Inorg. Chem. **2000,** *39,* 4651−4653

Effect of Zn Substitution on the Crystal Structure of $(ND_4)_2[Cu[Zn](D_2O)_6](SO_4)_2$

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Received March 28, 2000

Introduction

The Tutton salts of the general formula $M^I_2[M^{II}(H_2O)_6](SO_4)_2$ provide a convenient group of compounds for investigating the influence of crystal environments upon the electronic and geometric properties of hexahydrate complexes. The ammonium copper(II) Tutton salt is especially interesting because it exists in two distinct forms. When deuterated, it adopts a structure (form A) in which the long axis of the distorted $Cu(D_2O)_6^{2+}$ cation is directed to the pair of O(8) water molecules,[1] whereas in the hydrogenous salt (form B), this direction is to the O(7) pair of water molecules.[2] This change is accompanied by slight alterations in the orientations and hydrogen-bonding interactions of the ammonium and sulfate ions.[3,4] However, when the pressure is raised from ambient to 1.5 kbar, the deuterated compound switches to form B.[4] This change exhibits hysteresis when the pressure is decreased.[5] The deuterated compound has been the subject of charge-density analysis.[6] Both $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ and its deuterated analogue exhibit thermal equilibria involving the other crystal form,[3,7] and it has been suggested that cooperative interactions play a significant role in these equilibria.[8]

The chromium(II) Tutton salts differ from their copper(II) analogues in that both the hydrogenous and deuterated ammonium compounds adopt form A.[9] However, it was noted by Falvello et al. that when zinc(II) substitutes for chromium in the mixed-crystal series $(NH_4)_2[Cr_{1-x}Zn_x(H_2O)_6](SO_4)_2$ and $x \geq 0.07$, the structure switches to form B.[10] That is, substitution of Cr^{2+} with Zn^{2+} ions has an effect on the crystal structure similar to that of the application of pressure on deuterated ammonium copper(II) sulfate. This raises the possibility that the replacement of Cu^{2+} with Zn^{2+} ions might cause a structural switch for $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ also, and to investigate this, we have prepared several compounds in which small proportions of the Cu^{2+} ions are replaced with different fractions of Zn^{2+} ions.

Table 1. Crystallographic Data for $(ND_4)_2[Cu[Zn](D_2O)_6](SO_4)_2$ at 298 K

	Zn = 0.2%	Zn = 0.5%	Zn = 1.3%	Zn = 3.4%
formula	$D_{20}CuN_2O_{14}S_2$			
F_w	421.7			
space group	$P2_1/a$ (monoclinic)			
a (Å)	9.293(4)	9.281(6)	9.279(8)	9.208(6)
b (Å)	12.5051(5)	12.4999(8)	12.492(1)	12.4027(8)
c (Å)	6.194(1)	6.200(2)	6.208(2)	6.274(2)
β (deg)	106.35(3)	106.36(4)	106.38(5)	106.22(4)
V (Å^3)	690.7(3)	690.2(5)	690.4(7)	687.9(5)
Z	2			
D_{calc} (g cm^{-3})	1.93			
μ (cm^{-1})	20			
radiation	Mo Kα			
R^a	0.027	0.029	0.027	0.040
$R_w{}^b$	0.036	0.036	0.033	0.047

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, w (weight) $= [\sigma(F_o)]^{-2}$.

Experimental Section

Preparation of Compounds. The preparation of deuterated ammonium copper(II) sulfate hexahydrate has been described previously.[4] An identical procedure was used to prepare four samples in which 0.2%, 0.5%, 1.0%, and 2.0% of the $CuSO_4$, on a molar ratio basis, were replaced with $ZnSO_4 \cdot 7H_2O$. The resulting samples were recrystallized three times from 99.8% D_2O. The actual ratio of Zn/Cu was determined for each sample by analysis using a Varian SpectrAA-800 Atomic Absorption Spectrometer and was found to be 0.2%, 0.5%, 1.3%, and 3.4%, respectively. Comparison of the absolute determinations with the ratio of the Zn and Cu concentrations suggests that the values are accurate to better than 0.1%. A lower limit of 90% was obtained by mass spectroscopy for the deuterium concentration of the sample containing the greatest fraction of Zn.

Spectroscopy. EPR spectra were measured using a Bruker ESP300e spectrometer at X-band frequency (∼9 GHz) with the temperature measured and controlled using an Oxford Instruments ESR-910 flow cryostat with a ITC4 temperature controller.

