

Crystal Structure of {2,15-Dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene}(thiocyanato)lead(II) Thiocyanate

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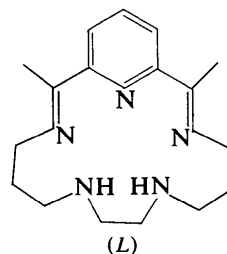
(Received 6 January 1979; accepted 19 March 1979)

Abstract

$C_{18}H_{27}N_6PbS^+ \cdot SCN^-$, $[Pb(C_{17}H_{27}N_5)(SCN)]^+ \cdot SCN^-$, $M_r = 624.5$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.170$ (7), $b = 15.108$ (11), $c = 18.794$ (13) Å, $\beta = 103.0$ (3)°, $U = 2260.3$ Å³, $d_c = 1.83$, $d_m = 1.80$ (4) Mg m⁻³, $F(000) = 1216$, $\mu(Mo K\alpha) = 7.65$ mm⁻¹. The structure has been refined by full-matrix least squares to $R = 0.081$ for 1767 counter reflections. The Pb atom is six-coordinate, being bonded to five N atoms of the quinquedentate macrocyclic ligand [2.47 (3)–2.64 (3) Å] and a S atom of a thiocyanate ion [3.095 (15) Å], leaving the remaining thiocyanate ligand uncoordinated. The geometry of the Pb^{II} coordination sphere shows that the lone pair is stereochemically active.

Introduction

In previous work we have investigated the structures of several complexes containing the quinquedentate macrocyclic ligand *L*. This 17-membered macrocycle does not form a planar girdle around the metal as do the 15- and 16-membered analogues. A common deviation from the pentagonal planar conformation is for the macrocycle to fold so that the pyridine N atom is well out of the plane of the metal and the other N atoms. The structures of $[MnL(NCS)_2]$ (Drew, Othman, McFall, McIlroy & Nelson, 1977), $[CdLBr]^+$ and $[HgLBr]^+$ (Drew, McFall, McIlroy & Nelson, 1979) and $[AgL]^+$ (Nelson, McFall, Drew, Othman & Mason, 1977) have been reported. In these three types of structure, the metal atom has coordination numbers 7, 6 and 5, respectively, and the conformation of the macrocycle is different in each case. A fourth conformation occurs in complexes of the smaller metal ion, Ni^{II}, where the macrocycle occupies five of the six sites of a distorted octahedron (Cairns, McFall, Nelson & Drew, 1979). In the present paper we report the structure of $[PbL(SCN)]SCN$.



Crystals of $[PbL(SCN)]SCN$ were prepared as reported previously (Cook, Fenton, Drew, Rodgers, McCann & Nelson, 1979). A crystal $0.4 \times 0.25 \times 0.7$ mm was mounted with *a** parallel to the instrument axis of a General Electric XRD 5 diffractometer equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zr-filtered Mo $K\alpha$ radiation was used. The stationary-crystal/stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background against 2θ . 2736 independent reflections were measured with $2\theta < 40^\circ$, of which 1767 with $I > 2\sigma(I)$ were used in subsequent calculations. The crystal was twinned with $0kl$ common. The twin ratio was *ca* 3:1 and we therefore subsequently allowed the $0kl$ reflections to have a different (and refineable) scale factor from the rest of the data. An absorption correction was applied.

The position of the Pb atom was located from a Patterson map and Fourier syntheses led to the positions of the remaining atoms. The structure was refined by full-matrix least squares with a weighting scheme that gave similar values for $w\Delta^2$ with ranges of F_o and $\sin \theta/\lambda$; $w^{1/2} = 1$ for $F_o < 120$ and $w^{1/2} = 120/F_o$ for $F_o > 120$. The Pb atom was refined anisotropically, the remaining atoms isotropically. There were 12 reflections for which $F_o \gg F_c$ and these were considered to be affected by the twinning and were omitted from the refinement but no other treatment of the twinning was deemed necessary. Calculations were made with

XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) at the University of London Computer Centre with a CDC 7600 computer. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The atomic coordinates are given in Table 1, bond lengths and angles in Table 2. The final difference map was

