

spectra of N,N' -bis(salicylidene)polymethylenediaminocobalt(II) complexes show differences in their reflectance and absorption spectra for the complexes with $n = 2, 3$, or 4 . For Co-Salen this is not due to coordination with the solvent as has been proposed,⁹ as there is no difference between the dichloromethane and 1-chloronaphthalene solutions.

To check whether this difference between reflectance and absorption spectra might be connected with a tetrahedral \rightleftharpoons square-planar transition, the magnetic susceptibilities of the 1-chloronaphthalene solutions were measured and are recorded in Table I. For all

TABLE I
ROOM-TEMPERATURE MAGNETIC SUSCEPTIBILITIES OF
QUADRIDENTATE COBALT(II) COMPLEXES
MEASURED IN 1-CHLORONAPHTHALENE SOLUTION

Ligand	μ_{eff} , BM
N,N' -bis(salicylidene)dimethylenediamino	2.28
N,N' -bis(salicylidene)trimethylenediamino	4.50
N,N' -bis(salicylidene)tetramethylenediamino	4.37
N,N' -bis(salicylidene)pentamethylenediamino	4.26
N,N' -bis(salicylidene)hexamethylenediamino	4.23
Bis(N -phenyl)salicylaldiminato	4.34

complexes the magnetic susceptibilities are not significantly different from those reported in the literature^{2,7,9} and it may be concluded that while Co-Salen in solution is square planar, the trimethylene and tetramethylene complexes are not.

Because of the uncommon features of the spectra of the latter two compounds, they were analyzed by mass spectrometry and C-H-N analysis to ascertain their composition. Results were identical with those reported previously and the absence of higher peaks in the mass spectrum showed that no polymer formation occurs during synthesis.²

The crystals of the tetramethylene complex are green and become orange after drying at 180° . Both forms showed the same absorption spectrum in solution. The dihydrate of the trimethylene complex and its dehydrated form, obtained by heating the crystals at 250° , also showed identical absorption spectra in solution. Apparently the complex loses the coordinated water molecules when dissolved in 1-chloronaphthalene. Summarizing, it can be said that N,N' -bis(salicylidene)-polymethylenediaminocobalt(II) complexes show significant differences between reflectance spectra of the solid phase and absorption spectra of their solutions for the compounds, where $n = 2, 3$, and 4 . This difference is caused neither by a specific solvent-solute interaction nor by a planar \rightleftharpoons tetrahedral transition and apparently reflects a less drastic change in structure.

For $n = 2$ we have seen that the spectra in dichloromethane and 1-chloronaphthalene solution are identical and that this complex is square planar in the solid state as well as in solution. It is likely that the differences of the solid-state spectrum are caused by intermolecular interactions between neighboring molecules in a direction perpendicular to that of the molecular plane.

For $n = 3$ and $n = 4$ the molecule is nonplanar in solution as well as in the solid state, and molecular

models show that the tetrahedral structure around the cobalt might be seriously distorted. With the chelating ligands in question this distortion opens possibilities of geometrical isomerism. Isomerization in solution could explain why differences between the two phases are found especially for the complexes with $n = 3$ and $n = 4$, where the greatest distortion occurs.

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The Electrochemical Behavior of Trichloro(2,2',2''-tripyridine)molybdenum, Tris(2,2'-bipyridine)molybdenum(0), and Bis(2,2',2''-tripyridine)molybdenum(0) in Dimethylformamide

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In a recent paper dealing with the electrochemistry of molybdenum(III) chloro complexes with pyridine, 2,2'-bipyridine, and 1,10-phenanthroline in acetonitrile,¹ it was found that the tendency for reduction of the metal is dependent upon the nature of the aromatic π system of the coordination sphere. Increase in the electron acceptor character of the aromatic π system of the coordination sphere causes a marked positive shift in the potential at which reduction occurs. In this note we report observations on molybdenum complexes in which the coordination sphere has, in each case, a more extensive aromatic π system than in the compounds previously studied. It was hoped that with greater ability of the coordination sphere to accept d electrons from the metal, there would be additional stabilization of lower oxidation states. This has been borne out.

