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Stable Homopolyatomic Anions. Synthesis and Crystal Structures of Salts Containing the Pentaplumbide(2−) and Pentastannide(2−) Anions[1]

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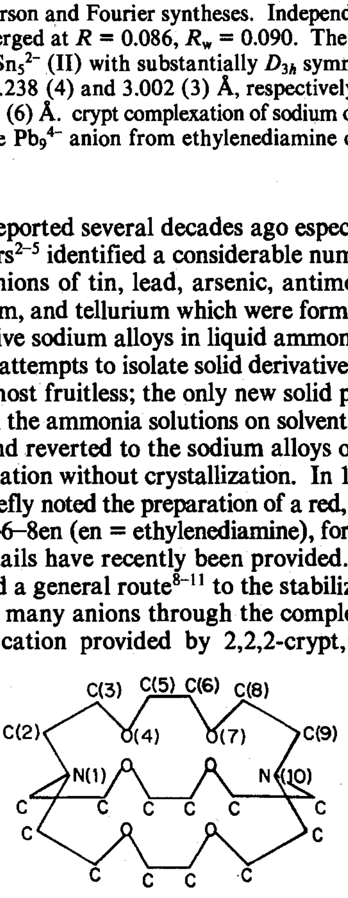
The synthesis and crystal structure are reported for two salts in which the pentaplumbide(2−) (I) and pentastannide(2−) (II) anions have been stabilized as a result of complexation of the sodium cations by 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane (2,2,2-crypt). The phases are prepared by the reaction of solutions of crypt in ethylenediamine with the intermetallic compositions $NaPb_{1.7-2}$ and $NaSn_{1-1.7}$. The compounds are trigonal and isostructural; for I $a = 11.615$ (3) Å and $c = 22.120$ (12) Å while for II $a = 11.620$ (1) Å and $c = 22.160$ (7) Å, the data applying at temperatures of ~5 and ~30 °C, respectively. For I integrated intensities were collected on an automatic diffractometer over four octants, yielding 499 averaged reflections ($\bar{3}m$) with $I > 3\sigma_I$. Heavy atoms were located by Patterson techniques and refined in space group $P\bar{3}c1$ by full-matrix least-squares techniques to conventional $R = 0.086$, $R_w = 0.091$. For II integrated intensities were collected over three octants, yielding 986 total (and 358 averaged) reflections with $I > 3\sigma_I$. For II an initial model based on the results for I was modified by addition of a rotational disorder for ~14% of the tin groups indicated by both Patterson and Fourier syntheses. Independent refinement of all atoms in the acentric group $P3c1$ required by the disorder converged at $R = 0.086$, $R_w = 0.090$. The compounds contain the trigonal-bipyramidal homopolyatomic anions Pb_5^{2-} (I) and Sn_5^{2-} (II) with substantially D_{3h} symmetry. In Pb_5^{2-} the equatorial–equatorial and axial–equatorial bond distances are 3.238 (4) and 3.002 (3) Å, respectively, while in Sn_5^{2-} the corresponding distances are 3.095 (10) and 2.887 (7) plus 2.854 (6) Å. crypt complexation of sodium or potassium cations is evidently not sufficient to allow isolation of these derivatives of the Pb_9^{4-} anion from ethylenediamine or ammonia solvents.

Introduction

Research reported several decades ago especially by Zintl and co-workers[2-5] identified a considerable number of homopolyatomic anions of tin, lead, arsenic, antimony, bismuth, sulfur, selenium, and tellurium which were formed by solution of the respective sodium alloys in liquid ammonia. However, until recently attempts to isolate solid derivatives of these ions have been almost fruitless; the only new solid products Zintl obtained from the ammonia solutions on solvent removal were amorphous and reverted to the sodium alloys of the element under investigation without crystallization. In 1970 Kummer and Diehl[6] briefly noted the preparation of a red, slightly stable phase Na_4Sn_9·6–8en (en = ethylenediamine), for which partial structural details have recently been provided.[7] Meanwhile we have found a general route[8-11] to the stabilization of solid derivatives of many anions through the complexation of the alkali metal cation provided by 2,2,2-crypt,[12,13] the high stability of the complex cation in many cases preventing reversion to the otherwise more stable alloy phase. The present paper presents the synthesis and structural characterization of the salts $[cryptNa^+]_2Pb_5^{2-}$ and $[cryptNa^+]_2Sn_5^{2-}$, the anions of which have hitherto been unknown for these elements save for a preliminary note on our results on the former.[9] The corresponding information for $(cryptNa^+)_3Sb_7^{3-}$ and $(cryptK^+)_2Te_3^{2-}$ has been published[10,11] and that for $(cryptNa^+)_4Sn_9^{4-}$ [9] is forthcoming.[14]



2,2,2-crypt

Experimental Section

Alloy samples were prepared as before[15] by fusion of appropriate amounts of the elements in sealed tantalum tubing. crypt was used as received from EM Laboratories and handled only in the drybox. The solvents were dried over CaH_2 and stored over Molecular Sieve in an evacuated flask after the usual degassing procedures. All syntheses were affected using standard high-vacuum techniques, about 0.1-g amounts of 2,2,2-crypt, and an apparatus equipped with Teflon needle valves (Fisher-Porter). All sample transfers were done in a drybox under inert atmosphere conditions.

