

was washed with oxygen-free benzene and dried under nitrogen, yield, 0.71 g. *Anal.* Calcd for $\text{MoC}_{30}\text{H}_{24}\text{N}_6$: Mo, 17.0; C, 63.8; H, 4.29; N, 15.0. Found: Mo, 17.0; C, 63.5; H, 4.47; N, 14.6.⁶

Bis(2,2',2''-tripyridine)molybdenum(0) was made according to directions of Behrens and Anders⁷ from molybdenum hexacarbonyl and the ligand. *Anal.* Calcd for $\text{MoC}_{30}\text{H}_{22}\text{N}_6$: Mo, 17.1; C, 64.1; H, 3.94; N, 14.9. Found: Mo, 16.3; C, 62.9; H, 3.98; N, 14.6. The compound could also be prepared in a manner similar to that described for tris(2,2'-bipyridine)molybdenum(0).⁸

Electrochemical Measurements.—The apparatus and experimental techniques for these measurements have already been described.¹

Acknowledgment.—Support from the National Science Foundation is acknowledged with gratitude by D. W. DuBois.

(6) Tris(2,2'-bipyridine)molybdenum(0) is not a new compound. It was synthesized earlier by a different procedure by S. Herzog and I. Schneider, *Z. Chem.*, **2**, 24 (1962).

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Proposed Structure of Bis(tri-*n*-butyltin) Sulfate and Related Molecules

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It is self-evident that the structures of compounds which are liquids (or gases) under ordinary conditions or to which X-ray diffraction methods cannot be applied for various reasons must be inferred from other spectroscopic data by indirect means. In the case of metal-organic tin compounds, *inter alia*, Mössbauer spectroscopy has proved to be a valuable tool with respect to structure elucidation,² and the present communication concerns the application of this technique to the problem of the structure of bis(tri-*n*-butyltin) sulfate and related molecules.

Experimental Section

Preparation of Compounds and Infrared Spectra.—Bis(tri-*n*-butyltin) sulfate, mp 140–144°, was prepared by oxidation of bis(tri-*n*-butyltin) sulfide with hydrogen peroxide³ and characterized by chemical analysis.

The molecular weight of bis(tri-*n*-butyltin) sulfate was determined by osmometry. In solution in polar solvents such as acetone or methyl ethyl ketone, the compound was found to be monomeric (mol wt: calcd, 676; found, 684). Infrared spectra of bis(tri-*n*-butyltin) sulfate were recorded, using a Perkin-Elmer Model 337 grating spectrometer in the range 2.5–24.5 μ , on KBr-wafer samples. Bis(tri-*n*-butyltin) sulfide and oxide were prepared by standard methods and gave satisfactory analytical results in agreement with previously reported values.

(1) Henry Rutgers Scholar supported in part by the National Science Foundation.

(2) See, for example, V. I. Gol'danskii, V. V. Khrapov, O. Yu. Okhlobystin, and V. Ya. Rochev in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter 6.

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Mössbauer Spectra.—Mössbauer spectroscopy, using the 23.8-keV transition in ¹¹⁹Sn, was effected using the constant-acceleration spectrometer described previously.⁴ All absorbers were run either at liquid nitrogen temperature (80 ± 1°K by calibrated thermocouple) or at room temperature using a BaSnO₃ source⁵ at room temperature. All source shifts are reported with respect to the center of a room-temperature BaSnO₃ absorber spectrum (whose position is identical with that of an SnO₂ absorber spectrum within the quoted experimental error). The constant-acceleration spectrometer was calibrated against a 0.5-mil natural iron absorber as described previously.⁶

Results and Discussion

The strong bands observed in the infrared spectrum of bis(tri-*n*-butyltin) sulfate at 1100 and 614 cm^{-1} can reasonably be assigned to the S–O asymmetric stretching and symmetric deformation bands of the sulfate group⁷ while other minor peaks at 667 and 523 cm^{-1} are obviously related to the tin-hydrocarbon bond vibrations.