In Table I there is summarized the oxidation and reduction steps involving the metal for the following complexes in dimethylformamide: trichloro(2,2',2''-tripyridine)molybdenum, tris(2,2'-bipyridine)molybdenum(0), and bis(2,2',2''-tripyridine)molybdenum(0). In addition, comparable data obtained in acetonitrile previously¹ for some pertinent molybdenum(III) complexes are shown. To compare the potentials in the two solvents, the values found in acetonitrile must be increased by 0.07 V. This increment was determined from the potentials of the ferricinium-ferrocene couple in the two solvent systems.^{2,3}

The compound $\text{MoCl}_3\text{tripy}$ in dimethylformamide exhibited four reduction waves at the dropping mercury electrode, with half-wave potentials at -0.75 , -1.57 , -2.12 , and -2.4 V *vs.* sce and limiting current ratios of

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TABLE I
 REDOX DATA FOR PROCESSES INVOLVING THE METAL
 FOR SOME MOLYBDENUM COMPLEXES WITH PYRIDINE,
 2,2'-BIPYRIDINE, AND 2,2',2''-TRIPYRIDINE

Compound	Half-wave potentials vs. sce				
	IV/III	III/II	II/I	I/0	0/-I
MoCl ₃ (py) ₃ ^d	+0.94 ^a	-1.47 ^c			
MoCl ₃ (py)bipy ^d	+0.83 ^a	-1.00 ^c			
MoCl ₃ tripy ^e	+0.60 ^a	-0.75 ^c	-1.57 ^{b,c}		
MoCl ₃ (bipy) ₂ ^d	+0.92 ^a	-0.63 ^c	-1.08 ^c		
Mo(bipy) ₃ ^f	...	-0.01 ^a	-0.42	-1.13	-1.77
Mo(tripy) ₂ ^f	...	+0.68 ^a	+0.28 ^a	-0.63 ^a	

^a Signifies an irreversible and anodic process. ^b $E_{pa} - E_{pc} \cong 75$ mV; i_{pc}/i_{pa} approaches 1 at high scan rates (1.3 at 18 V min⁻¹). ^c Values obtained at the dropping mercury electrode; all others at the rotating platinum electrode. ^d These compounds were studied in acetonitrile with 0.1 M (C₂H₅)₄NClO₄ as supporting electrolyte. ^e Supporting electrolyte, 0.1 M (C₂H₅)₄NClO₄. ^f Supporting electrolyte, 0.1 M (C₂H₅)₄NBF₄.

1:1:1:4. The limiting current of the first reduction wave was the same as that for the first one-electron reduction step for MoCl₃(py)₃¹ (with both compounds at the same concentration). The cyclic voltammogram of the same step at a hanging mercury drop electrode showed a peak potential separation of 66 mV and a cathodic to anodic peak current ratio of 1:1 at 5 V min⁻¹, values consistent with a reversible one-electron process. By cyclic voltammetry at high scan rates, the step at -1.57 V was demonstrated to approach reversibility for a one-electron reaction. The ligand itself (tripy) undergoes reduction in dimethylformamide at -2.05 and -2.43 V with limiting current ratio of 1:4 as was the case for the third and fourth reduction steps of MoCl₃tripy. Therefore, the third and fourth reduction waves, both of which were irreversible, must be attributed to ligand reductions in the complex, and the first two steps to reductions involving the central metal atom. The oxidation process, which occurred at +0.60 V, was irreversible. A comparison of the peak current with that for the one-electron step at -0.75 V indicated that the oxidation also involved one electron. Since the ligand itself does not undergo oxidation before at least +1.8 V, the step at +0.60 V is ascribed to oxidation of the metal.

For Mo(bipy)₃ the reversible one-electron nature of the steps at -1.77, -1.13, and -0.42 V involving the metal was established by a combination of limiting current, cyclic voltammetric, and epr data.⁴ The oxidation process at -0.01 V was irreversible, as shown by cyclic voltammetry, and current-voltage information was in accord with a one-electron transfer.

