

Binucleating N₆ 24- and 26-Membered Macrocyclic Ligands. Part 1. Dilead Complexes: X-Ray Crystal Structure Determination of a Macrocyclic Dilead Complex containing Nitrogen-only Bridging Thiocyanate *

Brian P. Murphy and Jane Nelson

The Open University, Milton Keynes MK7 6AA


S. Martin Nelson

Department of Chemistry, Queen's University, Belfast BT9 5AG

Michael G. B. Drew and Paul C. Yates

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The relatively restricting macrocycle 8,14,22,28-tetramethyl-9,13;23,27-dinitrilo-1,7,15,21-tetra-aza-cyclo-octacos-7,9,11,14,21,23,25,28-octaene (L¹) co-ordinates to two lead atoms in such a way that the preferred bonding mode for bridging thiocyanate is a single-atom N only bridge. Infrared absorption in the range 1 950—1 970 cm⁻¹ is observed with mono-, bis-, and tetra-thiocyanato dilead complexes of this ligand. X-Ray structural analysis has been carried out on the tetrathiocyanato complex Pb₂L¹(NCS)₄ and confirms the N only bridge, the first example of a

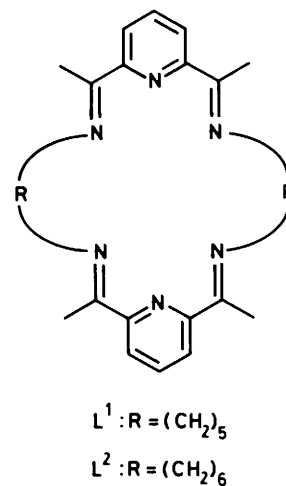
 NCS linkage. Spectroscopic evidence suggests that dilead thiocyanato complexes of a larger similar macrocycle (containing two more methylenes) may have a weakly bonded N only bridge, which is not retained on anion exchange. These macrocycles seem likely to generate binuclear transition metal complexes with interesting properties.

One reason for the current interest in macrocyclic binuclear complexes whose metal centres are bridged by exogenous (*i.e.* non-macrocyclic) ligands is the hope of observing unusual binding of the bridging substrate. In earlier work^{1,2} with other binucleating systems, we have established that exogenous bridging donors are most likely to be accommodated where (a) the macrocycle is either small enough or flexible enough to allow an appropriate intermetallic distance, and (b) the co-ordination requirements of the metal ion are not satisfied by the macrocyclic donors. In particular it is important that less than four equatorial donors should be offered by the macrocycle.

The macrocycles L¹ and L², examined in the present study, offer three equatorial donors to each metal ion, leaving a fourth equatorial site to be filled by a non-macrocyclic donor. A certain degree of flexibility is expected in the (CH₂)_n chain, suggesting that bridging ligands between 1 and 3 atoms in length could be accommodated to extend or complete the co-ordination requirements of the metal ion. With thiocyanate as bridging substrate, the options available are (a) the 'normal' long -NCS- bridge, or (b) the single-atom, N only or S only bridge.

Results and Discussion

Template reaction of the amines 1,5-diaminohexane and 1,6-diaminohexane with 2,6-diacetylpyridine (dap) on Pb(NCS)₂ yields respectively the 24- and 26-membered double macrocycles L¹ and L² by (2 + 2) condensation. The products of these template reactions analysed to the stoichiometry Pb₂L(NCS)₄, and were too insoluble for measurement of solution properties such as conductivity or ¹H n.m.r. spectra. These measurements, however, could be made on the sparingly soluble tetra-perchlorates (see Tables 1 and 2). The weak ¹H n.m.r. spectrum obtained was consistent with Schiff-base condensation. Formation of the 24- or 26-membered 'double' macrocycle was



confirmed for L¹ by an X-ray crystallographic structure determination, and for L² by borohydride reduction, the product of which gave a mass spectral molecular ion peak, M⁺, at *m/e* = 494.

