Metal Ion Size Selectivity of 1-Thia-4,7-diazacyclononane (9-aneN_2S), and other Tridentate Macrocycles. A Study by Molecular Mechanics Calculation, Structure Determination, and Formation Constant Determination of Complexes of 9-aneN_2S

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Abstract

Several aspects of the coordination chemistry of the tridentate cyclononane type macrocycles are examined using molecular mechanics calculations, crystallography and formation constant determinations. The molecular mechanics calculations show that small metal ions coordinate best to these ligands, such that metal ions with a covalent radius of 1.25 Å fit best into 9-aneS_3 and 1.40 Å fit best into 9-aneN_3 (9-aneS_3 = 1,4,7-trithiacyclononane, 9-aneN_3 = 1,4,7-triazacyclononane). For mixed donor members of the series such as 9-aneN_2S (1-thia-4,7-diazacyclononane) the disparity in M–L bond length between the M–N and M–S bond lengths leads to a much higher strain situation than expected from the strain energies of the 9-aneN_3 and 9-aneS_3 complexes. This accounts for the order of ligand field strength in complexes of these ligands of 9-aneS_3 > 9-aneN_3 > 9-aneN_2S. It is concluded that in the absence of the strain effects encountered in mixed donor ligands containing the thioether donor group, the latter group should always be higher in the spectrochemical series than ligands containing the secondary nitrogen donor. The formation constants of 9-aneN_2S with Ni(II), Zn(II), Cd(II), Co(II), Fe(II), and Pb(II) are reported. Comparison of these with the formation constants for the 9-aneN_2O and 9-aneN_3 complexes shows that the macrocyclic effect (the difference in stability between the complex of the macrocycle and of its open chain analogue) is much higher for small metal ions, and small with large metal ions, in agreement with the molecular mechanics calculations which show that the cyclononane macrocycles coordinate best with small metal ions. The crystal structure of the complex [Cu(9-aneN_2S)Br_2] is reported: monoclinic, space group $P2_1/n$, with cell dimensions a = 7.603(1), b = 13.167(2), and c = 10.873(2) Å, and β = 91.94(1)°, Z = 4. Final conventional R = 0.061. The unusual [234] conformation was found for the 9-aneN_2S ring in [Cu(9-aneN_2S)Br_2], instead of the usual [333] conformer found for other complexes of cyclononane macrocycles. Molecular mechanics calculations indicated that the strain energy for complexes of cyclononane macrocycles was always less for the [333] conformer than for the [234] conformer, in agreement with the rarity of the [234] conformer. However, the difference in strain energy between the [333] and [234] conformers was small for complexes of 9-aneN_2S, but large for 9-aneN_3 and 9-aneS_3 complexes, in agreement with the occurrence of the [234] conformer only in the 9-aneN_2S complexes.

Introduction

Cyclic nine-membered ring tridentate ligands such as 9-aneN_3 (see Fig. 1 for structure of ligands discussed here) have attracted growing interest since their coordinating properties were first reported in detail [1]. An interesting feature of these coordinating properties has been the high ligand field (LF) strength found in bis-9-aneN_3 complexes [1], which has been interpreted [2] in terms of the greater covalence of the secondary nitrogens found in these cyclic ligands as compared with the primary nitrogens found in the open chain analogues. This greater covalence leads to such interesting properties as low-spin Fe(II) and Fe(III) bis-9-aneN_3 complexes [3], in contrast to the high-spin complexes found for the open chain analogues such as dien. The structures of the low-spin 9-aneN_3 complexes of Fe(II) and Fe(III) have recently [4] been reported. Substitution of one or more of the nitrogens in the 9-aneN_3 ring with other donor atoms such as oxygen [5] or sulphur leads to interesting coordinating properties. The coordinating properties of 9-aneN_2S plus the structures of some of its complexes have been reported [6, 7], as well as those of 9-aneS_3 [8, 9]. Of particular interest is the fact that the

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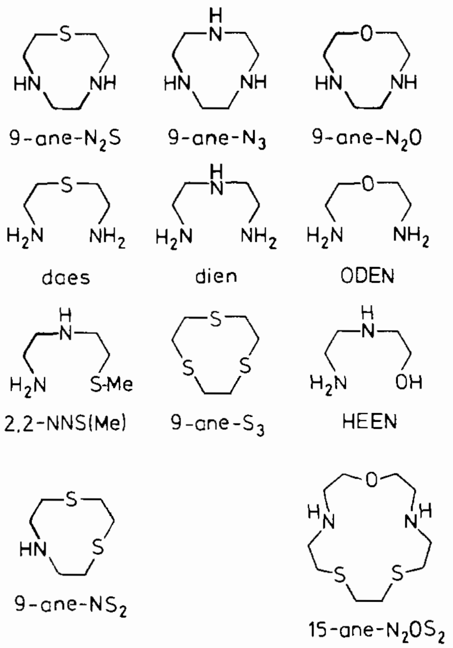

Fig. 1. Ligands discussed in this paper.

electronic spectra of the Ni(II) complexes indicate [9] that 9-aneS$_3$ exerts a stronger ligand field than does 9-aneN$_3$. In line with this it is found [9] that the Fe(II) complex $[Fe(9\text{-aneS}_3)_2]^{2+}$ is fully spin paired, whereas $[Fe(9\text{-aneN}_3)_2]^{2+}$ shows temperature dependent magnetic susceptibility corresponding to a low-spin to high-spin transition, and 10 *Dq*, the LF splitting parameter, is considerably higher in the 9-aneS$_3$ than in the 9-aneN$_3$ complex of Fe(II). What is puzzling in the light of this is that the complexes of the mixed donor ligand 9-aneN$_2$S show LF splitting which is considerably lower than that of either 9-aneS$_3$ or 9-aneN$_3$.

A further interesting property of these 9-aneX$_3$ (X = N, O, or S) ligands is their metal ion size selectivity. It has been shown recently [10] using molecular mechanics (MM) calculations that larger macrocyclic ligands such as the tetraaza-macrocycles are highly flexible, and that metal ions which are too large to be accommodated in the plane of the donor atoms of the macrocycle can be easily coordinated in conformers where the metal ion lies out of the plane of the donor atoms. In contrast, the 9-aneX$_3$ type of macrocycle is far more rigid, and cannot change to a variety of conformers so as to accommodate the particular needs of the metal ion as far as size and the L–M–L (L = ligand donor atom) angle are concerned, as is possible [10] with the tetraaza-macrocycles. This relatively greater rigidity of the 9-aneX$_3$ type of macrocycle thus means that, in contrast to the tetraaza-macrocycles [11], metal ion selectivity based on the match between the size of the cavity in the ligand, and the size of the metal ion, might actually be observed.