Table 1. Positional coordinates ($\times 10^4$) for $[\text{PbL}(\text{SCN})]\text{SCN}$ with *e.s.d.*'s in parentheses

	x	y	z
Pb	-139 (2)	2296 (1)	804 (1)
S(2)	3289 (21)	961 (11)	1960 (9)
C(2)	3221 (63)	17 (35)	2506 (27)
N(2)	3106 (57)	-523 (33)	2781 (26)
S(1)	1846 (16)	2336 (10)	-418 (7)
C(1)	3519 (50)	2488 (34)	175 (22)
N(1)	4686 (45)	2768 (25)	638 (21)
C(3)	176 (68)	2798 (34)	2606 (29)
C(4)	1135 (53)	3743 (29)	2607 (23)
C(5)	1927 (60)	3950 (31)	1928 (25)
N(6)	539 (35)	3822 (19)	1217 (15)
C(7)	-216 (57)	4535 (31)	947 (24)
C(8)	-1732 (45)	4399 (24)	307 (19)
N(9)	-1903 (31)	3552 (18)	115 (13)
C(10)	-2991 (49)	3334 (26)	-499 (20)
C(11)	-3207 (41)	2435 (29)	-737 (18)
N(12)	-2034 (44)	1933 (25)	-381 (19)
C(13)	-2091 (71)	919 (38)	-613 (30)
C(14)	-3029 (50)	384 (25)	-112 (21)
C(15)	-2445 (62)	365 (32)	689 (26)
N(16)	-2500 (40)	1259 (21)	1015 (17)
C(17)	-2143 (50)	1178 (27)	1791 (21)
C(18)	-2331 (54)	2080 (27)	2127 (23)
N(19)	-1210 (34)	2774 (18)	1974 (14)
C(20)	-159 (54)	5484 (29)	1373 (24)
C(21)	-2613 (52)	5098 (27)	-33 (22)
C(22)	-3891 (59)	4844 (31)	-636 (24)
C(23)	-4130 (53)	4026 (29)	-928 (22)
C(24)	-4555 (47)	2150 (23)	-1383 (20)

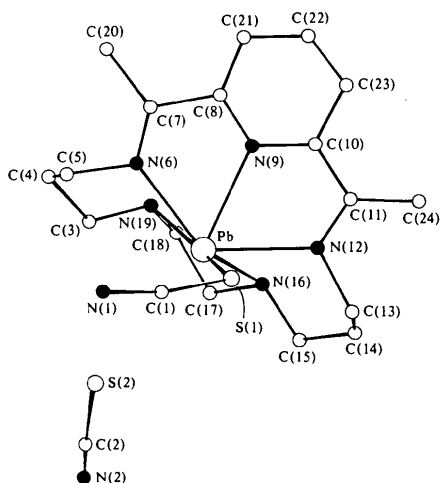


Fig. 1. A view of the title compound showing the atom numbering.

Table 2. Molecular dimensions for the Pb coordination sphere

Pb-S(1)	3.095 (15) Å	S(1)-Pb-N(6) ^(a)	95.6 (8)°
Pb-N(6)	2.46 (3)	S(1)-Pb-N(9)	86.5 (7)
Pb-N(9)	2.55 (2)	S(1)-Pb-N(12)	70.3 (9)
Pb-N(12)	2.47 (3)	S(1)-Pb-N(16)	131.3 (8)
Pb-N(16)	2.58 (3)	S(1)-Pb-N(19)	159.8 (6)
Pb-N(19)	2.64 (3)	N(6)-Pb-N(9)	61.6 (8)
		N(6)-Pb-N(12)	123.0 (10)
Pb-S(1)-C(1)	89.7 (17)°	N(6)-Pb-N(16)	130.0 (10)
		N(6)-Pb-N(19)	64.7 (9)
		N(9)-Pb-N(12)	62.6 (10)
		N(9)-Pb-N(16)	100.0 (9)
		N(9)-Pb-N(19)	87.9 (8)
		N(12)-Pb-N(16)	70.5 (11)
		N(12)-Pb-N(19)	123.6 (11)
		N(16)-Pb-N(19)	68.9 (9)

