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Synthesis, spectroscopy and magnetic properties of *cis*-(9,10-dihydro-9-oxo-10-acridineacetato-μ-O)copper(II). An unusual carboxylate-bridged chain with very weak magnetic exchange

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Abstract

The synthesis, crystal structure, spectroscopic and magnetic properties are reported for $Cu(CMA)_2(H_2O)_2$, where CMA^- is the 9,10-dihydro-9-oxo-10-acridineacetate ion. The complex $C_{30}H_{24}N_2O_8Cu$ crystallizes in the monoclinic space group $C2/c$, with cell dimensions $a=17.700(7)$, $b=19.266(8)$, $c=7.424(4)$ Å, $\beta=91.88(4)°$, $Z=4$. The structure was solved by direct methods and refined to a final R value of 0.035. The structure of $Cu(CMA_2)(H_2O)_2$ consists of unusual one-dimensional polymers which contain zigzag $(Cu–O_2–Cu–O_2)_\infty$ chains and stacks of acridone moieties. The 9,10-dihydro-9-oxo-10-acridineacetate ion coordinates in the monodentate manner. Each copper ion shows distorted (4+2) octahedral coordination. The four short bonds come from two acetate oxygen and two water oxygen atoms. The long apical bonds are to the basal acetate oxygen atoms from neighboring copper centers. The angle at the oxygen, in the planar Cu_2O_2 unit is 109.4(1)°, the Cu–Cu distance is 3.967(3) Å. The hydrogen atoms of each water molecule bind with the non-coordinated acetate oxygen atoms and 9-oxo oxygen atoms of the neighboring polymer. The acridone rings overlap with a 3.35 Å interlayer separation. The magnetic susceptibility of the compound has been examined between 4.2 and 300 K. The compound behaves as an $S=1/2$ paramagnet. The absence of coupling arises from the unfavorable relative orientation of the magnetic orbitals. The EPR and LF spectra are typical of the distorted octahedral environment of copper(II) ion.

Introduction

Although the most common bridging mode of carboxylates is known to be the μ-O,O′ mode, there are many examples in copper(II) chemistry [1–17] in which a monoatomic (μ-O) bridging mode is also present. In most cases, such copper(II) complexes are characterized by more than one type of bridging and exist in the form of dimers [1, 4–8, 10, 12–17] or polymers built from the dimeric units [3, 9, 11]. So far no chain-type complexes with μ-O bridging only are known for Cu carboxylates.

In a previous study [18] on the coordination compounds of a potential interferon inducer, sodium 9,10-dihydro-9-oxo-10-acridineacetate (NaCMA) [19], we reported some complexes of CMA^- with Ni(II), Co(II), Zn(II) and Cu(II); however, only microcrystalline solids were obtained.

In this article we describe the structure of $Cu(CMA)_2(H_2O)_2$ and its magnetic and spectroscopic properties. This compound is a new member of the monooxygen carboxylate bridged copper(II) series, and exerts hardly any magnetic interaction.

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Experimental

Preparation of complex

$CuCl_2(H_2O)_2$, EtOH and triethyl orthoformate (TEOF) were used as received. Sodium 9,10-dihydro-9-oxo-10-acridineacetate (NaCMA) was obtained according to the known method [19]. $CuCl_2(H_2O)_2$ (0.085 g, 0.5 mmol) was dissolved in 50 cm^3 of EtOH and 3 cm^3 TEOF. NaCMA (0.277 g, 1 mmol) was dissolved in 100 cm^3 of EtOH and 3 cm^3 TEOF, with heating and stirring. The NaCMA solution was added dropwise to the solution of the metal salt. An olive-green microcrystalline solid was precipitated immediately. The precipitate was kept in the mother liquor for six weeks. During this period the compound was converted into green crystals, while 90% of the solvent volume had evaporated.

Anal. Calc. for $C_{30}H_{24}N_2O_8Cu$: C, 59.65; H, 4.00; N, 4.64; Cu, 10.25. Found: C, 60.41; H, 3.70; N, 4.15; Cu, 10.45%.

