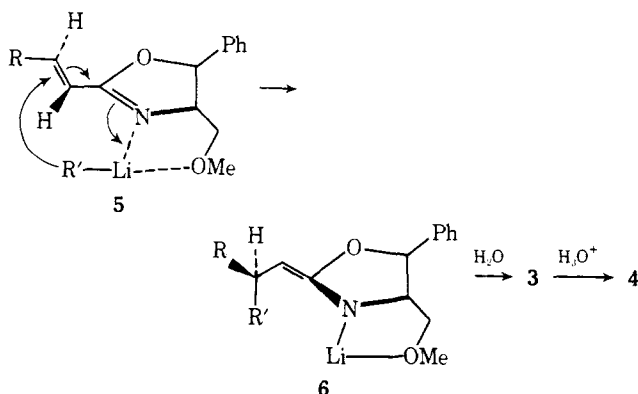


obtained in greater than 90% enantiomeric purity by simply reversing the order of introduction of the two substituents, R and R'. An asymmetric synthesis of *R*-(-)-3-phenylbutyric acid **4** (R = Ph, R' = Me) was reported by Tsuchihashi<sup>8</sup> to occur in 40% overall yield and in 95% enantiomeric purity by conjugate addition of malonate ion to a chiral  $\beta$ -styryl sulfoxide. However, the conjugate addition proceeded with 60% bias and the high optical yield was realized only after separation of the diastereomers. This result should be compared with the present study (entry 3) which gives *S*-(+)-3-phenylbutyric acid in 34% overall yield and at least 98% enantiomeric purity after simple hydrolysis of the intermediate **3**.<sup>13</sup> It should be noted that 3-phenylheptanoic acid (entry 7) obtained via this process possessed a specific rotation substantially greater than that previously reported from resolution techniques (ref 1, Table I). It is assumed that this higher value would represent 95–98% optical purity based upon the results from entries 5 and 6.

A mechanism which correctly predicts the proper configuration of the 3-substituted alkanolic acids and may tentatively be used as an operational scheme involves underside entry<sup>14</sup> of the organolithium reagent to the anti-*trans* conformer of the alkenyl oxazoline **5**. The lithio adduct **6**,



which is now a metalated "enamine" should also be capable of behaving as a nucleophile and is identical with the intermediates previously reported<sup>1</sup> to react with electrophiles producing  $\alpha$ -alkyl alkanolic acids. A study to evaluate additions of various nucleophiles to **2** as well as the creation of a second chiral center by electrophilic additions to **6** is underway.

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## References and Notes

- (1) A. I. Meyers and G. Knaus, *J. Am. Chem. Soc.*, **96**, 6508 (1974).
- (2) A. I. Meyers, G. Knaus, and P. M. Kendall, *Tetrahedron Lett.*, 3495 (1974).
- (3) A. I. Meyers and G. Knaus, *Tetrahedron Lett.*, 1333 (1974).
- (4) A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40**, 1186 (1975).
- (5) Y. Inouye and H. M. Walborsky, *J. Org. Chem.*, **27**, 2707 (1962).
- (6) M. Kawana and S. Emoto, *Bull. Chem. Soc. Jpn.*, **39**, 910 (1966).
- (7) R. A. Kretschmer, *J. Org. Chem.*, **37**, 2744 (1972).
- (8) G. Tsuchihashi, S. Mitamura, S. Inoue, and K. Ogura, *Tetrahedron Lett.*, 323 (1973).
- (9) Aldrich Chemical Co., Milwaukee, Wisc.
- (10) Recently, **2** (R = aryl) has been prepared in good yield by azeotropic removal of water from a toluene solution of aromatic aldehydes and **1** using ZnCl<sub>2</sub> as a catalyst.
- (11) We have observed that *cis*-**2** (R = Me), prepared in 40% yield from the 2-(trimethylsilylimethyl)oxazoline, LDA, and acetaldehyde<sup>12</sup> gave almost exclusively proton abstraction when treated with organolithium reagents. *cis*-**2**, upon standing (1 week) or heating above 90° isomerized to *trans*-**2**.
- (12) *Cis* olefins have been directly prepared using substituted trimethylsilyl carbanions and carbonyl compounds: P. F. Hudrik and D. Peterson, *J. Am. Chem. Soc.*, **97**, 1464 (1975), and references cited therein.
- (13) To date, we have been unable to effect an efficient addition of methyl-lithium to **2**, and thus synthesis of the optical antipodes in entries 1–3 has not been achieved.