(a) Analogous Br-Cd-N(*n*) angles in $[\text{CdLBr}]^+$ are 93.8, 131.9, 101.3, 99.5 and 110.4° for *n* = 6, 9, 12, 16, 19 respectively.

featureless. The other zero-weighted reflections gave no large discrepancies.*

Discussion

The structure consists of $[\text{PbL}(\text{SCN})]^+$ cations and SCN^- anions, separated by normal van der Waals contacts. The cation and atomic numbering are shown in Fig. 1. The Pb atom is bonded to the five N atoms of the macrocycle with bond distances ranging from 2.47 (3)–2.64 (3) Å. The coordination sphere is completed by a Pb-S(1) bond of 3.095 (15) Å. The closest approach of the other thiocyanate to the metal is 3.73 Å for S(2)⋯Pb. The geometry of the macrocycle is similar to that in $[\text{CdLBr}]^+$ (Drew *et al.*, 1979), for in

* Lists of structure factors, thermal parameters, intermolecular contacts and less important molecular dimensions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34303 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Torsion angles (°) in $[\text{PbL}(\text{SCN})]^+$ and $[\text{CdLBr}]^+$

	$[\text{CdLBr}]^+$	$[\text{PbL}(\text{SCN})]^+$
C(11)-N(12)-C(13)-C(14)	-105.1	-94 (1)
N(12)-C(13)-C(14)-C(15)	-59.3	-59 (1)
C(13)-C(14)-C(15)-N(16)	67.0	63 (1)
C(14)-C(15)-N(16)-C(17)	167.5	172 (1)
C(15)-N(16)-C(17)-C(18)	-177.3	-176 (1)
N(16)-C(17)-C(18)-N(19)	-64.7	-61 (1)
C(17)-C(18)-N(19)-C(3)	-87.1	-97 (1)
C(18)-N(19)-C(3)-C(4)	-160.4	-161 (1)
N(19)-C(3)-C(4)-C(5)	-71.0	-61 (1)
C(3)-C(4)-C(5)-N(6)	63.2	53 (1)
C(4)-C(5)-N(6)-C(7)	91.7	97 (1)

the two compounds all ring torsion angles in *L* are within 12° of each other (Table 3). Also, in both structures N(6), N(12), N(16) and N(19) are approximately planar (plane 2 in Table 4) with Pb, N(9) 0.90, -1.32 Å from the plane in $[\text{PbL}(\text{SCN})]^+$ and Cd, N(9) 0.43, -1.30 Å from the plane in $[\text{CdLBr}]^+$. If we describe the ring fold in the macrocycle as the angle between this plane and that of the pyridine ring (plane 7), then this angle is 63.1° in $[\text{PbL}(\text{SCN})]^+$ compared with 49.7° in $[\text{CdLBr}]^+$, 48.8° in $[\text{HgLBr}]^+$ and only 41.8° in $[\text{MnL}(\text{NCS})_2]$. The Pb atom is 0.18 Å from plane 7 compared with 0.13 Å for the Cd atom. This result therefore suggests a correlation* between the folding of the macrocycle and the size of the metal ion (Pb $^{2+}$ 1.23, Cd $^{2+}$ 1.03, Mn $^{2+}$ 0.90 Å; Shannon, 1976).† However, there is a major difference between the two cations in the position of the monodentate anion. This difference is illustrated in Fig. 2 which is a projection of the two coordination spheres down N(16)⋯N(19). In $[\text{CdLBr}]^+$, the Br atom is situated in a position approximately perpendicular to the Cd, N(6), N(12), N(16), N(19) plane (see angles in Table 2 and Fig. 2). This is not the case for the S atom in $[\text{PbL}(\text{SCN})]^+$ which is situated *trans* to N(19) and subtends an angle of only 70.3 (9°) at the metal with N(12) compared with 131.9 (6°) for the Br atom with N(12). Clearly the 63.1° fold in the Pb complex leads to a large gap on one side of the metal atom and it seems likely that this is occupied not only by the thiocyanate but also by a

