

Structure of Isothiocyanatothiocyano{3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene}lead(II)

BY I. W. NOWELL

Chemistry Department, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England

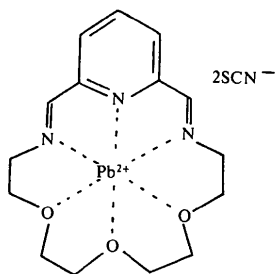
(Received 10 January 1979; accepted 9 April 1979)

Abstract. $C_{17}H_{21}N_5O_3PbS_2$, $Pb(C_{15}H_{21}N_3O_3)(NCS)-(SCN)$, $M_r = 614.7$, triclinic, $P\bar{1}$, $a = 9.546$ (2), $b = 14.744$ (4), $c = 7.672$ (2) Å, $\alpha = 100.97$ (4), $\beta = 89.19$ (3), $\gamma = 99.68$ (4)°, $U = 1044.8$ Å³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $Z = 2$, $D_m = 1.93$, $D_c = 1.95$ Mg m⁻³, $\mu = 7.97$ mm⁻¹, $F(000) = 592$. The structure was determined from two-circle diffractometer data by the heavy-atom method. Full-matrix refinement gave a conventional R factor of 0.0555 for 2960 reflections classified as observed. The Pb ion is located non-centrosymmetrically within the macrocyclic cavity, being displaced below the macrocycle ring and towards the N atoms. The mean Pb–N(macrocycle) distance of 2.617 Å is significantly smaller than the mean Pb–O distance (3.061 Å). The thiocyanate ions exhibit linkage isomerism and long-range Pb–S interactions [3.411 (5) Å] give rise to loosely held dimers in which the Pb ions have effective nine coordination.

Introduction. The use of template methods to prepare macrocyclic ligands has been well documented for a wide variety of metal ions (see, for examples, Lindoy & Busch, 1971; Nelson, McFall, Drew, Hamid bin Othman & Mason, 1977; Fenton, Cook, Nowell & Walker, 1978). In the absence of suitable metal ions, the reaction of pyridine-2,6-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane under a variety of conditions gives no recognizable macrocyclic products (Cook, 1977). If, however, the reaction is carried out in the presence of lead thiocyanate, the title compound (I) may be isolated as a crystalline product. In order to

examine the nature of the coordination in this macrocyclic complex and also to see the effect of metal-ion size upon the conformation adopted by the macrocycle, the structure has been determined (preliminary report, Fenton, Cook & Nowell, 1977). The complex crystallizes from warm, aqueous ethanol as yellow crystals, shown by preliminary photographic examination to be triclinic and by subsequent structure analysis to belong to space group $P\bar{1}$.

A crystal of dimensions 0.06 × 0.20 × 0.42 mm was mounted about the crystallographic c axis. Data were collected on a Stoe STADI-2 two-circle diffractometer, using monochromated $Mo K\alpha$ radiation ($\lambda = 0.71069$ Å) and the background- ω -scan-background technique. 4104 unique reflections were measured, of which 2900 had $I > 4\sigma(I)$ and were considered to be observed. [The net intensity, $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where c = scan time, t = time for background measurements at each end of the scan.] Lorentz and polarization factors were applied and intensities corrected for absorption effects with *ABSCOR* (Alcock, 1970). The Pb ion position was determined from the three-dimensional Patterson function, and the remaining atoms located from successive difference electron-density maps. H atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å) and were given a common isotropic temperature factor which refined to a final value of $U = 0.070$ (14) Å². Scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and analysis of structure factor agreement led to the adoption of unit weights throughout the refinement. Full-matrix refinement with anisotropic temperature factors for all non-hydrogen atoms gave the final $R = 0.0555$. The final atomic parameters are given in Table 1.*



(I)

