DALTON

Synthesis, stability and structure of the complex of bismuth(III) with the nitrogen-donor macrocycle 1,4,7,10-tetraazacyclododecane. The role of the lone pair on bismuth(III) and lead(II) in determining co-ordination geometry

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The complex [Bi(cyclen)(H_2O)(ClO_4)$_3$] (cyclen = 1,4,7,10-tetraazacyclododecane) has been synthesized and its crystal structure determined. The Bi has square-antiprismatic co-ordination to the four nitrogens of cyclen (mean Bi–N 2.39 Å) with the upper square being provided by one oxygen from each of the three perchlorates and a water molecule (mean Bi–O 2.77 Å). The formation constant (log K_1) of Bi^{III} with cyclen has been determined as 23.45 at $I = 0.5$ mol dm^{-3} and 25 °C by differential pulse polarography in an out-of-cell technique, where equilibration was slow and required 6 months. This is a high log K_1 value for a complex with cyclen, in accord with predictions made of the high affinity that Bi^{III} would have for polyamines on the basis of a model of acid–base interactions in aqueous solution. The structures of some complexes of Bi^{III} and the isoelectronic Pb^{II} were analysed in terms of the effect that the lone pair of electrons has on the M–L bond length (M = Bi or Pb, L = ligand donor atom). A relationship was found between the M–L bond length and the distance of L from the lone pair as quantified by the l.p.–M–L (l.p. = lone pair) angle, with M–L decreasing as l.p.–M–L increases. This observation is rationalized in terms of an analogy with the linear co-ordination geometry found in many complexes of Hg^{II}, where the lone pair on Bi^{III} or Pb^{II} occupies one of the two co-ordination sites in the analogous linear two-co-ordinate mercury(II) complex.

The chemistry of heavy post-transition elements such as Ga, In, Tl, Bi and Pb has been somewhat neglected. Standard texts[1–5] devote few pages to them as compared to the transition elements, for example. However, recent developments have highlighted the need for a deeper examination of this chemistry. Gallium and indium, as the ^{57}Ga and ^{111}In isotopes, are important[6] in body-imaging techniques in medicine. The chemistry of lead is of interest in relation to its toxicity and effects on intelligence in human populations.[7] Bismuth has become of increasing interest, as its ^{212}Bi isotope in potential cancer therapies,[8] and the use of complexes such as the subsalicylate in treating gastric and duodenal ulcers.[9] The increasing interest in bismuth has recently led to papers on its chemistry with chelating ligands.[10–16] Polarographic studies[10,11] have shown that the bismuth(III) ion has considerable affinity for nitrogen-donor ligands. Thus, log K_1 for Bi^{III} with[10,11] some polyamine ligands can be compared with values reported[17] for the same ligands with Cu^{II} and Hg^{II}, which are regarded as having a high affinity for ligands with neutral nitrogen donors (Table 1). Constants for the isoelectronic Pb^{II} are also included.

What was pleasing[10,11] about the observed high affinity of Bi^{III} for nitrogen-donor ligands was that it was predicted[18] several years before any attempt was made[10,11] to demonstrate it. In 1978 one of the present authors co-authored a paper[18] in which an equation was presented that allowed for prediction of log K_1 values for metal ions with unidentate ligands, similar to that proposed by Drago and Wayland[19] for predicting enthalpies of Lewis acid–base interactions in solvents of low relative permittivity. The estimate of log K_1(NH_3) for Bi^{III} of 5.0 suggested high affinity for polydentate ligands. The method of estimation of log K_1 has been discussed[10,11,18,20] in some detail, so that here we point out only that rearrangement of the Drago–Wayland equation,[19] adapted for use in aqueous solution,[18] yields equation (1).

Table 1 Formation constants of Bi(III) and other metal ions with nitrogen donor ligands

	log K_1				
Metal ion	NH_3	ampy	dien	trien	[15]aneN_4
Bi^{III}	(5.0)[a]	9.4	17.5	21.9	23.5
Cu^{II}	4.1	9.5	16.0	20.1	24.4
Hg^{II}	8.8	(10.0)[b]	21.8	24.8	23.7
Pb^{II}	1.6	3.95	7.5	10.4	10.5

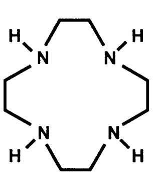
ampy = 2-(Aminomethyl)pyridine; dien = diethylenetriamine; trien = triethylenetetramine; [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane.
[a] Estimated[10,11,18] as discussed below. [b] Estimated as half log β_2. Formation constants from refs. 10, 11 and 17.

$$\log K_1(\mathrm{NH_3}) = 0.881 \log K_1(\mathrm{OH^-}) - 1.08 \log K_1(\mathrm{F^-}) \qquad (1)$$

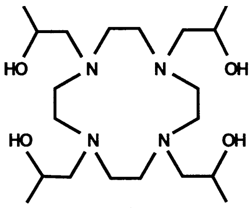
Equation (1) yields log K_1(NH_3) from the known values of log K_1 for the hydroxide and fluoride complexes to within about 0.4 log units for metal ions for which log K_1(NH_3) can be determined experimentally. The predicted value of log K_1(NH_3) for Bi^{III} of 5.0 suggests that the ammonia complexes of Bi^{III} will not exist in aqueous solution, because of hydrolysis according to equation (2). With log K_1(OH^-) for Bi^{III} of 12.36, pK_w of

$$[\mathrm{Bi(NH_3)}]^{3+}(\mathrm{aq}) + \mathrm{H_2O} \rightleftharpoons [\mathrm{Bi(OH)}]^{2+}(\mathrm{aq}) + \mathrm{NH_4^+}(\mathrm{aq}) \qquad (2)$$

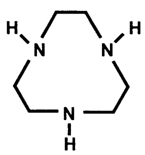
14.0, and with[17] the pK_a for NH_4^+ of 9.22, one calculates that reaction (2) will proceed to the right with a quotient of $10^{2.58}$. Many metal ions, such as Fe^{III}, Pu^{IV} and Bi^{III}, which are



