

Figure 1.—Absorption spectra of plutonium species in propane-1,2-diol carbonate solution: —, plutonium dissolved in chlorine-saturated propane-1,2-diol carbonate; ---,  $\text{PuCl}_6^{2-}$  in propane-1,2-diol carbonate; ····,  $\text{Cs}_2\text{PuCl}_6$  in propane-1,2-diol carbonate.

TABLE II  
COMPOSITION OF PLUTONIUM-CHLORIDE PRECIPITATES

Prepn	%		
	Pu	Cl	C
1	37.5	18.6	21.2
2	37.4	18.8	20.5
3	34.8	18.7	20.7
4	35.2	18.6	20.7
5	36.9	19.0	...
	Calcd		
$\text{Pu}_2(\text{PuCl}_6)_3 \cdot 12\text{PDC}$	39.1	20.9	18.8
$\text{Pu}_2(\text{PuCl}_6)_3 \cdot 14\text{PDC}$	36.6	19.6	20.6
$\text{Pu}_2(\text{PuCl}_6)_3 \cdot 16\text{PDC}$	34.5	18.4	22.2

and after drying, analysis indicated that it did not contain carbon. It was therefore concluded that the  $\text{PuCl}_6^{2-}$  anion does not contain any molecules of solvation and that all the solvent molecules in  $\text{Pu}_2(\text{PuCl}_6)_3 \cdot n\text{PDC}$  were coordinated to the  $\text{Pu}^{3+}$  ions.

Oxidation of Pu(III) to Pu(IV) is favored by stabilization of the latter as the hexachloro complex and is quantitative under favorable conditions. Thus, addition of a solution of  $(\text{C}_2\text{H}_5)_4\text{NCl}$  in propane-1,2-diol carbonate to a solution of  $\text{Pu}^{3+}$  and  $\text{PuCl}_6^{2-}$  in the same solvent (saturated with chlorine) caused all the  $\text{Pu}^{3+}$  to be oxidized to hexachloroplutonate(IV) by dissolved chlorine. In this case  $(\text{C}_2\text{H}_5)_4\text{NCl}$  supplied chloride anions to complex Pu(IV) and  $(\text{C}_2\text{H}_5)_4\text{N}^+$

cations necessary for charge balance. However, the presence of cations is not in itself sufficient to permit the oxidation; addition of  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  solution to another sample of the original solution did not alter the relative percentages of  $\text{Pu}^{3+}$  and  $\text{PuCl}_6^{2-}$ . In this case insufficient chloride ions were present to complex the Pu(IV).

The mechanism of dissolution of plutonium in chlorine-saturated propane-1,2-diol carbonate is not well understood. Initially it was thought likely that the metal was dissolved to form Pu(III), which was then oxidized to  $\text{PuCl}_6^{2-}$ , but this explanation was not supported by the observation that  $\text{PuCl}_3$  is relatively insoluble in chlorine-saturated propane-1,2-diol carbonate. Nevertheless, the bluish appearance of the metal when removed from the solvent suggests that dissolution does proceed through the formation of Pu(III).

In summary, solutions of plutonium in reasonable concentrations in propane-1,2-diol carbonate may be prepared by dissolution of the metal in chlorine-saturated solvent. The resulting solution contains Pu(III),  $\text{PuCl}_6^{2-}$ , and possibly a minor concentration of lower anionic complexes of Pu(IV) as the only ionic species. Addition of benzene to the solution causes precipitation of a compound containing only these ions, namely,  $[\text{Pu}^{\text{III}}(\text{PDC})_7]_2(\text{Pu}^{\text{IV}}\text{Cl}_6)_3$ . Future plans involve investigation of the plutonium-bromide and plutonium-iodide systems in propane-1,2-diol carbonate.

