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Triplet State of a Binuclear Copper *dl*-Tartrate and Electron Paramagnetic Resonance Spectra of the Copper Tartrates[1]

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This paper reports the electron paramagnetic resonance spectra of 1:1 complexes of copper with *meso*, active, and racemic tartaric acid in acidic (pH ~4) and basic (pH ~11) solutions at 80 and 300°K. The results show that when the compound Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$, which was isolated as pure single crystals, is dissolved in an aqueous solvent, the principal copper species is a binuclear anion having a structure analogous to that of binuclear vanadyl *dl*-tartrate. Under the imperfect assumption of axial symmetry, the relevant epr parameters of this $Cu_2(dl\text{-tart})_2^{4-}$ species in solution are $g_{\parallel} = 2.224$, $g = 2.139$, $g_{\perp} = 2.08$, $A = 0.0082\ \mathrm{cm}^{-1}$, $a = 0.0031\ \mathrm{cm}^{-1}$, and $D = 0.057 \pm 0.001\ \mathrm{cm}^{-1}$ (as derived from $\Delta M_s = \pm 1$ lines) or $0.060 \pm 0.005\ \mathrm{cm}^{-1}$ (as derived from the $|\Delta M_s| = 2$ lines), A and a being the nuclear hyperfine splittings exhibited by the full-field parallel and the room-temperature solution lines, respectively. From the zero-field parameter, D, and molecular models the Cu–Cu distance is estimated as ~3.5 Å. The interpretations of the epr spectra of the other complexes are less definitive but suggest that the *meso*- and *d*-tartrate complexes in alkaline solution and the *meso*-tartrate complex in acidic solution exist primarily as magnetically dilute species. The *dl*- and *d*-tartrate complexes form apparently identical species in acid solution and appear to be polymeric.

Introduction

The chelates formed in 1:1 copper–tartaric acid solutions at various pH values have been extensively investigated for over a century[2–11] and yet their structures remain very uncertain. As pointed out earlier,[12] part of the difficulty lies in the multidentate character of tartaric acid, $HO_2CCHOHCHOHCO_2H$, which can participate in polymeric complexes, and its several ionizable hydrogen atoms, which make complex formation very pH dependent.

Some of the precipitates isolated from acidic aqueous solution have been assigned the formulas Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$[3] and Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$,[2] in which both carboxyl protons have been ionized.[8] On the basis of infrared spectra, Kirschner and Kiesling[4] proposed a monomeric structure for copper *d*-tartrate trihydrate, with all three water molecules coordinated to copper. Their results were indirectly supported by the failure of Dunlop, *et al.*,[5] to observe any magnetic anomalies in solid or solution or any optical spectral difference between copper complexed with active or racemic tartrate in acidic media. Recent polarographic experiments indicate that only one species is formed at pH 2–5, copper tartrate in a 1:1 ratio for both active and racemic isomers.[6] However, from epr and magnetic susceptibility measurements on powdered samples, Ablov, *et al.*,[7] have proposed a polymeric chain model for copper *d*-tartrate trihydrate, each copper ion being coordinated with two halves of two different tartrate anions. The potentiometric titration data of Rajan and Martell[8] for solutions of 1:1 copper *dl*-tartrate suggest the existence of binuclear species in the pH range 2–3, where both carboxyl protons are ionized. It is noteworthy that an analogous Ni(II) complex with racemic tartaric acid is believed to be binuclear.[13]

The precipitates isolated from neutral 1:1 copper tartrate solutions have been generally formulated as 4:3 complexes of the type $Na_3Cu_4C_{12}O_{18}H_7 \cdot nH_2O$ and are considered to be polymeric. The recent results of Ablov, *et al.*, further support this contention.[7] Ample reference to the literature in this area can be found in ref 5.

Of particular interest are the chelates formed in basic copper tartrate solution (Fehling's solution). It has been established with reasonable certainty that at least some of the species present are polynuclear.[5] Conductometric, photometric, amperometric, and potentiometric titrations[8,9] all indicate 1:1 complexes. The colligative properties of alkaline copper *d*-tartrate imply polymeric species[10,11] and the observed Tyndall effect may be due to polymers of very large molecular weight.[5] Moreover, the racemic and active tartrate complexes exhibit markedly different optical spectra with departure from the Beer–Lambert law.[5] Similar spectral anomalies were noted for the vanadyl tartrates[5,14] which have since been shown to be 2:2 tartrato(4−)-bridged binuclear complexes both in the solid[15,16] and in solution.[14,17] *cis–trans* differences in coordination ge-

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[1] Support by ARPA Contract SD-131 through the Materials Research Laboratory at the University of Illinois and NDEA Title IV Predoctoral Fellowship awarded to N. D. C.