0567-7408/79/081891-04\$01.00

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34388 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters* ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
Pb	1999 (1)	2032 (1)	3491 (1)
S(1)	-2525 (5)	184 (3)	6364 (7)
S(2)	3732 (5)	3638 (3)	2231 (7)
O(1)	3854 (12)	3033 (8)	6612 (16)
O(2)	5304 (12)	2167 (9)	3655 (17)
O(3)	3772 (13)	1067 (8)	577 (17)
N(1)	-20 (12)	2796 (8)	2504 (18)
N(2)	1136 (14)	3364 (9)	5847 (18)
N(3)	987 (15)	1412 (10)	228 (17)
N(4)	-414 (16)	1221 (10)	4596 (23)
N(5)	1947 (19)	4950 (11)	2041 (23)
C(1)	-541 (15)	2544 (11)	855 (24)
C(2)	-1618 (18)	2985 (13)	289 (27)
C(3)	-2182 (17)	3633 (13)	1545 (30)
C(4)	-1654 (16)	3864 (11)	3222 (28)
C(5)	-551 (15)	3467 (10)	3693 (22)
C(6)	72 (16)	3715 (10)	5451 (23)
C(7)	1837 (18)	3673 (11)	7593 (21)
C(8)	3413 (17)	3880 (11)	7371 (22)
C(9)	5344 (19)	3128 (15)	6423 (27)
C(10)	5761 (19)	2266 (14)	5408 (32)
C(11)	5808 (19)	1413 (12)	2521 (28)
C(12)	5271 (19)	1352 (13)	664 (28)
C(13)	3199 (20)	1042 (12)	-1100 (24)
C(14)	1608 (21)	712 (13)	-997 (26)
C(15)	42 (17)	1815 (11)	-326 (24)
C(16)	-1289 (16)	789 (10)	5295 (23)
C(17)	2675 (18)	4408 (11)	2140 (22)
H(2)	-1990	2824	-1076
H(3)	-3042	3953	1173
H(4)	-2104	4361	4195
H(6)	-365	4205	6453
H(71)	1469	4298	8275
H(72)	1585	3126	8362
H(81)	3934	4159	8647
H(82)	3668	4382	6508
H(91)	5703	3695	5731
H(92)	5844	3284	7724
H(101)	5244	1672	5944
H(102)	6899	2304	5473
H(111)	6956	1540	2549
H(112)	5424	766	2969
H(121)	5761	846	-239
H(122)	5537	2030	293
H(131)	3401	1732	-1429
H(132)	3658	560	-2093
H(141)	1422	56	-531
H(142)	1124	614	-2298
H(15)	-326	1610	-1691

Table 2. *Bond lengths* (Å) *and angles* (°), *with estimated standard deviations in parentheses*

Symmetry code: None *x,y,z*; (') $-x, -y, 1 - z$.

