[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Six-coördinate Copper(II)[1]

BY STANLEY KIRSCHNER

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Evidence is offered for the existence of six-covalent copper(II) in its ethylenediaminetetraacetato and diaspartato complexes. Studies of the infrared spectra of these and related compounds indicate that all of the nitrogens and carboxyl groups are coördinated to the metal ion in both substances. A rotatory dispersion study of potassium ethylenediaminetetraacetatocuprate(II) in an aqueous solution of *levo*-quinine hydrobromide indicates that the complex anion is optically active, which is expected on the basis of the octahedral structure proposed for it.

Introduction

Interest recently has been aroused[2-4] in the possibility that, under certain conditions, the coördination number of the copper(II) ion may be greater than four. Earlier reports[5-8] of hexacovalent copper(II) have appeared, but well-defined evidence for the existence of six covalent or partially covalent bonds to the metal ion has been lacking.

Rosenblatt[7] postulated that $[Cu(en)_2(H_2O)_2]^{++}$[9] can exist in aqueous solution. Because the *cis* isomer of this material, supposedly containing six-covalent copper(II), is expected to be optically active, Wahl[10] attempted to resolve the compound and reported a successful resolution in 1927. However, Johnston and Bryant[11] were unable to repeat this work, so that verification of the existence of six-coördinate copper(II) in this complex is still lacking.

Jonassen and his co-workers[2] have presented convincing spectrophotometric evidence for the $[Cu(en)_2OH]^+$ ion in basic solution, and Basolo and his co-workers[3] have proposed that $[Cu(H_2O)_6]^{++}$ may exist in aqueous solutions of copper(II) salts—both compounds exhibiting copper(II) with a coordination number greater than four. In addition, Laitinen and his co-workers[12] have presented evidence, based on stability constants, for six-coördinate copper(II) in the bis-(diethylenetriamine) complex, although Martell and Calvin[13] feel that the stability constant of this material is not what would be expected for a six-covalent copper(II) complex. Keefer[14] and Riley and Gallafent[15] have presented polarographic and potentiometric evidence for the existence of the complex $[Cu(gly)_3]^-$ in aqueous solution, but did not investigate the coordination number of copper ion in this anion.

Davies and Dwyer[4] attempted to resolve the $[Cu(dipy)_3]^{++}$ and $[Cu(o\text{-phen})_3]^{++}$ ions, which were prepared by Jaeger and van Dijk,[6] but were unsuccessful. However, they[4] presented evidence to show that the ions are optically active, in that they enhance the optical rotation of ammonium *d*-bromocamphor-π-sulfonate in aqueous solution. This effect has been noted for other racemic complexes by Pfeiffer and Quehl[16] and has been attributed[4,17,18] to a shift in the equilibrium, $[d\text{-(complex)}]^{++} \rightleftarrows [l\text{-(complex)}]^{++}$, due to the different effects of the optically active anion on the activities of the complex cations in equilibrium. Davies and Dwyer[4] utilized the time required by the cation mixture to attain maximum rotation after the addition of an optically active anion as an indication of the possibility of resolution. The tris-(*o*-phenanthroline)-nickel(II) complex requires several days to reach maximum rotation and can be resolved into its optical enantiomers, but the copper(II) complexes show the effect practically instantaneously, indicating optical lability with little possibility of resolution.

Discussion

It is the purpose of this investigation to demonstrate that the copper(II) ion may have a coördination number of six. Complex inorganic compounds containing copper-(II) were prepared with ligands which would be expected to favor six-coördination. Two of these are potassium ethylenediaminetetraacetatocuprate(II), $K_2[Cu(edta)]$ (I) (ethylenediaminetetraacetate anion can be hexadentate, according to Busch and Bailar[19]), and potassium diaspartatocuprate(II), $K_2[Cu(asp)_2]$ (IV), the ligands of each of which easily can be oriented octahedrally about a metal ion, even if the tendency toward six-coördination on the part of the metal ion is not extremely strong (see Fig. 1).

