

Linkage isomers of dibromobis(1-(2-methoxyethyl)tetrazole)-copper(II) containing either a bromide or a unique tetrazole bridge

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Received 26th March 2003, Accepted 30th July 2003

First published as an Advance Article on the web 14th August 2003

The ligand 1-(2-methoxyethyl)tetrazole (teeOMe) reacts with copper(II) bromide to form two different isomers with the formula $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]_n$. The coordination details on the crystal packing are determined by the solvent from which the compound crystallises. In methanol, green crystals of α - $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ (**1**) are formed, and these have been characterised by X-ray crystallography (at three temperatures) and magnetic susceptibility measurements. The crystal structure of **1** is built up from square-planar *trans*- $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ units. Additional weak axial interactions between the copper centers and the N(2) tetrazole atoms of neighbouring complexes link the $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ units into two-dimensional layers. Compound **1** displays paramagnetic behaviour ($C = 0.41 \text{ cm}^3 \text{ K mol}^{-1}$). In ethanol, yellow-brown crystals of β - $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ (**2**) are formed, and these have been characterised by magnetic susceptibility measurements, in addition to IR, ligand field and EPR spectroscopy. The observed magnetic behaviour ($C = 0.41 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = 30.5 \text{ K}$ and $J/k_B = 16.4 \text{ K}$) is consistent with a structure containing two-dimensional bromide-bridged copper(II) grids. It is proposed that in **2** the square-planar $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ units are connected *via* axial Cu-Br interactions, as deduced from comparison of the magnetic properties.

Introduction

Only a limited number of crystal structures of copper(II) salts with 1-alkyltetrazole ligands have been published. The few structures known can be categorised in three groups. The first group consists of structures with BF_4^- or ClO_4^- anions. The majority contain copper(II) ions that are octahedrally surrounded by six 1-alkyltetrazole ligands.^{1,2} No magnetic coupling is observed for these mononuclear complexes.

Most complexes of tetrazoles with the halogens Br^- and Cl^- as anions crystallise in the space group $P2_1/c$ and adopt two-dimensional structures containing square grids of copper ions, bridged by the halogen ions.³⁻⁷ These structures are assembled from *trans*- $[\text{CuL}_2\text{Br}_2]$ monomers ($L = 1$ -alkyltetrazole). The copper ions are surrounded by tetragonally elongated octahedral coordination spheres: the equatorial plane consists of two 1-alkyltetrazole ligands and two halide anions: the axial positions are occupied by the halide anions of neighbouring $[\text{CuL}_2\text{Br}_2]$ units. Layers of tetrazole ligands, coordinated to the copper ions separate the copper-halide layers.³⁻⁶ Because of the axial distortion, magnetic orbitals centered on adjacent metal ions are strictly orthogonal, and superexchange interactions within the plane are expected to be ferromagnetic.^{8,9}

Finally, in complexes with nitrate anions,¹⁰⁻¹² two 1-alkyltetrazole ligands are *trans*-coordinated to the copper centers, and the other coordination sites are occupied by the nitrate anions (mono-coordinated,¹¹ bridging or chelating^{10,12}) and in one case, water molecules.¹¹ In $[\text{Cu}(\text{teec})_2(\text{NO}_3)_2]$ ($\text{teec} = 1$ -(2-chloroethyl)tetrazole),¹⁰ very weak ferromagnetic coupling is observed.

Few structures are known in which mono-substituted tetrazole rings act as bridging ligands. μ -1,2- η^2 Bridges are observed in *e.g.* $[\text{Ag}(5\text{-}(\text{trifluoromethyl})\text{tetrazolate})(\text{SbPh}_3)_2]_2$,¹³ whereas μ -2,3- η^2 bridges are observed¹⁴ in $[\text{Na}(\text{diglyme})_2][5\text{-}(\text{trifluoromethyl})\text{tetrazolate}]_3\text{Mn}_2(\text{CO})_6$. NMR and infrared measurements have indicated that 1-phenyltetrazole, 1-methyltetrazole

and 1-cyclohexyltetrazole also form μ -3,4- η^2 bridges in molybdenum carbonyl compounds.¹⁵ In all of these compounds, the tetrazole ring bridges *via* two neighbouring nitrogen atoms, as is also observed in structures containing 4-substituted 1,2,4-triazole ligands.¹⁶

In this paper, two compounds with the formula $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]_n$ ($\text{teeOMe} = 1$ -(2-methoxyethyl)tetrazole) are described. Depending on the solvent used, isomers are isolated differing in colour and magnetic properties. The yellow-brown β - $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ isomer (**2**) is crystallised from ethanol and displays ferromagnetic behaviour, and presumably adopts a structure comparable to that described for other tetrazole complexes with copper(II) bromide.³⁻⁶ The structure and magnetic properties of the green α - $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ isomer, (**1**) as crystallised from methanol differ dramatically from those of isomer **2**. No magnetic coupling between the copper(II) ions is observed. In the crystal structure of **1**, the bromide ions are monodentate, and the copper(II) ions are μ -2,4- η^2 -bridged by the tetrazole ligands. This is the first structure described in which a tetrazole ring bridges two copper(II) ions in this way.