Syntheses. Ethylenediamine (en) has been found to be the best solvent in both utility and convenience. Sodium–lead alloys of composition near $NaPb_{2.25}$ react only slightly with en but rapidly dissolve in the presence of crypt to give a dark brown solution. However, only the parent alloy (nonstoichiometric Cu_3Au-type structure[16]) is recovered when solvent is removed after a few hours. But small amounts of a microcrystalline brick orange phase deposit irreversibly from the foregoing solution after long standing or, in larger amounts, after heating to ~50 °C, especially if a more reduced alloy is used, e.g., $NaPb_{1.75}$. This microcrystal product turns out to be the subject Pb_5^{2-} salt. A more claret red solution is obtained in en from the composition $NaPb_{1.3}$ and crypt, and a very low yield of dark ruby red crystals of the desired polyplumbide salt which are suitable for structural analysis deposits on the wall of the reaction chamber at the meniscus during slow refluxing at about 90 °C.

Subsequent to the structure determination the phase has also been obtained from the $Na_{1.7}Pb$ composition in en and also after addition of NaOH. A good yield of the isostructural $(cryptK^+)_2Pb_5^{2-}$ precipitates as needles up to ~1 mm long from the brown-green solution obtained with $KPb_{2.25}$ plus crypt in en on heating to about 50 °C overnight. The emerald green solution color associated in the previous literature[2] with Pb_9^{4-} has not been obtained in en with any of these alloys. Green solutions are obtained with $MPb_{2.25}$ (M = Na, K) in NH_3 in the presence of crypt but only the $(cryptM^+)_2Pb_5^{2-}$ products or the starting alloy can be isolated either at −33 °C or at room temperature although traces of other materials have been seen in the powder patterns. With potassium the alloy phase which separates is the hitherto unknown $KPb_{2.2}$ (Cu_3Au structure with $a_0 = 4.95$ Å) paralleling the behavior of the sodium system.[16] At higher temperature this composition is reported to consist of the phases KPb_2 and KPb_4.[17]

Although the red Sn_9^{4-} is the usual product from $MSn_{2.25}$ in en or NH_3 with or without crypt, more yellow-brown to red-brown solutions are obtained from the slower solution of alloys NaSn to $Na_{1.7}Sn$ in en in the presence of crypt, and yellow brown (small) to claret red (larger) crystals slowly deposit from these on standing for days to weeks at room temperature. Oxidation with NaOH produces the same result faster.

Data Collection and Reduction. Crystals were selected under a microscope in the drybox and inserted into 0.2-mm thin-wall capillaries using silicone grease to hold their position. After preliminary oscillation photographs, a suitable crystal was mounted in a computer-controlled, four-circle diffractometer. This procedure and the programs utilized in the structure solution, refinements, and descriptions were as referenced before[10] unless otherwise noted.

For the lead compound a crystal ca. 0.1 × 0.1 × 0.3 mm was utilized and a total of 9745 reflections out to $2\theta \leq 50°$ in four octants spanning HKL to $H\bar{K}\bar{L}$ were measured at a temperature of ~5 °C using Mo

$K\alpha$ radiation. The crystal was cooled principally in the hope of reducing what appeared to be some disorder or thermal motion of ethylene groups at nitrogen bridgeheads that had been observed in $(\text{cryptNa}^+)_3\text{Sb}_7^{3-}$.[10] A 9% decay in the intensity sum of three standard reflections over the data collection period was neglected. Hexagonal unit cell parameters $a = 11.615$ (3) Å and $c = 22.120$ (12) Å at 5 °C were obtained from a least-squares refinement of twice the Ω angles of nine independent reflections, each of which was tuned by top–bottom left–right beam splitting on both Friedel-related peaks after the diffraction data set had been collected. The very small amount of the compound available at that time precluded a density determination but a unit cell of this volume (2583 Å^3) was expected to hold about four crypt-containing cations judging from the volume requirements found in related compounds of known structure.