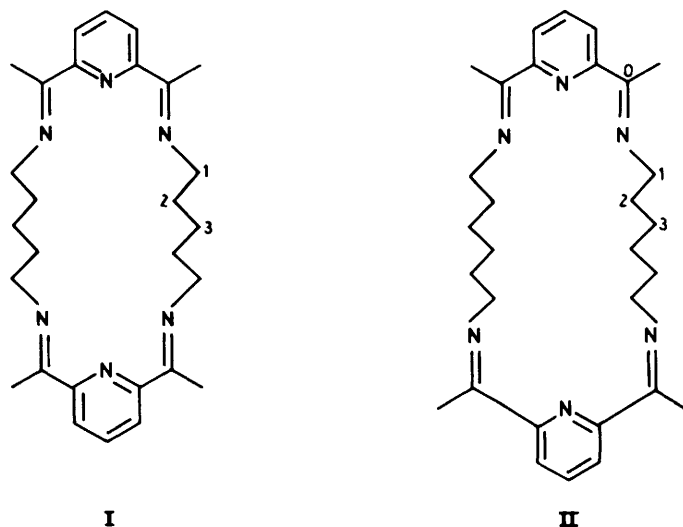
The template reaction products Pb₂L(NCS)₄ show complex i.r. spectra (Figure 1) in the ν_{NCS} region, indicating that thiocyanate exists in each of these complexes in several different co-ordination environments. Model exercises suggest that both L¹ and L² are large enough to accommodate a pair of lengthwise -NCS- bridges between the co-ordinated lead ions. However, the unusually low ν_{asym}(NCS) i.r. frequency observed for Pb₂L¹(NCS)₄ cannot be explained on the basis of lengthwise bridges only. The most intense feature in the i.r. spectrum of this complex is the broad band centred at 1 970 cm⁻¹. Appearance of ν_{asym}(NCS) below 2 000 cm⁻¹ is unusual and correlates, in the few cases where it has been reported³⁻⁵ with a single-atom (>N only) bridging role for the thiocyanate ligand. An X-ray crystallographic structural analysis was carried out (see next

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

section) to confirm the existence of the single-atom bridge in this complex. This analysis also revealed the presence of a second thiocyanate ion between, but remote from, the lead centres, which is best considered unco-ordinated. We attribute the i.r. frequency at $2\ 084\ \text{cm}^{-1}$, close to the free-ion value, to this ionic or weakly bonded thiocyanate group. The remaining ν_{NCS} frequencies at $2\ 041$ and $2\ 019\ \text{cm}^{-1}$ are then assigned to terminally S-bonded Pb-SCN groups.

Without the benefit of X-ray structural analysis, it is not easy to assign the various $\nu_{\text{asym}}(\text{NCS})$ frequencies for $\text{Pb}_2\text{L}^2(\text{NCS})_4$. The highest frequency, least intense absorption at *ca.* $2\ 085\ \text{cm}^{-1}$, may well correspond to a long -NCS- bridge, while the strongest feature, at $2\ 063\ \text{cm}^{-1}$, probably arises from terminally S-bonded Pb-SCN. It is not clear whether the lowest frequency absorption at $2\ 006\ \text{cm}^{-1}$ derives from terminal -SCN or from an -N only bridge, somewhat longer and weaker in this

Table 1. ^1H N.m.r. spectra^a of complexes of L^1 and L^2



$\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$ (structure I)^b

$\delta/\text{p.p.m.}$	R.i.	Assignment
8.35(m)	3	'pyridine' H
4.01(t)	4	H^1
2.43(s)	6	methyl H
2 ^d	—	H^3
1.7(cm)	4	H^2

$\text{Pb}_2\text{L}^2(\text{ClO}_4)_4$ (structure II)^b

$\delta/\text{p.p.m.}$	R.i.	Assignment
8.55(m)	3	'pyridine' H
4.02(t)	4	H^1
2.53(s)	6	methyl H
1.6(br m)	4	H^2 or H^3
1.2(m)	4	H^2 or H^3

Hydrogenated free ligand H_3L^2 (structure II)^c

$\delta/\text{p.p.m.}$	R.i.	Assignment
7.58(m)	3	'pyridine' H
3.73(m)	2	H^0
2.36(m)	6	$\text{NH} + \text{H}^1$
1.36(br m)	8	$\text{H}^2 + \text{H}^3$
1.19(s)	6	methyl H

^a R.i. = relative intensity; s = singlet, m = multiplet, cm = complex multiplet, br m = broad multiplet, t = triplet. ^b In CD_3CN . ^c In CDCl_3 ; H^0 are the protons from the hydrogenation. ^d Mainly obscured by solvent.