In order to investigate these two aspects of 9-aneX$_3$ chemistry, namely the variation in LF strength as N donors are replaced by S donors in complexes of 9-aneX$_3$, and the possibility of selectivity for metal ions based on the match between the cavity in the macrocycle and the size of the metal ion, we report here the formation constants of several metal ions with 9-aneN$_2$S, the crystal structure of [Cu(9aneN$_2$S)Br$_2$], and a MM force field for mixed N and S donor complexes of Ni(II), plus a molecular mechanics analysis of the problem of the metal ion size selectivity of 9-aneX$_3$ type ligands.

Experimental

Materials

The ligand 9-aneN$_2$S was synthesized as described previously [7]. To prepare [Cu(9-aneN$_2$S)Br$_2$], the ligand hydrobromide salt 9-aneN$_2$S·2HBr was neutralized with ethanolic sodium ethoxide, and added to an ethanolic solution of copper bromide. After standing for 6 h at 0 °C green crystals separated from the solution, and diffraction quality crystals were obtained after filtration and washing with ether. *Anal.* Calc. for $C_6H_{14}N_2SBr_2Cu$: C, 19.50; H, 3.82; N, 7.58. Found: C, 19.62; H, 3.87; N, 7.63%.

Metal solutions used in the potentiometric studies were prepared from the AR nitrate salts, and standardized by usual titration procedures.

Crystallographic Analysis

Oscillation and Weissenberg photographs were obtained using Cu Kα radiation. From these the apparent space group and approximate cell constants were determined. The cell constants were refined on an Enraf-Nonius CAD4 Four Circle Diffractometer by a least-squares fit on 25 ($16° \leqslant \theta \leqslant 18°$) reflections. The intensity data were collected in an ω–2θ scan mode with incident beam graphite monochromated Mo Kα radiation at room temperature. Three reference peaks were measured at regular intervals. Analysis of these showed no significant change in intensity with time. Empirical absorption corrections were applied to the data using the method of North *et al.* [12]. A Patterson map was used to place the heavy atoms, and the rest of the non-hydrogen atoms were found in the successive difference Fourier syntheses. The hydrogen atoms were placed in calculated positions, and refinement converged to an *R* value of 0.061. The crystal data for [Cu(9-aneN$_2$S)Br$_2$] are given in Table I, the fractional atomic coordinates in Table II, and the important bond lengths and angles in Table III. See also 'Supplementary Material'.

Potentiometric Titrations

These were carried out in a cell thermostatted to 25 °C in 0.1 M NaNO$_3$. Potentials were measured

TABLE I. Crystal Data for the Complex [Cu(9-aneN$_2$S)Br$_2$]

Formula	$C_6H_{14}N_2SBr_2Cu$
M_r	369.61
Crystal system	monoclinic
Space group	$P2_1/n$
Cell dimensions	
a (Å)	7.603(1)
b (Å)	13.167(2)
c (Å)	10.873(2)
β (°)	91.94(1)
V (Å^3)	1087.88
Z	4
D_{obs} (g cm^{-3})	2.22(2)
D_{calc} (g cm^{-3})	2.25
Radiation (Å)	λ(Mo Kα) 0.7107
Data collection	$\omega-2\theta$ scan
Theta range	$3° \leq \theta \leq 25°$
Scan speed (° min^{-1})	1.0 to 5.5
Scan angle (°)	$0.6 + 0.35 \tan\theta$
Octants	$-9 \leq h \leq 9, 0 \leq k \leq 15, 0 \leq l \leq 12$
No. reflections collected	1736
No. reflections used	1394
Absorption coefficient (μ_λ) (cm^{-1})	92.88
F(000)	716
Crystal size (μm)	220 × 200 × 180
Transmission	
maximum	79.33
minimum	99.88
average	91.12
Final R	0.061
Residual electron density (e Å^{-3})	1.3

TABLE II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors in [Cu(9-ane-N$_2$S)Br$_2$][a]

Atom	x	y	z	U_{eq}
Cu	0.6250	0.4931(1)	0.1650	0.0291(3)
Br(1)	0.3786(2)	0.6105(1)	0.1879(2)	0.0610(4)
Br(2)	0.8049(2)	0.6122(1)	0.0586(1)	0.0469(4)
S	0.7437(4)	0.4814(3)	0.3884(3)	0.038(1)
N(1)	0.467(1)	0.3749(9)	0.207(1)	0.038(3)
N(2)	0.805(1)	0.3832(9)	0.138(1)	0.034(2)
C(1)	0.589(2)	0.380(1)	0.420(1)	0.046(3)
C(2)	0.430(2)	0.373(1)	0.340(1)	0.044(3)
C(3)	0.540(2)	0.281(1)	0.155(1)	0.046(3)
C(4)	0.733(3)	0.282(1)	0.153(2)	0.089(6)
C(5)	0.963(2)	0.397(2)	0.213(1)	0.070(5)
C(6)	0.936(2)	0.411(2)	0.348(1)	0.059(4)
H1N1[b]	0.363	0.360	0.151	
H1N2	0.863	0.349	0.067	
H1C1	0.547	0.390	0.513	
H2C1	0.659	0.309	0.413	
H1C2	0.363	0.303	0.360	
H2C2	0.346	0.437	0.359	
H1C3	0.498	0.217	0.210	
H2C3	0.488	0.272	0.062	
H1C4	0.774	0.235	0.078	
H2C4	0.784	0.251	0.239	
H1C5	1.045	0.331	0.201	
H2C5	1.029	0.464	0.181	
H1C6	0.926	0.336	0.388	
H2C6	1.050	0.449	0.387	

[a] Non-hydrogen atoms were refined anisotropically (see 'Supplementary Material'). [b] Hydrogen atoms were refined with a common isotropic temperature factor of 0.096(17).

using a Radiometer G202B glass electrode with silver/silver nitrate reference electrode separated from the titration by a NaNO$_3$ salt bridge, and a Radiometer PHM 84 pH meter. For each of the metal ions studied, three separate titrations with differing metal to ligand ratios were carried out. Equilibration for all of the metal ions studied was rapid, except for Ni(II). For the latter metal ion, an 'out-of-cell' technique was employed [13], which involved making up solutions with the same amount of ligand and Ni(II) concentrations, but differing acid concentrations. These solutions were kept thermostatted at 25 °C in tightly stoppered flasks for one week, and thereafter the pH values were recorded. The formation constants were calculated from the potentiometric data using the program EQUILIBRIA [14]. The protonation constants of 9-aneN$_2$S, plus its formation constants with a variety of metal ions, as well as those of a variety of other 9-aneX$_3$ ligands, plus open-chain analogues of these ligands, are given in Tables IV and V.

