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A Mixed-Valence Tetranuclear Copper Cluster with Localized Valencies

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Introduction

Mixed-valence coordination compounds with short metal−metal distances involving bridging ligands have been of great and increasing interest during the last decade.[1,2] Their importance in biology is due to the total delocalization of the metal valencies over the cluster, which makes them very efficient in electron-transfer processes.[2−4] Worldwide, researchers have been studying clusters such as two,[5] three,[6] and four iron−sulfur clusters,[7] the four manganese cluster,[8] and polynuclear active sites in copper proteins,[3,4] both in the proteins and in synthetic analogues. In nature, mixed-valence clusters (often) contain metal ions in rigorously equivalent sites with totally delocalized valencies. On the contrary, mixed-valence compounds obtained by synthetic procedures are known to be of three types: those having totally localized (or trapped) valencies (class I), those in which the valencies may be essentially localized, with the possibility of (electron) hopping (class II), and those in which the valencies can be totally delocalized (in this case, the metal sites are rigorously equivalent) (class III).[9]

Mixed-valence compounds of each class have interesting physical properties (*e.g.*, magnetic behavior,[2] electrical conductivity,[10] bistability of the compounds, capability of electron transfer),[11] which makes them the compounds of choice for several applications (magnetic materials and in molecular electronics,[12] and also in electron-transfer processes).[11]

The coordination geometries of copper ions in (nonbiological) mixed-valence compounds are mostly highly different, and the unpaired electron tends to be localized on a certain metal ion; the valencies are trapped by stereochemical effects.

It is of interest to find out whether a rational choice of ligands and counterions can lead to mixed-valence species of either character. We now report on the synthesis, structure, and physical properties of an unusual tetranuclear class I Cu mixed-valence compound.

Experimental Section

Synthesis of 4-Amino-3,5-bis[(*N*-methylamino)methyl]-1,2,4-triazole (maamt). The maamt ligand has been prepared from glycine methyl ester hydrochloride and hydrazine monohydrate according to the method reported in the literature for the non-methylated derivative.[13,14]

Synthesis of $[Cu(maamt)(CuCl_3)]_2$ (1). To 17.6 mmol (3.00 g) of $CuCl_2\cdot 2H_2O$ in 50 mL of methanol was added 17.6 mmol (3.00 g) of maamt dissolved in 50 mL of methanol. The solution was filtered, and after a few days the dark blue compound crystallized upon slow evaporation of the solvent at room temperature. Yield: 25%. Anal. Calcd for $C_{12}H_{28}Cl_6Cu_4N_{12}$: C, 17.85; H, 3.50; N, 20.82; Cu, 31.48. Found: C, 17.80; H, 3.52; N, 21.14; Cu, 31.10.

X-ray Crystallography. A dark blue, block-shaped crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm^3 was sealed in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4-Turbo diffractometer, using a rotating anode X-ray source. Accurate unit cell parameters and an orientation matrix were determined at 298 K by least-squares refinement of 25 well-centered reflections (SET4) in the range $9.9^\circ < \theta < 15.4^\circ$ using graphite-monochromated Mo $K\alpha$ radiation (0.710 73 Å). Reduced cell calculations did not indicate higher lattice symmetry.[15] Crystal data and details on data collection and refinement are given in Table 1. Data were corrected for Lorentz and polarization effects. Three periodically measured reference reflections showed no significant linear decay (<1%) during 10 h of X-ray exposure. An empirical absorption and extinction correction was applied (DIFABS[16]). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[17]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-92[18]); an observance criterion was not applied during the refinement. Hydrogen atoms were included in the refinement at calculated positions (C−H = 0.98 Å) riding on their carrier atoms, except for the amine hydrogen atoms bonded to N31, N41, and N51, which were located on a difference Fourier map and subsequently included in the refinement. All non-hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 and 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms for the secondary amine and methyl hydrogen atoms and for the other hydrogen atoms, respectively. Convergence was reached at $R_1 = 0.053$, $wR_2 = 0.099$, for 1638 $F_o > 4\sigma(F_o)$, $S = 0.93$. Neutral atom scattering factors and anomalous dispersion corrections were taken from the

