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Structure of and Bonding in Copper Croconate and Zinc Croconate, $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$[1]

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Three-dimensional single crystal X-ray determinations of the isostructural compounds $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$ not only have established the general configuration of the first-row divalent transition metal croconates but also have revealed significant structural differences. Each compound crystallizes in the orthorhombic system with space group symmetry Pbca and with eight formula units in a unit cell of dimensions: $C_5O_5Cu(H_2O)_3$, a = 11.77 Å., b = 8.09 Å., c = 15.56 Å.; $C_5O_5Zn(H_2O)_3$, a = 11.99 Å., b = 8.16 Å., c = 15.38 Å. Anisotropic least-squares refinements have yielded final discrepancy factors of $R_1 = 9.1\%$ for copper(II) croconate and $R_1 = 9.2\%$ for zinc(II) croconate. Both complexes are one-dimensional coordination polymers with the infinite chains resulting from the bonding of each metal to two adjacent oxygens of one croconate and to a single oxygen of a second croconate such that two nonadjacent oxygens per croconate are not metal-coordinated. The oxygen environment of each six-coordinated metal is completed by the attachment of three molecules of water. A comparison of the detailed structural parameters of these homologous compounds allows a separation of the metal–oxygen distortions in $C_5O_5Cu(H_2O)_3$ due to the static Jahn–Teller effect from those due to the unsymmetrical oxygen environment of each metal. Examination of the geometries of the croconate rings in the two complexes shows that the D_{5h} symmetry of the free electron-delocalized croconate dianion is essentially retained in copper(II) croconate, whereas in zinc(II) croconate the idealized symmetry of the ring is reduced to C_{2v} such that the configuration is related to that of the localized α-enediol, croconic acid.

Introduction

Although copper(II) croconate was first reported as $Cu(C_5O_5)\cdot 3H_2O$ by Gmelin[3] in 1841, it was not until 1958 that Yamada, Mizuno, and Hirata[4] proposed a symmetric electron-delocalized structure for the croconate ion on the basis of infrared studies of the croconate salts of copper, potassium, barium, and silver. Extensive Raman and infrared studies, including a normal coordinate treatment by West and co-workers,[5] have substantiated the D_{5h} symmetry of the free croconate ion in aqueous solution. In addition, West and Niu[6] have prepared and characterized a series of divalent transition metal complexes of general formula $C_5O_5M(H_2O)_3$ (where M = Mn, Fe, Co, Ni, Cu, or Zn), which from similar X-ray powder patterns appear to be isostructural.

A three-dimensional single crystal X-ray investigation of $C_5O_5Cu(H_2O)_3$ was undertaken to determine the configuration of a typical divalent transition metal croconate in the solid state as well as to provide definite information concerning the croconate–copper interaction and its effect upon the delocalized π-bonding in the croconate ion. The subsequent structural determination of zinc(II) croconate permits an interesting comparison of the d^9 copper(II) and d^{10} zinc(II) configurations. Significant differences are shown to exist not only in the stereochemical environment about the metal atom but also in the symmetry (and thereby the electronic distribution) of the croconate dianion.

Preliminary single crystal X-ray work on the copper(II) complex has been carried out by Takehara and Yokoi.[7] Unit cell dimensions and the space group symmetry were determined, and from two-dimensional Patterson syntheses copper positions were proposed. However, their attempts to locate the carbon and oxygen atoms from two-dimensional electron density maps were unsuccessful, and our subsequent work has shown the coppers to be inaccurately placed in the unit cell.

Experimental

Crystals of $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$ were generously supplied to us by Professor West and Dr. Niu of the University of Wisconsin. The experimental densities were determined by the flotation method.

Lattice parameters for each compound were determined from $hk0$ and $0kl$ precession photographs. Multiple film equi-inclination Weissenberg photographs of reciprocal levels $h0l$ through $h9l$ yielded a total of 1356 independent intensity data for $C_5O_5Cu(H_2O)_3$. In addition, 72 reflections were obtained from timed precession photographs of the $0kl$ level. Similarly, a total of 1034 independent reflections were recorded for $C_5O_5Zn(H_2O)_3$ from the reciprocal Weissenberg levels $h0l$ through $h7l$. All X-ray data were taken with Zr-filtered Mo Kα radiation. The intensities were estimated visually by comparison with a calibrated set of intensities taken with the same crystal and then were corrected for Lorentz-polarization effects. Both of the crystals were sufficiently small (in each case μR was less than 0.5) that absorption errors were neglected.

Crystal Data

The unit cell of $C_5O_5Cu(H_2O)_3$ is orthorhombic with $a = 11.77 \pm 0.03$ Å., $b = 8.09 \pm 0.02$ Å., and $c = 15.56 \pm 0.03$ Å. These cell dimensions differ significantly from the values a = 11.48 Å., b = 7.83 Å., and c = 15.15

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[3] L. Gmelin, *Ann.*, **37**, 58 (1841).

[4] K. Yamada, N. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958).

[5] M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963); R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

[6] R. West and H. Y. Niu, *ibid.*, **85**, 2586 (1963).

[7] A. Takehara and M. Yokoi, *Shinshu Daigoku Sen Igakuba Kenkyu Hokoku*, **7**, 108 (1958).

Å. reported by Takehara and Yokoi.[7,8] For eight formula units of $C_5O_5Cu(H_2O)_3$ per unit cell, the calculated density of 2.31 g./cc. based on our lattice parameters agrees well with the measured density of 2.30 g./cc.

$C_5O_5Zn(H_2O)_3$ also crystallizes with eight formula units in an orthorhombic unit cell of dimensions a = 11.99 ± 0.03 Å., b = 8.16 ± 0.02 Å., c = 15.38 ± 0.04 Å.; $\rho_{\text{calcd}} = 2.28$ g./cc. *vs.* $\rho_{\text{obsd}} = 2.29$ g./cc. Comparison of the axial ratios $a/b = 1.455$, $c/b = 1.923$ for $C_5O_5Cu(H_2O)_3$ *vs.* the corresponding values of 1.469 and 1.885 for $C_5O_5Zn(H_2O)_3$ reveals that although these two compounds are isostructural they are not strictly isomorphous.[9]

Systematic absences for both compounds of $h = 2n + 1$ for $\{hk0\}$, $k = 2n + 1$ for $\{0kl\}$, and $l = 2n + 1$ for $\{h0l\}$ indicate the probable space group Pbca, (D_{2h}^{15}), later confirmed by the structural refinement, in agreement with that obtained by the Japanese workers[7,8] for $C_5O_5Cu(H_2O)_3$. All atoms were found to be in the eightfold set of general positions: $\pm(x, y, z; \; ^1/_2 + x, \, ^1/_2 - y, \, \bar{z}; \; \bar{x}, \, ^1/_2 + y, \, ^1/_2 - z; \; -x, y, \, ^1/_2 + z)$.[10] The asymmetric unit for each compound therefore consists of one metal, five carbons, eight oxygens, and six hydrogens, which necessitates the determination of 42 nonhydrogen positional parameters.

Solution of the Structure

A three-dimensional Patterson function of $C_5O_5Cu(H_2O)_3$ was calculated from the corrected intensity data, and its interpretation placed the asymmetric copper at $x = 0.127$, $y = 0.106$, and $z = 0.194$ in fractional coordinates. These coordinates differ considerably from those of $x = 0.15$, $y = 0.17$, and $z = 0.18$ derived by Takehara and Yokoi.[7,8]

Isotropic temperature factors of 2.0 Å.^{2} were arbitrarily estimated for the coppers, and structure factors were calculated from their positions. Least-squares refinement of the positional parameters of copper and of the scale factors yielded discrepancy factors of

$$R_1 = [\Sigma \,\big|\, |F_o| - |F_c| \,\big| / \Sigma\, |F_o|] \times 100 = 43\%$$

and

$$R_2 = [(\Sigma\, w(|F_o| - |F_c|)^2)^{1/2} / (\Sigma(\sqrt{w}F_o)^2)^{1/2}] \times 100 = 50\%$$

Since an attempt to vary the temperature factors of the coppers resulted in negative values, least-squares refinement was discontinued.

