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Highly Coordinated Lead. Crystal and Molecular Structure of (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)lead(II) Thiocyanate

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The crystal and molecular structure of the lead cryptate $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$ has been determined by three-dimensional X-ray crystallographic analysis using data collected on a Picker four-circle diffractometer. The colorless crystals are orthorhombic, space group *Pbca,* with unit cell parameters $a = 15.673$ (3), $b = 15.076$ (2), $c = 22.368$ (4) Å, and $Z = 8$. The structure has been refined to a final unweighted residual of 0.056 on 2986 independent observable reflections. It consists of discrete molecules of $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$ in which the lead atom occupies a central position in the cavity of the macrobicyclic ligand. Each lead atom is surrounded by one sulfur (Pb–S = 3.121 (3) Å), three nitrogen (Pb–N = 2.642 (10), 2.858 (9), 2.909 (9) Å), and six oxygen atoms (Pb–O range from 2.729 (7) to 2.980 (8) Å). The arrangement of the heteroatoms around the lead atom approximates a trigonal-capped irregular hexagonal pyramid.

Introduction

Recent investigations on synthetic macroheterocyclic and macroheterobicyclic systems have aroused considerable interest in numerous properties of these materials.[1-3] The diazapolyoxa macrobicycles generally display higher complexing abilities and formation selectivities with different cations than the cyclic systems.[2e,2i] The complexes with alkali, alkaline earth, and other metal ions so far studied show that there is always one cation in the central molecular cavity of the macrobicycles.[4] These complexes are called cryptates. More recently it has been shown that some macrotricyclic ligands can enclose two metal cations; by extension these new complexes are called [3]cryptates.[5]

The stability constants for a large number of cryptates with various cations have been determined in water and in methanol by the analysis of pH metric titration curves and in some cases with cation-specific electrodes. The complex between the ligand $C_{18}H_{36}N_2O_6$ (see Figure 1) and the Pb^{2+} ion has the greatest stability constant.[2e,2f] It should be noticed that this is also true when the ligand dicyclohexyl-18-crown-6 is used.[3] We report here a determination of the crystal structure of $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$.

Experimental Section

Crystals of composition $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$ were obtained by evaporating at room temperature a methanol–butanol solution of lead thiocyanate and the ligand in a 1:1 mole ratio. The transparent colorless crystals burnish very slowly under action of light or X-radiation.

Crystal Data. Precession photographs using Mo Kα radiation indicated that the crystals belong to the orthorhombic system. The systematic absences showed that the space group is *Pbca*. A crystal with dimensions of 0.15 × 0.37 × 0.17 mm in the $|100|$, $|010|$, and $|001|$ directions, respectively, was sealed in a Lindemann glass capillary. It was mounted with b approximately parallel to the ϕ axis of a Picker four-circle automatic X-ray diffractometer equipped with a graphite crystal incident-beam monochromator.

Twelve reflections in the 2θ range of 30–38° (Mo Kα_1) were automatically centered in the detector aperture. The setting angles were used to obtain the best values of the unit cell dimensions by least-squares refinement. All cell angles were constrained to 90° in the refinement which gave $a = 15.673$ (3), $b = 15.076$ (2), and $c = 22.368$ (4) Å. The crystal density of 1.75 ± 0.03 g/cm^3, measured by flotation in a mixture of bromoform and carbon tetrachloride at room temperature, compares favorably with the calculated value of 1.76 g/cm^3 based on eight molecules per unit cell (volume 5285.0 Å^3) and a molecular weight of 699.85.

Data Collection. An independent set of intensity data was collected at $18 \pm 2°$ by the θ–2θ scan technique within the angular range $6° \leqslant 2\theta$ (MoKα_1) $\leqslant 60°$. Attenuators were used whenever the scan count exceeded 7000 counts/sec. The intensities of three standard reflections were monitored throughout the data collection at intervals of 100 measurements. The intensities of two standards showed a steady decrease (about 5% at the end of the data collection). A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = |CT + (t_s/t_b)^2(B_1 + B_2) + (pI)^2|^{1/2}$ where CT is the total integrated peak count, B_1 and B_2 are background counts, t_s and t_b are respectively scan and background times, and p is an empirical coefficient of the net count I.[6] The factor p was given an initial value of 0.04. A total of 7955 reflections were recorded, using a takeoff angle of 1.3°, a scan rate of 2°/min, and a scan range of 1.4° symmetrical with respect to each calculated peak center. Background counts were taken for 20 sec at each end of the scan range. The raw intensities were corrected for background, Lorentz, and polarization effects; 2986 of these had $\sigma(I)/I$ less than 0.4 and were retained. Since the linear absorption coefficient of this compound is rather large (64.8 cm^{-1} for Mo Kα), an absorption correction was made.[7] The transmission factors varied from 0.33 to 0.43.

