All of the bond distances (Table V) appear to be within normal ranges. As expected, the axial bond lengths ($P–N_{ax}$ = 1.806 (2) Å and $P–C_{ax}F_3$ = 1.963 (3) Å) are longer than the equatorial bond lengths ($P–N_{eq}$ = 1.633 (2) Å and $P–C_{eq}F_3$ = 1.916 (3) Å). Also the C–F bond lengths for the axial CF_3 (1.354 Å, average) are longer compared to the C–F bond lengths for the equatorial CF_3 (1.322 Å, average).

The closest nonbonded intermolecular contacts (Table V) show that none are longer than the sum of the respective van der Waals radii.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (formerly the National Research Council) for support of this work.

Registry No. $[CH_3(CF_3)_2PNCH_3]_2$, 73506-03-3; $CH_3(CF_3)_3PCl$, 56420-21-4; CH_3NH_2, 74-89-5; $CH_3(CF_3)_3PN(H)CH_3$, 73506-04-4; $(CF_3)_3CH_3PF$, 57572-93-7; $(CH_3)_3SiN(H)CH_3$, 16513-17-0; $(CF_3)_2F(CH_3)PN(H)CH_3$, 73506-05-5.

Supplementary Material Available: A listing of observed ($10|F_o|$) and calculated $10|F_c|$) structure amplitudes (5 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination du CNRS Associé à l'Université Paul Sabatier de Toulouse, 31400 Toulouse, France

Crystal Structure and Magnetism of Sodium Bis(oxalato)cuprate(II) Dihydrate, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$. A Deductive Proposal for the Structure of Copper Oxalate, $CuC_2O_4 \cdot xH_2O$ ($0 \leq x \leq 1$)[1]

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Received December 13, 1979

Sodium bis(oxalato)cuprate(II) dihydrate, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, was synthesized from aqueous solutions of sodium oxalate and copper oxalate. It crystallizes in the triclinic system (space group $P\bar{1}$) with one formula unit in a cell of dimensions a = 7.536 (3) Å, b = 9.473 (4) Å, c = 3.576 (2) Å, α = 81.90 (6)°, β = 103.77 (5)°, and γ = 108.08 (4)°. The structure has been refined by full-matrix least-squares methods using 1734 independent observations to a final R factor of 0.027. It consists of columnar stacks of quasi-planar units $[(C_2O_4)Cu(C_2O_4)]^{2-}$ along the c axis, with Cu–Cu separation of 3.576 (2) Å and a tilt angle of 129.2 (5)° with respect to the stacking direction. Sodium atoms and water molecules develop independent chains running in the same c direction. This structure is markedly different from that of the potassium and ammonium derivatives. Derived models for ribbon-like structures of hydrated copper oxalate, $CuC_2O_4 \cdot xH_2O$ ($0 \leq x \leq 1$) are proposed. A weak antiferromagnetic intrastack coupling, brought to evidence from measurements of the magnetic susceptibility in the temperature range 4–300 K, is discussed in the light of the structural features of $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$.

Introduction

In their review on one-dimensional inorganic compounds, Miller and Epstein[2] have pointed out that "the crystal structures of various complexes which exhibit antiferromagnetic behavior reveal a chain structure formed through intermolecular bridging ligands and not through direct metal–metal bonding....An exception to this trend is α-Cu(msal)$_2$ which has a collinear array of Cu(II) atoms, with metal–metal spacings too large, 3.3 Å, for strong metal–metal bonding".

The study of sodium bis(oxalato)cuprate(II) dihydrate, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, was undertaken in the course of our investigations on compounds likely to have structures build from columnar stacks of nearly planar complex ions such as $Ni(S_2C_2O_2)_2{}^{2-}$[1] or $Cu(C_2O_4)_2{}^{2-}$. This latter anion has long been known as its potassium and ammonium salts[3] whose structures[4] and magnetism[5] have been investigated. On the other hand, its sodium salt was not known. We report here on the synthesis, crystal structure, and magnetic behavior of this compound which, unlike the potassium and ammonium derivatives, has a crystal structure made of columnar stacks of anions $Cu(C_2O_4)_2{}^{2-}$.