Molecular Mechanics Calculations

These were carried out as described previously [15], except that the interactions involving the Ni(II) and sulphur had to be parametrized. In the end a force field involving slightly different parametrization for Ni(II) and nitrogen as compared with the parameters used previously on complexes involving nitrogen donors only [15], was found to give the best results. The program MOLBD3 of Boyd [16] was used for all the MM calculations. Constants for the Ni(II) compounds with mixed nitrogen/sulphur donors were refined by fitting the calculated structures to those observed for the bis Ni(II) complexes of daes [17], 9-aneN$_2$S [6], 9-aneS$_3$ [8], and [Ni(15-aneN$_2$OS$_2$)·H$_2$O]$^{2+}$ [18]. The refined set of force field parameters is given in Table VI.

Results and Discussion

The formation constants determined here for the complexes of 9-aneN$_2$S are given in Table V. It is seen that in general the size of the macrocyclic effect as measured by $\log K$(mac) tends to be smaller in 9-aneN$_2$S complexes than in 9-aneN$_3$ complexes, but larger than in 9-aneN$_2$O complexes. ($\log K$(mac) is simply $\log K_1$ for the macrocyclic complex minus $\log K_1$ for the open-chain complex.) The small

TABLE III. Important Bond Lengths and Angles in the Complex [Cu(9-aneN_2S)Br_2][a]

Bond lengths (Å)			
Cu–S	2.567(3)	N(1)–C(2)	1.48(2)
Cu–N(1)	2.03(1)	N(1)–C(3)	1.48(2)
Cu–N(2)	2.02(1)	N(2)–C(4)	1.45(2)
Cu–Br(1)	2.449(2)	N(2)–C(5)	1.44(2)
Cu–Br(2)	2.403(2)	C(1)–C(2)	1.47(2)
S–C(1)	1.82(2)	C(3)–C(4)	1.47(2)
S–C(6)	1.80(2)	C(5)–C(6)	1.49(2)
Bond angles (°)			
N(1)–Cu–S	86.2(3)	C(2)–N(1)–Cu	111.3(8)
N(2)–Cu–S	82.9(3)	C(3)–N(1)–Cu	109.1(8)
N(1)–M–N(2)	83.8(4)	C(4)–N(1)–Cu	112(1)
Br(1)–Cu–Br(2)	94.9(1)	C(5)–N(2)–Cu	113(1)
Br(1)–Cu–S	100.8(1)	C(2)–N(1)–C(3)	116(1)
Br(2)–Cu–S	107.9(1)	C(4)–N(2)–C(5)	111(2)
Br(1)–Cu–N(1)	90.1(3)	C(2)–C(1)–S	117(1)
Br(2)–Cu–N(1)	163.8(3)	C(5)–C(6)–S	116(1)
Br(1)–Cu–N(2)	172.6(3)	C(1)–C(2)–N(1)	114(1)
Br(2)–Cu–N(2)	89.9(3)	C(4)–C(3)–N(1)	113(1)
Cu–S–C(1)	90.7(4)	C(3)–C(4)–N(2)	113(1)
Cu–S–C(6)	93.5(5)	C(6)–C(5)–N(2)	116(1)
C(1)–S–C(6)	101.6(8)		

[a] For key to atom numbering scheme, see Fig. 4.

TABLE IV. Protonation Constants for some 9-aneX_3 type Macrocycles (X = N, S or O) and Protonation Constants for some Open Chain Analogues of these Ligands

Ligand[a]	pK_1[b]	pK_2	pK_3	Reference
9-aneN_3	10.44	6.81		1
dien	9.84	9.02	4.23	21
9-aneN_2S	9.67	3.98		6
daes	9.68	8.82		21
9-aneN_2O	9.60	5.35		5
ODEN	9.75	8.90		21
HEEN	9.59	6.60		21
2,2-NNS(Me)	9.60	6.63		26

[a] For key to abbreviations for ligands see Fig. 1. [b] The protonation constant equilibria refer to pK_1, $L + H^+ = LH^+$; pK_2, $LH^+ + H^+ = LH_2^{2+}$; pK_3, $LH_2^{2+} + H^+ = LH_3^{3+}$.

value of log K(mac) for Cu(II) with 9-aneN_3 must reflect the extremely unfavourable effects produced by forcing a nitrogen of the 9-aneN_3 ligand to occupy an axial coordination site on Cu(II), which does not happen on the Cu(II) complex with dien. The effect of forcing the O or S (as evidenced by the structure of [Cu(9-aneN_2S)Br_2] below) to occupy the axial position appears to be much less serious for the value of log K(mac) for the Cu(II) complexes of 9-aneN_2S or 9-aneN_2O, reflecting the much weaker coordinating strength of S or O than N with Cu(II). What is particularly interesting in Table V is that for 9-aneN_2S and 9-aneN_2O complexes, there is a tendency for log K(mac) to become smaller as the size of the metal ion increases. This is seen in Fig. 2, where we have plotted log K(mac) as a function of the ionic radius [19] of the metal ions. It is seen that there is a good correlation between log K(mac) and ionic radius, such that the larger the metal ion becomes, the smaller is log K(mac). This is in line with MM calculations, which show that for complexes of 9-aneN_3 at least, the best fit in coordinating to the macrocycle is obtained with small metal ions

TABLE V. Formation Constants of 9-aneX_3 Type Macrocycles (X = N, O, or S) and their Open Chain Analogues, showing the Size of the Macrocyclic Effect in Each Case (log K(mac)), for a Variety of Metal Ions

