Lead(II) as a Template for the Synthesis of a [1 + 1] 18-Membered Hexadentate N_4S_2-Donor Macrocycle; Crystal and Molecular Structure of (Acetato-*O,O'*)[3,13-dithia-6,10-diaza-1,8(2,6)-dipyridinacyclotetradecaphane-6,9-diene]lead(II) Hexafluorophosphate†

Edwin C. Constable,*,[a] Cheryl Sacht,[a] Giuliana Palo,[b] Derek A. Tocher[c] and Mary R. Truter*,[c]
[a] *Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Dipartimento di Chimica, Viale Taramelli 12, I-27100 Pavia, Italy*
[c] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK*

The reaction of 2,6-pyridinedicarbaldehyde with 2,6-bis[(2-aminoethyl)thiomethyl)]pyridine in the presence of $Pb(O_2CMe)_2$ yields the mononuclear lead(II) complex of a [1 + 1] 18-membered, potentially hexadentate, N_4S_2 imine macrocycle, the crystal and molecular structure of which has been determined [space group *Pc*, $a = 8.358(3)$, $b = 15.158(5)$, $c = 10.127(4)$ Å, $\beta = 99.87(3)°$]. This structure represents a rare example of a structurally characterised lead(II) complex with a macrocyclic ligand containing both nitrogen and sulfur donor atoms.

Macrocyclic ligands incoporating both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems. A synthetic methodology based upon the metal-directed condensation of heterocyclic dialdehydes or diketones with linear α,ω-diamines to form macrocyclic polyimines has been applied to the synthesis of a wide-range of imine macrocyclic complexes and provides a well-established synthetic procedure for the preparation of these compounds.[1,2] We are interested in the design of macromolecular encapsulating environments for the incorporation of biomimetic metal–sulfur clusters, and have been investigating the metal-ion control in assembly of structured systems incorporating N and S donors.[3] We have been using 2,6-bis(mercaptomethyl)pyridine as a building block for the incorporation of NS_2 donor sites into macrocycles, and were specifically interested in the preparation of derivatised polynucleating macrocyclic ligands **I** (R = spacer group).[4] In this paper we describe our approaches to the synthesis of the parent non-functionalised tetraimine macrocyclic system L^1 by templated [2 + 2] condensations and the isolation and structural characterisation of a lead(II) complex of the [1 + 1] macrocyclic ligand L^4.

Experimental

Infrared spectra were recorded on Perkin Elmer 1710 or Philips PU9624 Fourier-transform spectrophotometers, with the samples in compressed KBr discs. Proton NMR spectra were recorded on Brüker WM250 or AM400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra. 2,6-Bis(bromomethyl)pyridine was prepared as described previously,[4] macrocycle L^2 was prepared by a slight modification of the method of Teixidor *et al.* [5] and 2,6-bis(hydroxymethyl)pyridine and $[HSCH_2CH_2NH_3]Cl$ were used as supplied by Aldrich.

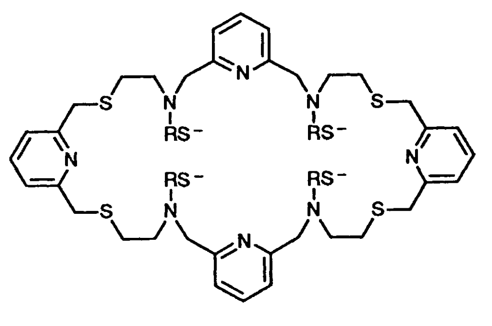
Preparations.—Macrocycle L^3. The salt $[HSCH_2CH_2NH_3]Cl$ (1.75 g, 0.015 mol) was added to a solution of KOH (1.716 g, 0.051 mol) in ethanol (75 cm^3) and the mixture heated to reflux under an inert atmosphere for 30 min, after which period a white precipitate of KCl had been deposited. A solution of 2,6-bis(bromomethyl)pyridine (2.10 g, 0.008 mol) in ethanol (50 cm^3) was then added, and the mixture heated to reflux for a further 3.5 h. The reaction mixture was cooled and filtered to remove inorganic solids. The filtrate was evaporated to dryness to yield an orange oil. This was dissolved in CH_2Cl_2 (30 cm^3), washed with water (4 × 150 cm^3), dried over $MgSO_4$ and the solvent removed *in vacuo* to give L^3 as an orange oil (0.62 g, 43%). IR: 3293w, 3054w, 2915s, 2831m, 1588vs, 1572vs, 1451vs, 1351w, 1266m, 1216m, 1152m, 1122m, 1086m, 992m, 733s and 700m cm^{-1}. Mass spectrum (EI): *m/z* 360. ^1H NMR ($CDCl_3$): δ 7.64 (d), 7.64 (t), 7.63 (t), 7.23 (d), 3.82 (m) and 2.78 (m).

$[ZnL^3(H_2O)][ZnCl_4]$. A solution of $ZnCl_2$ (0.348 g, 0.0025 mol) in MeOH (10 cm^3) was added to L^3 (0.62 g, 0.0017 mol) in EtOH (15 cm^3), and the white precipitate so obtained was collected by filtration and dried to give $[ZnL^3(H_2O)][ZnCl_4]$ (0.763 g), m.p. 164–167 °C. IR: 3469vs, 3236vs, 2926m, 1606vs, 1574vs, 1455vs, 1163m, 1088m, 1027m, 941m, 788m, 278s, 268s, 260m, 250s, 245vs and 235vs cm^{-1}. Mass spectrum (FAB): *m/z* 459 $\{[ZnL^3(Cl)]^+\}$, 423 $\{[ZnL^3]^+\}$ (Found: C, 33.2; H, 3.7; N, 8.7. Calc. for $C_{18}H_{26}Cl_4N_4OS_2Zn_2$: C, 33.2; H, 3.9; N, 8.6%). ^1H NMR (CD_3SOCD_3): δ 8.07 (t), 7.69 (t), 7.48 (d), 7.29 (d), 4.00 (m) and 2.75 (m).