The dimensions of the crystal were obtained from photomicrographs and the data set was corrected for absorption[18] using the program TALABS and a linear absorption coefficient of 160 cm^{-1}.[19] The data were then corrected for Lorentz–polarization and each observation was checked for statistical significance; 1878 reflections were considered observed with $I > 3\sigma_I$ and $F_o > 3\sigma_I$ as defined before,[10] and these exhibited extinction for $h\bar{h}l$ with $l \neq 2n$. The data set was then averaged to 499 independent reflections with trigonal Laue symmetry $\bar{3}m$ when it was observed that intensities of presumably equivalent reflections occurred in sets of three rather than in the sets of six expected for hexagonal Laue symmetry. The averaging program rejected 17 reflections by the criterion $\sum|F_o - \bar{F}_o|/\sum F_o \geq 0.20$. The trigonal space group $P3c1$ (No. 258) and the centric equivalent $P\bar{3}c1$ (No. 165) both have the appropriate extinction condition associated with them.[19]

For the tin compound a total of 3650 reflections in the three octants HKL, $HK\bar{L}$, and $H\bar{K}L$ were measured out to $2\theta \leq 40°$ at a temperature of ~30 °C. No decay of standard reflections with time was observed. Unit cell parameters $a = 11.620$ (1) Å and $c = 22.160$ (7) Å were similarly obtained from the tuned angles of 18 independent reflections. The data set exhibited the same extinction conditions as the lead compound investigated previously. An absorption correction was not employed because both the absorption coefficient (20 cm^{-1}) and the crystal were small (0.05 × 0.05 × 0.2 mm). After correction for Lorentz and polarization effects 986 reflections were found to qualify as "observed", viz., $I > 3\sigma_I$, and the data set was averaged for $\bar{3}m$ Laue symmetry to yield 358 independent reflections, about 70% as many as found with the lead compound. The HPR[20] test of the intensity distribution indicated acentricity.

Solution and Refinement of Structures. The scattering factors used were those of Hanson et al.,[21] modified for the real and imaginary parts of anomalous dispersion.[22] Positional parameters for all atoms, anisotropic temperature factors for heavier atoms, and isotropic temperature factors for all other (nonhydrogen) atoms were refined by full-matrix least squares through minimization of $\sum w\Delta^2$ where $w = 1/\sigma_F^2$ and $\Delta = |F_o| - |F_c|$.

Lead Structure. Lead positions were inferred and the two possible space groups confirmed by analysis of a three-dimensional Patterson function, aided especially by the distribution of heavy-atom vectors in the Harker sections U, V, 0 and U, V, $^1/_2$ and along 0, 0, W. Light-atom positions were thereafter deduced from successive Fourier syntheses and least-squares refinements. A solution was readily achieved in the centric $P\bar{3}c1$ space group, ultimately converging at $R = 0.086$ $(=\sum|\Delta|/\sum|F_o|)$ and $R_w = 0.091$ $(=(\sum w\Delta^2/\sum wF_o^2)^{1/2})$. Along the route the data set was reweighted in 12 groups when it was observed that $\sum w\Delta^2$ sorted on F_o was a significant function of the latter, the weaker reflections especially being overweighted by σ_F^{-2}. The largest shift in the final cycle was 0.03σ and the final difference electron density map exhibited scattered peaks of ≤1 e Å^{-3} near atoms except for peaks of 2 e Å^{-3} positioned so as to suggest that roughly 2% of the lead anions might be disordered as they are (to a greater extent) in the tin structure (vide infra).

Although thermal parameters and errors in the one unique cation appear quite normal (see Results), the observations that (1) Na^+ was displaced from the midpoint of the N–N axis by ~0.3 Å and (2) an HPR test of the intensity distribution mildly suggested acentricity both prompted an examination of the alternate $P3c1$ space group. This possibility really pertains only to the cation positions, in the following way. The heavy-atom entities found consist of two trigonal-bipyramidal pentalead (or tin) ions centered on the threefold axes at 0, 0, z and 0, 0, $z + {}^1/_2$ ($z = 0.25$ in $P\bar{3}c1$). One pair of cryptated sodium ions occur at $^1/_3$, $^2/_3$, z' and $^1/_3$, $^2/_3$, $z' + {}^1/_2$, with the N–Na–N axis lying on the crystallographic threefold axis. In the acentric space group $P3c1$ there is a second independent pair of cations centered at $^2/_3$, $^1/_3$, z'' and $^2/_3$, $^1/_3$, $^1/_2 + z''$, whereas in $P\bar{3}c1$ the latter pair is generated from the first by an inversion. Refinement in $P3c1$ naturally raises problems because of the major phasing provided by substantially centric lead anions. The cyclic refinement necessitated by parameter coupling and the inclusion of the imaginary component of the anomalous dispersion correction were both handled as described below for the tin structure. The results were quite reassuring with regard to correctness of the centric model. At convergence ($R = 0.093$, $R_w = 0.106$ for 1771 reflections) neither the parameters nor their errors for the two independent cations were significantly different from before (≥ 4–5σ) except that the inevitable coupling had introduced opposed distortions of the bond lengths at the ±0.1 Å level for those related by the center of symmetry. The largest difference in the Pb_5^{2-} anions from the two refinements was an asymmetric displacement of each of the axial atoms in the acentric case by 4σ (0.018 Å), a change of doubtful significance.