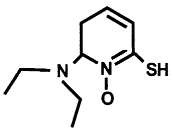
cyclen



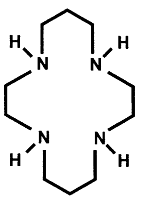
L^1



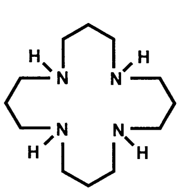
[9]aneN$_3$



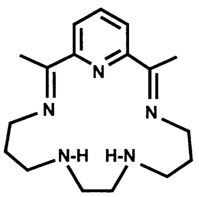
L^5



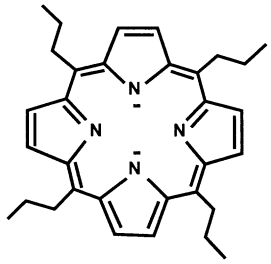
cyclam



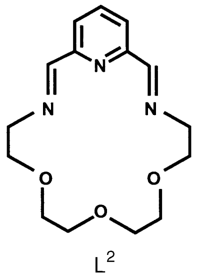
[16]aneN$_4$



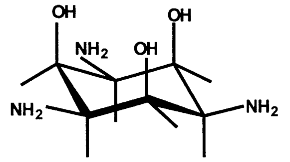
L^3



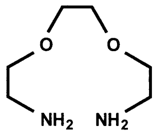
tprp



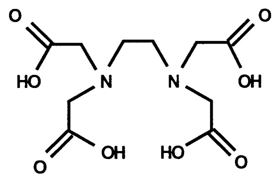
L^2



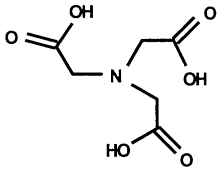
L^4



L^6



H$_4$edta



H$_3$nta

traditionally regarded[1–5] as having low affinity for amines, are predicted to have high log K_1 values with ammonia, but these complexes do not exist in solution because of the high affinity these metal ions have for OH^-. However, the chelate effect can stabilize[21] the complexes of these metal ions with polyamines, so that these are less prone to hydrolysis in aqueous solution. Thus it has been possible to measure the formation constants of Bi^{III} with polyamine ligands, both open-chain and macrocyclic.

In this paper the chemistry of Bi^{III} with nitrogen-donor macrocycles is investigated further. The synthesis and structure of a complex of Bi^{III} with the pendant-donor macrocycle L^1 has already been reported.[12] We report here the synthesis of the first example of a complex of Bi^{III} with a non-pendant-donor tetraazamacrocycle, $[Bi(cyclen)(H_2O)(ClO_4)_3]$, a crystallographic study of its structure, and a polarographic determination of the stability of the complex of Bi^{III} with cyclen in aqueous solution. Polarography has been shown[10,11] to be particularly suited to the study of complexes of hydrolysis-prone metal ions such as Bi^{III}.

The bismuth(III) and lead(II) ions have lone pairs of electrons, which can be stereochemically active,[22] and exert a considerable effect on the structures of their complexes. The stereochemically active lone pair can also[23] affect the thermodynamic stability of the complexes of these ions. An attempt is made here to rationalize further the thermodynamic and structural effects of the lone pair on these ions.

Experimental

Materials

The compound cyclen was synthesized according to the method of Richman and Atkins.[24] The complex $[Bi(cyclen)(H_2O)(ClO_4)_3]$ was synthesized by dissolving Bi_2O_3 in 70% $HClO_4$, together with 1 equivalent of cyclen. The pH was adjusted to approximately 1.0 by addition of Na_2CO_3. On standing, small colourless crystals were deposited, which were filtered off (Found: C, 30.0; H, 3.15; N, 8.15. Calc. for $C_8H_{22}BiCl_3N_4O_{13}$: C, 29.95; H, 3.2; N, 8.05%). **CAUTION**: Organic perchlorates may be explosive.

All reagents used for polarography were of analytical grade (Merck). Pure water was obtained by passing deionized water through a Milli-Q water-purification system. A 5.123×10^{-3} mol dm^{-3} stock solution of bismuth(III) nitrate was prepared in 0.5 mol dm^{-3} HNO_3. All experiments were carried out at an ionic strength of 0.5 mol dm^{-3}.

X-Ray crystallography

A colourless crystal of $[Bi(cyclen)(H_2O)(ClO_4)_3]$ **1** was mounted on a glass fibre at room temperature. Preliminary examination and data collection was performed on a Rigaku AFC5 (oriented graphite monochromator; Mo-Kα radiation) at 293(2) K. Cell parameters were calculated from least-squares fitting of 25 high-angle reflections ($2 < \theta < 15°$). ω Scans for several intense reflections indicated acceptable crystal quality. Data were collected for θ 2.29–25.05° at 163(2) K. The scan width was $1.54 + 0.3 \tan \theta$ in ω with a variable scan rate of 16° min^{-1}. Weak reflections were rescanned (maximum of two rescans) and the counts for each scan were accumulated. Three standards, collected every 150 reflections, showed no significant trends. Background measurement was by the stationary crystal–stationary counter technique at the beginning and end of each scan for half the total scan time. Lorentz-polarization corrections were applied to 1842 reflections. These unique observed reflections were used in further calculations. An empirical absorption correction was applied.[25] The structure was solved by direct methods.[26] Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $wR = 0.1762$ and $R = 0.0614$ at convergence.[27] Neutral atom scattering factors and anomalous scattering factors were taken from ref. 28. The structure analysis showed disorder of the cyclen ring, over a crystallographic mirror plane passing through Bi, O(1) and Cl(1). The two disordered cyclen moieties, corresponding to *RRRR* and *SSSS* enantiomers, were given 50% site occupancy factors. Rigid bond restraints were applied to all carbon and nitrogen atoms of the macrocyclic ring.[29] The nitrogens co-ordinated to the bismuth were common to both disordered moieties. The hydrogen atoms (only those of water were included) were found in a Fourier-difference map and fixed to ride on the water oxygen position

($U_{iso} = 0.08$). Crystal data and details of structure refinement and selected bond lengths and angles are given in Tables 2 and 3.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any requests to the CCDC for this material should quote the full literature citation and the reference number 186/322.

Polarography

Differential pulse (DP) polarograms were recorded on a Metrohm 626 POLARECORD instrument fitted with a 626 VA stand. A multimode electrode (Metrohm) was employed as working electrode, and used in the dropping mercury electrode mode with a drop time of 2 s. A Ag–AgCl electrode was used as the reference, and a platinum electrode as the auxiliary. A computer-generated DP waveform was used with the following characteristics: pulse height, 50 mV; step height, 4 mV; pulse width, 200 ms; integration time, 60 ms. High-purity nitrogen was used for deaeration of the cell. The pH of the solutions was recorded to ±0.002 pH unit on a PHI 72 pH meter and No. 39536 glass electrode (Beckman). The temperature of the cell was controlled to 25.0 ± 0.1 °C.

