the c axis with axial ratios of 2.3 and 1.8, respectively. In a refinement in which the weights of the reflections which had been modified by the twin factor were reduced by a factor of 2, these axial ratios both changed to 1.9. Thus the thermal parameters are at least not drastically sensitive to the twin factor correction, but this and the approximate absorption corrections are possible sources of systematic errors and the standard deviations should be regarded as minimal.

In view of the low scattering power of the lithium atom efforts were made to establish its position more conclusively. Structure (3), with lithium in a tetrahedral site of space group $P3m1$ gave $R = 0.104$ and $R_w = 0.136$. Refinement of this structure increased the lithium (isotropic) B to 43.8 Å^2 in three cycles showing conclusively that this site was incorrect. Refinement with no lithium in the structure converged with $R = 0.083$ and $R_w = 0.103$. The structure with lithium in the octahedral site is thus preferable at better than the 0.005 significance level. Structure (2) in which the atoms are essentially in the same positions as structure (1) but with small deviations resulting in a noncentrosymmetric arrangement was tested by refinement in the space group $P3m1$. Changes in positional parameters were all less than 1.5σ indicating that the space group is $P\bar{3}m1$ within experimental error, although, as in any structure, small deviations to lower symmetry may exist below this level.

Discussion

Our samples were prepared at higher temperatures and under different conditions from those used by Sergent and Prigent. There is a possibility that we may have obtained a different high-temperature form of $LiCrS_2$, but we feel that our material and theirs are of the same phase. First, the X-ray patterns of slowly cooled powders and single crystals were identical and there was no sign of a crystallographic change. The possibility of cubic indexing of the powder pattern arises from the fact that the c/a ratio is almost exactly $\sqrt{3}$. Second, the molar susceptibility of a powder sample at 4.5°K was 8×10^{-3}, which agrees well with a value extrapolated from high temperatures as measured by Sergent and Colin.[10]

The structure found for $LiCrS_2$ is derived from that of the NiAs type by an ordering of the lithium and chromium atoms in the octahedral sites. The strong tendency of chromium to occupy octahedral sites is well known, while in different structures lithium occupies either octahedral or tetrahedral sites. The interatomic distances found are as follows: Cr–S, 2.415 (3) Å; Li–S, 2.597 (4) Å; Li–Cr, 3.010 Å. The ionic radii for Li^+ and Cr^{3+} are 0.60 and 0.64 Å, respectively, while the corresponding metallic radii are 1.58 and 1.29 Å.[11] Since the Li–S distance is 0.18 Å greater than the Cr–S distance, some degree of metallic character is indicated. However, from the fact that the Li–Cr distance is 0.14 Å greater than the sum of the metallic radii, it appears that there is no direct interaction between these two atoms. This is in agreement with the high resistivity measured for $LiCrS_2$.[10]

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Circular Dichroism of Alkaline Copper(II) *d*-Tartrate Complexes

BY RICHARD S. TREPTOW

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Circular dichroism and anomalous rotatory dispersion, phenomena jointly known as the "Cotton effect," were first discovered in alkaline solutions of copper *d*-tartrate.[1] However, no systematic circular dichroism investigation of these solutions has previously been made. A wide variety of alkaline copper *d*-tartrate complexes have been proposed as the result of investigations by potentiometry,[2–6] optical rotation,[2–4] visible spectroscopy,[7] and esr.[8]

Because of its high stereochemical specificity circular dichroism has been previously found to have utility in elucidating the structure of copper complexes of amino acids[9] and dipeptides.[10] In this note three alkaline copper *d*-tartrate complexes have been verified and characterized by circular dichroism. From their diverse Cotton effect behavior deductions are made concerning the modes of chelation involved.

Experimental Section

All chemicals were reagent grade and were used as received. Solutions for optical measurements were prepared from standardized $Cu(ClO_4)_2$ and *d*-tartaric acid solutions with final pH levels adjusted by NaOH addition.

CD measurements in the 200–650-nm range were made on a Durrum JASCO ORD/UV/5 dichrograph and in the 650–1000-nm range on a Shimadzu QV-50 instrument. A Cary Model 15 spectrophotometer was employed for the absorption spectra. Values of ϵ and $\Delta\epsilon$ were calculated by the standard definitions and are based on the concentration of Cu(II).