However, infrared spectroscopy alone seems unable to resolve the controversy between quasiplanar trialkyltin ions linked to symmetric (T_d) sulfate ions and a reduced symmetry (C_{2v}) of the sulfate group accompanied by possible coordination between tin and oxygen.⁸

This difficulty has been discussed earlier with reference to $(\text{CH}_3)_3\text{SnSO}_4$ in the detailed study by Clark and Goel,⁹ who prepared both the anhydrous and solvated species by reaction of $(\text{CH}_3)_3\text{SnBr}$ and Ag_2SO_4 in dry methanol. The infrared bands at 2900–3000 cm^{-1} (C–H stretch), 780–785 cm^{-1} (Sn–CH₃ rocking), and 552 cm^{-1} (Sn–C asymmetric stretch) were interpreted as arising from a planar $(\text{CH}_3)_3\text{Sn}$ moiety, while the bands at 1090 and 630 cm^{-1} were ascribed to a sulfate entity having T_d symmetry. While the infrared data do not permit an unambiguous choice to be made between an ionic form [$(\text{CH}_3)_3\text{Sn}^+$ and SO_4^{2-}] and a structure involving a sulfate group bonded through all four oxygens, the authors prefer the latter structure in which there is a strong coordinative (covalent) interaction between the metal and the ligand.

The Mössbauer results obtained in the present study are summarized in Table I. The most dramatic feature of these data is the large difference in the quadrupole splitting parameter between the bis(tri-*n*-butyltin) sulfate and the related oxide and sulfide.

The data for bis(tri-*n*-butyltin) sulfate are in good agreement with related data for $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4$ and $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4$ which have been reported by Goel, *et al.*,¹⁰ and which are included in Table I.

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TABLE I
MÖSSBAUER PARAMETERS FOR COMPOUNDS
DISCUSSED IN THE TEXT^a

Absorber	Temp, °K	IS, mm/sec	QS, mm/sec	Ref
[(<i>n</i> -C ₄ H ₉) ₃ Sn] ₂ SO ₄	294	No effect		
	80	1.56 ± 0.02	4.01 ± 0.02	
[(<i>n</i> -C ₄ H ₉) ₃ Sn] ₂ O	80	1.24 ± 0.02	1.35 ± 0.02	
[(<i>n</i> -C ₄ H ₉) ₃ Sn] ₂ S	80	1.35 ± 0.02	1.58 ± 0.02	
[(CH ₃) ₃ Sn] ₂ SO ₄	(N ₂)	1.39	4.07	<i>b</i>
[(CH ₃) ₃ Sn] ₂ SeO ₄	(N ₂)	1.39	4.09	<i>b</i>
(CH ₃) ₃ SnNO ₃	80	1.45 ± 0.04	4.12 ± 0.04	
(CH ₃) ₃ SnNO ₃	80	1.44 ± 0.05	4.14 ± 0.05	<i>c</i>
(CH ₃) ₃ SnNO ₃ ·H ₂ O	90	1.38 ± 0.04	3.85 ± 0.04	

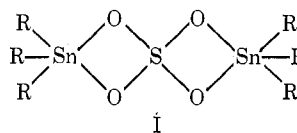
^a All isomer shifts are with respect to the centroid of a room-temperature SnO₂ absorption spectrum. ^b See ref 10. ^c M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, **29**, 1177 (1967).

As has been shown earlier in conjunction with Mössbauer data for trialkyltin halides and pseudohalides^{11,12} while changes in the electronegativity of the nonorganic ligand make a significant contribution to the range of quadrupole splittings which are observed in such compounds, a major effect is observed when there is a change in the coordination number (and hence overall symmetry) of the molecules. Indeed, as was suggested earlier,¹¹ this parameter (or more precisely the parameter $\rho = QS/IS$) can be used as a diagnostic measure of the departure from tetrahedral symmetry of organotin compounds.

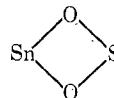
Taking into consideration the chemical and physical properties of the oxide and sulfide species, the only reasonable structure which suggests itself for these molecules is that of a distorted tetrahedral symmetry around each metal atom with the three alkyl groups nonplanar with respect to the metal atom and the two metal atoms joined by a tin-chalcogen-tin bond.

From these data it is clear that the ligand symmetry around the metal atom in the sulfate cannot correspond to a distorted tetrahedral configuration in which the sulfate moiety is bidentate, since the expected quadrupole splitting in this case should be very close to that observed for the oxide and/or sulfide, since the nearest neighbor environment in the two cases would be essentially the same. Such a distorted tetrahedral configuration would also be expected to give quadrupole splittings similar to those observed when three bulky organic ligands (*e.g.*, as in the case of the tri-n-phenyltin halides and pseudohalides) afford too much steric hindrance for the attainment of pentacoordination. The present results—in the context of the earlier data¹¹—clearly show that such a distorted tetrahedral structure does not obtain.

