

Notes

Influence of Deuteration on the Crystal Structure of $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$

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Introduction

The Tutton salts of general formula $\text{M}^{\text{I}}_2[\text{M}^{\text{II}}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ provide a convenient group of compounds to investigate the influence of various factors on the geometric and electronic properties of the hexahydrate complexes of divalent metal ions. The ammoniumcopper(II) Tutton salt is of particular interest because of the significant change in crystal structure that occurs upon deuteration.^{1,2} Deuteration causes the long axis of the distorted $\text{Cu}(\text{D}_2\text{O})_6^{2+}$ cation to switch from one pair of water molecules to another pair, this being accompanied by slight alterations in the orientations and hydrogen-bonding interactions of the ammonium and sulfate ions.³ However, the structural switch is reversed upon raising the pressure,³ this change exhibiting hysteresis when the pressure is decreased.⁴ Both $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ and its deuterated analogue exhibit thermal equilibria involving the other crystal form,^{1,5} and it has been suggested that cooperative interactions play a significant role in these.⁵ Thermal equilibria involving the orientations of the Jahn–Teller-distorted $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions formed when $\sim 1\%$ Cu^{2+} is doped into various diamagnetic Tutton salts also occur. These have been studied extensively by EPR spectroscopy,^{5–9} and a model has been developed that relates the geometry and orientation of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ to the influence of the surrounding host lattice.⁹

Ammoniumcopper(II) sulfate is unique in exhibiting a switch in the direction of the long axis of the Jahn–Teller distortion upon deuteration, and there has been speculation on the possible

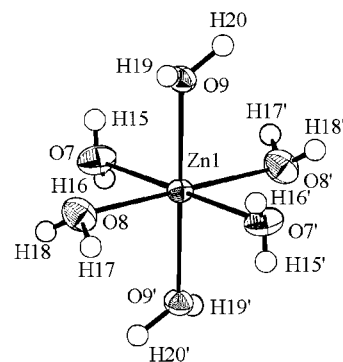


Figure 1. $\text{Zn}(\text{H}_2\text{O})_6^{2-}$ ion in $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ employing 50% probability thermal ellipsoids.

cause of the change in structure. It was suggested that the increase in ligand mass might play a role,¹⁰ but this may be discounted because no structural switch occurs when the water molecules are isotopically substituted with ^{18}O .¹¹ The most plausible explanation therefore seems to be that deuteration influences the lattice forces acting on the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion via its effect on the hydrogen-bonding interactions.¹¹ If this is the case, deuteration might also influence the bond lengths in the hexahydrate complex of a non-Jahn–Teller-active metal ion such as Zn^{2+} , and to test this hypothesis, we have determined the crystal structure of the ammoniumzinc(II) Tutton salt and its deuterated analogue. The structure determinations also allow the orientation of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions deduced from the EPR spectra of the Cu^{2+} -doped zinc(II) complexes to be related to the geometries of the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ ions in the host crystal lattices. To provide information on the way these interactions change with temperature, the structures were determined at both 298 and ~ 110 K.

Experimental Section

Preparation of Compounds. Ammoniumzinc(II) sulfate hexahydrate was prepared by recrystallizing equimolar proportions of the two salts from water. The preparation and characterization of the deuterated compound have been reported previously.⁵

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 MACH diffractometer with graphite monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 θ – 2θ 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 coordinates¹² 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

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Table 1. Crystallographic Data for $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ at $T = 298$ and 110 K and for $(\text{ND}_4)_2[\text{Zn}(\text{D}_2\text{O})_6](\text{SO}_4)_2$ at $T = 298$ and 115 K