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Results and Discussion

Potentiometric and polarimetric base titrations of 2:1 copper–*d*-tartaric acid solutions give an end point at pH 9.8 corresponding to 5 mol of base/mol of acid.[3] In concentrated 1:1 solutions an end point has been similarly detected at pH 12 with addition of 4 mol of base.[2,4,5] In order to demonstrate the existence of unique complexes at these end points, continuous variations plots[11] were constructed at appropriate pH and concentration levels (Figures 1A and 1B). The plots are based on circular dichroism measurements in the visible region and reveal both positive and negative Cotton effects in the copper(II) band. Maxima are indicated at 2:1 and 1:1 ratios for pH 9.8 and 12.0, respectively. The 2:1 maximum was found to be independent of C_T, the total copper plus ligand concentration, while the 1:1 maximum occurs only at high concentrations suggesting polymeric species. The titration results may now be formulated stoichiometrically by the equations

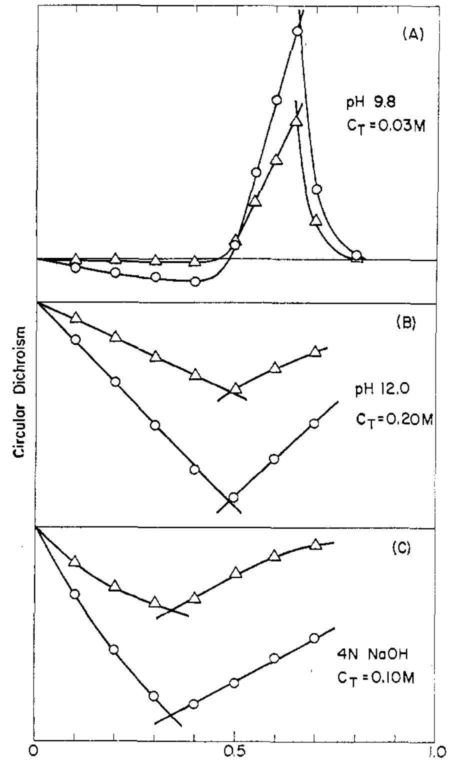

Figure 1.—Circular dichroism continuous variations plots of $Cu(ClO_4)_2$ and *d*-tartrate. Measurements were taken at 570 (Δ) and 650 nm (O).

$$2Cu^{2+} + H_4T + 5OH^- \longrightarrow Cu_2TOH^- + 4H_2O$$

$$Cu^{2+} + H_4T + 4OH^- \longrightarrow CuT^{2-} + 4H_2O$$

where T^{4-} represents the tetranegative *d*-tartrate ion resulting from ionization of all carboxyl and hydroxyl groups. A crystalline solid analog of CuT^{2-} is known, $Na_2[Cu(C_4H_2O_6)]\cdot 2H_2O$.[12] In the case of Cu_2TOH^- only the protonated form, $Cu_2C_4H_2O_6\cdot 2H_2O$, has been isolated.[13]

A 1:2 complex has also been demonstrated by the continuous variations method in 4 *N* NaOH (Figure 1C). Stoichiometry in OH^- cannot be determined by titration in this case. As has been done previously,[5] we have formulated the complex CuT_2^{6-} on the basis of the solid $Na_6[Cu(C_4H_2O_6)_2]\cdot 13H_2O$ which is obtained from such basic solutions.[12]

To characterize the complexes further, complete CD and absorption spectra were run on solutions known predominantly to contain each of the three complexes (Figure 2 and Table I). In the case of CuT_2^{6-} an excess of ligand is required to compensate for the dissociation indicated by the deviation from linearity in the continuous variations plot. The visible absorption spectra contain single, unresolved d–d transition bands typical of Cu(II) complexes. The CD spectra, on the other hand, reveal some unusual features which are subject to greater interpretation.

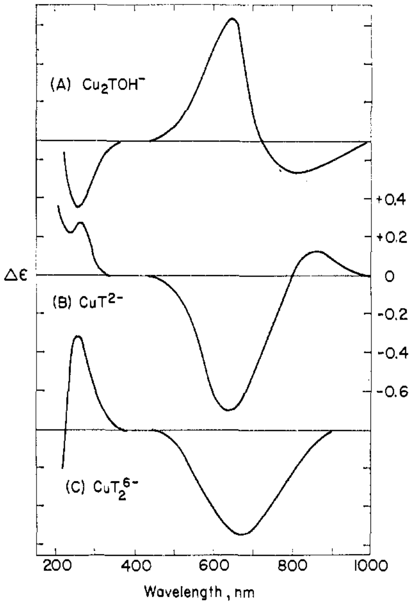

Figure 2.—Circular dichroism spectra of alkaline copper *d*-tartrate solutions with predominant complex indicated. Scale at right pertains to all three spectra; in the 200–400-nm region Δε/10 is plotted. Solution compositions are those listed in Table I.