Pb-S(1')	3.411 (5)		
Pb-S(2)	2.964 (5)	N(2)-C(7)	1.46 (2)
Pb-O(1)	2.990 (11)	C(7)-C(8)	1.50 (2)
Pb-O(2)	3.130 (12)	C(8)-O(1)	1.40 (2)
Pb-O(3)	3.063 (12)	O(1)-C(9)	1.41 (2)
Pb-N(1)	2.580 (13)	C(9)-C(10)	1.47 (3)
Pb-N(2)	2.637 (13)	C(10)-O(2)	1.39 (3)
Pb-N(3)	2.634 (13)	O(2)-C(11)	1.42 (2)
Pb-N(4)	2.619 (15)	C(11)-C(12)	1.50 (3)
N(1)-C(1)	1.33 (2)	C(12)-O(3)	1.42 (2)
N(1)-C(5)	1.37 (2)	O(3)-C(13)	1.40 (2)
C(1)-C(2)	1.42 (3)	C(13)-C(14)	1.52 (3)
C(1)-C(15)	1.45 (2)	C(14)-N(3)	1.46 (2)
C(2)-C(3)	1.39 (3)	N(3)-C(15)	1.28 (2)
C(3)-C(4)	1.35 (3)	N(4)-C(16)	1.15 (2)
C(4)-C(5)	1.37 (3)	C(16)-S(1)	1.66 (2)
C(5)-C(6)	1.44 (2)	N(5)-C(17)	1.16 (3)
C(6)-N(2)	1.28 (2)	C(17)-S(2)	1.65 (2)
S(2)-Pb-S(1')	133.5 (2)		
S(1')-Pb-N(4)	75.5 (4)	C(2)-C(3)-C(4)	120.2 (18)
S(2)-Pb-O(1)	75.5 (3)	C(3)-C(4)-C(5)	120.1 (16)
S(2)-Pb-O(2)	63.1 (3)	C(4)-C(5)-N(1)	120.8 (15)
S(2)-Pb-O(3)	77.4 (2)	C(4)-C(5)-C(6)	121.9 (15)
S(2)-Pb-N(1)	80.8 (3)	N(1)-C(5)-C(6)	117.3 (14)
S(2)-Pb-N(2)	83.2 (3)	C(5)-C(6)-N(2)	121.0 (14)
S(2)-Pb-N(3)	88.5 (3)	C(6)-N(2)-Pb	118.8 (10)
S(2)-Pb-N(4)	150.6 (4)	C(6)-N(2)-C(7)	120.8 (14)
O(1)-Pb-O(2)	55.3 (3)	C(7)-N(2)-Pb	120.4 (11)
O(1)-Pb-O(3)	110.3 (3)	N(2)-C(7)-C(8)	109.5 (13)
O(1)-Pb-N(1)	119.6 (3)	C(7)-C(8)-O(1)	107.3 (12)
O(1)-Pb-N(2)	59.5 (4)	C(8)-O(1)-Pb	110.8 (9)
O(1)-Pb-N(3)	162.7 (4)	C(8)-O(1)-C(9)	112.7 (13)
O(1)-Pb-N(4)	109.7 (4)	C(9)-O(1)-Pb	118.3 (10)
O(2)-Pb-O(3)	55.0 (3)	O(1)-C(9)-C(10)	116.6 (14)
O(2)-Pb-N(1)	143.8 (4)	C(9)-C(10)-O(2)	107.8 (18)
O(2)-Pb-N(2)	111.5 (4)	C(10)-O(2)-Pb	109.9 (10)
O(2)-Pb-N(3)	111.5 (4)	C(10)-O(2)-C(11)	111.9 (15)
O(2)-Pb-N(4)	144.3 (5)	C(11)-O(2)-Pb	113.6 (9)
O(3)-Pb-N(1)	117.4 (4)	O(2)-C(11)-C(12)	108.7 (16)
O(3)-Pb-N(2)	160.0 (3)	C(11)-C(12)-O(3)	109.9 (16)
O(3)-Pb-N(3)	58.7 (4)	C(12)-O(3)-Pb	118.1 (9)
O(3)-Pb-N(4)	124.1 (4)	C(12)-O(3)-C(13)	112.6 (14)
N(1)-Pb-N(2)	63.1 (4)	C(13)-O(3)-Pb	110.6 (10)
N(1)-Pb-N(4)	71.5 (5)	O(3)-C(13)-C(14)	106.5 (15)
N(2)-Pb-N(3)	125.9 (5)	C(13)-C(14)-N(3)	109.4 (13)
N(2)-Pb-N(4)	75.7 (4)	C(14)-N(3)-Pb	121.2 (12)
N(3)-Pb-N(4)	87.5 (5)	C(14)-N(3)-C(15)	120.1 (14)
C(1)-N(1)-Pb	120.3 (10)	C(15)-N(3)-Pb	118.3 (10)
C(5)-N(1)-Pb	119.6 (10)	N(3)-C(15)-C(1)	120.9 (16)
C(1)-N(1)-C(5)	120.1 (14)	Pb-S(2)-C(17)	106.9 (6)
N(1)-C(1)-C(2)	120.5 (15)	S(2)-C(17)-N(5)	178.5 (17)
N(1)-C(1)-C(15)	117.4 (15)	Pb-N(4)-C(16)	165.4 (15)
C(2)-C(1)-C(15)	122.0 (16)	N(4)-C(16)-S(1)	178.2 (15)
C(1)-C(2)-C(3)	118.1 (18)	Pb-S(1')-C(16')	114.8 (6)