- (14) All evidence points to a strong complexation of lithium ion to the nitrogen and methoxy group and hence to bottomside approach (A. I. Meyers et al., manuscript submitted as full account of earlier reports on asymmetric synthesis using chiral oxazolines). Furthermore, we have been able to solubilize LiCl with **1** in tetrahydrofuran over and above a blank solution indicating the strong affinity of lithium ion to the chelating environment of **1** or **4** (M. Druehlinger, research in progress).

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## Synthesis of Stable Homopolyatomic Anions of Antimony, Bismuth, Tin, and Lead. The Crystal Structure of a Salt Containing the Heptaantimonide(3-) Anion

Sir:

We wish to report the achievement of a solution to a long-standing problem, a general route to the isolation of stable derivatives of the polyatomic anions of the heavy post-transition metals that have long been known primarily as solutions of the corresponding alkali metal intermetallic phases in liquid ammonia. The method utilizes the strong complexing ability of 2,2,2-crypt<sup>1,2</sup> for the cation to prevent the usual decomposition reactions wherein electrons from the polyanions are partially transferred back to the alkali metal to form the parent alloy.

Zintl and coworkers<sup>3-5</sup> have provided the broadest and most thorough characterization of ammonia solutions of the polyatomic anions of tin, lead, arsenic, antimony, bismuth, sulfur, selenium, and tellurium through potentiometric titrations and alloy extractions. For the systems considered here they reported evidence for the nine species Sn<sub>9</sub><sup>4-</sup>, Pb<sub>7,9</sub><sup>4-</sup>, Sb<sub>3,5,7</sub><sup>3-</sup>, and Bi<sub>3,5,7(?)</sub><sup>3-</sup>. Evaporation of the ammonia yielded highly colored but amorphous solids which analyzed as the last-listed ion for each element together with Na(NH<sub>3</sub>)<sub>n</sub><sup>+</sup> cations. All such products lost ammonia before crystallization and reverted to known binary alloys. The latter in general do not exhibit compositions or structures which correspond to the observed solution species. Since that time results have substantially been peripheral,<sup>6,7</sup> and no synthesis and structural characterization of any phase containing an isolated polymetal "Zintl" anion has been reported although Kummer and Diehl<sup>8</sup> have briefly noted the preparation of a red, slightly stable phase Na<sub>4</sub>Sn<sub>9</sub>-6-8en (en = ethylenediamine).

The impetus for the present work was provided by the above observations coupled with the recent demonstration that the addition of crypt gives a considerable enhancement of the solubility of the alkali metals in diverse solvents<sup>9</sup> and allows the isolation and structural determination of the salt [Na(crypt)<sup>+</sup>]<sub>n</sub>Na<sup>-</sup>.<sup>10</sup> The extremely strong complexation of sodium and potassium ions by crypt, with formation constants of 10<sup>4</sup> to 10<sup>10</sup> in various solvents, suggested that the otherwise favorable delocalization of electrons from the polyanion back into the alkali metal ion to form a metallic structure could be prevented by this coordination. In all cases reported here a solution of crypt in en has been found to readily react with the appropriate alloy phase to yield a highly colored solution from which a crystalline derivative can be isolated.