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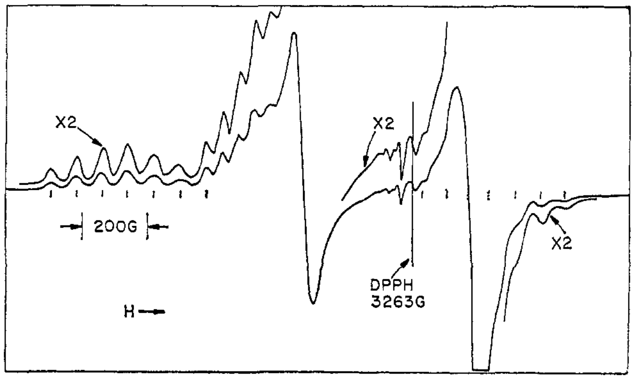

Figure 1.—"Full-field" $\Delta M_s = \pm 1$, first-derivative epr spectrum of saturated aqueous solution of Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$, pH 11.3, in 1:2 solution–ethylene glycol frozen glass at 77°K. The small solid vertical lines locate the parallel lines used in obtaining the parameters, and the dotted lines indicate probable positions of the other parallel lines.

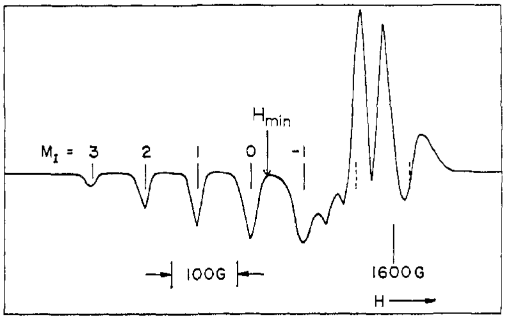

Figure 2.—"Half-field" $\Delta M_s = 2$, first-derivative epr spectrum of saturated aqueous solution of Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$ in 1:2 water–ethylene glycol frozen glass at 77°K. The arrow locates the choice of H_{min} for the $M_I = 0$ line; similar choices were made for the other hyperfine lines.

ometry about the vanadyl group are responsible for the striking spectral differences between the active and racemic vanadyl tartrate dimers,[18,19] and perhaps a similar situation exists in the copper tartrate system. Of the numerous compounds precipitated from basic copper tartrate solutions, some have been formulated as[2,11,20,21] $M_2CuC_4H_2O_6 \cdot nH_2O$, analogous to the vanadyl tartrates. Several other known potentially binuclear complexes have similar formulas.[12]

Epr spectroscopy has proven to be a valuable tool for the elucidation of the molecular structure of the binuclear vanadyl tartrates[17] and citrates[22] and the binuclear copper hydroxycarboxylate[23,24] and peptide[25] complexes in solution. In an attempt to elucidate the copper tartrate system, we have investigated epr spectra of room temperature and 77°K frozen solutions of 1:1 copper tartrate in acid (pH ~4) and alkaline (pH ~11) media.

Experimental Section

Preparation of Compounds.—Copper *meso*-, *d*-, and *dl*-tartrate salts were prepared by addition of a 0.1 *M* aqueous solution of sodium potassium tartrate, $NaKC_4O_6H_4$, to an equimolar solution of copper nitrate or sulfate; the crystalline precipitate which formed within 0.5 hr[4] was washed with cold water. Prolonged air-drying times of the *d* and *dl* salts resulted in loss of water of crystallization. Therefore, we followed the weight loss during the drying time and bottled the sample when an abrupt change in the slope of the drying curve occurred. Single crystals were obtained by slow diffusion of the sodium potassium tartrate solution into the copper sulfate solution. The copper content was analyzed as CuO cumbustion residue and the water content by weight loss under vacuum at 120° for 30 hr. *Anal.* Calcd for Cu-*d*- and Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$: C, 18.08; H, 3.77; Cu, 23.93. Found, respectively: C, 18.29, 18.11; H, 3.78, 3.77; Cu, 23.59, 23.77. Calcd for Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$: C, 19.76; H, 3.09; Cu, 26.14; H_2O, 12.95. Found: C, 19.94; H, 3.10; Cu, 26.09; H_2O, 12.98. Disodium copper(II) *dl*-tartrate pentahydrate was prepared by dissolving 10 g of copper *dl*-tartrate trihydrate, Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$, in 200 ml of 1 *M* carbonate-free sodium hydroxide followed by dropwise addition of 200 ml of 3:1 ethanol–water solution and then 50 ml of 95% ethanol, which brought about nearly complete precipitation of the compound. The crystalline product was washed twice with 100 ml of 1:1 ethanol–water solution and then with 3:1 solution and air dried. Single crystals were obtained by cooling a solution of the product in hot 1:1 ethanol–water or by slow diffusion of alcohol into an aqueous solution of the salt. The copper content was analyzed by EDTA titrations. This compound has been reported as the tetrahydrate,[2,11,20] but our results are more consistent with the pentahydrate. *Anal.* Calcd for Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$: C, 13.90; H, 3.49; Cu, 18.38; H_2O, 26.0. Found: C, 14.12; H, 3.53; Cu, 18.36; H_2O, 24.9. Attempts to isolate the analogous *d* and *meso* compounds as previously described[12] were unsuccessful; they resulted in precipitates of variable composition.

