

Hexaaqua Divalent Ions of the First Transition Series: New and Accurate Structures; Expected and Unexpected Trends

F. Albert Cotton,^{*,1a} Lee M. Daniels,^{1a} Carlos A. Murillo,^{*,1a,b} and Jaime F. Quesada^{1b}

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843–3255, and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Received February 26, 1993*

An accurate, X-ray crystallographic redetermination of the structures of both the ammonium Tutton salts and the hexafluorosilicates of the divalent hexaaqua species that are formed by the elements of the first transition series, namely, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, is presented here. For the Tutton salts, the metal-to-water bond distances show minima at vanadium and nickel as expected from ligand field theory considerations. For the second series of compounds, vanadium and chromium deviate unexpectedly from the pattern. A comparison of the variation of the metal-to-water distances in other hexaaqua compounds is also given and the general trends are discussed. Special attention is given to the suppression of the Jahn–Teller effect in the hexaaqua hexafluorosilicate compounds of Cr(II) and Cu(II).

Introduction

In our earlier studies of Jahn–Teller active compounds of chromium(II), our desire to make comparisons of the chromium-to-ligand bond distances with those in other compounds, both those of chromium(II) itself and those containing other divalent cations of the first transition series (FTS), has been generally frustrated by lack of reliable data. In all of our studies the ligand of preeminent interest has been H₂O.² Much to our surprise, we have found that the number of compounds containing [M(H₂O)_n]²⁺ moieties for which precise crystal structures are available is extremely small for chromium(II)³ and even smaller for vanadium(II).⁴ Even more surprisingly, accurate structural characterizations of compounds containing the very important [M(H₂O)₆]²⁺ ions of the FTS elements are very few in number.⁵

In addition to the limited data base of precise structures, there are other problems worth noting. One concerns the possible effect of unrecognized impurities on the crystal structures of compounds of Jahn–Teller active Cr^{II} and Cu^{II}. As our previous work has shown,⁶ solid solutions containing both Cr^{II} and Zn^{II} can easily be made and the metal–ligand distances found are then not the same as those in either of the pure compounds.

For chromium this is an important consideration since an easy way to prepare chromium(II) solutions in the laboratory is by reducing chromium(III) species with the Jones reductor (Zn/Hg). In the case of the crystallization of mononuclear compounds, many times both chromium and zinc are incorporated in the crystalline products.⁷ Many other possible combinations with other metals also occur, examples of which are [(V_{1-x}Ni_x)(H₂O)₆]-SO₄⁸ and (NH₄)₂[V_{0.45}Zn_{0.55}(H₂O)₆](SO₄)₂.⁹

Following our studies on the Cr/Zn solid solutions of the ammonium Tutton salts, (NH₄)₂[Cr_xZn_{1-x}(H₂O)₆](SO₄)₂,⁶ we decided to undertake a study of the entire series of pure Tutton salts and to redetermine each structure making sure of the purity with respect to the metal atom. The Tutton compounds are important because hundreds of studies have been reported for them and they afford a rare example of isotypic structures extending right across the FTS from which the least ambiguous structural comparisons can be drawn. Unfortunately many of the other known series of [M(H₂O)₆]²⁺ compounds of the FTS crystallize differently from metal to metal, as is the case, for example, with the nitrates.¹⁰ In other cases, such as in the sulfates, there are even changes in the stoichiometry. Hexaaqua compounds of the type [M(H₂O)₆]SO₄ are simply not known for chromium¹¹ or copper,¹² although they are known for others.¹³

The ammonium Tutton salts have already been studied extensively by diffraction methods.¹⁴ Unfortunately, not all of the structural data are available at one temperature. For comparison purposes, this is an important consideration since it has been shown, at least in the cases of the Jahn–Teller-active species chromium(II) and copper(II),³ that there are large variations in the structural parameters as the temperature is changed.^{15,16} Also, in some cases, data come from neutron

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

- (1) (a) Texas A&M University (b) University of Costa Rica.
- (2) (a) Cotton, F. A.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Valle, G. *Inorg. Chem.* **1984**, *23*, 4038. (b) Cotton, F. A.; Falvello, L. R.; Murillo, C. A.; Quesada, J. F. *J. Solid State Chem.* **1992**, *96*, 192 and references therein.
- (3) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Polyhedron* **1992**, *11*, 2475.
- (4) Cotton, F. A.; Daniels, L. M.; Montero, M. L.; Murillo, C. A. *Polyhedron* **1992**, *11*, 2767.
- (5) We have taken the arbitrary but practical threshold of accuracy to be an esd of 0.005 Å. On this basis the result is accurate to 0.01 Å at about the 99% confidence level.
- (6) Araya, M. A.; Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Murillo, C. A. *Inorg. Chem.*, preceding paper in this journal and references therein.
- (7) Broderick, W. E.; Pressprich, M. R.; Geiser, U.; Willet, R. D.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 3372.
- (8) Kutoglu, A. Z. *Kristallogr.* **1973**, *137*, 51.
- (9) Deeth, R. J.; Figgis, B. N.; Forsyth, J. B.; Kucharski, E. S.; Reynolds, P. A. *Aust. J. Chem.* **1988**, *41*, 1289.
- (10) (a) Ribár, B.; Petrović, D.; Djurić, S.; Krstanović, I. Z. *Kristallogr.* **1976**, *144*, 334. (b) Prelenski, B. V.; Gabela, F.; Ribár, B.; Krstanović, I. *Crystallogr. Struct. Commun.* **1973**, *2*, 581. (c) Bigoli, F.; Braibanti, A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Acta Crystallogr.* **1971**, *B27*, 1427. (d) Ferrari, A.; Braibanti, A.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Acta Crystallogr.* **1967**, *22*, 240.
- (11) (a) Hitchman, M. A.; Lichon, M.; McDonald, R. G.; Smith, P. W.; Stranger, R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1817. (b) Vaalstra, T. P.; Maslen, E. N. *Acta Crystallogr.* **1987**, *B43*, 448.
- (12) Bacon, G. E.; Curry, N. A. *Proc. R. Soc. London, A* **1962**, *266*, 95.
- (13) (a) Cotton, F. A.; Falvello, L. R.; Llusar, R.; Libby, E.; Murillo, C. A.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 3423. (b) Elerman, Y. *Acta Crystallogr.* **1988**, *C44*, 599. (c) Stadnicka, K.; Glazer, A. M.; Koralewski, M. *Acta Crystallogr.* **1987**, *B43*, 319.
- (14) Petruševski, V.; Aleksovskva, S. *Croat. Chem. Acta* **1991**, *64*, 577 and references therein.
- (15) Figgis, B. N.; Kucharski, E. S.; Reynolds, P. A. *Acta Crystallogr.* **1990**, *B46*, 577.
- (16) (a) Alcock, N. W.; Duggan, M.; Murray, A.; Tyagi, S.; Hathaway, B. J.; Hewat, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 7. (b) Hathaway, B. J.; Hewat, A. W. *J. Solid State Chem.* **1984**, *51*, 364.