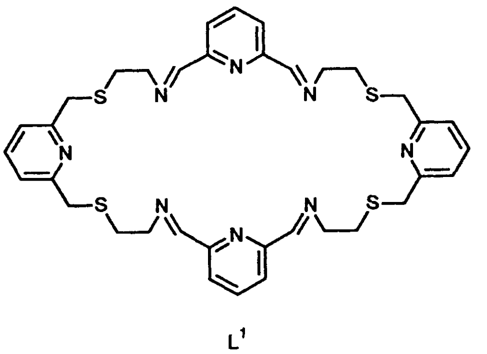
$[AgL^4][PF_6]$. Silver perchlorate (0.0452 g, 0.218 mmol), L^2 (0.0651 g, 0.253 mmol) and 2,6-pyridinedicarbaldehyde (0.0298 g, 0.224 mmol) were dissolved in methanol (100 cm^3) and the solution heated to reflux for 1 h, after which it was allowed to cool and a small amount of a brown solid removed by filtration. The yellow filtrate was treated with $[NH_4][PF_6]$ and the yellow precipitate of $[AgL^4][PF_6]$ was collected by filtration (0.048 g, 36%). IR: 3426w, 2924s, 2854m, 1654m, 1588s, 1572m, 1456s, 1406m, 1161m, 1099m, 1053m, 1006m, 840vs, 753m and 558vs cm^{-1}. Mass spectrum (FAB): *m/z* 463, 465 $\{[AgL^4]^+\}$ (Found: C, 35.0; H, 3.7; N, 9.5. Calc. for $C_{18}H_{20}AgF_6N_4PS_2$: C, 35.5; H, 3.3; N, 9.2%). ^1H NMR (CD_3CN): δ 8.07 (t), 7.69 (t), 7.48 (d), 7.29 (d), 4.00 (m) and 2.75 (m).

---

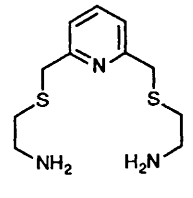
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



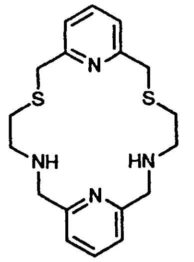
I



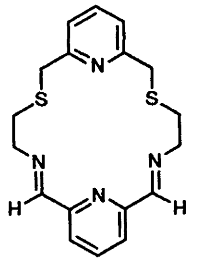
L^1



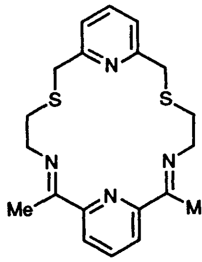
L^2



L^3



L^4



L^5

[PbL^5(NCS)$_2$]. Lead(II) thiocyanate (0.226 g, 0.699 mmol), L^2 (0.18 g, 0.699 mmol) and 2,6-diacetylpyridine (0.1157 g, 0.709 mmol) were dissolved in MeCN–MeOH (1 : 1, 120 cm^3) and the solution heated to reflux for 3 h, after which time the orange solution was filtered and the filtrate concentrated *in vacuo*. The complex [PbL^5(NCS)$_2$] precipitated as a brown powder (0.13 g, 13%). IR: 2925m, 2071vs, 2012vs, 1640s, 1628m, 1585s, 1571s, 1455s, 1426m, 1370m, 1200m, 1008m and 758m cm^{-1}. Mass spectrum (FAB): *m*/*z* 649 {[PbL^5(NCS)]$^+$}, 591 {[PbL^5]$^+$}.

[PbL^4(NCS)$_2$]. Lead(II) thiocyanate (0.185 g, 0.573 mmol), L^2 (0.15 g, 0.570 mmol) and 2,6-pyridinedicarbaldehyde (0.08 g, 0.594 mmol) were dissolved in MeCN–MeOH (1 : 1, 80 cm^3) and the solution heated to reflux for 3 h, after which time the yellow solution was filtered and the filtrate concentrated. The complex [PbL^4(NCS)$_2$] precipitated as a yellow powder (0.22 g, 28%). IR: 2923m, 2076s, 2032vs, 2015vs, 1654m, 1585s, 1453m and 1008m cm^{-1}. Mass spectrum (FAB): *m*/*z* 622 {[PbL^4(NCS)]$^+$}.

[PbL^4(O$_2$CMe)][PF$_6$]. Lead(II) acetate (0.181 g, 0.556 mmol), L^2 (0.154 g, 0.554 mmol) and 2,6-pyridinedicarbaldehyde (0.075 g, 0.56 mmol) were dissolved in MeCN–MeOH (1 : 1, 100 cm^3) and the solution heated to reflux for 2 h, after which time the red solution was filtered. The hot filtrate was treated with [NH$_4$][PF$_6$] and then left to cool, whereupon [PbL^4(O$_2$CMe)][PF$_6$] slowly precipitated as an orange solid. IR: 2924m, 1658m, 1585s, 1569s, 1553s, 1452s, 1413s, 1008m, 843vs, 802m, 669m and 559s cm^{-1}. Mass spectrum (FAB): *m*/*z* 563 {[PbL^4]$^+$}, 623 {[PbL^4(O$_2$CMe)]$^+$}.

Crystal Structure Determination of [PbL^4(O$_2$CMe)][PF$_6$].—Suitable single crystals of the complex were obtained by diffusion of diethyl ether vapour into an acetonitrile solution of the complex.

Crystal data. $C_{20}H_{23}F_6N_4O_2PPbS_2$, $M = 767.75$, monoclinic, space group *Pc*, $a = 8.358(3)$, $b = 15.158(5)$, $c = 10.127(4)$ Å, $\beta = 99.87(3)°$, $U = 1264$ Å^3, $Z = 2$, D_m not measured, $D_c = 2.02$ g cm^{-3}, $F(000) = 740$, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo-Kα) = 70.15 cm^{-1}.

