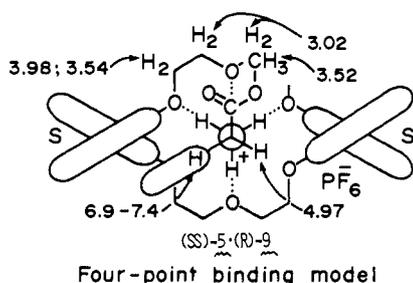
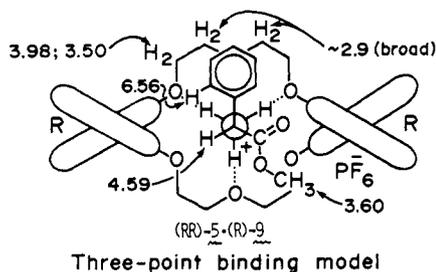


diastereomer support the structures written for (*R,R*)-5·(*R,R*)-9 and (*S,S*)-5·(*R*)-9, which are also arrived at by examination of CPK molecular models. The upfield shifts (0.19–0.38 ppm) of those protons shielded by the ring currents of the naphthalene and benzene rings are particularly informative. Their magnitudes indicate fairly rigid structures. The ortho proton of the phenyl and the CH<sub>2</sub>OCH<sub>2</sub> protons in (*R,R*)-5·(*R*)-9 would have moved much further upfield, had they not been averaging. Complex (*S,S*)-5·(*R*)-9 crystallized with 1 mol of chloroform.<sup>4a</sup>



Racemic amine hexafluorophosphates dissolved ( $\sim 1 M$ ) in D<sub>2</sub>O (1.0–4.0 *M* in LiPF<sub>6</sub> at pH  $\sim 4$ ) were shaken at the desired temperature with solutions of optically pure host ( $\sim 0.2 M$ ) in CDCl<sub>3</sub>. The pmr spectra indicated that in the CDCl<sub>3</sub> layer, [guest]/[host] = 0.7–1.0.<sup>6</sup> The layers were separated, the amines were isolated from each layer, and their optical purities and configurations were determined. The results provided *enantiomer distribution constants*, EDC =  $D_A/D_B$ , where  $D_A$  is the distribution coefficient of the enantiomer more complexed in CDCl<sub>3</sub> and  $D_B$  is that of the enantiomer less complexed (Table I).

Table I

Run no.	—RR'CHNH <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup> — R R'	Host	<i>T</i> , °C	EDC ( $D_A/D_B$ )	More stable complex
1	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	( <i>S,S</i> )-5	0	1.8	3-Point
2	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	-15	3	3-Point
3	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	24	2.5	3-Point
4	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	-15	5	3-Point
5	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	-1	1.8	4-Point
6	(CH <sub>3</sub> ) <sub>2</sub> CH CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	-10	1.5	4-Point
7	CH <sub>3</sub> S(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-5	-5	1.7	4-Point
8	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-8	24	12	3-Point
9	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-8	24	18	3-Point
10	CH <sub>3</sub> S(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	( <i>R,R</i> )-8	-5	2.2	3-Point

With no ester group present (run 1), the 3-point binding complex was more stable. In all of the more crowded complexes (runs 1, 2, 3, 4, and 8–10), the 3-point binding model applies. The methyl groups of 8 extended the chiral barrier, and increased the value of

EDC from 2.5 (run 3) to 12 (run 8). Introduction of a para-hydroxyl group into the phenyl of the guest in run 4 increased the EDC from 3 (run 2) to 5 (run 4). Possibly the  $\pi$ - $\pi$  repulsions between the phenyl and naphthalene in (*S,S*)-5·(*R*)-9 increased upon introduction of the para-hydroxyl group, and this diastereomer was relatively destabilized. In the less crowded complexes of runs 5–7, the 4-point binding diastereomers were the more stable. A comparison of runs 7 and 10 indicates that the methyl groups of host (*R,R*)-8 crowded the complex enough to cause a switch in model stability.