Table I. Crystal Data for $(\text{NH}_4)_2[\text{M}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, and Zn)

| | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| formula | $\text{MS}_2\text{O}_{14}\text{N}_2\text{H}_{20}$ | | | | | | | |
| fw | 387.23 | 388.29 | 391.23 | 392.14 | 395.23 | 395.00 | 399.83 | 401.66 |
| space group | $P2_1/c$ | | | | | | | |
| <i>a</i> , Å | 6.221(1) | 6.200(1) | 6.233(1) | 6.233(1) | 6.2358(7) | 6.238(1) | 6.297(1) | 6.254(2) |
| <i>b</i> , Å | 12.588(4) | 12.703(2) | 12.664(2) | 12.566(2) | 12.510(1) | 12.457(3) | 12.372(2) | 12.500(4) |
| <i>c</i> , Å | 9.283(4) | 9.431(1) | 9.353(1) | 9.270(1) | 9.253(1) | 9.177(1) | 9.201(1) | 9.224(2) |
| β , deg | 107.00(2) | 106.66(1) | 106.89(1) | 106.78(1) | 107.03(1) | 106.91(1) | 106.12(1) | 106.87(2) |
| <i>V</i> , Å ³ | 695.2(7) | 711.5(2) | 706.4(2) | 695.1(2) | 690.2(1) | 682.3(4) | 688.7(2) | 690.1(3) |
| <i>Z</i> | 2 | | | | | | | |
| <i>d</i> _{calc} , g/cm ³ | 1.850 | 1.812 | 1.839 | 1.873 | 1.902 | 1.923 | 1.928 | 1.933 |
| μ cm ⁻¹ | 95.32 | 11.32 | 110.88 | 122.37 | 15.98 | 17.90 | 19.48 | 21.80 |
| radiation (monochromated in incident beam) ^a | Cu | Mo | Cu | Cu | Mo | Mo | Mo | Mo |
| temp, °C | 22(1) | | | | | | | |
| transm factors: | | | | | | | | |
| max | 1.000 | 0.9979 | 1.000 | 1.000 | 0.9989 | 0.9998 | 0.9985 | 0.9982 |
| min | 0.784 | 0.9385 | 0.671 | 0.637 | 0.9263 | 0.7185 | 0.8576 | 0.7802 |
| <i>R</i> ^b | 0.029 | 0.024 | 0.045 | 0.026 | 0.020 | 0.026 | 0.021 | 0.032 |
| <i>R</i> _w ^c | 0.048 | 0.043 | 0.065 | 0.035 | 0.036 | 0.042 | 0.034 | 0.041 |

^a Mo K α ($\lambda_x = 0.71073$ Å); Cu K α ($\lambda_x = 1.54184$ Å). ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional and Equivalent Isotropic Displacement Parameters for the Non-Hydrogen Atoms of the Tutton Salts (for Each Atomic Site, Coordinates Given for All Eight Metals in the Study)^a

| atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eqv} | metal | atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eqv} |
|------|-------------|------------|-------------|-------------------------|-------|------|------------|-------------|-------------|-------------------------|
| M | 0.000 | 0.000 | 0.000 | 1.29(1) | V | O(2) | 0.0308(3) | 0.1131(1) | -0.1644(2) | 2.20(3) |
| | 0.000 | 0.000 | 0.000 | 1.600(9) | Cr | | 0.0415(3) | 0.1170(1) | -0.1802(1) | 3.07(3) |
| | 0.000 | 0.000 | 0.000 | 2.31(2) | Mn | | 0.0307(5) | 0.1152(2) | -0.1677(3) | 3.01(6) |
| | 0.000 | 0.000 | 0.000 | 0.69(1) | Fe | | 0.0311(3) | 0.1130(1) | -0.1650(2) | 1.53(3) |
| | 0.000 | 0.000 | 0.000 | 1.440(4) | Co | | 0.0336(2) | 0.11156(8) | -0.1619(1) | 2.27(2) |
| | 0.000 | 0.000 | 0.000 | 1.285(5) | Ni | | 0.0344(2) | 0.10976(9) | -0.1601(1) | 1.92(2) |
| | 0.000 | 0.000 | 0.000 | 1.441(4) | Cu | | 0.0311(2) | 0.10868(9) | -0.1639(1) | 2.42(2) |
| | 0.000 | 0.000 | 0.000 | 1.618(8) | Zn | | 0.0349(2) | 0.1123(2) | -0.1618(2) | 2.41(3) |
| S | -0.26034(8) | 0.36277(4) | -0.09249(5) | 1.62(1) | V | O(3) | 0.3078(2) | -0.0716(1) | 0.0000(2) | 2.07(3) |
| | -0.25665(6) | 0.35859(3) | -0.10452(4) | 1.90(1) | Cr | | 0.2968(2) | -0.07156(9) | 0.0002(1) | 2.20(2) |
| | -0.2589(2) | 0.36219(8) | -0.09304(9) | 2.42(2) | Mn | | 0.3103(4) | -0.0735(2) | -0.0010(3) | 3.13(6) |
| | -0.25869(8) | 0.36262(4) | -0.09340(6) | 0.92(1) | Fe | | 0.3044(2) | -0.0713(1) | 0.0001(2) | 1.47(3) |
| | -0.25979(5) | 0.36352(2) | -0.09163(3) | 1.681(5) | Co | | 0.3016(1) | -0.06891(7) | -0.00047(9) | 2.07(2) |
| | -0.26101(6) | 0.36346(3) | -0.09212(4) | 1.510(6) | Ni | | 0.2998(2) | -0.06639(9) | 0.0024(1) | 1.85(2) |
| | -0.25453(5) | 0.36102(3) | -0.08960(3) | 1.744(5) | Cu | | 0.2822(2) | -0.06510(8) | -0.0052(1) | 1.98(2) |
| | -0.26024(7) | 0.36318(5) | -0.09240(5) | 1.72(1) | Zn | | 0.3007(2) | -0.0678(2) | 0.0010(2) | 2.10(3) |
| O(1) | 0.1674(2) | 0.1076(1) | 0.1742(2) | 2.16(3) | V | O(4) | -0.4115(3) | 0.2734(1) | -0.0909(2) | 2.78(3) |
| | 0.1726(2) | 0.1065(1) | 0.1675(2) | 3.05(3) | Cr | | -0.4015(2) | 0.2656(1) | -0.1095(2) | 3.22(3) |
| | 0.1714(5) | 0.1096(2) | 0.1768(3) | 3.28(6) | Mn | | -0.4113(5) | 0.2727(3) | -0.0939(4) | 3.69(7) |
| | 0.1709(2) | 0.1084(1) | 0.1736(2) | 1.66(3) | Fe | | -0.4088(3) | 0.2724(1) | -0.0918(2) | 2.11(4) |
| | 0.1663(1) | 0.10762(8) | 0.17110(9) | 2.26(2) | Co | | -0.4098(2) | 0.27295(8) | -0.0870(1) | 2.89(2) |
| | 0.1621(2) | 0.10709(9) | 0.1677(1) | 1.92(2) | Ni | | -0.4103(2) | 0.2724(1) | -0.0856(1) | 2.51(2) |
| | 0.1766(2) | 0.1167(1) | 0.1757(1) | 2.66(2) | Cu | | -0.3995(2) | 0.26805(9) | -0.0840(1) | 2.76(2) |
| | 0.1646(2) | 0.1088(2) | 0.1707(2) | 2.30(3) | Zn | | -0.4081(3) | 0.2712(2) | -0.0879(2) | 2.73(3) |
| O(5) | -0.2141(3) | 0.4211(2) | 0.0476(2) | 3.50(4) | V | O(7) | -0.0500(3) | 0.3229(1) | -0.1149(2) | 2.44(3) |
| | -0.2286(3) | 0.4145(1) | 0.0350(1) | 3.54(3) | Cr | | -0.0363(2) | 0.3262(1) | -0.1206(1) | 2.73(3) |
| | -0.2167(6) | 0.4191(3) | 0.0474(3) | 4.37(8) | Mn | | -0.0462(4) | 0.3233(2) | -0.1129(3) | 3.20(6) |
| | -0.2168(3) | 0.4216(2) | 0.0466(2) | 2.72(4) | Fe | | -0.0477(3) | 0.3235(1) | -0.1142(2) | 1.70(3) |
| | -0.2129(2) | 0.4243(1) | 0.0488(1) | 3.50(2) | Co | | -0.0504(2) | 0.32289(8) | -0.1150(1) | 2.52(2) |
| | -0.2141(3) | 0.4251(1) | 0.0487(1) | 3.11(3) | Ni | | -0.0522(2) | 0.32268(9) | -0.1167(1) | 2.32(2) |
| | -0.2189(2) | 0.4239(1) | 0.0492(1) | 3.42(3) | Cu | | -0.0428(2) | 0.32110(9) | -0.1084(1) | 2.64(2) |
| | -0.2153(3) | 0.4239(2) | 0.0477(2) | 3.30(4) | Zn | | -0.0504(2) | 0.3221(2) | -0.1149(2) | 2.49(3) |
| O(6) | -0.3760(2) | 0.4331(1) | -0.2181(2) | 2.19(3) | V | N | 0.3573(3) | 0.3495(2) | 0.1338(2) | 2.52(4) |
| | -0.3711(2) | 0.42929(9) | -0.2279(1) | 2.44(2) | Cr | | 0.3657(3) | 0.3573(1) | 0.1264(2) | 2.67(3) |
| | -0.3713(4) | 0.4332(2) | -0.2173(3) | 2.95(6) | Mn | | 0.3599(6) | 0.3507(3) | 0.1332(4) | 3.42(8) |
| | -0.3728(2) | 0.4331(1) | -0.2197(2) | 1.47(3) | Fe | | 0.3577(3) | 0.3498(2) | 0.1330(2) | 1.79(4) |
| | -0.3771(1) | 0.43342(8) | -0.2189(1) | 2.26(2) | Co | | 0.3577(2) | 0.34803(9) | 0.1335(1) | 2.50(2) |
| | -0.3792(2) | 0.43309(8) | -0.2210(1) | 2.01(2) | Ni | | 0.3563(2) | 0.3465(1) | 0.1347(2) | 2.29(3) |
| | -0.3668(2) | 0.42939(8) | -0.2194(1) | 2.27(2) | Cu | | 0.3597(2) | 0.3480(1) | 0.1347(1) | 2.51(2) |
| | -0.3768(2) | 0.4324(1) | -0.2203(2) | 2.24(4) | Zn | | 0.3571(3) | 0.3483(2) | 0.1352(2) | 2.46(4) |