Solution and Refinement of the Structure. A three-dimensional Patterson map[7] readily yielded the position of the lead atom. The remaining nonhydrogen atoms were located from a three-dimensional Fourier synthesis map.[7] This structure hypothesis has been refined by a least-squares procedure.[7]

The least-squares refinements were carried out on F_o; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$; $|F_o|$ and $|F_c|$ are the observed

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(1) (a) C. J. Pedersen, *J. Amer. Chem. Soc.,* 89, 7017 (1967); (b) *ibid.,* 89, 2495 (1967); (c) *ibid.,* 92, 386 (1970); (d) *ibid.,* 92, 391 (1970); (e) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.,* 11, 16 (1972).

(2) (a) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.,* 2885 (1969); (b) *ibid.,* 2889 (1969); (c) *Chem. Commun.,* 1055 (1970); (d) J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Amer. Chem. Soc.,* 92, 2916 (1970); (e) J. M. Lehn and J. P. Sauvage, *Chem. Commun.,* 440 (1971); (f) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *J. Chem. Soc., Chem. Commun.,* 15 (1973); (g) *Tetrahedron,* 29, 1647 (1973); (h) B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzat, *ibid.,* 29, 1629 (1973); (i) J. M. Lehn, *Struct. Bonding (Berlin),* 16, 1 (1973).

(3) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science,* 174, 459 (1971).

(4) (a) B. Metz, D. Moras, and R. Weiss, *Chem. Commun.,* 217 (1970); (b) *J. Amer. Chem. Soc.,* 93, 1806 (1971); (c) *Chem. Commun.,* 444 (1971); (d) D. Moras, B. Metz, and R. Weiss, *Acta Crystallogr., Sect. B,* 29, 383 (1973); (e) *ibid.,* 29, 388 (1973); (f) D. Moras and R. Weiss, *ibid.,* 29, 396 (1973); (g) *ibid.,* 29, 400 (1973); (h) *ibid.,* 29, 1059 (1973); (i) B. Metz, D. Moras, and R. Weiss, *ibid.,* 29, 1377 (1973); (j) *ibid.,* 29, 1382 (1973); (k) *ibid.,* 29, 1388 (1973).

(5) (a) J. Cheney, J. M. Lehn, J. P. Sauvage, and M. E. Stubbs, *J. Chem. Soc., Chem. Commun.,* 1100 (1972); (b) J. M. Lehn, J. Simon, and J. Wagner, *Angew. Chem., Int. Ed. Engl.,* 12, 579 (1973); (c) R. Wiest and R. Weiss, *J. Chem. Soc., Chem. Commun.,* 678 (1973); (d) M. Mellinger, J. Fischer, and R. Weiss, *Angew. Chem., Int. Ed. Engl.,* 12, 771 (1973).

(6) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.,* 6, 197 (1967).

(7) In addition to local programs for the Univac 1108 computer, local versions of the following programs were used in this work: Prewitt's SFLS-5 least-squares program, the Wehe-Busing-Levy ORABS absorption correction program, and Johnson's ORTEP thermal ellipsoid plotting program.