Results and discussion

Crystal structure of α - $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]_n$ (**1**)

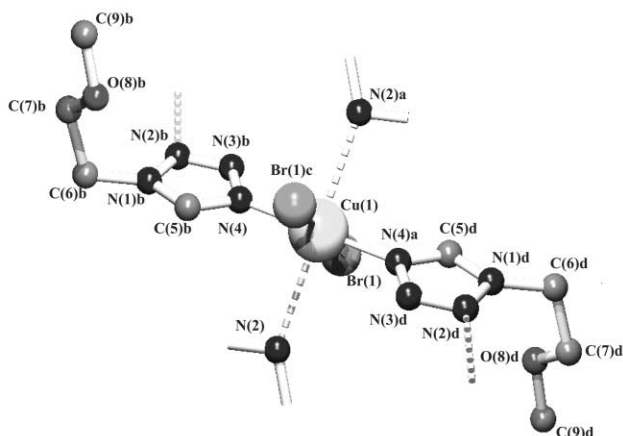
The crystal structure of **1** has been determined at 123 and 297 K for one crystal, and at 150 K for a second. Since the differences between the three structures are minimal, only the 297 K structure of **1** is depicted (Fig. 1) and discussed below. Crystal data are provided in Table 1 and selected bond distances and angles for all three structure determinations are presented in Tables 2 and 3.

The structure is built up from centrosymmetric square *trans*- $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ units: the asymmetric unit contains the copper ion, one bromide anion and one teeOMe ligand. Within the $[\text{Cu}(\text{teeOMe})_2\text{Br}_2]$ units, each copper(II) ion is coordinated

Table 1 Crystallographic data for α -[Cu(teeOMe)₂Br₂] (**1**) at 123, 150 and 297 K

	123 K	150 K	297 K
Chemical formula	C ₈ H ₁₆ Br ₂ CuN ₈ O ₂	C ₈ H ₁₆ Br ₂ CuN ₈ O ₂	C ₈ H ₁₆ Br ₂ CuN ₈ O ₂
Molecular weight	479.64	479.64	479.64
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	10.955(3)	11.0015(2)	11.116(7)
<i>b</i> /Å	8.3625(19)	8.3934(1)	8.489(5)
<i>c</i> /Å	8.957(2)	8.9823(1)	9.023(5)
β /°	105.909(4)	105.9890(10)	106.293(12)
<i>V</i> /Å ³	789.1(3)	797.34(2)	817.2(8)
<i>Z</i>	2	2	2
<i>D</i> _c /g cm ⁻³	2.0187(8)	1.9978(1)	1.9168(19)
μ (Mo-K α)/mm ⁻¹	6.464	6.397	6.231
<i>F</i> (000)	470.0	470.0	470.0
Crystal size/mm		0.06 × 0.21 × 0.21	
Crystal colour	Green	Green	Green
λ (Mo-K α)/Å	0.71073	0.71073	0.71073
θ_{\min} , θ_{\max} /°	1.9, 30.0	1.9, 27.5	1.9, 30.0
Dataset, <i>hkl</i>	-15 to 15; -11 to 11; -11 to 12	-14 to 14; -10 to 10; -11 to 10	-15 to 12; -8 to 11; -12 to 12
Total data, unique, <i>R</i> _{int}	8047, 2239, 0.036	11042, 1817, 0.079	5920, 2317, 0.028
Obs. data (<i>I</i> > 2.0 σ (<i>I</i>))	1944	1640	1990
<i>N</i> _{ref} , <i>N</i> _{par}	2239, 98	1817, 98	2317, 98
<i>R</i> , <i>wR</i> ₂ , <i>S</i>	0.0282, 0.0726, 1.03	0.0357, 0.0939, 1.08	0.0232, 0.0683, 0.80
<i>w</i> ⁻¹ _a	$\sigma^2(F_o^2 + 0.0475P)^2$	$\sigma^2(F_o^2 + 0.0649P)^2$	$\sigma^2(F_o^2 + 0.0521P)^2 + 0.2805P$
Max and av. shift/error	0.00, 0.00	0.00, 0.00	0.00, 0.00
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ /e Å ⁻³	-1.14, 1.23	-1.58, 1.27	-0.39, 0.49