Epr Spectra.—All spectra were recorded as described earlier.[17] Solutions as concentrated as feasible were prepared to favor dimer formation. Saturated Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$ (~2 *M*; the epr lines may be somewhat broadened at this high concentration) and Cu-*d*- and Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$ and Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$ (~0.005 *M*) solutions were used for the room-temperature spectra, the last three solutions having been prepared by stirring an excess of the sparingly soluble salt with water for at least 3 hr. Basic (0.1 *M*) copper *d*- or *meso*-tartrate solutions were prepared by dissolving Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$ or Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$ in 0.5 *M* sodium hydroxide, adjusting the pH to 11.3, and then diluting to volume with Na_2HPO_4–NaOH, pH 11.3, buffer[26] (the pH of 0.1 *M* Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$ solutions). Ethylene glycol–water solutions (2:1) were used for the liquid nitrogen frozen solution measurements. Dilutions below 0.1 *M* produced no significant narrowing of the epr lines.

Optical Spectra.—The optical spectra were recorded in the range 3000–15,000 Å with a Cary Model 14 RI recording spectrometer. We used Kel-F (3M Co.) grease as the suspension medium for the mull, which was sandwiched between two quartz plates. A sodium chloride mull served as a blank. Solutions were prepared in the same way as for the epr spectra.

Results

Copper *dl*-Tartrate, Basic Solution. A. Spectral Features.—The frozen solution spectra of disodium copper(II) *dl*-tartrate pentahydrate are shown in Figures 1 and 2. The apparent *D* splittings of the $\Delta M_s = \pm 1$

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("full-field") lines (*cf.* Figure 1) and the presence of the $\Delta M_s = 2$ ("half-field") lines (*cf.* Figure 2) are characteristic of binuclear triplet-state species.[17,22-25] Similar but less well-resolved half-field spectra have been reported for binuclear copper hydroxycarboxylate[24] and peptide[25] complexes. Kokoszka and coworkers[27] have found for polycrystalline samples of binuclear copper adenine complexes full-field lines which have the same general appearance as those in Figure 1.

To the first approximation, we assume that the system is axially symmetric (this assumption is not strictly true, as will be pointed out in the Discussion) and write the appropriate $S = 1$ Hamiltonian

$$\mathcal{H} = \beta(g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y))] + D[S_z^2 - (S(S + 1)/3)] + AS_zI_z + B(S_xI_x + S_yI_y) \quad (1)$$

where all the symbols have their usual meaning. The spectrum in Figure 1 consists of overlapping low- and high-field parallel and perpendicular lines, with the parallel lines separated by approximately $2D$ (1084 G) and the perpendicular lines by approximately D (502 G).

TABLE I

EPR AND OPTICAL SPECTRAL PARAMETERS OF THE COPPER TARTRATES[a]

	g	a^b	$g_{\|}$	$g_{\perp}$	A^b	B^b	D^b	Δ, kK[c]
Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$	2.139 (10)	30.8 (10)	2.224 (5)	2.086 (5)	81.9 (10)	5 (2)	605 (42)[e]	15.30, 15.25 (10)*
Basic pH 11.3 soln				2.08 (1)[d]			572 (7)[f]	
Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$	~2.14 (3)	~60 (10)	2.272 (5)	...	179 (2)	...	...	14.9 (1)
Basic pH 11.3 soln								
Cu-*meso*-$C_4O_6H_4 \cdot 1 \cdot 75H_2O$	~2.14 (3)	~60 (10)	2.271 (5)	...	178 (2)	...	...	14.8 (1)
Basic pH 11.3 soln								
Cu-*dl*- or Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$	2.17 (1)	...	...	...	...	...	...	12.2 (1)*
Acid pH 4.25 soln								
Cu-*meso*-$C_4O_6H_2 \cdot 1.75H_2O$	2.16 (1)	...	2.37 (1)	2.05 (3)	144 (5)	...	...	12.8 (1)*
Acid pH 4.53 soln								

[a] Estimated errors in the last digit are given in parentheses. [b] Values are given in units of 10^{-4} cm^{-1}. [c] Band maxima of optical spectra from mull samples are marked with an asterisk; others are from solution samples. [d] Estimated from frozen-solution spectrum in Figure 1. [e] Derived from the "half-field" lines. [f] Derived from the "full-field" lines.

One particularly interesting aspect of the frozen solution spectrum in Figure 1 is the appearance of a progression of about seven lines (spacing ~50 G) which follows the low-field parallel lines (average spacing 78.3 G). There are a number of possible explanations of this splitting and in an attempt to ascertain its origin, we measured the Q-band spectrum of a frozen solution at 77°K. Although the Q-band spectrum had the principal features of a binuclear compound, we were unable to assign completely all the lines as they were poorly resolved. (The resolution was adversely affected by an instrumental instability. It may be possible to improve the instrumentation and obtain definitive Q-band results at a later date.)

The poor resolution of the room-temperature solution spectrum in Figure 3 probably arises from magnetic dipole–dipole broadening of the resonance lines[17,28] and possibly from overlapping spectra of various species. The weak, relatively sharp lines just downfield from the DPPH mark in the frozen-solution spectrum (*cf.* Figure 1) may be due to monomeric species, similar lines are observed for polycrystalline samples of copper adenine dimers, in which case a careful study indicated a monomer origin.[27]

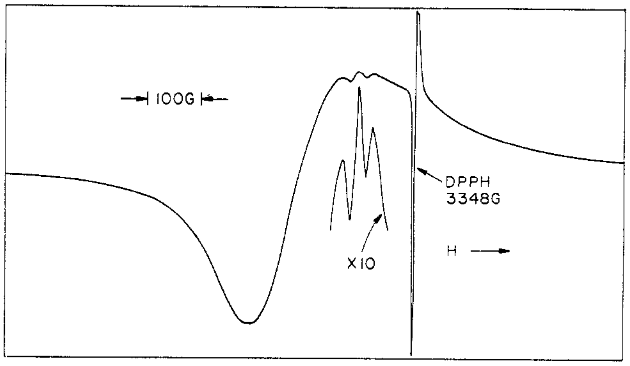

Figure 3.—"Full-field" $\Delta M_s = \pm 1$, first-derivative epr spectrum for a saturated aqueous solution of Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$, pH 11.3, at room temperature.