Table I. Positional Coordinates and Thermal Parameters[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb	45,776 (3)	26,828 (3)	38,466 (2)	288 (1)	328 (1)	164 (1)	9 (2)	13 (1)	3 (1)
S	26,937 (23)	32,834 (24)	36,443 (17)	389 (17)	441 (21)	363 (11)	−11 (15)	−19 (11)	11 (11)
C	19,935 (76)	24,967 (74)	38,046 (45)	416 (52)	528 (80)	143 (25)	−11 (49)	−1 (30)	−47 (46)
N	14,925 (70)	19,699 (82)	38,947 (54)	519 (59)	796 (74)	387 (37)	−184 (58)	83 (44)	−57 (47)
S′	72,696 (33)	44,485 (38)	35,640 (22)	827 (32)	1147 (38)	426 (15)	−589 (29)	−37 (17)	153 (20)
C′	65,210 (73)	39,156 (71)	39,095 (59)	375 (54)	318 (56)	363 (39)	−20 (46)	−114 (44)	−54 (45)
N′	59,881 (64)	35,335 (68)	41,464 (53)	327 (52)	511 (62)	419 (36)	−34 (46)	7 (36)	−110 (39)
N(1)	4,812 (6)	3,002 (6)	2,574 (4)	56 (6)	525 (6)	18 (2)	5 (5)	−3 (3)	0 (3)
C(2)	5,744 (8)	3,126 (8)	2,513 (6)	47 (6)	63 (7)	34 (4)	12 (6)	11 (4)	8 (5)
C(3)	6,234 (10)	2,320 (9)	2,694 (6)	71 (8)	77 (9)	27 (3)	11 (8)	15 (5)	8 (5)
O(4)	5,953 (5)	2,019 (5)	3,242 (3)	47 (4)	65 (5)	19 (2)	25 (4)	4 (2)	4 (2)
C(5)	6,392 (10)	1,288 (10)	3,486 (6)	62 (9)	88 (11)	34 (4)	44 (8)	5 (5)	0 (6)
C(6)	6,504 (9)	1,394 (11)	4,117 (7)	45 (8)	109 (13)	36 (4)	34 (8)	−11 (5)	−3 (6)
O(7)	5,677 (5)	1,444 (6)	4,402 (3)	38 (4)	64 (5)	23 (2)	10 (4)	−0 (2)	−2 (3)
C(8)	5,770 (9)	1,714 (9)	5,009 (6)	53 (8)	66 (9)	26 (4)	14 (7)	−7 (4)	2 (5)
C(9)	4,923 (9)	1,608 (9)	5,314 (6)	59 (8)	66 (9)	25 (4)	2 (7)	1 (4)	13 (5)
N(10)	4,269 (6)	2,209 (7)	5,064 (4)	42 (5)	59 (7)	15 (2)	−6 (5)	1 (2)	2 (3)
C(11)	3,407 (9)	1,795 (11)	5,083 (6)	44 (8)	116 (13)	35 (5)	−34 (8)	9 (5)	3 (6)
C(12)	3,356 (11)	975 (10)	4,702 (7)	89 (12)	79 (11)	37 (5)	−33 (9)	1 (6)	19 (6)
O(13)	3,599 (6)	1,181 (5)	4,125 (4)	62 (5)	43 (5)	30 (2)	−9 (4)	−5 (3)	3 (3)
C(14)	3,562 (12)	449 (10)	3,727 (7)	93 (12)	57 (9)	46 (6)	−11 (8)	−13 (6)	−15 (6)
C(15)	3,374 (11)	748 (10)	3,122 (7)	94 (12)	79 (11)	43 (5)	−38 (9)	10 (6)	−30 (6)
O(16)	4,018 (6)	1,360 (6)	2,938 (4)	62 (6)	73 (6)	25 (2)	−17 (5)	−1 (3)	−11 (3)
C(17)	3,792 (10)	1,797 (10)	2,430 (7)	56 (9)	123 (12)	35 (5)	−18 (10)	−13 (5)	−29 (7)
C(18)	4,498 (11)	2,299 (10)	2,170 (6)	104 (12)	86 (10)	21 (3)	−28 (10)	−8 (5)	−12 (5)
C(19)	4,373 (9)	3,822 (9)	2,435 (6)	60 (9)	83 (10)	20 (3)	7 (7)	−4 (4)	6 (5)
C(20)	4,584 (11)	4,591 (9)	2,822 (7)	84 (10)	61 (9)	39 (5)	31 (9)	10 (6)	22 (5)
O(21)	4,354 (5)	4,363 (5)	3,420 (4)	48 (5)	42 (4)	29 (2)	5 (3)	1 (3)	0 (3)
C(22)	4,499 (9)	5,074 (7)	3,829 (7)	57 (8)	35 (6)	45 (5)	8 (6)	2 (6)	−3 (5)
C(23)	4,008 (8)	4,896 (8)	4,384 (6)	40 (7)	46 (7)	39 (4)	12 (6)	−4 (4)	−13 (5)
O(24)	4,270 (5)	4,045 (5)	4,623 (3)	45 (4)	52 (5)	24 (2)	6 (2)	−4 (2)	−8 (3)
C(25)	3,826 (9)	3,804 (9)	5,127 (5)	59 (8)	79 (10)	20 (3)	11 (8)	0 (4)	−11 (5)
C(26)	4,238 (9)	3,026 (10)	5,432 (6)	62 (8)	86 (10)	20 (3)	−0 (8)	1 (4)	−9 (5)

[a] The values for Pb and the atoms of the anions are magnified by 10^5; the others, by 10^4. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

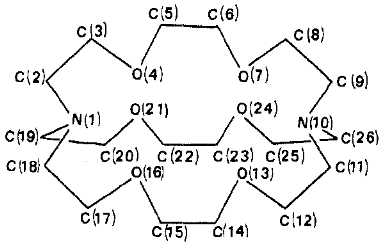

Figure 1. Schematic representation and notation used in the $C_{18}H_{36}N_2O_6$ compound.

and calculated structure factor amplitudes and the weight w was taken as $1/\sigma^2(F_o)$. The atomic scattering factors for the nonhydrogen atoms were those calculated by Cromer and Waber,[8] while those for hydrogen were taken from ref 9. The effects of anomalous dispersion for Pb and S were included; the values for $\Delta f'$ and $\Delta f''$ used are those given by Cromer.[10] The residual indices R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ and $R_2 = |\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2|^{1/2}$. After four cycles of least-squares refinement on the scale factor, the atomic coordinates and the thermal parameters (anisotropic for Pb; isotropic for the others) the residual index R_1 was equal to 0.077.

Hydrogen atoms were now included in calculated positions (1.00 Å from C, assuming sp^3 hybridization for the attached C), with isotropic thermal parameters $B_H = B_C + 1$ (B_C is the isotropic thermal parameter of the attached C). These atoms were not refined. Additional cycles of least-squares refinement with anisotropic refinement of all nonhydrogen atoms reduced R_1 and R_2 to 0.056 and 0.051, respectively.