Tin Structure. The analysis of the tin structure started with a confident introduction of leadlike parameters in a centric relationship since this compound exhibited the same extinctions and very similar dimensions for the unit cell. However, the refinement yielded a substantially higher R value and, most troubling, the final electron density difference map showed a substantial peak of ca. 7 e Å^{-3} in a position which would correspond to rotation of some heavy-metal anions by 60°. Since an incorrect choice of space group seemed possible, the structure was reconstructed in the lowest possible symmetry, $P3$, using the Patterson map together with Fourier syntheses. Significantly, the Patterson map contained all of the interset vectors expected if ca. 12–20% of the Sn_5^{2-} anions were indeed disordered by a rotation of about 60° together with a slight displacement in z. Electron density synthesis utilizing these disordered but unrefined Sn_5^{2-} groups readily allowed the location of all ligand and sodium atoms, and introduction of these gave an unrefined R of 0.19. As expected, oscillations characteristic of refinement into too low a symmetry were observed when the light-atom positions were let go. However the positions in all cases were within 3σ of those inferred for the lead compound in the $P3c1$ space group, which was assumed thereafter.

Several different refinements were pursued to ensure that both the position and fraction of the minor (rotated) equatorial tin atoms were real and reproducible. Initially positional coordinates and an occupancy consistent with the Patterson map were introduced and held constant while the principal Sn_5^{2-} group and then the light atoms were refined a few cycles (as described below). At this point the positional and isotropic temperature factors for all tin atoms were let go, whereafter only the occupancies of the two equatorial tin sites were refined with the temperature factor of the minor set fixed at that of the principal one. Different initial x and y coordinates of the minor atoms as well as occupancy refinements at different stages of the structure solution consistently yielded occupancies of 14–15 (±0.5)% for the rotated Sn_5 group, 85–87% for the principal one, and a reproducible separation of about 0.01 in z (0.25 Å).

It is principally this minor tin component which dictates the acentric symmetry and even so its contribution to the phasing is not large. Such pseudocentricity again leads to coupling and then to substantially increased errors and oscillations of positional and thermal parameters for those atoms related by the pseudocenter. In general this circumstance cannot be avoided without abandoning the least-squares refinement technique.[23-25] However, the opposing oscillations of parameters and bonds related to the pseudocenter can be suppressed (but not entirely eliminated) by cyclic refinement to convergence of five separate sets of parameters, each of which contains only those which are not significantly coupled (i.e., those of the two separate crypt cations, half the major anion parameters, and the minor waist atoms). Some small distortions especially in the ligands may still remain from cumulative effects of coupling, presumably from some near-zero terms in the denominator of sums for the calculations of shifts by the least-squares technique.

Although the imaginary component of the anomalous dispersion is a significant factor for tin (and lead), correction for it also presents special problems in the acentric space group since F_o values for Friedel-related peaks are no longer equal. This eliminates the improvement in the data set generated both by averaging of otherwise redundant observations with different l values and by the routine rejection of reflections which had been incorrectly measured. Re-

Table I. Final Positional and Thermal Parameters[a] for $(\text{cryptNa}^+)_2\text{Pb}_5{}^{2-}$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb(1)	0.1609 (2)	0.0	0.25	15.2 (3)	30.8 (6)	5.4 (1)	15.4 (3)	−2.5 (1)	−5.0 (2)
Pb(2)	0.0	0.0	0.1438 (2)	19.1 (3)	19.1 (3)	4.0 (1)	9.6 (2)	0	0
Na	0.667	0.333	0.457 (1)	11 (2)	10.2 (16)	4.0 (7)	5.1 (8)	0	0

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
N(1)	0.667	0.333	0.311 (2)	2.5 (7)	C(6)	0.738 (4)	0.081 (4)	0.470 (2)	6.5 (9)
C(2)	0.663 (4)	0.209 (3)	0.293 (1)	5.6 (9)	O(7)	0.748 (2)	0.193 (2)	0.504 (1)	4.7 (5)
C(3)	0.575 (3)	0.094 (3)	0.332 (1)	4.5 (7)	C(8)	0.727 (4)	0.161 (3)	0.568 (1)	5.1 (8)
O(4)	0.614 (2)	0.116 (2)	0.394 (1)	4.6 (5)	C(9)	0.755 (3)	0.267 (3)	0.603 (1)	4.7 (8)
C(5)	0.738 (3)	0.120 (4)	0.402 (1)	4.8 (7)	N(10)	0.667	0.333	0.577 (2)	6.1 (12)