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Table 1. Crystal Data and Details of the Structure Determination for $[Cu(maamt)(CuCl_3)]_2$

formula	$C_{12}H_{28}Cl_6Cu_4N_{12}$
mol wt	807.34
temp (K)	298
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	9.917(1)
b (Å)	11.541(1)
c (Å)	11.733(1)
β (deg)	100.39(1)
V (Å^3)	1320.9(2)
Z	2
d_{calc} (g/cm^3)	2.030
d_{obs} (g/cm^3)	2.00
μ (Mo Kα, cm^{-1})	38.3
θ range (deg)	1.77−27.49
hkl ranges	*h*, −12 to 12
	k, 0 to 14
	l, −10 to 15
no. of reflns measd	3556
no. of indep reflns	3018
R(int)	0.043
no. of reflns used ($I > 2.5\sigma(I)$)	3018
no. of params	162
$R_1{}^a$	0.053
$wR_2{}^a$	0.099
res el density (e Å^{-3})	−0.59, 0.48

[a] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 4\sigma(F_o)$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$. $w = 1/(\sigma^2(F^2) + (0.0394P)^2)$. $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for $[Cu(maamt)(CuCl_3)]_2$ with Esd's in Parentheses

	x	y	z	U(eq)^a
Cu	−0.14797(7)	0.89919(6)	−0.09175(6)	0.0313(2)
Cu(1)	−0.21343(9)	1.04330(8)	0.19159(7)	0.0483(3)
Cl(1)	−0.2797(2)	0.87591(13)	0.10422(12)	0.0398(5)
Cl(2)	−0.0098(2)	1.09912(15)	0.28407(13)	0.0446(5)
Cl(3)	−0.3856(2)	1.18292(14)	0.17331(13)	0.0410(5)
N(1)	0.1275(4)	0.9333(4)	0.0660(3)	0.0252(12)
N(2)	0.0274(4)	0.8651(4)	0.0042(4)	0.0271(14)
N(4)	0.2146(4)	0.7651(4)	0.0413(4)	0.0245(12)
N(31)	−0.1401(5)	0.7239(4)	−0.1257(4)	0.0306(16)
N(41)	0.3040(5)	0.6719(5)	0.0414(4)	0.0398(17)
N(51)	0.3337(5)	1.0471(4)	0.1808(4)	0.0301(17)
C(3)	0.0809(5)	0.7648(4)	−0.0108(4)	0.0254(17)
C(5)	0.2402(5)	0.8727(4)	0.0865(4)	0.0252(17)
C(31)	0.0010(6)	0.6763(5)	−0.0857(5)	0.0381(19)
C(32)	−0.2444(7)	0.6529(5)	−0.0827(6)	0.051(2)
C(51)	0.3691(6)	0.9296(5)	0.1413(5)	0.0372(19)
C(52)	0.3466(6)	1.0522(6)	0.3078(5)	0.046(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U.

International Tables for Crystallography.[19] Geometrical calculations and illustrations were performed with PLATON93.[20] All calculations were performed on a DECstation 5000/125. Positional and equivalent thermal parameters are given in Table 2.

Magnetic Measurements. Magnetic susceptibilities were measured and fitted to the theoretical expression as described in refs 21 and 22.

EPR Spectroscopy. X-band powder EPR spectra have been obtained on a JEOL RE2x electron spin resonance spectrometer.

Ligand Field Spectroscopy. UV/visible spectra were obtained on a Perkin Elmer 330 spectrophotometer using the diffuse reflectance technique with MgO as a reference.

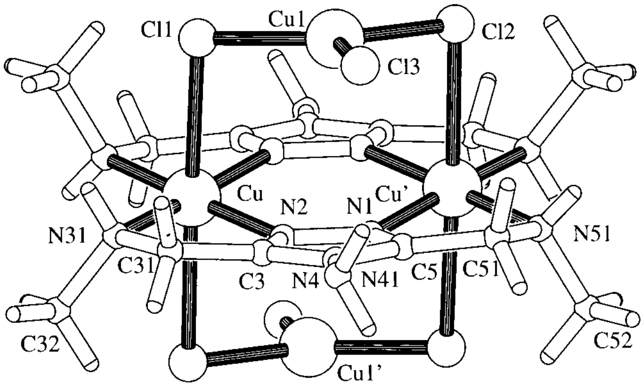

Figure 1. PLUTON[20] drawing and atomic labeling system showing the structure of $[Cu(maamt)(CuCl_3)]_2$. Primed atoms are generated by the symmetry operation $-x, 1 - y, 1 - z$.