B. Determination of Epr Parameters.—We determined the $g_{\|}$, A, and D values from the parallel lines through eq 2 for the transition energies, correct to the second order in perturbation theory, for the field direction along the symmetry axis,[29] where $I = 3$, $M_s = 1, 0$,

$$\omega_0 = g_{\|}\beta H + 2D(M_s - 1/2) + AM_I + (B^2/\omega_0)[I(I + 1) - M_I^2 + (2M_s - 1)M_I] \quad (2)$$

$M_I = \pm 3, \pm 2, \pm 1, 0$, and ω_0 is the radiation frequency. The resultant epr parameters are given in Table I. The hyperfine interaction A of Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$ is about half the splitting observed in the absence of strong exchange coupling.[30]

From the splitting (502 G) of the full-field perpendicular lines, we also determined a D which (with correction for g anisotropy) was identical with that obtained from the parallel lines. In addition, D was obtained from the positions of the $\Delta M_s = 2$ half-field lines through the relationship[31]

$$H_{\min} = [\omega_0^2 - {}^4/_3D^2]^{1/2}/2g\beta \quad (3)$$

$H_{\min}$ was determined from each of the four clearly dis-

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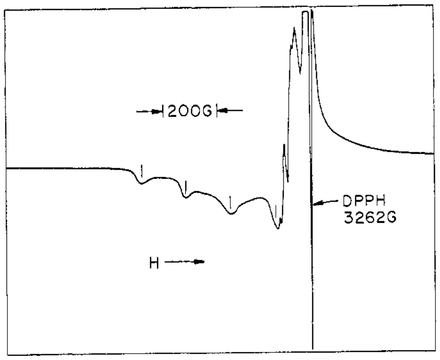

Figure 4.—First-derivative epr spectrum of 0.5 *M* Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$ + 1.0 *M* NaOH in aqueous $NaHPO_4$–NaOH pH 11.3 buffer in 1:2 solution–ethylene glycol frozen glass at 77°K. The small vertical lines locate the parallel lines used in obtaining the parameters.

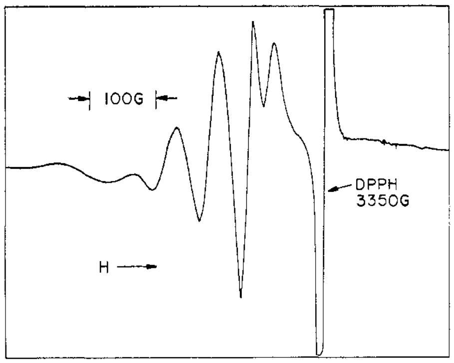

Figure 5.—First-derivative epr spectrum of 0.5 *M* Cu-*d*-$C_4O_6H_4 \cdot 3H_2O$ + 1.0 *M* NaOH in aqueous Na_2HPO_4–NaOH pH 11.3 buffer at room temperature.

cernible hyperfine lines (M_I = 3–0; *cf.* Figure 2) giving H_{min} values of 1413, 1413, 1421, and 1424 G (after correction for downfield shift of the hyperfine interaction) and corresponding D values (for $\omega_0 = 0.3052$ cm^{-1} and $g = 2.224$) of 0.0642, 0.0642, 0.0581, and 0.0556 cm^{-1} (average 0.0605 ± 0.040 cm^{-1}). The agreement with D from the full-field spectra is reasonable in view of the uncertainty in the position of H_{min}.

We calculated $g_\perp$ and B from equations

$$g = {}^1/_3 g_{\parallel} + {}^2/_3 g_{\perp} \tag{4}$$

$$a = {}^1/_3 A + {}^2/_3 B \tag{5}$$

where isotropic a and g were measured from the room-temperature spectrum. Assuming that the observed three-line splitting of about 30 G in Figure 3 corresponds to a of the binuclear complex, we calculate $B = 5 \times 10^{-4}$ cm^{-1}, which is rather small. A value of (10–25) $\times 10^{-4}$ cm^{-1} is perhaps more reasonable; however, B values less than 10^{-3} cm^{-1} have been reported for dimeric copper alkanoates[32–34] and citrates[23] and are in accord with our result.

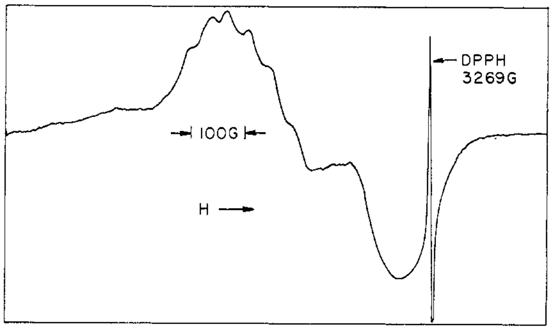

Figure 6.—First derivative epr spectrum of a concentrated aqueous solution of Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$, pH 4.25, in 1:2 solution–ethylene glycol frozen glass at 77°K.