These results demonstrate the feasibility of designing host compounds for optically resolving amino esters by selective complexation. A molecular basis has been provided for building an amino ester resolving machine.

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Roger C. Helgeson, Joseph M. Timko, Patrice Moreau  
Stephen C. Peacock, James M. Mayer,<sup>7</sup> Donald J. Cram\*

Contribution No. 3340, Department of Chemistry  
The University of California at Los Angeles  
Los Angeles, California 90024

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### Structure of the Dimer of Diphenylantimony Trichloride

Sir:

Diphenylantimony trichloride was first prepared by Michaelis and Reese<sup>1</sup> who obtained it as a monohydrate following recrystallization from dilute hydrochloric acid. The anhydrous compound was readily obtained by heating the hydrate to 100°. Although diphenylantimony trichloride has been frequently reported in the chemical literature,<sup>2</sup> a clear distinction between the hydrated and anhydrous material has not always been made.

In a preliminary paper in 1961 Polynova and Porai-Koshits,<sup>3</sup> on the basis of X-ray determination, concluded that the compound was a trigonal bipyramid with two equatorial phenyl groups. Although this paper clearly stated that (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SbCl<sub>3</sub> was used, the method cited for its preparation<sup>4</sup> should have yielded the monohydrate. Somewhat later, in a review paper,<sup>5</sup> these same authors state that the compound exists as a monohydrate with octahedral geometry but cite their earlier paper as the reference for this result. The issue has been further confused by a recent paper by Gukasyan and coworkers<sup>6</sup> who conclude, on the basis of the <sup>121</sup>Sb Mössbauer spectrum, that the compound exists as a trigonal bipyramid with three chlorine atoms in equatorial positions. Again it is unclear as to whether they used the hydrated or the anhydrous material.

(1) A. Michaelis and A. Reese, *Justus Liebigs Ann. Chem.*, **233**, 39 (1886).

(2) H. Schmidt, *Justus Liebigs Ann. Chem.*, **421**, 159 (1920); O. A. Reutov and O. A. Ptitsyna, *Dokl. Akad. Nauk SSSR*, **79**, 819 (1951); *Chem. Abstr.*, **46**, 6093 (1952); A. N. Nesmeyanov, O. A. Reutov, and O. A. Ptitsyna, *ibid.*, **91**, 1341 (1953); O. A. Reutov and V. V. Kondratyeva, *Zh. Obshch. Khim.*, **24**, 1259 (1954); E. Wiberg and K. Mödritzer, *Z. Naturforsch. B*, **12**, 131 (1957).

(3) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **2**, 477 (1961).

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(5) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **7**, 742 (1966).

(6) S. E. Gukasyan, V. P. Gor'kov, P. N. Zaikin, and V. S. Shpinel, *Zh. Strukt. Khim.*, **14**, 650 (1973).

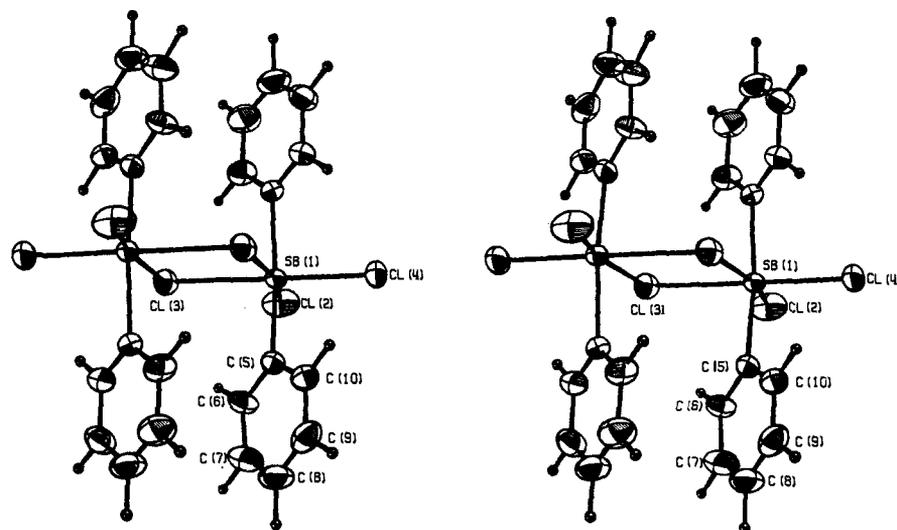


Figure 1. Stereoview of  $\text{Ph}_4\text{Sb}_2\text{Cl}_6$ .

