TABLE IV

PROMINENT INFRARED ABSORPTIONS FROM 3100 TO 650 CM.$^{-1}$ FOR THIOACETAMIDE AND METAL HALIDE-THIOACETAMIDE DERIVATIVES

T[k,l]	T·CuCl	T·CuBr	T_4·CuCl	T_4·AgCl	Probable assignments
3050s-br	3020s-br	3080s-br	3010s-br	3070s	NH_2str.[a,b] CH_3str[a,c,d]
2900w		2895w-sh			CH_3str[a,c,e]
1640s	1653s	1628s	1610s	1623s	—NH_2 amide II[f]
1478s	1477s	1475s			—C(=S)—N[g]
1453w-sh	1458m-s	1460w-sh	1433s	1441s	CH_3—C def[c]
1390m	1403m-s	1400m	1408m-s	1374m-s	C—N?[f,h]
1357s	1368m-s	1367m-s	1368m-s	1362m-s	CH_3—C def?[c,i]
1300s	1311s	1300s	1269s	1272s	C—N?[f,h,j]
1040m	1036w	1030w		970s	
974s	772w	966s	970s	704s-br	
708s-br	737s	699s-br	671s-br	674s-br	
	688s		662w	662m	

[a] K. W. K. Kohlrausch and J. Wagner, *Z. physik. Chem.*, **45B**, 229 (1940). [b] H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand, New York, N. Y., 1949, p. 47. [c] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 13. [d] Ref. b, p. 48. [e] Ref. b, p. 49. [f] Ref. c, p. 205. [g] Ref. c, p. 350. [h] Ref. c, p. 249. [i] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **77**, 171, 526 (1956). [j] R. Mecke and R. Mecke, *Ber. deut. chem. Ges.*, **89**, 343 (1956). [k] s, strong; m, medium; w, weak; sh, shoulder; br, broad. [l] See E. Spinner, *Spectrochim. Acta*, **15**, 95 (1959).

The X-ray diffraction pattern of the white precipitate was different from that of the reactants. The most intense diffraction lines had *d* values of 9.03, 6.34, 5.24, 3.614 and 2.583 Å. The fourteen diffraction lines observed could not be indexed as a cubic, tetragonal or hexagonal unit cell. This precipitate may be a mixture.

Elemental analysis gave results most closely corresponding to an empirical formula containing one mole of thioacetamide per mole of mercuric chloride (C, 5.44; H, 0.92; N, 3.12; Hg, 61.07; Cl, 18.65; S, 8.90%). The differences between the observed and calculated percentages, corresponding to the empirical formula $C_2H_5NSHgCl_2$, were outside the limits of experimental error. This is consistent with the conclusion that the precipitate is a mixture.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN]

The Structure of Copper(II) Tartrate Trihydrate[1a]

BY STANLEY KIRSCHNER AND ROBERT KIESLING

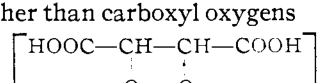
RECEIVED DECEMBER 11, 1959

Several proposed structures of copper(II) tartrate trihydrate in the solid state are discussed in the light of infrared studies of the compound. Only one of the proposed structures is fully consistent with the results of these studies.

Introduction

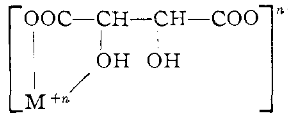
The composition and structure of copper(II) tartrate and tartrate complexes of copper have been subjects of much interest and speculation for many years.[1b–15] There is little doubt that the tartrate anion in copper(II) tartrate-3-hydrate is coördinated to the copper cation, but there has been a difference of opinion[1b,2,7,9] as to exactly how the anion is bonded to the copper and as to the location of the water molecules.

There are five principal proposals which describe the bonding of the tartrate ion in metal tartrate complexes. Various methods have been used in the study of these materials in order to verify each of the proposed structures. They include conductometric, spectrophotometric, potentiometric, *p*H and polarographic methods,[9] as well as polarimetric[15] and crystallization[1b,13] procedures. One proposed structure[1,2] for tartrate to copper bonding in copper-tartrate complexes involves coördination through the hydroxyl oxygens rather than carboxyl oxygens



$$\left[\begin{array}{c} HOOC-CH-CH-COOH \\ O\quad O \\ \diagdown\diagup \\ Cu \end{array}\right] \qquad I$$

A second proposal[12,14,15] implies that one carboxylate oxygen and one hydroxyl oxygen of the tartrate anion coördinate to a metal ion



$$\left[\begin{array}{l} OOC-CH-CH-COO \\ |\quad\ \ \ OH\ \ OH \\ M^{+n} \end{array}\right]^{n-2} \qquad II$$

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(1) (a) Presented in part before the Division of Physical and Inorganic Chemistry, 129th Meeting, American Chemical Society, Dallas, Texas, April 8–13, 1956; (b) F. Bullnheimer and E. Seitz, *Ber.*, **33**, 817 (1900); **32**, 2347 (1899).