In the final cycle of refinement the parameter shifts were less than 0.1σ. The estimated standard deviation of a unit weight ob-

Table II. Interatomic Distances (Å)

Pb–S	3.121 (3)	S–C	1.653 (12)
Pb–N′	2.642 (10)	C–N	1.126 (19)
Pb–N(1)	2.909 (9)	S′–C′	1.607 (16)
Pb–O(4)	2.734 (7)	C′–N′	1.163 (19)
Pb–O(7)	2.829 (8)		
Pb–N(10)	2.858 (9)	N(1)···N(10)	5.760 (13)
Pb–O(13)	2.805 (8)	N(1)···O(4)	2.761 (12)
Pb–O(16)	2.980 (8)	N(1)···O(16)	2.888 (13)
Pb–O(21)	2.729 (7)	N(1)···O(21)	2.882 (12)
Pb–O(24)	2.732 (8)	N(10)···O(7)	2.896 (12)
		N(10)···O(13)	2.814 (12)
N(1)–C(2)	1.479 (16)	N(10)···O(24)	2.938 (13)
C(2)–C(3)	1.494 (19)	O(4)···O(7)	2.770 (11)
C(3)–O(4)	1.379 (15)	O(4)···O(13)	4.371 (11)
O(4)–C(5)	1.409 (17)	O(4)···O(16)	3.264 (12)
C(5)–C(6)	1.431 (22)	O(4)···O(21)	4.350 (12)
C(6)–O(7)	1.447 (16)	O(4)···O(24)	5.081 (12)
O(7)–C(8)	1.424 (15)	O(7)···O(13)	3.339 (12)
C(8)–C(9)	1.502 (20)	O(7)···O(16)	4.185 (11)
C(9)–N(10)	1.477 (17)	O(7)···O(21)	5.337 (11)
N(10)–C(11)	1.491 (17)	O(7)···O(24)	4.525 (11)
C(11)–C(12)	1.504 (23)	O(13)···O(16)	2.750 (12)
C(12)–O(13)	1.381 (18)	O(13)···O(21)	5.186 (12)
O(13)–C(14)	1.419 (17)	O(13)···O(24)	4.581 (12)
C(14)–C(15)	1.457 (23)	O(16)···O(21)	4.684 (12)
C(15)–O(16)	1.429 (18)	O(16)···O(24)	5.545 (12)
O(16)–C(17)	1.359 (18)	O(21)···O(24)	2.735 (11)
C(17)–C(18)	1.461 (22)		
C(18)–N(1)	1.478 (18)	S···O(13)	3.635 (8)
N(1)–C(19)	1.448 (17)	S···O(16)	3.900 (8)
C(19)–C(20)	1.483 (20)	S···O(21)	3.110 (8)
C(20)–O(21)	1.429 (17)	S···O(24)	3.495 (8)
O(21)–C(22)	1.427 (15)	N′···O(4)	3.050 (13)
C(22)–C(23)	1.485 (20)	N′···O(7)	3.238 (13)
C(23)–O(24)	1.449 (15)	N′···O(21)	3.280 (13)
O(24)–C(25)	1.374 (15)	N′···O(24)	2.997 (13)
C(25)–C(26)	1.503 (20)		
C(26)–N(10)	1.481 (17)		

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(8) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(9) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 201-216.

(10) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

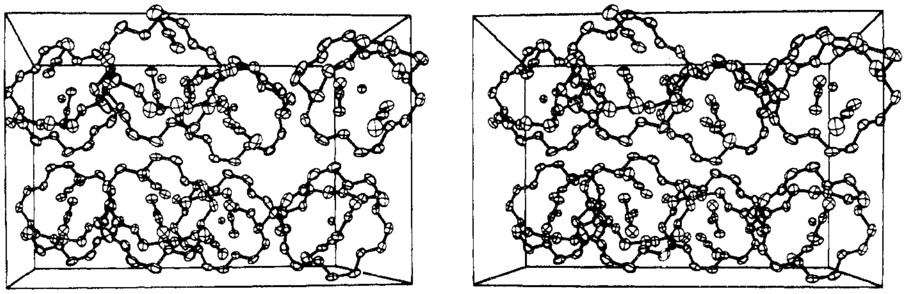

Figure 2. Stereoscopic view of the molecular packing in $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$. Atoms are represented by the envelopes of 30% probability.