^a Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^*B_{11} + b^2b^*B_{22} + c^2c^*B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

diffraction studies^{16b,17} while in others data were obtained from X-ray diffraction.¹⁵⁻¹⁸

Another series of compounds of the FTS that are of interest in this same context are the $[\text{M}(\text{H}_2\text{O})_6]\text{SiF}_6$ compounds. Because of the symmetry and rigidity of the crystal structure, the Jahn-Teller effect is completely suppressed for M = Cr^{2b} and partially

suppressed for Cu.¹⁹ The crystal structure of the vanadium compound was not heretofore known, and that of the manganese compound had not been reported in full.²⁰ This precluded discussion of any possible correlations of the structural parameters at the time of our earlier report^{2b} on the structure of $[\text{Cr}(\text{H}_2\text{O})_6]\text{SiF}_6$. For the rest of the metals of the first transition series there

was a neutron diffraction study for the iron compound in which the standard deviations for the Fe–O distances were high (0.013 Å),²¹ although apparently satisfactory X-ray structures for the Co, Ni, and Zn compounds²² were in the literature.

This series of hexaqua hexafluorosilicates is also of interest because phase transitions are common and the structures and internal dynamics have been subject to investigation by a variety of techniques.²³ Many of these studies have been done for the copper compound; however, this is the one member of the series that crystallizes differently from the others,¹⁹ with a unit cell containing four times as many molecules than that of the other members of the series.

In this paper we present consistently accurate data for both the Tutton salts and the $[M(H_2O)_6]SiF_6$ compounds for all metals in the FTS that form them, namely, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. We then examine the trends displayed within each series as well as the differences between the two series.

In our examination and discussion of trends we shall take as our point of departure the now well-known²⁴ graph of radii *vs* atomic number for the divalent ions of the FTS. This behavior was first noted and rationalized according to ligand field theory (LFT) in 1952 by van Santen and van Wieringen.²⁵ They pointed out that superimposed on an underlying monotonic decrease in 3d orbital radii with increasing atomic number would be the following contributions: each added t_{2g} electron should have a less than average effect and each added e_g electron should have a greater than average effect. Thus, actual radii (for high-spin species) should decrease for d^0 – d^3 , increase for d^4 and d^5 , again decrease for d^6 – d^8 , and increase for d^9 and d^{10} . If a smooth curve is drawn through the $d^0(Ca^{2+})$, $d^5(Mn^{2+})$, and $d^{10}(Zn^{2+})$ radii, all others lie below this curve, forming two festoons, with the minima at $d^3(V^{2+})$ and $d^8(Ni^{2+})$.

Experimental Section

In the preparation of divalent vanadium, chromium, and iron compounds, all operations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Water was deionized,

- (17) (a) Deeth, R. J.; Figgis, B. N.; Forsyth, J. B.; Kucharski, E. S.; Reynolds, P. A. *Aust. J. Chem.* **1988**, *41*, 1289. (b) Fender, B. E. F.; Figgis, B. N.; Forsyth, J. B.; Reynolds, P. A.; Stevens, E. *Proc. R. Soc. London, A* **1986**, *404*, 127. (c) Figgis, B. N.; Kucharski, E. S.; Reynolds, P. A. *Acta Crystallogr.* **1989**, *C45*, 942. (d) Figgis, B. N.; Keppert, C. J.; Kucharski, E. S.; Reynolds, P. A.; *Acta Crystallogr.* **1992**, *B48*, 753. (e) Maslen, E. N.; Ridout, S. C.; Watson, K. J.; Moore, F. H. *Acta Crystallogr.* **1988**, *C44*, 412. (f) Maslen, E. N.; Ridout, S. C.; Watson, K. J. *Acta Crystallogr.* **1988**, *B44*, 96. (g) Fender, B. E. F.; Figgis, B. N.; Forsyth, J. B. *Proc. R. Soc. London, A* **1986**, *404*, 139. (h) Figgis, B. N.; Khor, L.; Kucharski, E. S.; Reynolds, P. A. *Acta Crystallogr.* **1992**, *B48*, 144. (i) Maslen, E. N.; Watson, K. J.; Moore, F. H. *Acta Crystallogr.* **1988**, *B44*, 102.
- (18) (a) Montgomery, H.; Chastain, R. V.; Natt, J. J.; Witkowska, A. M.; Lingafelter, E. C. *Acta Crystallogr.* **1967**, *22*, 775. (b) Montgomery, H.; Chastain, R. V.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 731. (c) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1478. (d) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 659. (e) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1295.
- (19) Siddhartha, R.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1973**, *B29*, 2748.
- (20) Koder, E. Torii, A.; Osaki, K.; Watanabé, T. *J. Phys. Soc. Jpn* **1972**, *32*, 863.
- (21) Hamilton, W. C. *Acta Crystallogr.* **1962**, *15*, 353.
- (22) Siddhartha, R.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1973**, *B29*, 2741.
- (23) (a) Syoyama, S.; Osaki, K. *Acta Crystallogr.* **1972**, *B28*, 2626. (b) Weir, R. D.; Halsted, K. E.; Staveley, L. A. K. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 189. (c) Price, D. C. *Can. J. Phys.* **1987**, *65*, 1280. (d) Boiko, F. A.; Bochkovaya, G. Yu.; Bykov, A. M.; Duka, A. Ya.; Kovarskii, V. L.; Kolmanovich, V. Yu.; Pis'menova, W. E.; Sukharevskii, B. Ya.; Tsybul'skii, E. O.; Shatalova, G. E. *Izv. Akad. Nauk SSSR. Ser. Fiz.* **1989**, *53*, 1353. (e) Sukharevskii, B. Ya.; Tsybul'skii, E. O.; Shatalova, G. E.; Vitebskii, I. M. *Sov. Phys. Crystallogr.* **1983**, *28*, 288. (f) Boiko, F. A.; Bochkovaya, G. Yu.; Bykov, A. M.; Kovarsky, V. L.; Pismenova, W. E.; Ksenofontov, V. G.; Ruban, I. V.; Sukharevsky, B. Ya.; Tsybul'sky, E. O.; Shatalova, G. E. *Ferroelectrics* **1987**, *431*.
- (24) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1987, p 465.
- (25) van Santen, J. H.; van Wieringen, J. S. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 420.