The equilibration of the Bi^{III} cyclen system in aqueous solution is very slow, so that an 'out-of-cell' technique was used for the stability constant study. A series of sample solutions was measured in glass vials by metering out 10 cm^3 of 0.5 mol dm^{-3} HNO_3 and 0.5 cm^3 of 5.123×10^{-3} mol dm^{-3} $Bi(NO_3)_3$ stock solution and adding solid cyclen (22.1 mg). The initial concentration of Bi^{3+} was 2.44×10^{-4} mol dm^{-3}, and the cyclen to metal ratio was 50.8: 1. The pH of the solutions was adjusted by the addition of 0.5 mol dm^{-3} NaOH and varied from sample to sample over the range pH 0.3–1.0. Polarograms were run from time to time of these solutions kept at 25.0 ± 1.0 °C, and after 7 months it was apparent that equilibrium had been attained since the polarograms recorded showed no change from those recorded after 6 months.

In a typical run, the first polarogram was recorded for a solution containing 0.5 mol dm^{-3} HNO_3 to check for impurities. Then one of the Bi–cyclen solutions (*ca.* 10 cm^3) was transferred to the polarographic cell and deaerated. Two DP polarograms were recorded in the potential range 0.2 to −0.7 V. The solution was then transferred back to its vial, and the polarographic cell was cleaned with 0.5 mol dm^{-3} HNO_3 prior to examination of the next solution. The final solution for which a polarogram was recorded was a standard solution of Bi^{3+} (2.44×10^{-4} mol dm^{-3}) in 0.5 mol dm^{-3} HNO_3. This was done in order to provide a calibration for the concentration of free Bi^{3+} in the Bi–cyclen solutions. Polarograms were recorded on the samples once a month.

Calculation of formation constants

A computer program MLSPEC,[30] written for the IBM personal computer, which allowed for correction for the hydrolysis of Bi^{3+} to give species such as $[Bi(OH)]^{2+}$ or $[Bi_6(OH)_{12}]^{6+}$ using reported[17] formation constants, was used to analyse the Bi^{III}–cyclen solutions. It essentially solves the appropriate mass-balance equations incorporating the estimated formation constants for the complexes thought to be present in solution, equation (3), where x is the number of metal atoms M in the

$$M_T = \Sigma M_x L_y H_z \qquad (3)$$

solution species, y the number of ligands L present, and z the number of protons H (a hydroxide is a negative proton *i.e.* $z = -1$). For hydroxo complexes such as $[Bi(OH)]^{2+}$ ($x = 1$, $y = 0$, $z = -1$) the known[17] formation constants were kept fixed in solving the mass-balance equation. The predicted species distribution with trial values of the unknown formation constants and the relevant solution concentrations and pH were then compared with those indicated by the polarograms, and the formation constants adjusted to give as close a fit as possible. Peak currents rather than integrated peak currents were used as a measure of concentration. No evidence for adsorption effects or kinetic effects was found in the polarograms.

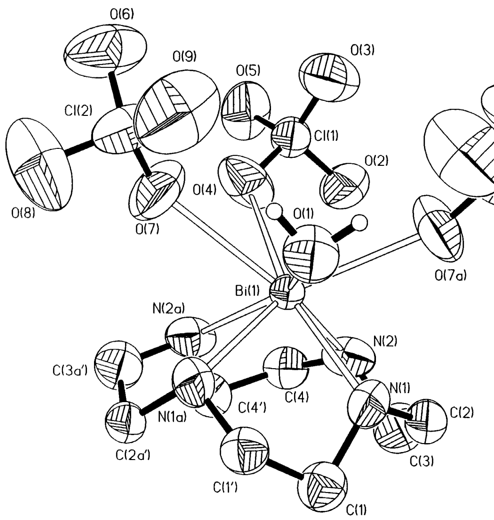


Fig. 1 Structure of $[Bi(cyclen)(H_2O)(ClO_4)_3]$, showing the numbering scheme. Only one of the disordered pair of cyclen ligands is shown for clarity. The complex lies over a crystallographic mirror plane containing O(1), Bi(1) and Cl(1). Atoms indicated with an 'a' only *e.g.* O(7a) are related to the corresponding atom O(7) by reflection through the mirror plane, while those indicated with a dash *e.g.* C(2a′) are related by reflection to an atom C(2′) of the other individual constituting the disordered pair (not shown). The water [O(1)] and perchlorates containing Cl(2) and Cl(2a) are common to both disordered moieties, but that containing Cl(1) has a second set of oxygens [O(2a) to O(5a)] present in the other disordered unit, related to O(2)–O(5) by reflection through the mirror plane. The thermal ellipsoids are at the 50% probability level

Results and Discussion

X-Ray crystallography

The structure of $[Bi(cyclen)(H_2O)(ClO_4)_3]$ **1** is seen in Fig. 1 (see also Tables 2 and 3), where only one disordered moiety is shown. The co-ordination geometry of Bi in **1**, and in its complex with L^1 is shown in Fig. 2. Also shown for comparison is the co-ordination geometry around the isoelectronic lead(II) ion in its complex with L^1.[23] The structure of **1** shows the similarity of the co-ordination geometry of Bi^{III} to that of Pb^{II}. The difference in bond lengths Bi–N (mean = 2.39 Å) and Bi–O (mean = 2.77 Å) compared to Pb–N 2.64, Pb–O 2.75 Å reflects the smaller ionic radius[31] of Bi^{III}. In **1**, the co-ordination geometry is square antiprismatic, with the four nitrogens of the macrocycle forming one square, and the four oxygen donors another. In the L^1 complexes of both Bi^{III} and Pb^{II} the structure is distorted from square antiprismatic towards cubic, probably due to the shortness of the pendant alcohol groups preventing rotation of the oxygen donors into a regular square-antiprismatic structure.