X-ray Studies. The X-ray crystallographic studies were conducted using an Enraf-Nonius CAD4 MACH diffractometer with graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell constants and their standard deviations were determined by a least-squares treatment (CELDIM) of the angular coordinates of 25 high-angle 2θ reflections. The $\theta - 2\theta$ scan mode was used with a variable scan rate. The intensities of three check reflections showed no discernible decrease. All diffraction intensities were corrected for Lorentz and polarization effects and for absorption using seven ψ scans. Previously determined atomic coordinates[3] were used as the initial input. The structures were refined using full-matrix least-squares methods with anisotropic displacement factors for the non-H atoms and fixed isotropic B-values for the H's. Refinements were based on F, and computations were performed on a Dec-alpha computer using the teXsan software package. Unit cell parameters are given in Table 1, while the full details of data acquisition techniques and structure refinement results are deposited as Table S1 (Supporting Information). All atomic positions and isotropic displacement parameters, bond lengths, bond angles, hydrogen bonding contacts, and anisotropic displacement parameters have been deposited as Tables S2−7.

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10.1021/ic000329l CCC: $19.00

Table 2. Comparison of the Metal Oxygen Bond Lengths (Å) for Different Crystals of $(ND_4)_2[Cu[Zn](D_2O)_2](SO_4)_2$ in which a small Percentage of Cu was Replaced with Zn or Pure Deuterated (deut.) or Hydrogenous (hydrog.) Compounds

bond	deut.[a]	0.2% Zn	0.5% Zn	1.3% Zn	3.4% Zn	hydrog.[a]
M−O(7)	2.078(3)	2.078(2)	2.081(2)	2.089(2)	2.177(3)	2.210(2)
M−O(8)	2.222(3)	2.216(2)	2.208(2)	2.199(2)	2.098(3)	2.071(2)
M−O(9)	1.960(2)	1.953(2)	1.956(2)	1.956(2)	1.965(2)	1.959(2)

[a] Ref 8.

Results and Discussion

The basic unit cells of the four Zn-doped samples of $(ND_4)_2[Cu[Zn](D_2O)_6](SO_4)_2$ were found to be very similar to one another and to the reported unit cells of the pure copper(II) compound.[3] The general disposition of the anions and cations in the unit cell and atomic numbering system are identical to those described previously.[3] The most important aspect of the structures is the orientation of the distorted $Cu(D_2O)_6^{2+}$ ions. The Cu−O bond lengths are listed in Table 2, together with those of the pure hydrogenous and deuterated copper(II) compounds for comparison. Three different Cu−O bond distances occur, and in every case, the shortest bond is to O(9). For the three samples with lower Zn substitution, the longest bonds are to O(8), and the bonds of intermediate length are to O(7), as is characteristic of the form (A) adopted by pure deuterated ammonium copper(II) sulfate at ambient pressure.[1] For the sample where 3.4% of the Cu^{2+} ions are replaced by Zn^{2+} ions, the longest bonds are to O(7) and the bonds of intermediate length to O(8), as observed for the crystal structure of hydrogenous ammonium copper(II) sulfate (form B).[2]

It has been noted previously[3,7] that for deuterated ammonium copper(II) sulfate, the Cu−O(7) and Cu−O(8) bond lengths are much closer in value at room temperature than at low temperature (Cu−O(7) = 2.009(1) Å, Cu−O(8) = 2.300(1) Å, and Cu−O(9) = 1.960(1) Å at 8 K).[3] This has been explained in terms of a thermal equilibrium involving the higher-energy crystal structure, form B.[4] Because the lengths of the two bonds are interchanged in forms A and B, this leads to their partial averaging in the high-temperature crystal structure determination.[11] Detailed analysis of the temperature dependence of the Cu−O bond lengths and *g*-values suggests that the thermal behavior is strongly influenced by cooperative interactions.[8] It is of interest to see how this is influenced by Zn^{2+} ion substitution. The temperature dependence of the EPR spectrum of a powdered sample of $(ND_4)_2[Cu[Zn](D_2O)_6](SO_4)_2$ with 3.4% Zn substitution was measured between 4 and 295 K. The observed behavior was found to be very similar to that reported for the pure deuterated[8] and hydrogenous compounds,[12] suggesting that, at least at these low levels, the cooperative interactions are unaffected by the replacement of Cu^{2+} ions with Zn^{2+}. Thus, the *g*-values were found to be 2.055, 2.235, and 2.325 for the Zn-doped sample at 295 K and 2.075, 2.120, and 2.425 at 4 K, the change being almost complete upon cooling to ~150 K; for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, the *g*-values of 2.055, 2.215, and 2.355 were observed at 300 K, and 2.065, 2.110, and 2.426 were observed at 4 K, with the change also occurring predominantly in the 150−300 K region.[8,12] The influence of the metal ion substitution on the position of the equilibrium may be seen from the variation of the Cu−O bond lengths as a function of Zn^{2+} ion concentration plotted in Figure 1. The values observed for the hydrogenous salt are included for comparison. It can be seen that there is a slight convergence of the Cu−O(7) and Cu−O(8) lengths as the concentration increases from zero to 1.3%, with the structure then switching sharply when the Zn level rises to 3.4%. While a slight change in the position of the equilibrium is apparent, it appears to be relatively insensitive to Zn substitution, at least at these low levels.