We have now determined by means of single-crystal X-ray diffraction studies that the anhydrous compound  $(\text{C}_6\text{H}_5)_2\text{SbCl}_3$  exists as a dimer with chlorine bridges. The monohydrate was prepared by a method previously described from this laboratory<sup>7</sup> and was dehydrated by heating *in vacuo* over  $\text{P}_4\text{O}_{10}$  at  $100^\circ$ . It was recrystallized from carbon tetrachloride. Elemental analyses were in agreement with the formula  $(\text{C}_6\text{H}_5)_2\text{SbCl}_3$ .

Crystals suitable for a single-crystal X-ray analysis were grown by the slow evaporation technique. Crystals of an appropriate size were surveyed and a  $1\text{-}\text{\AA}$  data set collected on a Syntex P1 diffractometer equipped with a graphite monochromator and molybdenum radiation ( $\lambda$  0.71069  $\text{\AA}$ ). All diffraction data were collected at room temperature. Details of the crystal and data collection parameters are summarized in Table I. The systematic extinctions initially had led

led to the final assignment of space group  $Pnmm$ . A trial structure was derived by conventional Patterson and Fourier techniques. This trial structure refined routinely to a final  $R$  index of 0.042 ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ). Hydrogen positions were calculated, and while their parameters were added to the structure factor calculations, their parameters were not refined. The final cycles of full-matrix least-squares refinement contained all atomic coordinates, scale factor, and anisotropic temperature factors in one matrix. The shifts calculated in the final cycle of least squares were all less than one-seventh of the standard deviation. A final difference Fourier revealed no missing or misplaced electron density.

The refined structure was plotted using the ORTEP computer program of Johnson<sup>8</sup> (Figure 1). Bond distances and angles, along with their standard deviations, are presented in Table II. Atomic coordinates,

Table I. Crystal and Data Collection Parameters

Compound	$\text{C}_{24}\text{H}_{20}\text{Sb}_2\text{Cl}_6$ (764.6)
Crystallization medium	Benzene
Crystal size	$0.1 \times 0.1 \times 0.1$ mm
Cell dimensions	$a = 10.550$ (2) $\text{\AA}$ $b = 8.525$ (2) $\text{\AA}$ $c = 14.763$ (3) $\text{\AA}$ $V = 1327.7$ (4) $\text{\AA}^3$
Density observed	1.90 $\text{g/cm}^3$
Density calculated	1.91 $\text{g/cm}^3$ (for $Z = 2$ )
$\mu$	26.6 $\text{cm}^{-1}$
Scan mode	$\theta/2\theta$
Scan rate	$2^\circ/\text{min}$ in $2\theta$
Background count time	Peak scan time/2 (at both ends of scan)
Number of reflections	755
Nonzero reflections <sup>a</sup>	733

<sup>a</sup> Reflections with intensities less than  $2\sigma$  were set equal to zero with zero weight.

to an ambiguity in space group ( $Pnmm$  or  $Pnn2$ ). Density calculations had also indicated that the molecule contained twofold or  $2/m$  symmetry. Subsequent refinement and the establishment of  $2/m$  symmetry

(7) G. O. Doak and J. M. Summy, *J. Organometal. Chem.*, **55**, 143 (1973).