A three-dimensional Fourier map then was calculated with phases based on the coppers only. Peaks corresponding to the probable positions of the light atoms as well as to the asymmetric copper were readily discernible from the Fourier map with twelve of the fourteen peaks lying approximately in a plane perpendicular to the a axis at $x = 0.125$ and the other two peaks above and below the copper. An identification of the thirteen new nonhydrogen peaks as carbon and oxygen atoms was made on the basis of the presumed conformation and the relative peak heights.

The carbons and oxygens were assigned isotropic temperature factors of 3.0 Å.^{2}, and a least-squares refinement was attempted. Negative thermal parameters resulted, and convergence was not obtained. Fourier refinement followed by least-squares refinement with more realistic starting thermal parameters of 1.0 Å.^{2} for the light atoms did lead to convergence. After five cycles all parameter shifts were negligible, and the values of R_1 and R_2 were 13.6 and 11.1%, respectively.

Since a three-dimensional difference map revealed some thermal anisotropy, further least-squares refinement was undertaken with individual anisotropic temperature factors of the form

$$\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$$

The discrepancy factors after anisotropic refinement were $R_1 = 9.1\%$ and $R_2 = 11.3\%$.

The positions of the 14 asymmetric nonhydrogen atoms of zinc croconate were obtained from three-dimensional Patterson and electron density maps and as expected were similar to those found in copper croconate. A three-dimensional isotropic least-squares refinement in which initial thermal parameters of 1.0 Å.^{2} were assumed proceeded routinely with resulting discrepancy factors of $R_1 = 11.2\%$ and $R_2 = 12.0\%$. The zinc compound then was refined further by the anisotropic least-squares method which yielded final discrepancy factors of $R_1 = 9.2\%$ and $R_2 = 9.5\%$.[11] In order for anisotropic thermal parameters to be physically meaningful, they must form a positive-definite matrix; however, for $C_5O_5Zn(H_2O)_3$ the thermal parameters of three atoms (C_1, C_5, O_3) were slightly nonpositive-definite. The misbehavior of these thermal parameters is attributed mainly to the unusual sensitivity of thermal parameters to systematic errors in the photographic data which make it difficult to attach physical significance to any thermal analysis.

Examination of the correlation matrices obtained from the final least-squares refinements for both compounds showed the positional parameters to be essentially independent of the thermal parameters. Consistent with this observation is the fact that in the anisotropic refinement of each compound the coordinates of all atoms do not differ by more than two standard deviations from those obtained from the respective isotropic refinements. Final difference maps of both compounds showed no residual electron density greater

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(8) The following transformation has been applied to the coordinate system of Takehara and Yokoi[7] in order to clarify the relation between their results (primed) and ours (unprimed): $a = b'$, $b = c'$, $c = a'$. It should be noted that the space group Pbca is invariant to this transformation.

(9) *Cf.* A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1962, p. 186.

(10) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 150.

(11) Calculated and observed structure factors for both the copper(II) and zinc(II) croconates are deposited as Document No. 8091 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

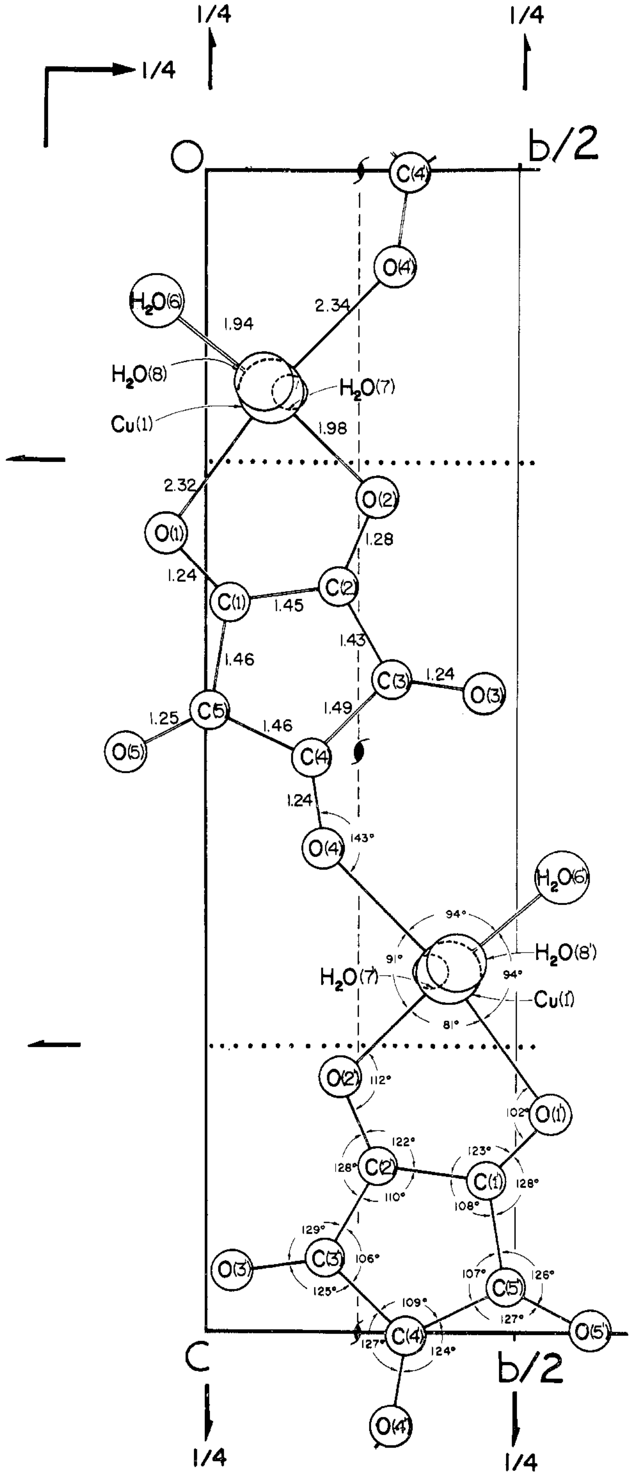

Fig. 1.—The configuration of $C_5O_5Cu(H_2O)_3$. The crystallographic repeating unit of the infinite chain located at $a/8$ is viewed down the [100] direction.

than 1.5 electrons/Å.^{3}; no peaks were assigned to the hydrogen positions.

Weights were assigned throughout according to the functions $\sqrt{w} = (2/F_o)(I_o/I_{\min})^2$ if $I_o < \sqrt{10}\, I_{\min}$ and $\sqrt{w} = 20/F_o$ if $I_o \geq \sqrt{10}\, I_{\min}$.