Ligand	Cu(II)		Ni(II)		Zn(II)		Cd(II)		Pb(II)	Co(II)	Fe(II)	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_1	log K_1	log K_2
9-aneN_3[a]	15.5		16.2	14.2[b]	11.6		9.4		11.0			
dien[a]	15.9	5.0	10.5	8.1	8.8	5.5	8.3	5.8	7.5			
log K(mac)[c]	−0.4		5.7	6.1	2.8		1.1		3.44			
9-aneN_2S[d]	12.42[e]	9.87[e]	10.82(6)	9.95(6)	7.31(3)	5.84(5)	6.65(2)	5.81(3)	6.76(2)	7.85(4)	5.9(2)	6.1(2)
daes[a]	9.02	5.24	7.38	6.14	5.31	3.57	5.47	3.52	(6.0)[d]	5.09		
log K(mac)	3.40	4.63	3.44	3.81	2.00	2.27	1.18	2.29	0.8	2.76		
9-aneN_2O[e]	10.86	8.68	8.49	7.2	6.36	5.07	4.48	3.40	5.17			
ODEN[a]	8.70	4.4	5.62	3.39	5.74	4.12	5.27[e]	4.06[e]	6.10[e]			
log K(mac)	2.16	4.28	2.87	3.81	0.62	0.95	−0.79	−0.66	−0.93			

[a] Ref. 21. [b] Ref. 36. [c] The value of log K(mac) is simply log K_1 for the macrocycle, e.g. 9-aneN_3, minus log K_1 for the open chain analogue, e.g. dien. [d] This work, 25 °C in 0.1 M $NaNO_3$; the value of log K_1 for Pb(II) with daes is only approximate, as the titrations were bedevilled by the formation of lead hydroxide precipitates almost from the onset of complex-formation. [e] Ref. 5.

TABLE VI. Parameters Used in the Molecular Mechanics Calculations Discussed in this Paper (where parameters are not indicated, they are the same as used in refs. 15 and 27.)

Bond type	K_r (mdyn A)	$r°$ (Å)	Reference
Bond length deformation constants[a]			
C–O	5.36	1.50	28
C–S	2.64	1.82	29
N–LP[b]	6.16	1.00	30
O–H	6.00	0.99	30
O–LP	6.00	1.00	30
S–LP	6.00	1.00	30
Ni–N	0.85	2.10	31, this work
Ni–O	0.85	2.10	this work
Ni–S	1.00	2.45	this work
Cu–N	0.85	2.03	this work, 10
Cu–S (axial)	1.00	2.78	this work

Angle type	K_θ (mdyn A rad^{-1})	$\theta°$ (radians)	Reference
Bond angle deformation constants[c]			
H–C–S	0.30	1.911	32
C–C–S	0.42	1.911	32
H–C–O	0.43	1.911	28
C–C–O	0.56	1.911	28
H–N–LP	0.53	1.911	33
C–N–LP	0.56	1.911	33
H–O–H	0.53	1.911	33
H–O–LP	0.53	1.911	33
LP–O–LP	0.53	1.911	33
C–O–C	0.62	1.911	28
C–O–LP	0.35	1.911	28
C–S–C	0.85	1.745	this work
C–S–LP	0.30	2.056	this work
Ni–O–C[d]	0.20	1.911	this work
Ni–O–H[d]	0.10	1.911	this work
Ni–O–LP[d]	0.10	1.911	this work
Ni–S–LP[d]	0.10	1.911	this work
Ni–S–C[d]	0.20	1.911	this work
N–Ni–N[d]	0.20	1.571/3.142	this work
N–Ni–S[d]	0.25	1.571/3.142	this work
S–Ni–S[d]	0.25	1.571/3.142	this work
O–Ni–O[d]	0.20	1.571/3.142	this work
O–Ni–N[d]	0.20	1.571/3.142	this work
O–Ni–S[d]	0.25	1.571/3.142	this work

Atoms	*a*	*b*	*c*	Reference
Non-bonded potentials[e]				
C---S	2180	4.05	5.380	30
C---Ni[d]	689	3.64	1.990	30
H---Ni[d]	114	3.52	0.807	30
N---S	2320	4.16	4.410	30
N---Ni[d]	724	3.73	1.630	30
S---Ni[d]	854	3.41	5.170	30
O---O[f]	1754	4.59	1.510	30
O---C[f]	1691	4.45	1.770	30
O---H[f]	272	4.33	0.720	30
O---N[f]	1791	4.57	1.450	30

(continued)

TABLE VI. *(continued)*

Atoms	*a*	*b*	*c*	Reference
Non-bonded potentials[e]				
O---S[f]	2317	4.18	4.600	30
O---M[f]	736	3.75	1.700	30

[a] The constants are for use in the equation $U_B = \frac{1}{2}K_r(r - r^\circ)^2$, as discussed in refs. 27 to 33. [b] LP is abbreviation for lone pair of electrons on N, O, or S. [c] The constants are for use in the equation $U_\theta = \frac{1}{2}K_\theta(\theta - \theta^\circ)^2$, as discussed in refs. 27 to 33. [d] For all these constants the metal can also be Cu(II) instead of Ni(II). [e] These constants are for calculating the non-bonded interaction potential, U_{NB}, from the expression $U_{NB} = a\ \exp(-br) - cr^{-6}$, as discussed in refs. 27 to 34. [f] These parameters are the same as reported in refs. 30, except that *a* has been calculated using a van der Waals radius of 1.65 Å, referring to sp^3 hybridized oxygen, rather than the 1.60 Å (30) which refers to sp^2 hybridized oxygen.

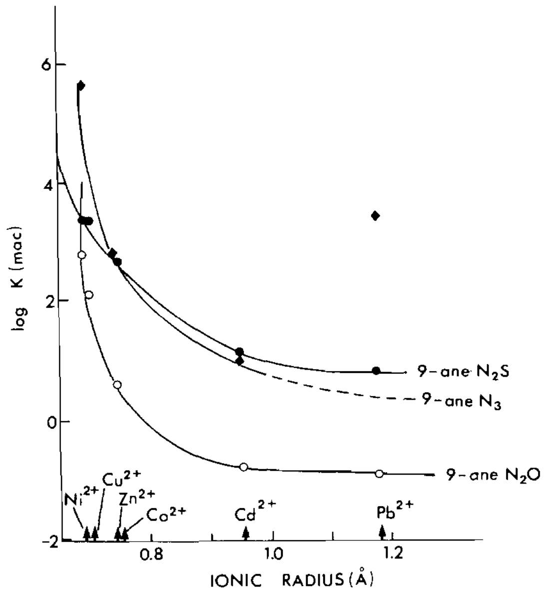

Fig. 2. The relationship between the size of the macrocyclic effect, log *K*(mac), in complexes of 9-aneX_3 macrocycles, and the ionic radius [19] of the metal ions. The value of log *K*(mac) is taken from Table V, and is simply the difference in the formation constant, log K_1, for the formation of the macrocyclic complex and its open chain analogue. It is seen that log *K*(mac) increases strongly towards smaller ionic radii, in agreement with molecular mechanics calculations which show that small metal ions fit best into 9-aneX_3 type macrocycles. The points are for the complexes of 9-aneN_2O (○), 9-aneN_2S (●), and 9-aneN_3 (◆). The anomalous position for the Pb^{2+} point with 9-aneN_3 is discussed in the text.