$$^a P = (F_o^2 + 2F_c^2)/3.$$

**Fig. 1** Molecular structure of α -[Cu(teeOMe)₂Br₂] (**1**) at 297 K (hydrogen atoms have been omitted for clarity).^{28,29}

to two *trans*-bromide anions (Cu(1)–Br(1) 2.4335(15) Å and two nitrogen atoms from two teeOMe ligands (Cu(1)–N(4) 2.004(2) Å), at distances comparable to those found in [Cu(teeOMe)₂Br₂] (Cu–Br 2.4520(3) Å, Cu–N 1.9747(16) Å), for example.⁶ The N(2) atoms of the tetrazole rings of two neighbouring [Cu(teeOMe)₂Br₂] units occupy the axial positions above and below the square plane, completing a tetragonally distorted octahedron with bond angles ranging from 88.62(4) to 91.76(6)°. The axial Cu(1)–N(2) distance of 2.781(2) Å is considerably longer than normal coordination bonds; however, in view of the bond angles involving N(2), the copper ion and the other donor atoms, which are close to 90°, the Cu(I)–N(2) bond may be regarded as semi-coordinated.

The tetrazole rings act as μ -2,4- η^2 bridges between the copper(II) ions, forming two-dimensional layers stacked perpendicular to the *bc* plane (Fig. 2) in a way very similar to the triazole rings¹⁷ in Cu(triazole)₂(NCS)₂. The layers are separated by the methoxyethyl substituents of the tetrazole rings and the bromide anions. The closest distance between the copper centers are 6.194(4) Å within a layer and 11.116(7) Å between two neighbouring layers.

Table 2 Selected bond lengths (Å) of α -[Cu(teeOMe)₂Br₂] (**1**) at 123, 150 and 297 K

	123 K	150 K	297 K
Br(1)–Cu(1)	2.4325(7)	2.4367(2)	2.4335(15)
Cu(1)–N(2)	2.7165(19)	2.7319(25)	2.781(2)
Cu(1)–N(4)	1.9935(18)	1.9974(26)	2.004(2)
N(1)–N(2)	1.349(3)	1.3548(35)	1.350(3)
N(2)–N(3)	1.288(2)	1.2863(37)	1.286(3)
N(3)–N(4)	1.357(2)	1.3593(35)	1.358(3)
N(4)–C(5)	1.321(3)	1.3213(37)	1.315(3)
N(1)–C(5)	1.331(2)	1.3294(37)	1.333(2)
N(1)–C(6)	1.468(3)	1.4687(37)	1.463(3)
C(6)–C(7)	1.506(3)	1.5050(46)	1.496(4)
C(7)–O(8)	1.407(3)	1.4040(42)	1.405(4)
O(8)–C(9)	1.421(4)	1.4141(53)	1.430(6)
Cu(1)–Cu(1)a	6.1270(17)	6.1468(1)	6.194(4)
Cu(1)–Cu(1)d	8.957	8.982	9.023

Symmetry codes: (a) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (d) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

The structure of **1** changes very little upon cooling. The main difference observed is a reduction in the Cu(1)–N(2) semi-coordination distance from 2.781(2) to 2.7165(19) Å at 123 K. This contraction is associated with a decrease in the intra-layer distance Cu(1) \cdots Cu(1) from 6.194(4) to 6.1270(17) Å.

Structure of β -[Cu(teeOMe)₂Br₂]_{*n*} (**2**)

Unfortunately, due to the lack of suitable single crystals, the structure of β -[Cu(teeOMe)₂Br₂] (**2**) could not be determined. However, since all other bis(1-alkyltetrazole)copper(II) halides of which the structure has been solved^{3–6} adopt crystal structures containing two-dimensional grids of halide-bridged copper ions with axial N donor ligands, it is plausible that **2** adopts a similar structure. This is especially likely because the magnetic properties of **2** are almost identical to the magnetic behaviour⁶ observed in *e.g.* [Cu(teeOMe)₂Br₂]_{*n*}. It is indeed possible to envision that the square-planar [Cu(teeOMe)₂Br₂] units observed in **1** could be linked by weak axial Cu–Br interactions to form two-dimensional [CuBr₂]_{*n*} layers separated by the teeOMe ligands (see Fig. 3 for a schematic representation).