(2) K. Jellinek and H. Gordon, *Z. physik. Chem.*, **112**, 207 (1924).

(3) E. E. Wark and I. W. Wark, *J. Chem. Soc.*, 2474 (1930).

(4) W. Traube, F. Kuhbier and W. Schroeder, *Ber.*, **69B**, 2655 (1936).

(5) J. P. Mathieu, *Comp. rend.*, **198**, 251 (1934); *Bull. soc. chim.*, (5), **1**, 1713 (1934).

(6) P. Pfeiffer, H. Simons and E. Schmitz, *Z. anorg. Chem.*, **256**, 318 (1948).

(7) P. Pfeiffer and E. Schmitz, *Pharmazie*, **4**, 451 (1949).

(8) J. B. Hakomori, *Sci. Repts. Tohoku Imp. Univ.*, **16**, 841 (1927).

(9) M. Bobtelsky and J. Jordan, THIS JOURNAL, **67**, 1824 (1945).

(10) R. N. Sen Sarma, *J. Indian Chem. Soc.*, **27**, 683, 443 (1950); *Science and Culture*, **15**, 200 (1949).

(11) M. E. Tsimbler, *Ukrain. Khim. Zhur.*, **17**, 587 (1951).

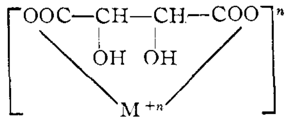
(12) A. V. Ablov and G. A. Popovich, *J. Gen. Chem. U.S.S.R.*, **24**, 975 (1954).

(13) S. U. Pickering, *J. Chem. Soc.*, **99**, 169 (1911).

(14) J. L. Delsal, *J. chim. phys.*, **35**, 314, 350 (1938).

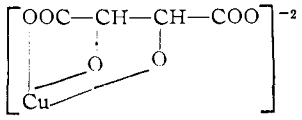
(15) Yeu Ki Heng, *ibid.*, **33**, 356 (1936).

A third proposal[14] states that a metal ion can be coördinated to the tartrate anion through the oxygens of the two carboxylate groups



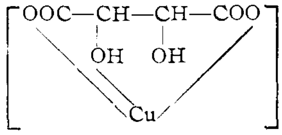
III

A fourth proposal[6,7] states that two of the hydroxyl oxygens and one of the carboxylate oxygens of the tartrate can be involved in the coördination to copper(II), resulting in a camphor-like structure with a bridge



IV

A fifth proposal[8,9] puts forth the idea that tartrate can coördinate through a hydroxyl group and two of the carboxylate groups



V

Discussion

The experimental procedures resulting in the various proposed structures described above were carried out in solution. One reason for the confusion and large number of proposals is the fact that copper(II) tartrate, which is only very slightly soluble in water, will dissolve in basic solution, thereby creating much speculation about the role of the alcoholic hydroxyl groups in copper-tartrate complexes.

A study of the infrared spectra of copper(II) tartrate trihydrate and of tartaric acid[16a] reveals something of the structure of the former compound in the solid state.

The infrared spectrum of *d*-tartaric acid shows a peak at 1750 cm.$^{-1}$ which is indicative of free carboxyl groups.[16b] It is a sharp peak indicating that both such groups are quite similar in this compound. The spectrum of copper(II) tartrate-3-hydrate, however, shows a single sharp peak at 1634 cm.$^{-1}$, which is indicative of coördinated carboxylate groups.[17,18] The sharp peak indicates that both groups are alike (coördinated carboxylate groups), and, therefore, structures I, II and IV (assuming two hydrogen ions are present to balance the negative charge in IV) are ruled out for copper(II) tartrate trihydrate in the solid state.

