1)	O(5)	−0.202(6)	−0.056(1)	0.258(4)
C(3)	0.492(2)	0.053 1(5)	0.567(1)	O(15)	−0.103(8)	−0.076(2)	0.240(5)
C(4)	0.656(2)	0.041 6(5)	0.610(1)	O(6)	−0.004(4)	−0.074(1)	0.157(4)
C(5)	0.778(2)	0.039 5(5)	0.542(1)	O(16)	0.013(5)	−0.047(1)	0.111(4)
C(6)	0.736(2)	0.048 5(5)	0.429(1)	Cl(2)	0.282 3(7)	0.275 1(1)	0.195 2(5)
C(7)	0.572(2)	0.060 9(4)	0.385(1)	O(7)	0.205(6)	0.316(1)	0.207(3)
C(8)	0.617(2)	0.063 8(5)	0.200(1)	O(17)	0.348(6)	0.314(1)	0.185(3)
C(9)	0.573(2)	0.080 7(5)	0.089(1)	O(8)	0.201(5)	0.241(1)	0.228(3)
C(10)	0.677(2)	0.074 7(5)	0.008(1)	O(18)	0.328(7)	0.243(2)	0.144(4)
C(11)	0.629(2)	0.095 4(5)	−0.096(1)	O(9)	0.268(5)	0.267(1)	0.069(3)
C(12)	0.486(2)	0.119 3(5)	−0.113(1)	O(19)	0.350(7)	0.267(1)	0.314(3)
C(13)	0.392(2)	0.123 3(5)	−0.026(1)	O(10)	0.453(4)	0.275(2)	0.235(3)
C(14)	0.233(2)	0.148 4(5)	−0.041(1)	O(20)	0.121(4)	0.273(1)	0.206(4)
C(15)	0.001(2)	0.174 0(5)	0.036(1)	N(4)	0.619(2)	0.168 6(5)	0.469(1)
C(16)	−0.055(2)	0.202 9(5)	−0.050(1)	C(23)	0.680(2)	0.171 0(5)	0.558(2)
C(17)	−0.213(2)	0.223 9(6)	−0.053(1)	C(24)	0.763(2)	0.173 0(7)	0.671(2)

Table 6. Fractional atomic co-ordinates for complex (**2**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	0.123 9(1)	0.132 07(4)	0.324 3(2)	C(4)	0.365(1)	0.304 1(4)	0.598(2)
Cl(1)	0.333 5(4)	0.065 2(1)	0.231 4(5)	C(5)	0.230(1)	0.316 4(4)	0.446(2)
Cl(2)	−0.198 2(3)	0.177 7(1)	0.276 3(3)	C(6)	0.140(1)	0.283 3(3)	0.317(1)
S(1)	0.384 4(3)	0.170 4(1)	0.526 6(4)	C(7)	0.189(1)	0.238 1(3)	0.346(1)
S(2)	0.215 6(3)	0.103 1(1)	0.641 9(4)	C(8)	−0.006(1)	0.208 7(3)	0.049(1)
O(1)	0.229(1)	0.100 7(4)	0.182(2)	C(9)	−0.092(1)	0.168 7(3)	−0.052(1)
O(2)	−0.044 3(8)	0.166 4(3)	0.390(1)	C(10)	−0.205(1)	0.168 2(3)	−0.245(1)
O(3)	0.405(1)	0.061 1(4)	0.429(1)	C(11)	−0.280(1)	0.128 0(3)	−0.324(1)
O(4)	0.278(2)	0.026 8(4)	0.158(2)	C(12)	−0.243(1)	0.089 1(4)	−0.215(1)
O(5)	0.429(1)	0.080 8(3)	0.196(1)	C(13)	−0.126(1)	0.092 1(3)	−0.026(1)
O(6)	−0.226(1)	0.211 2(3)	0.146(1)	C(14)	−0.074(1)	0.054 8(4)	0.106(1)
O(7)	−0.280(1)	0.139 7(3)	0.181(1)	C(15)	0.109(1)	0.028 8(3)	0.416(1)
O(8)	−0.232(1)	0.194 3(4)	0.393(1)	C(16)	0.090(1)	−0.017 8(4)	0.380(1)
N(1)	0.097 8(8)	0.202 4(2)	0.223(1)	C(17)	0.167(1)	−0.047 7(4)	0.526(2)
N(2)	−0.055 2(7)	0.131 0(3)	0.048(1)	C(18)	0.264(1)	−0.032 0(4)	0.706(2)
N(3)	0.038 2(8)	0.062 2(2)	0.273(1)	C(19)	0.281(1)	0.013 8(4)	0.746(1)
C(1)	0.449(1)	0.159 4(4)	0.764(2)	C(20)	0.202(1)	0.044 6(3)	0.596(1)
C(2)	0.327(1)	0.226 8(3)	0.502(1)	C(21)	0.413(1)	0.111 9(4)	0.781(2)
C(3)	0.421(1)	0.260 8(4)	0.633(1)				

The space groups for complexes (**1**) and (**2**) were assigned from systematic absences in the data $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). Data were collected in the θ ranges 3—28° for (**1**) and 3—27° for (**2**) with scan widths of 0.8°. The methods of data collection and data processing have been described previously.[16] No absorption corrections were applied. Equivalent reflections were averaged to give 3 128 unique reflections with $I/\sigma(I) > 3.0$ for (**1**) and 1 887 with $I/\sigma(I) > 2.0$ for (**2**).

Structure solution and refinement.[17] The zinc and sulphur atoms for both structures were located from Patterson syntheses. The remaining non-hydrogen atoms were obtained from subsequent difference Fourier maps. The perchlorate anions in complex (**1**) were disordered and difference Fourier syntheses indicated two distinct orientations. Two positions, each with half occupancy, were assigned to each perchlorate oxygen atom, except for O(3) which was common to both orientations. Blocked full-matrix refinement for (**1**) and full-matrix refinement for (**2**) converged at R and R' 0.092 and 0.090 for (**1**) and 0.059 and 0.063 for (**2**), with $w = 1/\sigma^2(F)$. The Zn, Cl, S, and O atoms were assigned anisotropic thermal parameters in the final cycles of refinement of both structures. For (**2**) the hydrogen atoms were included in calculated positions (C–H 1.08, N–H 1.04 Å; U_{iso} 0.075 Å^2). The final fractional atomic co-ordinates for (**1**) and (**2**) are given in Tables 5 and 6 respectively.

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