Table 2. Analytical, i.r. (cm^{-1}), and conductance data

Complex	Colour	Analysis ^a (%)			$\Lambda^b/\text{S cm}^2\ \text{mol}^{-1}$	$\nu_{\text{asym}}(\text{NCS})$	$\nu(\text{C}=\text{N})$	$\nu_3(\text{ClO}_4^-)$	$\nu_4(\text{ClO}_4^-)$
		N	C	H					
$\text{Pb}_2\text{L}^1(\text{NCS})_4$	Yellow	12.4 (12.7)	34.7 (34.8)	3.7 (3.5)	insol.	2 084s, 2 041s, 2 019s, 1 970s	1 636m		
$\text{Pb}_2\text{L}^2(\text{NCS})_4$	Yellow	11.6 (12.4)	35.5 (36.0)	3.7 (3.7)	insol.	2 085s, 2 063s, 2 006s	1 635m		
$\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{ClO}_4)_2$	Primrose	9.4 (9.4)	30.1 (30.3)	3.2 (3.2)	insol.	2 090s, 1 965s	1 640m	1 090s, br, 1 050br (sh)	628m, 622m
$\text{Pb}_2\text{L}^1(\text{NCS})(\text{ClO}_4)_3$	Cream	7.7 (8.0)	28.7 (28.3)	3.1 (3.1)	520 ^c	1 947s	1 645m	1 130s, 1 090s, 1 035s	628m, 622m, 617m
$\text{Pb}_2\text{L}^2(\text{NCS})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$	White	7.2 (7.6)	28.7 (28.8)	3.2 (3.4)	461 ^c	2 085s	1 642m	1 090s, br	625m
$\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{NO}_3)_2$	Cream	12.9 (12.6)	32.2 (32.3)	3.5 (3.4)		1 990ms	1 638m		
$\text{Pb}_2\text{L}^1(\text{NCS})_2\text{Cl}_2$	Primrose	11.5 (11.3)	36.1 (36.4)	4.1 (3.9)		2 009ms	1 642m		
$\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$	White	6.0 (6.6)	26.0 (26.5)	3.1 (3.0)	480		1 643m	1 090s, br	625m
$\text{Pb}_2\text{L}^2(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	White	6.3 (6.4)	27.5 (27.4)	3.4 (3.4)	460		1 634m	1 030s, 1 090s, br	617m, 625m

^a Calculated values in parentheses. ^b Concentration $10^{-3}\ \text{mol dm}^{-3}$ in MeCN; insol. = insoluble. ^c Decomposition: initial rapid change observed.

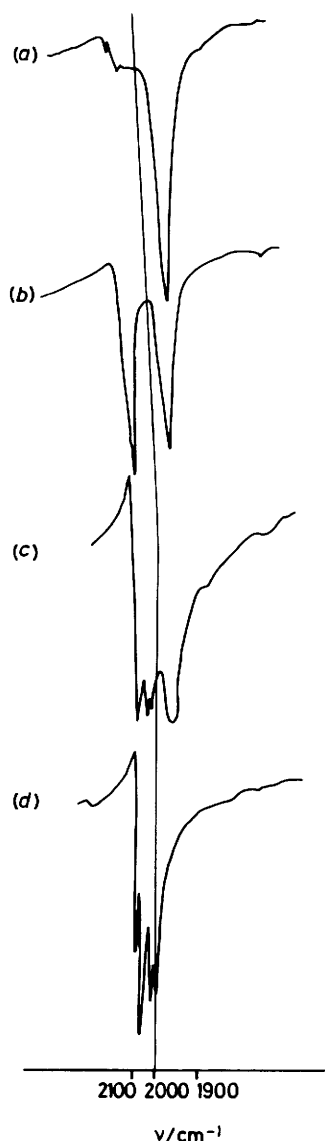


Figure 1. Infrared spectra in the $\nu_{\text{asym}}(\text{NCS})$ stretching region: (a) $\text{Pb}_2\text{L}^1(\text{NCS})(\text{ClO}_4)_3$, (b) $\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{ClO}_4)_2$, (c) $\text{Pb}_2\text{L}^1(\text{NCS})_4$, (d) $\text{Pb}_2\text{L}^2(\text{NCS})_4$

case because of the larger distance between the lead ions co-ordinated by the 26-membered macrocycle.