In addition, the spectrum of *d*-tartaric acid shows a peak at 1097 cm.$^{-1}$ indicative of a secondary alcohol group (C–O stretching)[16] whereas the spectrum of copper(II) tartrate trihydrate shows a split or double peak which has been shifted to lower frequencies (1080 and 1063 cm.$^{-1}$). The alcoholic hydroxyl groups both remain as OH groups (no loss of the protons, as evidenced by the O–H bending peak at 1450 cm.$^{-1}$ for both tartaric acid and copper(II) tartrate trihydrate), but the conversion of a single peak into a double one and the shift to lower frequencies indicate that the alcoholic hydroxyl groups are not alike in the copper compound. The coördination of an oxygen to the metal ion is expected to result in a reduction of the C–O stretching frequency, and the fact that both peaks are at a lower frequency than the corresponding single peak in tartaric acid indicates that there is an attraction between the hydroxyl groups and the copper ion. However, the split peak indicates a much stronger attraction for one hydroxyl group by the copper ion than for the second. The increase in bond order and coördination to a metal ion by the carboxylate groups are both expected to reduce the carbon–oxygen stretching frequency, which is observed.

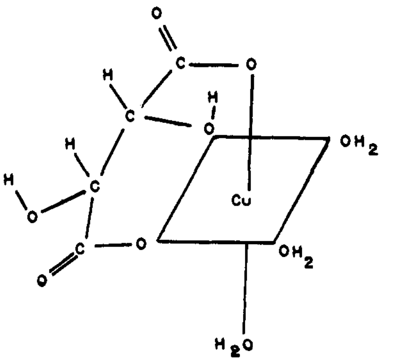


Fig. 1.—Probable structure of copper(II) tartrate trihydrate in the solid state.

Consequently, structure III is eliminated since it shows no coördination of a hydroxyl group to the metal. The elimination of this structure is not unexpected[19] since the formation of seven-membered rings is not accomplished easily.

Structure V fits the infrared data quite well and, as far as the bonding of tartrate to copper is concerned, the structure proposed by Bobtelsky and Jordan[9] holds in the solid state as well as in solution. Concerning the location of the water molecules, since it is possible for the copper(II) ion to be six-covalent in certain compounds,[18] it is quite probable that the structure of copper(II) tartrate trihydrate in the solid state is that given in Fig. 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. The technique of pressing the samples into discs[20] using anhydrous potassium bromide also was employed and the results were similar to those obtained with the mulls.

Compounds.—Copper(II) tartrate trihydrate was prepared by the addition of dilute potassium-*d*-tartrate (*ca.* 0.1 *M*) to an equimolar solution of copper(II) nitrate. Pre-

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(16) (a) These spectra have been deposited as Document number 6231 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting a check or money order for $1.25 for a photoprint or a 35 mm. microfilm; (b) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

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

(18) S. Kirschner, *ibid.*, **78**, 2372 (1956).

(19) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1952, pp. 144 ff.; L. A. Tschugaeff and E. Serbin, *Compt. rend.*, **151**, 1361 (1910).

(20) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

cipitation occurred after several minutes and the crystals were filtered after standing for one hour, washed with cold water, and air-dried at room temperature. The spectral measurements were made on relatively fresh samples, and the effects of any structure changes in the compound on standing for several months have not yet been studied.

Acknowledgment.—One of the authors (R. K.) wishes to express his appreciation to the National Science Foundation for a research fellowship grant which contributed materially to the progress of this investigation.

[CONTRIBUTION FROM THE BOSTON UNIVERSITY DEPARTMENT OF CHEMISTRY, BOSTON, MASSACHUSETTS]

The Identical Diffusion Coefficients of Isostructural Heteropoly Anions. The Complete Independence of D from Ionic Weight

BY LOUIS C. W. BAKER AND MICHAEL T. POPE[1,2]

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The "self"-diffusion coefficients of $[SiMo_{12}O_{40}]^{-4}$ and its isomorph, $[SiW_{12}O_{40}]^{-4}$, were measured at 30° by the open capillary method. These ions are very stable, virtually unsolvated, and almost spherical. Their ionic weights differ greatly. The diffusion coefficients are identical, demonstrating the complete non-validity of "Riecke's Law." Diffusion and dialysis rates are independent of molecular weight *per se*. Similar measurements were made for the isomorphs: $[CoMo_6O_{21}]^{-3}$ and $[CrMo_6O_{21}]^{-3}$. The results also test recent postulates for relating diffusion rates of polyanions to the numbers of exterior oxygen atoms available for H-bonding to the solvent. The results discourage hopes for that correlation. For polyanions and coördination complexes, even the most approximate estimations of ionic weight from diffusion data are almost completely unreliable, and chemical interpretations which have been based on such evidence should be disregarded.