Data collection and processing. A suitable off-white crystal of size 0.4 × 0.4 × 0.35 mm was mounted on a glass fibre and all geometric and intensity data were obtained using an automated four-circle diffractometer (Nicolet R3m/V). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections ($14 \leqslant 2\theta \leqslant 29°$) taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 2477 reflections (2290 unique) in the range $5° \leqslant 2\theta \leqslant 50°$. Three standard reflections were remeasured every 97 scans and showed no significant loss in intensity during the data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied (maximum transmission 0.88, minimum transmission 0.23).[6]

Structure analysis and refinement. The structure was solved from the Patterson synthesis and successive Fourier difference syntheses using all 1975 reflections for which $|F_o| \geqslant \sigma(F_o)$; these comprised 1158 having $k + l = 2n$, the 'even' planes, and 817 having $k + l = 2n + 1$, the 'odd' planes. With lead allowed anisotropic thermal parameters and the other non-hydrogen atoms isotropic ones, *R* was 0.0615 (0.0618 for the 'even' and 0.0605 for the 'odd' planes). Reversal of polarity gave the lower values of 0.0549 (0.0540 and 0.0557) respectively. Inclusion of hydrogen atoms in calculated positions with C–H distances of 0.96 Å and a fixed U_{iso} of 0.08 Å^2 and allowance for anisotropic vibration of the seven atoms of the hexafluorophosphate ion reduced *R* to 0.0488. The six largest peaks in the electron density difference map of 1.6 to 0.7 e Å^{-3} were all within 1.2 Å of the lead atom. Refinement on 183 parameters was continued with 1827 reflections for which $|F_o| \geqslant 2\sigma(F_o)$ to give $R = 0.0444$, 0.0445 for the 1158 'even' planes and 0.0444 for the 513 'odd' planes. [An identical refinement with a weighting scheme $w = 1/(\sigma^2F_o + 0.001\,797\,F^2)$ yielded $R = 0.0435$, 0.0377 for 'even' and 0.0520 for 'odd' planes, and so we preferred the more uniform distribution given by unit weights.] The final *R* was 0.0566 for all 2225 planes, with the difference map showing peaks ranging from 1.56 to −0.80 e Å^{-3}. The six highest, in the range 1.56–0.63 e Å^{-3}, were all within 1.0 Å of the lead atom. Structure solution was carried out using SHELXTLPLUS on a MicroVax II computer.[6] Atomic coordinates are presented in Table 1 and selected bond lengths and angles in the co-ordination sphere in Table 2.

Additional material available from the Cambridge Crystallographic Data centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

We considered the synthesis of macrocycles of type **I** by the [2 + 2] template condensation of 2,6-bis[(2-aminoethyl)thiomethyl]pyridine L^2 with 2,6-pyridinedicarbaldehyde, followed

Table 1 Atomic coordinates ($\times 10^4$) for $[PbL^4(O_2CMe)][PF_6]$

Atom	*x*	*y*	*z*
Pb	0	−7 458(1)	0
S(1)	−3 588(7)	−7 837(4)	394(6)
C(2)	−3 573(29)	−6 947(14)	1 612(23)
C(3)	−3 392(27)	−6 091(14)	963(22)
N(4)	−2 285(22)	−6 010(11)	132(17)
C(5)	−2 007(31)	−5 225(17)	−346(25)
C(6)	−775(27)	−5 209(16)	−1 262(23)
S(7)	1 225(8)	−5 505(4)	−350(7)
C(8)	2 425(35)	−5 687(19)	−1 616(29)
C(9)	2 291(37)	−6 452(18)	−2 408(29)
N(10)	2 166(22)	−7 268(12)	−1 719(18)
C(11)	2 979(27)	−7 928(14)	−1 955(21)
C(12)	2 832(28)	−8 815(14)	−1 305(22)
N(13)	1 756(21)	−8 826(11)	−469(17)
C(14)	1 552(25)	−9 589(13)	117(21)
C(21)	3 685(31)	−9 508(16)	−1 628(25)
C(22)	3 430(35)	−10 297(19)	−1 060(27)
C(23)	2 325(21)	−10 384(18)	−179(25)
C(15)	373(26)	−9 602(14)	1 082(22)
N(16)	−408(20)	−8 934(11)	1 266(17)
C(17)	−1 547(23)	−8 937(13)	2 289(19)
C(18)	−3 282(32)	−8 750(17)	1 509(25)
C(31)	−4 218(31)	−5 311(15)	1 281(25)
C(32)	−3 812(32)	−4 504(17)	800(26)
C(33)	−2 728(31)	−4 473(17)	−30(25)
O(1)	2 368(18)	−7 436(11)	1 783(15)
O(2)	254(21)	−6 908(11)	2 405(17)
C(19)	1 706(25)	−7 122(15)	2 644(21)
C(20)	2 595(37)	−6 990(21)	4 000(30)
P	−2 413(9)	−8 200(5)	−3 886(7)
F(1)	−2 986(29)	−7 701(11)	−5 219(16)
F(2)	−2 571(27)	−9 075(11)	−4 717(19)
F(3)	−1 722(33)	−8 684(13)	−2 573(18)
F(4)	−2 258(35)	−7 362(12)	−3 032(20)
F(5)	−4 158(28)	−8 298(25)	−3 725(29)
F(6)	−684(28)	−8 102(24)	−4 102(32)

by the reduction of the tetraimine ligand L^1. Fenton and others have demonstrated the selective formation of [2 + 2] macrocycles related to **I** by the use of large metal ions such as lead(II), barium(II), silver(I) or lanthanides as templates,[2,7] and we initially considered that the use of metal ion size to control the formation of [2 + 2] as opposed to [1 + 1] products would be successful in this case. However, these previous studies have illustrated that hole-size is not an infallible guide to the selection of a metal ion for a specific template condensation, and a surprising number of examples of lead(II)-, strontium(II)- and barium(II)-directed condensations lead to [1 + 1] products. Furthermore, the number and type of donor atoms have a considerable influence upon the direction of the reaction over and above the simple constraints of hole-size. The introduction of flexibility into the macrocyclic framework renders the concepts of hole-size difficult to apply.