Treatment of the thiocyanato complexes with AgClO_4 results in replacement of thiocyanate by perchlorate. (Characterisation of the resulting complexes is reported in Table 2.) In the case of L^1 , replacement can be carried out sequentially, substituting perchlorate for two, three, or four of the thiocyanate groups, according to the stoichiometry used. An unusually low i.r. $\nu_{\text{asym}}(\text{NCS})$ frequency persists throughout the series, suggesting that the >N only bridging thiocyanate is more strongly co-ordinated by lead in these complexes than the other (terminal or unco-ordinated) thiocyanates.

Infrared spectra of the perchlorate groups in this series of complexes are also informative. In the tetraperchlorate $\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$ single broad absorptions are observed for both ν_3 and ν_4 ClO_4^- modes. As it seems unlikely that lead is only three-co-ordinate in the complex, the splitting of these bands due to co-ordinated perchlorate must be masked by the broad unsplit absorption of ionic perchlorate.

However, in the monothiocyanato complex $\text{Pb}_2\text{L}^1(\text{NCS})$ -

$(\text{ClO}_4)_3$, both ν_3 and ν_4 perchlorate modes are split into three components each, while the normally forbidden ν_2 mode appears as a medium intensity band at 918 cm^{-1} . These splittings suggest C_{2v} symmetry for at least one of the ClO_4^- groups resulting from either a chelating or bridging role for the ion. It seems possible that one ClO_4^- acts as a second bridge between the lead ions.

$\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{ClO}_4)_2$ shows two well separated $\nu_{\text{asym}}(\text{NCS})$ frequencies and a lesser splitting of ClO_4^- ν_3 and ν_4 into two components, which suggests that the lead centres are bridged by thiocyanate in both 'long' and 'short' modes with ClO_4^- being co-ordinated in monodentate fashion.

Where thiocyanate was partly replaced by more strongly co-ordinating anions such as nitrate or chloride, the monothiocyanato complex was not obtained. The $\nu_{\text{asym}}(\text{NCS})$ frequency observed for the bis-thiocyanato complexes $\text{Pb}_2\text{L}^1(\text{NCS})_2\text{X}_2$ ($\text{X} = \text{Cl}$ or NO_3) was ca. 30 cm^{-1} higher, at 2009 and 1990 cm^{-1} respectively, than in the case of $\text{X} = \text{ClO}_4^-$. An >N only thiocyanate bridge is still a possible, though not definite, assignment of these frequencies.

The monothiocyanato complex of L^2 , $\text{Pb}_2\text{L}^2(\text{NCS})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ has a normal $\nu_{\text{asym}}(\text{NCS})$ frequency (at 2085 cm^{-1}) which can be explained either by terminal N-co-ordination or a long $-\text{NCS}-$ bridge, so it seems that even if an >N only bridge exists in $\text{Pb}_2\text{L}^2(\text{NCS})_4$, it is not retained on anion exchange.

X-Ray Crystallography.—The geometry of the $[\text{Pb}_2\text{L}^1(\text{NCS})_3]^+$ cation is shown in Figure 2 together with the atomic numbering scheme. We make the assumption that the fourth thiocyanate anion is not part of the co-ordination sphere. As stated in the Experimental section, its position could not be located with any certainty and no regions of electron density were found within 3.5 \AA of the metal.

Each lead atom is therefore considered as five-co-ordinate, being bonded to three nitrogen atoms of the macrocycle [$\text{Pb}-\text{N}(4)$ $2.525(17)$, $\text{Pb}-\text{N}(7)$ $2.459(16)$, $\text{Pb}-\text{N}(10)$ $2.484(16)\text{ \AA}$], a terminal thiocyanate ligand through sulphur [$\text{Pb}-\text{S}(27)$ $2.879(6)\text{ \AA}$], and a bridging thiocyanate ligand through nitrogen [$\text{Pb}-\text{N}(18)$ $2.667(13)\text{ \AA}$]. A search of the Cambridge Data Centre files revealed ten structures which contained lead bonded to a thiocyanate ligand. In most cases the thiocyanate ligand is terminal and bonded through sulphur, with a range of $\text{Pb}-\text{S}$ bond lengths between 2.7 and 3.3 \AA . There is one example⁶ which could be categorised as containing a $\text{Pb}-\text{N}-\text{C}-\text{S}-\text{Pb}$ bridge although the bond lengths are long ($\text{Pb}-\text{N}$ 2.619 , $\text{Pb}-\text{S}$ 3.421 \AA) and two examples which contain terminal thiocyanate ligands bonded through nitrogen with $\text{Pb}-\text{N}$ 2.89^7 and 2.42 \AA .⁸ There is no precedent for the $\text{Pb}-\text{N}-\text{Pb}$ linkage in the present structure. The $\text{Pb}-\text{N}$ bond length is $2.667(13)\text{ \AA}$.