Infrared Studies. 1. Ethylenediaminetetraacetate Complexes.—The infrared spectra of the crystalline complexes in mineral oil mulls and in

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(2) H. B. Jonassen, R. E. Reeves and L. Segal, THIS JOURNAL, **77**, 2748 (1955).

(3) F. Basolo, Y. T. Chen and R. K. Murmann, THIS JOURNAL, **76**, 956 (1954).

(4) N. R. Davies and F. P. Dwyer, *J. Proc. Roy. Soc. N.S.W.*, **86**, 64 (1954).

(5) P. Pfeiffer and K. Pimmer, *Z. anorg. Chem.*, **48,** 98 (1905).

(6) J. M. Jaeger and J. A. van Dijk, *Proc. Koninkl. Akad. Amsterdam*, **37**, 395 (1934).

(7) F. Rosenblatt, *Z. anorg. Chem.*, **204**, 351 (1932).

(8) G. Peyronel, *Gazz. chim. ital.*, **71**, 363 (1941); G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1259 (1927); F. G. Mann, *ibid.*, 466 (1934); J. C. Breckenridge, *Can. J. Research*, **26B**, 11 (1948); J. V. Dubsky and J. Trtilek, *J. prakt. Chem.*, **140**, 47 (1934); P. Pfeiffer, H. Simons and E. Schmitz, *Z. anorg. Chem.*, **256,** 318 (1948).

(9) The coördinating agents are designated as follows: en = ethylenediamine, dipy = 2,2′-dipyridyl, *o*-phen = *o*-phenanthroline, edta = ethylenediaminetetraacetate anion, gly = glycinate anion, asp = racemic aspartate anion.

(10) W. Wahl, *Soc. Sci. Fennica*, **4,** (14), 1 (1927).

(11) C. H. Johnston and S. A. Bryant, *J. Chem. Soc.*, 1783 (1934).

(12) H. Laitinen, E. Onstott, J. Bailar, Jr., and S. Swann, THIS JOURNAL, **71**, 1550 (1949).

(13) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 285–286.

(14) R. M. Keefer, THIS JOURNAL, **68**, 2329 (1946).

(15) H. L. Riley and V. Gallafent, *J. Chem. Soc.*, 2029 (1931).

(16) P. Pfeiffer and K. Quehl, *Ber.*, **65**, 560; **66**, 415 (1932).

(17) E. E. Turner and M. H. Harris, *Quart. Rev.*, **1**, 299 (1947).

(18) F. P. Dwyer, E. C. Gyarfas and M. F. O'Dwyer, *Nature*, **167**, 1036 (1951).

(19) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953).

potassium bromide disks[20] were studied. The infrared spectrum of I was compared with that of dihydrogen ethylenediaminetetraacetatocopper(II), [Cu(H_2edta)] (II), in which two carboxyl groups of the ligand are protected from coördination by being bound to protons. The ligand of II is therefore tetradentate—and this is evidenced by an infrared absorption peak at 1718 cm.$^{-1}$ (indicating uncoördinated carboxyls) as well as a peak of similar intensity at 1615 cm.$^{-1}$ (indicating coördinated carboxylate groups). It is expected that there should be two uncoördinated carboxyl groups and two coördinated carboxylate groups in this compound, and the approximately equal intensities of the observed absorption peaks are in conformity with this expectation.