Table I. Experimental Crystallographic Data

(1) Physical and Crystallographic Data

formula: $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$
cryst system: triclinic
space group: $P\bar{1}$
a = 7.536 (3) Å
b = 9.473 (4) Å
c = 3.576 (2) Å
α = 81.90 (6)°
β = 103.77 (5)°
γ = 108.09 (4)°

mol wt: 321.6
V = 235 Å^3
ρ_m = 2.24 ± 0.03 g/cm^3
ρ_x = 2.27 ± 0.02 g/cm^3
Z = 1
abs factor: $\mu_{MoK\alpha}$ = 24.58 cm^{-1}
morphology: parallelogram, 0.004 × 0.005 × 0.05 cm

(2) Data Collection

temp: 293 K
radiation: λ (Mo Kα) = 0.710 69 Å
crystal-detector distance: 208 mm
detector window: height = 4 mm; width = 4 mm
scan mode: θ–2θ
maximum Bragg angle: 37°
scan angle: $\Delta\theta = \Delta\theta_0 + B \tan\theta$; $\Delta\theta_0{}^a$ = 1°, B^a = 0.347
values determining scan speed: SIGPRE^a = 0.66; SIGMA^a = 0.018; VPRE^a = 10°/min; TMAX^a = 80 s
std intensity reflctns: $22\bar{1}$, 300, $0\bar{1}1$ measured every 3600 s

[a] These parameters have been described in: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, *33*, 2633.

Experimental Section

Synthesis and Characterization. Copper oxalate was prepared as described in ref 6 and dissolved in an aqueous solution of sodium

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[1] Presented at the 5th European Crystallographic Meeting, Cophenhagen (Abstract No. 15-P3-2), along with studies on bis(dithiooxalato)nickelates(II) of alkali elements. A study of $K_2Ni(S_2C_2O_2)_2$ has been published: Gleizes, A.; Cléry, F; Bruniquel, M.-F.; Cassoux, P. *Inorg. Chim. Acta* **1979**, *37*(1), 19. Results concerning the compounds $M_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ with M = Li and Na, which are isostructural with $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, are to be published in *Inorg. Chim. Acta*.

[2] Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 127.

[3] von Groth, P. *Chem. Krist.* **1910**, *3*, 158.

[4] Viswamitra, M. A. *J. Chem. Phys.* **1962**, *37*, 1408. Viswamitra, M. A. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1962**, *117*, 437.

[5] Jeter, D. Y.; Hatfield, W. E. *Inorg. Chim. Acta* **1972**, *6*(3), 523.

Table II. Positional and Thermal Parameters for the Atoms of $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	1.11 (1)	0.84 (1)	1.92 (2)	0.067 (5)	0.51 (1)	−0.54 (1)
Na	0.2979 (1)	0.57239 (7)	0.6073 (2)	2.63 (2)	2.17 (2)	2.53 (3)	0.50 (2)	0.69 (2)	−0.49 (2)
O(1)	0.2327 (1)	0.1623 (1)	0.0424 (3)	1.29 (4)	1.16 (3)	2.31 (5)	0.11 (3)	0.62 (3)	−0.61 (3)
O(2)	−0.0914 (1)	0.1244 (1)	0.2459 (3)	1.31 (4)	1.15 (3)	2.41 (5)	0.13 (3)	0.68 (3)	−0.59 (3)
O(3)	0.3436 (2)	0.3952 (1)	0.2198 (4)	1.49 (4)	1.15 (3)	2.46 (5)	−0.16 (3)	0.47 (3)	−0.58 (3)
O(4)	0.0019 (2)	0.3564 (1)	0.4265 (4)	1.85 (4)	1.43 (4)	2.72 (6)	0.52 (3)	0.45 (4)	−0.92 (4)
C(1)	0.2200 (2)	0.2756 (1)	0.1794 (4)	1.21 (4)	1.10 (4)	1.27 (5)	0.23 (3)	0.22 (4)	−0.23 (3)
C(2)	0.0279 (2)	0.2544 (1)	0.2939 (4)	1.23 (4)	1.02 (4)	1.44 (6)	0.35 (3)	0.15 (4)	−0.26 (3)
O_w	0.3945 (2)	0.7525 (2)	0.1073 (4)	1.58 (5)	2.42 (5)	2.94 (7)	0.70 (4)	0.56 (4)	0.05 (4)

atom	x	y	z	B_{iso}	atom	x	y	z	B_{iso}
H(1)	0.5279	0.8117	0.0895	2	H(2)	0.3282	0.8304	−0.0006	2

[a] Estimated standard deviations in the least significant figure are given in parentheses. Isotropic B's and anisotropic B_{ij}'s thermal parameters have units of Å². Anisotropic parameters enter the expression of the structure factor in the form $\exp[0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

Table III. Selected Interatomic Distances (Å) and Bond Angles (Deg) in $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$[a]