Carbon and oxygen atomic scattering factors were taken from Berghuis, *et al.*,[12] and atomic scattering factors for copper(II) and zinc(II) were those of Watson and Freeman.[13]

Table I

Positional Parameters with Standard Deviations from Anisotropic Least-Squares Refinements^a

	x	$10^4\sigma(x)$	y	$10^4\sigma(y)$	z	$10^4\sigma(z)$
Cu	0.1276	1	0.1059	1	0.1885	1
(Zn)	(0.1245)	(1)	(0.1193)	(2)	(0.1860)	(1)
C_1	0.1250	70	0.0400	10	0.3681	6
	(0.1120)	(10)	(0.0727)	(12)	(0.3654)	(6)
C_2	0.1324	9	0.2161	10	0.3534	5
	(0.1347)	(10)	(0.2437)	(18)	(0.3536)	(7)
C_3	0.1353	9	0.3023	10	0.4338	5
	(0.1335)	(11)	(0.3296)	(17)	(0.4380)	(6)
C_4	0.1338	9	0.1724	10	0.5018	6
	(0.1298)	(11)	(0.1924)	(15)	(0.5030)	(7)
C_5	0.1248	10	0.0110	12	0.4605	5
	(0.1254)	(10)	(0.0306)	(15)	(0.4590)	(5)
O_1	0.1169	7	−0.0626	8	0.3089	4
	(0.1169)	(8)	(−0.0259)	(12)	(0.3036)	(4)
O_2	0.1322	8	0.2787	8	0.2781	4
	(0.1353)	(10)	(0.3085)	(11)	(0.2791)	(5)
O_3	0.1307	6	0.4535	9	0.4470	4
	(0.1321)	(8)	(0.4762)	(11)	(0.4522)	(4)
O_4	0.1418	6	0.1931	9	0.5804	4
	(0.1388)	(8)	(0.2082)	(10)	(0.5851)	(5)
O_5	0.1215	8	−0.1226	8	0.4968	5
	(0.1193)	(8)	(−0.0978)	(11)	(0.4948)	(5)
O_6	0.1144	6	−0.0758	8	0.1081	4
	(0.1086)	(7)	(−0.0882)	(9)	(0.1147)	(5)
O_7	−0.0413	6	0.1334	7	0.1827	5
	(−0.0503)	(6)	(0.1586)	(9)	(0.1800)	(6)
O_8	0.3011	6	0.0967	9	0.1800	5
	(0.3042)	(7)	(0.1075)	(11)	(0.1751)	(5)

^{a} The values for $C_5O_5Cu(H_2O)_3$ are listed first followed by the corresponding values for $C_5O_5Zn(H_2O)_3$ in parentheses.

All Fourier and Patterson maps were computed on the IBM 704 with the program of Shoemaker and Sly.[14] The full matrix least-squares[15] and function and error[16] programs of Busing and Levy were used throughout the refinement of the copper(II) croconate. The anisotropic least-squares refinement and analysis of zinc(II) croconate were carried out with the Fortran versions[17,18] of the above programs in order to refine nonpositive-definite temperature factors. The least-squares refinements were based upon the weighted structure factors, and all standard deviations were calculated from a full variance–covariance matrix.[15–18]

The final anisotropic positional and thermal parameters with their standard deviations are listed in Tables I and II. The intrachain bond lengths and angles with their standard deviations are given in Tables III and IV.

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(13) R. F. Watson and A. J. Freeman, *ibid.*, **14**, 231 (1961).

(14) W. G. Sly and D. P. Shoemaker, "Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer," MIFR1 (1960).

(15) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

(16) W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," Oak Ridge National Laboratory Report 59-12-3 (1959).

(17) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Report TM-305 (1962).

(18) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory Report TM-306 (1964).

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	19 ± 1	29 ± 1	5 ± 0	1 ± 1	0 ± 1	-4 ± 1
(Zn)	(22 ± 1)	(32 ± 2)	(5 ± 0)	(-2 ± 1)	(1 ± 1)	(-4 ± 1)
C_1	33 ± 6	20 ± 11	11 ± 3	-3 ± 8	-7 ± 5	4 ± 4
	(19 ± 7)	(-1 ± 18)	(11 ± 3)	(7 ± 9)	(1 ± 6)	(3 ± 5)
C_2	24 ± 6	9 ± 10	12 ± 3	-2 ± 7	4 ± 4	9 ± 4
	(8 ± 6)	(64 ± 21)	(10 ± 4)	(14 ± 10)	(-3 ± 5)	(11 ± 7)
C_3	17 ± 6	37 ± 12	9 ± 3	-8 ± 7	-12 ± 4	-3 ± 4
	(22 ± 7)	(64 ± 22)	(5 ± 3)	(-20 ± 10)	(-10 ± 5)	(6 ± 6)
C_4	12 ± 5	58 ± 13	11 ± 2	-13 ± 8	-3 ± 4	11 ± 5
	(16 ± 7)	(59 ± 20)	(10 ± 3)	(-13 ± 13)	(0 ± 6)	(1 ± 7)
C_5	18 ± 5	73 ± 14	4 ± 2	2 ± 8	1 ± 4	8 ± 4
	(14 ± 6)	(51 ± 18)	(1 ± 3)	(-14 ± 10)	(8 ± 5)	(6 ± 6)
O_1	54 ± 6	30 ± 9	10 ± 2	-8 ± 6	-4 ± 4	-9 ± 3
	(41 ± 6)	(78 ± 16)	(6 ± 3)	(-6 ± 9)	(-8 ± 4)	(-5 ± 5)
O_2	56 ± 7	12 ± 8	6 ± 2	0 ± 6	-8 ± 4	1 ± 3
	(44 ± 7)	(40 ± 14)	(9 ± 3)	(-4 ± 10)	(-4 ± 5)	(4 ± 5)
O_3	27 ± 5	52 ± 10	10 ± 2	6 ± 6	-6 ± 4	3 ± 4
	(40 ± 6)	(37 ± 17)	(8 ± 3)	(0 ± 8)	(-3 ± 4)	(-17 ± 5)
O_4	21 ± 6	70 ± 11	6 ± 2	4 ± 6	-5 ± 3	4 ± 4
	(39 ± 7)	(36 ± 13)	(5 ± 2)	(5 ± 8)	(-2 ± 4)	(-3 ± 5)
O_5	52 ± 6	39 ± 10	21 ± 3	-3 ± 7	12 ± 4	19 ± 4
	(45 ± 6)	(41 ± 14)	(13 ± 3)	(-5 ± 9)	(5 ± 5)	(5 ± 6)
O_6	28 ± 5	49 ± 10	14 ± 2	6 ± 6	-3 ± 3	-4 ± 3
	(28 ± 7)	(33 ± 12)	(13 ± 3)	(6 ± 7)	(0 ± 4)	(-9 ± 5)
O_7	42 ± 5	6 ± 9	15 ± 2	-2 ± 5	4 ± 3	2 ± 3
	(23 ± 5)	(28 ± 13)	(12 ± 3)	(2 ± 6)	(-1 ± 4)	(-9 ± 5)
O_8	36 ± 5	60 ± 12	12 ± 3	20 ± 6	0 ± 3	-2 ± 4
	(38 ± 6)	(12 ± 12)	(18 ± 4)	(5 ± 8)	(0 ± 4)	(-3 ± 6)

TABLE III

BOND LENGTHS (Å.) WITH STANDARD DEVIATIONS FROM ANISOTROPIC LEAST-SQUARES REFINEMENTS[a]

	$C_5O_5Cu(H_2O)_3$	$C_5O_5Zn(H_2O)_3$
Cu(Zn)-O(1)	2.320 ± 0.007	2.164 ± 0.009
Cu(Zn)-O(2)	1.975 ± 0.006	2.116 ± 0.010
Cu(Zn)-O(4^I)	2.343 ± 0.007	2.103 ± 0.010
Cu(Zn)-H_2O(6)	1.938 ± 0.007	2.027 ± 0.009
Cu(Zn)-H_2O(7)	2.003 ± 0.008	2.122 ± 0.009
Cu(Zn)-H_2O(8)	2.048 ± 0.008	2.164 ± 0.010
C(1)-C(2)	1.446 ± 0.011	1.415 ± 0.018
C(2)-C(3)	1.432 ± 0.012	1.475 ± 0.016
C(3)-C(4)	1.491 ± 0.012	1.501 ± 0.016
C(4)-C(5)	1.459 ± 0.014	1.484 ± 0.017
C(5)-C(1)	1.457 ± 0.011	1.480 ± 0.013
C(1)-O(1)	1.244 ± 0.011	1.247 ± 0.013
C(2)-O(2)	1.276 ± 0.010	1.254 ± 0.012
C(3)-O(3)	1.243 ± 0.012	1.217 ± 0.017
C(4)-O(4)	1.240 ± 0.010	1.274 ± 0.012
C(5)-O(5)	1.249 ± 0.011	1.186 ± 0.014

[a] Superscript I refers to the position: $x, {}^1/_2 - y, -{}^1/_2 + z$.

