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$Cu(en)_2SiF_6$ and $[Cu(dmen)_2(H_2O)]SiF_6$ (*en* = 1,2-diaminoethane; *dmen* = *N*,*N*-dimethyl-1,2-diaminoethane): Preparations, crystal structures, spectroscopic properties and hydrogen bonding mediated magnetism

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ABSTRACT

Crystals of $Cu(en)_2SiF_6$ (*en* = 1,2-diaminoethane) (**1**) and $[Cu(dmen)_2(H_2O)]SiF_6$ (*dmen* = *N*,*N*-dimethyl-1,2-diaminoethane) (**2**) were isolated from aqueous–ethanolic systems Cu^{2+}-*en* or *dmen*-SiF_6^{2-}. The chain-like crystal structure of **1** is built up of $[Cu(en)_2]^{2+}$ complex cations linked by bridging μ_2-SiF_6^{2-} anions with *trans* positions of the bridging fluorine atoms. Copper ion exhibits usual distorted octahedral coordination; there are two chelate coordinated *en* ligands in the equatorial plane with Cu—N1 bonds of 1.9994(14) Å (4*x*), while the axial positions are occupied by fluorine atoms from SiF_6^{2-} anions with Cu—F2 bond of 2.6065(14) Å (2*x*). The individual chains are linked by N—H···F type hydrogen bonds. In **2** the coordination polyhedron of the Cu(II) atom can be described as slightly deformed square pyramid (τ = 13.0%) with four N atoms from two chelate *dmen* ligands placed in the basal plane (Cu—N bonds are from the range 2.0164–2.0599 Å) while the apical position is occupied by an aqua ligand at Cu—O distance is 2.293 (2) Å. The structure of **2** is stabilized by O—H···F and N—H···F hydrogen bonds between complex cations and the hexafluoridosilicate anions. The EPR spectra show the rhombic anisotropy of *g*-factor in both complexes. Magnetic measurements indicate the presence of two-dimensional antiferromagnetic structure in both complexes. A weak exchange coupling J/k_B = −0.85 K was found in **1**. Much stronger exchange coupling J/k_B = −3.69 K present in **2** allowed us to identify spatial anisotropy of the exchange coupling, α = 0.2, and to describe **2** by rectangular antiferromagnetic lattice model.

1. Introduction

Hydrogen bonds as an important non-bonding interaction are well described from geometric as well as energetic point of view and they play an important role in chemistry, physics and biology [1,2]. It was also demonstrated that hydrogen bonds can serve as the path of the magnetic exchange interactions, especially in case of Cu(II) (S = 1/2) compounds [3–5]; nevertheless, quantum chemical calculations indicated that the role of the hydrogen bonds in mediating magnetic exchange interactions is mainly limited to structural role, i.e. to hold the paramagnetic centers in a suitable geometric arrangement [6].

In our previous papers we have studied correlation between the crystal structures and the magnetic and thermodynamic properties of low-dimensional complexes of the general formula $Cu(L)_2M(CN)_4$ in which *L* were bidentate chelate ligands *en* or its *N*-methylated derivates and M was Ni, Pd or Pt [7–9]. The formed complexes generally exhibit one-dimensional (1D) crystal structure in which complex cations $[Cu(L)_2]^{2+}$ are linked by square tetracyanidocomplex anions $[M(CN)_4]^{2-}$ with *trans*-positions of the bridging cyanido ligands in both complex ions forming a 2,2-TT type 1D (from covalent bonds point of view) structure (for the nomenclature see Ref. [10]). The main differences between the formed structures are represented by the formed pattern of the hydrogen bonding system. The obtained results on M = Ni and Pd complexes were later confirmed on the analogous, often isostructural tetracyanidoplatinate complexes [11,12].

The observed antiferromagnetic interactions between the Cu(II) atoms (S = 1/2) were weak, so it was concluded that magnetic exchange paths between the Cu(II) atoms through hydrogen bonds were competitive to the path through the —N≡C—M—C≡N— five-atomic bridge formed by the cyanidocomplex anion. This conclusion was supported also by the orientation of the d_{z^2} orbital of the Cu(II) atoms containing two paired electrons; this orbital is oriented toward the five-atomic cyanidocomplex bridge while the $d_{x^2-y^2}$ orbital containing the unpaired electron and thus most of the spin density lies within the plane of hydrogen bonds. As an example we can mention the case of $Cu(en)_2Ni(CN)_4$; despite its structurally 1D character from covalent bonds point of view its

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specific heat study revealed that it behaves as a 2D square lattice Heisenberg antiferromagnet (AFM) with the exchange constant of $J/k_B = -180$ mK and the 2D–3D crossover was observed at 128 mK [13]. In order to shorten this five-atomic bridge as well as to preserve the possibility of magnetic exchange interactions through hydrogen bonds we decided to replace the square tetracyanidocomplex anion $[M(CN)_4]^{2-}$ in the $Cu(L)_2M(CN)_4$ type compounds by the hexafluoridosilicate anion. Literature data show that hexafluoridosilicate anion can act simply as a counter ion, e.g. in $[Cu(bipy)_2(H_2O)_2]SiF_6$ (*bipy* = 4,4′-bipyridine) [14,15] or also as a bridging unit linking metal atoms; in this case $\{\mu_2\text{-}SiF_6\}$ (*trans*) and $\{\mu_4\text{-}SiF_6\}$ (*trans*) bridging modes were observed. As examples we can mention $Cu(bipy)_2(SiF_6)\cdot 8H_2O$ (*bipy* = 4,4′-bipyridine) [15] and $Cu_2(dpya)_2F_2(SiF_6)\cdot CH_3OH$ (*dpya* = 2,2′-dipyridylamine) [16].