[11] of the size of high-spin Ni(II). Figure 2 shows a very sharp increase in log *K*(mac) for 9-aneN_3 and 9-aneN_2O towards metal ions of the size of Ni(II), but for 9-aneN_2S the increase is less sharp, and the plot suggests that a peak might be found at metal ions of a size somewhat smaller than Ni(II), *i.e.* the presence of S donors might lead to a preference for smaller metal ions than when N or O are present. This question is dealt with in considering the results of MM calculations below. The flattening out of the log *K*(mac) *versus* ionic radius curve at larger ionic radii presumably reflects more ionic metal to ligand bonding as metal ion size increases. The value of log *K*(mac) for the Pb(II) complex of 9-aneN_3 appears anomalous in relation to the curves of log *K*(mac) *versus* ionic radius obtained for 9-aneN_2O and 9-aneN_2S. At first we suspected that the reported value of log K_1 for Pb(II) with 9-aneN_3 was incorrect. We have, however obtained a result in tolerably close agreement (log K_1 = 10.6*) with the reported value. The answer to the apparently anomalous behaviour of the value of log *K*(mac) for Pb(II) in Fig. 2 is possibly to be found in the structure recently reported [20] for the mono complex of 9-aneN_3 with Pb(II). Unlike other reported structures of Pb(II) with nitrogen donor ligands in the literature, the Pb(II) is only six-coordinate, with the coordination sphere comprising the three nitrogens of the 9-aneN_3 plus three oxygens from the anions (nitrate in one complex and perchlorate in another [20]) present. Of particular importance is that, accompanying this unusually low coordination number, there appears to be a sterically active lone pair on the Pb(II) [20]. The flat O–Pb–O angles indicate [20] that the lone pair is situated between the three oxygen atoms on the opposite side of the Pb to the 9-aneN_3 ligand. At the same time, the Pb–N bonds appear to be unusually short, being some 0.3 Å shorter than found in other Pb(II) amine complexes. We would tentatively suggest that the anomalously high stability of the 9-aneN_3 complex of Pb(II), in comparison to its complexes with 9-aneN_2S and 9-aneN_2O, is associated with the collecting together of the electron density associated with the 'inert pair' of Pb(II) from being spread evenly around the metal ion into a sterically active lone pair. This change in electron distribution

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*R. D. Hancock and M. P. Ngwenya, to be published.

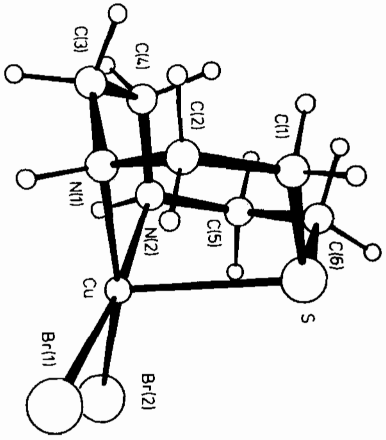

Fig. 3. The complex [$Cu(9\text{-}aneN_2S)Br_2$] showing the atom numbering scheme used.

then accounts for the unusually short Pb–N bond lengths in the 9-aneN_3 complexes and the high complex stability. This would imply that the 9-ane-N_2S and 9-aneN_2O complexes of Pb(II) should not have a sterically active lone pair, and would have normal Pb–N bond lengths in the vicinity of 2.7 Å. We are currently attempting to grow crystals of the mono-complexes of these two ligands with Pb(II) to test this hypothesis.

The structure of [$Cu(9\text{-}aneN_2S)Br_2$]

In Fig. 3 is seen the structure of the complex [$Cu(9aneN_2S)Br_2$], plus the numbering scheme for this complex. The structure is similar to that reported for [$Cu(9\text{-}aneN_3)Br_2$] [22], in that the coordination geometry around the copper is square pyramidal, with two nitrogens and two bromines lying in the plane. In the 9-aneN_3 complex the third nitrogen from the macrocycle occupies the axial coordination site, while in [$Cu(9\text{-}aneN_2S)Br_2$] the sulphur occupies the axial position. In the 9-aneN_2S complex, the copper lies some 0.19 Å above the plane formed by the two nitrogen donors and the two bromines, while in its 9-aneN_3 analogue the copper lies 0.22 Å out of the plane [22]. The Cu–N bond lengths to the in-plane nitrogens in the 9-aneN_3 complex (2.05 Å) are also very similar to those found here for the 9-aneN_2S complex, namely 2.03(1) and 2.04(1) Å, and also the bis-9-aneN_2S complex of Cu(II) [7]. Unlike the 9-aneN_3 complex, where the macrocyclic ring has the [333] conformation, the macrocyclic ring, like that for the bis-9-aneN_2S complex of Cu(II) [7], has the [234] conformation*. Apart from this, the Cu–S bond length in [$Cu(9\text{-}aneN_2S)Br_2$] at

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*For a definition of the [234] and [333] conformations, see Fig. 5.

TABLE VII. The Accuracy of Prediction of Geometry Using the Parameters in Table VI for Molecular Mechanics. A Comparison of Selected Bond Lengths and Angles for A = [$Ni(9\text{-}ane\text{-}N_2S)_2$]$^{2+}$, B = [$Ni(daes)_2$]$(ClO_4)_2$, C = [$Ni(daes)_2$]$_2(NO_3)(BPh_4)_3$, D = [$Ni(9\text{-}ane\text{-}S_3)_2$]$^{2+}$, E = [$Ni(15\text{-}ane\text{-}N_2OS_2)H_2O$]$^{2+}$, F = [$Cu(9\text{-}ane\text{-}N_2S)_2$]$^{2+}$ and G = [$Cu(daes)_2$]$^{2+}$

