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X-ray Structural Characterization of a Pair of Isotypic Tetraaqua Compounds of the Jahn–Teller Species Chromium(II) and Copper(II)

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The recrystallization of hexaaquachromium(II) hexafluorosilicate and its copper analog from hexafluorosilicic acid gives the $[M(H_2O)_4]SiF_6$ compounds. These compounds are isotypic and crystallize in the monoclinic space group $P2_1/c$ forming an extended structure of nearly square tetraaqua species that are weakly linked by SiF_6^{2-} ions into infinite chains. For the chromium compound $[Cr(H_2O)_4]SiF_6$, $a = 5.444(1)$ Å, $b = 9.813(2)$ Å, $c = 7.350(1)$ Å, and $\beta = 104.91(1)°$. The structure has been refined to a final R factor of 0.025 based on 784 observed independent reflections. For the copper analog the cell dimensions are $a = 5.3434(7)$ Å, $b = 9.619(1)$ Å, $c = 7.234(1)$ Å, and $\beta = 105.16(1)°$. The structure has been refined to a final R factor of 0.020 based on 733 observed independent reflections. In each case, the central atom resides on a crystallographic inversion center. The M–OH_2 bonds are short (average values of 2.041 and 1.951 Å for Cr and Cu, respectively) while the M···F distances are very long (2.3964(8) and 2.3399(8) Å, for Cr and Cu, respectively).

Introduction

While studying the series of hexaaqua compounds of the divalent cations of the first transition series[2] (FTS), we found that the nature of the hexafluorosilicate products was different depending on the concentration of acid used during the crystallization for the cases of the Jahn–Teller active species Cr and Cu. Upon recrystallization from water, the very unstable $[M(H_2O)_6]SiF_6$[2,3] species were obtained, but from solutions containing a high concentration of hexafluorosilicic acid different, more stable compounds could be isolated. For copper, that product had been correctly identified as the tetraaqua species, but only a rough crystal structure had been reported.[4]

Since there are very few precise crystal structure determinations of compounds containing divalent chromium with water as a ligand[2,5] we decided to undertake the structural characterization of the chromium compound. We found that it was isotypic with the copper compound (*vide infra*). To our knowledge, there is only one other example of tetraaqua metal species for copper and chromium, namely, the $MSO_4{\cdot}5H_2O$ compounds for which precise structural data are available.[6,7] Their formulae are best described as $\{[M(H_2O)_4]SO_4\}H_2O$. We also decided to do a more precise structural study of $[Cu(H_2O)_4]SiF_6$.

Table I. Crystal Data for $[M(H_2O)_4]SiF_6$ (M = Cr, Cu)

	Cr	Cu
formula	$MSiF_6O_4H_8$	
fw	266.13	277.7
space group	$P2_1/c$	
a, Å	5.444(1)	5.3434(7)
b, Å	9.813(2)	9.619(1)
c, Å	7.350(1)	7.234(1)
β, deg	104.91(1)	105.16(1)
V, Å^3	379.4(2)	358.9(1)
Z	2	
d_{calcd}, g/cm^3	2.33	2.57
μ(Mo Kα), cm^{-1}	17.17	33.09
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)	
temp, °C	22(1)	
transm factors		
max	0.9960	0.9996
min	0.8735	0.7845
R^a	0.025	0.020
$R_w{}^b$	0.041	0.040

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

Experimental Section

For the preparation of the divalent chromium compounds, all operations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Deionized water was deoxygenated by prolonged refluxing in a nitrogen atmosphere and distilled just before it was used. Metals were purchased from Johnson Matthey Electronics with a purity of 99.95% or better. Purified ammonium carbonate (Fisher Scientific) was used as received. Hexafluorosilicic acid and copper carbonate were prepared as reported before.[2]

$[Cr(H_2O)_4]SiF_6$. The compound was prepared in an entirely analogous manner to $[Cr(H_2O)_6]SiF_6$,[3] except that the crystals were filtered and redissolved in a minimum amount of hexafluorosilicic acid to which a layer of ethanol was added. After several days at 0 °C, long crystals were collected. The same product was also obtained simply by recrystallization of pure $[Cr(H_2O)_6]SiF_6$ in hexafluorosilicic acid followed by of the addition of an ethanol layer.

$[Cu(H_2O)_4]SiF_6$. Copper carbonate hydrate was slowly added to a solution of hexafluorosilicic acid until the solid no longer dissolved. Another equivalent volume of hexafluorosilicic acid was added, and the solution was allowed to stand in air for several days until long blue crystals formed. The same product was obtained by dissolving $[Cu(H_2O)_6]SiF_6$ in hexafluorosilicic acid followed by slow evaporation of water.