Copper Surrounding			
Cu–O(1)	1.929 (1)	O(1)–Cu–O(2)	85.42 (6)
Cu–O(2)	1.930 (1)	O(1)–Cu–O(2)^{iv}	95.0 (7)
Cu–O(2)^{iv}	2.803 (2)	O(2)–Cu–O(2)^{iv}	83.6 (6)
Cu–Cu^{ii}	3.576 (2)		
Oxalate Group			
C(1)–O(1)	1.279 (2)	C(1)–O(1)–Cu	112.54 (9)
C(2)–O(2)	1.286 (2)	C(2)–O(2)–Cu	112.21 (9)
C(1)–O(3)	1.225 (2)	O(1)–C(1)–C(2)	114.7 (1)
C(2)–O(4)	1.220 (2)	O(2)–C(2)–C(1)	114.8 (1)
C(1)–C(2)	1.543 (2)	O(1)–C(1)–O(3)	125.8 (1)
O(1)–O(3)	2.229 (2)	O(2)–C(2)–O(4)	125.6 (1)
O(2)–O(4)	2.229 (2)	O(3)–C(1)–C(2)	119.4 (1)
O(1)–O(2)	2.618 (2)	O(4)–C(2)–C(1)	119.6 (1)
O(3)–O(4)	2.749 (2)		
O(1)–O(2)^{i}	2.836 (2)		
O(4)–O(4)^{vi}	2.852 (2)		
Sodium Surrounding			
Na–O_w	2.372 (2)	Na–O(4)^{vi}	2.523 (2)
Na–O_w^{ii}	2.471 (2)	Na–Na^{ii}	3.576 (2)
Na–O(3)	2.469 (2)	Na–Na^{ix}	4.060 (2)
Na–O(3)^{viii}	2.553 (2)	Na–Na^{viii}	3.969 (2)
Na–O(3)^{ii}	2.587 (2)	Na–Na^{vi}	4.179 (2)
Na–O(4)	2.536 (2)		
Water Molecule and Hydrogen Bonds			
O_w–H(1)	1	H(1)–O_w–H(2)	99 (3)
O_w–H(2)	1	O_w–H(1)–O(1)^{v}	153 (4)
O_w–O(1)^{v}	2.832 (2)	O_w–H(2)–O(2)^{vii}	148 (4)
O_w–O(2)^{vii}	2.835 (2)	O(1)^{v}–O_w–O(2)^{vii}	127.83 (7)
H(1)–O(1)^{v}	1.91 (3)	Na–O_w–Na^{iii}	95.15 (6)
H(2)–O(2)^{vii}	1.94 (3)	Na–O_w–O(1)^{v}	123.08 (7)
		Na^{iii}–O_w–O(1)^{v}	88.10 (7)
		Na–O_w–O(2)^{vii}	108.91 (7)
		Na^{iii}–O_w–O(2)^{vii}	91.60 (7)

[a] Code of equivalent positions relative to x, y, and z used in this table: (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $x, y, 1 + z$; (iii) $x, y, \bar{1} + z$; (iv) $\bar{x}, \bar{y}, 1 - z$; (v) $1 - x, 1 - y, \bar{z}$; (vi) $\bar{x}, 1 - y, 1 - z$; (vii) $\bar{x}, 1 - y, \bar{z}$; (viii) $1 - x, 1 - y, 1 - z$; (ix) $1 - x, 1 - y, 2 - z$.

oxalate. Complete dissolution occurs when the molar ratio (sodium oxalate)/(copper oxalate) is nearly 2, depending on the temperature. On evaporation of the solution, long prismatic blue single crystals separated. The density was measured by flotation in a mixture of 1,1,2,2-tetrabromoethane and carbon tetrachloride and was found equal to 2.24 ± 0.03 g/cm³; X-ray photographs of a single crystal were taken by using a Stoe precession camera (Mo Kα radiation); a triclinic cell with approximate parameters was determined: $a = 7.52$ Å, $b = 9.44$ Å, $c = 3.58$ Å, $\alpha = 82°$, $\beta = 104°$, $\gamma = 108°$. These values combined with the measured density were consistent with $Z = 1$ unit of formula $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$ per cell (calculated density = 2.27 g/cm³). This formula was fully confirmed by the structure analysis.

Collection of X-ray Data. A single crystal was mounted on an Enraf-Nonius CAD-4 computer-controlled four-circle X-ray diffractometer. The dimensions of the crystal were 0.004 × 0.005 × 0.05 cm. The accurate unit-cell constants were derived from a least-squares refinement of the setting angles of 25 reflections and are reported in Table I.

Reflections in the range $4° < 2\theta < 74°$ were scanned as described in Table I for the Miller indices hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$. The three standard reflections showed no significant variation of intensity. The data were processed[7] by using an ignorance factor p of 0.02 in the estimation of standard deviations. Intensities were measured at ψ angles minimizing path lengths as much as possible, and scans around the diffusion vectors of some reflections showed no significant changes in intensities; therefore, data were not corrected for absorption.