Alloy samples have been prepared by fusing the appropriate amounts of the elements in sealed tantalum tubing as before.<sup>7</sup> Because of the cost of crypt (\$115 g<sup>-1</sup>, EM Laboratories) most preparations have been on the milligram scale and characterizations, by crystallography. For example, the reaction of powdered NaSb or NaSb<sub>3</sub> with crypt in

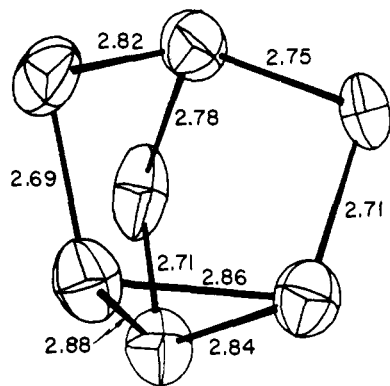


Figure 1. Configuration of the ion  $\text{Sb}_7^{3-}$  in the salt  $[\text{Na}(\text{crypt})^+]_3\text{Sb}_7^{3-}$

dry en produces a deep brown solution in 10–15 min. Evaporation of the solvent yields brown needles and chunks that have been shown to be  $[\text{Na}(\text{crypt})^+]_3\text{Sb}_7^{3-}$  (see below). No other phase appears to be formed from Na–Sb alloys save for small amounts of the blue “sodium crypt electronide”<sup>10</sup> obtained from samples with the higher sodium activities.

The compositions  $\text{NaSn}_{2.25}$  and  $\text{NaSn}_{1.32}$  both dissolve in en alone<sup>8</sup> and redeposit alloy on thorough solvent removal, but crypt complexation allows the isolation of intensely colored orange-red needles and rods in pure form. The coloration is similar to that reported by others for  $\text{Sn}_9$  derivatives.<sup>3,4,8</sup> The compound is somewhat unstable to X-rays but usable data can be secured when the crystal is cooled. Use of  $\text{Na}_{1.7}\text{Sn}$  yields a more reduced yellow-brown polytin phase, a coloration also noted in liquid ammonia solutions.<sup>11</sup> The compositions  $\text{NaPb}_{2.25}$ ,  $\text{NaPb}_{1.75}$ , and  $\text{NaPb}_{1.3}$  all dissolve relatively rapidly in en only in the presence of crypt, but these redeposit brown mud and rods which are only polycrystalline composites of the alloy phase  $\text{MPb}_{2.2}$ . However, slow refluxing of a solution of  $\text{NaPb}_{1.3}$  and crypt in en at  $\sim 90^\circ$  gives a low yield of ruby red crystals which are close to  $[\text{Na}(\text{crypt})^+]_4\text{Pb}_9^{4-}$  in composition but which do not have the green color associated with  $\text{Pb}_9^{4-}$  in liquid ammonia.<sup>4,11</sup> The sodium–bismuth–crypt reactions appear to be the most complex and, among those systems considered, the least productive of good crystals. Samples of  $\text{NaBi}$  or  $\text{NaBi} + \text{Bi}$  react with crypt in en to produce an immediate blue-green color, and this eventually deepens to a dichroic green-ruby red solution. No coloration is observed with en alone. The crypt solution deposits a microcrystalline green to rose colored polybismuth salt on evaporation of solvent.

X-Ray data have been obtained from a single crystal of the polyantimony derivative described above with a four-circle automatic diffractometer using  $\text{Mo K}\alpha$  radiation. The monoclinic cell dimensions are  $a = 23.292(7) \text{ \AA}$ ,  $b = 13.791(6) \text{ \AA}$ ,  $c = 25.355(6) \text{ \AA}$ ,  $\beta = 108.56(2)^\circ$ , and observed extinctions uniquely fixed the space group as  $P2_1/n$ . Utilizing 4662 unique reflections with  $I_{\text{obsd}} > 3\sigma_1$  the correct location of the seven antimony atoms in general positions was deduced by direct methods.<sup>12</sup> Successive refinement followed by electron density synthesis located three sodium atoms and, after some care, the three independent crypt molecules surrounding the sodium atoms. Full-matrix least-squares refinement of all 88 independent (nonhydrogen) atoms with anisotropic thermal parameters for the ten heavy atoms and isotropic parameters for those in the crypt ligands yielded a conventional  $R$  of 0.111 and a difference Fourier map with ripples  $< 5 \text{ e}/\text{\AA}^3$  near the antimony atoms and  $\leq \pm 1 \text{ e}/\text{\AA}^3$  elsewhere.