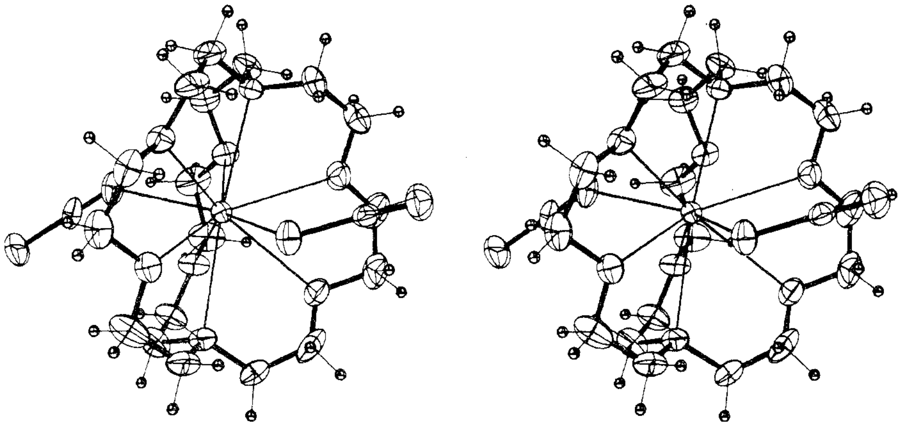

Figure 3. Stereoscopic view of the $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$ molecule. Atoms are represented by 35% probability thermal ellipsoids.

servation was 1.349. A final inspection did not show any systematic dependence of the residues $\Delta F/\sigma$ on θ or F_o. A Fourier difference map computed at this stage showed no peaks greater than 1.0 $e/Å^3$, except for a small region around the Pb atom. The final positional and thermal parameters for all nonhydrogen atoms are presented in Table I along with their estimated standard deviations as derived from the inverse matrix. The values of $|F_o|$ and F_c (in electrons × 10) for the 2986 reflections included in the refinement are available.[11] Selected bond lengths and angles are given in Tables II and III, along with their estimated standard deviations. Table IV lists the observed values of the torsion angles. Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter, unless otherwise indicated.

Description of the Structure and Discussion

A stereoview of the packing in the cell is shown in Figure 2. The crystal consists of discrete molecular units of $C_{18}H_{36}N_2O_6Pb(SCN)_2$ which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts; the closest approaches occur between N at x, y, z and C(22) at $\frac{1}{2} - x, -1 + (\frac{1}{2} + y), z$ and between S′ at x, y, z and C(5) at $1 + (\frac{1}{2} - x), \frac{1}{2} + y, z$. The corresponding distances are respectively equal to 3.26 and 3.48 Å.

One molecule is shown in Figure 3. The lead atom occupies a central position in the molecular cavity of the bicyclic ligand. As in the other cryptates of bivalent cations with this ligand so far studied, interactions of the central ion with other molecules or anions are possible.[4i,4j,4k] Here the two anions interact: one is S and the other N bonded (they are respectively noted (SCN) and (SCN)′). This dissimilar behavior is certainly due to steric effects; two strong Pb-S interactions are not possible in presence of the bicycle.

Figure 4 presents a view of the inner coordination sphere about the lead atom. It can be seen that the decacoordinate lead possesses a geometry which approximates a hexagonal pyramid, the base of which is trigonally capped. The sulfur atom is at the top of the pyramid, and the N′, O(4), and O(7) atoms constitute the trigonal cap. The plane of the trigonal cap is nearly parallel to the mean plane containing O(13), O(16), O(21), and O(24) (see Table V).

Table III. Bond Angles (deg)

N(1)-C(2)-C(3)	112.3 (8)	S-Pb-N(1)	85.9 (2)
C(2)-C(3)-O(4)	110.1 (8)	S-Pb-N(10)	92.9 (2)
C(3)-O(4)-C(5)	116.4 (10)	S-Pb-O(13)	75.5 (2)
O(4)-C(5)-C(6)	110.8 (8)	S-Pb-O(16)	79.4 (2)
C(5)-C(6)-O(7)	109.2 (8)	S-Pb-O(21)	63.8 (2)
C(6)-O(7)-C(8)	110.0 (9)	S-Pb-O(24)	73.0 (2)
O(7)-C(8)-C(9)	108.2 (7)	N′-Pb-O(4)	69.1 (3)
C(8)-C(9)-N(10)	112.1 (8)	N′-Pb-O(7)	72.5 (3)
C(9)-N(10)-C(11)	111.2 (9)	N′-Pb-O(21)	75.2 (3)
C(9)-N(10)-C(26)	108.8 (9)	N′-Pb-O(24)	67.7 (3)
C(11)-N(10)-C(26)	107.6 (9)	N′-Pb-N(1)	93.5 (4)
N(10)-C(11)-C(12)	112.1 (8)	N′-Pb-N(10)	91.2 (4)
C(11)-C(12)-O(13)	109.3 (8)	N(1)-Pb-O(4)	58.5 (3)
C(12)-O(13)-C(14)	113.6 (10)	N(1)-Pb-N(10)	174.4 (3)
O(13)-C(14)-C(15)	110.6 (9)	N(1)-Pb-O(16)	58.7 (3)
C(14)-C(15)-O(16)	108.9 (9)	N(1)-Pb-O(21)	61.3 (3)
C(15)-O(16)-C(17)	111.8 (11)	N(10)-Pb-O(7)	61.2 (3)
O(16)-C(17)-C(18)	112.7 (9)	N(10)-Pb-O(13)	59.6 (3)
C(17)-C(18)-N(1)	112.3 (9)	O(4)-Pb-O(7)	59.7 (3)
C(18)-N(1)-C(2)	111.3 (9)	O(4)-Pb-O(13)	104.2 (3)
C(18)-N(1)-C(19)	108.8 (9)	O(4)-Pb-O(16)	69.5 (3)
C(19)-N(1)-C(2)	109.9 (8)	O(4)-Pb-O(21)	105.5 (3)
N(1)-C(19)-C(20)	115.8 (8)	O(4)-Pb-O(24)	136.7 (3)
C(19)-C(20)-O(21)	107.6 (7)	O(7)-Pb-O(13)	72.7 (3)
C(20)-O(21)-C(22)	112.3 (9)	O(7)-Pb-O(16)	92.2 (3)
O(21)-C(22)-C(23)	108.5 (7)	O(7)-Pb-O(21)	147.6 (3)
C(22)-C(23)-O(24)	108.7 (7)	O(7)-Pb-O(24)	108.9 (3)
C(23)-O(24)-C(25)	113.2 (9)	O(13)-Pb-O(16)	56.7 (3)
O(24)-C(25)-C(26)	111.2 (8)	O(13)-Pb-O(21)	139.2 (3)
C(25)-C(26)-N(10)	114.2 (8)	O(13)-Pb-O(24)	111.6 (3)
S-C-N	177.0 (8)	O(16)-Pb-O(21)	110.2 (3)
S′-C′-N′	179.0 (8)	O(16)-Pb-O(24)	152.2 (3)
Pb-N′-C′	137.5 (6)	O(21)-Pb-O(24)	60.1 (3)
		Pb-S-C	112.8 (2)