Copper *d*- and *meso*-Tartrate, Basic Solution.—Epr spectra typical of either complex are shown in Figures 4 and 5. The frozen solution spectrum (Figure 4) has the general appearance of one derived from monomeric species,[35] while the interpretation of the room-temperature spectrum (*cf.* Figure 5) is not completely straightforward. The complexity of the room-temperature spectrum suggests incomplete rotational averaging of **g** and **A** tensors as might be expected of polymeric species; however, we observed no $\Delta M_s = 2$ lines characteristic of exchange-coupled dimers or low molecular weight polymers. It is possible that in a chain-structured model for a polymer, the Cu^{2+} ions may be far enough removed from one another (>6 Å) that direct dipolar and direct- or superexchange interactions are very small and therefore do not substantially change the spectrum from one characteristic of essentially isolated Cu^{2+} units. Other experiments[5,10,11] do suggest the existence of polymers in solution (see Introduction).

Copper *d*- and *dl*-Tartrate, Acid Solution.—The epr spectra of room-temperature and frozen solutions of copper *d*- and *dl*-tartrate trihydrate (*cf.* Figures 6 and 7) are the same for both complexes, as is consistent with their identical elemental analyses, stabilities,[6] and mull and solution[5] optical spectra. Since these are 1:1 complexes, any dimers[8] [our failure to observe any half-field transitions characteristic of copper dimers (*cf.* Figure 2) makes the presence of these species less likely] or oligomers[7] present must consist largely of molecules containing *d* or *l* but not both isomers of tartaric acid in the same structure. The structureless room-temperature spectrum and the broad complicated low-temperature spectrum probably arise from polymeric species of various molecular weights or possibly from overlapping spectra of different complexes; however, contamination of the solution by substantial amounts of quite different complexes is not supported by polarographic measurements.[6]

Copper *meso*-Tartrate, Acid Solution.—The room-temperature and frozen-solution spectra of the solutions of Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$ are quite different from those of the active and racemic complexes (*cf.* Figures 8 and 9 compared to Figures 6 and 7) and could arise from

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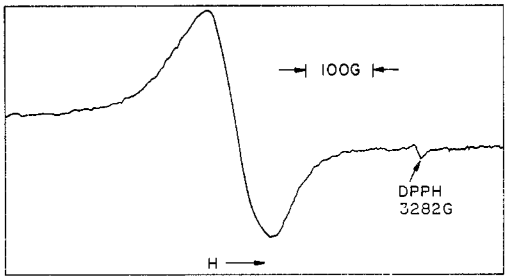

Figure 7.—First-derivative epr spectrum of a concentrated aqueous solution of Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$, pH 4.25, at room temperature.

monomeric and polymeric species having very weak magnetic interactions between metal centers (see the discussion on copper *d*- and *meso*-tartrate, basic solution).

Optical Spectra.—The optical spectra of all the tartrates consist of one broad band in the range 650–850 mμ, with the alkaline solution species exhibiting an additional more intense band at about 330 mμ (see ref 5 for representative spectra). The 655-mμ band maximum for Na_2Cu-*dl*-$C_4O_6H_2 \cdot 5H_2O$ occurs 3000 cm^{-1} higher in energy than that of Cu-*dl*-$C_4O_6H_4 \cdot 3H_2O$. Similarly, a blue shift is also observed for the *meso* and active tartrates (see Table I). These shifts suggest an increase in crystal field strength produced by coordination of "negatively charged" hydroxyl oxygens of the tartrate(4−) anion.

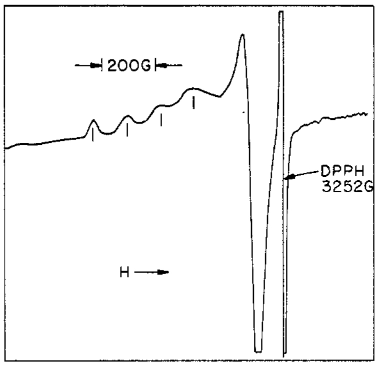

Figure 8.—First-derivative epr spectrum of a concentrated aqueous solution of Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$, pH 4.53, in 1:2 solution–ethylene glycol frozen glass at 77°K. The small vertical lines locate the parallel resonances used in obtaining the parameters.

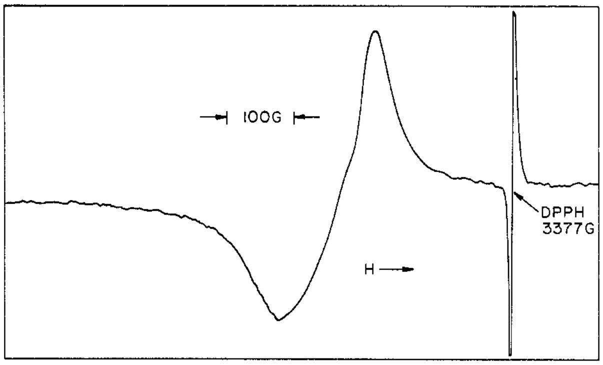

Figure 9.—First-derivative epr spectrum of a concentrated aqueous solution of Cu-*meso*-$C_4O_6H_4 \cdot 1.75H_2O$, pH 4.53, at room temperature.