Physical measurements

Variable temperature magnetic susceptibility data were measured using a Cahn RH electrobalance by the Faraday method. The magnetic field applied was 0.429 T (4.28 kOe). Elemental analyses were performed at the Analytical Laboratory, Department of Chemistry, Technical University, Wrocław. IR spectra were recorded as KBr pellets or nujol mulls by using Perkin-Elmer 180 and Specord 80 spectrophotometers.

Solid-state ligand spectra were measured in the diffuse reflectance mode on a Perkin-Elmer 330 instrument equipped with a data station (33 000–5000 cm^{-1}) fitted with a reflectance attachment using $MgSO_4$ as reference material.

EPR powder spectra were recorded on a Jeol RES-J2X instrument (at X-band frequencies) using standard conditions at 77 and 300 K.

Crystallography

Crystals of the title compound suitable for X-ray study were readily found from material synthesized for other studies. Weissenberg photographs showed the space group to be *Cc* or *C2/c*. The choice of the centrosymmetric *C2/c* space group was confirmed by the successful solution and refinement of the structure. Characteristics of the data collection on a Kuma KM4 four-circle diffractometer (κ-geometry), processing crystal data and refinement are given in Table 1.

The structure was solved by direct methods. The C bonded H atoms were introduced in calculated positions with d(C–H) = 1.08 Å. The O bonded H atoms were found from difference synthesis. The block-diagonal least-squares [20] was completed by using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for water H atoms. Neutral-atom scattering factors [21] and real as well as imaginary components of anomalous dispersion were included for all non-H atoms. Absorption and extinction were ignored. The final difference synthesis was essentially featureless; the largest peak of 0.30 e/$Å^3$. The results of the X-ray study are given in Tables 2 (atomic

TABLE 1. Crystal data for $Cu(CMA)_2(H_2O)_2$

Color	green
Crystal dimensions (mm)	0.07 × 0.1 × 0.2
Space group	*C2/c*
Cell dimensions (25 reflections)	
a (Å)	17.700(7)
b (Å)	19.266(8)
c (Å)	7.424(4)
β (°)	91.88(4)
Molecules/cell	4
Volume ($Å^3$)	2530(2)
Density (calc.) (g/cm^3)	1.586(2)
Density (meas.) (g/cm^3)	1.58
Wavelength (Å)	1.5418
Molecular weight	604.07
Linear absorption coefficient (cm^{-1})	17.6
No. unique reflections	2877
No. with $F > 6.0\sigma(F)$	2115
Final residuals	
$R(F)$	0.035
$R_w(F)$	0.035
Max. Δ/σ for last cycle	0.02

TABLE 2. Final atomic parameters for $Cu(CMA)_2(H_2O)_2$ crystal

Atom	x	y	z	B_{eq} ($Å^2$)
Cu	0.5	0.53633(2)	0.25	2.61(2)
O(1)	0.55557(10)	0.46797(9)	0.1205(3)	3.19(8)
O(2)	0.64044(12)	0.44408(11)	0.3423(3)	3.90(9)
O(3)	0.89850(12)	0.22885(10)	0.2415(3)	3.59(9)
O(4)	0.55528(13)	0.60773(10)	0.1237(3)	4.19(10)
N	0.71652(11)	0.35396(10)	0.1191(3)	2.46(8)
C(1)	0.61425(13)	0.43854(12)	0.1873(4)	2.43(9)
C(2)	0.65118(14)	0.39272(14)	0.0495(4)	2.82(11)
C(3)	0.80169(17)	0.44424(13)	0.0149(5)	3.45(12)
C(4)	0.87334(19)	0.46441(15)	−0.0236(5)	4.12(14)
C(5)	0.93559(18)	0.42107(17)	0.0111(5)	4.20(15)
C(6)	0.92440(15)	0.35719(15)	0.0870(5)	3.34(12)
C(7)	0.75175(18)	0.18260(14)	0.3336(4)	3.28(12)
C(8)	0.67983(20)	0.16347(16)	0.3744(5)	4.02(14)
C(9)	0.61970(19)	0.20820(17)	0.3356(5)	4.12(15)
C(10)	0.63109(16)	0.27101(15)	0.2525(4)	3.36(12)
C(11)	0.78883(14)	0.37746(12)	0.0894(4)	2.40(9)
C(12)	0.85167(13)	0.33477(12)	0.1294(4)	2.42(9)
C(13)	0.84231(14)	0.26668(12)	0.2093(4)	2.49(10)
C(14)	0.76567(14)	0.24687(12)	0.2492(4)	2.52(9)
C(15)	0.70436(14)	0.29097(13)	0.2066(4)	2.50(10)
H(41)[a]	0.577(3)	0.652(2)	0.166(5)	6.9(11)
H(42)[a]	0.588(2)	0.590(2)	0.042(4)	6.4(10)