The spectrum of the free acid, H_2edta (III), shows only one absorption peak in the carboxyl region, that at 1700 cm.$^{-1}$ indicating free carboxyl groups only, whereas the spectrum for I, the ligand of which differs from II in the absence of the two protecting protons, shows only one carbonyl peak, that at 1615 cm.$^{-1}$. The band in the 1700 cm.$^{-1}$ region has completely disappeared in I, indicating the absence of uncoördinated carboxyl groups. The sharp peak at 1615 cm.$^{-1}$ indicates that all of the carboxylate groups are similar (coördinated) which supports the proposed existence of six-coördinate copper(II) in this compound. As expected[19] the carbonyl peak of the carboxyl groups is shifted toward lower frequencies upon coördination. This most probably is due to greater electron localization in the coördinated carbonyl groups than in the carbonyls of the uncoördinated carboxyl groups of the free acid (or even of the uncoördinated carboxylate groups of the disodium salt[21a]).

In addition, the carbonyl peak due to the free carboxyl groups of II is shifted toward a higher frequency than that of the carboxyl groups of the free acid. This is indicative of an expected[19] reduction of intramolecular hydrogen bonding in the complex, since all of the carboxyl groups are no longer so favorably oriented for this type of bonding in II as they are in the free acid.

The nitrogens remain coördinated to the metal ion in all of these copper(II) complexes, as evidenced by the peak of medium intensity at 1112 cm.$^{-1}$ which is present in the spectra of both I and II.[21b] It is not expected that the nitrogens would be uncoördinated in I, since this would result in the formation of one eleven-member and two eight-member chelate rings—not a likely situation in this case.

The possibility that one (or two) of the carboxylate groups is uncoördinated is remote, since the peak for the coördinated groups of I in the carboxylate region is sharp, indicating that all of these groups are quite similar. In addition, the infrared spectra of materials expected to contain uncoördinated as well as coördinated carboxylate groups (*e.g.*, di-(glutamato)-cuprate(II) ion) show a broad band extending over a wide range (from 1560 to 1660 cm.$^{-1}$) instead of a sharp peak in the carboxylate region, indicating that more than one kind of carboxylate group exists in such complexes.

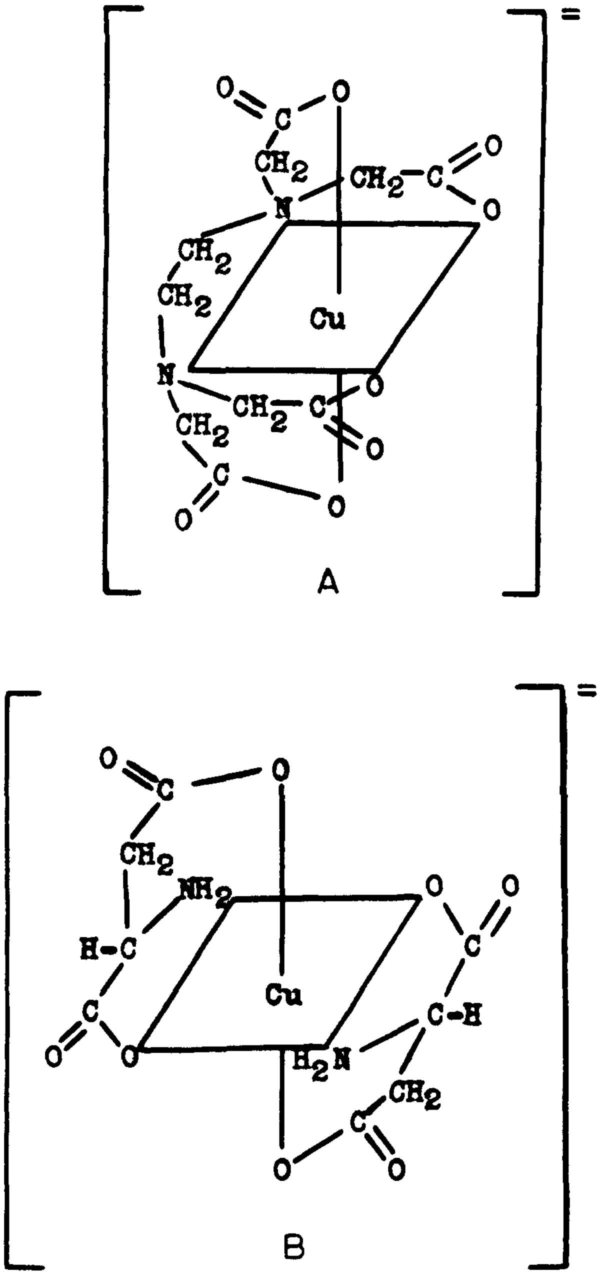

Fig. 1.—Possible orientation of ligands about the copper (II) ion: A, the ethylenediaminetetraacetatocuprate(II) anion; B, diaspartatocuprate(II) anion.