The desired precursor L^2 was prepared from 2,6-bis(hydroxymethyl)pyridine was converted to 2,6-bis(bromomethyl)pyridine by reaction with 48% hydrobromic acid, and typical yields in the range 50–60% were obtained.[4] Initial attempts to prepare L^2 by the reaction of 1 equivalent of 2,6-bis(bromomethyl)pyridine with 2 equivalents of $[HSCH_2CH_2NH_3]Cl$ in ethanol in the presence of 2 equivalents of KOH were unsuccessful. After boiling for 3.5 h a yellow solution containing solid KCl had been obtained. Removal of the inorganic salts and concentration *in vacuo* gave an orange oil. The IR spectrum of this oil suggested that it was a single compound, and the presence of strong absorptions at 1588 and 1572 cm^{-1} was strongly indicative of the presence of the 2,6-disubstituted pyridine. The EI mass spectrum of the compound exhibits a strong parent ion at *m/z* 360, which is in accord with the formation of the 16 membered-ring macrocycle L^3. The ^1H NMR spectrum of a $CDCl_3$ solution of the oil is also consistent with this formulation, and exhibits resonances for two non-equivalent pyridine rings [δ 7.63 (t), 7.64 (t), 7.23 (d), 7.64 (d)] and two multiplets at δ 3.82 and 2.78. The addition of a methanolic solution of $ZnCl_2$ to a methanol solution of L^3 resulted in the immediate precipitation of the complex $[ZnL^3(H_2O)][ZnCl_4]$ as a white solid. A strong absorption in the IR spectrum of this complex at 278 cm^{-1} is in accord with the formulation as a tetrachlorozincate salt. The FAB mass spectrum of the complex exhibited intense peaks at *m/z* 423 $\{[ZnL^3]^+\}$ and 459 $\{[ZnL^3(Cl)]^+\}$. The ^1H NMR spectrum of a CD_3SOCD_3 solution of the complex was sharp and well-resolved, and clearly indicated that the macrocyclic ligand L^3 was intact, and that the two pyridine rings were non-equivalent [δ 8.07 (t), 7.69 (t), 7.48 (d), 7.29 (d)]. The aliphatic protons were observed as sets of overlapping multiplets centred at δ 4.00 and 2.75. The complex is almost completely insoluble in water, acetone and acetonitrile, and only sparingly soluble in hot methanol. The addition of $[NH_4][PF_6]$ solution to the hot methanolic solution of the salt resulted in the precipitation of an off-white hexafluorophosphate salt. The ^1H NMR spectrum of a CD_3SOCD_3 solution was identical to that of a solution of the tetrachlorozincate salt. The FAB mass spectrum of the complex exhibited intense peaks at *m/z* 423 $\{[ZnL^3]^+\}$ and 569 $\{[ZnL^3(PF_6)]^+\}$, and the IR spectrum no longer exhibited the 278 cm^{-1} absorption assigned to the $[ZnCl_4]^{2-}$ anion. Microanalysis of this compound suggests that a formulation $[ZnL^3(H_2O)]Cl[PF_6]$ is appropriate.

The desired intermediate L^2 was obtained in good yield by a slight modification of the literature method involving the reaction of 1 equivalent of 2,6-bis(bromomethyl)pyridine with 4 equivalents of $[HSCH_2CH_2NH_3]Cl$ in methanol in the presence of 8 equivalents of Na(OMe).[3] The product was obtained as a yellow oil, with ^1H NMR and IR properties which matched those previously described. It appears that it is necessary to generate an excess of the thiolate species $H_2NCH_2CH_2S^-$ to prevent the formation of the macrocyclic ligand L^3. In our hands, the unmodified literature method gave an orange oil which consisted of a mixture of L^3 and L^2.

Upon heating L^2 with 2,6-pyridinedicarbaldehyde in the presence of silver(I) perchlorate in methanol a pale brown solution was obtained. Upon cooling, a small amount of brown solid was deposited leaving a clear yellow solution. Treatment of this solution with $[NH_4][PF_6]$ gave a yellow precipitate. The IR spectrum of this yellow solid showed no absorptions which could be assigned to unreacted carbonyl groups, but exhibited absorptions at 1654, 1588 and 1572 cm^{-1} assigned to imine functionalities and pyridine rings. The ^1H NMR spectrum of solutions of the complex in CD_3CN are broad and poorly resolved at ambient temperature. However, the ratio of aromatic to aliphatic protons is 1 : 2, as would be expected for a complex of the desired ligand L^1 or the [1 + 1] product L^4. No significant changes to the spectrum were noted upon warming or cooling the solution. The FAB mass spectrum of this yellow solid exhibited high intensity peaks at *m/z* 463 and 465 corresponding to $[AgL^4]^+$. No peaks to higher mass were observed. This strongly suggests that a complex of the [1 + 1] ligand L^4 has been formed instead of one with the desired [2 + 2] product L^1. Microanalysis of the complex is compatible with a formulation $[AgL^4][PF_6]$ for this yellow product.

As silver(I) was unsuccessful in acting as a template for the formation of the [2 + 2] product, we investigated some other cations with varying charge and size properties. Initially we considered the use of a slightly larger dication, and attempted the condensation in the presence of barium(II) (radius ≈ 1.35 Å). The reaction of L^2 with 2,6-pyridinedicarbaldehyde in methanol in the presence of barium carbonate gave a transient orange colouration, after which a white solid was precipitated from the reaction mixture. This material had a very broad IR spectrum, and appeared to be largely polymeric and was not further investigated. No further tractable

Table 2 Bond lengths (Å) and angles (°) for $[PbL^4(O_2CMe)][PF_6]$

Pb–N(10)	2.733(20)	Pb–N(13)	2.630(17)	N(13)–C(14)	1.324(26)	C(14)–C(23)	1.422(34)
Pb–N(16)	2.630(17)	Pb–O(1)	2.440(14)	C(14)–C(15)	1.503(33)	C(21)–C(22)	1.359(38)
Pb–O(2)	2.548(17)	Pb–S(1)	3.145(6)	C(22)–C(23)	1.396(41)	C(15)–N(16)	1.236(27)
Pb–S(7)	3.172(6)	Pb–N(4)	2.928(17)	N(16)–C(17)	1.523(28)	C(17)–C(18)	1.554(31)
S(1)–C(2)	1.827(23)	S(1)–C(18)	1.776(26)	C(31)–C(32)	1.381(36)	C(32)–C(33)	1.338(40)
C(2)–C(3)	1.473(31)	C(3)–N(4)	1.359(31)	O(1)–C(19)	1.207(28)	O(2)–C(19)	1.239(27)
C(3)–C(31)	1.433(33)	N(4)–C(5)	1.320(31)	C(19)–C(20)	1.458(35)		
C(5)–C(6)	1.500(37)	C(5)–C(33)	1.354(37)				
C(6)–S(7)	1.822(22)	S(7)–C(8)	1.779(32)	P–F(2)	1.565(19)	P–F(1)	1.550(18)
C(8)–C(9)	1.403(40)	C(9)–N(10)	1.433(34)	P–F(4)	1.530(20)	P–F(3)	1.542(19)
N(10)–C(11)	1.255(29)	C(11)–C(12)	1.510(30)	P–F(6)	1.506(26)	P–F(5)	1.502(26)
C(12)–N(13)	1.337(31)	C(12)–C(21)	1.342(34)				