X-ray Structure Analyses. Similar procedures were used for both the Cr and Cu compounds. Crystals were mounted on glass fibers and preliminary orientation reflections were taken from 360° ϕ-rotation photographs. In each case data were collected in the $+h,\pm k,\pm l$ hemisphere, and a series of azimuthal scans of reflections having Eulerian angle χ near 90° were used as the basis of an empirical absorption

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[Cr(H_2O)_4]SiF_6$ and $[Cu(H_2O)_4]SiF_6$[a]

	M = Cr				M = Cu			
atom	*x*	*y*	*z*	*B*, Å²	*x*	*y*	*z*	*B*, Å²
M	0.000	0.000	0.000	1.396(5)	0.000	0.000	0.000	1.206(5)
Si	0.500	0.000	0.500	1.285(9)	0.500	0.000	0.500	1.08(1)
F(1)	0.3088(2)	0.0417(1)	0.2920(1)	3.28(2)	0.2992(2)	0.0485(1)	0.2923(1)	2.25(2)
F(2)	0.7228(2)	0.10566(8)	0.4564(1)	2.79(2)	0.7301(2)	0.10545(9)	0.4543(1)	2.08(2)
F(3)	0.6201(2)	–0.13094(7)	0.3990(1)	2.61(2)	0.6098(2)	–0.13357(8)	0.3894(1)	1.92(2)
O(1)	–0.1395(2)	–0.15868(9)	0.1227(1)	2.24(2)	–0.1254(2)	–0.1575(1)	0.1209(2)	1.79(2)
O(2)	–0.2304(2)	0.13334(8)	0.0908(1)	2.27(2)	–0.2380(2)	0.1258(1)	0.0800(1)	1.78(2)
H(1)	–0.198(3)	–0.146(2)	0.187(2)	1.4(4)*	–0.208(3)	–0.207(2)	0.049(2)	0.02(2)*
H(2)	–0.215(3)	–0.228(2)	0.052(2)	1.2(4)*	–0.227(3)	–0.148(2)	0.195(3)	0.2*
H(3)	–0.234(3)	0.209(2)	0.066(2)	1.2(4)*	–0.237(3)	0.123(2)	0.171(3)	0.2*
H(4)	–0.244(3)	0.129(2)	0.180(3)	1.3(4)*	–0.232(3)	0.197(2)	0.045(2)	0.2*

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. An asterisk denotes values for atoms refined isotropically.

Table III. Bond Distances (Å) and Angles (deg) for $[M(H_2O)_4]SiF_6$ (M = Cr, Cu)[a]

distances	M = Cr	M = Cu	distances	M = Cr	M = Cu
M–F(1)	2.3964(8)	2.3399(8)	Si–F(1)	1.6640(8)	1.6686(8)
M–O(1)	2.042(1)	1.953(1)	Si–F(2)	1.6879(9)	1.6916(9)
M–O(2)	2.040(1)	1.949(1)	Si–F(3)	1.6968(8)	1.6973(9)

angles	M = Cr	M = Cu	angles	M = Cr	M = Cu
F(1)–M–O(1)	89.40(3)	89.05(4)	F(1)–Si–F(2)	89.13(4)	89.18(4)
F(1)–M–O(2)	86.92(3)	87.29(4)	F(1)–Si–F(3)	90.25(4)	90.42(5)
O(1)–M–O(2)	90.84(4)	91.23(4)	F(2)–Si–F(3)	90.32(4)	90.19(4)
M–F(1)–Si	155.47(6)	152.19(6)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

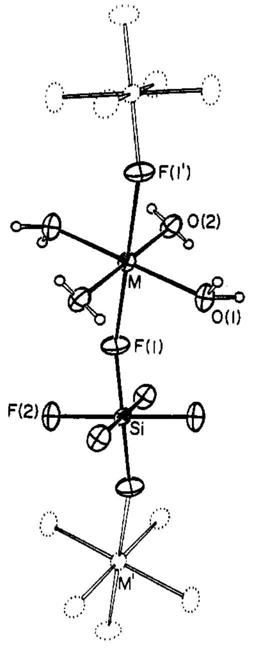

Figure 1. Representation of the chain structure of the $[M(H_2O)_4]SiF_6$ compounds (M = Cr, Cu).

correction. Following Lorentz, polarization, and absorption corrections, equivalent data were averaged with $R_{int} = 0.011$ for both the Cr and the Cu data sets.

The starting positions of the non-hydrogen atoms used for least-squares refinement of the Cr structure were taken from a direct-methods *E*-map. Hydrogen atoms were later located in a difference map and were included in the final stages of refinement with isotropic temperature factors. Starting positions of the non-hydrogen atoms for the copper compound were taken directly from the chromium structure. Hydrogen atoms were also included in the refinement, but in this case a single common temperature factor was refined for the hydrogen atoms.[8] Important data collection and refinement parameters are recorded in Table I. Table II contains positional parameters for both structures. Some important distances and angles are given in Table III.