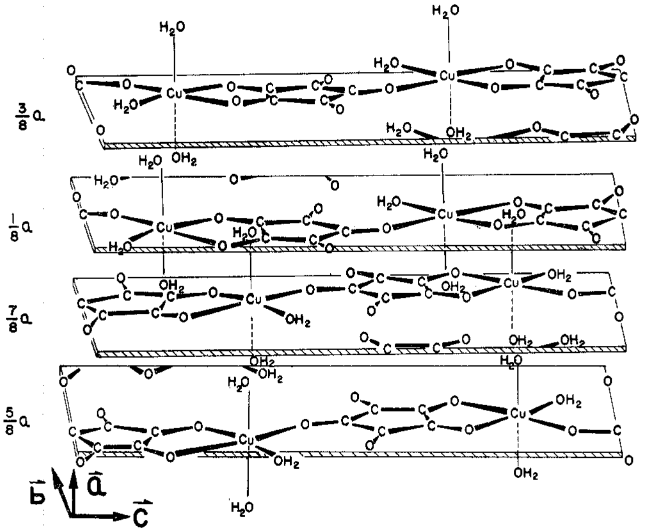

Fig. 2.—The packing of the infinite chains of $C_5O_5Cu(H_2O)_3$ in the unit cell.

Results and Discussion

General Configuration.—Copper(II) and zinc(II) croconates both consist of infinite chains with the asymmetric repeating unit composed of one metal, one croconate, and three waters (shown in Fig. 1 for $C_5O_5Cu(H_2O)_3$). The metal is surrounded by six oxygens at the corners of a distorted octahedron. Each polymeric chain results from the bonding of a metal to two croconates *via* a chelate linkage to one croconate and through an interaction with a single oxygen of a second croconate, such that only two nonadjacent oxygens per croconate are uncoordinated. The oxygen environment about each metal is completed by the coordination of the three water molecules.

The chains (shown in Fig. 2 for copper(II) croconate) are parallel to the *c*-axis, and the resulting crystallographic identity period corresponds to two $C_5O_5M(H_2O)_3$ units which are related by a c_b symmetry operation. In each asymmetric unit all nonhydrogen atoms, except for two oxygens, H_2O(7) and H_2O(8), lie approximately in planes perpendicular to the *a* axis. The chains are packed in a zigzag fashion such that each is surrounded by four others displaced by *a*/4, *b*/2, and two others located *a*/2 away.

Although the gross geometries of the two complexes are the same (as indicated by the similar powder patterns), a comparison of the detailed structural features

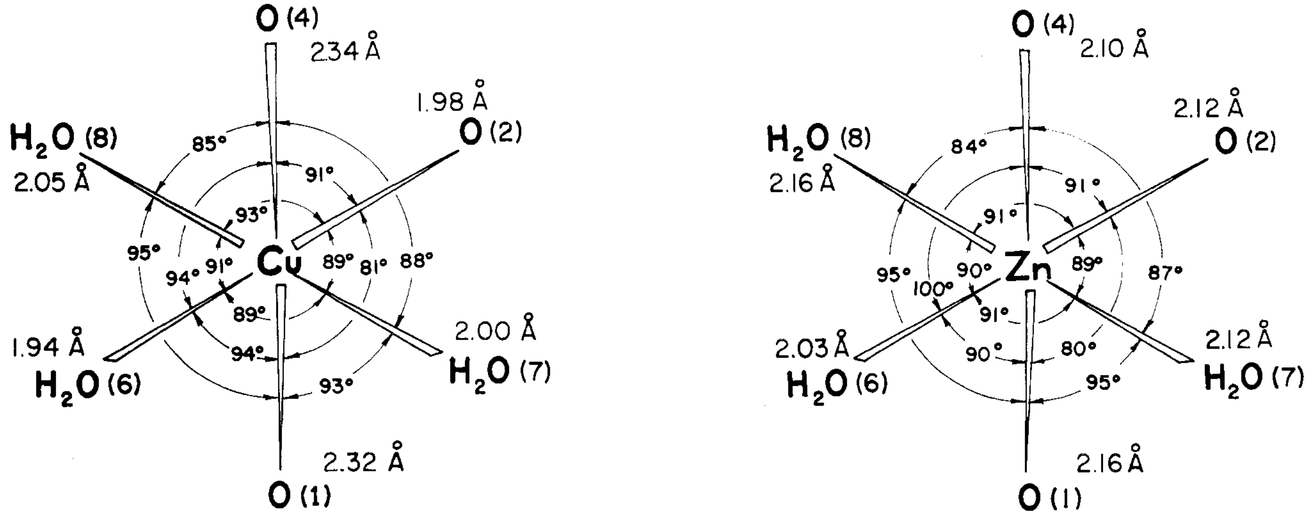

Fig. 3.—Comparison of the oxygen environments about the central metals in $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$.

Table IV

Bond Angles (degrees), with Standard Deviations[a]

	$C_5O_5Cu(H_2O)_3$	$C_5O_5Zn(H_2O)_3$
O(1)–Cu(Zn)–O(2)	81.2 ± 0.2	80.4 ± 0.3
O(1)–Cu(Zn)–H_2O(6)	94.1 ± 0.3	89.5 ± 0.4
O(1)–Cu(Zn)–H_2O(7)	92.7 ± 0.3	94.5 ± 0.3
O(1)–Cu(Zn)–H_2O(8)	94.9 ± 0.3	94.7 ± 0.3
O(2)–Cu(Zn)–H_2O(7)	88.9 ± 0.3	88.9 ± 0.4
O(2)–Cu(Zn)–H_2O(8)	92.5 ± 0.4	91.4 ± 0.4
O(2)–Cu(Zn)–O(4^{I})	90.8 ± 0.3	90.5 ± 0.4
H_2O(6)–Cu(Zn)–H_2O(7)	88.6 ± 0.3	90.6 ± 0.3
H_2O(6)–Cu(Zn)–H_2O(8)	90.6 ± 0.3	90.8 ± 0.3
H_2O(6)–Cu(Zn)–O(4^{I})	93.9 ± 0.3	99.7 ± 0.4
H_2O(7)–Cu(Zn)–O(4^{I})	87.8 ± 0.3	87.0 ± 0.3
H_2O(8)–Cu(Zn)–O(4^{I})	84.7 ± 0.3	83.7 ± 0.4
O(1)–Cu(Zn)–O(4^{I})	172.0 ± 0.2	170.8 ± 0.3
O(2)–Cu(Zn)–H_2O(6)	174.6 ± 0.3	169.8 ± 0.3
H_2O(7)–Cu(Zn)–H_2O(8)	172.4 ± 0.2	170.7 ± 0.3
Cu(Zn)–O(1)–C(1)	101.6 ± 0.6	106.4 ± 0.8
Cu(Zn)–O(2)–C(2)	111.5 ± 0.6	108.0 ± 0.9
Cu(Zn)–O(4^{I})–C(4^{I})	142.9 ± 0.6	142.4 ± 0.8
C(1)–C(2)–C(3)	110.0 ± 0.7	110.8 ± 0.9
C(2)–C(3)–C(4)	106.1 ± 0.7	103.4 ± 1.0
C(3)–C(4)–C(5)	108.6 ± 0.7	111.2 ± 0.9
C(4)–C(5)–C(1)	106.9 ± 0.7	103.8 ± 0.9
C(5)–C(1)–C(2)	108.3 ± 0.7	110.5 ± 0.9
O(2)–C(2)–C(3)	127.5 ± 0.8	126.7 ± 1.2
C(2)–C(3)–O(3)	128.6 ± 0.7	128.7 ± 1.1
O(3)–C(3)–C(4)	125.1 ± 0.8	127.8 ± 1.1
C(3)–C(4)–O(4)	127.2 ± 0.8	125.6 ± 1.1
O(4)–C(4)–C(5)	124.2 ± 0.8	123.0 ± 1.0
C(4)–C(5)–O(5)	126.9 ± 0.8	124.3 ± 0.9
O(5)–C(5)–C(1)	126.2 ± 0.8	130.9 ± 1.0
C(5)–C(1)–O(1)	128.5 ± 0.8	126.4 ± 1.0
O(1)–C(1)–C(2)	123.1 ± 0.8	122.9 ± 1.0
C(1)–C(2)–O(2)	122.4 ± 0.8	122.2 ± 1.1