N(10)–Pb–N(13)	61.1(5)	N(10)–Pb–N(16)	123.7(5)	Pb–N(10)–C(11)	118.5(15)	C(9)–N(10)–C(11)	120.6(22)
N(13)–Pb–N(16)	62.6(6)	N(10)–Pb–O(1)	85.9(5)	N(10)–C(11)–C(12)	122.6(22)	C(11)–C(12)–N(13)	113.7(19)
N(13)–Pb–O(1)	74.8(5)	N(16)–Pb–O(1)	78.9(5)	C(11)–C(12)–C(21)	120.2(22)	N(13)–C(12)–C(21)	126.0(21)
N(10)–Pb–O(2)	128.2(5)	N(13)–Pb–O(2)	118.2(5)	Pb–N(13)–C(12)	124.1(13)	Pb–N(13)–C(14)	119.3(14)
N(16)–Pb–O(2)	79.0(5)	O(1)–Pb–O(2)	50.5(5)	C(12)–N(13)–C(14)	116.5(18)	N(13)–C(14)–C(23)	123.2(22)
N(10)–Pb–S(1)	148.2(4)	N(13)–Pb–S(1)	116.9(4)	N(13)–C(14)–C(15)	116.9(18)	C(23)–C(14)–C(15)	119.9(19)
N(16)–Pb–S(1)	64.9(4)	O(1)–Pb–S(1)	125.4(4)	C(12)–C(21)–C(22)	117.2(26)	C(21)–C(22)–C(23)	121.5(27)
O(2)–Pb–S(1)	82.2(4)	N(10)–Pb–S(7)	64.5(4)	C(14)–C(23)–C(22)	115.4(25)	C(14)–C(15)–N(16)	120.6(19)
N(13)–Pb–S(7)	121.0(4)	N(16)–Pb–S(7)	156.9(4)	Pb–N(16)–C(15)	120.5(15)	Pb–N(16)–C(17)	118.8(11)
O(1)–Pb–S(7)	80.4(4)	O(2)–Pb–S(7)	80.0(4)	C(15)–N(16)–C(17)	120.6(18)	N(16)–C(17)–C(18)	106.9(16)
S(1)–Pb–S(7)	121.2(2)	N(10)–Pb–N(4)	117.3(5)	S(1)–C(18)–C(17)	119.0(18)	C(3)–C(31)–C(32)	119.7(25)
N(13)–Pb–N(4)	171.1(5)	N(16)–Pb–N(4)	118.4(5)	C(31)–C(32)–C(33)	119.1(25)	C(5)–C(33)–C(32)	119.7(25)
O(1)–Pb–N(4)	114.1(5)	O(2)–Pb–N(4)	70.2(5)	Pb–O(1)–C(19)	97.3(12)	Pb–O(2)–C(19)	91.1(13)
S(1)–Pb–N(4)	59.2(4)	S(7)–Pb–N(4)	62.0(4)	O(1)–C(19)–O(2)	121.1(19)	O(1)–C(19)–C(20)	120.8(21)
Pb–S(1)–C(2)	93.1(7)	Pb–S(1)–C(18)	100.7(8)	O(2)–C(19)–C(20)	118.2(22)		
C(2)–S(1)–C(18)	99.4(11)	S(1)–C(2)–C(3)	109.8(16)				
C(2)–C(3)–N(4)	119.3(20)	C(2)–C(3)–C(31)	122.4(22)	F(1)–P–F(3)	176.0(15)	F(1)–P–F(2)	87.7(10)
N(4)–C(3)–C(31)	118.0(20)	Pb–N(4)–C(3)	118.6(13)	F(1)–P–F(4)	94.1(10)	F(2)–P–F(3)	92.6(10)
Pb–N(4)–C(5)	120.1(13)	C(3)–N(4)–C(5)	119.4(20)	F(3)–P–F(4)	85.7(11)	F(2)–P–F(4)	178.1(12)
N(4)–C(5)–C(6)	115.1(22)	N(4)–C(5)–C(33)	124.0(25)	F(2)–P–F(5)	88.9(16)	F(1)–P–F(5)	89.0(15)
C(6)–C(5)–C(33)	120.9(23)	C(5)–C(6)–S(7)	110.5(16)	F(4)–P–F(5)	90.6(18)	F(3)–P–F(5)	95.0(16)
Pb–S(7)–C(6)	90.0(7)	Pb–S(7)–C(8)	99.7(10)	F(2)–P–F(6)	90.0(16)	F(1)–P–F(6)	89.2(16)
C(6)–S(7)–C(8)	104.7(12)	S(7)–C(8)–C(9)	122.7(23)	F(4)–P–F(6)	90.6(18)	F(3)–P–F(6)	86.8(16)
C(8)–C(9)–N(10)	116.2(25)	Pb–N(10)–C(9)	120.8(16)			F(5)–P–F(6)	177.9(18)

material could be precipitated from the mother-liquor with $[NH_4][PF_6]$.