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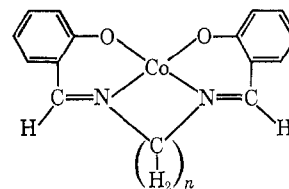
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## The Structure of Cobalt(II) Complexes with Quadridentate Schiff Bases in Solution and the Solid State

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In a recent publication<sup>2</sup> the synthesis was described of a series of cobalt(II) complexes with  $N,N'$ -bis-(salicylidene)polymethylenediamine ligands



The complexes with  $n$  ranging from 3 to 6 were said to

(1) Weizmann Institute of Science, Rehovoth, Israel. Work performed while on leave of absence.

(2) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).

be insoluble in nondonor solvents and only properties of the solid state were described. As these compounds were important to us for our studies concerning their catalytic properties,<sup>3</sup> we repeated the synthesis and have found that 1-chloronaphthalene is a suitable solvent. Therefore, we measured the spectral and magnetic properties of these complexes in solution and compared them with those in bis(N-phenylsalicylaldiminato)cobalt(II) and N,N'-ethylene(salicylideneiminato)cobalt(II).

#### Experimental Section

**Ligands.**—The ligands were prepared as described in ref 2.

**Complexes.**—The N,N'-bis(salicylidene)polymethylenecobalt(II) complexes with  $n$  ranging from 3 to 6 were synthesized as described in ref 2. Best results were obtained when the solutions of the ligand and those of the cobalt chloride were combined as quickly as possible under vigorous stirring. The bis(N-phenylsalicylaldiminato)cobalt(II) was prepared according to ref 4, substituting aniline for toluidine. The complex with  $n = 2$  (to be called Co-Salen) was prepared according to ref 5.

**Optical Spectra.**—All spectra were recorded on a Cary Model 14 spectrophotometer, using 0.01  $M$  solutions and quartz cells of 2-cm path length.

**Magnetic Susceptibility Measurements.**—The procedure described by Evans<sup>6</sup> was used. Paramagnetic shifts were measured on the signals of TMS which was added to both sample solution and solvent. The instrument was a Varian A-60 spectrometer and two concentric sample tubes were used.

**Preparation of Solutions.**—To a weighed quantity of the solid a measured volume of 1-chloronaphthalene (Baker grade) was added; the solution was brought to boil and cooled to room temperature under a stream of nitrogen. Crystallization could be postponed sufficiently to allow performance of the physical measurements. Only Co-Salen and the pentamethylene complex gave some trouble in this respect. All solutions were extremely sensitive to air and great care had to be taken to work under anaerobic conditions. The trimethylene and tetramethylene complexes showed the greatest tendency to be oxidized; even more than Co-Salen.

**Mass Spectra.**—Mass spectra were recorded on a CEC 21-104 mass spectrometer with a direct-introduction probe. Conditions were identical with those described in ref 2.

#### Results and Discussion

In Figure 1 the optical spectra are shown of the pentamethylene and the hexamethylene complexes, which are compared with that of bis(N-phenylsalicylaldiminato)cobalt(II). The spectrum of the latter is almost identical with that recorded for its benzene solution<sup>7</sup> which shows that no decomposition occurs during dissolution in the high-boiling solvent. The similarity of the three spectra shows that all three have the same stereochemistry around the cobalt which has been described as pseudotetrahedral. The same conclusion was reached from the reflectance spectra.<sup>2</sup>

In Figure 2 the optical spectra are shown of the solutions of the trimethylene and the tetramethylene complexes which are compared to that of the square-planar Co-Salen. The spectra of both compounds show no resemblance either to that of the Co-Salen or to those recorded in Figure 1. They are also different from the