[a] Superscript I refers to the position (x, $^1/_2 - y$, $-^1/_2 + z$).

of the copper(II) and zinc(II) complexes yields highly significant differences.

The Coordination Symmetry of the Central Metals and the Jahn–Teller Effect.—The stereochemical oxygen environment about each copper(II) is characterized by the usual distortion into four short and two longer Cu–O bonds.[19] The four nearest oxygens are the three water oxygens and the approximately coplanar croconate oxygen O(2). The two Cu–OH_2 distances out of the plane of the chain average 2.02 Å. compared to the in-plane Cu–OH_2 distance of 1.94 Å. The fourth short Cu–O distance of 1.98 Å. results in an average Cu–O distance of 1.99 Å. The mean value of the two symmetrically elongated Cu–O bond lengths is 2.33 Å. These Cu–O bond lengths are consistent with those reported for other six-coordinated copper(II) complexes, which usually have four short Cu–O bond lengths of about 2.0 Å. and two longer Cu–O bonds of from 2.3 to 2.7 Å. Examples of such complexes include Cu-$(CHO_2)_2 \cdot 4H_2O$[20] (four O at 2.00 Å., two H_2O at 2.36 Å.), $Cu(C_6H_5CO_2)_2 \cdot 3H_2O$[21] (two O at 1.91 Å., two H_2O at 1.97 Å., two H_2O at 2.51 Å.), and $Cu(NH_4)_2(C_2O_4)_2 \cdot 2H_2O$[22] (two O at 2.12 Å., two O at 1.98 Å., two H_2O at 2.49 Å., and two O at 1.97 Å., two O at 2.13 Å., two O at 2.74 Å.).

The marked distortion in bond lengths of six-coordinated copper(II), as illustrated above, has been attributed[19] on the basis of ligand field theory to a Jahn–Teller coercion.[23] For a d^9 copper(II) of octahedral point group symmetry O_h, the ground electronic state is E_g, which is doubly degenerate. The Jahn–Teller theorem predicts[24] that the degeneracy of this unstable electronic state will be removed by a distortion of the octahedron. Although the theory does not predict the direction of the distortion, a tetragonal-type deformation usually is observed involving the formation of four short and two long bond lengths.[19,23,25] with theoretical expectations.[27]

In order to obtain a quantitative estimate of the

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(19) *Cf.* L. E. Orgel and J. D. Dunitz, *Nature*, **179**, 462 (1957); J. D. Dunitz and L. E. Orgel, *Advan. Inorg. Chem. Radiochem.*, **2**, 15 (1960).

(20) R. Kiriyama, H. Ibamata, and K. Matsua, *Acta Cryst.*, **7**, 482 (1954).

(21) H. Koizumi, K. Osaki, and T. Watanabe, *J. Phys. Soc. Japan*, **18**, 117 (1963).

(22) M. A. Viswamitra, *J. Chem. Phys.*, **37**, 1408 (1962).

(23) For extensive theoretical and experimental discussion and references cited therein see (a) A. D. Liehr, *Progr. Inorg. Chem.*, **3**, 281 (1962); (b) A. D. Liehr, *J. Phys. Chem.*, **67**, 389, 471 (1963).

(24) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937).

(25) An inverse directional distortion of octahedral copper(II) to give two near and four more distant neighbors has been ascertained for K_2CuF_4 by an X-ray study[26] in agreement with theoretical expectations.[27]

(26) K. Knox, *J. Chem. Phys.*, **30**, 991 (1959).

(27) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958)

Jahn–Teller distortion for the oxygen-coordinated copper(II) in the croconate complex, a subsequent structural investigation of zinc(II) croconate was undertaken. A comparison of the detailed structural parameters of these isostructural compounds allows a separation of the distortions due to the static Jahn–Teller effect in $C_5O_5Cu(H_2O)_3$ from those due to the unsymmetrical oxygen environment (*viz.*, three H_2O and three croconate O) and the stereochemical requirements of the polymeric chains. *Inherent in such a comparison is the assumption that all disturbing influences about the central metal except those due to the Jahn–Teller effect are common to both complexes.*

The X-ray analysis showed each zinc(II) to be coordinated to five approximately equidistant oxygens at an average distance of 2.13 Å. (range 2.10–2.16 Å.) and to a sixth oxygen, $H_2O(6)$, at a distance of 2.03 Å. The resulting average value of 2.11 Å. for the six bonds is consistent with the average Zn–O bond lengths found for $Zn_5(OH)_8Cl_2 \cdot H_2O$(six OH at 2.16–2.17 Å.)[28] and Zn-$(CH_3CO_2)_2 \cdot 2H_2O$ (four O at 2.17–2.18 Å. and two H_2O at 2.14 Å.).[29]

A comparison of the corresponding metal–oxygen bond lengths in the two croconate complexes (Fig. 3) shows that the localized environment of the copper(II) is a distorted version of the more regular environment of the zinc(II). In the removal of a single electron from the d^{10} zinc(II) to give the d^9 copper(II) configuration, each of four metal–oxygen bonds has shortened an average of 0.12 Å., while each of the other two metal–oxygen bonds has lengthened an average of 0.20 Å. These results are consistent with ligand field theory which, *via* the Jahn–Teller mechanism, predicts for the usual tetragonal type distortion of a d^9 copper(II) complex the formation of four short*er* and two long*er* metal–ligand bond lengths relative to those of the undistorted octahedral complex. Of interest is that the magnitudes of bond shortening and lengthening (which depend on the variation of potential energy with internuclear distance) are similar to the differences of corresponding distances found for copper(II) and zinc(II) difluorides[30–32]; in these ionic fluoride compounds of the rutile series (CuF_2: four F at 1.93 Å., two F at 2.27 Å.; ZnF_2: six F at 2.02–2.04 Å.), each of four bonds in CuF_2 is shortened 0.10 Å. while each of the other two bonds is lengthened 0.24 Å. relative to those in the undistorted ZnF_2 structure.