[a] Estimated standard deviations in the least significant figures are given in parentheses. Values of $\beta \times 10^3$ are listed. The form of the anisotropic thermal parameter expression employed is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Final Positional and Thermal Parameters for $(\text{cryptNa}^+)_2\text{Sn}_5{}^{2-}$

Atom	Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn(1)	0.86	−0.0054 (5)	0.1510 (3)	0.3145	14.4 (4)	28.2 (6)	5.2 (1)	12.9 (3)	−2.4 (7)	−4.9 (2)
Sn(2)	0.14	0.1320 (18)	0.1795 (19)	0.3244 (11)	$B = 5.1$ (7) Å^2					
Sn(3)	1.0	0	0	0.4177 (3)	23.5 (7)	23.5 (7)	4.9 (3)	11.8 (4)	0	0
Sn(4)	1.0	0	0	0.2155 (3)	20.8 (6)	20.8 (6)	2.9 (2)	10.4 (3)	0	0
Na(1)		0.667	0.333	0.514 (1)	13 (2)	13 (2)	3.5 (10)	6 (1)	0	0
Na(2)		0.333	0.667	0.602 (1)	11 (2)	11 (2)	2 (1)	5 (1)	0	0

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
N(11)	0.667	0.333	0.646 (2)	3.2 (12)	N(21)	0.333	0.667	0.757 (2)	4.4 (13)
C(12)	0.708 (3)	0.483 (3)	0.660 (2)	2.9 (9)	C(22)	0.361 (3)	0.800 (3)	0.776 (2)	3.2 (9)
C(13)	0.847 (3)	0.593 (3)	0.633 (2)	3.3 (9)	C(23)	0.405 (3)	0.902 (4)	0.735 (2)	3.5 (10)
O(14)	0.801 (2)	0.554 (2)	0.570 (1)	4.4 (6)	O(24)	0.389 (3)	0.870 (3)	0.673 (1)	7.0 (8)
C(15)	0.927 (4)	0.660 (3)	0.538 (2)	4.1 (10)	C(25)	0.279 (3)	0.898 (3)	0.661 (1)	1.9 (8)
C(16)	0.862 (4)	0.624 (4)	0.465 (2)	5.9 (12)	C(26)	0.246 (4)	0.907 (4)	0.600 (2)	4.0 (9)
O(17)	0.891 (2)	0.509 (2)	0.461 (1)	2.5 (5)	O(27)	0.254 (2)	0.810 (2)	0.563 (1)	3.6 (6)
C(18)	0.912 (3)	0.450 (4)	0.400 (1)	3.2 (8)	C(28)	0.296 (4)	0.848 (4)	0.494 (2)	4.8 (10)
C(19)	0.784 (3)	0.465 (3)	0.361 (1)	2.4 (8)	C(29)	0.267 (4)	0.736 (4)	0.456 (1)	2.7 (7)
N(110)	0.667	0.333	0.379 (2)	2.3 (11)	N(210)	0.333	0.667	0.483 (2)	4.9 (14)

Table III. Metal–Metal Bond Distances and Angles within $\text{M}_5{}^{2-}$ Anions

	$\text{Pb}_5{}^{2-}$		$\text{Sn}_5{}^{2-}$ [a]	
Equatorial–equatorial, Å	3.238 (4)	3.319 (4)[b]	3.095 (10)	3.24 (4)[c]
Equatorial–axial, Å	3.002 (3)	3.075 (3)[b]	2.877 (7)[d]	2.854 (6)
Equatorial–axial–equatorial, deg	65.26(9)		65.1 (2)[d]	65.7 (2)
Axial–equatorial–axial, deg	103.0 (1)		102.8 (2)	
Equatorial–equatorial–axial, deg	57.37 (5)		57.5 (2)[d]	57.2 (2)

[a] Occupation-weighted z coordinate of 0.1841 used for equatorial tin atoms. [b] Distances averaged over thermal motion, independent atoms. [c] Within minor (14%) component. [d] To axial Sn(3).