The most remarkable feature of the structure is the  $\text{Sb}_7^{3-}$  ion, Figure 1, in which the atoms occur in an end-

capped trigonal prism of approximately  $C_{3v}$  symmetry with the capped face opened up to substantially nonbonding distances (4.19–4.34  $\text{\AA}$ ). The  $\text{Sb}_7^{3-}$  ion is the first characterized polyatomic anion of a metallic element although it is quite similar in configuration and presumably bonding to that briefly described for  $\text{P}_7^{3-}$  (in the ionic limit) in the phase  $\text{Sr}_3\text{P}_{14}$  prepared at high temperatures.<sup>13</sup> The three sodium–crypt cations exhibit configurations and average distances which are quite comparable to those found in  $[\text{Na}(\text{crypt})^+]^-$ .<sup>14</sup>

In general a fertile synthetic field appears indicated, and several derivatives are presently under structural investigation.

## References and Notes

- (1) 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane,  $\text{N}(\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4)_3\text{N}$ .
- (2) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, **34**, 2885 (1969).
- (3) E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. Phys. Chem., Abt. A*, **154**, 1 (1931).
- (4) E. Zintl and A. Harder, *Z. Phys. Chem., Abt. A*, **154**, 47 (1931).
- (5) E. Zintl and W. Dullenkopf, *Z. Phys. Chem., Abt. B*, **16**, 183 (1932).
- (6) H. Schafer, B. Eisenmann, and W. Müller, *Angew. Chem., Int. Ed. Engl.*, **12**, 694 (1973).
- (7) M. Okada, R. A. Guidotti, and J. D. Corbett, *Inorg. Chem.*, **7**, 2118 (1968).
- (8) D. Kummer and L. Diehl, *Angew. Chem., Int. Ed. Engl.*, **9**, 895 (1970).
- (9) M. T. Lok, F. J. Tehan, and J. L. Dye, *J. Phys. Chem.*, **72**, 2975 (1972).
- (10) F. J. Tehan, B. L. Barnett, and J. L. Dye, *J. Am. Chem. Soc.*, **98**, 7203 (1974).
- (11) C. A. Kraus and H. F. Kurtz, *J. Am. Chem. Soc.*, **47**, 43 (1925).
- (12) P. Main, M. M. Woolfson, and F. Germain, “MULTAN, A Computer Program for the Automatic Solution of Crystal Structures”, University of York Printing Unit, York, U.K., 1971.
- (13) W. Dahlmann and H. G. v. Schnering, *Naturwissenschaften*, **59**, 420 (1972).
- (14) D. Moras, B. Metz, and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 396 (1973).

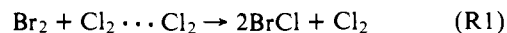
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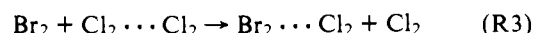
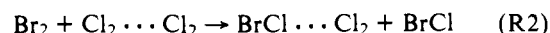
## Molecular Beam Chemistry. Reactions Exchanging van der Waals Bonds among Three or More Halogen Molecules

Sir:

Under the single-collision conditions provided in crossed-beam experiments,  $\text{Br}_2 + \text{Cl}_2$  at collision energies up to  $\sim 25$  kcal/mol yields no product attributable to bimolecular reaction.<sup>1</sup> However, even at thermal collision energies of only  $\sim 3$  kcal/mol evidence was found<sup>2</sup> for a facile termolecular reaction,



The dimeric chlorine reactant,  $\text{Cl}_2 \cdots \text{Cl}_2$ , is held together by a weak van der Waals bond<sup>3</sup> with dissociation energy  $\sim 1$ –2 kcal/mol and bond length  $\sim 4.3 \text{ \AA}$ . Here we report further experiments which confirm (R1) and give evidence for two other facile reaction paths,



The (R2) path is a corollary of the reaction sequence suggested for the (R1) process.<sup>2</sup> Six-center bond exchange is assumed to occur in a cyclic transition state which disso-