A conspicuous feature of the structures of the complexes of Bi^{III} and Pb^{II} is the effect of the lone pair of electrons on L–M–L bond angles and lengths.[31] In an initial study of this problem[23] the structure of $[PbL^1][NO_3]_2 \cdot Pr^nOH$ was determined. Although it was concluded[23] that the Pb^{II} might in fact not have a stereochemically active lone pair, in light of the present work it seems clear that the lone pair in $[PbL^1][NO_3]_2 \cdot Pr^nOH$ is active. The structure showed the geometry around Pb^{II} to possess features associated[22,33,34] with a stereochemically active lone pair, namely, (1) a gap in the co-ordination where the

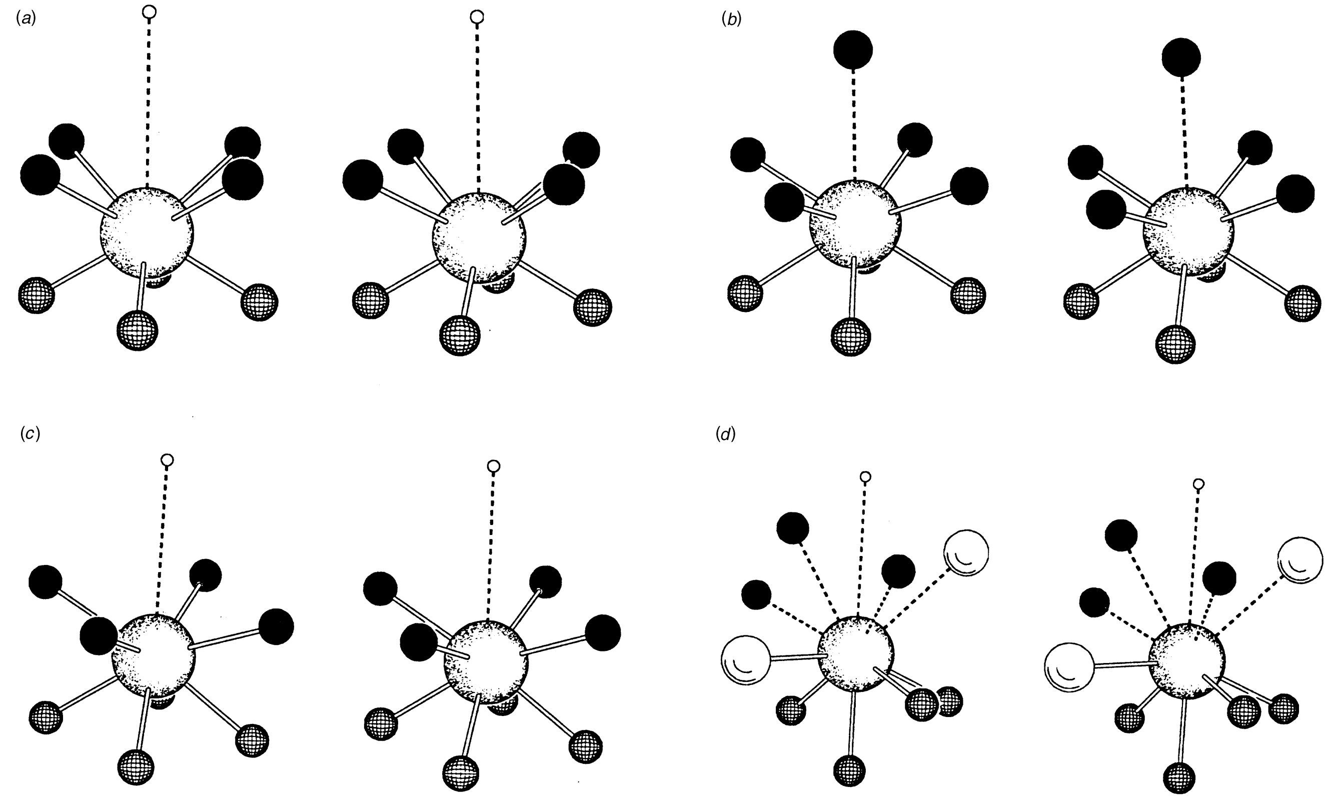


Fig. 2 Stereoviews of the co-ordination geometry around Pb^{II} and Bi^{III}. The geometry around Bi^{III} is shown (*a*) in $[Bi(cyclen)(H_2O)(ClO_4)_3]$, determined in this work, and (*b*) in $[BiL^1][ClO_4]_3$.[12] The geometry around Pb^{II} is shown (*c*) in $[PbL^1][NO_3]_2{\cdot}Pr^nOH$,[31] and (*d*) in $[PbL^2(SCN)_2]$.[32] Oxygen atoms are shown as black circles, nitrogen as cross-hatched and sulfurs as larger open circles. The Pb and Bi atoms are shown as large shaded circles. The proposed positions of the lone pairs are indicated as very small circles at the end of broken lines. Metal–ligand bonds which are longer than expected from the sums of the ionic radii are indicated as broken lines. Drawings made with coordinates available in the original papers[12,31,32]

Table 2 Crystal data and structure refinement for $[Bi(cyclen)(H_2O)(ClO_4)_3]$

Empirical formula	$C_8H_{22}BiCl_3N_4O_{13}$
λ/Å	0.710 73
Crystal system	Orthorhombic
Space group	*Pnma*
a/Å	17.784(4)
b/Å	13.429(5)
c/Å	8.390(2)
U/Å^3	2003.7(10)
Z	4
D_c/mg m^{-3}	2.30
D_m/mg m^{-3}	2.29
μ/mm^{-1}	9.270
F(000)	1328
Crystal size/mm	0.44 × 0.44 × 0.38
Index ranges	$0 \leqslant h \leqslant 21, -16 \leqslant k \leqslant 0, -9 \leqslant l \leqslant 0$
Reflections collected	1842
Independent reflections	1842 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least squares on F^2
Data, restraints, parameters	1806, 269, 190
Goodness of fit on F^2	1.050
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0517, 0.1446
(all data)	0.0614, 0.1762
Largest difference peak and hole/e Å^{-3}	1.572, −1.616

$wR2 = \Sigma[(F_o^2 - F_c^2)^2]^{\frac{1}{2}}/(F_o^2)^2$. Weighting, $w = 1/[\sigma(F_o^2) + (aF_o^2 + bF_o^2)]$ where $a = 0.1096$ and $b = 13.7278$.