Table III. Bond Distances (Å) and Angles (deg) for the $M(H_2O)_6$ Units of the Tutton Salts^a

| M | M–O(1) | M–O(2) | M–O(3) |
|----|-----------|----------|-----------|
| V | 2.133(1) | 2.136(2) | 2.116(1) |
| Cr | 2.122(1) | 2.327(1) | 2.052(1) |
| Mn | 2.185(3) | 2.191(3) | 2.149(3) |
| Fe | 2.143(2) | 2.136(2) | 2.098(2) |
| Co | 2.1054(9) | 2.102(1) | 2.0699(9) |
| Ni | 2.065(1) | 2.064(1) | 2.039(1) |
| Cu | 2.222(1) | 2.070(1) | 1.964(1) |
| Zn | 2.109(2) | 2.105(2) | 2.061(2) |

| M | O(1)–M–O(2) | O(1)–M–O(3) | O(2)–M–O(3) |
|----|-------------|-------------|-------------|
| V | 89.58(6) | 91.67(5) | 90.77(6) |
| Cr | 89.93(5) | 91.21(5) | 89.81(5) |
| Mn | 89.6(1) | 92.1(1) | 91.1(1) |
| Fe | 89.25(6) | 91.02(6) | 90.86(6) |
| Co | 88.94(3) | 91.16(3) | 89.69(4) |
| Ni | 88.45(4) | 90.30(4) | 89.50(5) |
| Cu | 88.76(4) | 90.62(4) | 88.82(4) |
| Zn | 88.32(6) | 90.85(6) | 89.74(7) |

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

Table IV. Distances (Å) and Angles (deg) for Atoms Involved in Hydrogen Bonds in the Fe Tutton Salt^a

| Bond Distances | | | |
|----------------|----------|-----------|----------|
| H(1)–O(1) | 0.83(3) | H(3)–O(2) | 0.89(3) |
| H(2)–O(1) | 0.83(3) | H(4)–O(2) | 0.75(3) |
| H(1)–O(6) | 1.95(3) | H(3)–O(5) | 1.82(3) |
| H(2)–O(7) | 2.01(3) | H(4)–O(7) | 2.00(3) |
| O(1)–O(6) | 2.778(2) | O(2)–O(5) | 2.709(2) |
| O(1)–O(7) | 2.829(3) | O(2)–O(7) | 2.755(2) |
| H(5)–O(3) | 0.95(3) | H(6)–O(3) | 0.94(3) |
| H(5)–O(4) | 1.74(3) | H(6)–O(6) | 1.82(3) |
| O(3)–O(4) | 2.686(2) | O(3)–O(6) | 2.753(2) |

| Bond Angles | | | |
|----------------|--------|----------------|--------|
| O(1)–H(1)–O(6) | 170(3) | O(2)–H(4)–O(7) | 175(3) |
| O(1)–H(2)–O(7) | 173(2) | O(3)–H(5)–O(4) | 173(3) |
| O(2)–H(3)–O(5) | 174(3) | O(3)–H(6)–O(6) | 169(2) |

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

deoxygenated by prolonged refluxing in a nitrogen atmosphere, and distilled just before it was used. All metals were purchased from Johnson Matthey Electronics with a purity of 99.95% or better. Purified ammonium carbonate (Fisher Scientific), ammonium sulfate (Fisher Scientific), silicic acid (Baker), and HF (48–51%, Baker) were used as received.

Metal Carbonate Hydrates. These were typically prepared by first dissolving the metal in an appropriate acid, such as HCl or HNO₃, and then evaporating to dryness. The solids were redissolved, and an ammonium carbonate solution was added. The precipitated carbonates were filtered and washed with abundant amounts of water. In the case of vanadium, the carbonate was prepared by beginning with $[V(H_2O)_6]SO_4$ instead of the metal.

Hexafluorosilicic Acid. HF, 48–51%, was carefully added to an excess amount of silicic acid in a plastic beaker. After several days it was decanted and stored in polypropylene bottles.

$M(H_2O)_6SiF_6$. The hexafluorosilicic acid solution was carefully added to an aqueous suspension of the metal carbonate. Upon complete dissolution of the solid, the solvent was allowed to slowly evaporate for those compounds that are air-stable. In the case of copper, a desiccator with a small amount of potassium hydroxide was used. For the others, a layer of ethanol was carefully added and the mixtures were placed in a refrigerator at 4 °C. After several days crystals formed. In each case the compound was recrystallized from aqueous solution.

$(NH_4)_2M(H_2O)_6(SO_4)_2$. A dilute sulfuric acid solution (ca. 1 M) was added to an aqueous suspension of the metal carbonate. When the solid had dissolved, an equivalent amount of an ammonium sulfate solution was added. Then, a few drops of ethanol were added, and the mixture was cooled to 4 °C. After several days, the crystals were filtered. In each case, they were then recrystallized from aqueous solution.

X-ray Structure Analyses

Tutton Salts. A crystal of each sample was mounted on the tip of a glass fiber and covered with a very thin coat of epoxy cement. Geometrical and intensity data were collected on a Rigaku AFC5R for the V, Mn,

Table V. Crystal Data for $[M(H_2O)_6]SiF_6$ ($M = V, Mn, Fe, Co, Ni, \text{ and } Zn$)

| | V | V | Mn | Fe | Co | Ni | Cu | Zn |
|---|----------|----------|----------|--|-----------|----------|-----------|----------|
| formula | | | | MSiF ₆ O ₆ H ₁₂ | | | | |
| fw | 301.11 | 301.11 | 305.11 | 306.02 | 309.10 | 308.88 | 313.71 | 315.54 |
| space group | | | | $R\bar{3}$ (hexagonal setting) | | | | |
| <i>a</i> , Å | 9.391(1) | 9.427(1) | 9.660(2) | 9.636(2) | 9.3664(7) | 9.309(1) | 18.066(1) | 9.361(3) |
| <i>c</i> , Å | 9.703(1) | 9.775(1) | 9.801(2) | 9.690(3) | 9.731(1) | 9.619(2) | 9.842(1) | 9.689(5) |
| <i>V</i> , Å ³ | 741.0(1) | 752.3(3) | 792.1(5) | 779.1(6) | 739.3(2) | 721.9(3) | 2781.8(6) | 735.3(8) |
| <i>Z</i> | 3 | 3 | 3 | 3 | 3 | 3 | 12 | 3 |
| <i>d</i> _{calcd.} , g/cm ³ | 2.02 | 1.99 | 1.92 | 1.96 | 2.08 | 2.13 | 2.25 | 2.14 |
| μ cm ⁻¹ | 11.86 | 11.68 | 123.8 | 16.54 | 19.51 | 22.44 | 25.89 | 27.81 |
| radiation (monochromated in incident beam) ^a | Mo | Mo | Cu | Mo | Mo | Mo | Mo | Mo |
| temp, °C | -60(1) | 22(1) | 22(1) | 22(1) | 22(1) | 22(1) | -60(1) | 22(1) |
| transm factors | | | | | | | | |
| max | 0.9997 | 0.9981 | 1.000 | 0.9948 | 0.9969 | 0.9972 | 0.9926 | 0.9992 |
| min | 0.9211 | 0.9086 | 0.8211 | 0.8057 | 0.8620 | 0.8703 | 0.7469 | 0.9256 |
| <i>R</i> ^b | 0.014 | 0.021 | 0.032 | 0.022 | 0.018 | 0.017 | 0.065 | 0.015 |
| <i>R</i> _w ^c | 0.021 | 0.037 | 0.048 | 0.036 | 0.024 | 0.027 | 0.086 | 0.019 |