Among 2381 independent collected reflections, 1734 had $F_o^2 \geq 3\sigma(F_o^2)$ and were used to determine and to refine the structural parameters of the title compound.

Structure Determination and Refinement. Structure determination was effected by using Patterson and Fourier map techniques and the refinement by applying full-matrix least-squares techniques.[7] Throughout the refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight $w = 4F_o^2/\sigma^2(F_o^2)$. The reliability coefficients are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. The atomic scattering factors and anomalous terms are from the tabulations in ref 8.

Space group $P\bar{1}$ was assumed, implying that the copper atom lies on a center of symmetry, the positions of the other nonhydrogen atoms being then readily observed on the tridimensional Patterson map. The anisotropic refinement of all nonhydrogen atoms led to $R = 0.033$ and $R_w = 0.047$. On a subsequent difference Fourier map, two peaks, closely related to the oxygen atom O_w of the water molecule, were attributed to the hydrogen atoms. Their positions were introduced in the refinement with isotropic thermal coefficients, and two more cycles, including also Zacchariasen's secondary extinction parameter, were run. Then the resulting coordinates of hydrogen atoms were corrected in such a way as to get H–O_w bond lengths equal to 1 Å while keeping the angle H(1)–O_w–H(2) equal to the value resulting from previous refinements. In the next and last cycle, these new hydrogen coordinates and the corresponding isotropic thermal coefficients taken equal to 2 Å² were not varied. The final reliability factors were $R = 0.027$ and $R_w = 0.029$ for the 1734 reflections and 80 variables, and the error in an observation of unit weight was 1.48 electron. A final difference Fourier map did not show peaks higher than $^1/_{18}$th of peaks corresponding to a carbon atom in a Fourier map.

A listing of observed and calculated structure amplitudes is available as supplementary material. Refined atomic parameters are listed in Table II, and selected interatomic distances and angles in Table III.

Magnetic Measurements. The magnetic susceptibility of $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$ was measured in the Laboratoire de Spectrochimie des Eléments de Transition (Orsay, France), over the temperature

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(6) McGregor, K. T.; Soos, Z. G. *Inorg. Chem.* **1976**, *15*(9), 2159.

(7) In addition to local programs for the CII-IRIS 80, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Ibers and Doedens' NUCLS least-squares program, Busing and Levy's ORFLS program, and Johnson's ORTEP II thermal plotting program.

(8) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2.A and 2.1.C.

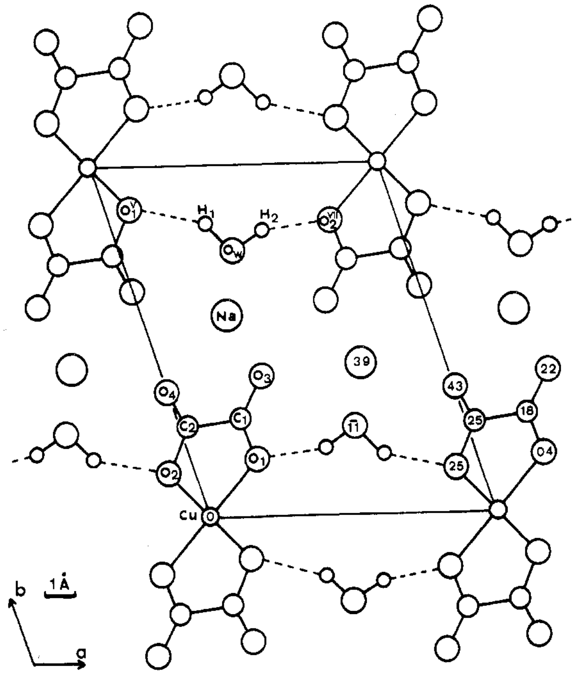

Figure 1. A ball and spoke drawing of the structure of $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$, projected onto the (001) plane.

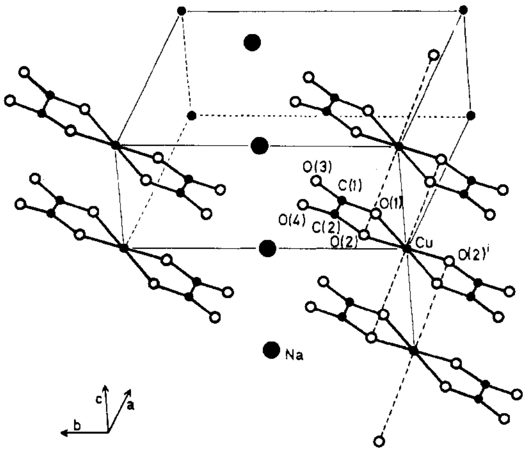

Figure 2. Stacking of the $Cu(C_2O_4)_2^{2-}$ units in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$.

range 4–300 K, on a Faraday type magnetometer equipped with a continuous-flow cryostat designed by Oxford Instruments. The sample was made of a few, needle-shaped, single crystals and weighed about 8 mg. It was positioned in such a way that the elongation axis of the crystals (*c* axis) was perpendicular to the magnetic field. The correction for diamagnetism was estimated to -102×10^{-6} cm^3 mol^{-1}.