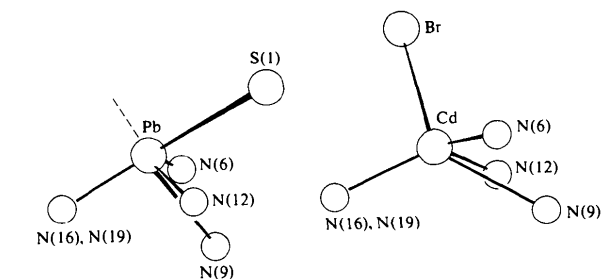


Fig. 2. Comparison of the coordination spheres of $[\text{PbL}(\text{SCN})]^+$ and $[\text{CdLBr}]^+$. Projections are down the N(16)⋯N(19) vector.

stereochemically active lone pair, in a position approximately *trans* to N(9). This position seems most likely as no angle subtended at the metal involving N(9) is $>100^\circ$. S(2) from the unbonded thiocyanate is situated in this vacant area (Fig. 1), though at a distance well above a Pb—S bond length.

It is difficult to rationalize from a consideration of available Pb II structures the variable stereochemical activity of the lone pair. Attempts to do so in terms of the soft or hard nature of the ligands seem inconclusive (Wynne, 1973). In the present case, there might be some correlation between the observed activity of the lone pair and the fact that the thiocyanate is S-bonded rather than N-bonded. It is conventional to describe the geometry of an MX_6E molecule (*M* a metal, *X* a ligand, *E* a lone pair) in terms of seven-coordinate geometry (Drew, 1977; Wynne, 1973). Thus the geometry of $[\text{PbL}(\text{SCN})]^+$ approximates to a pentagonal bipyramid with N(9) and the lone pair in axial positions, and S(1), N(6), N(19), N(16), N(12) in equatorial positions. The major distortion from this geometry is the requirement that the N(6)—Pb—N(9) and N(9)—Pb—N(12) angles are *ca* 62° .

S(1) is fairly weakly bound to the Pb atom at 3.095 (15) Å and the Pb—S—C angle of 89.7 (17°) is remarkably small. Values can be compared with those found in other macrocyclic complexes, *viz* 2.975 Å, 105.8° (Fenton, Cook, Nowell & Walker, 1977) and 2.91 Å, 102° ; 3.00 Å, 104° (Drew, Rodgers, McCann & Nelson, 1978). The Pb—N distances in $[\text{PbL}(\text{SCN})]^+$ are also comparable with the Pb—N distances in these two structures.

There are no intermolecular distances significantly less than the sum of the van der Waals radii. A list of values <3.5 Å has been deposited.*

We thank A. W. Johans for his assistance with the crystallographic investigations.

* See deposition footnote.

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* This correlation is only valid for complexes in which the ring folds in this way, *i.e.* those complexes with Pb $^{2+}$, Cd $^{2+}$, Hg $^{2+}$ and Mn $^{2+}$. In $[\text{AgL}]^+$ and $[\text{NiLX}]^+$ [Ag^+ 1.22, Ni $^{2+}$ 0.69 Å], the conformations of *L* are completely different for reasons discussed elsewhere (Drew & Nelson, 1979; Cairns *et al.*, 1979).

† Values quoted are seven-coordinate radii except for Ni $^{2+}$ which is a six-coordinate radius.

Table 4. Distances (Å) of atoms from least-squares planes

Atoms marked with an asterisk do not contribute to the plane.