In an attempt to force the formation of a [2 + 2] product by introducing sterically demanding substituents, we investigated the reaction of L^2 with 2,6-diacetylpyridine in the presence of $Pb(NCS)_2$ (radius $Pb^{2+} \approx 1.2$ Å) in MeOH–MeCN. This resulted in the formation of a pale orange solution from which an orange-brown solid was obtained upon concentration. The IR spectrum of the solid exhibited two strong absorptions at 2071 and 2012 cm^{-1} assigned to thiocyanate ligands and no carbonyl absorptions. An absorption at 1640 cm^{-1} is characteristic of a conjugated imine. The complex is not soluble in methanol, acetonitrile or chlorinated solvents, but is sparingly soluble in CD_3SOCD_3. The ^1H NMR spectrum of a solution of the complex in CD_3SOCD_3 clearly demonstrates the presence of two pyridine environments [ring A, δ 8.57 (AB_2); ring B, δ 7.83 (t), 7.4 (d)]. The methylene protons are observed as two broad, unresolved resonances at δ 4.2 and 3.2 in a ratio of 2 : 1, and the methyl groups as a sharp singlet at δ 2.6. The FAB mass spectrum of the solid exhibits intense peaks at *m*/*z* 649 and 591 which are assigned to $[PbL^5(NCS)]^+$ and $[PbL^5]^+$ respectively. These data strongly suggest that only complexes of the [1 + 1] macrocyclic ligand L^5 rather than the [2 + 2] ligand are obtained in the template reaction with lead(II).

The reaction of L^2 with 2,6-pyridinedicarbaldehyde in the presence of $Pb(NCS)_2$ in MeOH–MeCN resulted in the formation of an intense yellow solution. After cooling and filtration to remove small amounts of unreacted lead salts, the yellow solution was allowed to evaporate slowly and a fine yellow powder was precipitated. The IR spectrum of the solid exhibited strong absorptions at 2032 and 2015 cm^{-1} assigned to co-ordinated thiocyanate and also an absorption at 2076 cm^{-1} corresponding to ionic thiocyanate. No absorptions due to carbonyl groups were observed. An absorption at 1654 cm^{-1} is characteristic of a conjugated imine, whilst bands at 1585 and 1453 cm^{-1} are assigned to pyridine ring modes. The complex is sparingly soluble in CD_3SOCD_3. The ^1H NMR spectrum of a solution of the complex in CD_3SOCD_3 clearly demonstrates the presence of two pyridine environments [ring A, δ 8.58 (t), 8.28 (d); ring B, δ 7.86 (t), 7.5 (d)] with the similarity to the [1 + 1] product obtained from the reaction with 2,6-diacetylpyridine being marked. A sharp singlet at δ 9.4 as assigned to an imine proton. The methylene protons are observed as three resonances at δ 4.3 (s, pyridyl-CH_2S, 4 H), 4.27 (m, CH_2CH_2S, 4 H) and 3.2 (m, CH_2CH_2S, 4 H). The FAB mass spectrum of the solid exhibits an intense peak at *m*/*z* 622 corresponding to $[PbL^4]^+$. Once again, this is indicative of the formation of the [1 + 1] product L^4 rather than the desired [2 + 2] ligand.

In an attempt to further control the reaction, we investigated the condensations in the presence of lead(II) acetate. The reaction of L^2 with 2,6-pyridinedicarbaldehyde in the presence of lead(II) acetate in MeOH–MeCN resulted in the formation of a clear red solution. After concentration and filtration to remove small amounts of unreacted lead salts, the solution was treated with $[NH_4][PF_6]$ to give an orange-brown precipitate. The IR spectrum of this compound closely resembled that of the yellow product obtained from the condensation in the presence of lead(II) thiocyanate, except that the thiocyanate absorptions were absent and new bands at 1569 and 1413 cm^{-1} (co-ordinated acetate) and 843 and 559 cm^{-1} (hexafluorophosphate) were observed. The ^1H NMR spectrum of a solution of the complex in CD_3CN (Fig. 1) differs slightly from that of the thiocyanate complex in CD_3SOCD_3, and clearly demonstrates the presence of two pyridine environments [ring A, δ 8.39 (t), 8.03 (d); ring B, δ 7.77 (t), 7.4 (d)] and an imine (δ 9.07). A sharp singlet at δ 1.52 is assigned to an acetate group. The aliphatic protons are observed as two broad, unresolved resonances at δ 4.3 (CH_2S, m) and δ 3.2 (CH_2N, m). The positive ion FAB mass spectrum exhibited high intensity peaks at *m*/*z* 563 and 623 corresponding to $[PbL^4]^+$ and $[PbL^4(O_2CMe)]^+$. No peaks assigned to lead complexes of L^1 were observed. Microanalysis of the complex is in accord with the fomulation $[PbL^4(O_2CMe)][PF_6]$. All of the experiments described above suggest that the products of the condensation of L^2 are [1 + 1] macrocyclic species rather than the [2 + 2] macrocycle expected. However, the ^1H NMR data and microanalysis results will not distinguish between [1 + 1] and [2 + 2] products, and we have previously found that mass spectroscopy is not an infallible tool in assigning stoichiometry to macrocyclic products. In order to resolve this ambiguity we have determined the crystal and molecular structure of the lead complex.

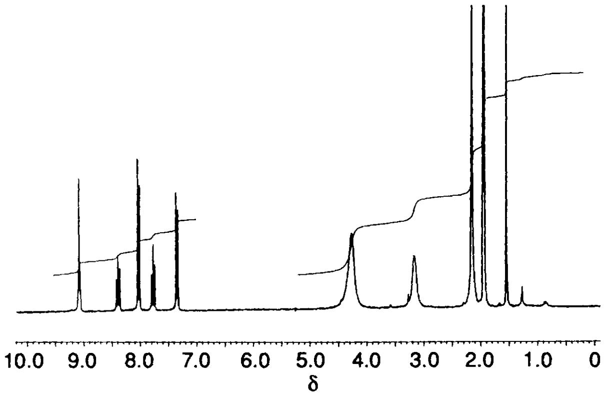


Fig. 1 Proton NMR spectrum of a CD_3CN solution of $[PbL^4(O_2CMe)][PF_6]$

Suitable single crystals of the complex were obtained by diffusion of diethyl ether vapour into an acetonitrile solution of the complex, and the crystal and molecular structure of the complex is shown in Fig. 2. The compound is a monolead complex of the [1 + 1] macrocycle L^4. The molecule consists of a co-ordinated acetatolead(II) with a definite, but weak, interaction with a hexafluorophosphate ion, as shown in Fig. 2. The difference between the Pb–O distances, 2.440(14) and 2.548(17) Å, to the acetate is not chemically significant. Examples of bidentate acetate ligands co-ordinated to lead(II) are known in which the acetate is symmetrical with Pb–O and C–O bond lengths both equivalent, and in which the bonding mode is unsymmetrical with Pb–O lengths in the ranges 2.42–2.45(1) and 2.65–2.74(1) Å.[8]