^a Mo K α ($\lambda_{\alpha} = 0.71073$ Å), Cu K α ($\lambda_{\alpha} = 1.54184$ Å). ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table VI. Positional and Equivalent Isotropic Displacement Parameters for the $[M(H_2O)_6]SiF_6$ Structures^a

| atom [occ] | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eqv} ^b | metal | atom [occ] | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eqv} |
|-------------|-------------|-------------|-------------|--------------------------------------|------------|-------------|-----------|-----------|------------|-------------------------|
| M | 0.000 | 0.000 | 0.000 | 1.734(8) | V | H(1) | -0.074(3) | 0.201(3) | -0.119(2) | 5.1(5)* |
| | 0.000 | 0.000 | 0.000 | 1.439(4) | V (-60 °C) | | 0.015(1) | -0.172(1) | -0.216(1) | 1.5(3)* |
| | 0.000 | 0.000 | 0.000 | 2.44(3) | Mn | | 0.288(7) | 0.199(7) | -0.114(8) | 19(3)* |
| | 0.000 | 0.000 | 0.000 | 1.78(1) | Fe | | 0.203(2) | 0.107(2) | -0.212(2) | 7.8(2)* |
| | 0.000 | 0.000 | 0.000 | 1.794(5) | Co | | 0.273(2) | 0.088(2) | -0.116(1) | 2.2(4)* |
| | 0.000 | 0.000 | 0.000 | 1.623(3) | Ni | | -0.076(2) | 0.194(2) | -0.1148(9) | 2.2(2)* |
| | 0.000 | 0.000 | 0.000 | 1.920(6) | Zn | | -0.267(1) | -0.196(2) | -0.110(2) | 4.0(3)* |
| O | -0.0120(1) | 0.1767(1) | -0.12699(8) | 3.01(2) | V | H(2) | 0.015(2) | 0.193(2) | -0.212(2) | 4.0(3)* |
| | -0.01024(7) | -0.18848(6) | -0.12741(7) | 2.31(1) | V (-60 °C) | | -0.075(1) | -0.282(1) | -0.122(1) | 2.2(3)* |
| | 0.2039(4) | 0.1004(6) | -0.1311(4) | 8.2(2) | Mn | | 0.194(7) | 0.072(7) | -0.219(5) | 10(2)* |
| | 0.2030(2) | 0.1015(3) | -0.1271(1) | 5.46(6) | Fe | | 0.299(2) | 0.125(3) | -0.116(2) | 11.1(3)* |
| | 0.1860(1) | 0.0114(1) | -0.12442(8) | 3.12(2) | Co | | 0.178(2) | -0.006(2) | -0.206(1) | 2.7(4)* |
| | -0.00630(8) | 0.17647(8) | -0.12172(6) | 2.55(1) | Ni | | 0.175(2) | 0.167(1) | 0.209(1) | 2.2* |
| | -0.0089(1) | -0.18539(9) | -0.12397(8) | 2.93(2) | Zn | | -0.167(2) | -0.184(2) | 0.204(2) | 5.1(3)* |
| Si | 0.000 | 0.000 | 0.500 | 1.67(1) | V | F(2) [0.45] | 0.1021(3) | 0.1657(2) | 0.5981(2) | 2.83(4) |
| | 0.000 | 0.000 | 0.500 | 1.313(6) | V (-60 °C) | [0.30] | 0.1294(3) | 0.1570(2) | 0.5996(2) | 3.13(4) |
| | 0.000 | 0.000 | 0.500 | 2.25(5) | Mn | [0.47] | 0.1505(4) | 0.0190(4) | 0.4019(3) | 3.3(1) |
| | 0.000 | 0.000 | 0.500 | 1.65(2) | Fe | [0.52] | 0.1475(2) | 0.0104(3) | -0.6010(2) | 2.95(5) |
| | 0.000 | 0.000 | 0.500 | 1.708(9) | Co | [0.49] | 0.1555(2) | 0.1317(2) | 0.4001(1) | 3.94(5) |
| | 0.000 | 0.000 | 0.500 | 1.542(7) | Ni | [0.30] | 0.1590(3) | 0.1297(4) | 0.3982(2) | 4.03(7) |
| | 0.000 | 0.000 | 0.500 | 1.658(9) | Zn | [0.33] | 0.1316(3) | 0.1562(3) | 0.5994(2) | 3.80(7) |
| F(1) [0.55] | -0.0343(5) | -0.1585(2) | 0.3992(1) | 4.75(8) | V | | | | | |
| | [0.70] | -0.0727(1) | -0.16792(8) | 0.39968(8) | 2.43(1) | V (-60 °C) | | | | |
| | [0.53] | 0.1293(4) | -0.0214(5) | 0.5988(4) | 3.9(1) | Mn | | | | |
| | [0.48] | 0.1375(2) | -0.0096(3) | 0.3993(2) | 2.49(5) | Fe | | | | |
| | [0.51] | 0.0643(2) | -0.1026(2) | 0.6000(1) | 3.14(3) | Co | | | | |
| | [0.70] | 0.1023(1) | 0.1686(1) | 0.60102(7) | 2.92(2) | Ni | | | | |
| | [0.67] | -0.0683(2) | -0.1678(2) | 0.3989(1) | 3.32(3) | Zn | | | | |

^a For each atomic site, the coordinates are given for the six isotopic structures and the low-temperature vanadium structure. The same starting positional parameters were not necessarily used for each structure. The refined occupancy for each fluorine site is indicated. ^b Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$. Starred values denote atoms that were refined isotropically.

and Fe salts; data for the remainder of the series were taken on a P3/F (equivalent) diffractometer. Orientation reflections on the AFC5R diffractometer were found via an automated search routine. On the P3 diffractometer, initial orientation reflections were taken from a 360° rotation photograph. A set of 25 reflections, ranging from approximately 22 to 35° in 2θ , was selected from a preliminary data set taken on the Co salt for the determination of accurate lattice dimensions. These same reflections were then used for the remainder of the samples studied on the P3 diffractometer.

Intensity data were taken at 22 ± 1 °C for each sample. For the V, Cr, Mn, Fe, and Co salts, data were collected in the $+h, +k, \pm l$ quadrant. For the Ni, Cu, and Zn salts, data were measured in the $+h, \pm k, \pm l$ hemisphere. In each case the ω - 2θ scan technique was used, and azimuthal scans were measured for use as the basis of an empirical absorption correction. Normal-beam oscillation photographs were used to verify the primary lattice repeats and the mirror symmetry perpendicular to the *b* axis. Lorentz and polarization corrections were applied to each data set, and equivalent data were averaged. Only those data having $F_o^2 \geq 3\sigma(F_o^2)$ were used in the refinements of the structures.

The known approximate positions of the non-hydrogen atoms were used as starting parameters for the refinement of each structure.^{18a} Peaks

corresponding to hydrogen atoms were seen in a difference Fourier map in each case, and the hydrogen positions were included in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The isotropic thermal parameters for hydrogen atoms were refined with constraints in each case except the Co and Cu structures, in which each hydrogen isotropic thermal parameter was allowed to refine independently.^{26a} Table I presents a summary of the geometrical and refinement results. Positional parameters are listed in Table II; metal-oxygen bond distances and angles appear in Table III, and a sample of hydrogen-bonding interactions is shown in Table IV.

Hexaqua Hexafluorosilicates. Each sample crystal for room-temperature analysis was mounted on the tip of a glass fiber and covered with a very thin coat of epoxy cement. The low-temperature sample crystals (the copper salt and one of the vanadium samples) were attached to the fiber with a small bit of stopcock grease. Geometrical and intensity data were collected on a Rigaku AFC5R for the Mn salt; the low-temperature data sets for the V and Cu samples were taken on a

(26) (a) Refinement calculations were carried out on a Local Area VAX cluster using the SDP programs. (b) The SHELX-76 programs were used for refinement.