Description of the Crystal Structure

A ball and spoke drawing of the structure projected on to the (001) plane is given in Figure 1. The structure consists of stacked, quasi-planar (vide infra) $Cu(C_2O_4)_2$ units and of linear chains of sodium atoms and of water molecules. Both columns and chains run parallely to the *c* axis, with Cu–Cu, Na–Na, and O_w–O_w intervals equal to the *c* parameter, i.e., 3.576 (2) Å. The $Cu(C_2O_4)_2$ units are not perpendicular to the stacking direction; indeed the plane of atoms Cu, O(1), and O(2) makes an angle of 129.2 (5)° with the *c* axis (Figure 2).

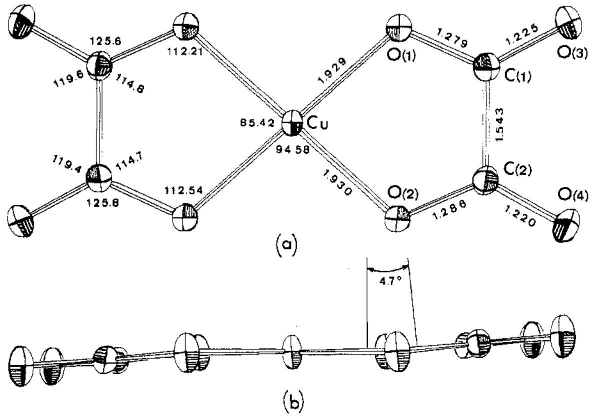

Figure 3. A drawing of the anion $Cu(C_2O_4)_2^{2-}$ in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$, parallel (a) and perpendicular (b) to the plane of coordination of Cu. The atoms are drawn at their 50% probability ellipsoid, in this and subsequent drawings.

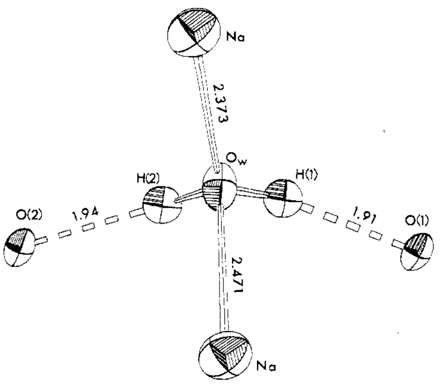

Figure 4. The water molecule in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$.

The detailed geometry of the anion $Cu(C_2O_4)_2^{2-}$ is shown in Figure 3. The copper atom lies on a center of symmetry. It is coordinated to two oxalate groups through O(1)- and O(2)-like oxygen atoms located at the corners of a quasi-square parallelogram. Cu–O(1) and Cu–O(2) bond lengths are equal within the experimental error: 1.929 (1) and 1.930 (1) Å. The environment of a copper atom is octahedrally completed with two centrosymmetrically related oxygen atoms $O(2)^{ii}$ from neighboring $Cu(C_2O_4)_2$ groups, one above and one below, in the same stack, with Cu–$O(2)^{ii}$ distances equal to 2.803 (2) Å (Figure 2). The versatility of coordination of Cu(II) ions has been recently illustrated and discussed about the crystal structure of $Cu_5Se_2O_8Cl_2$.[9] It is not surprising to find again this (4 + 2) coordination type which is very similar to the one found in the simple CuO structure[10] where Cu–O bond lengths in the square CuO_4 are equal to 1.951 and 1.961 Å, while the apical oxygen atoms are at 2.784 Å. The copper atom may be considered as being inserted in an octahedron elongated consequently to a Jahn–Teller effect, but the elongation does not take place along the fourfold axis but is tilted by 8° (17° in CuO).

The oxalate groups may be described as planar since their component atoms do not deviate by more than 0.009 Å from the least-squares plane which fit them. In these groups, chemically but not symmetrically equivalent bond lengths and angles are remarkably close to each other within the experimental error range. The two C–O bonds corresponding to oxygen atoms coordinated to Cu are slightly but significantly longer (1.279 (2) and 1.286 (2) Å) than the two others (1.220 (2) and 1.225 (2) Å). It is remarkable that the C–C bond length of 1.543 (2) Å and the average value of the C–O bond lengths 1.253 (2) Å are exactly the same as in the oxalate groups in the ribbons ...$Sn(C_2O_4)Sn(C_2O_4)$... of tin(II) oxalate:[11] 1.542 (4) and 1.253 (2) Å, respectively.

