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The First Dinuclear μ-Hexafluorosilicato Copper(II) Compound. Synthesis and Crystal Structure of (μ-Hexafluorosilicato-κ*F*:κ*F*′)-bis[aqua(*N*³-salicyloylpyridine-2-carboxamidrazonato-κ³*N*′,*N*²,*O*)copper(II)] Dihydrate

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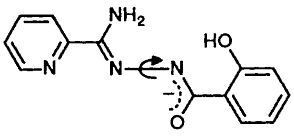
The X-ray structure of a unique dinuclear copper(II) compound containing a single hexafluorosilicato bridge, $[Cu_2L_2(H_2O)_2(SiF_6)]\cdot 2H_2O$ (HL = *N*³-salicyloylpyridine-2-carboxamidrazone), is reported.

Recently, linear-chain compounds of general composition $[M^{II}L_4(SiF_6)]$ [L = *N*-vinylimidazole (Hvim), M = Mn, Fe, Co, Ni, Cu or Zn;[1] L = 3(5)-phenylpyrazole (Hppz), M = Co, Ni or Cu[2]] have been described. They have a structure related to that of $[Cu(H_2O)_4(SiF_6)]$[3] *i.e.* CuL_4^{2+} units linked by SiF_6^{2-} anions. These compounds can either be prepared starting from the $M^{II}SiF_6$ salts, or from solutions containing $M^{II}(BF_4)_2\cdot 6H_2O$, where tetrafluoroborate decomposition followed by attack of the fluoride ions on the glass surface of the reaction vessel is responsible for the slow formation and crystallization of hexafluorosilicate ions.[1,2]

In the framework of a program on the magnetic properties of polynuclear copper(II) compounds containing 1,2,4-triazole ligands or their precursors, the *N*³-salicyloyl-2-carboxamidrazone ligand HL was selected for study.† Reaction of equimolar amounts of $Cu^{II}(BF_4)_2\cdot 6H_2O$ and HL in aqueous solution in Pyrex glass vessels led to the formation of a unique dinuclear compound of composition $[Cu_2L_2(H_2O)_2(SiF_6)]\cdot 2H_2O$.‡

The molecular structure of the dinuclear unit together with the atomic labelling is shown in Fig. 1. The structure consists of two five-co-ordinated distorted square-pyramidal copper(II) ions linked by a single hexafluorosilicato bridge. The basal plane is formed by the three donor atoms of the anionic ligand L [Cu–N(1) 2.001(2), Cu–N(9) 1.883(2), Cu–O(12) 1.951(2) Å] and the co-ordinated water molecule [Cu–O(1) 1.929(2) Å]. The copper(II) ion is located 0.0075(1) Å above this plane. The apical ligand is a fluoride atom of a hexafluorosilicate anion [Cu–F(1) 2.528(1) Å] at 2.573(2) Å from the least-squares plane [N(1), N(9), O(12), O(1)]. This Cu–F distance is significantly larger than those found in linear-chain compounds, such as $[Co(Hvim)_4(SiF_6)]$ [2.143(2) Å],[1] $[Cu(Hppz)_4(SiF_6)]$ [2.245(3), 2.251(3) Å][2] and $[Cu(H_2O)_4(SiF_6)]$ [2.336(5) Å].[3]



L

The ligand L is nearly planar with the largest deviation from planarity being less than 0.19 Å. The intramolecular hydrogen bond between atoms O(19) and N(10) [O(19)–H(19) ··· N(10) 146.90(9)°, O(19)–H(19) 0.6994 Å, N(10) ··· H(19) 1.995(3) Å] contributes to the planarity of the ligand and together with the