This sort of linkage is quite rare for all metals, two examples being $[\text{Re}_2(\text{NCS})_{10}]^3$ which contains a $\text{Re}-\text{Re}$ bond, and $[\text{K}_2\text{C}_{24}\text{H}_{32}\text{O}_8][\text{NCS}]_2$ ($\text{C}_{24}\text{H}_{32}\text{O}_8 = 6,7,9,10,12,13,20,21,23,24,26,27$ -dodecahydrodibenz[*b,n*][$1,4,7,10,13,16,19,22$]octa-oxacyclotetracosin).⁹ The dimensions in this latter molecule are quite different, however, from those in Figure 2 ($\text{K}-\text{N}$ lengths are 2.84 and 2.87 \AA , with $\text{K}-\text{N}-\text{K}$ 73 and $\text{K}-\text{N}-\text{C}$ 130 , 137°). In $\text{Pb}_2\text{L}^1(\text{NCS})_4$ comparable angles are $\text{Pb}-\text{N}-\text{Pb}$ $109.2(8)$ and $\text{Pb}-\text{N}-\text{C}$ $122(2)$, $122(2)^\circ$.

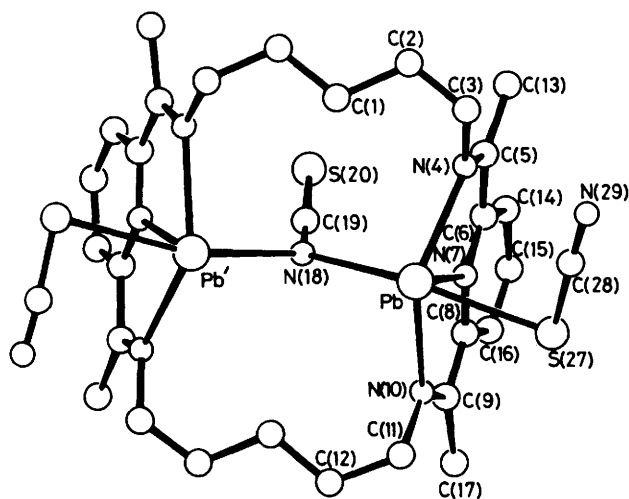
The geometry of the lead atom in the co-ordination sphere is a distorted trigonal bipyramid. The three N atoms of L^1 make up the equatorial girdle, albeit highly distorted by steric constraints, and the terminal thiocyanate S(27) and the bridging thiocyanates make up the axial positions [$\text{N}(18)-\text{Pb}-\text{S}(27)$ $160.0(4)^\circ$]. There is a vacant area in the co-ordination sphere *trans* to the pyridine nitrogen N(7) and this may be where the Pb lone pair is stereochemically active. This lone-pair activity may be the cause of the fourth thiocyanate not being bonded to