	$T = 298$ K	$T = 110$ K	$T = 298$ K	$T = 115$ K
formula	$\text{H}_{20}\text{ZnN}_2\text{O}_{14}\text{S}_2$	$\text{H}_{20}\text{ZnN}_2\text{O}_{14}\text{S}_2$	$\text{D}_{20}\text{ZnN}_2\text{O}_{14}\text{S}_2$	$\text{D}_{20}\text{ZnN}_2\text{O}_{14}\text{S}_2$
fw	401.7	401.7	421.7	421.7
space group	$P2_1/a$ (monoclinic)	$P2_1/a$ (monoclinic)	$P2_1/a$ (monoclinic)	$P2_1/a$ (monoclinic)
a (Å)	9.2360(4)	9.1515(7)	9.230(3)	9.1434(5)
b (Å)	12.5122(5)	12.3836(7)	12.5106(4)	12.3689(6)
c (Å)	6.2460(3)	6.2791(5)	6.2461(8)	6.2828(3)
β (deg)	106.860(4)	106.963(7)	106.83(2)	106.918(4)
V (Å ³)	690.78(5)	680.64(9)	690.4(3)	679.79(6)
Z	2	2	2	2
D_{calc} (g cm ⁻³)	1.93	1.96	2.03	2.06
μ (cm ⁻¹)	21.5	21.8	21.5	21.5
radiation	Mo K α	Mo K α	Mo K α	Mo K α
R^a	0.026	0.025	0.028	0.035
R_w^b	0.038	0.036	0.040	0.050

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

Table 2. Comparison of the Metal Oxygen Bond Lengths (Å) for $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_2](\text{SO}_4)_2$ and $(\text{ND}_4)_2[\text{Zn}(\text{D}_2\text{O})_2](\text{SO}_4)_2$ at High and Low Temperatures^a

bond	$(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_2](\text{SO}_4)_2$				$(\text{ND}_4)_2[\text{Zn}(\text{D}_2\text{O})_2](\text{SO}_4)_2$		Cu[H]	Cu[D]] ^b
	$T = 298$ K X-ray ^b	$T = 295$ K X-ray ^c	$T = 295$ K neutron ^c	$T = 110$ K X-ray ^b	$T = 298$ K X-ray ^b	$T = 115$ K X-ray ^b	$T = 9.5$ K X-ray ^d	$T = 15$ K neutron ^e
M–O(7)	2.110(2)	2.109(1)	2.115(2)	2.108(1)	2.114(2)	2.112(2)	2.2758(9)	2.022(2)
M–O(8)	2.107(2)	2.106(1)	2.113(2)	2.100(1)	2.107(2)	2.099(2)	2.0042(8)	2.310(2)
M–O(9)	2.061(2)	2.062(1)	2.061(2)	2.066(1)	2.057(2)	2.060(2)	1.9737(9)	1.966(3)

^a Values at low temperature for the corresponding hydrogenous (Cu[H]) and deuterated (Cu[D]) copper(II) salts are also given. ^b Present work. ^c Reference 12. ^d Reference 11. ^e Reference 3.

were performed on a Dec-alpha computer using the teXsan software package. Unit cell parameters and structure refinement results are summarized in Table 1. The atomic numbering is shown in Figure 1.

Results and Discussion

The basic unit cell of the ammoniumzinc(II) salt is similar to those of other Tutton salts^{1–3,10,11} and to that reported previously from a comparative neutron and X-ray diffraction study of the hydrogenous salt at room temperature.¹² The metal–oxygen bond lengths in the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ groups are shown in Table 2, and the room temperature values for the hydrogenous salt are in excellent agreement with those of the previously reported X-ray study of this compound.¹² The bond to O(9) is shortest, with that to O(7) being marginally but consistently slightly longer than that to O(8). Deuteration causes no significant change in the Zn–O distances. For both the hydrogenous and deuterated compound, cooling from 298 to ~110 K causes slight decreases in the lengths of the bonds to O(7) and O(8) but a small increase in that to O(9). The hydrogen-bonding contacts to the water molecules are also essentially identical for the two compounds (Table 5 of Supporting Information).