Table 3 Selected bond lengths (Å) and angles (°) in $[Bi(cyclen)(H_2O)(ClO_4)_3]$

Bi(1)–N(1)	2.375(10)	Bi(1)–N(2)	2.412(9)
Bi(1)–O(4)	2.81(2)	Bi(1)–O(1)	2.810(14)
Bi(1)–O(7)	2.690(10)		
N(1)–Bi(1)–N(1′)	72.3(4)	N(1)–Bi(1)–N(2′)	113.3(4)
N(1)–Bi(1)–N(2)	73.5(4)	N(2)–Bi(1)–N(2′)	70.4(5)
N(1)–Bi(1)–O(7)	143.3(3)	N(1)–Bi(1)–O(7′)	77.4(4)
N(2)–Bi(1)–O(7′)	76.2(5)	N(2)–Bi(1)–O(7)	139.3(3)
O(7)–Bi(1)–O(7′)	119.7(9)	N(1)–Bi(1)–O(4)	154.4(6)
N(1)–Bi(1)–O(4)	126.6(5)	N(2)–Bi(1)–O(4)	65.6(6)
N(2)–Bi(1)–O(4)	83.3(6)	O(7)–Bi(1)–O(4)	62.6(6)
O(7)–Bi(1)–O(4)	89.3(5)	N(1)–Bi(1)–O(1)	72.2(4)
N(2)–Bi(1)–O(1)	141.0(3)	O(7)–Bi(1)–O(1)	79.3(3)
O(4)–Bi(1)–O(1)	126.1(7)	Cl(1)–O(4)–Bi(1)	132.3(13)
C(2′)–N(1)–Bi(1)	123.2(10)	C(2)–N(1)–Bi(1)	103.5(10)
C(1)–N(1)–Bi(1)	108.4(9)	C(1′)–N(1)–Bi(1)	115.4(10)
C(4′)–N(2)–Bi(1)	118.4(14)	C(3′)–N(2)–Bi(1)	108.6(11)

lone pair is thought to be located and (2) shortening of the Pb–L bonds on the side of the Pb^{II} away from the proposed site of the lone pair. The structures in Fig. 3 all show this feature with short Pb–N or Bi–N and long M–O bonds. In most cases, M–N bonds are longer than M–O bonds, which relates to the smaller size[29] of oxygen than nitrogen. Bismuth(III) in its complexes with cyclen in **1**, and with L^1, also shows Bi–N bonds that are shorter than the Bi–O bonds. What is of particular interest is the presence in the $[BiL^1][ClO_4]_3$ and $[PbL^1][ClO_4]_2{\cdot}Pr^iOH$ complexes of very long M–O contacts at the spot where the lone pair is presumed to be. There is thus a Bi–O contact at 3.34 Å with an oxygen from a perchlorate, and the Pb^{II} is 3.50 Å from the oxygen of the solvent Pr^iOH molecule. The nature of this type of contact in these structures is not yet clear. There is no sign of similar contacts over the proposed sites of the lone pairs in **1**, or in the $[PbL^1][NO_3]_2{\cdot}Pr^nOH$ complex,[31] with the nearest oxygens being over 4.5 Å away. However, the structure of the $[PbL^1]^{2+}$ cation is almost identical in the nitrate, where no contact with a donor atom is present over the site of the lone pair, and in the perchlorate, where such a contact is present.

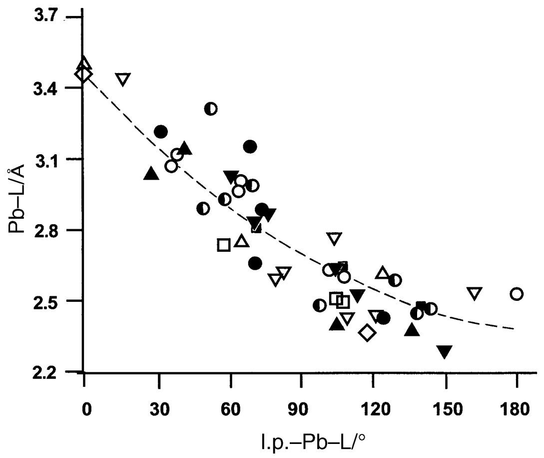


Fig. 3 Relationship between the Pb–L distance in some complexes of Pb^{II} and the l.p.–Pb–L angle (l.p. = lone pair on Pb^{II}). The structures from which bond length and angle data were taken were [PbL^1]$^{2+}$ (Δ), [Pb([9]aneN$_3$)(NO$_3$)$_2$] (●), [PbL^2]$^{2+}$ (○), [Pb([14]aneN$_4$)][NO$_3$]$_2$ ([14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane) (◐), [Pb(tprp)] (◇), [Pb([16]aneN$_4$)]Cl$_2$ (□), [PbL^3]$^{2+}$ (▽), [PbL^4][NO$_3$]$_{12}$ (▼), [PbL^5$_2$] (▲) and [Pb{HB(pz)$_3$}$_2$] (pz = pyrazolyl) (■), from refs. 23, 34, 32, 35–41 respectively. The Pb–L distance decreases approximately as the donor atom L is further from the proposed position of the lone pair

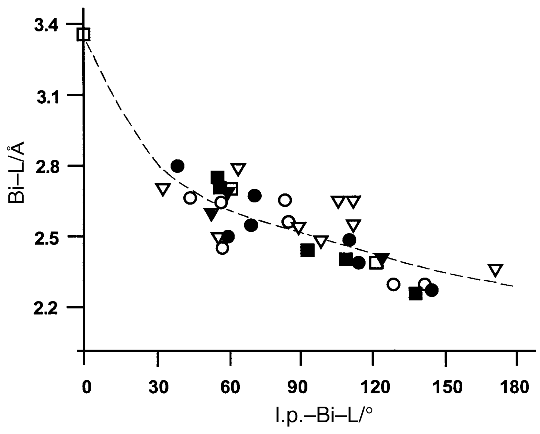


Fig. 4 Relationship between Bi–L length in some complexes of Bi^{III}, and l.p.–Bi–L angle: [Bi(cyclen)(H$_2$O)(ClO$_4$)$_3$] (▼), [BiL^1][ClO$_4$]$_3$ (□), [Bi(nta)(H$_2$O)$_2$] (●), [Bi(Hedta)] (○), [Bi(dtpa)]$^{2-}$ (▽) {H$_5$dtpa = [(carboxymethyl)imino]bis(ethylenedinitrilo)tetraacetic acid}, [(BiL^4)$_3$]Cl$_9$ (■). Structural data from this work, and refs. 12, 16 and 39. The Bi–L distance decreases approximately as the donor atom L is further from the proposed position of the lone pair