	A		B	C		D		E			F		G	
	exp.[a]	calc.	exp.[b]	exp.[b]	calc.	exp.[c]	calc.	exp.[d]	calc.		exp.[e]	calc.	exp.[e]	calc.
Ni–S	2.42	2.43	2.46	2.45	2.42	2.39	2.42	2.42	2.45	Cu–S	2.71	2.72	2.76	2.73
Ni–N	2.12	2.12	2.10	2.11	2.11			2.06	2.08	Cu–N	2.03	2.03	2.06	2.06
S–Ni–S	180	180	97.3	98.6	95.8	88.5	87.4	86.9	85.9		2.07	2.07		
S–Ni–N	85.1	84.7	84.2	83.5	84.5			85.2	84.0	S–Cu–N	84.2	85.2	82.4	82.4
N–Ni–N	80.5	80.7	93.1	94.9	94.4			164	167		79.8	79.3	80.4	81.4
Ni–S–C	93.1	92.7	94.6	95.5	95.0	99.5	98.8	96.1	96.4	N–Cu–N	84.1	83.9	91.4	91.4
	97.6	97.3	97.0	97.1	97.9	103.8	103.2	103.8	103.2	Cu–S–C	90.9	89.5	89.5	89.6
C–S–C	104.2	105.9	102.4	102.4	103.0	103.3	104.3	103.8	104.3		93.2	92.9	92.2	92.5
S–Ni–N[f]			172	174	177			172	177	C–S–C	103.2	103.7	100.8	102.2
S–Ni–N[f]			172	172	169			167	168					
N–Ni–N[f]			178	174	176			164	167					

[a]Ref. 6. [b]Refs. 17 and 37. [c]Ref. 8. [d]Ref. 18. [e]Ref. 7. [f]These refer to the bond angles involving the *trans* donor atoms in N–Ni–N, N–Ni–S, etc.

2.57 Å is considerably shorter than that in the bis-9-aneN_2S complex, which is 2.71 Å [7]. This possibly reflects the five-coordination around copper in [Cu(9-aneN_2S)Br_2], where the coordination site opposite the sulphur is empty, whereas in the six-coordinate $[Cu(9\text{-ane}N_2S)_2]^{2+}$ the coordination sites have the two sulphur donors opposite to each other. What is of interest here is the unique [234] ring conformation found in these complexes, whereas all other 9-aneX_3 complexes so far studied have the [333] conformation. The question is raised as to whether this is a response to the rather long ligand to metal bonds found on the axial coordination sites of the Jahn–Teller distorted Cu(II). We attempt to answer this question with the aid of molecular mechanics calculations below.

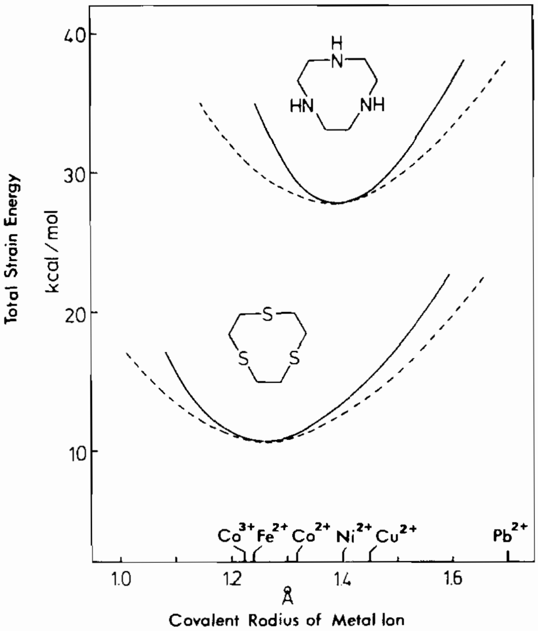

Fig. 4. The strain energy of the bis- complex of 9-aneN_3 and 9-aneS_3 calculated as a function of the strain-free (- - - -) length of the M–N bond (r°) or final energy minimised M–N bond length (——) of $[M(9\text{-ane}S_3)_2]^{n+}$ and $[M(9\text{-ane}N_3)_2]^{n+}$ complexes, as a function of the covalent radii of the metal ion, M. The minima in the curves are the best-fit size for a metal ion to coordinate to the ligand. It is seen that the best-fit size for the 9-aneS_3 complexes is for smaller metal ions than is the case for 9-aneN_3. This possibly accounts for the greater ability of the 9-aneS_3 to cause spin-pairing in the small low-spin ions of Co(II) and Fe(II), whose covalent radii are indicated on the x-axis.

Molecular Mechanics Calculations

As seen in Table VII, the MM calculations reproduce the important structural features of the complex of high-spin complexes of Ni(II) with mixed donor ligands containing nitrogen and sulphur donors, with the parameters shown in Table VI. We may now attempt to use this force field to analyse some of the problems mentioned in the introduction. The first problem of interest is the question of the metal ion size selectivity of 9-aneN_3 relative to 9-aneS_3 type ligands. A very useful technique [10] for analyzing the best-fit size for metal ions into macrocycles is to keep all the parameters in the force field constant except for the ideal, or strain-free, metal to ligand bond length. The value of the ideal metal to ligand bond length is varied systematically, and the total strain energy of the complex obtained as a function of the ideal metal to ligand bond length. Calculations for the bis-9-aneN_3 and bis-9-aneS_3 complexes are seen in Fig. 3, where all the parameters for the force field are kept at the values for high-spin Ni(II) compounds, except for the M–L bond length, which has been systematically varied. In order to facilitate comparisons between the 9-aneN_3 and the 9-aneS_3 complex, the strain energy has in Fig. 3 been plotted as a function of the metal covalent radius, rather than M–L bond length. This is to allow for the fact that the covalent radius of sulphur at 1.04 Å is much larger than that for nitrogen at 0.70 Å [23]. Thus, to obtain the metal covalent radii, 1.04 Å has been subtracted from the M–S bond lengths, and 0.70 Å has been subtracted from the M–N bond lengths in Fig. 4. What is of particular interest is that in Fig. 4 the minimum in the curve of strain energy *versus* metal ion covalent radius comes at a much smaller metal covalent radius for the bis-9aneS_3 than for the bis-9-aneN_3 complexes. This is quite easily understood by examining the causes of the increasing strain as the metal ion becomes smaller in these bis-9-aneX_3 ligands. As discussed previously [10], the rise in steric strain as the metal ion becomes too small is caused by steric repulsions between the hydrogen atoms on the two 9-aneX_3 ligands. The much larger covalent radius of sulphur than of nitrogen means that for any given metal covalent radius, the 9-aneS_3 ligands are much further apart than are the 9-aneN_3 ligands, and the van der Waals repulsions between the two ligands are accordingly less for the 9-aneS_3 than the 9-aneN_3 complexes. The calculations thus show that the bis-9-aneS_3 ligand system is capable of accommodating a much smaller metal ion than is the case for the bis-9-aneN_3 system. This has some important implications. In the first instance, the Fe(II) ion is what might be termed [2] 'supersmall'. This means that the covalent radius of the metal ion is such that in virtually all its complexes inter- and intraligand van der Waals repulsions prevent the donor atoms from approaching their equilibrium, or strain free, bond length with the metal ion. Only in unusual circumstances, such as the bis-9-aneS_3 system, can the ligand pack efficiently enough around the metal so as to allow for relatively strain-free coordination. We would thus suggest that in the absence of steric