Results and Discussion

The crystal structures of $[M(H_2O)_4]SiF_6$ (M = Cr, Cu) are isotypic. They crystallize in space group $P2_1/c$. The metal atom occupies a site of $\bar{1}$ symmetry, as does the silicon atom. As shown in Figure 1 the structure consists of infinite chains formed by nearly regular square planar $[M(H_2O)_4]^{2+}$ moieties linked by the SiF_6^{2-} anions. An extensive array of hydrogen bonds links the chains. The structures are also isotypic with those of $[Cu(H_2O)_4]MF_6$ (M = Ti, Zr), described by Fischer and Weiss[9] in a study which included structures of compounds of the type $NH_4CuMF_7 \cdot 4H_2O$ (M = Si, Ti, Sn).[10]

Both tetraaqua hexafluorosilicate compounds described here display a highly distorted octahedral arrangement of the ligands about the metal center as would be expected from the Jahn–Teller effect. In both cases one of the axes is very elongated while the others are compressed. The atom arrangement can almost be considered as square planar. When the average of the short distances is used, the magnitude of the change is *ca.* 0.35 and 0.39 Å for chromium and copper, respectively. This change is slightly smaller than those found for the only other isotypic tetraaqua species known, the $MSO_4 \cdot 5H_2O$ compounds. In that case, there are two independent molecules in the crystal and the differences are 0.37 and 0.40 Å for chromium and 0.41 and 0.49 Å for copper. With the limited amount of data available it is difficult to generalize, but if the considerations of the preceding paper[2a] are followed, it seems reasonable to expect a larger dispersion of the distances for the copper compounds. Also it is noteworthy that the bond that stretches the most is normally the one to the less basic ligand. This is in accord with our previous observations[5] in which it was shown that if more basic ligands such as pyridine or pyridine-like ligands are coordinated to the chromium atom along with water molecules, then it is one of the trans pairs of Cr-to-water distances that elongates.

In general, as shown in Table IV, the variation in the short distances is very small, namely 0.04 Å for chromium and 0.08 Å for copper. However, the longer bonds vary over a larger

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(8) Refinement calculations were carried out on a Local Area VAX cluster using the SDP programs.

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Table IV. Comparison of the Metal(II)–Ligand Distances in Six-Coordinate $M(H_2O)_4L_2$ Species for M = Cr and Cu and L ≠ H_2O

compound	M–O(water)–Distances(Å)			M–L			ref
$Cr(H_2O)_4SiF_6$	2.042(1)			2.3964(8)			this work
	2.040(1)						
$CrSO_4 \cdot 5H_2O$[a]	I	II		I	II		6
	2.0532(13)	2.0535(9)		2.4216(8)	2.4587(8)		
	2.0521(8)	2.0535(9)					
$Cr(H_2O)_4Cl_2$	2.081(25)			2.758(9)			11
	2.074(25)						
$Cu(H_2O)_4SiF_6$	1.953(1)			2.3399(8)			this work
	1.949(1)						
$CuSO_4 \cdot 5H_2O$[a]	I	II		I	II		7
	1.964(1)	1.960(1)		2.382(1)	2.434(1)		
	1.971(1)	1.932(1)					
$CuSO_4 \cdot 5H_2O$[a–c]	I	II		I	II		12
	1.986	1.980		2.380	2.436		
	1.983	1.944					
$CuBF_4 \cdot 5H_2O$	I	II		I	II		13
	1.966(2)	1.949(2)		2.318(1)	2.380(2)		
	1.964(2)	1.926(2)					
$[Cu(H_2O)_4](ClO_3)_2$[d]	i	ii		i	ii		14
	1.938(2)	1.939(2)		2.396(2)	2.388(2)		
	1.979(2)	1.977(2)					
$Cu_3V_2F_{12} \cdot 12H_2O$[e]	I	II	III	I	II	III	15
	1.975(2)	1.962(2)	1.973(2)	2.200(1)	2.412(2)	2.327(2)	
	1.983(2)	1.941(2)	1.948(2)				
$Cu_3Fe_2F_{12} \cdot 12H_2O$[e]	I	II	III	I	II	III	15
	1.979(2)	1.967(2)	1.968(2)	2.205(2)	2.412(2)	2.327(2)	
	1.979(2)	1.938(2)	1.950(2)				
$Cu_3Cr_2F_{12} \cdot 12H_2O$[e]	I	II	III	I	II	III	15
	1.977(2)	1.962(2)	1.967(2)	2.204(1)	2.427(2)	2.325(2)	
	1.976(2)	1.935(2)	1.951(2)				
$Cu(H_2O_4ZrF_6$[f]	2.011(6)			2.246(6)			9a
	1.947(5)						

[a] Two independent metal centers in the crystal. [b] Standard deviations were not reported. [c] Neutron diffraction study. [d] Two different temperatures: (i) 296 K; (ii) 223 K. [e] Three independent metal centers in the crystal. [f] Distances calculated from positional parameters given in the reference.

range in this type of compound. For chromium the change is 0.36 Å and that for copper is 0.23 Å.[11-15]

It is clear that the metal-to-ligand distances are quite flexible and we presume that in many cases they are governed by the efficiency with which the hydrogen bonds can be formed.

As mentioned in the Introduction, the chemical stability of the $[M(H_2O)_4]SiF_6$ compounds of Cr and Cu relative to that of the corresponding hexaaqua species is very enhanced. While crystals of the first type persist for long periods of time, crystals of the hexaaqua compounds are extremely unstable, even toward water.

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Supplementary Material Available: Complete tables of crystallographic parameters, bond distances, bond angles, and general displacement parameters (6 pages). Ordering information is given on any current masthead page.