Plane 1:	Pb -0.13 (1), N(6) 0.12 (2), N(9) -0.10 (2), N(12) 0.11 (2)
Plane 2:	Pb* 0.90 (1), N(6) 0.12 (2), N(12) -0.11 (2), N(16) 0.17 (2), N(19) -0.18 (2), N(9)* -1.32 (2)
Plane 3:	Pb 0.02 (1), S(1) -0.01 (1), N(16) -0.00 (2), N(19) -0.01 (2), N(6)* -0.70 (2), N(9)* -2.47 (5), N(12)* -1.47 (3)
Plane 4:	Pb, N(12), N(16) 0.00, C(13)* 1.29 (4), C(14)* 1.26 (4), C(15)* 1.24 (4)
Plane 5:	Pb, N(6), N(19) 0.00, C(3)* 1.31 (4), C(4)* 1.45 (4), C(5)* 1.32 (4)
Plane 6:	Pb, N(16), N(19) 0.00, C(17)* 0.86 (3), C(18)* 0.22 (2)
Plane 7:	C(7) -0.07 (2), C(8) 0.05 (2), N(9) 0.08 (2), C(10) -0.02 (2), C(11) -0.02 (2), C(21) -0.01 (2), C(22) 0.03 (2), C(23) -0.04 (2), Pb* 0.19 (1)

Angles between planes:

$$1 \wedge 2 \ 61.1, 1 \wedge 3 \ 84.9, 2 \wedge 3 \ 24.7, 2 \wedge 7 \ 63.1^\circ$$

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The Crystal and Molecular Structure of [Bromobis(tetrahydrofuran)magnesium]-bis(η -cyclopentadienyl)hydridomolybdenum

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(Received 7 September 1978; accepted 13 February 1979)

Abstract

The crystal and molecular structure of the title compound has been determined by Patterson heavy-atom methods and refined to $R = 0.066$ {triclinic, $a = 11.708$ (5), $b = 11.596$ (5), $c = 7.750$ (3) Å, $\alpha = 86.33$ (2), $\beta = 82.92$ (2), $\gamma = 73.26$ (3)°, space group $P\bar{1}$, Mo $K\alpha$ radiation, 1334 reflections [$I > 3\sigma(I)$]}. The bis(η -cyclopentadienyl)molybdenum moiety has the eclipsed configuration and the Mo–Mg bond length is 2.732 Å. The presence of the hydrido ligand is inferred from the molecular geometry. The Mg atom has a distorted tetrahedral configuration.

Introduction

The crystals were prepared by the recrystallization from tetrahydrofuran of the reaction product of (η -C₅H₅)₂MoH₂ with the Grignard reagent isopropylmagnesium bromide. The preparation, reactions and structure of this compound have been the subject of a preliminary report (Davies, Green, Prout, Coda & Tazzoli, 1977). It was expected to have a structure analogous to that of the previously reported compound

bis- μ -[bis-(η -cyclopentadienyl)hydridomolybdenum]-bis{di- μ -bromo-[cyclohexylmagnesium](diethyl ether)magnesium} (I) (Prout & Forder, 1975), but the structure analysis showed it to be a new type of compound (II). An irregular fragment, 0.3–0.4 mm thick, was chosen from the sample of air-unstable orange crystals, and was sealed under nitrogen in a glass capillary.

Experimental

Crystal data

(η -C₅H₅)₂Mo(H)Mg(C₄H₈O)₂Br, C₁₈H₂₇BrMgMoO₂, [Mo{(C₅H₅)₂H[MgBr(C₄H₈O)₂]}], $M_r = 475.1$, triclinic, $a = 11.708$ (5), $b = 11.596$ (5), $c = 7.750$ (3) Å, $\alpha = 86.33$ (2), $\beta = 82.92$ (2), $\gamma = 73.26$ (3)°, $U = 1002.9$ Å³; $D_c = 1.57$ Mg m⁻³ for $Z = 2$; space group $P\bar{1}$ (C_i^1 , No. 2) from intensity statistics and structure analysis, four-circle diffractometer data, Mo $K\alpha$ radiation (graphite monochromator), $\mu = 4.93$ mm⁻¹, 1334 independent reflections [$I > 3\sigma(I)$].

The unit-cell dimensions were determined on a Philips PW 1100 four-circle automatic diffractometer using the manufacturer's routine *LAT*: this performs an accurate scan of the rows $h00$, $0k0$, $00l$, $hh0$, $h0h$, $0kk$, $0kk$, hhh , $h\bar{h}h$, $h\bar{h}h$ and $h\bar{h}\bar{h}$ in the range $\theta = 2$ –20°, and afterwards minimizes the differences between

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