2. **Aspartate Complexes.**—The infrared spectra of potassium diaspartatocuprate(II), K_2[Cu(asp)$_2$] (IV), and bis-(monohydrogen aspartato)-copper(II), [Cu(Hasp)$_2$] (V), were also compared. The spectrum of V shows a peak at 1705 cm.$^{-1}$ indicative of free carboxyl groups and a strong peak at 1630 cm.$^{-1}$, indicative of the absorption due to the coördinated carboxylate groups[21b] as well as to the amino groups. This is expected since two of the carboxyl groups are prevented from coördination by protons, which results in the presence of both uncoördinated carboxyl and coördinated carboxylate groups.

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[20] M. M. Stimson and M. J. O'Donnell, This Journal, **74**, 1805 (1952).

[21] (a) "Sequestrene," Alrose Chemical Company, Providence, R. I., 1952, p. 4; (b) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

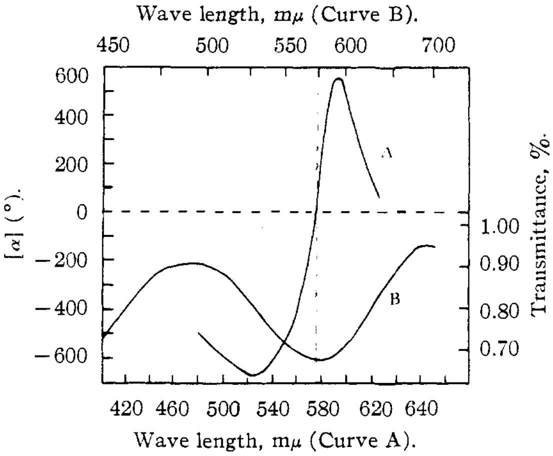

Fig. 2.—The Cotton effect: A, rotatory dispersion of $K_3[Cr(C_2O_4)_3]$; B, absorption spectrum of $K_3[Cr(C_2O_4)_3]$.

However, when the protecting protons are removed to form IV, only a single, sharp peak appears, and it is in the region of coördinated carboxylate groups (at 1620 cm.$^{-1}$) indicating that all of these groups are alike and coördinated, which is strong support for the existence of six-coördinate copper(II) in this compound. The shift of this peak to a lower frequency is indicative of the expected increase in electron localization of the carbonyl groups upon coördination, as was noted for ethylenediaminetetraacetate complexes.

In addition, the shift of the carbonyl peak indicating the free carboxyl groups of V to a higher frequency than the corresponding peak for racemic aspartic acid (VI), indicates that there is an expected[19] reduction or elimination of hydrogen bonding upon formation of V, similar to the situation found with ethylenediaminetetraacetatic acid.

Optical Rotation Studies.—The structure of a six-coördinate complex containing the ethylenediaminetetraacetate anion is expected[13] to be octahedral (see Fig. 1), and there should be an asymmetric center at the metal ion. In addition to the infrared evidence, proof of optical activity would lend additional support to the conclusion that the copper(II) ion is six-coördinate in this complex, although taken alone, this optical activity would not preclude other degrees of covalency in the material.