Table 3 Selected bond angles (°) of α -[Cu(teeOMe)₂Br₂] (**1**) at 123, 150 and 297 K

	123 K	150 K	297 K
Br(1)–Cu(1)–N(2)a	91.09(4)	91.19(5)	91.38(4)
Br(1)–Cu(1)–N(2)b	88.91(4)	88.81(5)	88.62(4)
Br(1)–Cu(1)–N(4)	91.28(5)	91.26(7)	91.01(5)
Br(1)–Cu(1)–N(4)c	88.72(5)	88.74(7)	88.99(5)
N(2)a–Cu(1)–N(4)	88.16(6)	88.34(9)	88.24(6)
N(2)b–Cu(1)–N(4)	91.84(6)	91.66(9)	91.76(6)
N(1)–N(2)–N(3)	107.24(16)	107.20(23)	107.19(16)
N(2)–N(3)–N(4)	109.51(17)	109.66(23)	109.62(17)
N(3)–N(4)–C(5)	107.03(16)	106.85(24)	106.95(15)
N(4)–C(5)–N(1)	107.71(17)	107.98(25)	107.95(16)
C(5)–N(1)–N(2)	108.51(16)	108.30(24)	108.28(15)
N(2)–N(1)–C(6)	122.10(17)	121.97(24)	121.99(17)
C(5)–N(1)–C(6)	129.33(18)	129.68(24)	129.70(18)
N(1)–C(6)–C(7)	110.8(2)	110.70(24)	111.20(19)
C(6)–C(7)–O(8)	106.9(2)	107.54(26)	107.5(2)
C(7)–O(8)–C(9)	112.0(2)	113.03(29)	112.5(3)
Cu(1)–N(4) \cdots N(2)–Cu(1)d	–19.94(4)	–18.5(5)	–15.3(4)
C(6)–C(7)–O(8)–C(9)	178.1(2)	178.4(3)	178.9(3)

Symmetry codes: (a) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (b) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (c) $-x, -y, -z$; (d) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

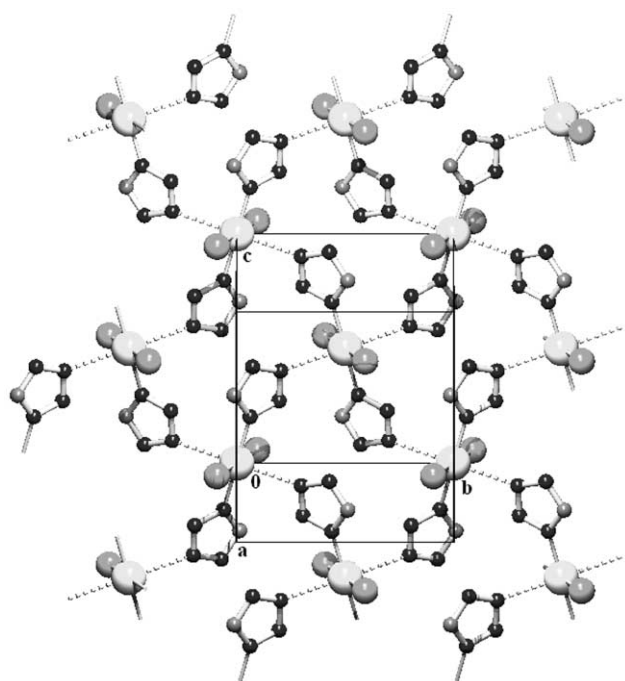


Fig. 2 View down the a -axis of the two-dimensional μ -2,4- η^2 tetrazole-bridged layer in α -[Cu(teeOMe)₂Br₂] (**1**) (hydrogen atoms and the 2-methoxyethyl groups have been omitted for clarity, the unit cell is indicated by the black box).^{28,29}

Because of the tetragonally elongated octahedral coordination geometry, the unpaired electron of each copper(II) ion occupies a d -type orbital with lobes pointing toward the two bromide anions and the two tetrazole nitrogen atoms of the [Cu(teeOMe)₂Br₂] unit. If it is assumed that in the crystal structure neighbouring [Cu(teeOMe)₂Br₂] units are orthogonal, the orbitals centred on adjacent metal ions will also be orthogonal; therefore, according to this model, superexchange interactions within the two-dimensional layer are predicted to be ferromagnetic.^{8,9}

Ligand field, IR and EPR spectroscopy

Ligand field spectra have been recorded for both the green compound **1** and the brown compound **2**. The spectrum of **1** shows broad signals associated with the LMCT transitions at 40.0×10^3 and 23.8×10^3 cm^{-1} . Furthermore, a broad signal is present at 14.0×10^3 cm^{-1} , which is in the normal range for d – d transitions of the copper(II) ion.¹⁸ In compound **2**, similar trans-