2. Experimental

2.1. Materials

Copper(II) tetrafluoridoborate hydrate $Cu(BF_4)_2\cdot H_2O$, 98%, 19–22% Cu, Aldrich), ammonium hexafluoridosilicate $(NH_4)_2SiF_6$, 98%, Aldrich), 1,2-diaminoethane (*en*, $C_2H_8N_2$, 99.5%, Aldrich), *N,N*-dimethyl-1,2-diaminoethane (*dmen*, $C_4H_{12}N_2$, 98%, Aldrich), ethanol (analytical grade) were used as received.

2.2. Synthesis of bis(1,2-diaminoethane)-hexafluoridosilicate copper(II) complex, $Cu(en)_2SiF_6$ (**1**)

To an aqueous–ethanolic (1:1 in vol.) solution of $Cu(BF_4)_2\cdot H_2O$ ($x \cong 6$, 0.273 g, approx. 1.0 mmol, 10 cm^3 of the solvent) were successively added 0.13 cm^3 (2 mmol) of *en* and aqueous solution of $(NH_4)_2SiF_6$ (0.178 g, 1.0 mmol, 10 cm^3 of water). The formed violet solution was filtered in order to remove any solid impurity. Violet needles separated from the filtrate within 3 weeks, they were separated by filtration and dried on air. Yield: 32% (0.101 g).

Anal. Calc. for $CuC_4H_{16}N_4F_6Si$: C, 14.74; H, 4.94; N, 17.19; Cu, 19.50. Found: C, 14.64; H, 5.01; N, 16.85 Cu, 18.95%.

IR (cm^{-1}): 3309s; 3217s; 3138m; 2965w; 2892w; 1622w; 1609w; 1583vs; 1430w; 1044vs; 756s; 525s; 483s.

2.3. Synthesis of bis(N,N-dimethyl-1,2-diaminoethane)-(aqua)-hexafluoridosilicate copper(II) complex, $[Cu(dmen)_2(H_2O)]SiF_6$ (**2**)

The violet crystals of $[Cu(dmen)_2(H_2O)]SiF_6$ were prepared by similar method to that used for preparation of **1** but instead of the *en* ligand *dmen* ligand (0.22 cm^3, 2 mmol) was used. Within 1 month violet prisms crystallized, these were separated by filtration and dried on air at laboratory temperature. Yield: 21% (0.084 g).

Anal. Calc. for $CuC_8H_{26}N_4F_6OSi$: C, 24.02; H, 6.55; N, 14.00; Cu, 15.89. Found: C, 24.12; H, 6.48; N, 13.78; Cu, 15.94.

IR (cm^{-1}): 3439m; 3191vs; 3097vs; 2963w; 2901w; 1635w; 1609w; 1459m; 1153m; 1063s; 746vs; 476vs.

2.4. Physical measurements

Elemental analyses (C, H, N) were performed on a Flash EA 1112 Elemental Analyzer (ThermoFinnigan).

Infrared spectra were recorded on a FT-IR Avatar 330 Thermo-Nicolet instrument using KBr pellets technique (1:100) in the range of 4000–400 cm^{-1}.

Electronic absorption spectrum was recorded on a Specord 250 spectrometer (Analytik Jena) in Nujol suspension.

Electron-paramagnetic resonance (EPR) data were collected at 2.5 K in an X-band Bruker ELEXSYS E500 spectrometer. The magnetic susceptibility (determined using the relation $\chi = M/H$) was taken at 0.1*T* using a Quantum Design SQUID magnetometer (MPMS-XL5) in the temperature range from 1.8 to 300 K. The background contribution from the gelatine capsule to the magnetic moment of the sample has been subtracted. The obtained data were corrected to diamagnetic contribution using Pascal's constants

Table 1
Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_4H_{16}CuF_6N_4Si$	$C_8H_{26}CuF_6N_4OSi$
Formula weight	325.84	399.96
T (K)	290(2)	290(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Cmca*	*C*2/*c*
Unit cell dimensions		
a (Å)	14.397(5)	15.9306(4)
b (Å)	7.861(3)	6.96650(10)
c (Å)	10.002(3)	15.4700(4)
β (°)	90	117.070(3)
V (Å^3)	1131.97(7)	1528.79(6)
Z	4	4
D_{calc} (g cm^{-3})	1.912	1.738
Absorption coefficient (mm^{-1})	2.097	1.575
Crystal dimensions (mm)	0.23 × 0.23 × 0.10	0.54 × 0.36 × 0.35
Theta range for data collection (°)	3.59–26.50	3.04–26.97
Index ranges	$-18 \leqslant h \leqslant 18$	$-20 \leqslant h \leqslant 20$
	$-9 \leqslant k \leqslant 9$	$-8 \leqslant k \leqslant 8$
	$-12 \leqslant l \leqslant 12$	$-19 \leqslant l \leqslant 19$
Reflections collected/independent	5469/610 [R_{int} = 0.0402]	15440/1664 [R_{int} = 0.0203]
Absorption correction	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Maximum and minimum transmission	0.651and 0.839	0.571 and 0.644
Data/restraints/parameters	610/0/42	1664/0/104
Goodness-of-fit (GOF) on F^2	1.035	1.169
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0203, wR_2 = 0.0590	R_1 = 0.0268, wR_2 = 0.0766
R indices (all data)	R_1 = 0.0265, wR_2 = 0.0604	R_1 = 0.0306, wR_2 = 0.0781
Largest difference in peak and hole (e Å^{-3})	0.26(5) and −0.22(5)	0.58(7) and −0.27(7)