Table II. Bond Distances and Angles

Atom		Distance ( $\text{\AA}$ )	Atom			Angle (deg)
Sb(1)	Cl(2)	2.346 (4)	Cl(3)	Sb(1)	Cl(2)	87.4 (2)
Sb(1)	Cl(3)	2.620 (4)	Cl(4)	Sb(1)	Cl(2)	94.8 (2)
Sb(1)	Cl(4)	2.388 (4)	C(5)	Sb(1)	Cl(2)	97.4 (2)
Sb(1)	C(5)	2.125 (9)	Cl(4)	Sb(1)	Cl(3)	177.9 (2)
Sb(1)	Cl(3') <sup>a</sup>	2.839 (4)	C(5)	Sb(1)	Cl(3)	88.8 (2)
C(5)	C(6)	1.39 (1)	C(5)	Sb(1)	Cl(4)	90.9 (2)
C(5)	C(10)	1.39 (1)	Cl(3') <sup>a</sup>	Sb(1)	Cl(2)	168.5 (2)
C(6)	C(7)	1.38 (1)	Cl(3)	Sb(1)	Cl(3') <sup>a</sup>	81.2 (1)
C(7)	C(8)	1.37 (1)	Cl(4)	Sb(1)	Cl(3') <sup>a</sup>	96.7 (1)
C(8)	C(9)	1.38 (1)	C(5)	Sb(1)	Cl(3') <sup>a</sup>	82.4 (2)
C(9)	C(10)	1.39 (1)	Sb(1)	Cl(3)	Sb(1') <sup>a</sup>	98.8 (2)
			C(6)	Sb(1)		117.9 (6)
			C(10)	C(5)	Sb(1)	119.9 (6)
			C(10)	C(5)	C(6)	122 (1)
			C(7)	C(6)	C(5)	118 (1)
			C(8)	C(7)	C(6)	121 (1)
			C(9)	C(8)	C(7)	120 (1)
			C(10)	C(9)	C(8)	120 (1)
			C(9)	C(10)	C(5)	117 (1)

<sup>a</sup> Generated by symmetry operation:  $\bar{x} + 1.0, \bar{y} + 1.0, \bar{z} + 1.0$ .

(8) C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn.

temperature factors, and structure factor table appear in Tables III-V.<sup>9</sup>

**Supplementary Material Available.** Tables III-V will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6763.

(9) See paragraph at end of paper regarding supplementary material.

Jon Bordner, G. O. Doak,\* John R. Peters, Jr.

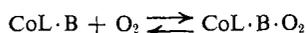
Department of Chemistry, North Carolina State University  
Raleigh, North Carolina 27607

Received July 10, 1974

### Evidence against the O<sub>2</sub><sup>-</sup> Formulation of Cobalt(II) Adducts of Dioxygen

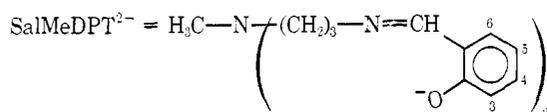
Sir:

The reversible binding of dioxygen, O<sub>2</sub>, to form six-coordinate cobalt(II) Schiff base and porphyrin complexes has led to much recent work concerning the electronic structure of the cobalt-oxygen adduct<sup>1-6</sup> and the enthalpy of adduct formation.<sup>7-10</sup> Binding of O<sub>2</sub> usually takes place in the presence of a coordinating base, B, and can be represented as



where CoL represents the Schiff base or porphyrin complex. These adducts have been formulated as superoxo (O<sub>2</sub><sup>-</sup>) adducts of Co(III) through esr<sup>2-6</sup> and X-ray diffraction studies.<sup>11</sup> In this communication we present results on a complex which is best viewed as one involving bound singlet O<sub>2</sub> and show its esr spectral behavior is not very different than other reported cobalt-oxygen complexes formulated as O<sub>2</sub><sup>-</sup>.

We report nmr and esr investigations of the O<sub>2</sub> and CO adducts of the pentadentate Schiff base complex Co<sup>II</sup>(salMeDPT), salMeDPT = bis(salicylidene-γ-



iminopropyl)methylamine, as shown below. Nmr studies on this system are more feasible than those previously reported due to enhanced solubility. Co(salMeDPT) is high spin ( $\mu = 4.29$  BM in solid, 4.28 BM

(1) R. G. Wilkins, *Advan. Chem. Ser.*, No. 100, 111 (1971), and references within.