TABLE II

INTERMETALLIC DISTANCES FROM ZERO-FIELD SPLITTING PARAMETERS

Dimer	$10^4 D_{\text{exptl}}/\text{cm}^{-1}$	J/cm^{-1}	10^4 $D_{\text{pseudo}}/$ cm^{-1}	$R_{\text{calcd}}/\text{Å}^a$	$R_{\text{calcd}}/\text{Å}^b$	$R_{\text{exptl}}/\text{Å}^c$
$(VO)_2$(*d*-tart)$_2^{4-}$	-335 ± 4^d	$<50^e$	<10	>4.15	4.19	4.35 ± 0.06^f
$(VO)_2$(*d*-tart)(*l*-tart)$^{4-}$	$\sim -336^d$	$<50^e$	<10	>4.15	~4.19	4.082 ± 0.006^g
$Cu_2(C_5H_4N_5)_4 \cdot 4H_2O^h$	-1210 ± 50^i	-160 ± 60^i	130	2.84	2.92	2.947 ± 0.006^j
$Cu_2(C_5H_5N_5)_4(ClO_4)_4 \cdot 3H_2O^k$	-1100 ± 50^i	-300 ± 60^i	280	2.85	3.08	...
Cu_2(*d*-tart)(*l*-tart)$^{4-}$	-572 ± 7^l	...	...	...	3.85 (3.3^m)	(3.4^n)

[a] Calculated from eq 8 and $D_{dd} = D_{exptl} - D_{pseudo}$. [b] Calculated from eq 8 and $D_{dd} = D_{exptl}$. [c] Metal–metal distances from X-ray data; errors quoted are 3σ. [d] Reference 7. [e] The exchange energy is unknown for the vanadyl tartrates; for these calculations J is taken to be negative, and previous susceptibility and epr measurements[14,17,18] indicate its magnitude to be between 0.1 and 50 cm^{-1}. [f] Reference 15. [g] Reference 16. [h] $g_{\parallel} = 2.10 \pm 0.03$ and $g_{\perp} = 2.05 \pm 0.01$.[27] [i] Reference 27. [j] E. Sletten, *Chem. Commun.*, 1119 (1967). [k] $g_{\parallel} = 2.22 \pm 0.03$ and $g_{\perp} = 2.05 \pm 0.01$.[27] [l] This work. [m] Estimated with inclusion of covalency corrections in the dipole calculation. [n] Estimated from molecular models; see text.

Discussion of Binuclear Copper *dl*-Tartrate

The most interesting and definitive result of this study is the synthesis and characterization of binuclear sodium copper *dl*-tartrate, which we now formulate as $Na_4[Cu_2(d\text{-}C_4O_6H_2)(l\text{-}C_4O_6H_2)] \cdot 10H_2O$. In addition to verifying the existence of a triplet-state binuclear complex, epr data provide some evidence for its detailed molecular structure.

Consideration of Pseudodipolar Contributions.—Both magnetic dipole–dipole interactions and pseudodipolar terms (originating in spin–orbit coupling) can contribute to the zero-field splitting parameter, $D_{\text{exptl}} = D_{\text{dd}} + D_{\text{pseudo}}$. Pseudodipolar contributions, D_{pseudo}, can be estimated from the relation[33]

$$D_{\text{pseudo}} \approx -J\{[(g_{\parallel} - 2)^2/4] - (g_{\perp} - 2)^2\}/8 \qquad (6)$$

where $-J$ is the energy separation between the singlet ground state and the first excited triplet state. Since our interest here is in the use of the measured D value to estimate an unknown intermetallic distance, which is obtained from D_{dd},[17,36] we must estimate D_{pseudo}. Table II gives values for similar binuclear complexes for which J, $g_{\parallel}$, $g_{\perp}$, and D_{exptl} are known. Clearly the agreement between the experimental metal–metal distance (R_{exptl}) and those estimated from the zero-field splitting is good and moreover is relatively insensitive to the pseudodipolar contributions. This insensitivity results di-

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(36) K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A214**, 237 (1952).

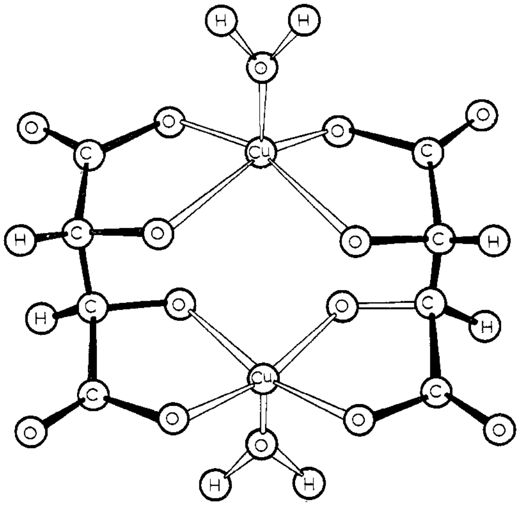

Figure 10.—Proposed structure of binuclear $Cu_2(dl\text{-}C_4O_6H_2)_2^{4-}$ anion.

rectly from the cube-root dependence of R_{calcd} upon D_{dd}, so that $|\delta R_{\text{calcd}}/R_{\text{calcd}}| \approx {}^1/_3|\delta D_{\text{dd}}/D_{\text{dd}}|$. Furthermore, D_{pseudo} is typically an order of magnitude or two smaller than D_{exptl} in systems which we would suppose to be analogous to binuclear copper *dl*-tartrate.

