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Synthesis, Spectroscopy and X-ray Structure of Hexakis(μ-3-methyl-4-ethyl-1,2,4-triazolo-N^1,N^2)tetraaquatricopper(II) Hexakis(trifluoromethylsulfonate)

W. VREUGDENHIL*, J. G. HAASNOOT**, J. REEDIJK

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

and J. S. WOOD**

Department of Chemistry, University of Massachusetts, Amherst, MA (U.S.A.)

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Abstract

The synthesis, characterization and X-ray structure determination of $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6 \cdot (H_2O)_4$ is described. The compound crystallizes in the space group $R\bar{3}$, with $a = b = 14.075(3)$ and $c = 34.655(8)$ Å. The complex cation consists of linear trinuclear clusters positioned on the crystallographic three-fold axis, and in which the Cu atoms are bridged by triple N^1,N^2-coordinating triazole ligands. The terminal copper atoms are in addition coordinated by two water molecules, and thus have a distorted tetragonal pyramidal geometry. The central copper ion is located at a three-fold inversion center and thus should exhibit dynamic Jahn–Teller behaviour. In the crystal one observes the average of three such trimers related by the three-fold axis, and due to this disorder and also to that in the triflate anions, the structure could be refined only to $R = 0.17$ ($R_w = 0.20$). The infrared and ligand-field spectroscopic data and magnetic susceptibility are in agreement with the observed structure.

Introduction

In the past decades, a variety of coordination compounds has been reported containing N^4 substituted 1,2,4-triazoles as a ligand coordinating to first-row transition metal ions [1–9]. Structures and magnetic properties of di- and trinuclear compounds have been described. From those studies it was concluded, that 1,2,4-triazoles easily form triple bridges, coordinating through their N^1 and N^2 atoms. These oligonuclear, triple-bridged compounds show rather weak magnetic interactions.

The research on 4-alkyltriazoles has recently been extended to the asymmetric 3,4-disubstituted triazoles [10, 11]. The structures and magnetic properties of the compounds with 3-methyl-4-ethyl-1,2,4-triazole (abbreviated as metz) (Fig. 1) strongly resemble those of the compounds containing 4-alkyltriazoles [10, 4–7]. In the trinuclear compounds two types of coordination sites are present; one MN_6 and two MN_3O_3 configurations occur. The research on the asymmetric ligands aims at increasing the differences between the two coordination sites. In the present paper we report the structural, spectroscopic and magnetic properties of a trinuclear copper(II) compound with metz as a ligand. In the series of trinuclear compounds with metz as a ligand reported sofar, a well-defined Cu(II) compound was lacking [10].

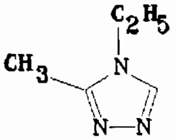

Fig. 1. 3-Methyl-4-ethyl-1,2,4-triazole.

Experimental

Syntheses

The synthesis of the ligand has been described previously [10].

Synthesis of $[Cu_2(metz)_6(H_2O)_4](CF_3SO_3)_6 \cdot (H_2O)_4$: a solution of 2 mmol of $Cu(CF_3SO_3)_2$ in 5 ml of water was added to a solution of 2 mmol of metz in 5 ml of water. The compound crystallizes upon standing at room temperature. After crystallization the compound was filtered off, washed with a small amount of ethanol and dried in air.

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*Present address: Research Centre Amsterdam, AKZO Chemicals, P.O. Box 15, 1000 AA Amsterdam, The Netherlands.

**Authors to whom correspondence should be addressed.

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Metal determinations were carried out using standard complexometric titrations. C, H and N analyses were carried out by the Microanalytical Laboratory of University College, Dublin, Ireland. Found: Cu, 10.28; C, 22.12; H, 3.21; N, 12.82. Calc.: Cu, 10.05; C, 22.81; H, 3.73; N, 13.30%.

Spectroscopic Measurements

Infrared spectra (4000–180 cm^{-1}) were recorded as KBr pellets on a Perkin-Elmer 580B spectrophotometer. UV–Vis spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique with MgO as a reference.

Magnetic susceptibilities were measured on a PAR vibrating sample magnetometer model 150 in the temperature range 4–80 K and also on a automatic Faraday balance in the temperature range 80–300 K. $HgCo(NCS)_4$ was used as a calibrant.