For the ammoniumcopper(II) Tutton salt at 1 bar pressure the long and intermediate Cu–O bonds occur to different pairs of water molecules for the deuterated salt compared with the hydrogenous compound (Table 2).^{1,2} However, when the pressure is raised to above ~500 bar at room temperature, the structure of the deuterated compound switches to that of the hydrogenous form.^{3,4} The hydrogenous and high-pressure form of the deuterated copper(II) salt have structures in which the longest metal–oxygen bond is to O(7) and the bond of intermediate length is that to O(8), a trend similar to that observed for the hydrogenous and deuterated zinc(II) compounds (Table 2). However, the deuterated ammoniumcopper(II) salt has the longest and intermediate Cu–O bonds to O(8) and to O(7), respectively. It was hoped that the ammoniumzinc(II) Tutton salt would exhibit structural changes on deuteration,

Table 3. Deviations in the Zn–O Bond Lengths from Their Average Values for the Ammoniumzinc(II) Tutton Salt and Its Deuterated Analogue Compared with Estimates Derived from the EPR Spectra of the Cu²⁺-Doped Salts

compound	temp (K)	deviations from the average bond length (Å)		
		Zn–O(7)	Zn–O(8)	Zn–O(9)
$(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$	298	0.017	0.014	–0.032
	110	0.017	0.009	–0.025
$(\text{ND}_4)_2[\text{Zn}(\text{D}_2\text{O})_6](\text{SO}_4)_2$	298	0.021	0.014	–0.036
	115	0.022	0.009	–0.030
EPR analyses ^a	4.6–298	0.019	0.009	–0.028

^a Data from refs 3 and 9. The analyses treated data obtained over the temperature range 4.6–298 K, and similar results were obtained for the hydrogenous and deuterated host lattices.

which might indicate why the copper(II) compound switches structure when deuterated, but this is not the case.

The EPR spectra of ~1% Cu²⁺ doped into single crystals of hydrogenous and deuterated $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ have been reported.^{5,7,9} The orientations of the g tensors were used to deduce the orientation of the distorted guest $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions in the host lattices, and both the hydrogenous and deuterated compounds follow the sequence Cu–O(9) < Cu–O(8) < Cu–O(7). The same sequence occurs for the hydrogenous and deuterated zinc(II) compounds, the hydrogenous ammonium-copper(II) Tutton salt,² and the deuterated salt at high pressure,³ though the distances to O(7) and to O(8) are reversed in the latter at ambient pressure. In the doped compounds it is thus the structure of the host lattice that determines the orientation of the distorted $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion, and for both the hydrogenous and deuterated zinc(II) salts, this favors an orientation similar to that of the pure hydrogenous copper(II) compound.

The g anisotropies and temperature dependence of the g values were used to deduce the strains induced on the guest $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions by the hydrogenous and deuterated zinc(II) host lattices.^{5,9} Similar results were obtained for the two host lattices, with the copper(II) complex experiencing a relative

compression along the direction of the Zn–O(9) bond, a lesser compression along Zn–O(8), and the least interaction along Zn–O(7). The lattice strain parameters derived from the EPR spectra of the Cu²⁺ complexes may be used to estimate the changes in bond length, which such interactions would cause in the non-Jahn–Teller-active Zn(H₂O)₆²⁺ ion,⁹ and these are compared with the data from the present structure determinations in Table 3. Agreement with the bond length deviations observed at ~110 K is excellent, suggesting that similar lattice interactions act on the guest Cu(H₂O)₆²⁺ ion as on the host complex.

Comparison of the structures at 298 and ~110 K suggests that the Zn(H₂O)₆²⁺ ions experience a slightly stronger compression along the Zn–O(9) direction and that the strains along Zn–O(7) and Zn–O(8) are more nearly equal at 298 K than at low temperature. If a similar trend also occurs for the guest Cu²⁺ complexes, it implies that the lattice strain parameters should change with temperature, with the axial strain decreasing and the orthorhombic component increasing on cooling. The effect is relatively small, and the treatments of the temperature

dependence of the *g* values of Cu²⁺-doped hydrogenous and deuterated (NH₄)₂[Zn(H₂O)₆](SO₄)₂ and other zinc(II) Tutton salts have not required such a refinement.^{5–9} However, recent measurements of the EPR spectra of Cu²⁺-doped Cs₂[Zn(H₂O)₆](ZrF₆)₂ and the ammoniummagnesium Tutton salt suggest that the lattice strain parameters do alter as a function of temperature, the behavior being consistent with changes in structure directly analogous to those observed in the present determinations.¹³

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Supporting Information Available: Tables giving atomic coordinates and isotropic thermal parameters, selected bond lengths, hydrogen bond lengths, intramolecular distances, bond angles, and full experimental details for all crystal structure determinations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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