Since the first-row transition metal(II) croconates all possess the same basic crystal structure (as indicated by the nearly identical powder patterns), further X-ray investigations of these compounds should provide experimental evidence concerning possible Jahn–Teller implications for other oxygen-coordinated divalent ions.[33] To date systematic X-ray studies of isostructural octahedral type complexes of the first-row transition metals have been limited mainly to homologous series of fluoride compounds (*cf.*, the rutile series, MF_2; the perovskite series, KMF_3; and the vanadium trifluoride series, MF_3).[23]

TABLE V

INTRA- AND INTERCHAIN NONBONDING DISTANCES[a,b]

Intrachain	$C_5O_5Cu(H_2O)_3$	$C_5O_5Zn(H_2O)_3$
$O(1)\cdots O(2)$	2.81	2.76
$O(2)\cdots O(3)$	2.98	2.99
$O(3)\cdots O(4)$	2.96	2.99
$O(4)\cdots O(5)$	2.91	2.87
$O(5)\cdots O(1)$	2.97	3.00
$O(3)\cdots H_2O(6^{I})$	2.70	2.68
$O(4)\cdots H_2O(8^{I})$	2.97	2.85
Interchain		
$O(1)\cdots H_2O(7^{II})$	2.62	2.71
$O(3)\cdots H_2O(7^{VII})$	2.70	2.70
$H_2O(7)\cdots H_2O(8^{IV})$	2.84	2.86
$H_2O(6)\cdots H_2O(8^{V})$	3.04	2.85
$O(4)\cdots H_2O(8^{III})$	2.89	3.02
$C(5)\cdots O(3^{V})$	2.92	2.94
$O(5)\cdots H_2O(8^{III})$	2.92	3.00
$O(5)\cdots H_2O(6^{VI})$	2.98	3.16

[a] Individual standard deviations are 0.011 Å. for $C_5O_5Cu(H_2O)_3$ and 0.013 Å. for $C_5O_5Zn(H_2O)_3$. [b] Superscripts refer to the following positions

I	x,	$^1/_2 - y$,	$^1/_2 + z$
II	$1 - x$,	$-^1/_2 + y$,	$^1/_2 - z$
III	$^1/_2 - x$,	$-y$,	$^1/_2 + z$
IV	$-x$,	$-y$,	$1 - z$
V	$^1/_2 - x$,	$-^1/_2 + y$,	z
VI	x,	$-^1/_2 - y$,	$-^1/_2 + z$
VII	$-x$,	$^1/_2 + y$,	$^1/_2 - z$

The short $M\text{–}OH_2(6)$ bond in both the copper(II) and zinc(II) croconates is presumably a manifestation of the unsymmetrical field of the ligands. The fact that the two long bonds in $C_5O_5Cu(H_2O)_3$ are to two croconate oxygens can be attributed either to the lower field strength of the croconate oxygens relative to the waters and/or to a stereochemical "locking-in" of this configuration.

The angles about the central metal atoms are relatively close to 90° except for $O(4^{I})\text{–}Zn\text{–}H_2O(6)$ (100°) and O(1)–M–O(2) (M = Cu, 81°; Zn, 80°). The considerable deviations from 90° of these latter bond angles are not unexpected for a metal-chelated linkage of croconate oxygens which are constrained by the stereochemistry of the croconate rings. Examination of the nonbonding croconate oxygen–oxygen distances for both complexes (Table V) reveals that the two oxygens, O(1) and O(2), in coordinating with the metal are distorted from the *idealized* D_{5h} positions *toward* one

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[28] W. Nowacki and J. N. Silverman, *Z. Krist.*, **15**, 21 (1961).

[29] J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Cryst.*, **6**, 720 (1953).

[30] R. D. Peacock, *Progr. Inorg. Chem.*, **2**, 193 (1960).

[31] C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, **79**, 1049 (1957).

[32] W. H. Baur, *Acta Cryst.*, **11**, 488 (1958).

(33) Although both theoretical considerations and available experimental evidence indicate that the Jahn–Teller effect arising from octahedral t_{2g} degeneracies is not an important factor in determining the stereochemistry of the first-row transition metal ions,[19] it is noteworthy that one possible exception involving considerable distortion from octahedral symmetry is observed in the rutile MF_2 series[30–32] for FeF_2; the deformation of the idealized rutile structure for this compound is such that each high-spin d^6 iron(II) is surrounded by two near fluorides (1.99 Å.) and four more distant fluorides (2.12 Å.). In order to assess whether this otherwise inexplicable crystallographic deviation can be attributed to the Jahn–Teller phenomena (as differentiated from anisotropic coulombic forces), structural investigations of the homologous high-spin d^5 manganese(II) and d^6 iron(II) croconates are being undertaken. A detailed comparison of these four isostructural compounds (the manganese(II) and zinc(II) configurations do not exhibit Jahn–Teller instability) should reveal whether a distortion similar to that present in iron(II) difluoride also occurs in the iron(II) croconate.

another, thereby resulting in smaller O(1)–M–O(2) angles but larger M–O(1)–C(1) and M–O(2)–C(2) angles (102 and 112° in copper(II) croconate, 106 and 107° in zinc(II) croconate). The observed nonbonding O(1) · · · O(2) distance is considerably shorter than those of the other ring oxygens in the metal complexes (*viz.*, 2.81 Å. *vs.* 2.96 Å. (av.) for $C_5O_5Cu(H_2O)_3$ and 2.76 Å. *vs.* 2.96 Å. (av.) for $C_5O_5Zn(H_3O)_3$) and those found by Baenziger and co-workers[34,35] for the free croconate dianion (O · · · O = 2.95 Å. (av.)) in diammonium croconate.

For each complex "best planes" of the metal–oxygen system (Table VI; B, C, D) have been computed with the Smith least-squares program.[36] These calculations show that the four oxygens lying in the plane of the chain and the central metal are approximately coplanar but that the other two groups of four oxygens show deviations of 0.1–0.2 Å. from planarity. The dihedral angles between the pairs of "best planes" are essentially 90° for each complex.

The Geometry of the Croconate Rings.—An interesting and unexpected feature of these structures is revealed in the geometry of the croconate rings (Fig. 4). The D_{5h} symmetry and presumably the π-electron delocalization of the free croconate ring is essentially retained in the copper(II) croconate, whereas in zinc(II) croconate the croconate ring possesses *idealized* C_{2v} symmetry and bond lengths and angles such as to suggest an electronic structure related to that of the α-enediol, croconic acid.

Examination of the molecular parameters of the croconate ring in $C_5O_5Cu(H_2O)_3$ shows five approximately equivalent C–C bonds (1.45, 1.43, 1.49, 1.46, and 1.46 Å.; individual e.s.d. 0.013 Å.) of average value 1.46 Å. and five essentially equal C–O bonds (range 1.24–1.28 Å.; individual e.s.d. 0.011 Å.) of average value 1.25 Å. These *mean* C–C and C–O values compare favorably with the corresponding value of 1.46 and 1.26 Å. found for the free croconate dianion of D_{5h} symmetry in the diammonium salt, $(NH_4)_2C_5O_5$.[34,35] The π-bond orders of 0.45 and 0.77 assigned by Baenziger and Hegenbarth[35] from the above distances to the C–C and C–O bonds, respectively, in the free croconate dianion therefore are equally applicable to the corresponding bonds in the congruent croconate ring of $C_5O_5Cu(H_2O)_3$. The inner angles of the croconate ring in copper(II) croconate (and the diammonium salt) are equivalent within experimental error (range 106–110°; individual e.s.d. 0.7°) and have the average value of 108° required for a regular pentagon. The five croconate carbons in $C_5O_5Cu(H_2O)_3$ are coplanar within 0.015 Å. (Table VI; E); of the croconate oxygens only O(3) and O(4) deviate significantly from this "best least-squares plane." The deviations may be explained on the basis of *intra*- and *inter*chain interactions (*vide infra*).

However, in zinc(II) croconate the bond length of the two carbons attached to the zinc(II)-chelated oxygens has shortened to 1.42 Å. (e.s.d. 0.018 Å.) relative to the values of 1.48–1.50 Å. (individual e.s.d. 0.016 Å.) for the other four C–C bonds. The resulting partially localized croconate structure of lower symmetry C_{2v} is related to that of the triketocyclopentenediol, croconic acid. Consistent with this observation is that the three zinc(II)-coordinated C–O bonds have lengths of 1.25, 1.25, and 1.27 Å. (individual e.s.d.