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† Ligand HL was synthesized starting from commercially available 2-cyanopyridine and salicylic acid hydrazide. 2-Cyanopyridine (0.13 mol, 13.0 g) was treated with a solution of sodium (0.46 g) in dry methanol (120 cm³) to yield the methyl ester of imidopicolinic acid. After addition of salicylic acid hydrazide (0.13 mol, 19.0 g) in methanol (100 cm³) the solution was refluxed for 2 h. From the filtrate the ligand HL precipitated as a white solid, m.p. 236 °C; mass spectrum, *m/z* 256 (M^+). The complex $[Cu_2L_2(H_2O)_2(SiF_6)]\cdot 2H_2O$ was synthesized by the addition of $Cu(BF_4)_2\cdot 6H_2O$ (3 mmol, 1.04 g) dissolved in methanol (50 cm³) to a suspension of HL (4 mmol, 1.02 g) in water (20 cm³). The resulting dark green solution was filtered. The compound crystallized by slow reaction of BF_4^- ions with the interior wall of the glass flask and upon evaporation of the solvent at room temperature after a few days. The dark green crystals were filtered, washed with water and dried in air. Yield: 65% (Found: C, 36.80; H, 3.55; Cu, 14.80; N, 13.15. $C_{26}H_{30}Cu_2F_6N_8O_8S$: requires C, 35.50; H, 3.40; Cu, 14.45; N, 12.75%).

‡ *Crystal data.* $C_{26}H_{30}Cu_2F_6N_8O_8Si$, $M = 851.7$, crystal size = 0.2 × 0.2 × 0.3 mm, monoclinic, space group = $P2_1/n$, $a = 10.0147(2)$, $b = 8.8510(2)$, $c = 18.1899(2)$ Å, $\beta = 92.0583(1)°$, $Z = 2$ (dinuclear molecules), $U = 1611$ Å³, $D_c = 1.802$ Mg m⁻³ and $F(000) = 864$ at 293 K. Intensities for 3894 independent reflections were measured on an Enraf-Nonius CAD-4 automated diffractometer using Mo-Kα radiation [$\lambda(\alpha_1) = 0.709\ 30$ Å] for $2 < 2\theta < 35°$. The structure was solved using Patterson and Fourier techniques (program AUTOFOUR[4]) and refined by least-squares methods. Absorption correction was carried out by the program DIFABS.[5] The four hydrogen atoms of the water molecules, the two amine hydrogens and the phenolic hydrogen were located in a Fourier difference map and were refined together with the corresponding non-hydrogen atoms with a different thermal parameter for each group of hydrogens, [H(1A), H(1B), H(2A), H(2B)], [H(8A), H(8B)], [H(19)]. The remaining hydrogen atoms were placed in calculated positions (C–H 1.00 Å) and refined together with the corresponding non-hydrogen atoms. A unique common thermal parameter was refined for these hydrogens. Final refinement converged to $R = 0.0354$ ($R' = 0.0500$) with weighting scheme $w = 1/[\sigma^2(F) + 0.0025F^2]$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

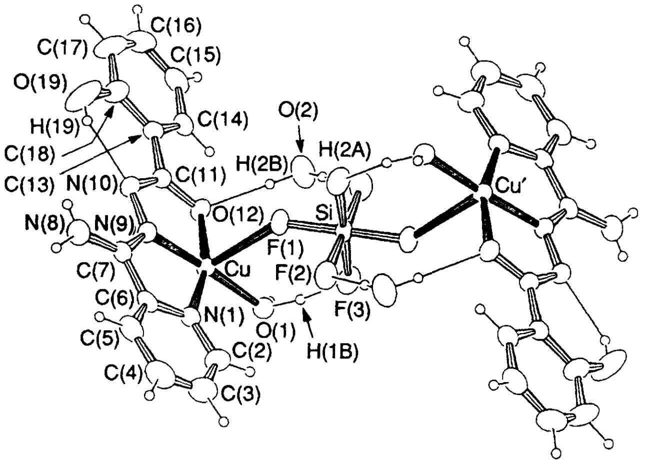

Fig. 1 ORTEP[6] drawing and atomic labelling system showing the structure of $[Cu_2L_2(H_2O)_2(SiF_6)]\cdot 2H_2O$. The single lines represent hydrogen bonds. Selected bond distances (Å) and angles (°): Cu ⋯ Cu′ (1 − *x*, 1 − *y*, −*z*) 7.9507(6), Cu–F(1) 2.528(1), Cu–N(1) 2.001(2), Cu–N(9) 1.883(2), Cu–O(12) 1.951(2), Cu–O(1) 1.929(2), Si–F(1) 1.691(1), Si–F(2) 1.673(1), Si–F(3) 1.680(1); F(1)–Cu–N(1) 91.82(7), F(1)–Cu–N(9) 101.83(7), F(1)–Cu–O(12) 93.99(6), F(1)–Cu–O(1) 84.04(6), N(1)–Cu–N(9) 81.12(8), N(1)–Cu–O(12) 161.20(7), N(1)–Cu–O(1) 98.96(8), N(9)–Cu–O(12) 80.19(7), N(9)–Cu–O(1) 174.13(8), O(12)–Cu–O(1) 99.41(7), Cu–F(1)–Si 140.07(8)