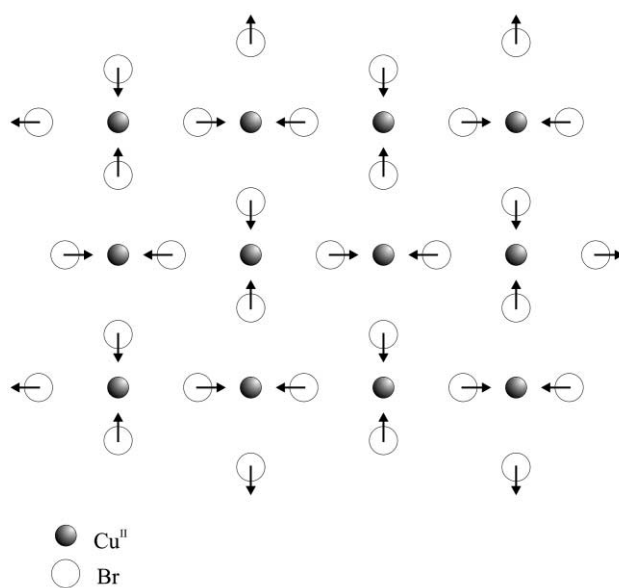


Fig. 3 Model for the two-dimensional [CuBr₂] layer in β -[Cu(teeOMe)₂Br₂] (**2**), with arrows indicating the shortest Jahn–Teller axis.⁹

itions are observed, although at slightly different energies: the LMCT transitions are observed at 40.0×10^3 and 21.5×10^3 cm^{-1} and the d – d transition is observed at 13.4×10^3 cm^{-1} .

The main difference between the infrared spectra of **1** and **2** is the position of the aromatic C–H stretching vibration. In compound **1**, the $\nu(\text{C–H})$ vibration is observed at 3141 cm^{-1} , whereas in compound **2**, this vibration is moved 21 cm^{-1} to 3120 cm^{-1} . In the stretching frequency of the bond between the N1 atom of the tetrazole ring and the first carbon of the methoxymethyl group a shift of 8 cm^{-1} is observed ($\nu(\text{N}_1\text{–C}_{\text{alkyl}})$ is 1364 cm^{-1} in **1** vs. 1356 cm^{-1} in **2**). No other large shifts are present in the infrared spectra. The infrared spectrum of compound **2** has been compared with the spectra of bromide-bridged [CuL₂Br₂]_n compounds, in which L = 1-ethyltetrazole,⁴ 1-(2-fluoroethyl)tetrazole, 1-(2-chloroethyl)tetrazole and 1-(2-bromoethyl)tetrazole.^{6,19} The $\nu(\text{C–H})$ vibration in these compounds was at 3126 , 3113 , 3116 and 3117 cm^{-1} , respectively, indicating that in compound **2** the tetrazole ring is only coordinated to the copper ion, and not bridging, as in compound **1**.

X-Band EPR spectra of polycrystalline powder of compounds **1** and **2** were recorded at 77 K. The complexes show an

isotropic $S = 1/2$ signal with g -values of 2.07 for compound **1** and 2.12 for compound **2**. No hyperfine splittings are observed.

Magnetic susceptibility

In Fig. 4, the magnetic susceptibility of compounds **1** and **2** is shown, plotted as χ^{-1} vs. the temperature.

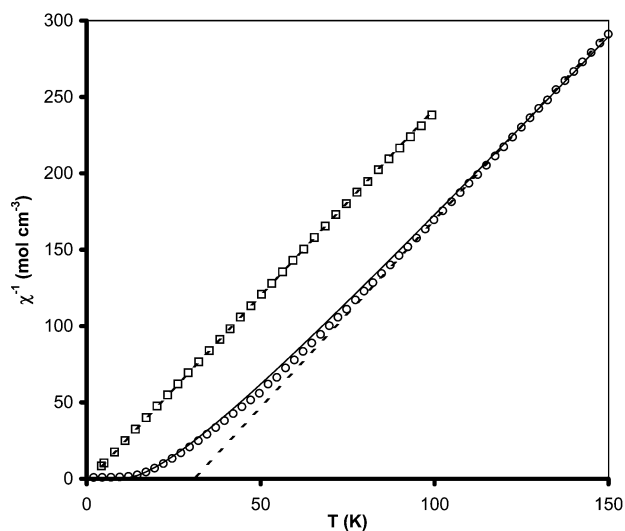


Fig. 4 Magnetic susceptibility plotted as χ^{-1} vs. T ; (\square) α -[Cu(teeOMe)₂Br₂] (**1**); (\circ) β -[Cu(teeOMe)₂Br₂] (**2**) (solid line is the fit of the prediction for the two-dimensional Heisenberg $S = 1/2$ ferromagnet from high-temperature series expansion; dashed lines are the Curie-Weiss plots from mean-field theory).