In more symmetric complexes such as [ML^1]$^{n+}$ (M^{n+} = Bi^{3+}or Pb^{2+}), the position of the lone pair is unambiguous, and it must lie along the four-fold axis through the square planes formed by the four nitrogen donors and the four oxygen donors. Its position is further indicated by the gap between the four oxygen donors, where it must be situated, and by the long M–O bonds. The proposed positions of the lone pair in the more symmetric complexes of Bi^{III} and Pb^{II} are indicated in Fig. 2. Lawton and Kokatailo[33] have pointed out that in complexes of Pb^{II} the lengths of the M–L bonds decrease approximately as they are further away from the position of the lone pair. The distance of the donor atom from the lone pair on Bi^{III} or Pb^{II} can be quantified with the angle that the M–L bonds form with the line passing through the centre of the postulated lone pair and Pb^{II} or Bi^{III}. One can thus obtain (Fig. 3) a relationship between the M–L distance and l.p.–M–L angle (l.p. = lone pair), which shows bond lengthening with decreasing l.p.–M–L angle. The further away a bond is from the lone pair, which is to say the larger the l.p.–M–L angle, the shorter it is. The geometry around metal ions such as Pb^{II} and Bi^{III}[16] can be very irregular, as seen in Fig. 2, where the co-ordination geometry around Pb^{II} in its complex[32] [PbL^2(SCN)$_2$] is shown. The position of the lone pair, as proposed here, is also shown. For irregular complexes the lone pair can be located by examination of the bond lengths, and adjustment of the position of the lone pair to produce a relationship as shown in Fig. 3. Fig. 3 shows that this type of relationship holds quite well for complexes of Pb^{II} and a variety of its complexes,[30,32,34–40] and a similar relation is seen for some complexes[11,16,23] of Bi^{III} in Fig. 4. The bond lengths to sulfur are corrected in Figs. 3 and 4 for the larger size of sulfur[31] (with respect to nitrogen and oxygen) by subtraction of 0.3 Å, and for chloride are corrected by subtraction of 0.25 Å. The very long Bi–O and Pb–O bonds observed in structures such as that of the L^1 complexes[12,30] can be seen to be the extreme case of extension of the M–L bond when it is situated directly over the lone pair of electrons on the metal ion. The fairly large scatter of points in Figs. 3 and 4 may reflect steric effects, which are in addition to the effects of the lone pair on the M–L bond length. Thus, one Bi–O bond in the [Bi(Hedta)] complex,[16] which is rather shorter than might have been anticipated from its closeness to the lone pair, may be short because it is part of a chelate ring, and its ability to move out to long Bi–O lengths is limited sterically. On the other hand, oxygen atoms that form bridges between two metal ions appear to form M–O bonds that are longer than might be expected, which again might be due to steric effects preventing closer approach of the two complexes forming the dimer. One should point out that the structures used in drawing Figs. 3 and 4 were not selected for any particular reason, except that they were those which had already been extracted from the Cambridge Crystallographic Data Base for other purposes.

The curves that have been drawn tentatively through the points in Figs. 3 and 4 suggest that Bi^{III} and Pb^{II} can be viewed as being ovoid, rather than effectively spherical as are pre-transition-metal ions of similar charge and size such as La^{III} or Sr^{II}. An extensive analysis of the many structures available for complexes of Pb^{II} is presently being carried out, with the hope that a molecular mechanics model can be developed where the strain-free Pb–L bond length is a function of the angle made by the Pb–L bond with the position of the lone pair. It should also be possible to develop a similar model for Bi^{III}, for which fewer structures are available.

The observation that Pb–L or Bi–L bonds become shorter as the l.p.–M–L angle approaches 180° suggests an analogy with the co-ordination geometry of Hg^{II}. The typical geometry for mercury(II) compounds is[42] a distorted octahedron with two short bonds along one axis, which in the extreme case with highly covalent Hg–L bonds such as in Hg(CN)$_2$ becomes linear two-co-ordinate. This linear co-ordination may represent sp (or sd) hybridization of the Hg^{II}. In the VSEPR (valence shell electron pair repulsion) formalism[22] the geometry of atoms having one lone pair on them (*e.g.* N in NH$_3$) is derived from similar compounds of atoms where a co-ordinated atom is present instead of a lone pair (*e.g.* C in CH$_4$). Ions such as Pb^{II} and Bi^{III} may be regarded as isoelectronic with Hg^{II} if the lone pair of electrons on Pb^{II} and Bi^{III} is considered to be a pair of electrons donated by a donor atom, as required by the VSEPR formalism. Thus, Pb^{II} and Bi^{III} would have a preference for a linear co-ordination geometry similar to that of Hg^{II}, with the lone pair on Pb^{II} and Bi^{III} occupying one of the two co-ordination sites found in linearly co-ordinated Hg^{II}, in line with VSEPR ideas.[22] This suggestion is illustrated in Fig. 5. The analogy accounts for the fact that bonds at right angles to the lone pair on Pb^{II} and Bi^{III} are longer than those opposite the lone pair. The preference[1–5] of Hg^{II} for linear co-ordination geometry is also reflected in the formation constants of its complexes. Complexes of ligands where two donor atoms can occupy the two co-ordination sites 180° apart are more stable than those where they cannot. Thus, for Hg^{II}, log K_1 for the ethane-1,2-diamine (en) complex is[17] much lower than that