Table 3. Selected Distances (Å) and Angles (deg) for $[Cu(maamt)(CuCl_3)]_2{}^a$

Cu···Cu′	4.048(1)	Cu−N2	1.934(4)
Cu1···Cu1′	6.782(1)	Cu−N31	2.066(5)
Cu···Cu1	3.875(1)	Cu′−Cl2	2.969(2)
Cu′···Cu1	4.022(1)	Cu1−Cl1	2.230(2)
Cu−N1′	1.962(5)	Cu1−Cl2	2.209(2)
Cu−N51′	2.043(5)	Cu1−Cl3	2.329(2)
Cu−Cl1	2.855(2)		
Cu−Cl1−Cu1	98.57(7)	Cl2−Cu1−Cl3	115.69(7)
Cu′−Cl2−Cu1	100.90(6)	Cu′−N1−N2	133.9(3)
Cl1−Cu1−Cl2	130.24(8)	Cu−N2−N1	133.0(4)
Cl1−Cu1−Cl3	114.00(7)		

[a] Primed atoms are generated by the symmetry operation $-x, 1 - y, 1 - z$.

Results and Discussion

The structure of **1** is shown in Figure 1, with relevant bond length and bond angle information given in Table 3. The monoclinic cell contains two $[Cu(maamt)(CuCl_3)]_2$ units. The molecular structure can be described as a dinuclear $[Cu^{II}(maamt)]_2{}^{4+}$ cation to which two $[Cu^{I}Cl_3]^{2-}$ anions are weakly coordinated. The $[Cu(maamt)]_2{}^{4+}$ unit resembles previously reported compounds obtained with 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole.[14,23] The maamt ligand acts as a doubly bidentate ligand, linking the metal ions which are related by a crystallographic center of symmetry. This 1,2,4-triazole bridging mode *via N*1,*N*2 is quite well known in copper(II) coordination compounds.[14,21−25] The Cu−Cu′ distance within the cation of 4.048(1) Å is in the same range as for related dinuclear compounds.[14,21−25] The Cu(II) atom is in a distorted octahedral environment. The equatorial plane is formed by four N-donor atoms of two maamt ligands. The $[CuCl_3]^{2-}$ unit is linked *via* Cl1 to Cu (2.855(2) Å) and *via* Cl2 to Cu′ (2.969(2) Å). The Cu−Cl1−Cu1 and Cu′−Cl2−Cu1 angles are 98.57(7)° and 100.90(6)°. The resulting Cu−Cu1 and Cu′−Cu1 distances are 3.875(1) and 4.022(1) Å, respectively. These approximately trigonal planar $[CuCl_3]^{2-}$ units with C_{2v} symmetry are stacked above the triazole ring at a distance of 3.193(1) Å. This stacking position is further stabilized by the intramolecular hydrogen bond between Cl3 and the amino group attached to the triazole ring (N41···Cl3 ($-x, 1 - y, 1 - z$) = 3.247(5) Å; N41-H41A = 0.88(7) Å; H41A···Cl3 ($-x, 1 - y, 1 - z$) = 2.60(7) Å; N41−H41A···Cl3 ($-x, 1 - y, 1 - z$) =

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131(6)°). The steric features of the complex require the methyl groups of the aminomethyl substituents of maamt to be twisted out of the equatorial plane and away from the copper(I) trichloride anion that is stacked above the triazole ring. As a result, these two amino groups are also involved in hydrogen bonding with Cl3 (N51···Cl3 ($x - 1, y, z$) = 3.210(5) Å; N51−H51 = 0.77(6) Å; H51···Cl3 ($x - 1, y, z$) = 2.47(6) Å; N51−H51···Cl3 ($x - 1, y, z$) = 161(6)°). The lattice structure is further stabilized by hydrogen bonds.[26]

Although the trichlorocopper(I) unit is known as a noncoordinating anion,[27,28] also two examples of bidentate bridging $[CuCl_3]^{2-}$ anions are known.[29,30]