Solutions of Mo(tripy)₂ showed three anodic waves of equal height at -0.63, +0.28, and +0.68 V. Cyclic voltammetry revealed all three processes to be irreversible. The only reasonable interpretation of the limiting current data is the assignment of a one-electron change for each oxidation step. Since the ligand itself does not undergo oxidation before the background current due to solvent-supporting electrolyte appears, the potentials noted above must be for oxidation of the metal in the complex. At a dropping mercury elec-

trode, cathodic waves were observed at -1.92, -2.25, -2.4, and -2.7 V, with relative heights of 1:2:4:2. The limiting current of the first wave was equal to that of the oxidation wave which occurred at -0.63 V. Cyclic voltammetry with a hanging mercury drop electrode showed only a small anodic return peak. Since the first step in the reduction of the ligand alone takes place at -2.05 V, it is possible, but not at all certain, that the reduction for the complex at -1.92 V is due to conversion of the metal from the zero to the mono-negative state, a process observed for the comparable bipyridine complex.

A comparison of the data for the first three compounds of Table I establishes that 2,2',2''-tripyridine with its more extensive aromatic π character has a greater stabilizing effect on lower oxidation states of molybdenum than does either pyridine or a combination of pyridine and 2,2'-bipyridine. Not only is the potential of the molybdenum(III)-molybdenum(II) couple shifted in a more positive direction by replacement of the other amine ligands by tripyridine, but, in addition, further reduction of the molybdenum to the (I) state can be realized, a phenomenon not observed for the complexes with pyridine and bipyridine. Similar features are evident for the MoCl₂(bipy)₂⁺-Mo(bipy)₃ pair. In the latter compound, in contrast to the first, all the ligands have aromatic π character and there is found not only a positive shift in the II-I couple, but also the stabilization of even lower oxidation states (0, -I). Although no quantitative comparison can be made between the potentials obtained for Mo(bipy)₃ and Mo(tripy)₂ because of the irreversibility of the redox systems for the latter complex, nevertheless it is apparent that with tripyridine as ligand lower oxidation states are similarly stabilized.

Experimental Section

Materials.—Reagent grade dimethylformamide (Baker) was found to be satisfactory without further purification as a solvent for polarography. 2,2',2''-Tripyridine (G. Frederick Smith Chemical Company) and 2,2'-bipyridine (Aldrich Chemical Company) were used as obtained from the suppliers. Tetraethylammonium perchlorate was prepared as previously described.¹ Tetraethylammonium tetrafluoroborate was precipitated by reaction between aqueous solutions of tetraethylammonium hydroxide and fluoroboric acid. The product was recrystallized twice from water and vacuum dried under an infrared heating lamp.

Trichloro(2,2',2''-tripyridine)molybdenum was prepared as follows. Tetraethylammonium tetrachlorodiamolybdate(III)¹ (1.26 g) was added to a solution of 0.73 g of 2,2',2''-tripyridine in 100 ml of acetonitrile and the mixture refluxed under nitrogen for 2 hr. The product, a black crystalline powder, was isolated by filtration, washed with solvent, and dried under a stream of nitrogen; yield, 0.86 g. *Anal.* Calcd for MoCl₃C₁₅H₁₁N₃: Mo, 22.0; Cl, 24.4. Found: Mo, 22.0; Cl, 23.4.

Tris(2,2'-bipyridine)molybdenum(0) was prepared from bis(benzene)molybdenum(0)⁶ and 2,2'-bipyridine. Oxygen-free xylene (4 ml), Mo(C₆H₆)₂ (0.42 g), and 2,2'-bipyridine (1.63 g) were mixed in a Pyrex tube (25-ml volume) under a nitrogen atmosphere. The tube was sealed and heated to 250° for 90 min. The reaction mixture was cooled and the resulting permanganate-colored solid collected on a sintered glass filter. The product

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(5) This compound was obtained by the method of E. O. Fischer and H. O. Stahl, *Chem. Ber.*, **89**, 1805 (1956).

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.

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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 ($80 \pm 1^\circ\text{K}$ 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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