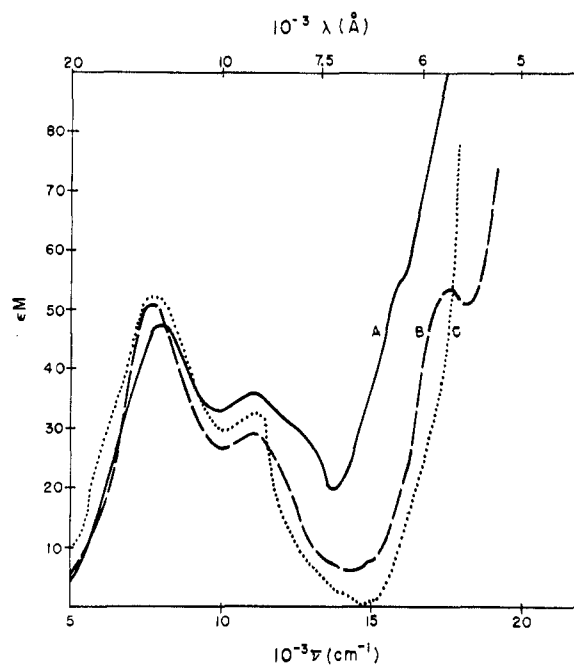


Figure 1.—Absorption spectra of 0.01  $M$  solutions in 1-chloronaphthalene: A, N,N'-bis(salicylidene)pentamethylenediaminocobalt(II); B, N,N'-bis(salicylidene)hexamethylenediaminocobalt(II); C, bis(N-phenylsalicylaldiminato)cobalt(II)

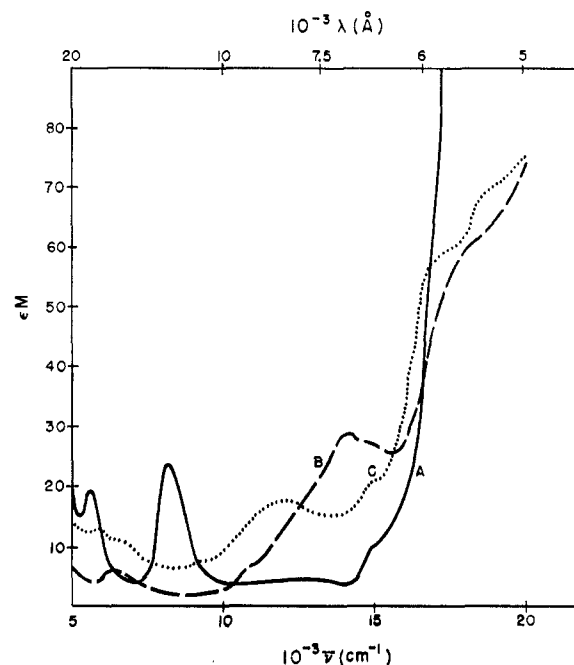


Figure 2.—Absorption spectra of 0.01  $M$  solutions in 1-chloronaphthalene: A, N,N'-ethylene(salicylideneiminato)cobalt(II); B, N,N'-bis(salicylidene)trimethylenediaminocobalt(II); C, N,N'-bis(salicylidene)tetramethylenediaminocobalt(II).

reflectance spectra given in ref 2. The absorption spectrum of Co-Salen in 1-chloronaphthalene is almost identical with that of its dichloromethane solution,<sup>8</sup> whereas its reflectance spectrum is said to show a maximum at 11,400  $\text{cm}^{-1}$ , which does not occur in the absorption spectrum in solution.<sup>9</sup> Therefore, the

(3) J. Manassen, *J. Catalysis*, submitted for publication.

(4) B. O. West, *J. Chem. Soc.*, 1374 (1962).

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(8) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, **37**, 8 (1964).

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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,<sup>9</sup> 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	$\mu_{\text{eff}}$ , 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<sup>2,7,9</sup> 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.<sup>2</sup>

The crystals of the tetramethylene complex are green and become orange after drying at  $180^\circ$ . 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  $250^\circ$ , 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,<sup>1</sup> it was found that the tendency for reduction of the metal is dependent upon the nature of the aromatic  $\pi$  system of the coordination sphere. Increase in the electron acceptor character of the aromatic  $\pi$  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  $\pi$  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 previously<sup>1</sup> 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.<sup>2,3</sup>

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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(2) H. M. Koepp, H. Wendt, and H. Strehlow, *Z. Elektrochem.*, **64**, 483 (1960).

(3) I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, **35**, 867 (1963).