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[11] See paragraph at end of paper regarding supplementary material.

Table IV. Torsion Angles (deg)[a]

A-B-C-D		A-B-C-D	
N(1)-C(2)-C(3)-O(4)	−49	O(16)-C(17)-C(18)-N(1)	−62
O(4)-C(5)-C(6)-O(7)	61	N(1)-C(19)-C(20)-O(21)	−61
O(7)-C(8)-C(9)-N(10)	−65	O(21)-C(22)-C(23)-O(24)	57
N(10)-C(11)-C(12)-O(13)	−55	O(24)-C(25)-C(26)-N(10)	−62
O(13)-C(14)-C(15)-O(16)	58		
C(3)-O(4)-C(5)-C(6)	140	C(2)-N(1)-C(18)-C(17)	146
C(5)-O(4)-C(3)-C(2)	−176	C(2)-N(1)-C(19)-C(20)	−61
C(6)-O(7)-C(8)-C(9)	−170	C(18)-N(1)-C(2)-C(3)	−63
C(8)-O(7)-C(6)-C(5)	−169	C(18)-N(1)-C(19)-C(20)	177
C(12)-O(13)-C(14)-C(15)	150	C(19)-N(1)-C(2)-C(3)	176
C(14)-O(13)-C(12)-C(11)	−179	C(19)-N(1)-C(18)-C(17)	−93
C(15)-O(16)-C(17)-C(18)	−169	C(9)-N(10)-C(11)-C(12)	−63
C(17)-O(16)-C(15)-C(14)	−167	C(9)-N(10)-C(26)-C(25)	161
C(20)-O(21)-C(22)-C(23)	162	C(11)-N(10)-C(9)-C(8)	147
C(22)-O(21)-C(20)-C(19)	−177	C(11)-N(10)-C(26)-C(25)	−78
C(23)-O(24)-C(25)-C(26)	−168	C(26)-N(10)-C(9)-C(8)	−95
C(25)-O(24)-C(23)-C(22)	−177	C(26)-N(10)-C(11)-C(12)	177

[a] Defined as the angle, measured counterclockwise, that the projection of bond A-B makes with the reference bond C-D when viewed in the direction B-C. The estimated standard deviations are all less than 0.9°.

Table V. Weighted Least-Squares Planes and Distances (Å) of Atoms from These Planes

Plane I: O(13), O(16), O(21), O(24)

Eq: $-0.9739X + 0.2008Y - 0.1055Z + 6.2590 = 0$

O(13)	0.148 (9)	Pb	−0.824 (0)
O(16)	−0.156 (9)	N(1)	−0.785 (10)
O(21)	0.126 (8)	N(10)	−0.785 (9)
O(24)	−0.126 (8)	N′	−2.79
		O(4)	−2.98
		O(7)	−3.00

Plane II: O(4), O(7), O(21), O(24)

Eq: $-0.8366X - 0.5024Y - 0.2183Z + 10.8064 = 0$

O(4)	−0.112 (8)	Pb	0.893 (0)
O(7)	0.117 (8)	N(1)	0.965 (10)
O(21)	0.122 (8)	N(10)	1.060 (10)
O(24)	−0.115 (8)		