finement of the tin (and lead) salt in the acentric $P3c1$ space group therefore employed the reduced but unaveraged data set. In order to correct for poor data 44 of 986 reflections for which $|\Delta|/F_o \geq 0.80$ were omitted in the final refinement stages. Comparison with data-averaging results showed that this rejection level accomplishes about the same thing for the weaker reflections but generally bypasses stronger ones which appear in error. Notwithstanding, inclusion of the anomalous dispersion correction did produce both observably smaller errors and faster convergence. A reweighting of the data set was also included, as already described for the lead problem, while the absolute configuration was established by inversion of the structure without refinement. The latter gave a 0.01 reduction in both residuals, a trend confirmed by comparison of structure factors for individual reflections where the effect was largest. Residuals at convergence were $R = 0.086$ and $R_w = 0.090$, with final shifts of $\leq 0.09\sigma$ for the heavy atoms and up to 0.3σ for a few of the light-atom parameters. The final difference map was very flat save for scattered residual density of ≤ 1 e Å^{-3} near some atoms. Although some disorder in the cations presumably accompanies that of the $\text{Sn}_5{}^{2-}$ anion, the effect is too small for treatment.

Results and Discussion

The compounds studied are properly formulated $(\text{cryptNa}^+)_2\text{Pb}_5{}^{2-}$ and $(\text{cryptNa}^+)_2\text{Sn}_5{}^{2-}$, with heavy-metal anions which are very similar in all respects. The final parameters for the centric lead compound are given in Table I, while Figure 1, the [110] section of this structure, aids in the perception of the structure type and its problems. Final parameters for the polytin salt in the acentric space group $P3c1$ are listed in Table II. Observed and final calculated structure factors for both structures are given in the supplementary material.

Bond lengths and angles exhibited by the $\text{Pb}_5{}^{2-}$ and $\text{Sn}_5{}^{2-}$ anions are summarized in Table III. The centric space group of the lead compound requires that $\text{Pb}_5{}^{2-}$ have D_{3h} symmetry, while that for $\text{Sn}_5{}^{2-}$ only restricts it to C_{3v} symmetry. Nonetheless the difference of axial–equatorial distances in the latter, 0.023 (9) Å, is not significant and $\text{Sn}_5{}^{2-}$ is properly classified as D_{3h} as well. Although the presence of ~14% of the $\text{Sn}_5{}^{2-}$ ions disordered by a rotation of ~50° can be resolved for the waist atoms, the apices corresponding to the two presumed anion locations cannot be because of the small displacement (~0.2 Å). In this case the distances and angles presented in Table III for $\text{Sn}_5{}^{2-}$ have been deduced using the occupation-weighted mean for the z coordinate of the equatorial atoms.

The two polymetal anions are illustrated in Figure 2. Both $\text{Pb}_5{}^{2-}$ and $\text{Sn}_5{}^{2-}$ ions exhibit remarkable similar thermal el-

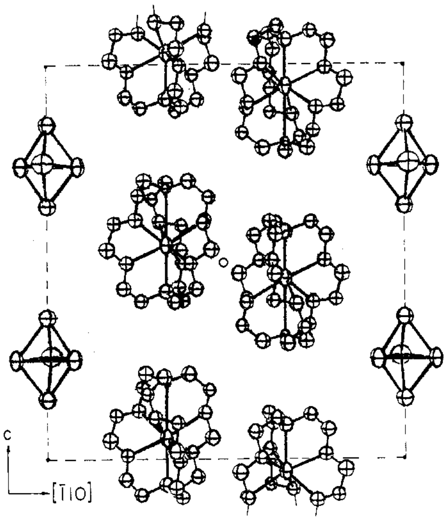


Figure 1. The [110] section of the centric structure of $(\text{cryptNa}^+)_2\text{Pb}_5{}^{2-}$.

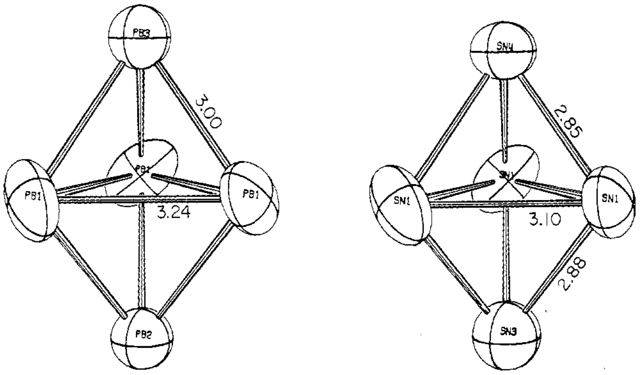


Figure 2. Configurations of and distances within the $\text{Pb}_5{}^{2-}$ (left) and $\text{Sn}_5{}^{2-}$ (right) ions.