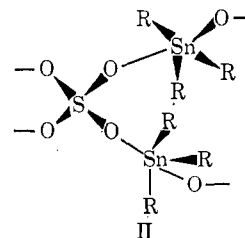
On this basis one can account for the very much larger quadrupole splittings in the case of the related sulfate molecule by postulating a structure in which the sulfate group is tetradentate, being bridged through two oxygen atoms to one R₃Sn moiety (I). As noted



above, such a structure has been suggested⁹ to account for the infrared results obtained for trimethyltin sulfate. Since the quadrupole splitting which is observed in (*n*-C₄H₉)₃SnF (presumed to be five-coordinate with $\sim C_{3v}$ symmetry along the F-SnF axis) and (*n*-C₄H₉)₂-SnF₂ (presumed to be six-coordinate with *trans* alkyl groups) is 3.75 and 4.00 mm/sec, respectively,¹³ it is reasonable to associate the large quadrupole splitting observed in [(*n*-C₄H₉)₃Sn]₂SO₄ with the steric requirements imposed by the postulated four-membered cyclic arrangement



The other plausible structure which satisfies the stoichiometry of this compound is one which involves the formation of a two-dimensional polymer (II). This possibility for the solid configuration can however be ruled out on several grounds. The molecular weight of the sulfate in ketones shows unambiguously that [(*n*-C₄H₉)₃Sn]₂SO₄ is monomeric in solution. While it is possible that a monomer-polymer conformational change occurs in going from the solution to the neat solid phase, the absence of an observable Mössbauer resonance effect at room temperature suggests¹⁴ that the strong intermolecular forces implied in a polymeric structure must be absent in the solid, and hence the monomeric structure found in solution is preserved. Moreover the Mössbauer parameters for [(*n*-C₄H₉)₃Sn]₂SO₄ dissolved in methylhydrofuran and frozen to a glassy matrix are identical with those observed for the neat solid (within the quoted experimental error), again suggesting the absence of a monomer-polymer equilibrium in going from solution to the solid phase.



Whether the conclusions reached above for the structure of trialkyltin sulfates can be extended to other trialkyltin species must be examined in the light of the available evidence, which, in the case of those compounds which can be obtained in the form of single crystals, must ultimately be X-ray diffraction data. That a large quadrupole splitting (>4 mm/sec)

(13) Y. Gosciniy, private communication. These data were obtained (in part) at the Université Libre de Bruxelles and will be reported in detail in a subsequent publication. The authors are indebted to Professors M. Gielen and J. Nazielsky for permission to quote these results.

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for trialkyltin species may not be unambiguously diagnostic of the cyclic nature of the ligand is illustrated by the Mössbauer data¹⁵ for $(\text{CH}_3)_3\text{SnNO}_3$ included in Table I. A variety of structural inferences, including a model with a nitrate group bidentate to a single $(\text{CH}_3)_3\text{Sn}$ fragment, have been drawn earlier from infrared data.^{16,17} These data were, however, partially beclouded by the fact that $(\text{CH}_3)_3\text{SnNO}_3$ picks up water on standing and that consequently some of the infrared bands which are observed are, in fact, characteristic of the hydrated species.

An X-ray diffraction study of the anhydrous material, which can be obtained by vacuum sublimation of the hydrate, has now been carried out¹⁸ and shows that the neat solid compound does *not* contain bidentate NO_3 groups bound to a single $(\text{CH}_3)_3\text{Sn}$ moiety. The details of this structure will be reported by these authors in a separate communication.

It is clear, then, that Mössbauer data for R_3SnX species must be examined with considerable care, preferably in conjunction with all other available spectroscopic information, before structural inferences are drawn. When this is done, however, a consistent model for the architecture of such molecules can be obtained.

Acknowledgment.—The authors are very grateful to Professor H. C. Clark for making the X-ray diffraction results on $(\text{CH}_3)_3\text{SnNO}_3$ available to us prior to publication. This work has been supported in part by the U. S. Atomic Energy Commission and constitutes Document No. NYO-2472-63. Support from the Petroleum Research Fund, administered by the American Chemical Society, and the Research Council of Rutgers University is also gratefully acknowledged.

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(18) This work (unpublished) was undertaken by Dr. T. C. Mak, then in the Department of Chemistry of the University of Western Ontario, and has been communicated to us by Professor H. C. Clark.