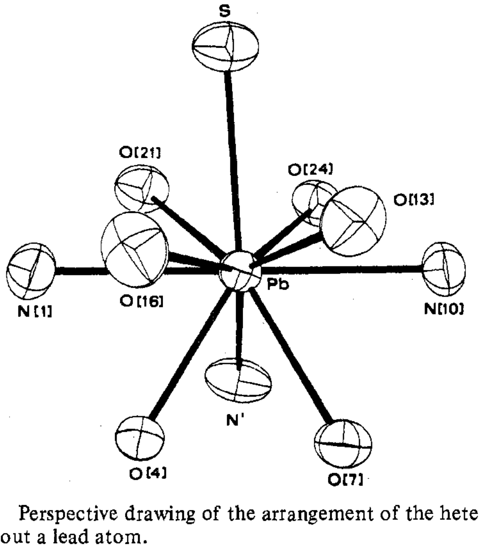

Figure 4. Perspective drawing of the arrangement of the hetero atoms about a lead atom.

The Pb-S bond length, 3.121 (3) Å, is longer than the value 2.97 Å found in cubic PbS (NaCl structure) in which lead contains a delocalized lone pair of electrons.[12] It also is longer than the value 2.895 (3) Å recently observed in 1,7,10,16-tetraoxa-4,13-diazacyclooctadecanelead(II) thiocyanate, $C_{12}H_{26}N_2O_4{\cdot}Pb(SCN)_2$; in this compound the 6s lone pair of the lead atom has been localized.[13] However same values have been found in lead(II) *O,O′*-diisopropylphosphorodithioate, in which the lead atom has sixfold coordination; the lone pair occupies an equatorial position in the irregular pentagonal bipyramid.[14]

The Pb-O distances range from 2.729 (7) to 2.980 (8) Å (mean value 2.80 Å); they are longer than the sum of the van der Waals radius of oxygen and the ionic radius of lead(II) of 2.67 Å.[15,16] The same remark is true for the two Pb-N distances with the two nitrogen atoms belonging to the bicycle. The mean value of these two distances is 2.88 Å whereas the sum of the radii equals 2.77 Å.[15,16] The Pb-N′ bond distance of 2.642 (10) Å indicates the presence of a slight covalent character. In the lead(II) isopropyl xanthate-pyridine compound in which lead is five-coordinated the Pb-N bond is equal to 2.55 (1) Å.[17]

An example of structure which elegantly displays a stereochemically active lone pair of electrons in six-coordination has been reported recently by Lawton and Kokotailo.[14] They have shown that the bonds most remote from the lone pair tend to be shorter than the adjacent bonds. In our compound, although the Pb-O (4), Pb-O (21), and Pb-O (24) bonds are the shortest (ranging from 2.729 (7) to 2.734 (7) Å) and although the Pb-O (16) bond is significantly lengthened (2.980 (8) Å), it seems that the lone pair is delocalized. The lead atom appears to be a simple cation, according to the Pb-O, Pb-N, and Pb-S distances. These bonds are mainly due to electrostatic interactions and the noted shortenings or lengthenings are probably consequences of steric requirements.

In the lead cryptate the organic ligand presents the in-in conformation.[2b] The distance between the two nitrogen atoms is equal to 5.76 Å, whereas in the uncomplexed ligand 6.87 Å separates the two atoms.[18] The shortest distance of this type has been found in the two silver cryptates $C_{18}H_{36}N_2O_6{\cdot}4AgSCN$ and $2C_{18}H_{36}N_2O_6{\cdot}4AgSCN$ as 4.91 Å (mean value).[19] As in the other cryptates so far studied, the diazahexaoxa macrobicyclic ligand adapts the

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(12) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, England, 1962, p 527.

(13) B. Metz and R. Weiss, *Acta Crystallogr., Sect. B,* **29,** 1088 (1973).

(14) S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.,* **11,** 363 (1972).

(15) L. H. Ahrens, *Geochim. Cosmochim. Acta,* **2,** 155 (1952).

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 221-264, 538.

(17) H. Hagihara, N. Yoshida, and Y. Watanabe, *Acta Crystallogr., Sect. B,* **25,** 1775 (1969).

(18) R. Weiss, B. Metz, and D. Moras, *Proc. Int. Conf. Coord. Chem., 13th,* **2,** 85 (1970).

(19) B. Metz, D. Moras, and R. Weiss, unpublished results.

dimension of its cavity to the size of the cation. The conformational changes are drastic upon complexation: anti forms pass to gauche forms and anti clinal forms pass to anti forms. The mean values of the torsion angles about the C-C and C-O bonds in the lead complex are respectively equal to 59 and 167° (Table IV).

Registry No. $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$, 51567-34-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036 Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2094.