TABLE VIII. Calculated Strain Energies for bis-9-aneX$_3$ Complexes of Ni(II) (X = N and/or S), Showing the Effect of Composition of the Donor Set, and of Conformation of the Macrocyclic Ring, on Strain Energy

Complex	Strain energy (kcal mol^{-1})		Δ [234]/[333][b]	Deviation from interpolated value[c]
	[234]	[333]		
[Ni(9-aneN$_3$)$_2$]$^{2+}$	35.7	28.1	7.6	(0.0)
[Ni(9-aneN$_2$S)$_2$]$^{2+}$	28.6	25.1	3.5	+2.1
[Ni(9-aneNS$_2$)$_2$]$^{2+}$	27.8	19.2	8.6	+1.3
[Ni(9-aneS$_3$)$_2$]$^{2+}$	21.4	12.8	8.6	(0.0)

[a]For explanation of the nature of the [234] and [333] conformers of cyclononane type rings, see Fig. 5. [b]This is the difference in strain energy between the [234] and the [333] conformers, and shows that in all cases the [333] conformer is more stable than the [234], although this difference is much smaller for the 9-aneN$_2$S complex than for the other 9-aneX$_3$ macrocycles. [c]This is calculated by calculating an interpolated value for the 9-aneN$_2$S and 9-aneNS$_2$ from the strain energies of the 9-aneN$_3$ and 9-aneS$_3$ complexes, assuming that the strain energy would be a linear function of the number of N or S donor atoms. The value shown is the amount by which the observed value of the strain energy is larger than the value estimated by interpolation. The calculations refer to the [33] conformer of the macrocyclic ring only.

effects, sulphur donor ligands would always show a greater ligand field strength than comparable nitrogen donor ligands. Thus, the higher ligand field strength for the 9-aneS$_3$ complexes [9] as compared with the 9-aneN$_3$ complexes is really the 'normal' situation. In virtually all cases where the sulphur donor has shown itself to occupy a low position in the spectrochemical series, this has been ascertained from the spectra of mixed donor ligands [24]. We now consider the question of why the complexes of 9-aneN$_2$S exhibit much lower LF strengths than their 9-aneS$_3$ and 9-aneN$_3$ analogues.

In Table VIII is shown the total strain energies calculated for the Ni(II) complexes of the type [Ni(9-aneX$_3$)$_2$]$^{2+}$, where 9-aneX$_3$ is 9-aneN$_3$, 9-aneN$_2$S, 9-aneNS$_2$, and 9-aneS$_3$. The decrease in strain energy which occurs as nitrogen donors are replaced by sulphur donors along this series is due to the longer Ni–S bonds which lessen steric repulsion between the two 9-aneX$_3$ ligands coordinated to the Ni(II). What is of interest, however, is that the decrease in steric strain which occurs as the nitrogen donors are replaced by sulphur donors is not uniform, and as shown in the Table, the strain energy of the mixed donor ligand complexes of 9-aneN$_2$S and 9-aneNS$_2$ is higher than would be expected from interpolating between the strain energies of the 9-aneN$_3$ and 9-aneS$_3$ complexes. Examination of the MM calculations shows that this extra strain energy for the mixed donor complexes is chiefly due to strain in the metal to ligand bonds. This arises because of the mismatch in M–L bond length of the Ni–N and Ni–S bonds. In other words, the mixed donor ligands 9-aneN$_2$S and 9-aneNS$_2$ are rather like three-legged stools which do not stand well because two of the legs are very different in length from the remaining leg. One would thus account for the lower 10 *Dq* value in the complex [Ni(9-aneN$_2$S)$_2$]$^{2+}$ than in either [Ni(9-aneS$_3$)$_2$]$^{2+}$ or [Ni(9-aneN$_3$)$_2$]$^{2+}$ in terms of the relatively higher steric strain in the M–L bonds of the complexes of the mixed donor ligand brought about by the difficulty of coordinating to the metal ion with two short Ni–N and one very much longer Ni–S bond.

The final question which we consider here is why the 9-aneN$_2$S ring has the [234] conformation in [Cu(9-aneN$_2$S)Br$_2$] and [Cu(9-aneN$_2$S)$_2$]$^{2+}$ [7] when in all other 9-aneX$_3$ complexes examined to date the macrocyclic ring has the [333] conformation. Our first thought here was that this was related to the long Cu–S bonds brought about by the fact that the sulphur donor in the 9-aneN$_2$S complexes of Cu(II) occupies the axial coordination site. In order to test this hypothesis, the strain energy of the regular Ni(II) complexes, given the [234] conformation was calculated (Table VIII), and it was found that for all the 9-aneX$_3$ complexes of Ni(II), the [333] conformer was lower in strain energy than the [234] conformer, agreeing with the rarity of the [234] conformer in reported structures of complexes of 9-aneX$_3$ ligands. What is of interest in Table VIII, however, is that the difference in strain energy between the [333] and [234] conformers is at a minimum for the 9-aneN$_2$S ligand, suggesting why the [234] conformer has been found only in the complexes of this ligand, and not for 9-aneN$_3$ or 9-aneS$_3$. One would predict on the basis of the calculations in Table VIII that should complexes of 9-aneNS$_2$ by synthesized, the macrocyclic rings would all have the [333] conformation. Table VIII shows that, although the difference in strain energy between the [234] and [333] conformers is at a minimum for 9-aneN$_2$S in the 9-aneX$_3$ macrocycles, the strain energy of the [333] form is still considerably lower than that of the [234] form, and one should therefore seek further contributing factors for the occurrence of this conformer in the Cu(II) complexes of 9-aneN$_2$S. Repeating the calculations