Of the six heteroatoms of the 18-membered ring, five are certainly co-ordinated to the lead. The plane of the seven atoms N(10), C(11), C(12), N(13), C(14), C(15) and N(16) essentially includes the lead atom (which is −0.050 Å out of the plane), but not N(4) [−0.56(2) Å], S(1) [−1.759(6) Å] or S(7) [+1.095(6) Å], where the positive direction is defined in the direction of the acetato group. The distances Pb–N(10) and Pb–N(16) differ by 0.103 Å, which, with an e.s.d. of 0.026 Å, is statistically significant or, more probably, an indication that the errors are underestimated. These lengths are in the range usually found for lead(II) imine complexes,[9] while the distance Pb–N(13) is slightly longer than the usually observed $Pb–N_{pyridine}$ distances.[9,10] The distance Pb···N(4) of 2.928(17) Å is considerably longer than the unequivocal Pb–N bonds. The Pb–S bond lengths are equal and comparable with those in two of the three compounds containing $Pb–S_{thioether}$ bonds located in the files of the Cambridge Crystallographic Data Centre. Lead complexes with 1,4,7-trithiacyclononane and 1,5-dithiacyclo-

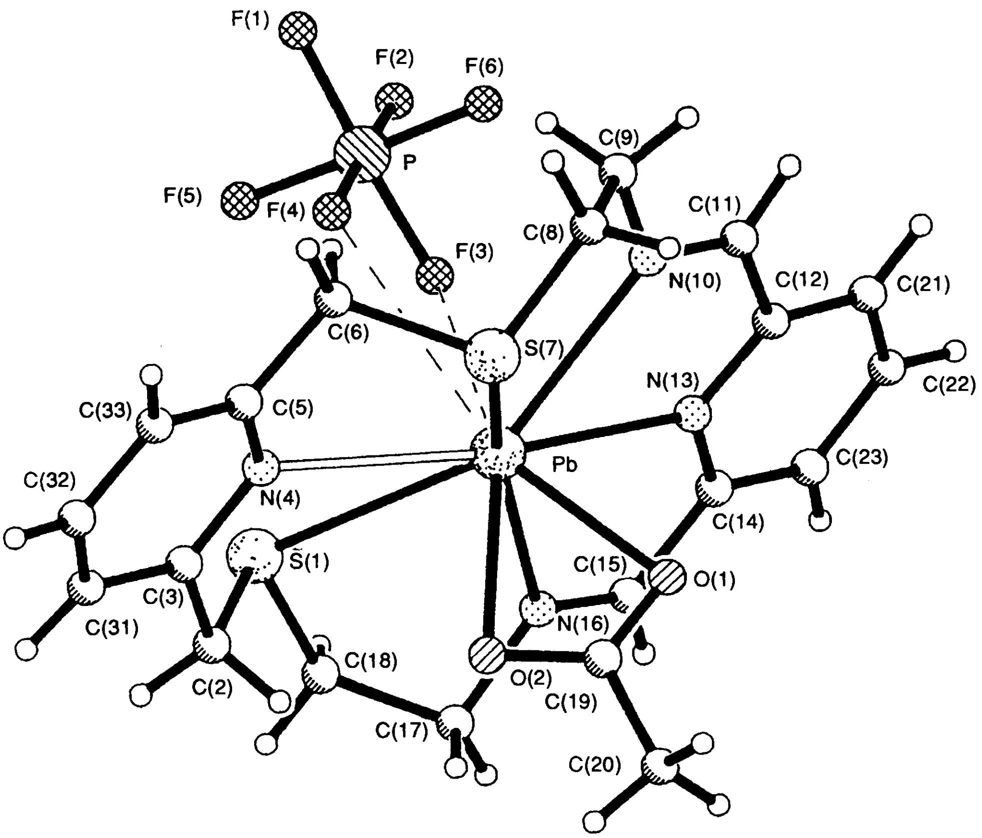


Fig. 2 The complex $[PbL^4(O_2CMe)][PF_6]$ as found in the crystal showing the designations of the atoms. Bond lengths (Å) are Pb–O(1) 2.44(1), Pb–O(2) 2.55(2), Pb–N(10) 2.73(2), Pb–N(13) 2.63(2), Pb–S(1) 3.145(6), Pb–S(7) 3.172(6), additional contacts are Pb···N(4) 2.93(2), Pb···F(3) 3.32(2), Pb···F(4) 3.32(2). The 2,6-bis(iminomethyl)pyridine unit is planar, torsion angles in the rest of the macrocyclic ring run −119° for C(15)–N(16)–C(17)–C(18) through −50, −78, 166, −44, −173, 180, −65, 168, −76, −43 to −135 for C(8)–C(9)–N(10)–C(11)

octan-3-ol give Pb–S distances in the range 3.015(5)–3.209(3) Å.[11] The only structurally characterized macrocyclic complex of lead with a mixed NS donor ligand contains a seven-coordinate metal centre and exhibits a Pb–N distance of 2.55(2) Å and very short Pb–S distances of 2.860(5) Å.[12] In the present work the lead is 'nested' within the macrocyclic cavity, whereas in the other compounds reported it is 'perched' above the cavity.

Bond lengths in the ligand have an e.s.d. ranging from 0.02 to 0.04 Å and, except for 1.40 Å for C(8)–C(9) which may be affected by disorder, are within the values expected for the bond types shown in conventional structural diagrams.

Correction for the libration of the hexafluorophosphate anion suggested ($R = 0.098$) that the rigid-body approximation is reasonable and the corrected values for the P–F bond lengths average 1.63 Å compared with 1.54 Å for the uncorrected ones. The corrected values agree with those obtained similarly by correction of room-temperature measurements, in a more favourable case (e.s.d. 0.009 Å),[13] while numerous low-temperature measurements give values in the range 1.58–1.62 Å.