TABLE I

VISIBLE ABSORPTION BANDS OF ALKALINE COPPER *d*-TARTRATE SOLUTIONS

	Predominant complex	Concn, *M* Cu-$(ClO_4)_2$	Concn, *M* *d*-Tartrate	pH	λ_{max}, nm	ϵ_{max}
A	Cu_2TOH^-	0.02	0.01	9.8	667	39
B	CuT^{2-}	0.1	0.1	12.0	679	30
C	CuT_2^{6-}	0.05	0.25	4 *N* NaOH	638	29

For both the d–d and the charge-transfer bands at higher energy, Cu_2TOH^- has a CD spectrum which is nearly a perfect inversion of that of CuT^{2-}. The spectrum of CuT_2^{6-} is unlike either of the above although it

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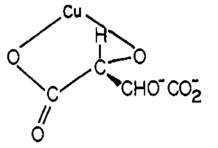
more closely resembles that of CuT^{2-}. Such diverse CD behavior for the copper complexes of a single ligand is without precedent and undoubtedly can be attributed to the many chelation modes available to *d*-tartrate.

The unique feature of this ligand is its two hydroxyl groups capable of deprotonating and binding to the metal ion. That such deprotonation and metal binding does occur is supported by the fact that basic solutions of copper(II) succinate or malate do not contain complexes analogous to the alkaline copper(II) tartrates. Of the various proposed modes of chelation,[4,5,8,12] three can be shown possible by the molecular models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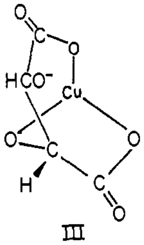
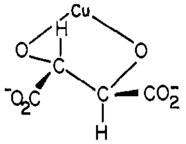

III


II

The circular dichroism characteristics of each chelate mode can be predicted from correlations with known copper(II) complexes of optically active amino acids,[9,14] peptides,[10,15] and diamines.[16] The correlations are concerned with the sign and magnitude of the predominant d–d band occurring at 600–700 nm for the present complexes. Because of their empiric nature no theoretical model for optical activity need be assumed.[9,15,17] Chelate mode I can be expected to display a prominent positive CD band since it is structurally related to the common copper(II) chelates of simple L-amino acids but is of opposite absolute configuration. Similarly, III is enantiomerically related to the tridentate L-histidine complexes; it is predicted to display a negative CD band of greater magnitude than the bidentate structures.[9] A negative band can be expected for II on the basis of its correlation with L-amino acid or *d*-propylenediamine chelates.

Chelate mode I enables a bridging *d*-tartrate ion to bind two copper ions equivalently with a positive visible-region CD band resulting. In keeping with its observed spectrum Cu_2TOH^- is assigned this structure. Apparently one coordinated water molecule of the complex is deprotonated; the position of this bound OH^- cannot be determined from the present data. Molecular models indicate it may form a second bridge between the two copper ions. With chelate mode II a single copper ion can be bound by two *d*-tartrate ions in a square-planar fashion. A negative CD band should result. Based on its CD behavior CuT_2^{6-} is assigned this tetracoordinate structure. A more difficult situation arises in the case of CuT^{2-} since the continuous variations and other results[5-8] imply a polynuclear complex. Its negative CD band indicates either chelate mode II or III. The intensity, however, is less than expected for tridentate chelation. Therefore, the structure proposed is one employing mode II with the carboxylate groups forming the bridges for polymerization.

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Observations on Some Cobalt(III) Complexes with Aminopolycarboxylic Acids and Nitrite Ion

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Earlier studies of the complexes formed by ethylenediaminetetraacetic acid (EDTA)[1] and similar potentially sexadentate ligands (*e.g.*, propylenediaminetetraacetic (PDTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA), and hydroxyethylethylenediaminetriacetic acid (HOEDTA)) with cobalt(III) have shown that the ligands can occupy five or six coordination sites of the metal ion.[2-12] Thus, complexes of the types CoY^- and $Co(HY)X^-$, where Y^{4-} denotes the full ligand anion, HY^{3-} the monoprotonated anion, and X a monodentate ligand (H_2O, OH^-, Cl^-, Br^-, NO_2^-) have been identified in aqueous solution and several have been isolated. For $X^- = NO_2^-$, pentadentate complexes $Co(HY)NO_2^-$ and $Co(Y)NO_2^{2-}$ have been isolated for EDTA, PDTA, and HOEDTA and studied in solution by infrared and spectrophotometric methods.[2-5,7-10] Their general method of preparation[2] is *via* the oxidation of the corresponding Co(II) complex with nitrous acid. $Co(HEDTA)NO_2^-$ has also been obtained by treating sodium cobaltinitrite (Na_3Co-

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