Compound **1** shows paramagnetic behaviour, with a Curie-Weiss constant of $C = 0.41 \text{ cm}^3 \text{ K mol}^{-1}$ and a Curie temperature θ of 0 K. Despite being bridged by the tetrazole rings, the copper(II) ions in **1** are magnetically isolated, due to the fact that the magnetic orbitals do not overlap. Related two-dimensional layers of copper(II) ions with μ -2,4- η^2 bridging triazole ligands are found in the structure of poly-bis(thiocyanato- N)bis-(1,2,4-triazole- N^2, N^4)copper(II) described by Engelfriet *et al.*¹⁷ In this compound, a weak ferromagnetic coupling is observed.²⁰

Compound **2** displays a strong ferromagnetic coupling with a Curie temperature θ of 30.5 K, (Fig. 4). The Curie-Weiss constant ($C = 0.41 \text{ cm}^3 \text{ K mol}^{-1}$) is almost identical to that of compound **1**. Magnetisation measurements at constant temperature (2 K) indicate that compound **2** behaves as a nearly ideal soft ferromagnet, since no hysteresis effect is observed (Fig. 5).

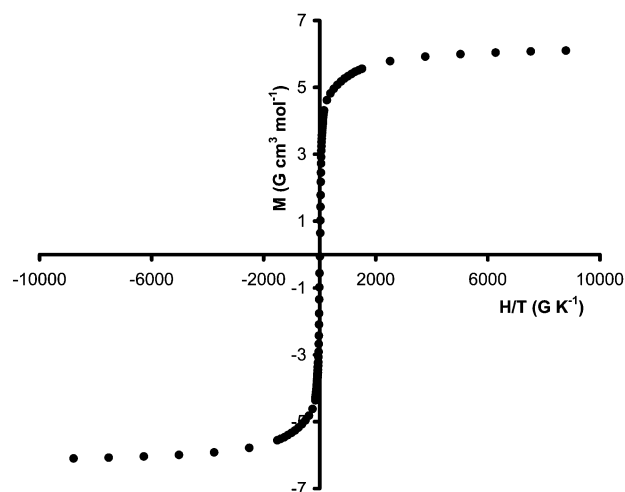


Fig. 5 Field dependence of the magnetisation of β -[Cu(teeOMe)₂Br₂] (**2**) at 2 K.

A saturation magnetisation of $M_S = 6.1 \text{ G cm}^3 \text{ mol}^{-1}$ is observed at 7 T. This value is identical to the theoretical value of $M_S (= N\mu_B g S) = \sim 6.1 \text{ G cm}^3 \text{ mol}^{-1}$ (with g calculated from the measured Curie-Weiss constant).²¹ This magnetic behaviour is similar to the magnetic behaviour of comparable compounds.^{6,22}

The critical temperature T_c for the ferromagnetic ordering derived from zero-field ac susceptibility measurements is clearly indicated (Fig. 6) at 8.5 K. This temperature is slightly lower than those of comparable compounds, reported by De Jongh *et al.*²² (*i.e.* 10.5–16 K) and is in good agreement with the critical temperature observed for [Cu(teecc)₂Br₂]_n ($T_c = 8.0 \text{ K}$).⁶ The fact that the T_c value is much lower than the Curie-Weiss temperature θ can be ascribed to the pronounced two-dimensional character of this material. Because sufficiently large single crystals were not available, all measurements were performed on polycrystalline samples: therefore no distinction could be made between the different crystal axes.

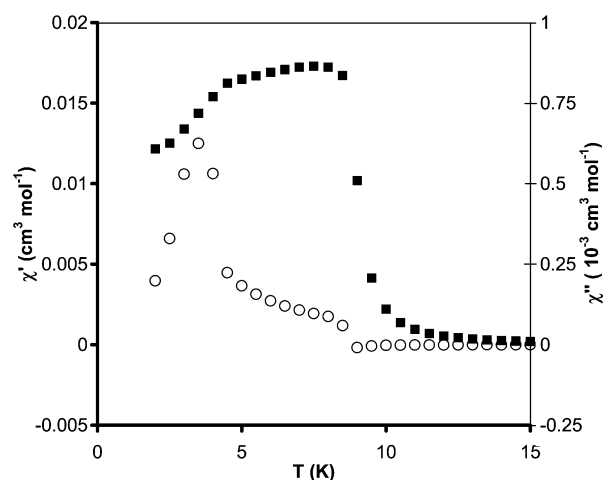


Fig. 6 Temperature dependence of the real part (χ') (\blacksquare) and the imaginary part (χ'') (\circ) of the ac magnetic susceptibility of β -[Cu(teeOMe)₂Br₂] (**2**).

Below T_c , a slight slope is visible in the plot of χ' vs. T . In the χ'' vs. T curve, two steps are visible, one at 8.5 K which is associated with the critical temperature T_c and one at 3.5 K, which may be caused by an inter-layer ordering.