The distances for Pb–F(3) and Pb–F(4) suggest that there is a weak interaction between the lead(II) and the hexafluorophosphate anion. The crystal consists of these ion pairs packed with the shortest contacts being several F···C of 3.3 Å and S(1)···C(11) along the *a* axis at 3.4 Å. The volume per non-hydrogen atom is 17.56 Å^3.

Although mononuclear lead(II) complexes derived from imine Schiff-base macrocycles with N_x, N_xO_y and N_xS_y donor atom sets have been described, the crystal structure of the complex presented here represents only the second reported structure of a lead(II) complex with a macrocyclic ligand incorporating both nitrogen and sulfur donor atoms. An interesting feature of this structure is that the lead is surrounded by both hard and soft donor atoms, and that the soft lead ion binds preferentially to the hard end of the macrocyclic ligand.

These results reinforce the caveat that matching up macrocyclic cavity sizes with template ion sizes does not always result in the assembly of the anticipated macrocycle!

Acknowledgements

We thank the Foundation for Research Development, Republic of South Africa, for support (to C. S.), the SERC, the Royal Society of Great Britain and the Isaac Newton Trust for funds towards the purchase of diffractometers and spectrometers. The Cambridge Structural Database System was implemented on the University of London Computer by A. Quick.

References

1 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461; D. E. Fenton, *Pure Appl. Chem.*, 1986, **58**, 1437.

2 *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979; L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.

3 E. C. Constable and J. Lewis, *J. Organomet. Chem.*, 1983, **254**, 105; E. C. Constable, P. J. Stotereau and M. G. B. Drew, *Inorg. Chim. Acta*, 1988, **145**, 3; E. C. Constable, P. J. Stotereau and M. G. B. Drew, *Polyhedron*, 1989, **8**, 2749; E. C. Constable, A. C. King, C. A. Palmer and P. R. Raithby, *Inorg. Chim. Acta*, 1991, **184**, 43; E. C. Constable and P. R. Raithby, *Inorg. Chim. Acta*, 1991, **183**, 21; E. C. Constable, C. A. Palmer and D. A. Tocher, *Inorg. Chim. Acta*, 1990, **176**, 57.

4 E. C. Constable, J. Lewis, V. E. Marquez and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1986, 1747; E. C. Constable, A. C. King, V. E. Marquez and C. A. Palmer, *Inorg. Chim. Acta*, in the press.

5 F. Teixidor, L. Escriche, J. Casabo, E. Molins and C. Miravitlles, *Inorg. Chem.*, 1986, **25**, 4060.

6 G. M. Sheldrick, SHELXTLPLUS, University of Göttingen, 1986.

7 See, for example, A. Bashall, M. McPartlin, B. P. Murphy, D. E. Fenton, S. J. Kitchen and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1990, 505; H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton and G. Rossi, *J. Chem. Soc., Dalton Trans.*, 1990, 1271; D. E. Fenton, S. J. Kitchen, C. M. Spencer, P. A. Vigato and S. Tamburini, *J. Chem. Soc., Dalton Trans.*, 1987, 55; B. P. Murphy, J. Nelson, S. M. Nelson, M. G. B. Drew and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1987, 123; D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, 1988, **17**, 69; *Inorg. Chim. Acta*, 1987, **139**, 39, 57 and refs. therein.

8 R. G. Bryant, V. P. Chacko nd M. C. Etter, *Inorg. Chem.*, 1984, **23**, 3580; R. J. Rajaram and J. K. M. Rao, *Z. Kristallogr.*, 1982, **160**, 225; P. G. Harrison and A. T. Steel, *J. Organomet. Chem.*, 1982, **239**, 105; P. G. Jones, R. Schelbach, E. Schwarzmann and C. Thöne, *Acta Crystallogr., Sect. C*, 1988, **44**, 1198.

9 A. Bashall, M. McPartlin, B. P. Murphy, D. E. Fenton, S. J. Kitchen and A. J. Smith, *J. Chem. Soc., Dalton Trans.*, 1990, 505; J. Nelson, B. P. Murphy, M. G. B. Drew, P. C. Yates and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1988, 1001; B. P. Murphy, J. Nelson, S. M. Nelson, M. G. B. Drew and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1987, 123; H. Adams, N. A. Bailey, D. E. Fenton, R. J. Good, R. Moody and C. O. Rodriguez-Barbarin, *J. Chem. Soc., Dalton Trans.*, 1987, 207; D. H. Cook, D. E. Fenton, M. G. B. Drew, A. Rodgers, H. McCann and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1979, 414; M. Tadokoro, H. Okawa, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1991, 1657; S. S. Tandon and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1989, 19; A. E. Koziol, R. C. Palenik and G. J. Palenik, *Inorg. Chim. Acta.*, 1986, **116**, L51; J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers and S. M. Nelson, *Inorg. Chim. Acta*, 1978, **30**, L313; M. G. B. Drew, A. Rodgers, M. McCann and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1978, 415; M. G. B. Drew, J. de O. Cabral, M. F. Cabral, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 1033; N. A. Bailey, D. E. Fenton, I. T. Jackson, R. Moody and C. R. de Barbarin, *J. Chem. Soc., Chem. Commun.*, 1983, 1463; M. G. B. Drew and S. M. Nelson, *Acta Crystallogr., Sect. B*, 1979, **35**, 1594; I. W. Nowell, *Acta Crystallogr., Sect. B*, 1979, **35**, 1891.

10 L. M. Engelhardt, B. M. Furphy, J. McB. Harrowfield, J. M. Patrick and A. H. White, *Inorg. Chem.*, 1989, **28**, 1410.

11 M. M. Olmstead, R. M. Kessler, H. Hope, M. D. Yanuck and W. K. Musker, *Acta Crystallogr., Sect. C*, 1987, **43**, 1890; H.-J. Kuppers, K. Wieghardt, B. Nuber and J. Weiss, *Z. Anorg. Allg. Chem.*, 1989, **577**, 155.

12 P. Hoffmann, F.-J. Hermes and R. Mattes, *Z. Naturforsch., Teil B*, 1988, **43**, 567.

13 N. Thoruf, G. Rindorf. H. Soling and K. Bechgaard, *Acta Crystallogr., Sect. B*, 1981, **37**, 1236.

Received 24*th August* 1992; *Paper* 2/04565F