TABLE VI

EQUATIONS OF "BEST PLANES," DISTANCES (IN Å.) FROM THESE PLANES, AND ANGLES (IN DEGREES) BETWEEN PLANES[a,b]

(A) Plane through Cu(Zn), C(1), C(2), C(3), C(4), C(5), O(1), O(2), O(3), O(4), O(5), $H_2O(6)$, $O(4^I)$

$$0.999x - 0.054y - 0.004z - 1.441 = 0$$
$$(0.998x - 0.063y - 0.007z - 1.407 = 0)$$

Cu(Zn)	0.002 (0.001)	O(3)	−0.129 (−0.120)
C(1)	−0.012 (−0.025)	O(4)	0.106 (0.082)
C(2)	−0.001 (0.041)	O(5)	0.010 (0.015)
C(3)	−0.009 (−0.027)	$H_2O(6)$	−0.071 (−0.075)
C(4)	0.025 (−0.009)	$O(4^I)$	0.088 (0.096)
C(5)	−0.007 (0.026)		
O(1)	−0.060 (−0.029)	$H_2O(7)$	−2.00 (−2.11)
O(2)	−0.025 (0.024)	$H_2O(8)$	2.05 (2.16)

(B) Plane through O(1), O(2), $H_2O(6)$, $O(4^I)$, and Cu(Zn)

$$-0.996x + 0.086y - 0.012z + 1.440 = 0$$
$$(-0.995x + 0.101y - 0.001z + 1.394 = 0)$$

O(1)	−0.031 (−0.028)	Cu(Zn)	−0.002 (0.004)
O(2)	0.031 (0.027)	$H_2O(7)$	1.98 (2.121)
$H_2O(6)$	0.025 (0.024)	$H_2O(8)$	−2.06 (−2.150)
$O(4^I)$	−0.025 (−0.024)		

(C) Plane through O(1), $O(4^I)$, $H_2O(7)$, and $H_2O(8)$

$$-0.060x - 0.761y - 0.646z + 2.172 = 0$$
$$(-0.088x - 0.788y - 0.610z + 2.733 = 0)$$

O(1)	−0.089 (−0.071)	Cu(Zn)	0.076 (0.091)
$O(4^I)$	−0.087 (−0.086)	O(2)	−1.89 (−2.02)
$H_2O(7)$	0.085 (0.079)	$H_2O(6)$	2.02 (2.11)
$H_2O(8)$	0.095 (0.079)		

(D) Plane through $H_2O(6)$, O(2), $H_2O(7)$, and $H_2O(8)$

$$0.044x + 0.676y - 0.736z + 1.488 = 0$$
$$(0.044x + 0.615y - 0.788z + 1.594 = 0)$$

O(2)	−0.106 (−0.175)	Cu(Zn)	−0.026 (0.005)
$H_2O(6)$	−0.105 (−0.181)	O(1)	−2.33 (−2.15)
$H_2O(7)$	0.104 (0.182)	$O(4^I)$	2.32 (2.10)
$H_2O(8)$	0.109 (0.174)		

(E) Plane through C(1), C(2), C(3), C(4), and C(5)

$$0.998x - 0.057y - 0.013z - 1.375 = 0$$
$$(0.998x - 0.057y - 0.001z - 1.459 = 0)$$

C(1)	−0.001 (−0.036)	O(1)	−0.037 (−0.051)
C(2)	0.009 (0.036)	O(2)	−0.006 (0.015)
C(3)	−0.014 (−0.020)	O(3)	−0.140 (−0.104)
C(4)	0.014 (−0.001)	O(4)	0.083 (0.099)
C(5)	−0.008 (0.022)	O(5)	0.007 (0.009)
		Cu(Zn)	0.038 (−0.027)

Dihedral angles

A–B	2° (3°)
B–C	89° (90°)
B–D	89° (89°)
C–D	92° (90°)
A–E	2° (0°)
A–(100)	3° (3°)
B–(100)	5° (6°)
E–(100)	3° (3°)
B–E	2° (3°)
$B–E^I$	8° (9°)

[a] The values are given first for $C_5O_5Cu(H_2O)_3$ followed in parentheses by those for $C_5O_5Zn(H_2O)_3$. [b] Superscript I refers to the position $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$.

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(34) N. C. Baenziger, J. J. Hegenbarth, and D. G. Williams, *J. Am. Chem. Soc.*, **85**, 1539 (1963).

(35) N. C. Baenziger and J. J. Hegenbarth, to be published.

(36) D. L. Smith, "A Least-Squares Planes Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

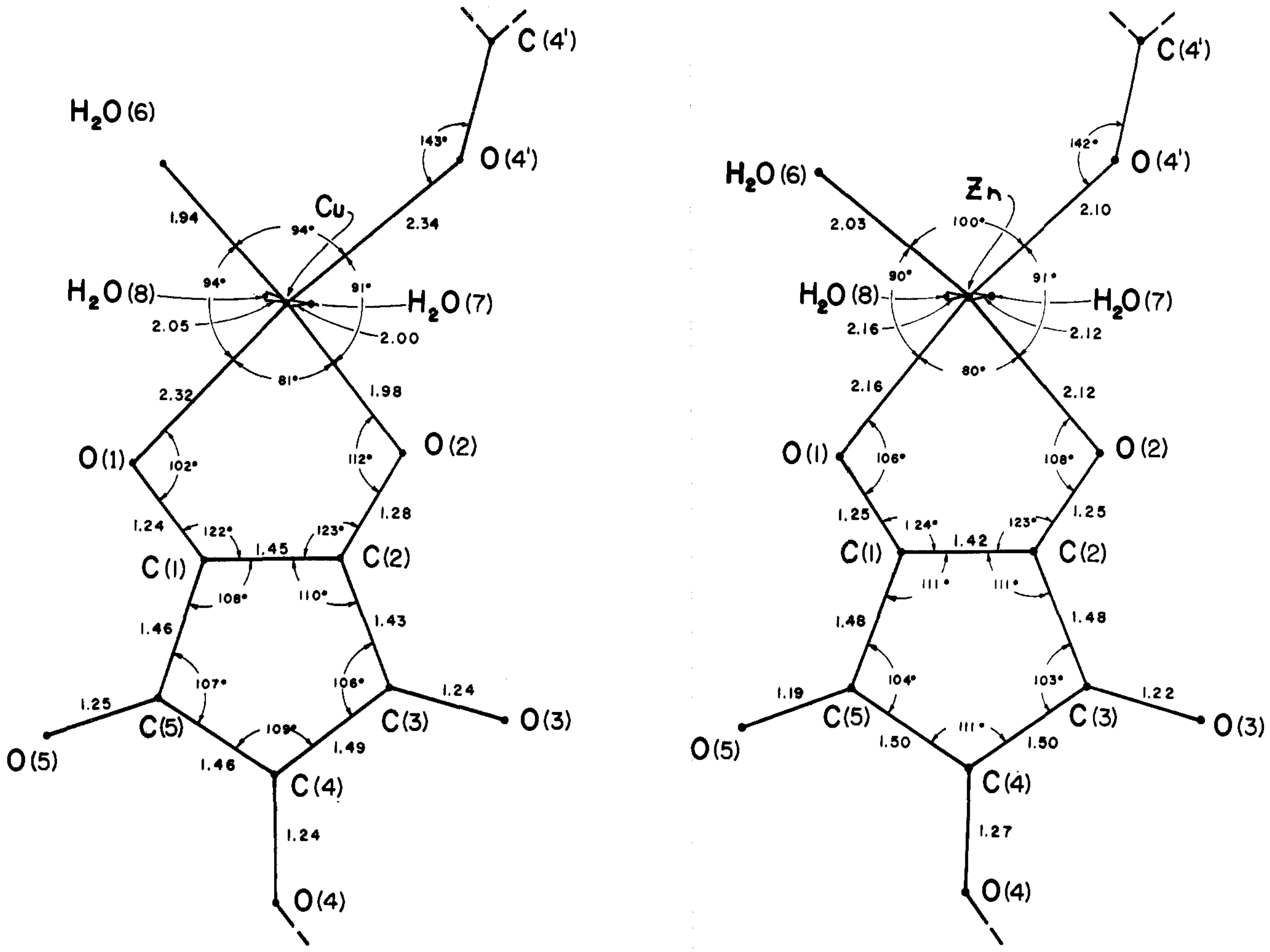

Fig. 4.—Comparison of the configurations of $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$.