To prove that the observed ferromagnetic interaction can indeed be caused by the presence of a two-dimensional square grid, values for the exchange parameter J/k_B have been obtained by fitting the data above 20 K to an expression for the susceptibility derived from high-temperature series expansion results for an isotropic ferromagnetic quadratic lattice with spin $S = 1/2$. The results of Baker *et al.*²³ for the two-dimensional Heisenberg model have been used to fit the data. The series take the following form:

$$\chi = \left(\frac{C}{T}\right) \cdot \left[1 + \sum_{n \geq 1} \frac{a_n}{2^n n!} x^n\right]$$

where $n = 1, 2, \dots, 10$, $x = J/k_B T$ and a_n is the coefficient for the square lattice (for $S = 1/2$, a_n are known for $n = 1, 2, \dots, 10$). The fit was accomplished by minimisation of the reliability factor, defined as $R = \sum (\chi_m T_{\text{calc}} - \chi_m T_{\text{obs}})^2 / (\chi_m T_{\text{obs}})^2$, by a least-squares procedure. The best fit was obtained for $C = 0.42 \text{ cm}^3 \text{ K mol}^{-1}$ and the interlayer exchange parameter $J/k_B = 16.4 \text{ K}$ with an R value of 3.5×10^{-4} . Considering that the Curie-Weiss temperature θ corresponds to $2J/k_B$, the value derived from the fit to the two-dimensional $S = 1/2$ Heisenberg model ($\theta = 2J/k_B = 32.8 \text{ K}$) is in very good agreement with the Curie-Weiss temperature.

The value of $k_B T_c / J$ can be regarded as an indication for the ratio of the inter-layer exchange parameter J'/k_B and the

intra-layer exchange parameter J .²² For compound **2**, $k_B T_c/J = 0.52$, comparable to the value published for $(C_4H_9NH_3)_2CuBr_4$,²² which would indicate that the ratio $|J'/J|$ is approximately 1×10^{-3} . From this comparison it can be concluded that in **2** the interlayer-exchange coupling J' is several orders smaller than the intralayer-exchange coupling J . It is therefore appropriate to consider compound **2** to be built up from nearly perfectly isolated ferromagnetic layers.

Solvent effect

The solvent effect observed here, whereby two different linkage isomers of $[Cu(\text{teeOMe})_2Br_2]$ are obtained after crystallisation under different conditions, has not been observed with other, comparable, ligands. Crystallisation attempts in various solvents (e.g. methanol, ethanol, water, DMSO) for complexes $[CuL_2Br_2]$ with several different ligands (with shorter side chains: L = 1-methyltetrazole, 1-propyltetrazole, 1-(2-chloroethyl)tetrazole,⁶ with side chains of equal length: L = 1-butyltetrazole and with longer side chains: L = 1-pentyltetrazole and 1-hexyltetrazole) all resulted in complexes with magnetic properties resembling those of compound **2**. No compounds comparable in structure and magnetism to compound **1** have been identified.

Only the ligand teeOMe appears to be able to form a $[CuL_2Br_2]$ complex containing μ -2,4- η^2 bridging tetrazole rings.

Conclusions

The crystal structure of α - $[Cu(\text{teeOMe})_2Br_2]$ (**1**), which remains fundamentally unchanged between 123 and 297 K, contains two-dimensional layers of copper(II) ions with μ -2,4- η^2 bridging tetrazole ligands. No magnetic interactions are observed between the copper(II) ions. From 2 to 300 K, **1** exhibits paramagnetic behaviour, with a Curie constant of $0.41 \text{ cm}^3 \text{ K mol}^{-1}$ and a Curie–Weiss temperature of 0 K. Despite being bridged by the tetrazole rings, the copper(II) ions are magnetically isolated, due to the fact that the magnetic orbitals do not overlap.

Unfortunately, due to the lack of suitable single crystals, the structure of β - $[Cu(\text{teeOMe})_2Br_2]$ (**2**) could not be determined. However, since all other bis(1-alkyltetrazole)-copper(II) halides, of which the crystal structure is known,^{3–6} adopt structures containing two-dimensional grids of halide-bridged copper ions, it is plausible that **2** adopts a similar structure. It is indeed possible to envision that the square-planar $[Cu(\text{teeOMe})_2Br_2]$ units observed in **1** could be linked by weak axial Cu–Br interactions to form two-dimensional $[CuBr_2]$ layers separated by the teeOMe ligands (Fig. 3).

Because of the tetragonally elongated octahedral coordination geometry, the unpaired electron of each copper(II) ion occupies a d-type orbital with lobes pointing toward the two bromide anions and the two tetrazole nitrogen atoms of the $[Cu(\text{teeOMe})_2Br_2]$ unit. It is assumed that in the crystal structure, neighbouring $[Cu(\text{teeOMe})_2Br_2]$ units are orthogonal, the orbitals centered on adjacent metal ions will also be orthogonal; therefore, according to this model, superexchange interactions within the two-dimensional layer are expected to be ferromagnetic,^{8,9} as is observed in this compound.