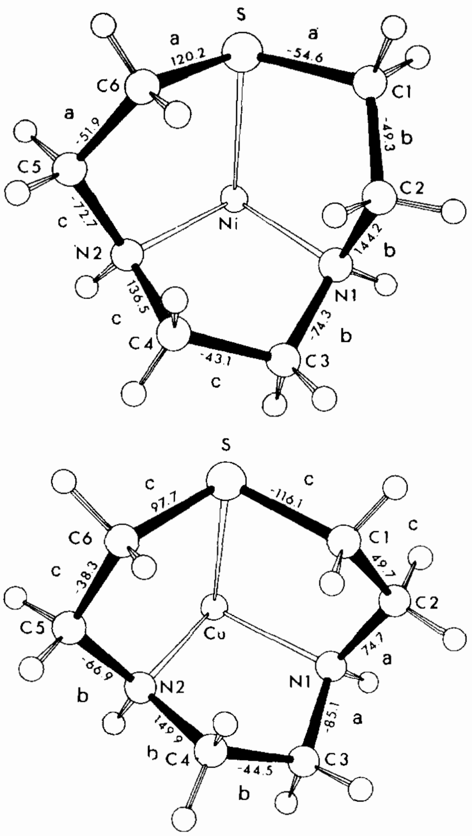

Fig. 5. The macrocycle 9-aneN_2S shown bound to Ni(II) and Cu(II) to illustrate the difference between the [333] and the [234] conformers. The numbers inside the square brackets indicate the lengths of the sides which are present in the macrocycle, *i.e.* in the [333] conformer the ligand is considered to be a triangle with three sides each comprised of three bonds, indicated as a, b, and c in the diagram. For the [234] conformer, the macrocycle is considered to have three sides of unequal length, *i.e.* there is a short side consisting of the two bonds marked 'a', a longer side consisting of the three bonds marked 'b', and the longest side consisting of the four bonds each marked 'c'. A corner is seen to be an angle, when the macrocycle is looked at in projection from above, which is sharp, and is defined [34] as occurring at a ring atom where the torsional angles on either side of the ring atom fall in the range −90° to +90°. The corners in the [333] and [234] conformers are indicated. Sterically, the important difference between the [333] and [234] conformers lies at the ring atom C_1, which lies more or less flat in the [333] conformer, but is twisted up out of the plane of the paper in the [234], with the result that the 'corner' occurs at C_1 in the [333] conformer, but at C_2 in the [234] conformer. For a more complete discussion of this nomenclature as applied to macrocyclic ligands, ref. 35 should be consulted.

of strain energy for the Cu(II) complex, with the now much longer M–S bond than in the case for Ni(II) (see Table VI) did not bring the strain energy of the [234] conformer of $[Cu(9\text{-ane}N_2S)_2]^{2+}$ down lower than for its [333] conformer, and in fact the difference in strain energy between the two conformers actually increases somewhat. The MM calculations on Ni(II) in Table VIII thus suggest that the [234] conformation is most stable in 9-aneN_2S complexes out of all the 9-aneX_3 complexes, but the strain energy calculations on the Cu(II) complexes suggest that the occurrence of the [234] conformer in $[Cu(9\text{-ane}N_2S)Br_2]$ and $[Cu(9\text{-ane}N_2S)_2]^{2+}$ is not related to the longer M–S bonds when M is Cu(II). We also considered the possibility that hydrogen bonding within the crystal determined whether the [234] or [333] conformer was observed, which effect was postulated by Cramer and Huneke [25] to account for the conformers of $[M(en)_3]^{n+}$ found with different counterions present in the crystal. However, the N--Br distances found here for adjacent complex molecules in crystals of $[Cu(9\text{-ane}N_2S)Br_2]$ at 3.5 Å are a little too long to be indicative of H--Br hydrogen bonding. Since there does not appear to be strong hydrogen bonding in the crystal of $[Cu(9\text{-ane}N_2S)Br_2]$, it does not seem that one can advance hydrogen bonding as a reason for the occurrence of the [234] conformer in the Cu(II) complexes with 9-aneN_2S (Fig. 5).

In conclusion, one can say from the results presented in this paper that

(a) Macrocycles of the 9-aneX_3 type are shown by molecular mechanics calculations to fit best, *i.e.* coordinate with the lowest strain energy, to metal of small size. In the case of 9-aneN_3 this is to metal ions of covalent radius 1.4 Å, and for 9-aneS_3 to metal ions of covalent radius 1.25 Å.

(b) The high ligand field strength found in 9-aneS_3 complexes is due to the fact that the ligand can coordinate in a very low-strain manner. For mixed donor ligands such as 9-aneN_2S the great differences in M–N and M–S bond lengths lead to a mismatch when coordinating to a metal ion, and the resulting steric strain lowers the ligand field strength. Since the position of sulphur donor ligands in the spectrochemical series has been determined exclusively from the spectra of mixed donor ligands, the implication of this is that the low position of thioether-type sulphur donors in the spectrochemical series [24] is misleading. Thus, in the absence of steric effects, the thioether group should occupy a higher position in the spectrochemical series than do secondary nitrogen donors.

(c) The fact that the ligand field strength, dependent on the factors described above, increases 9-aneN_2S < 9-aneN_3 < 9-aneS_3 in the complexes of these ligands, accounts for the spin-states observed in the complexes of these ligands with metal ions such as Fe(II) and Co(II).

(d) The fact that very small metal ions fit best into the 9-aneX_3 macrocycles accounts for the fact that the macrocyclic effect shows a dependency on metal ion size such that the macrocyclic effect is larger with small metal ions such as Ni(II), and smaller with metal ions such as Cd(II) and Pb(II), which are too large for the cavity in the 9-aneX_3 type of macrocycle. An exception to this type of behaviour is Pb(II) with 9-aneN_3. Here, the collecting together of the 'inert pair' of electrons to become a sterically active unshared pair of electrons appears to change the chemistry of the Pb(II) in that the metal ion becomes effectively much smaller with more covalent M–N bonding.

(e) Molecular mechanics calculations show that the [333] conformer of 9-aneX_3 type macrocycle is always of lower strain energy in its complexes with metal ions than is the case for the [234] type of conformer. However, for the 9-aneN_2S ligand in its complexes with metal ions, the difference in strain energy between the [234] and [333] conformer is very much less than is the case for the 9-aneN_3, 9-aneS_3, or 9-aneNS_2 complexes. This partly accounts for the occurrence of the [234] conformer in the complexes of Cu(II) with 9-aneN_2S, and nowhere else. It is at this stage not clear what other factors contribute to the stabilization of the [234] conformer in these complexes.

Supplementary Material

The calculated and observed structure factors, and the anisotropic temperature factors are available on request.

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