Discussion. Bond lengths and angles are given in Table 2, torsion angles in Table 3, and mean planes in Table 4. The Pb ion is located non-centrosymmetrically within the macrocyclic cavity, being displaced below the macrocycle and towards the N atoms (Fig. 1). The overall 'saucer' shape of the complex is reflected by a N(1)-Pb-O(2) bond angle of 143.8(4)° and the cation is found to lie significantly (-0.41 Å) below the N(2), N(3), O(1), O(3) mean plane. N(2) and N(3) lie +0.15 and -0.16 Å respectively out of the pyridine mean plane and torsion angles about the N(2)-C(7)

and C(14)-N(3) bonds have values of 132.0 and -118.6°. Of the donor atoms available within the macrocycle, Pb shows a strong preference for the N atoms. Thus the mean Pb-N(macrocycle) bond length of 2.617 Å is less than the sum of the van der Waals

Table 3. Torsion angles (°) in the macrocyclic ring

C(5)–N(1)–C(1)–C(15)	178.5	C(7)–C(8)–O(1)–C(9)	176.7	C(11)–C(12)–O(3)–C(13)	–177.0
C(1)–N(1)–C(5)–C(6)	179.3	C(8)–O(1)–C(9)–C(10)	172.2	C(12)–O(3)–C(13)–C(14)	–179.0
N(1)–C(5)–C(6)–N(2)	–4.2	O(1)–C(9)–C(10)–O(2)	–69.3	O(3)–C(13)–C(14)–N(3)	–65.6
C(5)–C(6)–N(2)–C(7)	–175.2	C(9)–C(10)–O(2)–C(11)	–173.0	C(13)–C(14)–N(3)–C(15)	–118.6
C(6)–N(2)–C(7)–C(8)	132.0	C(10)–O(2)–C(11)–C(12)	–179.9	C(14)–N(3)–C(15)–C(1)	177.1
N(2)–C(7)–C(8)–O(1)	64.7	O(2)–C(11)–C(12)–O(3)	67.7	N(3)–C(15)–C(1)–N(1)	–2.3

Table 4. Mean planes through groups of atoms

Deviations from the plane are in Å, designations in italics are of atoms excluded from the calculation of the plane.

Plane A

N(1)	–0.003	C(1)	–0.021	C(2)	0.027
C(3)	–0.009	C(4)	–0.016	C(5)	0.022
C(6)	0.057	N(2)	0.145	C(7)	0.285
C(15)	–0.081	N(3)	–0.158	C(14)	–0.153
Pb	–0.008	O(1)	1.015	O(2)	1.829

Plane B

N(2)	0.045	N(3)	–0.045	O(1)	–0.042
O(3)	0.042	O(2)	0.470	N(1)	0.471
Pb	–0.407				

Plane C

Pb	–0.068	S(2)	0.030	N(4)	0.025
S(1')	0.013	N(1)	1.099	O(2)	–1.194
C(16)	–0.125	S(1)	–0.393	C(17)	0.293

Angles between planes (°)

Plane 1	Plane 2	Angle
A	B	19.9
A	C	92.9
B	C	81.8

radius of N and the ionic radius of Pb^{II} of 2.88 Å (Bondi, 1964; Shannon & Prewitt, 1969) and is far shorter than the corresponding mean Pb–O(macrocycle) distance of 3.061 Å. The Pb–N(macrocycle) distances indicate the presence of some covalent character in the bonding whereas the Pb–O distances are significantly longer than the sum of the van der Waals radius of O and the ionic radius of Pb^{II} (2.83 Å) and the Pb–O interactions appear to be essentially electrostatic.