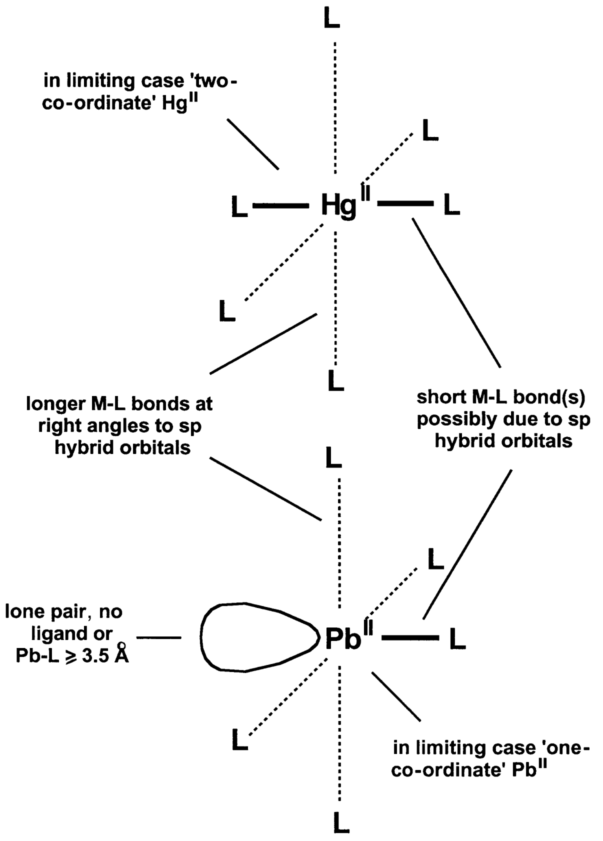


Fig. 5 The VSEPR[22] analogy proposed here between the preferred linear two-co-ordination found in complexes of Hg^{II} above, and the 'one-co-ordinate' geometry towards which Pb^{II} (and Bi^{III}) tends, although a definite one-co-ordinate structure of Pb^{II} (or of Bi^{III}) has not so far been observed. This proposal accounts for the fact that Pb–L and Bi–L bonds are shortest when directly opposite the lone pair, which is held to occupy one of the two co-ordination sites found on linearly co-ordinated Hg^{II}

with L[6], presumably because the long connecting bridge of the latter allows the two nitrogens to co-ordinate 180° apart on the Hg^{II}, while for en the bridge is too short. For Pb^{II}, high stability would be expected for unidentate ligands which would occupy only the site opposite the lone pair, and as the donor atoms were forced to be further apart, and hence closer to the lone pair, so complex stability would diminish. Thus, it has been found[43] that tertiary monoamines such as triethylamine form complexes of unprecedented stability with Pb^{II}, with a log K_1 value of about 5.3, which can be contrasted with log K_1 with en[17] of only 5.04. It is presumed that in the triethylamine complexes the unidentate amine occupies a position 180° from the lone pair, with a short Pb–N bond, which Fig. 3 suggests may be between 2.2 and 2.3 Å in length. The Pb^{II} may be effectively one-co-ordinate in such a complex, with only long bonds to co-ordinated solvent molecules, or counter ions, similar to the long bonds at right angles to the sp hybrid orbitals in mercury(II) complexes.

A further problem to be dealt with is that of complexes where there does not appear to be a stereochemically active lone pair on Bi^{III} or Pb^{II}, such as the lead(II) complex with cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane),[44] the tris-terpy complex[45] (terpy = 2,2′ : 6′,2″-terpyridine) and the bis-tren complex[46] [tren = tris(2-aminoethyl)amine]. The cause of the non-stereochemically active lone pair may be electronic, or it can also be steric, as has been shown[41] for complexes of Pb^{II} with methyl-substituted tris(pyrazolyl)borate. It has been pointed out[47] that in complexes of Pb^{II} and Sn^{II} where the structure suggests that the lone pair is not stereochemically active, the metal atom has very large thermal parameters. This is not true for the above complexes of Pb^{II} where the lone pair is not stereochemically active. It may be that in some complexes where the lone pair does not appear to be stereochemically active there is dynamic disorder between two identical structures each with a stereochemically active lone pair, which gives an overall apparently higher symmetry to the complex, and an appearance of there being no stereochemically active lone pair.

Table 4 Formation constant for Bi^{III} with cyclen determined polarographically, together with protonation constants of cyclen and hydrolysis constants of Bi^{III} used to calculate log K_1. Ionic strength 0.5 mol dm^{-3}, 25 °C

Equilibrium	log K	Ref.
$H^+ + OH^- \rightleftharpoons H_2O$	13.74	17
$H^+ + L \rightleftharpoons HL^+$	10.82	17
$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	9.72	17
$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	1.15	17
$Bi^{3+} + L \rightleftharpoons [BiL]^{3+}$	23.45 ± 0.05	This work
$Bi^{3+} + OH^- \rightleftharpoons [Bi(OH)]^{2+}$	12.42	17
$Bi^{3+} + 3OH^- \rightleftharpoons Bi(OH)_3$	31.88	17
$Bi^{3+} + 4OH^- \rightleftharpoons [Bi(OH)_4]^-$	32.98	17
$6Bi^{3+} + 12OH^- \rightleftharpoons [Bi_6(OH)_{12}]^{6+}$	162.78	17
$9Bi^{3+} + 20OH^- \rightleftharpoons [Bi_9(OH)_{20}]^{7+}$	266.92	17
$9Bi^{3+} + 21OH^- \rightleftharpoons [Bi_9(OH)_{21}]^{6+}$	276.76	17
$9Bi^{3+} + 22OH^- \rightleftharpoons [Bi_9(OH)_{22}]^{5+}$	287.30	17

Complex formation of Bi^{III} with cyclen

In Fig. 6 are shown selected DP polarograms for the Bi^{III}–cyclen system at various pH values, after 7 months of equilibration. These polarograms show typical non-labile behaviour. With increase of pH the height of the Bi^{3+} peak decreases, and a well separated peak for the Bi^{III}–cyclen complex appears at a value some 400 mV more negative. The peak referred to as the Bi^{3+} peak in fact corresponds[10] to a mixture of Bi^{3+} and hydrolysed species, the composition of which varies with pH, so that its height cannot be used in a simple direct way to calculate the concentration of uncomplexed Bi^{3+}. It represents a labile mixture of $[Bi_m(OH)_n]^{(3m-n)+}$ species, so that the concentration of free Bi^{3+} has to be calculated by solving the appropriate mass-balance equation (4) where $[M]_{T(lab)}$ is the total metal-ion

$$[M]_{T(lab)} = [M]_{free} + \sum_{j=1}^{m} \sum_{i=1}^{n} j\beta_{ij}[M]_{free}{}^{j}[OH]^{i} \qquad (4)$$