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(9) Galy, J.; Bonnet, J. J.; Andersson, S. *Acta Chem. Scand., Ser. A* **1979**, *33*, 383.

(10) Åsbrink, S.; Åström, A. *Acta Crystallogr., Sect. B* **1970**, *26*, 8.

(11) Gleizes, A.; Galy, J. J. *Solid State Chem.* **1979**, *30*, 23.

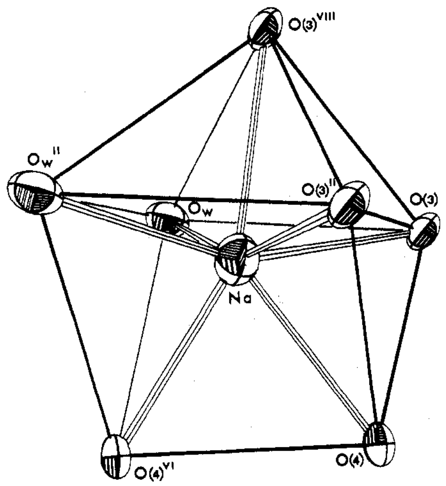

Figure 5. Coordination polyhedron around sodium in $Na_2Cu(C_2O_4)_2·2H_2O$.

The dihedral angle along O(1)–O(2) between the plane of atoms Cu, O(1), and O(2) and the mean plane of the attached oxalate group is 4.7°, which gives to the $(O_2C_2O_2)Cu(O_2C_2O_2)$ entities a slightly "chair" distorted planar configuration (Figure 3b). The perpendicular plane passing by the copper atom position and the middles of the two C–C bonds is almost a perfect mirror for the anion $Cu(C_2O_4)_2^{2-}$.

Each water molecule is pseudotetrahedrally surrounded by two sodium ions at 2.372 (2) and 2.471 (2) Å and two oxygen atoms $O(1)^v$ and $O(2)^{vii}$ at 2.832 (2) and 2.835 (2) Å belonging to different oxalate groups and bridged via hydrogen bonds (Figure 4). As a matter of fact, the distances $H(1)–O(1)^v$ and $H(2)–O(2)^{vii}$, which measure 1.91 (3) and 1.94 (3) Å, are markedly shorter than the sum of the van der Waals radii.[12] Two water molecules bridge two units $Cu(C_2O_4)_2$ related one to the other through the translation $\vec{a}$ (Figure 1).

Each sodium atom is environed with seven oxygen atoms, two from water molecules and five from oxalate groups, at distances ranging from 2.37 to 2.59 Å and located at the vertices of a distorted monocapped trigonal prism (Figure 5).

Then the whole structure appears as a packing of parallel thick layers of infinite ribbons $[Cu(C_2O_4)_2·(H_2O)_2]_n$ running along the *a* axis and piled up along the *c* axis. These ribbons are held together by the sodium atoms.

Structural Relationships: A Proposal for the Structures of Hydrated Copper Oxalates, $Cu(C_2O_4)·xH_2O$ ($0 \le x \le 1$)

The crystal structure of hydrated copper oxalates is still not yet known because all attempts to grow single crystals suitable for X-ray analysis have failed.

Preliminary Hypothesis. In a previous paper about tin(II) oxalate[11] it has been shown that the ribbon type structure of SnC_2O_4 could be deduced from that of $Na_2Sn(C_2O_4)_2$, made of stacks of nonplanar units $(C_2O_4)Sn(C_2O_4)$ and chains of sodium atoms, by applying the crystallographic shear $^1/_8$-$[34\bar{2}](001)$ of *c*/2 periodicity. Such an operation squeezes out the sodium atoms and generates the ribbon chains of tin oxalate. A hypothetical structure, showing remarkable similarities to the actual one, was also deduced for $Na_2C_2O_4$.

Applying similar structural relationships to $Na_2Cu(C_2O_4)·2H_2O$ permits us to deduce a hypothetical structure for the structurally unknown hydrated copper oxalate $Cu(C_2O_4)_2·xH_2O$ particularly studied for its remarkable magnetic behavior.[6]