Coordination about the Pb is completed by the thiocyanate ions, which exhibit linkage isomerism (Fig. 2). The S atom of the N-bonded thiocyanate ion is linked to a neighbouring Pb ion by a long-range Pb–S interaction (3.411 Å) to give loosely held dimers. The Pb ion is almost coplanar with S(2), N(4), S(1') and the coordination of the metal is increased to nine. The Pb–S(2) distance of 2.964 (5) Å is comparable with the Pb–S(CN) distances of 3.121 (3) and 2.894 (3) Å found respectively in the lead cryptate C₁₈H₃₆N₂O₆.Pb(SCN)₂ (Metz & Weiss, 1974) and the macrocyclic complex C₁₂H₂₆N₂O₄.Pb(SCN)₂ (Metz &

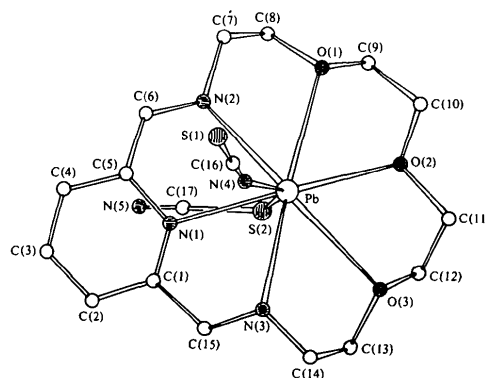
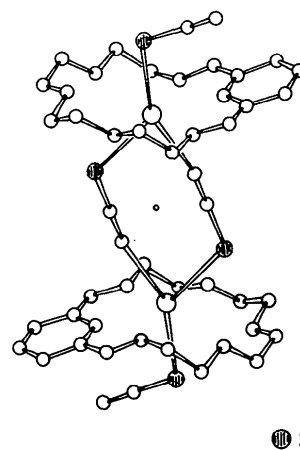
Fig. 1. Molecular structure of Pb(macrocycle)(NCS)₂.

Fig. 2. Intermolecular interactions.

Weiss, 1973). Unlike the latter compound, where localization of the 6s lone pair has been proposed, there appears to be no stereochemical activity of the Pb lone pair in the present complex.

I wish to thank the SRC for an equipment grant.

References

- ALCOCK, N. W. (1970). *The Analytical Method for Absorption Correction in Crystallographic Computing*, edited by F. R. AHMED. Copenhagen: Munksgaard.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

- COOK, D. H. (1977). PhD Thesis, Sheffield Univ., England.
 FENTON, D. E., COOK, D. H. & NOWELL, I. W. (1977).
Chem. Commun. pp. 274–275.
 FENTON, D. E., COOK, D. H., NOWELL, I. W. & WALKER,
 P. E. (1978). *Chem. Commun.* pp. 279–280.
International Tables for X-ray Crystallography (1974). Vol.
 IV, Table 2.2B. Birmingham: Kynoch Press.
 LINDOY, L. F. & BUSCH, D. H. (1971). *Prep. Inorg. React.* **6**,
 1–61.

- METZ, B. & WEISS, R. (1973). *Acta Cryst.* **B29**, 1088–1093.
 METZ, B. & WEISS, R. (1974). *Inorg. Chem.* **13**, 2094–2098.
 NELSON, S. M., MCFALL, S. G., DREW, M. G. B., HAMID BIN
 OTHMAN, A. & MASON, N. B. (1977). *Chem. Commun.*
 pp. 167–168.
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**,
 925–946.