The differences in the coordination environment clearly indicate that the Cu atoms are Cu(II), whereas the atoms marked Cu1 are Cu(I). The valencies are expected to be (essentially) localized. This is confirmed by the EPR (below) and magnetic susceptibility data recorded in the temperature range 6-292 K. The typical behavior of a copper(II) dinuclear compound has been found with a maximum in the χ *vs* T curve at *ca*. 130 K. The magnetic data have been fitted to the modified Bleaney and Bowers expression for the molar magnetic susceptibility for S = $^1/_2$ dimers,[31] based on the spin Hamiltonian $\mathbf{H} = -2J[\mathbf{S}_{Cu1}\cdot\mathbf{S}_{Cu2}]$, yielding $J = -78(2)$ cm^{-1}, $g = 2.05(1)$, and a fraction of paramagnetic contribution of 0.0277. The J value can be explained on the basis of the localized valencies and the geometry around Cu(II). The unpaired electron for the d^9 ion clearly resides in the d(x^2-y^2) orbital, with hardly any density in the direction of the axial Cl ligands. The magnitude of the antiferromagnetic interaction between Cu(II) ions can, therefore, be explained by the superexchange pathway involving the σ orbitals of the *N*1,*N*2-diazine moiety of the bridging triazole network.[14,21−25]

The X-band powder EPR spectra (77 and 298 K) are typical of a triplet spin state showing the $\Delta m_s = \pm 1$ transition at g = 2.10 and $|D| = 0.05$ cm^{-1}, as well as the transition forbidden by the selection rule, $\Delta m_s = 2$ at $g = 4.29$, due to the coupling of the two Cu(II) $S = {}^1/_2$ spins.

The UV/visible spectrum shows a broad asymmetric band with a maximum at 15.6 × 10^3 cm^{-1}, with a shoulder at 11.7 × 10^3 cm^{-1}, which is in agreement with the presence of a tetragonal $Cu^{II}N_4Cl_2$ chromophore.[32] There is no evidence for intervalence charge-transfer bands.

In conclusion, $[Cu(maamt)(CuCl_3)]_2$ represents a novel example of a tetranuclear copper mixed-valence cluster with localized valencies. The compound shows some similarity to the tetranuclear complex $[Cu_2(H_2L1][Cu_2Cl_4]$, where H_2L1 is the 20-membered macrocycle obtained from the template condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane.[33] However, this compound contains the planar $[Cu_2Cl_4]^{2-}$ anions coordinated monodentately to the Cu(II) ions, and the unique stacking does not occur. Consequently, the topology of the cluster is entirely different from that in our compound. The topology of the present cluster is remarkable: the Cu(II) ions are linked by a double diazine bridge, whereas the Cu(II) and Cu(I) ions are only bridged by a single chloride anion. The stacking of $Cu^ICl_3{}^{2-}$ anions upon the triazole ring is unique. The Cu(I)−Cu(II) distances are even shorter than the Cu(II)−Cu(II) distances. The magnetic properties of this cluster indicate the presence of localized valencies, in agreement with the presence of different Cu(I) and Cu(II) coordination environments.

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Supporting Information Available: Figure S1 showing the χ *vs* T curve for $[Cu(maamt)(CuCl_3)]_2$; details of the structure determination, including atomic coordinates, bond lengths and angles, and (an)isotropic thermal parameters; and an ORTEP projection (9 pages). Ordering information is given on any current masthead page.

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(26) The lattice structure is further stabilized by hydrogen bonds between the (methylamino)methyl N31 and Cl1 of a neighboring tetranuclear cluster (N31···Cl1 (x, 0.5 − y, 0.5 + z) = 3.421(5) Å; N31−H31 = 0.84(6) Å; N31···Cl1 (x, 0.5 − y, 0.5 + z) = 2.70(6) Å; N31−H31···Cl1 (x, 0.5 − y, 0.5 + z) = 146(5)°), as well as between amino nitrogen N41 and Cl3 of another tetranuclear unit (N41···Cl3 (−x, −0.5 + y, 0.5 − z) = 3.301(5) Å; N41−H41B = 0.95(7) Å; H41B···Cl3 (−x, −0.5 + y, 0.5 − z) = 2.41(7) Å; N41−H41B···Cl3 (−x, −0.5 + y, 0.5 − z) = 156(5)°).

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