Table 3. Atomic co-ordinates ($\times 10^4$) for $\text{Pb}_2\text{L}^1(\text{NCS})_4$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Pb	4 677(1)	2 883(0)	6 501(0)	C(9)	2 462(16)	4 200(15)	6 142(9)
N(18)	5 000(0)	3 927(15)	7 500(0)	C(8)	3 378(16)	4 787(13)	6 003(9)
C(19)	4 619(21)	4 616(16)	7 516(18)	N(7)	4 403(13)	4 400(11)	6 047(7)
S(20A)	4 003(26)	5 630(15)	7 528(12)	C(6)	5 264(16)	4 892(12)	5 916(9)
S(20B)	4 629(32)	5 779(14)	7 520(21)	C(5)	6 385(15)	4 399(16)	5 954(9)
S(20C)	3 519(36)	5 353(29)	7 565(24)	N(4)	6 377(14)	3 580(12)	6 123(8)
S(27)	3 861(4)	2 287(4)	5 278(3)	C(3)	7 415(19)	3 027(20)	6 152(13)
C(28)	5 099(16)	1 838(15)	5 164(9)	C(2)	8 187(18)	3 159(17)	6 690(11)
N(29)	5 931(17)	1 605(16)	5 062(10)	C(1)	7 729(19)	2 952(19)	7 312(11)
N(21)	3 454(51)	603(107)	7 200(36)	C(12)	1 424(21)	2 967(24)	7 147(10)
C(22)	4 154(0)	620(0)	7 581(0)	C(11)	1 851(18)	2 789(15)	6 531(10)
S(23)	5 541(22)	748(38)	7 856(22)	C(17)	1 307(18)	4 582(16)	6 021(11)
S(26)	5 839(25)	1 001(36)	7 558(22)	C(16)	3 221(19)	5 658(14)	5 784(9)
C(25)	4 545(0)	883(0)	7 156(0)	C(15)	4 101(24)	6 166(17)	5 638(11)
N(24)	3 892(65)	692(90)	6 783(44)	C(14)	5 159(19)	5 776(12)	5 705(9)
N(10)	2 723(13)	3 421(11)	6 363(7)	C(13)	7 390(23)	4 889(18)	5 789(12)

Table 4. Molecular dimensions in the co-ordination sphere: distances (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

Pb-N(18)	2.667(13)	Pb-N(7)	2.459(16)
Pb-S(27)	2.879(6)	Pb-N(4)	2.525(17)
Pb-N(10)	2.484(16)		
N(18)-Pb-S(27)	160.02(36)	N(18)-Pb-N(4)	88.96(43)
N(18)-Pb-N(10)	87.88(38)	S(27)-Pb-N(4)	91.65(40)
S(27)-Pb-N(10)	76.30(37)	N(10)-Pb-N(4)	129.2(5)
N(18)-Pb-N(7)	78.6(5)	N(7)-Pb-N(4)	64.8(5)
S(27)-Pb-N(7)	83.62(35)	Pb-N(18)-Pb	109.2(8)
N(10)-Pb-N(7)	64.9(5)		

**Figure 2.** The structure of $[\text{Pb}_2\text{L}^1(\text{NCS})_3]^+$

the metal. A contributory cause may be the steric constraints of the macrocycle which may preclude some of the preferred types of bridging from occurring. In particular, a model in which two thiocyanates form three-atom bridges of the type $\text{Pb}-\text{N}-\text{C}-\text{S}-\text{Pb}$ may be too crowded to exist within the macrocycle. The $\text{Pb}\cdots\text{Pb}$ distance within the macrocycle is 4.347(1) \AA .

The conformation of the macrocycle is most interesting as can be seen from Figure 2. The five carbon atoms in the pentane linkage are approximately planar with a maximum deviation of the C_5 plane of 0.27 \AA . This plane is almost coplanar with the

symmetry-related C_5 plane, the angle of intersection being 4.2° . Atoms Pb, N(4), N(7), and N(10) are coplanar within 0.08 \AA and these two PbN_3 moieties intersect each other at an angle of 47.9° . The two PbN_3 planes intersect the C_5 planes at angles of 65.8 and 66.3° . There are no intermolecular contacts of note between molecules.

Experimental

Template Syntheses.— $\text{Pb}_2\text{L}^1(\text{NCS})_4$. Solid $\text{Pb}(\text{NCS})_2$, dap, and 1,5-diaminopentane were combined in 0.01 mol proportions in methanol-acetonitrile (1:1, ca. 1 dm^3) and the suspension stirred vigorously at 60°C for 3 h, after which a grey powder was filtered off. The orange filtrate on cooling gave yellow crystals of the product in 75% yield.

$\text{Pb}_2\text{L}^2(\text{NCS})_4$. Solid $\text{Pb}(\text{NCS})_2$, dap, and 1,6-diaminohexane were combined in 0.01 mol proportions in methanol (ca. 1 dm^3) and stirred vigorously at reflux for 1–2 h, followed by 10 h at room temperature. The bright yellow product, obtained in 72% yield, was contaminated with unreacted $\text{Pb}(\text{NCS})_2$, but was suitable for further syntheses. A small quantity of pure material was obtained for characterisation by Soxhlet extraction with acetonitrile over ca. 6 h.