Davies and Dwyer[4] were unable to resolve the copper(II) complexes they studied by chemical means, and the D,L-[Cu(edta)]$^{=}$ ion used in this investigation defied resolution by adsorption on optically active powdered quartz. However, this is not unexpected,[4] since the addition of this ion to an aqueous solution of *levo*-quinine hydrobromide results in an almost immediate change in the observed rotation, indicating[4,16] that the complex is optically active but probably cannot be resolved into its enantiomers.

However, it should be shown that this observed change of rotation of the *levo*-quinine cation is actually due to the presence of an asymmetric complex anion (*i.e.*, D,L-[Cu(edta)]$^{=}$ which undergoes a shift in the equilibrium $D^{=} \rightleftarrows L^{=}$), and not to the presence of an extraneous ion (*i.e.*, a salt or solvent effect). Consequently, the experiment with *levo*-quinine hydrobromide was repeated using the dioxalatocuprate(II) anion, $[Cu(C_2O_4)_2]^{=}$, which is similar to the complex anion used, but which is not optically active, and no shift in rotation of the *levo*-quinine hydrobromide was observed.

Additional evidence to demonstrate that the change in rotation of the *levo*-quinine cation is due to the presence of an optically active complex inorganic anion is to be found in a study of the rotatory dispersions of these compounds.

Cotton[22,23] has shown that the optical rotation of a "colored" compound undergoes a marked change in direction in the region of the absorption band (whether in the visible or ultraviolet region), usually passing through zero rotation at the absorption peak. Figure 2 illustrates this behavior for an optically active enantiomer of $K_3[Cr(C_2O_4)_3]$. For "colorless" compounds, the rotatory dispersion usually follows a curve similar to that given in Fig. 3A.

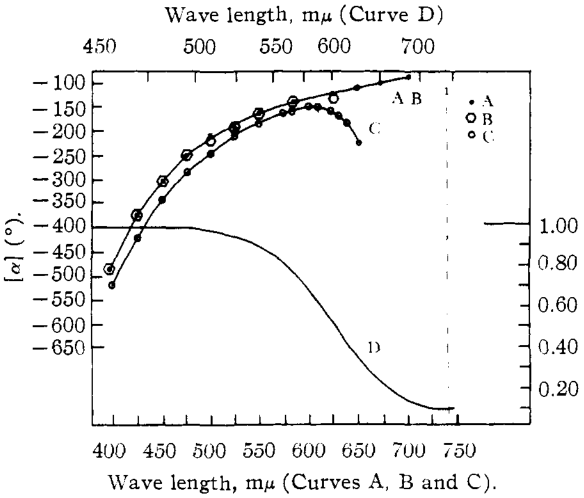

Fig. 3.—A, rotatory dispersion of *levo*-quinine hydrobromide; B, rotatory dispersion of *levo*-quinine hydrobromide and racemic $K_2[Cu(C_{10}H_{12}N_2O_8)]$ in separate polarimeter tubes in series; C, rotatory dispersion of *levo*-quinine hydrobromide in solution with racemic $K_2[Cu(C_{10}H_{12}N_2O_8)]$; D, absorption spectrum of racemic $K_2[Cu(C_{10}H_{12}N_2O_8)]$.

When two polarimeter tubes, one containing an aqueous solution of *levo*-quinine hydrobromide and the other containing racemic potassium ethylenediaminetetraacetatocuprate(II) are placed in series in a polarimeter, the rotatory dispersion curve, as expected, is found to be identical with that for the *levo*-quinine hydrobromide alone (see Figs. 3A and 3B). However, if the two solutions are mixed, not only is there an immediate change in rotation at all points of the rotatory dispersion curve (Fig. 3C), but the curve changes direction in the vicinity of the absorption band of the complex, indicating that the colored complex is itself optically active and is exhibiting the Cotton effect in the vicinity of its absorption band. This supports the conclusion that there is a shift in the equilibrium, D-[Cu-(edta)]$^{=}$ $\rightleftarrows$ L-[Cu(edta)]$^{=}$, in the

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(22) A. Cotton, *Compt. rend.*, **120**, 989, 1044 (1895).