Table VII. Positional Parameters and Their Estimated Standard Deviations for $[\text{Cu}(\text{H}_2\text{O})_6]\text{SiF}_6$

| atom | x | y | z | B_i^a Å ² |
|-------|-----------|-----------|-----------|------------------------|
| Cu(1) | 0.000 | 0.000 | 0.000 | 1.06(3) |
| Cu(2) | 0.500 | 0.000 | 0.000 | 1.18(2) |
| Si(1) | 0.000 | 0.000 | 0.500 | 1.15(7) |
| Si(2) | 0.500 | 0.000 | 0.500 | 1.22(5) |
| F(1) | 0.0803(2) | 0.0714(2) | 0.4009(4) | 1.84(9) |
| F(2) | 0.4105(3) | 0.2072(3) | 0.2854(5) | 2.8(1) |
| F(3) | 0.2639(3) | 0.1709(3) | 0.2751(5) | 2.6(1) |
| F(4) | 0.3043(3) | 0.0683(3) | 0.2207(5) | 3.3(1) |
| O(1) | 0.0969(3) | 0.0896(3) | 0.1198(5) | 2.0(1) |
| O(2) | 0.2516(3) | 0.4276(3) | 0.4434(5) | 1.9(1) |
| O(3) | 0.0753(3) | 0.3346(3) | 0.4396(6) | 1.9(1) |
| O(4) | 0.1750(3) | 0.2384(3) | 0.4920(5) | 1.7(1) |

^a Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

Table VIII. M–O Distances (Å) and Angles (deg) for the Isotypic Hexafluorosilicates^a

| M | M–O dist | O–M–O angle | M | M–O dist | O–M–O angle |
|------------|-----------|-------------|----|-----------|-------------|
| V | 2.125(1) | 89.33(3) | Co | 2.080(1) | 89.53(4) |
| V (–60 °C) | 2.1214(7) | 89.46(2) | Ni | 2.0418(8) | 90.39(3) |
| Mn | 2.135(3) | 87.6(2) | Zn | 2.0776(9) | 89.92(3) |
| Fe | 2.095(1) | 88.93(8) | | | |

^a The O–M–O angle is the one generated by the crystallographic 3-fold axis. Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IX. Cu–O Distances (Å) and Angles (deg) in $[\text{Cu}(\text{H}_2\text{O})_6]\text{SiF}_6^a$

| Bond Distances | | | |
|------------------|----------|-----------------|----------|
| Cu(1)–O(1) | 2.059(4) | Cu(2)–O(3) | 1.964(6) |
| Cu(2)–O(2) | 1.954(4) | Cu(2)–O(4) | 2.379(5) |
| Bond Angles | | | |
| O(1)–Cu(1)–O(1') | 90.5(2) | O(2)–Cu(2)–O(4) | 87.7(2) |
| O(2)–Cu(2)–O(3) | 89.6(2) | O(3)–Cu(2)–O(4) | 90.9(2) |

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

Table X. Distances (Å) and Angles (deg) for Atoms Involved in Hydrogen Bonds in $[\text{Co}(\text{H}_2\text{O})_6]\text{SiF}_6^a$

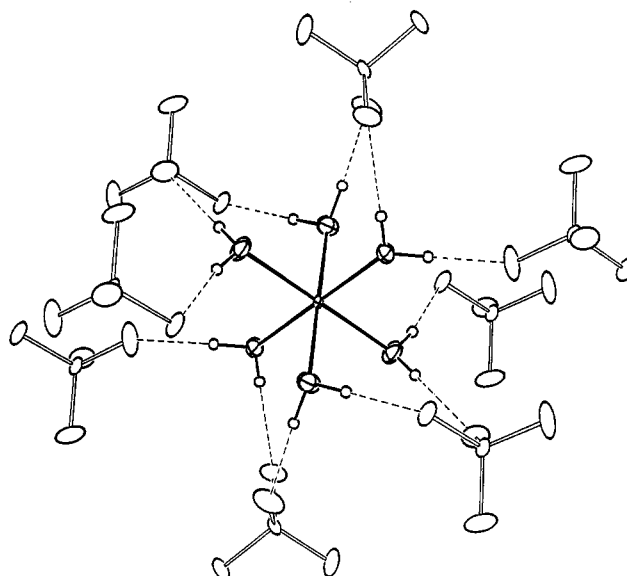
| Bond Distances | | | |
|----------------|----------|-------------|----------|
| H(1)–O | 0.78(1) | H(1)–F(1) | 2.00(1) |
| H(2)–O | 0.80(1) | H(1)–F(2) | 1.99(1) |
| F(1)–O | 2.900(2) | F(1)–O | 2.772(2) |
| | | F(2)–O | 2.709(2) |
| | | F(2)–O | 2.720(2) |
| Bond Angles | | | |
| F(1)–H(1)–O | 171(2) | F(1)–H(2)–O | 159(2) |
| F(2)–H(1)–O | 154(2) | F(2)–H(2)–O | 167(2) |

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

CAD4 diffractometer; data for the remainder of the series were taken on a P3/F (equivalent) diffractometer.

Orientation reflections on the AFC5R and CAD4 diffractometers were found via automated search routines. Initial orientation reflections for crystals on the P3 diffractometer were taken from rotation photographs and a final set of reflections selected either from a fast preliminary data set ($20^\circ < 2\theta < 35^\circ$) or from one of the data sets previously collected on another of the samples. In each case the initial primitive rhombohedral cell was transformed to the triple hexagonal setting before data collection.

All of the room temperature data sets included at least one redundant measurement for each reflection. The low-temperature measurements on the vanadium compound included an entire sphere of data. Only the $+h, +k, \pm l$ region was measured for the copper compound. The ψ -scans were used as the basis of an empirical absorption correction in each case. Lorentz and polarization corrections were applied to each data set, and equivalent data were averaged. Only those data having $F_o^2 \geq 3\sigma(F_o^2)$ were used in the refinements of the structures.

**Figure 1.** Representation of the nature of the hydrogen bond network in crystals of the Tutton salts. Hydrogen bonds between H_2O molecules and SO_4^{2-} units are indicated as dashed lines.

In each case except one, the metal and silicon atoms were placed at 0, 0, 0 and 0, 0, 0.5, respectively, and the scale and temperature factors were refined. (The copper crystals are not isotypic with the remainder of the series; handling of its structure is described below.) The oxygen and (disordered) fluorine atoms were then found in difference Fourier syntheses. In each case the fluorine atoms of the SiF_6 unit were modeled as two distinct sets, and the refinement included a factor defining the occupancy ratio of these two orientations. The two unique hydrogen atoms were taken from later difference maps in every case; positional and isotropic temperature factors for the hydrogen atoms were included in the final refinement cycles. Intensity statistics for the Mn, Co, and Ni structures indicated a secondary extinction effect, so a correcting coefficient was refined for these structures.

Starting positional parameters for the Cu structure were taken from the previously published report.¹⁹ Following least-squares convergence with all of the non-hydrogen atoms anisotropic, peaks corresponding to all of the expected hydrogen atoms were seen in a difference map. It was not possible, however, to successfully refine their positions and isotropic thermal parameters; this is the same result that the original authors reported. When the hydrogen positions were held fixed and only a common isotropic thermal parameter was varied, the residuals were further reduced to their final values.^{26b}

A summary of important data collection and refinement results is given in Table V. Positional parameters for the isotypic hexaaqua hexafluorosilicates are given in Table VI, and for the copper compound in Table VII. Metal–water distances and angles are given in Tables VIII and IX, and Table X lists the hydrogen contacts for the Co compound (as an example).

Results and Discussion

Tutton Salts. The compounds of the FTS elements from an isotypic series. In this structure there exists a network of strong hydrogen bonds (Figure 1) which is probably the chief reason why the structure type persists across the whole series. The special stability of the structure doubtless plays a role in the unusual stability toward oxidation shown by the dry crystals of the vanadium and chromium compounds.

In this work we have re-refined all of the structures of the $(\text{NH}_4)_2[\text{M}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ compounds ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$), employing new data, collected for the purpose at room temperature (22 °C). The new results agree well (to within a few standard deviations) with those of previously reported, room-temperature X-ray structures.

As shown in Figure 2, the variation in M–OH₂ bond lengths, for the independent bond distances as well as for the average values, follows the expected pattern predicted by LFT for these octahedral high spin species. There are maxima at manganese (d^5) and zinc (d^{10}) and a minimum at nickel (d^8) and the results

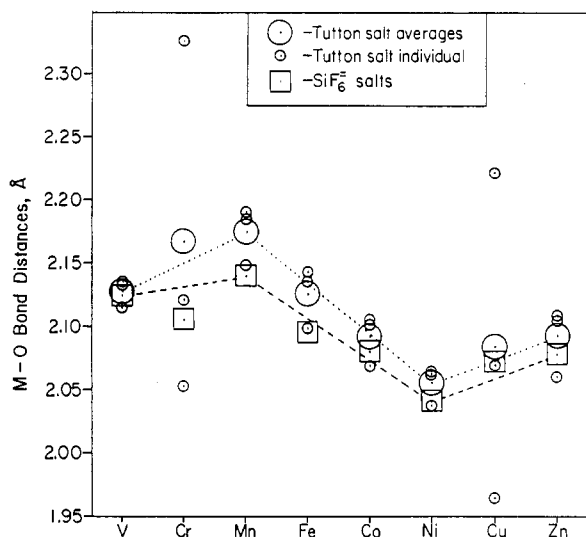


Figure 2. Variation in metal-to-water distances in the Tutton salts and the hexaqua hexafluorosilicates of the first transition series.