Anion Exchange.— $\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$ and $\text{Pb}_2\text{L}^2(\text{ClO}_4)_4$. The white precipitate produced on mixing the appropriate dilead tetrathiocyanato complex (0.0005 mol) and AgClO_4 (0.003 mol) in acetonitrile (80 cm^3) was filtered off and the solvent evaporated until crystallisation began. The product was recrystallised from acetonitrile. Yield 60–70%.

$\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{ClO}_4)_2$. The complex $\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$ (0.0002 mol) was dissolved on warming in dry acetonitrile (100 cm^3), and LiNCS (0.0004 mol) dissolved in the minimum quantity of dry acetonitrile was added with stirring. The solution was filtered to remove turbidity and left to cool slowly when primrose-yellow crystals of product were obtained as the first crop (yield 15%). (Subsequent crops were impure.) This product could also be obtained by treatment of $\text{Pb}_2\text{L}^1(\text{NCS})_4$ with AgClO_4 in 1:2 proportions in acetonitrile, but it was more difficult to obtain a pure product by this method.

$\text{Pb}_2\text{L}^1(\text{NCS})(\text{ClO}_4)_3$. The complex $\text{Pb}_2\text{L}^1(\text{NCS})_4$ (0.001 mol) and AgClO_4 (0.003 mol) were stirred together in dry acetonitrile (300 cm^3). The resulting precipitate was filtered off, and the filtrate evaporated to ca. 120 cm^3 , when the product was obtained as pale cream crystals (yield 60%). This complex could also be obtained by reaction of LiNCS and $\text{Pb}_2\text{L}^1(\text{ClO}_4)_4$ (mol ratio 1:1) in acetonitrile.

$\text{Pb}_2\text{L}^1(\text{NCS})_2(\text{NO}_3)_2$. The complex $\text{Pb}_2\text{L}^1(\text{NO}_3)_4$ was made by treating $\text{Pb}_2\text{L}^1(\text{NCS})_4$ with excess of AgNO_3 . LiNCS (0.0001 mol) was added to $\text{Pb}_2\text{L}^1(\text{NO}_3)_4$ (0.0001 mol) and the solution, on concentration and cooling, gave small crystals of a product analysing not for the expected monothiocyanato stoichiometry but for the bis-thiocyanate complex above.

$\text{Pb}_2\text{L}^1(\text{NCS})_2\text{Cl}_2$. The complex $\text{Pb}_2\text{L}^1(\text{NCS})_4$ (0.002 mol) was stirred with LiCl (0.004 mol) in MeCN (ca. 200 cm^3) at 60 °C for 20 min. The clear yellow solution, on reducing its volume, yielded tiny primrose-yellow crystals of product.

Hydrogenated ligand ($\text{L}^2 + 8\text{H}$). The complex $\text{Pb}_2\text{L}^2(\text{NCS})_4$ (2 mmol) was reduced as described elsewhere.¹⁰ The ^1H n.m.r. spectrum (Table 1) confirms that the product is the free hydrogenated macrocycle (H_8L^2).

$\text{Pb}_2\text{L}^2(\text{NCS})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. Silver perchlorate (0.003 mol) was stirred vigorously with $\text{Pb}_2\text{L}^2(\text{NCS})_4$ (0.001 mol) at 60 °C for 20 min and the resulting white precipitate was filtered off. On cooling and concentrating the filtrate, the monothiocyanato complex was obtained as a finely crystalline cream solid (yield 50%).

Physical measurements were carried out as described in earlier publications.¹¹

X-Ray Crystallography.—Crystal data. $\text{Pb}_2\text{L}^1(\text{NCS})_4$, $\text{C}_{32}\text{H}_{38}\text{N}_{10}\text{Pb}_2\text{S}_4$, $M = 1105.4$, monoclinic, $a = 12.12(1)$, $b = 14.78(1)$, $c = 21.85(1)$ Å, $\beta = 96.5(1)^\circ$, $U = 3888.9$ Å³, $D_m = 1.89$ g cm^{-3} , $D_c = 1.89$ g cm^{-3} , $Z = 4$, $F(000) = 2104$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 22.95$ cm^{-1} , space group $C2/c$ from the successful structure determination.