Acta Cryst. (1979). **B35**, 1894–1895

Nitrato(1,4,7,10-tetraazacyclododecane)copper(II) Nitrate

BY ROBERT CLAY, PETER MURRAY-RUST AND JUDITH MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

(Received 5 April 1979; accepted 23 April 1979)

Abstract. [Cu(C₈H₂₀N₄)(NO₃)⁺.NO₃⁻, C₈H₂₀CuN₅O₃.NO₃⁻, *M_r* = 359.8, monoclinic, *P*2₁/*n*, *a* = 12.00 (1), *b* = 13.76 (1), *c* = 8.86 (2) Å, β = 90.10 (3)° from diffractometer measurements (Mo *K*α radiation), *V* = 1463.8 Å³, *Z* = 4, *D_m* = 1.60, *D_c* = 1.63 Mg m⁻³, *F*(000) = 748, μ = 1.409 mm⁻¹. The complex contains five-coordinate Cu^{II} in a square-pyramidal environment, the Cu being 0.5 Å above the plane containing the four N atoms of the macrocycle.

Introduction. Systematic absences from precession photographs *h*0*l*: *h* + *l* odd, 0*k*0: *k* odd indicated space group *P*2₁/*n*. Data were collected for *hk*0–8 with θ_{max} = 25° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo *K*α radiation). This gave 2803 data of which 1862 unique reflexions with *I* > 3σ(*I*) were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by direct phasing methods with *SHELX* 76 (Sheldrick, 1976), which was used for all calculations. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Weighted full-matrix least-squares refinement (including isotropic H atoms) converged at *R* = 0.052 for 1862 observed reflexions (*R* = ∑||*F_o*| – |*F_c*||/∑|*F_o*|); *R_w* = 0.059 {*R_w* = ∑ (||*F_o*| – |*F_c*|| *w*^{1/2})/∑ (|*F_o*| *w*^{1/2}), *w* = 3.43/[σ²(*F_o*) + 0.000656*F_o*²]}. In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, bond distances and angles in Table 2.*

In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, bond distances and angles in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34416 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates (×10⁴) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	3468 (0)	5711 (0)	2922 (1)
C(2)	1678 (6)	6187 (5)	4787 (9)
C(3)	2642 (7)	6374 (5)	5797 (8)
C(5)	3941 (5)	7447 (4)	4385 (8)
C(6)	4875 (5)	7375 (5)	3237 (9)
C(8)	3906 (7)	7127 (5)	794 (9)
C(9)	3398 (7)	6340 (5)	–162 (7)
C(11)	1611 (6)	5872 (7)	1161 (10)
C(12)	1196 (5)	5251 (6)	2482 (12)
O(14)	4529 (3)	4426 (3)	3080 (5)
O(15)	3094 (4)	3579 (3)	2458 (7)
O(16)	4685 (4)	2900 (3)	2620 (6)
O(18)	3112 (4)	3940 (4)	8666 (6)
O(19)	2580 (5)	3758 (5)	6382 (7)
O(20)	1569 (4)	4524 (4)	7940 (8)
N(1)	1973 (4)	5371 (4)	3827 (7)
N(4)	3712 (4)	6460 (3)	4859 (6)
N(7)	4539 (4)	6671 (4)	1994 (7)
N(10)	2749 (5)	5619 (4)	889 (6)
N(13)	4102 (3)	3637 (3)	2683 (5)
N(17)	2423 (4)	4069 (4)	7652 (7)
H(1A)	1957	4727	4516
H(2A)	1518	6817	4093
H(2B)	944	6024	5447
H(3A)	2505	7041	6409
H(3B)	2721	5778	6581
H(4A)	4256	6119	5675
H(5A)	3208	7764	3878
H(5B)	4202	7885	5333
H(6A)	5622	7115	3787
H(6B)	5029	8083	2758
H(7A)	5279	6277	1662
H(8A)	3260	7588	1254
H(8B)	4460	7560	109
H(9A)	2832	6660	–969
H(9B)	4044	5949	–751
H(10A)	2770	5014	100
H(11A)	1550	6637	1449
H(11B)	1128	5736	154
H(12A)	363	5469	2787
H(12B)	1192	4498	2133