Table IV. Bonding Distances in cryptNa^+ in the $\text{M}_5{}^{2-}$ Salts, Å

	$\text{Pb}_5{}^{2-}$	$\text{Sn}_5{}^{2-}$	
		Cation 1	Cation 2
Na-N(1)	3.23 (5)	2.91 (5)	3.43 (7)
Na-O(4)	2.66 (2)	2.56 (3)	2.63 (3)
Na-O(7)	2.48 (2)	2.65 (2)	2.43 (2)
Na-N(10)	2.66 (6)	3.01 (5)	2.66 (6)
N(1)-C(2)	1.47 (4)	1.59 (3)	1.48 (4)
C(2)-C(3)	1.50 (4)	1.60 (4)	1.37 (4)
C(3)-O(4)	1.42 (3)	1.48 (4)	1.42 (4)
O(4)-C(5)	1.43 (4)	1.54 (4)	1.49 (4)
C(5)-C(6)	1.57 (5)	1.73 (5)	1.41 (4)
C(6)-O(7)	1.46 (4)	1.54 (4)	1.45 (4)
O(7)-C(8)	1.46 (4)	1.59 (3)	1.58 (4)
C(8)-C(9)	1.45 (4)	1.80 (4)	1.44 (4)
C(9)-N(10)	1.56 (3)	1.50 (3)	1.49 (3)

Table V. Debye-Scherrer Pattern for $(\text{cryptNa}^+)_2\text{Pb}_5{}^{2-}$ above 2.1 Å

hkl	*d*, Å	*I*(calcd)	*hkl*	*d*, Å	*I*(calcd)
002	11.06	245	131	2.768	80
100	10.06	1000	223	2.702	76
102	7.44	878	108	2.665	125
110	5.81	378	216	2.646	115
112	5.14	90	313	2.609	62
200	5.03	70	224	2.571	102
202	4.58	108	306	2.480	40
113	4.56				
			217	2.429	127
114	4.00	44	225	2.427	
210	3.80	54	135	2.359	50
121	3.75	327	321	2.295	71
204	3.72				
212	3.60	40	226	2.281	55
213	3.38	102	316	2.224	78
124	3.13	208	140	2.195	49
206	2.97	30	1,0,10	2.159	110
215	2.883	212	324	2.130	101
221	2.879				
304	2.867				

lipsoid distributions, but the impeller shape for the waist atoms in both seems unusual. A small positional disorder might be suggested except that the apex-atom distribution does not follow such a circumstance. A disorder involving $\text{M}_5{}^{2-}$ ions of C_{3v} symmetry (distorted axially and symmetrically) and oriented equally "up" and "down" could be involved but there is no obvious evidence or test for this rather tenuous postulate.

Bond distances within the three cryptNa^+ ions investigated are given in Table IV. The distances between light atoms in the unique cation in the lead compound are fairly reasonable, 1.42 (3)–1.57 (5) Å, though the sodium is off the midpoint of the N–N axis by 0.29 (5) Å. This does not appear especially unusual when compared with the range of Na–N distances found in other cryptNa^+ compounds containing lower field anions and with cells of low symmetry.[10,14] The Na^+ ion is considered undersized for the 2,2,2-crypt ligand cavity.[26] Some distortion from parameter coupling during refinement of the tin structure owing to its near-centricity does appear in the results for those two cations, one exhibiting generally somewhat smaller distances than the other. The sodium ions are noticeably acentric, while six of the light atoms deviate from centricity by 10σ or more. As an aid to identification the indexed powder pattern of $(\text{cryptNa}^+)_2\text{Pb}_5{}^{2-}$ with calculated[27] intensities is listed in Table V.

The pentaplumbide(2−) and pentastannide(2−) anions are the first five-atom members of a small but growing number of solid homopolyatomic anions of the heavy post transition metals which have been structurally characterized, joining $\text{Sn}_9{}^{4-}$, $\text{Sb}_7{}^{3-}$, and $\text{Te}_3{}^{2-}$. These ions are important not only because they are differentiated from both heteroatomic cluster anions and homopolyatomic anions of nonmetals but also because they contain no "central" atom which structurally distinguishes them from the usual coordination compounds (ML_n).

The detection of the pentaplumbide ion is itself somewhat surprising. The nonaplumbide ion $\text{Pb}_9{}^{4-}$ had been expected because it is isoelectronic with both the known $\text{Bi}_9{}^{5+}$ cation[28] and the $\text{Sn}_9{}^{4-}$ anion. Moreover, the green $\text{Pb}_9{}^{4-}$ anion has been relatively unambiguously characterized as the principal ion formed in liquid ammonia solutions of alkali metal alloys of lead, the analytical uncertainty reported[2] appearing to be well less than that which could allow $\text{Pb}_5{}^{2-}$. In addition the colors are distinctly different. However $\text{Pb}_5{}^{2-}$ is a somewhat pleasant surprise because the trigonal-bipyramidal structure is the same as predicted by MO calculations[29] for the isoelectronic species $\text{Bi}_5{}^{3+}$. Although this bismuth cation is well established,[29,30] we have so far been frustrated by twinning problems in attempts at structure analysis of the ion in either $\text{Bi}_5{}^{3+}(\text{AlCl}_4{}^-)_3$ or $\text{Bi}_5{}^{3+}(\text{AlBr}_4{}^-)_3$.