concentration excluding that bound up as the non-labile ML complex, $[M]_{free}$ is the free metal-ion concentration, and β_{ij} is the formation constant of the hydrolysed species $Bi_j(OH)_i$. The free metal-ion concentration is thus calculated with MLSPEC[30] and the known[17] formation constants of the $M_j(OH)_i$ species, from the height of the 'Bi^{3+}' peak. The free pro-ligand concentration was calculated from the appropriate mass-balance equation and the protonation constants[17] of cyclen at ionic strength 0.5 mol dm^{-3}. The concentration of the Bi^{III}–cyclen complex was calculated from the sum of the bismuth(III) species (Bi^{3+} plus hydrolysed species) not complexed by cyclen. The set of Bi^{III}–cyclen solutions gave calculated values of log K_1 of 23.17, 23.37, 23.45 and 23.45 after 1, 3, 6 and 7 months had elapsed. Table 4 shows the formation constant determined for Bi^{III} with cyclen, together with the constants for formation of hydrolysed bismuth(III) species used in the calculation of log K_1.

The Bi^{III}–cyclen complex is of high stability, as was found[10,11] for the bismuth(III) complexes of [14]aneN$_4$ and [15]aneN$_4$. The pattern that is emerging with the bismuth(III) complexes of the tetraazamacrocycles is that the variation of the formation constants with macrocyclic ring size resembles that of Cd^{II}, which is similar in size[31] to Bi^{III} (Table 5).

Extensive work has shown[48,49] that the metal-ion selectivity of the tetraazamacrocycles is more complex than envisaged in the simple 'size match selectivity' concept. If the complexes are allowed to adopt whichever ligand conformation and metal-

Table 5 Formation constants of tetraazamacrocyclic ligands with a selection of metal ions

		log K_1				
Metal ion	r^+/Å	[12]aneN_4 (cyclen)	[13]aneN_4	[14]aneN_4 (cyclam)	[15]aneN_4	[16]aneN_4
Cu^{II}	0.57	23.4	24.4	27.2	24.4	21.6
Zn^{II}	0.74	16.2	15.6	15.5	15.0	13.1
Cd^{II}	0.95	14.3	12.7	11.2	12.1	12.7
Bi^{III}	1.03	23.45	—	21.5	23.5	—
Pb^{II}	1.18	15.9	13.5	10.8	10.2	9.6

Formation constants from refs. 10, 11, 17 and this work. Ionic radii (r^+) from ref. 31. [13]aneN_4 = 1,4,7,11-Tetraazacyclotridecane.

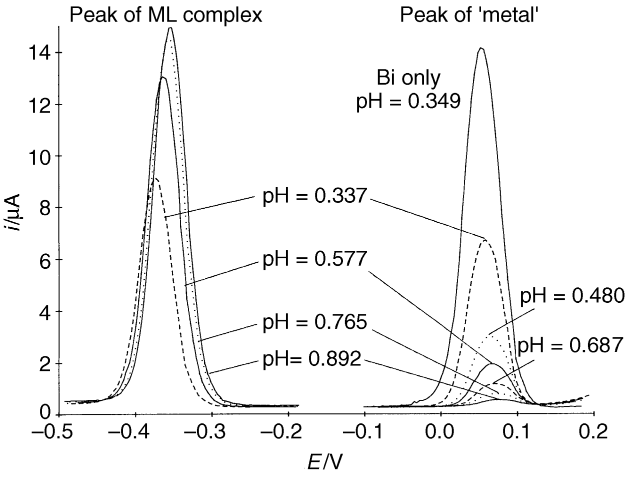


Fig. 6 A selection of polarograms at different pH values recorded for Bi^{III}–cyclen solutions after equilibration for 7 months. The total Bi^{III} was initially, before addition of base to raise the pH, 2.44×10^{-4} mol dm^{-3} and the L : M ratio 50.8 : 1

ion geometry that is of lowest strain energy, then in fact[49] the cavities of the tetraazamacrocycles decrease from [12]aneN_4 (square pyramidal) through [14]aneN_4 (square planar) to [16]aneN_4 (tetrahedral). The upturn in complex stability from [14]aneN_4 to [15]aneN_4 found only for Bi^{III} and the similarly sized Cd^{II} must relate to some unusual feature of the co-ordination in these complexes.

This study has attempted to analyse the structure and stability of complexes of Bi^{III}, and also of Pb^{II}. The complex effects of the lone pair of electrons on these metal ions may be understood through the analogy presented here, where the lone pair occupies one co-ordination site in linear two-co-ordinate geometry like that of Hg^{II}, that tends towards, but so far has not been observed to achieve, a one-co-ordinate status in Bi^{III} and Pb^{II}. The M–L bonds in Bi^{III} and Pb^{II} thus lengthen as they move further away from the preferred site of co-ordination opposite the lone pair. The lone pair can be located more accurately by an analysis where its position is related to the extent of lengthening of the M–L bonds observed. There does therefore not have to be an obvious gap in the co-ordination geometry on Pb^{II} and Bi^{III} to locate the lone pair. The presence of the latter can be indicated simply by the pattern of long and short bonds to the metal ion. The previous suggestion[23] that the lone pair in the L^1 and the L^2 complexes of Pb^{II} was not stereochemically active should therefore be revised. An important question is the nature of the attraction that occurs for donor atoms which lie directly over the lone pair, with very long contacts of about 3.5 Å. Although MOPAC[50] does not perform particularly well in our experience in calculations aimed at predicting the structures of complexes of Pb^{II} or Bi^{III}, the calculations we have so far carried out, and which will be reported in a future paper together with more ambitious *ab initio* calculations, give an indication of the nature of these very long contacts. In compounds of more electronegative atoms such as nitrogen, wave-mechanical calculations at all levels of complexity show regions of significant negative charge at the position of the lone pair. In MOPAC calculations on BiL_3 complexes, however, there is no negative charge at the position of the lone pair, but rather a region where the positive charge is lower than on the rest of the Bi atom. There is thus still a positive charge, although it is closer to neutral, in the region of the lone pair on Bi^{III}, and it is this which would produce the weak interactions with donor atoms in the vicinity of the lone pair, resulting in the long contacts observed in some structures.

Acknowledgements

The authors thank the University of the Witwatersrand and Texas A&M University, as well as the Foundation for Research Development, for generous financial support for this work.

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Received 22*nd July* 1996; *Paper* 6/05068I

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