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(5) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 61 (1970).

(6) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969).

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(8) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1154 (1973).

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(10) R. M. Guidry and R. S. Drago, *J. Amer. Chem. Soc.*, **95**, 6645 (1973).

(11) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).

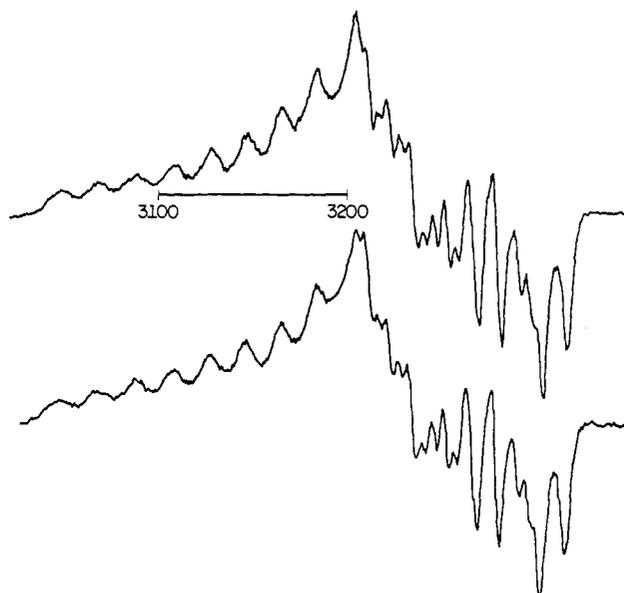


Figure 1. X-Band esr spectra of Co(salMeDPT) adducts in CH<sub>2</sub>Cl<sub>2</sub>-toluene glass: O<sub>2</sub> (top), CO (bottom).

in CH<sub>2</sub>Cl<sub>2</sub> solution) and is likely five-coordinate, as is the case with the Ni(II) complex of this ligand.<sup>12</sup> Since the combined effects of spin-orbit coupling and zero-field splitting cause a short  $T_1$ , the contact-shifted <sup>1</sup>H nmr is easily observable. The isotropic shifts exhibit Curie behavior.

Addition of 1 atm of O<sub>2</sub> to the complex in degassed CDCl<sub>3</sub> solution produces a marked change in the nmr. As the temperature is lowered below -10°, new peaks appear in the 0-6 ppm range and they gain intensity as the temperature is lowered. The 4, 5, and 6 ring proton peaks lose intensity, but their chemical shifts remain identical with those of a low temperature degassed sample. At -50°, the 4-H peak has lost ~40% of its room temperature intensity. These observations are reversible with temperature. We attribute these new peaks to the O<sub>2</sub> adduct. Since separate resonances are observed for the adduct and free complex, there is slow exchange of O<sub>2</sub> over the temperature range observed. Further evidence for slow exchange comes from the fact that resonances due to free Co(salMeDPT) in the O<sub>2</sub> solution fall on the same Curie plot as the degassed sample.

The esr of free Co(salMeDPT) in a degassed solution of CH<sub>2</sub>Cl<sub>2</sub>-toluene or a dilute powder in Zn<sup>II</sup>(salMeDPT) shows a very broad signal observable at 77°K with a  $g$  value of approximately 4.3, consistent with its high spin configuration. Upon addition of O<sub>2</sub> to a CH<sub>2</sub>Cl<sub>2</sub>-toluene solution, the spectrum sharpens and  $g$  value anisotropy is evident and is better resolved than in any previously reported spectra of O<sub>2</sub> adducts. A precise computer simulation has not as yet been obtained because of field dependent line widths as seen in Figure 1 and the possible misalignment of the  $g$  and  $A$  tensors. The spectrum observed when CO is complexed to the cobalt is practically identical with that of the O<sub>2</sub> adduct. Coordination of CO is established from the very broad infrared absorption of complexed CO at ~2090 cm<sup>-1</sup> and from a +23.8 ppm shift

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