A crystal of approximate size 0.30 × 0.25 × 0.30 mm was mounted on a Stoe Stadi-2 diffractometer and data collected via variable-width ω scan. Background counts were 30 s and the scan rate of 0.0167° s^{-1} was applied to a width of $(2.0 + \sin \mu / \tan \theta)^\circ$. 3394 Independent reflections with $2\theta < 50^\circ$ were measured of which 2008 with $I > 3\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied. The position of the metal atom was obtained from the Patterson function and Fourier methods gave the positions of the macrocycle atoms and the terminal thiocyanate ligands. The molecule has crystallographically imposed C_2 symmetry. The remaining two thiocyanates in the molecule were found to be disordered. One thiocyanate was located with N(18) lying on the two-fold axis between the two lead atoms. The carbon atom C(19) was located slightly off this axis. Both N(18) and C(19) were given an occupancy of 0.50. Three possible positions were observed in the difference-Fourier map for the sulphur atom and these were given occupancy factors of 0.25, 0.125, and 0.125 respectively. The remaining thiocyanate anion proved hard to locate. A difference-Fourier map showed a long thin cylinder of continuous electron density parallel to x with ends at positions (0.38, 0.10, 0.74) and (0.48, 0.08, 0.74) with heights between 1.5 and 2.2 e Å⁻³. No distinct peaks were observed.

This region of electron density is ca. 3.5 Å from the lead atom. Taking into account the symmetry-related cylinder at (0.62, 0.10, 0.76) to (0.52, 0.08, 0.76) it proved possible to fit two thiocyanate groups within this region each with occupancy of

0.25. The atoms of these groups were given a common thermal parameter and the positions of the central carbon atoms fixed. The bonded and 1,3-non-bonded distances in all these $-\text{NCS}$ groups were given a common value. A final difference-Fourier map showed no significant peaks in this area. Hydrogen atoms were positioned in trigonal or tetrahedral positions and those in the methyl groups, in the pyridine ring, and those in the remainder of the macrocycle were each given a common thermal parameter.

All ordered atoms were refined anisotropically; disordered atoms and hydrogen atoms were refined isotropically. Calculations were performed using full-matrix least-squares methods with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Scattering factors were taken from ref. 12. Calculations were performed using SHELX 76¹³ on the Amdahl V7A computer at the University of Reading. The final R value was 0.062 ($R' = 0.060$). Final atomic co-ordinates are given in Table 3 and bond lengths and angles in the metal co-ordination spheres are given in Table 4.

Acknowledgements

We thank the Open University for the award of a higher degrees studentship (to B. P. M.), and Harriet Ardill who carried out some of the work as part of an undergraduate project. We also thank the S.E.R.C. for funds for the diffractometer and A. W. Johans for his assistance with the crystallographic investigations.

References

- M. F. Cabral, B. Murphy, and J. Nelson, *Inorg. Chim. Acta*, 1984, **90**, 169.
- M. G. B. Drew, S. M. Nelson, F. S. Esho, V. McKee, and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1982, 1837.
- F. A. Cotton, A. Davidson, W. H. Ilsley, and H. S. Trop, *Inorg. Chem.*, 1979, **18**, 279.
- M. G. B. Drew, F. S. Esho, and S. M. Nelson, *Inorg. Chim. Acta*, 1983, **76**, 1269.
- G. A. Hasnoot and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 1404.
- D. E. Fenton, D. H. Cook, and I. W. Nowell, *Acta Crystallogr., Sect. B*, 1978, **35**, 1891.
- N. A. Bailey, D. E. Fenton, I. T. Jackson, R. Moody, and C. R. de Barbarin, *J. Chem. Soc., Chem. Commun.*, 1983, 1463.
- 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.
- D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1972, 66.
- M. McCann, Ph.D. Thesis, Queen's University, Belfast, 1980.
- See, for example, D. H. Cook, D. E. Fenton, M. G. B. Drew, A. Rodgers, M. McCann, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1979, 414.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
- SHELX 76, Package for Crystal Structure Determination, G. M. Sheldrick, University of Cambridge, 1976.

Received 6th February 1986; Paper 6/255