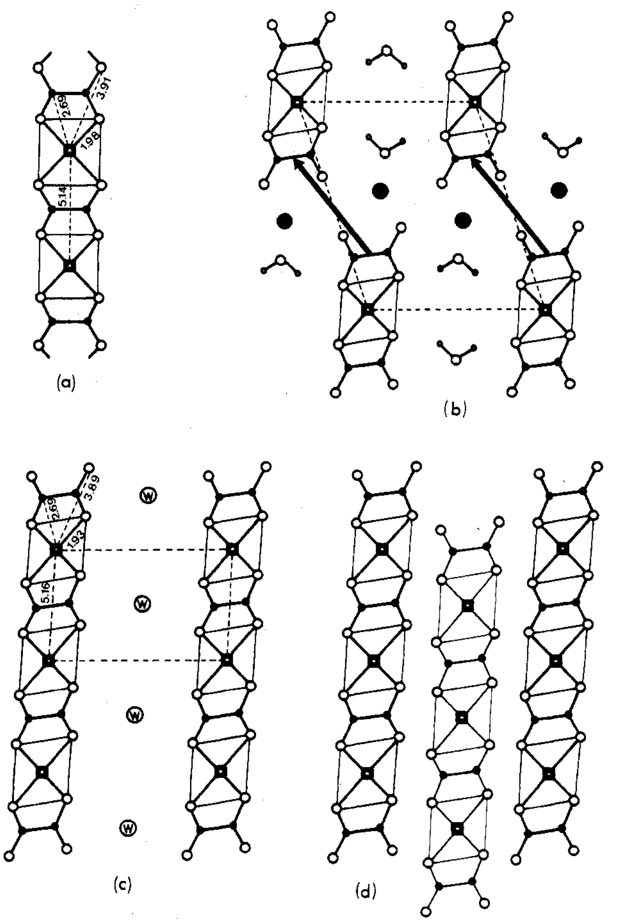

Figure 6. Structural relationship between $Na_2Cu(C_2O_4)_2·2H_2O$ and copper oxalate: (a) a sketch of a ribbon-like chain in copper oxalate as determined from EXAFS; (b) the crystallographic shear operation $^1/_4[\bar{1}2\bar{2}](010)$, illustrated by arrows, in $Na_2Cu(C_2O_4)_2·2H_2O$, yielding ribbon-like chains of copper oxalate; (c) proposal for the structure of $Cu(C_2O_4)·H_2O$; (d) the final stage, structure of CuC_2O_4.

Available Data. Concerning the copper oxalates, $Cu(C_2O_4)_2·xH_2O$, we have to mention a work by Schmittler,[13] who showed that the water content ranged over $0 \le x < ^1/_2$ and concluded to the existence of chains ...$(C_2O_4)Cu(C_2O_4)Cu$.... More recently, McGregor and Soos emphasized the need for single crystals because their thorough EPR study of the magnetic properties of $Cu(C_2O_4)·^1/_3H_2O$[6] did not allow them to choose between two suggested structures: one is based on a ribbon type arrangement of square-planar oxalate groups bound to adjacent copper(II) ions; the other is based on the adjacent ions being bridged by two different oxalate groups. The latter structure is consistent with the relatively large exchange interaction, the former one being more consistent with the EPR data.

Recent results following an EXAFS study performed in the Laboratoire d'Utilisation du Rayonnement Electromagnêtique (LURE) in Orsay, France, argue in favor of ribbon-like chains;[14] a sketch of such a chain with interatomic distances as derived from EXAFS data is presented in Figure 6a.

Structural Relationships. It is possible to reach similar conclusions by applying the crystallographic shear operation $^1/_4[\bar{1}2\bar{2}](010)$ of periodicity *b* to the structure of $Na_2Cu(C_2O_4)_2·2H_2O$. This operation generates ribbon-like chains $(CuC_2O_4)_n$, and one water molecule is kept (Figure 6b). Figure 6c illustrates the final result corresponding to a possible

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(12) This is true whether the van der Waals radius of hydrogen is given the Pauling value of 1.2 Å or the value of 1 Å deduced from recent neutron diffraction studies, the van der Waals radius of oxygen being given the Pauling value of 1.40 Å.

(13) Schmittler, H. *Monatsber. Dtsch. Akad. Wiss. Berlin* **1968**, *10*, 581.

(14) Michalowicz, A.; Girerd, J. J.; Goulon, J. *Inorg. Chem.* **1979**, *18*(11), 3004.