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Transition Metal σ-Acyls. II.[1] Crystallographic Determination of the Molecular Structure of (π-C_5H_5)Ni[$C_5H_5(Me_2C_2O)_2$], Including the Location and Refinement of All Hydrogen Atoms

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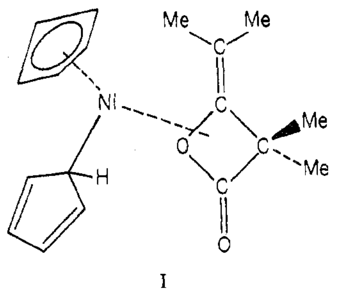
The reaction of bis(π-cyclopentadienyl)nickel with dimethylketene has previously been shown to produce a complex of stoichiometry $(C_5H_5)_2(Me_2C_2O)_2Ni$. A single-crystal X-ray diffraction study of this complex shows it to be (*pentahapto*-cyclopentadienyl)-1,3′,4′-*trihapto*{2-methyl-2-(6′,6′-dimethylbicyclo[3.2.0]hept-3′-en-7′-on-2′-yl)propionyl}nickel(II). The complex crystallizes in the centrosymmetric triclinic space group $P\overline{1}$ [C_i^1; No. 2] with a = 9.0048 (16) Å, b = 15.5241 (33) Å, c = 6.0445 (12) Å, α = 94.17 (2)°, β = 109.94 (1)°, γ = 94.04 (2)°, and Z = 2. Observed and calculated densities are 1.378 (5) and 1.386 g cm^{-3}, respectively. All atoms, including hydrogen atoms, were accurately located from an analysis based on 2794 symmetry-independent reflections (representing data complete to 2θ = 50°, using Mo Kα radiation) collected with a Picker FACS-1 automated diffractometer. Final discrepancy indices are R_F = 3.04% and R_{wF} = 3.05%. The nickel atom is bonded to a π-cyclopentadienyl ligand [Ni–C = 2.066 (2)–2.172 (2) Å], an olefin [Ni–C = 2.004 (2) and 2.024 (2) Å], and a σ-acyl residue [Ni–C = 1.895 (2) Å].

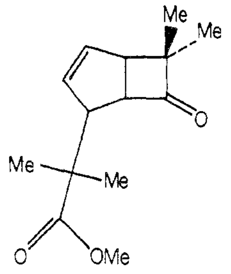
Introduction

The reaction of bis(π-cyclopentadienyl)nickel(II) with dimethylketene ($Me_2C{=}C{=}O$) was originally reported by Sato, Ichibori, and Sato in 1971.[2] On the basis of infrared and ^1H nmr spectroscopy, the product of this reaction (which has the stoichiometry $(C_5H_5)_2(Me_2C_2O)_2Ni$ or $C_{18}H_{22}O_2Ni$) was assigned a structure in which a four-membered lactone ring was bonded to the nickel atom *via* π electrons (see I).

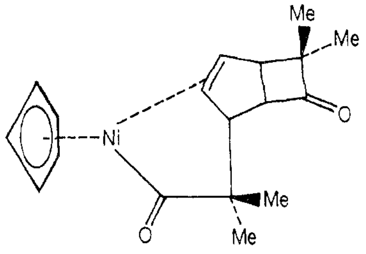


I

However, degradation of this complex with ceric ammonium nitrate in methanol produces a good yield of the bicyclic species II.[3] A more reasonable structure for the complex $C_{18}H_{22}O_2Ni$, in which the bicyclic fragment of II is retained, is shown in III.



II



III

In order to determine unambiguously the molecular geometry of the complex $C_{18}H_{22}O_2Ni$, we have undertaken a three-dimensional X-ray diffraction study. Our results, which confirm the correctness of structure III, are reported below.

Collection and Treatment of the X-Ray Diffraction Data

Orange crystals of the complex were provided by Dr. D. A. Young of Tennessee Eastman Co. The material was recrystallized from methanol under an inert atmosphere.

The crystal chosen for the X-ray diffraction study was an approximately rectangular plate between {100} faces, 0.066 mm apart and bounded by {010}, 0.137 mm apart, and {001}, 0.780 mm apart. The crystal was placed within a lightly greased 0.2-mm diameter thin-walled Lindemann glass capillary, which was then flushed with nitrogen, flame sealed, fixed into a brass pin with melted paraffin wax, and transferred to a eucentric goniometer.

Preliminary $hk(0\text{-}1)$ Weissenberg photographs, a c-axis rotation photograph, $(0\text{-}1)kl$ and $h(0\text{-}1)l$ precession photographs, and a and b cone-axis photographs gave approximate unit cell dimensions, indicated only C_i ($\overline{1}$) Laue symmetry, and showed no systematic absences. These conditions are compatible only with the triclinic space groups $P1$ [C_1^1; No. 1] or $P\overline{1}$ [C_i^1; No. 2].

The crystal was transferred to a Picker FACS-1 computer-con-

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[1] Part I: M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

[2] M. Sato, K. Ichibori, and F. Sato, *J. Organometal Chem.*, **26**, 267 (1971).

[3] Personal communication from Dr. D. A. Young, Tennessee Eastman Co.