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Isocyanatopentaamminecobalt(III) Bromide: Synthesis and Oxidation-Reduction Reactivity Studies

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Although the first pseudohalogenopentaamminecobalt(III) complex, $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, was synthesized by Werner¹ and the corresponding azido complex has also been known² for some time, the syn-

theses of the cyano^{3,4} and isoselenocyanato⁵ complexes were not accomplished until this decade, due to the special synthetic problems encountered. The synthesis of the remaining member of the series, $[\text{Co}(\text{NH}_3)_5\text{NCO}]^{2+}$, has heretofore been thwarted by the tendency of the cyanate ion to hydrolyze in acidic or basic media, the limited solubility of MNCO salts in all solvents except water, and, most important, the fact that the reaction between $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$ and NCO^- yields the carbamato complex, $[\text{Co}(\text{NH}_3)_5\text{O}_2\text{CNH}_2]^{2+}$, with retention of the original Co-O bond.⁶ We now wish to report the synthesis of $[\text{Co}(\text{NH}_3)_5\text{NCO}]\text{Br}_2$ and the results of our study of the electron mediating ability of the cyanate group in oxidation-reduction reactions of the complex with $[\text{Co}(\text{CN})_6]^{3-}$ and chromium(II).

Experimental Section

Preparation of Reactants.—The chloride² and perchlorate⁷ salts of azidopentaamminecobalt(III), (triethyl phosphate)pentaamminecobalt(III) perchlorate,⁷ nitrosyl perchlorate,⁸ and tetraphenylarsonium cyanate dihydrate⁹ were prepared by methods given in the literature.

Preparation of $[\text{Co}(\text{NH}_3)_5\text{NCO}]\text{Br}_2$.—A solution of 2.0 mmol of tetraphenylarsonium cyanate dihydrate (0.92 g) in 5 ml of dimethyl sulfoxide was added, with stirring, to a solution of 1.0 mmol of $[\text{Co}(\text{NH}_3)_5\text{OP}(\text{OC}_2\text{H}_5)_3](\text{ClO}_4)_3$ (0.62 g) dissolved in 5 ml of DMSO. After the mixture had been stirred for 12 hr at room temperature, the precipitated tetraphenylarsonium perchlorate was removed by filtration. The addition of 10 ml of 8 M aqueous sodium bromide to the red filtrate resulted in the immediate formation of a pink precipitate which was isolated by filtration, washed with ethanol and ethyl ether, and air dried after the mixture had been stirred for 15 min in an ice bath. The pink solid was then slurried in 75–100 ml of distilled water for 30 min. Filtration of the mixture yielded a white solid (a mixture of tetraphenylarsonium perchlorate and bromide) and a pink filtrate. The product was precipitated from the latter by the addition of solid sodium bromide, isolated by filtration, washed with ethanol and ethyl ether, and dried over calcium sulfate; yield 26%; mp 256–258° dec (uncorrected from DTA thermogram). *Anal.* Calcd for $\text{CH}_{15}\text{N}_6\text{Br}_2\text{OCo}$: C, 3.47; H, 4.37; N, 24.29. Found: C, 3.33; H, 4.49; N, 24.09.

Reaction with $[\text{Co}(\text{CN})_6]^{3-}$.—To a solution of 4.1 mmol of potassium cyanide (0.27 g) in 5 ml of distilled water was added 0.82 mmol of $[\text{Co}(\text{NH}_3)_5\text{NCO}]\text{Br}_2$ (0.28 g). The addition of a small crystal of cobalt(II) nitrate hexahydrate resulted in partial dissolution of the cyanate complex and the evolution of ammonia. After the slurry had been stirred for 1 min at room temperature, it was filtered directly into 200 ml of 95% ethanol, which had been precooled to 0° in an ice bath. This resulted in the formation of a pale yellow solid. (The solid remaining in the filter proved to be some unreacted $[\text{Co}(\text{NH}_3)_5\text{NCO}]\text{Br}_2$.) The product, $\text{K}_3[\text{Co}(\text{CN})_6] \cdot \text{H}_2\text{O}$ (*vide infra*), was isolated by filtration, washed with ethanol and ether, and dried over calcium sulfate. A small amount of potassium cyanide impurity ($\nu_{\text{C}\equiv\text{N}}$ at 2173 cm^{-1}) was removed by dissolving the product in 1 ml of distilled water and reprecipitating the $\text{K}_3[\text{Co}(\text{CN})_6] \cdot \text{H}_2\text{O}$ by the addition of 75 ml of cold ethanol. It was isolated, washed, and dried as above; yield, based on available cyanide, 71%. *Anal.* Calcd for $\text{C}_6\text{H}_2\text{N}_6\text{OCoK}_3$: C, 20.57; H, 0.57; N, 23.99. Found: C,

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