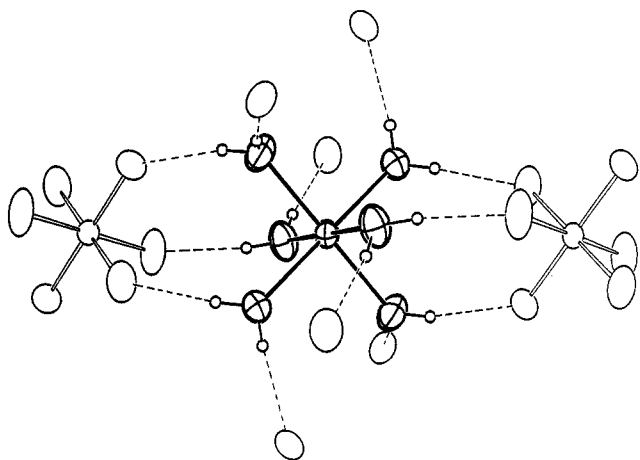


Figure 3. Hydrogen bonding in crystals of the $[M(H_2O)_6]SiF_6$ compounds. For clarity, some of the SiF_6^{2-} groups are represented only by the fluorine atom interacting with the $[M(H_2O)_6]^{2+}$ unit shown.

are consistent with there being a minimum at vanadium (d^3), although no data are available for Ca^{2+} , Sc^{2+} , or Ti^{2+} . It is also clear that qualitatively, the d^4 chromium(II) ion and the d^9 copper(II) ion have large and similar deviations from the regular patterns, as expected from the Jahn–Teller theorem. The octahedron is distorted in such a way that one of the axes is markedly elongated while the other two axes are slightly compressed. (Note, however, that the elongated M–O bond is not the same one in the Cr and Cu structures;⁶ i.e. Cr–O(2) vs Cu–O(1).) Overall, the behavior of the Tutton salts is similar to that found in the saccharinate complexes of the FTS.^{2a}

$[M(H_2O)_6]SiF_6$ Compounds. We again have an isotopic series of compounds, all of which crystallize in the space group $R\bar{3}$. The copper compound is an exception, having a unit cell containing more molecules (*vide infra*). In all other cases, the SiF_6^{2-} ion was found to be disordered, with a single silicon position surrounded by two sets of fluorine atoms. However, the hexaqua metal ion is fully ordered. All hydrogen atoms participate in hydrogen bonding forming an extensive network, as shown in Figure 3. The metal atom resides on a site of $\bar{3}$ symmetry that necessitates the crystallographic equality of all metal-to-water bonds. This leads to a suppression of the Jahn–Teller effect for chromium, as discussed previously.^{2b}

The lower part of Figure 2 shows the variation of the crystallographically unique metal-to-water distance for the different metal ions of the FTS. The two maxima at manganese and zinc and the minimum at nickel correspond to the same pattern found for the Tutton salts. However, the left side of the figure

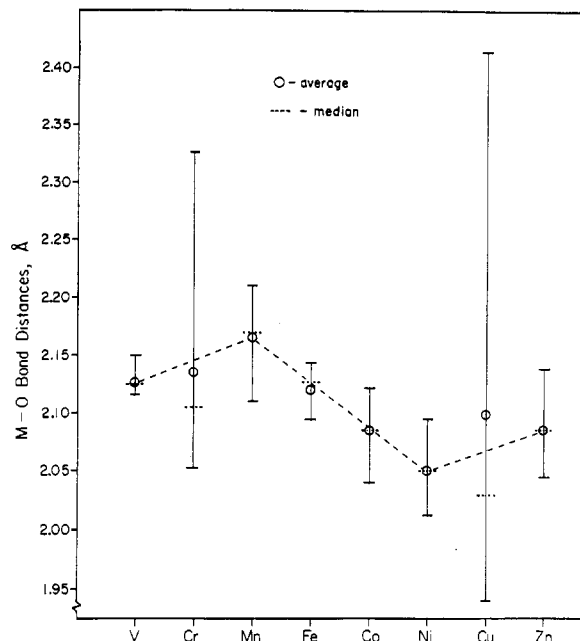


Figure 4. Ranges and averages of metal-to-oxygen distances in hexaqua compounds of the first transition series. See the text for a detailed description.

indicates puzzling results. The slope of the line from vanadium to manganese is extremely small. Furthermore, the chromium-to-water bond length is far shorter than would be expected from the standard assumptions of LFT. So far, we have been unable to find a completely satisfactory explanation for this fact. Although it is possible that the crystal forces are stronger for the hexafluorosilicates than for the Tutton salts, since in each case the bond distances around the metal atom are shorter for the former by several hundredths of an Angstrom than for the averages for the latter, as seen in Figure 2. It is possible that what we observe is the result of varying degrees of libration in the different specimens. A thorough study of this question, which is beyond the scope of the present manuscript, is underway. It is also interesting to note that the difference in the M–O bond distances in the two compound types is essentially negligible for vanadium.

To make sure that this result is genuine and not due to some contamination, we prepared samples independently at both of our laboratories. The results were the same. We also decided to check the effect of temperature on the vanadium compound and found no anomalous behavior for the bond distance. The V–O distance is 2.125(1) Å at 20 °C and 2.1214(7) Å at –60 °C.

Other $[M(H_2O)_6]^{2+}$ Species. To be able to put our observations in the correct context, we searched the literature for additional precise structures of hexaqua ions of the FTS determined by X-ray diffraction at room temperature.

Figure 4 shows the general trends found. As indicated in the Introduction, we are using only crystal structures for which the average standard deviation in the M–O distance is 0.005 Å or less. The upper limit is the maximum bond length found and the lower limit represents the smallest M–O distance. Open circles represent the average values (unit-weighted, including each individual bond), and the median values are shown by horizontal broken lines. In each case, we used the values for the Tutton salts and the hexaqua hexafluorosilicate, as well as those for any other published structure meeting the aforementioned standard of accuracy that we were able to find. Other data were included for V,²⁷ Mn,²⁸ Fe,²⁹ Co,^{10b,13b,30} Ni,^{13c,30b,31} Cu,^{30a,31d,32} and Zn.³³

Several features are immediately evident in this figure. In general, the average values follow the pattern expected from LFT considerations, showing well defined maxima for manganese and

(27) Holt, D. G. L.; Larkworthy, L. R.; Povey, D. C.; Smith, G. W.; Leigh, G. J. *Inorg. Chim. Acta* **1990**, *169*, 201.

zinc and minima for vanadium and nickel. Also noteworthy is the fact that the median is generally very close to the average, except for the Jahn–Teller active chromium and copper ions for which the median is significantly smaller than the average. This is, of course, a result of the form taken by the Jahn–Teller distortion in which one axis of the octahedron elongates while the other two axes contract.

The case of vanadium is atypical. The dispersion of the bond lengths is very narrow. All distances are within the range of 2.12–2.13 Å with the single exception of one of the axes in $[\text{V}(\text{H}_2\text{O})_6]\text{SO}_4$ for which the distance is 2.150 Å.^{13a} Is this because the vanadium ion is more rigid than the others or is it just because we do not have enough data? We hope that future work will answer that question.

Copper Hexafluorosilicate Hexahydrate. An earlier report of the crystal structure of this compound¹⁹ showed a number of interesting features and left several questions open. In contrast to the remaining ions of the FTS, copper forms a compound that crystallizes in the same space group but with a unit cell that is four times larger and contains two independent copper centers. One-fourth of the copper atoms occupy a site with $\bar{3}$ symmetry, requiring all Cu–O bonds to be equal. The remaining copper atoms occupy a position on a center of symmetry in which there is a considerable Jahn–Teller distortion. The original structure was determined using a very limited amount of data, and it was also reported that the crystal decomposed and moved during data collection. In addition, there had been published reports both claiming^{23d,f} and disclaiming the occurrence of phase transitions in this compound. Thus, for these several reasons, and others,^{34,35,36,37,38} we considered it worthwhile to try to establish the structure of this substance more precisely.