X-ray Structure Determination

A hexagonal platelet-shaped crystal of $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$ of dimension, 0.35 × 0.25 × 0.06 mm was mounted on an Enraf Nonius CAD-4 diffractometer and data were collected in the $\omega/2\theta$ scan mode at 295 K. Crystal data: unit $Cu_3S_3C_{36}H_{70}N_{18}O_{26}F_{18}$, $a = b = 14.075(3)$, $c = 34.655(8)$ Å, space group $R\bar{3}$, hexagonal, $Z = 3$, $D_{calc} = 1.59$ g/cm³, Mo Kα radiation (graphite monochromator). Intensity data were collected in the reverse setting, in the range $1.5 < \theta < 18°$. A total of 1952 reflections were measured and yielded 954 independent reflections on averaging. Of these 599 were considered to be observed, ($I > 2\sigma(I)$). The reflections were corrected for absorption using an analytical method as described in the literature [12]. The copper and sulfur atoms were located via a Patterson map and the remaining atoms from successive difference Fourier maps. The structure was refined on F by least squares methods, the function minimized being $\Sigma w(|F_o|) - (|F_c|)^2$ with weights $w = [2L_pF_o/\sigma(I)]^2$. The refinement was considerably complicated by the presence of rotational disorder in the $CF_3SO_3^-$ ion, statistical disorder in the water molecules and the high level of thermal motion in the crystal.

The model giving the best fit to the data, as judged by the R_w value, the 'goodness-of-fit' index and consistency among thermal parameters for atoms in the complex cation had the following features.

(i) A fixed geometry for the $CF_3SO_3^-$ group. C and S atoms were refined conventionally and partially occupied positions of oxygen and fluorine atoms were constrained to give approximate tetrahedral geometries about S and C. The remaining densities (*c.* 1/3 per atom) associated with the O and F atoms were refined as toroidal distributions to simulate the apparent hindered rotational disorder of the $-SO_3$ and $-CF_3$ units. The scattering factors for this density had the form $f_{rotor} = f^*J_0(2\pi rS \sin\phi)$, where f is the spherical atom scattering factor, J_0 is the zero-order Bessel function, r is the radius vector defining the torus of density and ϕ is the angle between r and the scattering vector $\boldsymbol{S}$.

(ii) The oxygen atoms O(1) (coordinated to Cu(2)) and O(2) of the water molecules were refined with 2/3 occupancy. These atoms, atom C(5), and all the atoms of CF_3SO_3, apart from sulfur, were treated isotropically.

No hydrogen atoms were included in the refinement. Anomalous dispersion corrections were included for Cu [13]. The final agreement indices are $R = 0.17$ and $R_w = 0.20$ and the 'goodness-of-fit index' $S = 1.91$. See also 'Supplementary Material'.

Results and Discussion

Description of the Structure of $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)$

The structure consists of linear trinuclear cationic units, which lie on a three-fold axis. The central copper ion is positioned at a $\bar{3}$ inversion centre. An ORTEP [14] drawing of the cluster is given in Fig. 2. Listings of positional and thermal parameters and of geometrical data are given in Tables 1 and 2 respectively. The copper ions are linked to each other by means of triple triazole bridges. The best structural model indicates that two water molecules are coordinated to the terminal metal ions, the crystal symmetry thus requiring that, on average, these positions are 2/3 occupied. As a result the terminal Cu ions are in a tetragonal square pyramidal environment, so that, in each cluster one of the three water molecules at each terminal copper ion, as depicted in Fig. 2, is missing. These open coordination sites are therefore randomly distributed through the whole crystal and each individual cluster actually only possesses a centre of symmetry. The observed three-fold symmetry is due to the positional averaging of the clusters. Because of this asymmetry, all distances from the ligand N^1 atom to the central copper ion appear to be equal, which can be interpreted either in terms of dynamic Jahn–Teller behaviour for this ion at room temperature, or as a statistical average of three ions having a static Jahn–Teller geometry. It is noted that the C3 methyl substituents in this compound are all crystallographically equal and, therefore, must be positioned in the same way, i.e. pointed to the terminal sites of the complex cation. A hydrogen bond is apparently formed between the coordinated water molecules and the lattice water molecules O(1)..O(2) distances: 3.06(6) and 2.55(6) Å).

The structure of the present trinuclear compound strongly resembles that of several other linear trinuclear compounds containing 1,2-bridging triazoles.