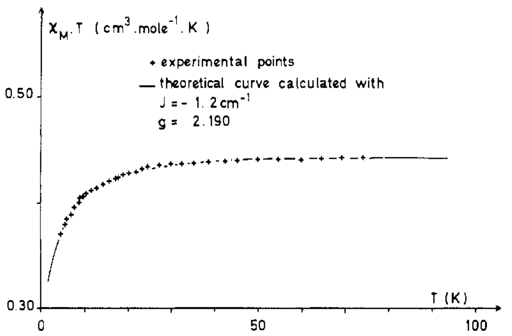

Figure 7. Temperature dependence of the product χ_mT for $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$ (χ_m is the molar susceptibility).

structure for $Cu(C_2O_4){\cdot}H_2O$. It is reasonable to think that the chains pile up in such a way that the coordination geometry of Cu(II) ions is close to that observed in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$. Figure 6c indicates also how close are the interatomic distances issued both from this operation and from EXAFS. The predicted Cu–Cu separation of 5.16 Å is especially in very close agreement with that of 5.14 Å found by EXAFS techniques. If the piling is also maintained, like along *c* in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$, it could explain the weak interchain coupling brought into evidence in EPR studies.[6]

The progressive removing of the water molecules from this layered structure should lead to the limit structure of anhydrous copper oxalate in which the layers would be linked by van der Waals contacts between oxygen atoms (Figure 6d), as in tin(II) oxalate. But it is easy to see the difficulty to remove all the water molecules, and such a fact can also explain the difficulty to obtain samples well crystallized and their ability to have compositions $Cu(C_2O_4){\cdot}xH_2O$ with $0 \leq x < 1$. The X-ray powder patterns are of poor quality exhibiting wide and diffuse lines.

Magnetic Behavior

The results of the magnetic measurements are shown in Figure 7, where are plotted the experimental values of the product χ_mT (χ_m is the molar susceptibility and T the temperature) vs. the temperature, below 100 K. The decrease of χ_mT below 30 K testifies to a weak antiferromagnetic coupling within chains of stacked units $Cu(C_2O_4)_2$. Experimental data are interpreted satisfactorily by using the theoretical expression giving the magnetic susceptibility within a chain of spin doublets, as recently proposed by Estes et al.[15] The values found for the exchange parameter J and the parameter g are $J = -1.2 \pm 0.05$ cm⁻¹ and $g = 2.190 \pm 0.003$.

This weak intrachain antiferromagnetic coupling is due to a δ type interaction between the magnetic orbitals of units $Cu(C_2O_4)_2$. These magnetic orbitals are built from the $d_{x^2-y^2}$ metallic orbitals pointing toward oxygen atoms O(1) and O(2) of oxalate groups bound to Cu(II) ions. Indeed, it has been shown that the absolute value of J increases with the square integral of overlap of magnetic orbitals of next neighboring ions.[16]

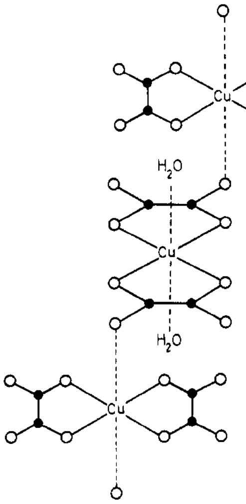

Figure 8. A sketch from ref 5 of the chaining of the anion $Cu(C_2O_4)_2^{2-}$ in $K_2Cu(C_2O_4)_2{\cdot}2H_2O$ and $(NH_4)_2Cu(C_2O_4)_2{\cdot}2H_2O$.

It is interesting to compare these results with those which can be deduced from the study of the complexes $K_2Cu(C_2O_4)_2{\cdot}2H_2O$ and $(NH_4)_2Cu(C_2O_4)_2{\cdot}2H_2O$.[5] The authors of this work have found that these complexes followed a Curie–Weiss law with $\Theta = 0.7$ K and $\Theta = 0.6$ K, respectively. If those deviations from the Curie law are attributed to an intrachain coupling, one can deduce $J = -0.7$ cm⁻¹ and $J = -0.6$ cm⁻¹, respectively. Thus, the couplings in the potassium and the ammonium salts appear to be even weaker than in the sodium salt. This discrepancy is to be related to the structural differences between these compounds. $K_2Cu(C_2O_4)_2{\cdot}2H_2O$ and $(NH_4)_2Cu(C_2O_4)_2{\cdot}2H_2O$ are isostructural.[4] But, unlike what happens in $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$, their structures are not made of columnar stacks of units $[Cu(C_2O_4)_2]^{2-}$ but contain units $[Cu(C_2O_4,H_2O)_2]^{2-}$ and units $[Cu(C_2O_4)_2]^{2-}$ disposed in such a way (Figure 8) that the interaction occurs through weak oxalate bridges over distances of more than 5 Å, whereas in the sodium salt the structural arrangement allows for direct, even if weak, δ type overlap of the magnetic orbitals.

Acknowledgment. This work has been supported by CNRS, DGRST, and DESR. We thank Professor O. Kahn and Dr. J. J. Girerd from the Laboratoire de Spectrochimie des Elêments de Transition, Université de Paris-Sud, Orsay, for fruitful discussions about magnetism.

Registry No. $Na_2Cu(C_2O_4)_2{\cdot}2H_2O$, 73505-53-0.

Supplementary Material Available: A listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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