co-ordination of the metal ion is the main cause for the conformation adopted by the ligand. The tautomeric structure of the deprotonated ligand is evident from the X-ray structure. Two hydrogen atoms are located at N(8) [N(8)–H(8A) 0.9876, N(8)–H(8B) 0.7744 Å, H(8A)–N(8)–H(8B) 109.96°]. Ligand L is deprotonated at O(12).

The SiF_6^{2-} unit, which lies on an inversion centre, links two of the cationic $CuL(H_2O)^+$ units together to form a unique single-bridged hexafluorosilicato dinuclear copper(II) co-ordination compound. The Cu ⋯ Cu′ distance is 7.9507(6) Å. The bridging mode can be described as two copper(II)-containing square pyramids containing fluoride in the apical position which point towards each other and are linked by a hexafluorosilicato anion with a Cu–F(1)–Si angle of only 140.07(8)°. The M–F–Si angles are much larger in other six-co-ordinated metal(II) chains, such as $[Co(Hvim)_4(SiF_6)]$ (180°),[1] $[Cu(Hppz)_4(SiF_6)]$ [171.4(2), 173.8(2)°][2] and $[Cu(H_2O)_4(SiF_6)]$ [152.2(3)°][3]. The observed low angle of 140.07(8)° must be due to the stabilization by the hydrogen bonding network. Both water molecules are involved in hydrogen bonding with fluoride atoms of the hexafluorosilicate [O(1) ⋯ F(3) (1 − *x*, 1 −*y*, −*z*) 2.645(2) Å, O(1)–H(1B) ⋯ F(3) 164.27(8)°, O(1)–H(1B) 1.0399, F(3) ⋯ H(1B) 1.629(2) Å; O(2) ⋯ F(2) (1 − *x*, −*y*, −*z*) 2.749(3) Å, O(2)–H(2A) ⋯ F(2) 176.30(7)°, O(2)–H(2A) 0.8653, F(2) ⋯ H(2A) 1.885(3) Å]. In addition, hydrogen bonds are present between the non-co-ordinated water molecule and the co-ordinated oxygen of L [O(2) ⋯ O(12) 2.814(2) Å, O(2)–H(2B) ⋯ O(12) 176.28(8)°, O(2)–H(2B) 0.9193, O(12) ⋯ H(2B) 1.896(2) Å] and between the water molecules [O(1) ⋯ O(2) (1 −*x*, −*y*, −*z*) 2.593(2) Å, O(1)–H(1A) ⋯ O(2) 176.85(9)°, O(1)–H(1A) 0.8797, O(2) ⋯ H(1A) 1.715(2) Å]. The presence of these hydrogen bonds is also reflected in the IR spectrum, where the very broad absorptions at 2850 and 3220 cm^{-1} correspond to hydrogen bonds with lengths around 2.60–2.65 Å and 2.75–2.81 Å respectively.[7]

Vibration absorptions of SiF_6^{2-} in the IR spectrum are situated at 720 (ν_1) and 484 cm^{-1} (ν_4), in agreement with the symmetry of the anion being lowered from O_h to D_{4h}.[8]

The X-band powder EPR spectra recorded at 298 and 77 K shows only an isotropic signal at $g = 2.05$ and no indication of Cu ⋯ Cu exchange splittings are observed.

This is in agreement with the magnetic data recorded in the temperature range 7.2–300 K, where the product of the magnetic susceptibility (χ) and the temperature remains relatively constant over the whole temperature range studied, with a value of 0.335 cm^3 K mol^{-1}, which agrees with the theoretical value for isolated $S = \frac{1}{2}$ ions. This is as expected, since the copper(II) ions are widely separated [Cu ⋯ Cu′ 7.9507(6) Å] and are linked only by a single hexafluorosilicato bridge *via* apical Cu–F bonds.

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