(23) A. Cotton, *Ann. chim. phys.*, [7] **8**, 347 (1896).

asymmetric environment of *levo*-quinine hydrobromide (see Figs. 3C and 3D) and there is little question that the complex is optically active, even though the ligand itself is not.

Experimental

Reagents.—The inorganic salts, acids, and bases used were of the standard reagent or C.P. quality. The ethylenediaminetetraacetic acid was purchased from the Antara Division of the General Dyestuff Company. Calcd. for $C_{10}H_{16}N_2O_8$: C, 41.09; H, 5.54; N, 9.59. Found: C, 40.87; H, 5.45; N, 9.38. The infrared spectrum of this material is practically identical with that published in the literature.[17,19] The *levo*-quinine hydrobromide-1-hydrate was purchased from Merck and Company, and its specific rotation was determined to verify the purity of the compound. The racemic aspartic acid was purchased from the Eastman Kodak Company and was recrystallized from hot water.

Compounds.—1. **Preparation of Dihydrogen Ethylenediaminetetraacetatocopper(II)-1-hydrate, $[Cu(C_{10}H_{14}N_2O_8)]\cdot H_2O$.**—To a solution of 12.5 g. (0.05 mole) of $CuSO_4\cdot 5H_2O$ in 100 ml. water, 14.6 g. (0.05 mole) of ethylenediaminetetraacetic acid was added slowly with stirring. The mixture was warmed to 90° and stirring was continued until the acid completely dissolved. The solution was allowed to cool slowly (4 hours) to 25° during which time the inner complex $[Cu(H_2edta)]\cdot H_2O$ crystallized as minute, light blue crystals, which melt with decomposition at 242°. The product[24] was filtered and washed with two 20-ml. portions of cold water, and was dried in an oven at 80° for 24 hours. The yield was 15.5 g. (87.5%).

Anal. Calcd. for $[Cu(C_{10}H_{14}N_2O_8)]\cdot H_2O$: C, 32.30; H, 4.34; N, 7.54. Found: C, 32.20; H, 4.19; N, 8.07.

2. **Preparation of Racemic Potassium Ethylenediaminetetraacetatocuprate(II)-4-hydrate, D,L-$K_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$.**—This was prepared by a modification of the method[25] used for the sodium salt. To a slurry of 3.7 g. (0.01 mole) of $[Cu(C_{10}H_{14}N_2O_8)]\cdot H_2O$ in 10 ml. of water there was added a solution of 2.2 g. (0.04 mole) of potassium hydroxide in 10 ml. of water. Stirring was continued until the blue complex dissolved (any material which did not dissolve was filtered). The solution was then poured slowly (10 ml./minute) with vigorous stirring into one liter of absolute ethanol, and intermittent stirring was continued for 15 minutes. The finely divided blue crystals of $K_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$, which are extremely hygroscopic and which melt at 109°, were filtered and washed with two 20 ml. portions of absolute ethanol. The material was quickly placed in a vacuum desiccator and dried at room temperature under vacuum over anhydrous $CaCl_2$ for 12 hours; yield 5.0 g. (96%).

Anal. Calcd. for D,L-$K_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$: C, 23.93; H, 4.02; N, 5.58. Found: C, 24.20; H, 4.15; N, 5.60. The log $K_{\text{stab.}}$ for $[Cu(edta)]^=$ in aqueous solution is 18.38 ± 0.07, according to Schwarzenbach and Freitag.[26]

3. **Preparation of Potassium Dioxalatocuprate(II)-2-hydrate, $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$.**—This compound was prepared by a method similar to that used for the sodium salt.[27]

4. **Preparation of Bis-(monohydrogen aspartato)-copper-(II)-hemihydrate, $[Cu(C_4H_6NO_4)_2]\cdot {}^1/_2H_2O$.**—To a solution of 4.0 g. (0.02 mole) of copper(II) acetate-1-hydrate in 25 ml. of water at 75° there was added with stirring 5.4 g. (0.04 mole) of racemic aspartic acid. Stirring was continued for one minute, after which the solution was quickly filtered to remove any undissolved material. The filtrate was then poured slowly and with vigorous stirring into one liter of absolute methanol. The resulting precipitate was filtered, washed with two 25-ml. portions of absolute methanol, and dried at room temperature under vacuum for 24 hours over anhydrous phosphorus pentoxide; yield 4.9 g. (73%).