0.013 Å.), whereas the C–O bond lengths of the two uncoordinated oxygens have smaller values of 1.19 and 1.22 Å. (individual e.s.d. 0.016 Å.) in agreement with the double bond value of 1.23 Å. (e.s.d. 0.01 Å.) reported for other ketonic C–O bonds.[37]

Although the molecular parameters of croconic acid are not available, a structural determination[34] of ammonium hydrogen croconate, $NH_4HC_5O_5$, which has a *quasi*-croconic acid structure, has yielded bond lengths consistent with those obtained in $C_5O_5Zn(H_3O)_3$. The partial π-electron localization in the monohydrogen croconate ion results from strong hydrogen bonding in the crystalline state as indicated by two adjacent hydrogen-bonded C–O bonds of 1.25 and 1.33 Å. and three shorter free C–O bonds of 1.20–1.21 Å. The bond between the two carbons attached to the hydrogen-bonded oxygens is only 1.39 Å. as contrasted with the other four ring C–C bond lengths of 1.45–1.51 Å.

The reduced symmetry of the croconate ring in zinc(II) croconate is also evidenced by the variation of the inner angles of the ring from 108°. The bond angles subtended by the adjacent ring carbons at C(1), C(2), and C(4) are 111° (individual e.s.d. 0.9°) whereas the remaining two ring angles subtended at the essentially ketonic carbons, C(3) and C(5), which are related to each other by an *idealized* vertical mirror plane, have significantly smaller values of 103 and 104° (individual e.s.d. 1.0°). The resulting *idealized* C_{2v} symmetry of the croconate group approximately holds for the *entire* asymmetric unit of zinc(II) croconate.

The above geometric features all suggest a significant localization of the π-electrons in the croconate ring of zinc(II) croconate relative to that in copper(II) croconate. These facts and the resulting conclusion imply that the Cu–O bonds in copper(II) croconate are essentially ionic such that the copper(II) does not appreciably disturb the molecular geometry (and presumably the electron delocalization) of the croconate ring, whereas in the zinc(II) complex a significant covalent contribution to the metal–ring bonding must be considered.

These conclusions drawn from a comparison of the molecular parameters obtained from the anisotropic least-squares refinements are in complete agreement with those made from the isotropic least-squares refinements, which emphasize even more strongly the different symmetries of the croconate rings for the two complexes.

A complete understanding of the bonding must await further experimental and theoretical studies; however

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[37] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, Burlington House, London, 1958, p. S17.

it is noteworthy that the two chelating metal–oxygen bonds in zinc(II) croconate are *equivalent*, in contrast to those in copper(II) croconate, which possess *different lengths* and therefore *different energies*. These equivalent bonds in the zinc compound may allow a more significant interaction between the metal and ring than do the nonequivalent bonds present in the copper complex. Hence, the ring dimensions may be partly a consequence of the different stereochemical requirements of the central metals in forming these coordination polymers linked through oxygen atoms. It is hoped that this problem will be further clarified by the structural studies of the homologous manganese(II) and iron(II) croconates. For the high-spin d^5 manganese(II), a partially localized croconate system similar to that found for zinc(II) would be predicted.

A geometric feature common to both complexes is that the same two croconate oxygen atoms, O(3) and O(4), are distorted out of the *mean* plane of the carbon atoms (Table VI; E) in opposite directions to each other. The bending down of O(3), which amounts to 0.13 Å. in copper(II) croconate and 0.11 Å. in zinc(II) croconate, is in the direction of a water from another chain to which O(3) is hydrogen-bonded (*vide infra*), as indicated by the resulting shortened oxygen–oxygen distance of 2.70 Å. in each complex. The bending up from the *mean* croconate carbon plane of the other oxygen, O(4), which is 0.08 and 0.07 Å. in the copper(II) and zinc(II) compounds, respectively, is such as to preserve the approximate coplanarity (Table VI; B) of the central metal with the three coordinated croconate oxygens and the water, $H_2O(6^{I})$.

Hydrogen Bonding.—Although the coordinates of the hydrogen atoms were not determined, inspection of the crystallographically independent nonbonding oxygen–oxygen distances (Table V) certainly suggests that the small but directionally significant shifts of the croconate and water oxygens from their undistorted positions in the polymeric chains are largely due to intrachain and interchain hydrogen bonds. Three strong hydrogen bonds, consisting of one intrachain and two interchain $CO\cdots H_2O$ interactions, are indicated from $O\cdots O$ distances of less than 2.72 Å. These latter two and other weaker interchain hydrogen bonds are a dominant part of the forces which bind the polymeric chains.

Of particular interest is the interchain $O(3)\cdots H_2O(7^{VII})$ interaction, as the strong hydrogen bonding distances of 2.70 Å. for both complexes are achieved by the previously discussed deformation of O(3) from the *mean* croconate carbon plane. This croconate oxygen, O(3), also participates in the formation of the strongest intrachain hydrogen bond with $H_2O(6^{I})$ as indicated by the equally short $O\cdots O$ distances of 2.70 and 2.68 Å. for the copper(II) and zinc(II) complexes, respectively. In this connection $H_2O(6^{I})$ in both complexes is distorted by 0.07 Å. from the intrachain plane of the asymmetric metal croconate unit (Table VI; A) such that the intrachain $O(3)\cdots H_2O(6^{I})$ distance is decreased. The resulting $H_2O(6^{I})\cdots O(3)\cdots H_2O(7^{VII})$ angles are 114 and 119° for the copper and zinc croconates, respectively.

The other strong interchain interaction is $O(3)\cdots H_2O(7^{II})$ as evidenced by the $O\cdots O$ distances of 2.62 and 2.71 Å. for the copper(II) and zinc(II) complexes, respectively. It should be noted that $H_2O(7)$ forms two strong hydrogen bonds to C=O groups with the $CO\cdots HOH\cdots OC$ bond angle being 114 and 119° for the copper(II) and zinc(II) compounds, respectively.

Although in general hydrogen bond interactions appear to be relatively insensitive to the angle between the C=O and the $O\cdots O$ lines,[38] calculations for both complexes show that the generically similar angle between the $M-OH_2$ bond and the $H_2O\cdots OC$ line varies from only 102 to 116° for these strongest hydrogen bonds.

One manifestation of the hydrogen bonding is that the "best plane" of the asymmetric $C_5O_5MH_2O(6)$ intrachain fragment (Table VI; A) is not perpendicular to the *a* axis but is tipped slightly to give for each complex a dihedral angle of 3° with respect to the (100) plane; the resulting dihedral angle between the "best planes" of the two adjacent crystallographically identical units of a given polymeric chain is 6°. Figures 1 and 4 show that the out-of-plane waters, $H_2O(7)$ and $H_2O(8)$, are shifted from directly above the metal such that the $H_2O-M-OH_2$ line remains approximately normal to the $C_5O_5MH_2O(6)$ fragment.

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(38) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 255–295.