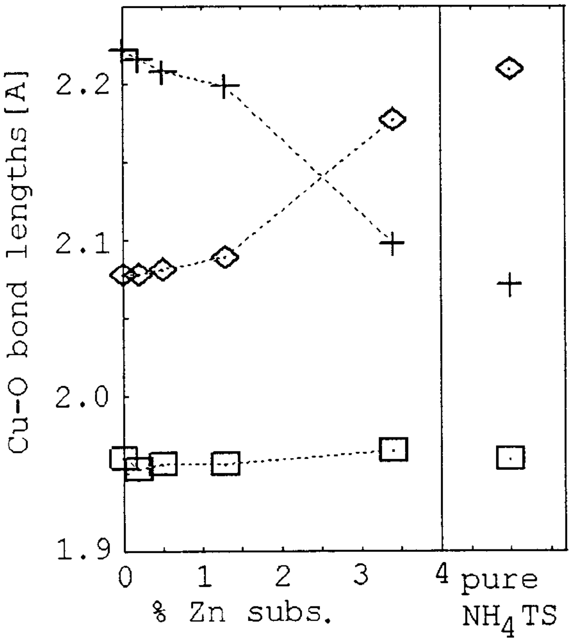

Figure 1. Variation in Cu−O(7), Cu−O(8), and Cu−O(9) bond lengths (diamonds, crosses, and squares, respectively) for $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ as a function of the percentage of Cu^{2+} ions replaced by Zn^{2+}. The values for the hydrogenous salt are shown for comparison.

In this respect, the influence of Zn^{2+} ion substitution is similar to that observed upon the increase of pressure. When the pressure rises progressively from 0 to ~400 bar at room temperature, comparatively little change in the unit cell parameters and molecular *g*-values of deuterated ammonium copper(II) sulfate is observed. However, when the pressure is raised further to 450 bar, a switch to the unit cell and EPR parameters of form B occurs.[5] It has been suggested[8] that the reason the compound tends to adopt either one crystal form or the other, with an intermediate structure being unfavorable, relates to the cooperative interactions in the compound. The switching of directions for the bonds of one complex makes it energetically more favorable for neighboring complexes, and, indeed, for the whole surrounding lattice, to change to the higher-energy form. For this reason, it was proposed that the equilibrium may largely involve fluctuating domains of the two forms rather than changes of isolated complexes,[8] with hydrogen bonding interactions playing a key role in this process. Indeed, the fact that deuterated and hydrogenous ammonium copper(II) sulfate adopt different crystal forms at ambient pressure is due presumably to the influence of isotopic substitution upon the hydrogen-bonding interactions. The hydrogen bond lengths in the Zn-doped salts should potentially provide useful information on this question, but the uncertainties in the data from the present X-ray study (Table S4) are too large for useful conclusions to be drawn. Low-temperature neutron-diffraction studies are planned to investigate this aspect.

Since Zn substitution in deuterated ammonium copper(II) sulfate has an effect on the structure similar to that of the application of pressure, it might be thought that the replacement of Cu^{2+} with the larger Zn^{2+} ions simply generates an “internal”

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pressure in the crystal lattice and that this pressure causes the switch. However, such reasoning appears to be too simplistic. The dynamic behavior of the ammonium copper(II) sulfate in some ways resembles that of iron(II) complexes which exhibit "high-spin−low-spin equilibria".[13] Such iron(II) complexes have a smaller volume in the low-spin state, and the application of pressure invariably shifts the equilibrium in the direction of this form. However, when a fraction of the Fe^{2+} ions are replaced by larger Zn^{2+} ions, the equilibrium shifts in favor of the larger high-spin iron(II) complex. This occurs because the substitution induces a general expansion of the crystal lattice, causing, in effect, a "negative" pressure to act on the Fe(II) complexes, and this favors the larger high-spin form. If similar reasoning is applied to the effect of Zn^{2+} ion substitution on the structure of deuterated ammonium copper(II) sulfate, Zn^{2+} substitution should inhibit the change to the more dense form B rather than cause it. However, unlike the iron(II) spin isomers, the structural difference between the two forms of ammonium copper(II) sulfate involves the packing of highly distorted complexes with essentially identical volumes, and it seems probable that the replacement of Cu^{2+} (and Cr^{2+}) with Zn^{2+} influences the structure by its effect on this packing, though the precise mechanism is not clear.

Acknowledgment. The authors thank the Magnetic Resonance Centre of the University of Queensland for the facilities used in measuring the EPR spectra. M.A.H. thanks the Australian Research Commission for financial assistance.

Supporting Information Available: Full crystallographical details (Table S1), positional and thermal parameters for all structures (Table S2), bond lengths S3, intermolecular hydrogen bonds, intramolecular hydrogen bonds (Table S5), bond angles (Table S6), and anisotropic displacement parameters (Table S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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