Structural Evidence from the Zero-Field Splitting.—Having established that the D value provides a reasonable estimate of metal–metal distances for some systems, we now proceed to examine binuclear copper *dl*-tartrate. The increased line broadening in the room-temperature spectrum of copper *dl*-tartrate as compared to vanadyl *dl*-tartrate[17] probably reflects the greater magnetic dipole–dipole interaction[17,28] of the former ($D \approx 0.06$ *vs.* 0.03 cm^{-1}). The magnetic dipole interaction between two spins is given by the equation[36]

$$D_{\text{dd}} = (3/4)g^2\beta^2\left\langle\frac{1 - 3\cos^2\theta}{r_{12}^3}\right\rangle_{\max} \qquad (7)$$

where r_{12} is the interelectronic distance and θ is the angle between the r_{12} direction and the magnetic field direction. For a point dipole model with each electron located on a copper nucleus, eq 7 becomes

$$R_{\text{calcd}} = (0.650g_{\parallel}^2/D_{\text{dd}})^{1/3} \qquad (8)$$

where R_{calcd} is the copper–copper distance. Using the experimental D values of 0.0572 and 0.0605 cm^{-1} from the "full-field" and "half-field" lines, respectively, we calculate R_{calcd} = 3.85 and 3.78 Å. Of course, these distances are only approximate but they do suggest a structure quite similar to that of the vanadyl *dl*-tartrate dimer (V–V distance 4.08 Å).

The proposed structure of copper *dl*-tartrate dimer is shown in Figure 10; it consists of two Cu^{2+} ions bridged by one *d*- and one *l*-tartrate(4−) anion with chelating oxygens in a *cis* arrangement about the five-coordinate metal ion in a manner analogous to the vanadyl system. We have replaced the vanadyl group (VO) with an aquocopper group, $Cu \cdot H_2O$, since a number of other copper binuclear complexes are known to be five-coordinate.[37–40] In the vanadyl structure the vanadium atom lies ~ 0.55 Å above the plane of the chelating tartrate oxygen atoms, but in the case of copper complexes distances of 0.10–0.30 Å above the plane[37–42] are generally found. Assuming the Cu^{2+} ion lies 0.25 Å above the plane with the same ligand framework as vanadyl *dl*-tartrate, we predict a Cu–Cu distance of 3.4 Å, which is lower than the value of R_{calcd} = 3.8 Å obtained from the point dipole calculation. However, the ground-state orbitals of Cu^{2+} complexes (unlike typical vanadyl complexes) involve considerable covalency; a rough accounting for covalency in the dipole calculation as described previously[17] would probably reduce R_{calcd} to about 3.3 Å, in agreement with the molecular model. (Unfortunately, the same effect causes R_{calcd} for the copper adenine complexes to be somewhat smaller than an experimental value of R; see Table II.)

Hyperfine and Forbidden-Line Clues to Structure.—The "forbidden" $\Delta M_s = 2$ transitions arise when the magnetic field direction does not coincide with a symmetry axis.[29] We observe in the half-field lines a hyperfine splitting which is 3.5 G greater than that of the full-field parallel lines (81.8 *vs.* 78.3 G). Since $A > B$, this difference immediately suggests that the principal axes of the **g** and **A** tensors are not coincident. However, the interpretation is complicated by noncoincidence of the principal axes of the **D** tensor with those of **A** and **g**. A similar 3-G difference was noted for vanadyl *dl*-tartrate, which is known to have nonaxial symmetry[16] (*i.e.*, the V—V and V=O directions differ by 28°), whereas vanadyl *d*-tartrate with approximate axial symmetry (deviation less than 3°)[15] exhibited normal behavior. This further demonstrates the similarity in structure between the binuclear copper and vanadyl *dl*-tartrates.

It is clear that *accurate* hyperfine and zero-field splitting parameters cannot safely be extracted from these spectra without an analysis of considerable (possibly unwarranted) sophistication, including a theoretical duplication of the frozen-solution spectra with general noncoincident axes for all of the magnetic interaction parameters. The epr work on the vanadyl tartrates and the results given here suggest that the error in the derived epr parameters under the axial symmetry approximation is not very large.

Stereochemistry.—Tapscott, Belford, and Paul[12] have proposed on the basis of stereochemical arguments that the stabilities of tartrato(4−)-bridged binuclear complexes should have the ordering *dl* > *dd* = *ll* > *meso,meso* when the coordination of the tartrate oxygen atoms about the metal ion is square planar. Our observation of a binuclear copper complex with only racemic tartrate is in agreement with this prediction.