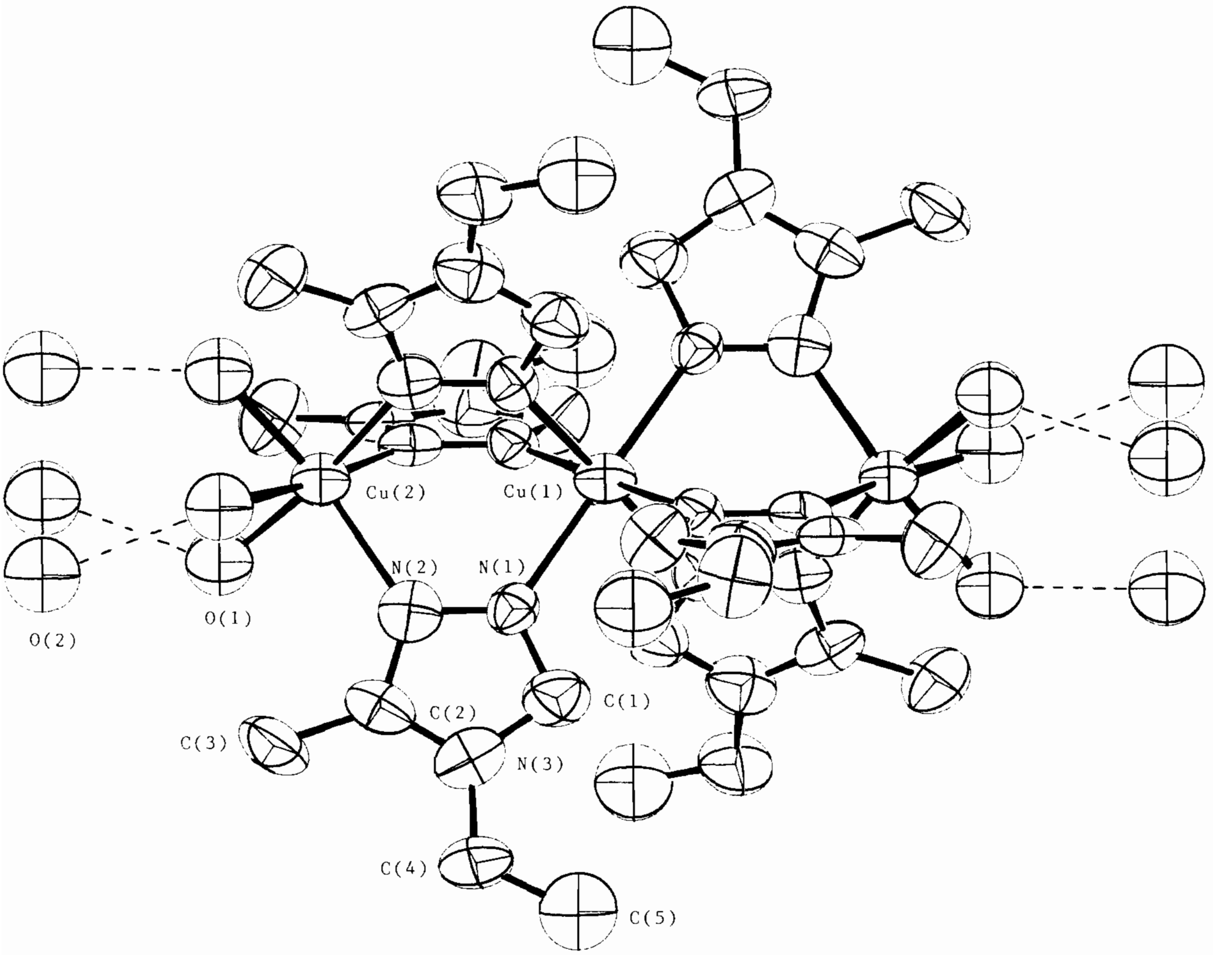

Fig. 2. ORTEP [14] drawing of $[Cu_3(metz)_6(H_2O)_4](H_2O)_4{}^{6+}$. All three partially occupied positions of the water molecules are depicted.

TABLE 1. Fractional atomic coordinates and isotropic thermal parameters of metal and ligand atoms for $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_5$ (e.s.d.s in parentheses)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(iso)[a]	Atom	*x/a*	*y/b*	*z/c*	U_{eq}(iso)[a]
Cu(1)	0	0	0	0.083(5)	O(1)[b, c]	0.113(3)	0.016(3)	0.146(1)	0.12(2)
Cu(2)	0	0	0.1073(2)	0.084(5)	O(2)[b, c]	0.125(3)	0.092(3)	0.212(1)	0.16(2)
N(1)	0.113(2)	0.135(3)	0.035(1)	0.08(3)	S	0.345(1)	0.279(1)	0.091(1)	0.15(1)
N(2)	0.116(3)	0.137(3)	0.074(2)	0.11(3)	O(3)[b, d]	0.352	−0.050	0.066	0.18(3)
C(1)	0.189(5)	0.228(6)	0.19(2)	0.10(4)	O(4)[b, d]	0.295	0.087	0.071	0.18
C(2)	0.200(5)	0.236(6)	0.085(2)	0.10(4)	O(5)[b, d]	0.295	−0.014	0.128	0.18
N(3)	0.245(3)	0.289(3)	0.051(2)	0.12(4)	C(6)	0.477(6)	0.129(5)	0.100(3)	0.17(3)
C(3)	0.239(4)	0.275(4)	0.125(2)	0.12(4)	F(1)[b, d]	0.538	0.161	0.066	0.16(3)
C(4)	0.337(4)	0.398(4)	0.049(2)	0.11(4)	F(2)[b, d]	0.477	0.022	0.117	0.16
C(5)[b]	0.362(5)	0.452(5)	0.011(2)	0.16(3)	F(3)[b, d]	0.524	0.087	0.125	0.16