A great deal of effort, especially on the part of persons interested in the chemistry of heteropoly and isopoly electrolytes, has been expended upon determining diffusion coefficients, dialysis coefficients and coefficients of electrodialysis, for the purpose of estimating ionic weights of species in solution. The results of recent researches along these lines appear in leading journals. Further, several of the most authoritative recent inorganic texts and reference works expound relationships between ionic weights and diffusion or dialysis coefficients and describe various detailed chemical interpretations which derive ultimately from "ionic weights" so determined. Although supposed difficulties in successfully relating ionic weights to diffusion or dialysis data are commonly mentioned, these works hold that (1) the ionic weight *per se* of the diffusing species is the main factor in determining diffusion and dialysis coefficients and (2) rough estimates, at least, of ionic weight may be obtained from such data.

On the other hand, the most valuable modern theories of diffusion in liquids[3-8] predict that the molecular or ionic weights will play no role whatever[9] in determining rates of diffusion. These treatments take the view that, for a given solvent, only the size and shape of the diffusing species, plus the magnitude of its interactions with adjacent particles, will affect the diffusion coefficient.

One object of the present experiments was to provide an unambiguous test of the conflicting postulates in this regard. Heretofore all the ions studied have been sufficiently dissimilar that discrepancies between observed diffusion rates and those predicted on the basis of ionic weight variation could be ascribed to a number of other factors.

This paper reports diffusion coefficients, measured in exactly comparable manner, for two pairs of isomorphous polyanions. The first pair was 12-tungstosilicate, $[SiW_{12}O_{40}]^{-4}$ (ionic weight = 2875), and 12-molybdosilicate, $[SiMo_{12}O_{40}]^{-4}$ (ionic weight = 1820). These ions are very stable under the conditions used.[10-12] They are almost spherical and virtually identical in size, structure,[13] charge and negligible degree of solvation.[14]

The results show that for these two anions the diffusion coefficients at infinite dilution are identical, within the small experimental error, despite the large difference in ionic weight. The diffusion coefficients change very little with concentration, such changes being linear in the regions studied.

The diffusion coefficients of another pair of isostructural[15] unsolvated[16] anions, 6-molybdocobaltiate and 6-molybdochromiate, were also measured in an identical manner. The results for all four ions

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[1] U. S. Atomic Energy Commission Research Associate at Boston University.

[2] St. Peter's Hall, Oxford University, England.

[3] R. H. Stokes, *Rev. Pure and Appl. Chem.*, **5**, 60 (1955).

[4] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

[5] J. Frenkel, *Z. Physik*, **36**, 652 (1926).

[6] G. S. Hartley, *Phil. Mag.*, **12**, 473 (1931).

[7] A. E. Stearn, E. M. Irish and H. Eyring, *J. Phys. Chem.*, **44**, 981 (1940).

[8] B. Ottar, "Self-Diffusion and Fluidity in Liquids," Oslo University Press, Oslo, Norway, 1958.

[9] In the course of an excellent modern treatment, Ottar[8] estimates (p. 74) that roughly 0.17×10^{-5} is the fraction of the activation energy used to accelerate the molecular mass during a molecular jump in aqueous diffusion.

[10] L. Malaprade, *Ann. Chim.*, [10], **11**, 159, 172 (1929).

[11] L. C. W. Baker, "Properties of Heteropoly Molybdates," Climax Molybdenum Co., Information Bulletin Cdb-12, New York, N. Y., 1956, p. 7.

[12] M. C. Baker, P. A. Lyons and S. J. Singer, THIS JOURNAL, **77**, 2011 (1955).

[13] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934); J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. 1, Elsevier Publishing Co., Inc., Amsterdam, the Netherlands, 1950, p. 192.

[14] T. Kurucsev, A. M. Sargeson and B. O. West, *J. Phys. Chem.*, **61**, 1569 (1957).

[15] G. A. Tsigdinos, M. T. Pope and L. C. W. Baker, THIS JOURNAL, **82**, in press (1960). See also Abstracts of Papers Presented before the Division of Inorganic Chemistry, Am. Chem. Soc. National Meeting, Boston, Massachusetts, 1959.

[16] M. T. Pope and L. C. W. Baker, *J. Phys. Chem.*, **63**, 2083 (1959).