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We intend to investigate these systems in more detail and in particular to study the crystal structures and magnetic susceptibilities of $Na_2Cu\text{-}dl\text{-}C_4O_6H_2 \cdot 5H_2O$, $Cu\text{-}dl\text{-}C_4O_6H_4 \cdot 3H_2O$, and $Cu\text{-}meso\text{-}C_4O_6H_4 \cdot 1.75H_2O$.

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O-Trialkylstannyl Oximes

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Fourth-group oximes have been synthesized from (a) the organoelement chlorides and the oxime in the presence of a strong Lewis base, (b) organotin chlorides with the O-lithio oxime to split out lithium chloride, and (c) bis(organotin) oxides and organotin hydroxides, ethoxides, and diethylamines with the oxime to split out water, ethanol, and diethylamine, respectively. The products are monomeric in solution; all are liquids except O-trimethylstannylcyclohexanone oxime whose ir spectrum differs from that in solution and whose mass spectrum shows peaks above the parent mass which are revealed by high-resolution work to contain the Sn–O–Sn backbone, presumably resulting from cyclic Sn–O–Sn–O structures in the solid. Confirmation of the high-coordination solid state structure comes from Sn^{119m} Mössbauer quadrupole splitting values which are *ca.* 1 mm/sec higher for the trimethyltin derivatives. The O-trialkyltin oximes undergo metathetical reactions with water and hydrogen chloride and with other fourth group chlorides to give the silicon and germanium analogs, and insertion reactions with isocyanates, isothiocyanates, chloral, bromal, etc., to give novel adducts where reactivity is seen to be in the orders Sn > Ge ≫ Si and $SnOR > SnON{=}C{<}$ and $X_3CCHO > C_6H_5NCO > RNCO > C_6H_5NCS$.

The O–group III derivatives of acetoxime are all dimers in benzene, with the dimethylboron compound somewhat dissociated. In the vapor the dimethylboron oxime is a monomer, while the other dimethyl derivatives retain their dimeric character. Six-membered "BONBON"-type ring structures seem likely for these compounds, although the evidence does not allow the four-membered "BOBO" structures to be ruled out.[1] The methylzinc derivative of acetoxime is a tetramer in which zinc atoms in a six-membered "ZnONZnON" achieve four-coordination by binding two such rings into a cage structure.[2]

In tin chemistry there is precedent for the four-membered SnOSnO ring structure in the stannoxanes,[3] and adducts with nitrogenous ligands are easily formed as well. Thus it seemed of interest in investigating the oxime derivatives of the fourth group to concentrate on the organotin oximes in order to take advantage of the more powerful Lewis acidity of tin and also to be able to bring to bear additional evidence from nmr, ir, and Sn^{119m} Mössbauer spectroscopies. Because Lewis acids are known to catalyze the rearrangement of oximes to amides,[4] cyclohexanone oxime was chosen to ensure that all of the group IV derivatives would have the $R_3MO\text{-}N{=}C{<}$ structure.

Discussion

The organotin cyclohexanone oxime derivatives reported here were prepared by the five routes

$$\begin{tikzcd} n\text{-}C_4H_9Li + HON{=}C_6H_{10} \arrow[r, "\text{ether–petroleum ether}", "{-10^\circ,\ -C_4H_{10}}"'] & LiON{=}C_6H_{10} \quad (1) \arrow[d, "-LiCl"', "R_3SnCl"] \\ & R_3SnON{=}C_6H_{10} \end{tikzcd}$$

$$0.5(R_3Sn)_2O + HON{=}C_6H_{10} \xrightarrow{-0.5H_2O} R_3SnON{=}C_6H_{10} \quad (2)$$

$$R_3SnOH + HON{=}C_6H_{10} \xrightarrow[-H_2O]{\text{benzene}} R_3SnON{=}C_6H_{10} \quad (3)$$

$$R_3SnOC_2H_5 + HON{=}C_6H_{10} \xrightarrow{-C_2H_5OH} R_3SnON{=}C_6H_{10} \quad (4)$$

$$R_3SnN(C_2H_5)_2 + HON{=}C_6H_{10} \xrightarrow{-HN(C_2H_5)_2} R_3SnON{=}C_6H_{10} \quad (5)$$

Unlike the third group element and zinc alkyls which react directly with acetoxime to liberate methane and generate the oxime derivative,[1,2] tetraphenyltin pyrolyzes when heated at 190° with cyclohexanone oxime. Other fourth-group oximes were prepared in the presence of a strong Lewis base

$$R_3MCl + HON{=}C_6H_{10} \xrightarrow{(C_2H_5)_3N} R_3MON{=}C_6H_{10} + (C_2H_5)_3NHCl \quad (6)$$

where $R = CH_3$ and $M = Si, Ge$.

The trialkyl fourth-group cyclohexanone oxime derivatives are sensitive to hydrolysis except for the trimethylsilyl derivative which is air stable. They are colorless, mobile liquids except the trimethyltin derivative which is a solid. All of the compounds studied are monomeric in dilute benzene (osmometry) at ambient temperatures, and this is reflected in the infrared and nmr data. The absorption assigned to $\nu(C{=}N)$ is at 1665 cm^{-1} in cyclohexanone oxime. In the group III series, the frequency of this band in the free oxime is lowered by *ca.* 30 cm^{-1} in the partially associated

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