[a] $U_{eq}(\mathrm{iso}) = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i{}^* a_j{}^* a_i a_j$. [b] Atoms refined isotropically. [c] Atoms refined with occupation factors of 2/3. [d] Atoms treated as rigid groups with occupancies of 0.63, and defined by S–O = 1.47 Å and C–F = 1.39 Å. The remaining density (occupancy 0.37) was treated by toroidal distributions with the same isotropic thermal parameters as for O(3)....F(3).

Although this is the first copper compound in the series for which the crystal structure has been determined, the most striking difference between this compound and the previously described trinuclear compounds with triazole bridges is the coordination sphere of the terminal Cu ions, which have a square

TABLE 2. Relevant interatomic distances (Å) and angles (°) for $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_5$ (e.s.d.s in last significant digits given in parentheses)

Bond distances			
Cu(1)–Cu(2)	3.719(7)	Cu(1)–N(1)	2.14(5)
Cu(2)–N(2)	2.14(5)	Cu(2)–O(1)	1.99(4)
N(1)–N(2)	1.34(6)	N(1)–C(1)	1.33(7)
N(2)–C(2)	1.36(7)	C(1)–N(3)	1.40(8)
C(2)–N(3)	1.36(8)	C(2)–C(3)	1.49(8)
N(3)–C(4)	1.44(7)	C(4)–C(5)	1.49(8)
S–C(6)	1.71(6)	O(1)–O(2)	2.55(6)
O(1)–O(2)^a	3.06(6)		
Bond angles			
N(1)–Cu(1)–N(1)^a	91.0(1.6)	N(1)–Cu(1)–N(1)^b	89.0(1.6)
N(2)–Cu(2)–N(2)^a	93.3(1.6)	O(1)–Cu(2)–O(1)^a	80.6(1.6)
O(1)–Cu(2)–N(2)	92.2(1.4)	O(1)–Cu(2)–N(2)^a	93.2(1.4)
C(1)–N(1)–N(2)	113.7(3.5)	C(2)–N(2)–N(1)	108.4(3.3)
N(1)–C(1)–N(3)	101.1(3.9)	N(2)–C(2)–N(3)	103.4(3.9)
C(1)–N(3)–C(2)	113.0(4.1)	N(2)–C(2)–C(3)	128.1(4.3)
C(1)–N(3)–C(4)	123.2(4.3)	N(3)–C(4)–C(5)	116.4(4.2)
C(2)–N(3)–C(4)	123.8(4.3)		

$^a -y, x - y, z$. $^b y, -x + y, -z$.

pyramidal arrangement. So, in this example the aim of increasing the differences between the coordination sites by using asymmetric triazole ligands has been met. This observation might open a route to the synthesis of heteronuclear compounds.

Spectroscopic and Magnetic Measurements

The presence of two different coordination sites in this compound as determined by the crystal structure determination is also reflected in the ligand-field spectrum. Two band maxima are observed, i.e. one at 10000 and a second one at 14300 cm^{-1}. It cannot be excluded, however, that each Cu(II) contributes to each of these bands.

The infrared spectrum of this compound is almost identical to the spectra of the previously reported trinuclear compounds with these triazole ligands [10, 11], which in fact could be expected from the structural similarity. The infrared spectrum is dominated by the vibrations of the trifluoromethanesulfonate anion.

The magnetic data, recorded from 4–80 K, reveal only small metal–metal interaction, as deduced from a θ value of 2K in a $1/\chi$ versus T plot. Fitting of the data to a theoretical prediction for a linear trinuclear copper cluster did not give any interpretable results [15].

Supplementary Material

Details of the structural constraints, anisotropic thermal parameters and lists of observed and calculated structure factors are available from author J.S.W.

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