We first set out to study the structure at room temperature, but soon found (as had our predecessors) that the crystals were highly unstable and lost water readily. We tried different techniques to mount the crystals, but under all conditions the crystals continued to move while in the beam. Therefore, we decided that we had no recourse but to study the low temperature (–60 °C) crystal structure. Even at this temperature we observed a small but nonnegligible decay of the intensity standards.

The structure we obtained is essentially the same as that described previously at room temperature. The copper-to-water distance at the $\bar{3}$ site at –60 °C is 2.059(4) Å, which is about 0.01 Å shorter than that in the room temperature report. The three independent Cu–O bond lengths at the inversion center follow the usual pattern of two short ones, 1.954(4) and 1.964(6) Å, and one long one, 2.379(5) Å.

The long bond is 0.012 Å longer at –60 °C than the one reported at room temperature. While this difference is small, the same trend has been frequently observed in Jahn–Teller active species.^{15,16a,b}

An analysis of the displacement parameters, similar to that carried out for $[\text{Cr}(\text{H}_2\text{O})_6]\text{SiF}_6$,^{2b} shows that all distances are indeed identical, and not just an average of long and short distances statistically distributed over the three directions. However, we believe that the M–O distances for both Cr and Cu at the $\bar{3}$ sites may be to some extent modified by libration and averaged to an as yet unknown extent by the dynamics of the Jahn–Teller effect.

Note Added in Proof: Just as this paper was being submitted an *ab initio* study of the hexaaquo M^{2+} ions of the first transition series appeared (Akesson, R.; Petterson, L. G. M.; Sandström, M.; Siegbahn, P. E. M.; Wahlgren, U. *J. Phys. Chem.* **1992**, *96*, 10773.). The bimodal variation of the M–O distances already predicted by simple crystal field theory is again found. Values for the Cr^{2+} and Cu^{2+} ions in undistorted octahedral environments were obtained by averaging those for the actual tetragonal structures. Because of assumptions made in the theoretical model that are not consistent with the situation prevailing in the compounds we have studied experimentally, numerical agreement is not necessarily to be expected. However, the theoretical results do confirm that the behavior of $[\text{V}(\text{H}_2\text{O})_6]\text{SiF}_6$ and/or $[\text{Cr}(\text{H}_2\text{O})_6]\text{SiF}_6$ has no obvious explanation.

Acknowledgment. We are grateful to the Vicerrectoría de Investigación, U.C.R. (Grant No. 115–87–516) for support of work at the University of Costa Rica, and to the Robert A. Welch Foundation (Grant No. A-494) for support of work at Texas A&M University. We also thank Mr. Miguel A. Araya for the preparation of the chromium Tutton salt crystal and Prof. Larry R. Falvello for helpful discussions.

Supplementary Material Available: Full tables of crystallographic parameters, bond distances and angles, and anisotropic displacement parameters for the eight Tutton salts for the eight hexaaqua hexafluorosilicate structures and hydrogen atom parameters for the eight Tutton salts (56 pages). Ordering information is given on any current masthead page.

- (28) (a) Herdtweck, E.; Massa, W. *Z. Anorg. Allg. Chem.* **1989**, *579*, 191. (b) Carrell, H. L.; Glusker, J. P. *Acta Crystallogr.* **1973**, *B29*, 638. (c) Tamura, H.; Ogawa, K.; Sakurai, T.; Nakahara, A. *Inorg. Chim. Acta* **1984**, *92*, 107. (d) Glusker, J. P.; Carrell, H. L. *J. Mol. Struct.* **1973**, *15*, 151.
- (29) (a) Strouse, J.; Layten, S. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 562. (b) Ruiz-Valero, C.; Monge, A.; Gutiérrez-Puebla, E.; Gutiérrez-Rios, E. *Acta Crystallogr.* **1984**, *C40*, 811.
- (30) (a) Cousson, A.; Abazli, H.; Jové, J.; Gasperin, M. *J. Less-Common Met.* **1985**, *109*, 155. (b) Vicat, J.; Tranguit, D.; Aléonard, S. *Acta Crystallogr.* **1977**, *B33*, 1180. (c) Blackburn, A. C.; Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr.* **1990**, *B46*, 712. (d) Riley, P. E.; Pecoraro, V. L.; Carrano, C. J.; Raymond, K. N. *Inorg. Chem.* **1983**, *22*, 3096. (e) Viossat, B.; Khodadad, P.; Rodier, N. *Bull. Soc. Chim. Fr.* **1981**, 1–69. (f) Ganesh, V.; Seshasayee, M.; Aravamudan, G.; Heijdenrijk, D.; Schenk, H. *Acta Crystallogr.* **1990**, *C46*, 949. (g) McCandlish, E. F. K.; Michael, T. K.; Neal, J. A.; Lingafelter, E. C.; Rose, N. J. *Inorg. Chem.* **1978**, *17*, 1383. (h) Knuuttila, P. *Inorg. Chim. Acta* **1981**, *52*, 141.
- (31) (a) Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr.* **1990**, *C46*, 350. (b) Blackburn, A. C.; Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr.* **1991**, *C47*, 1786. (c) Gallucci, J. C.; Gerkin, R. E.; Reppart, W. *Acta Crystallogr.* **1990**, *C46*, 1580. (d) Shchegoleva, T. M.; Iskhakova, L. D.; Ovanesyan, S. M.; Shakhnazaryan, A. A.; Trunov, V. K. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1983**, *28*, 1286. (e) Cingi, M. B.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Acta Crystallogr.* **1984**, *C40*, 56. (f) Jouini, A. Dabbabi, M. *Rev. Chim. Miner.* **1986**, *23*, 776.
- (32) (a) Blackburn, A. C.; Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr.* **1991**, *C47*, 2019. (b) Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr.* **1989**, *C45*, 1279.
- (33) (a) Stadnicka, K.; Glazer, A. M.; Koralewski, M. *Acta Crystallogr.* **1988**, *B44*, 356. (b) Cariati, F.; Erre, L.; Micera, G.; Panzaneli, A. *Inorg. Chim. Acta* **1983**, *80*, 57. (c) Mak, T. C. W.; Huang, S.-H. *Polyhedron* **1987**, *6*, 111. (d) Knuuttila, P. *Polyhedron* **1984**, *3*, 303.
- (34) Very few other compounds are known in which symmetry imposes the equality (or apparent equality) of all metal-to-ligand distances in chromium(II) and copper(II) compounds. The best known examples are provided by $\text{K}_2\text{M}[\text{Cu}(\text{NO}_2)_6]$, for $\text{M} = \text{Pb}, \text{Ba}, \text{Ca}$.^{35a,b} $\text{TlPb}[\text{Cu}(\text{NO}_2)_6]$,^{35c} $[\text{Cu}(\text{en})_2]\text{SO}_4$,³⁶ tris(octamethylpyrophosphoramide)copper(II) perchlorate,³⁷ $[\text{Cu}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$,^{32a} CrZrF_6 ³⁸ and $[\text{Cr}(\text{H}_2\text{O})_6]\text{SiF}_6$.^{2b}
- (35) (a) Elliot, H.; Hathaway, B. J.; Slade, R. C. *Inorg. Chem.* **1966**, *5*, 669. (b) Cullen, D. L.; Lingafelter, E. C. *Inorg. Chem.* **1971**, *10*, 1264. (c) Takagi, S.; Joesten, M. D.; Lenhart, P. G. *Acta Crystallogr.* **1976**, *B32*, 326.
- (36) Cullen, D. L.; Lingafelter, E. C. *Inorg. Chem.* **1970**, *9*, 1858.
- (37) Joesten, M. D.; Hussain, M. S.; Lenhart, P. G. *Inorg. Chem.* **1970**, *9*, 151.
- (38) Mayer, H. W.; Reinen, D.; Heger, G. *J. Solid State Chem.* **1983**, *50*, 213.