Anal. Calcd. for $[Cu(C_4H_6NO_4)_2]\cdot {}^1/_2H_2O$: C, 28.53; H, 3.89; N, 8.32. Found: C, 28.69; H, 3.86; N, 8.20.

5. **Preparation of Racemic Potassium Diaspartatocuprate(II)-1-hydrate, D,L-$K_2[Cu(C_4H_5NO_4)_2]\cdot H_2O$.**—To a slurry of 15.76 g. (0.05 mole) of barium hydroxide-8-hydrate and 5.61 g. (0.1 mole) of potassium hydroxide in 150 ml. of water, 13.3 g. (0.1 mole) of racemic aspartic acid was added with stirring. The mixture was heated to 90° and a solution of 12.5 g. (0.05 mole) of copper(II) sulfate-5-hydrate in 70 ml. of water was added with vigorous stirring. The solution was allowed to cool to room temperature (three hours) and the barium sulfate was filtered, washed, and dried. Calcd. yield of $BaSO_4$, 11.7 g.; found, 12.0 g.

The filtrate was allowed to evaporate to 70 ml. at 50° (any material which precipitated was filtered and discarded) and was then poured slowly (10 ml./min.) and with vigorous stirring into three liters of absolute ethanol. The finely divided, extremely hygroscopic blue crystals which melt at 66° were filtered after being washed by decantation with 100 ml. of absolute ethanol and were quickly transferred to a vacuum desiccator, where they were dried under vacuum for 24 hours at room temperature over anhydrous calcium chloride; yield 16.9 g. (80%).

Anal. Calcd. for D,L-$K_2[Cu(C_4H_5NO_4)_2]\cdot H_2O$: C, 22.78; H, 2.87; N, 6.64. Found: C, 23.39; H, 3.03; N, 6.74.

Instruments. 1. **Infrared Studies.**—Spectra were recorded on a Baird Associates Recording Infrared Spectrophotometer equipped with a sodium chloride prism. The samples were mulled with mineral oil or pressed into discs[20] using KBr as a diluent.

2. **Visible Absorption Studies.**—These were carried out on a Warren "Spectracord"-recording visible and ultraviolet spectrophotometric attachment used in conjunction with a Beckman DU spectrophotometer. The samples were in aqueous solution in 1 cm. cells.

3. **Optical Rotation Studies.**—Determinations of optical rotation at single wave lengths (either Na_D or Hg_{5461}) were carried out on a Rudolph High Precision Visual Polarimeter Model 80. Rotatory dispersion measurements were obtained on a Rudolph Spectrophotometric Photoelectric High Precision Polarimeter, which utilizes a Model DU Beckman spectrophotometer as a monochromator.

For the experiment in which the rotatory dispersion of *levo*-quinine hydrobromide and racemic potassium ethylenediaminetetraacetatocuprate(II) in series was determined (see Fig. 3B), the concentration of *levo*-quinine hydrobromide-1-hydrate, $C_{20}H_{22}N_2O_2\cdot HBr\cdot H_2O$, was 0.2598 g./100 ml. of water, and that of $K_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$ was 0.5332 g./100 ml. of water. The path of light through each solution was 1 dm. For the rotatory dispersion determination of the mixture of the two compounds (see Fig. 3C), the concentration of each solution was half that in the previous experiment and the light path through the solution was 2 dm.

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