Experimental

Physical measurements

Vis-NIR spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-Band powder EPR spectra were obtained on a JEOL RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using

the diffuse reflectance technique ($4000\text{--}300 \text{ cm}^{-1}$, resolution 4 cm^{-1}). Magnetic susceptibility measurements ($2\text{--}300 \text{ K}$) were carried out at 0.1 Tesla using a Quantum Design MPMS-5 5T SQUID magnetometer. Ac magnetic susceptibility measurements were made at a frequency of 9.9 Hz. Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.²⁴ C, H, N determinations were performed on a Perkin Elmer 2400 Series II analyser. ¹H and ¹³C NMR measurements were performed in d^6 -dmsO, using a Bruker 300 MHz spectrometer.

Synthesis

1-(2-Methoxyethyl)tetrazole (teeOMe) was synthesised by refluxing a mixture of 0.5 mol of 1-methoxyethylamine and 0.5 mol of sodium azide in 200 ml of acetic acid and 400 ml of triethylorthoformate for 5 h. After evaporation of the excess of solvents and removal of the formed salts by filtration, the yellow oil obtained was dissolved in water. The acetic acid was neutralised by the addition of sodium carbonate, until the pH is above 6. The product was extracted with dichloromethane. After drying on sodium sulfate and evaporation of the dichloromethane, the product was isolated as a yellow oil, in a yield of approximately 90%. ¹H NMR (d^6 -dmsO): δ 9.34 (s); 4.66 (t); 3.75 (t); 3.22 (s).

α - $[Cu(\text{teeOMe})_2Br_2]$ (**1**) was prepared by dissolving 0.1 mmol (0.22 g) of $CuBr_2$ and 0.2 mmol (0.26 g) of teeOMe in 10 ml of methanol. Green plate-shaped crystals suitable for X-ray analysis formed after one week after slow evaporation of the solvent. Elemental analysis for $C_8H_{16}N_8O_2CuBr_2$: found (calc.): C, 19.9 (20.0); H, 3.2 (3.4); N, 23.4 (23.4); Cu, 13.4 (13.2); Br, 32.9 (33.3%).

β - $[Cu(\text{teeOMe})_2Br_2]$ (**2**) was prepared by dissolving 0.1 mmol (0.22 g) of $CuBr_2$ and 0.2 mmol (0.26 g) of teeOMe in 20 ml of ethanol. Yellow–brown plate-shaped crystals formed overnight. Unfortunately, these were not of suitable quality for X-ray analysis. Elemental analysis for $C_8H_{16}N_8O_2CuBr_2$: found (calc.): C, 20.1 (20.0); H, 3.2 (3.4); N, 23.5 (23.4); Cu, 13.0 (13.2); Br, 32.7 (33.3%).

Crystal structure determination of α - $[Cu(\text{teeOMe})_2Br_2]$

At 123 K and 297 K: Intensity data were collected for a single crystal on a Bruker SMART CCD three-circle diffractometer using Mo-K α radiation from a sealed X-ray tube, at 123 and at 297 K. A semi-empirical correction was applied (SADABS²⁵). The structures were solved by automated direct methods using SHELXS97²⁶ and refined on F^2 by least-squares techniques using SHELXL97.²⁷

At 150 K: Intensity data were collected for a single crystal on a Nonius Kappa CCD diffractometer using Mo-K α radiation from a rotating anode, at 150 K. A multi-scan absorption correction was applied using MULABS in PLATON.²⁸ The structure was solved by automated direct methods using SHELXS97,²⁶ and refined on F^2 by least-squares procedures using SHELXL97.²⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure validation and molecular graphics preparation were performed with the PLATON package.²⁸

CCDC reference numbers 207021–207023.

See <http://www.rsc.org/suppdata/dt/b3/b303422d/> for crystallographic data in CIF or other electronic format.

Acknowledgements

The work described in the present paper has been supported by the Leiden University Study Group WFMO and has been

performed under the auspices of the Graduate Research School HRSMC. Financial support was provided by the European Union, allowing regular exchange of preliminary results with several European colleagues in the TOSS network, under contract ERB-FMNRX-CT98-0199, and by the ESF Programme Molecular Magnets (1998–2003). This work was also supported in part (A. M. M. and A. L. S.) by the Netherlands Foundation of Chemical Research (CW) with financial aid from the Netherlands Organisation for Scientific Research (NWO). Jos van Brussel is kindly acknowledged for the elemental analysis.

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