So far we have been unable to isolate other polyplumbide anions from reactions involving either Na–Pb or K–Pb alloys with crypt in either en or NH_3. The compositions $\text{MPb}_{2.25}$ to $\text{M}_{1.7}\text{Pb}$ dissolve readily in en in the presence of crypt but the solutions deposit only the pentaplumbide salt and the nonstoichiometric alloy phase $\text{MPb}_{2.2}$. Although green solutions characteristic of $\text{Pb}_9{}^{4-}$ are obtained in liquid NH_3 in the presence of crypt as well, only the $\text{Pb}_5{}^{2-}$ salt forms in any amount. These reactions may be driven by the insolubility of the $\text{Pb}_5{}^{2-}$ and $\text{Sn}_5{}^{2-}$ salts in most solvents. The structure is roughly an antitype of CdI_2 except that the elongated shape of the crypt cations allows more interpenetration of what would be the nonmetal layers in CdI_2.

The isolation of the pentastannide ion is also a pleasant surprise, the red Sn_9^{4-} anion having been the only species identified by Zintl[2] in ammonia solutions of the tin alloys and more recently verified in the solid state.[7,9] A yellow-brown color like that of Sn_5^{2-} was observed in liquid ammonia solutions by Kraus and Kurtz.[31]

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Registry No. $(cryptNa^+)_2Pb_5^{2-}$, 58862-91-2; $(cryptNa^+)_2Sn_5^{2-}$, 61665-35-8.

Supplementary Material Available: Listings of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dicarbonyl(η-cyclopentadienyl)(2-propanoneoximato-*O,N*)molybdenum, a Complex Containing a Novel Chelating Oximato Ligand

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A crystallographic study has shown the product of the reaction of 2-bromo-2-nitrosopropane with $NaMo(C_5H_5)(CO)_3$ to contain an oximato ligand bound in a novel chelating fashion. Crystals of the title compound are orthorhombic, of space group $Pna2_1$, with $a = 7.745$ (11) Å, $b = 12.810$ (18) Å, $c = 11.301$ (16) Å, and $Z = 4$. The structure determination was based upon 865 independent nonzero reflection data; full-matrix least-squares refinement converged to a final conventional R factor of 0.053. The monomeric molecules contain a molybdenum atom bound to an η-cyclopentadienyl ring, two carbonyl groups, and a bidentate $(CH_3)_2C{=}NO$ ligand. The 2-propanoneoximato group is bound in chelating fashion with Mo–N and Mo–O bond lengths of 2.089 (12) and 2.139 (12) Å, respectively. The molecular structure is rationalized on the basis of a bonding model in which the oximato ligand occupies two coordination sites of a seven-coordinate metal atom. The N–O bond distance of 1.336 (27) Å and the N–C distance of 1.253 (18) Å are close to the values expected for a single and a double bond, respectively. The pertinence of the structural results to the chemistry of metal–nitroso and metal–nitrosyl systems is discussed.

Introduction

In a recent study of the reactions of metal carbonylate anions with 2-bromo-2-nitrosopropane, King and Douglas obtained several types of products.[1] These included metal complexes containing dimethyl ketimine and isopropylidenamido ligands, as well as two compounds believed to contain a novel $(CH_3)_2CNO$ ligand. One of these latter two complexes, a bis(tricarbonyliron) species, was formulated as containing a 2-propanoneoximato group linking the iron atoms through a diatomic Fe–N–O–Fe bridge. This structure was recently confirmed by a crystallographic study[2] and a second example of a bis(tricarbonyliron) complex containing an identical bridging group has subsequently appeared.[3] A less straightforward structural problem was presented by the mononuclear molybdenum complex $[(CH_3)_2CNO]Mo(C_5H_5)(CO)_2$, obtained by the reaction of 2-bromo-2-nitrosopropane with $NaMo(C_5H_5)(CO)_3$. At least four possible modes for the binding of the $(CH_3)_2CNO$ ligand to the metal atom were considered, including binding through C and N, C and O, and N and O or via a delocalized π system involving C, N, and O. Spectroscopic data provided no basis for clear distinction among these four possibilities.[1] We have now completed a crystal structure analysis of the molybdenum complex because of the novelty of the proposed structures and because of our continuing interest in metal complexes derived from azo and nitroso ligands.