[a] Only these two H atoms are at refined positions; the other H atoms have been placed at calculated positions.

TABLE 3. Principal interatomic distances (Å) and angles (°)^a

Cu···Cu$^{i,\,ii}$	3.967(3)	Cu–O(1$^{0,\,iii}$)	1.921(2)
Cu–O(4$^{0,\,iii}$)	1.947(2)	Cu–O(1$^{ii,\,iv}$)	2.892(3)
C(1)–O(1)	1.270(3)	C(1)–O(2)	1.231(3)
C(1)–C(2)	1.515(4)	C(2)–N	1.457(3)
N–C(11)	1.382(3)	N–C(15)	1.397(3)
C(11)–C(12)	1.407(3)	C(15)–C(14)	1.406(3)
C(12)–C(13)	1.452(3)	C(13)–C(14)	1.449(4)
C(11)–C(3)	1.422(4)	C(15)–C(10)	1.405(4)
C(3)–C(4)	1.366(5)	C(10)–C(9)	1.376(4)
C(4)–C(5)	1.400(5)	C(9)–C(8)	1.392(5)
C(5)–C(6)	1.371(4)	C(8)–C(7)	1.369(5)
C(6)–C(12)	1.403(4)	C(7)–C(14)	1.413(4)
C(13)–O(3)	1.250(3)		
O(4)···O(3^{v})	2.657(3)	O(4)···O(2^{vi})	2.800(3)
O(4)–H(41)	0.99(4)	O(4)–H(42)	0.91(4)
H(41)···O(3^{v})	1.68(4)	H(42)···O(2^{vi})	1.90(4)
O(1)–Cu–O(1^{ii})	70.6(1)	O(1)–Cu–O(1^{iv})	107.0(1)
O(1)–Cu–O(4)	88.3(1)	O(1)–Cu–O(4^{iii})	178.3(1)
O(1^{ii})–Cu–O(4)	73.9(1)	O(1^{ii})–Cu–O(4^{iii})	108.5(1)
O(1)–Cu–O(1^{iii})	93.4(1)	O(1^{ii})–Cu–O(1^{iv})	176.7(1)
O(4)–Cu–O(4^{iii})	90.1(1)	Cu–O(1)–Cu^{ii}	109.4(1)
Cu–O(1)–C(1)	122.4(2)	Cu^{ii}–O(1)–C(1)	127.4(2)
O(1)–C(1)–O(2)	127.2(3)	C(2)–C(1)–O(1)	111.2(3)
C(2)–C(1)–O(2)	121.6(3)	N–C(2)–C(1)	114.5(3)
C(2)–N–C(11)	120.3(3)	C(2)–N–C(15)	118.5(3)
N–C(11)–C(3)	121.3(3)	N–C(15)–C(10)	120.5(3)
N–C(11)–C(12)	120.3(3)	N–C(15)–C(14)	120.0(3)
C(3)–C(11)–C(12)	118.4(3)	C(10)–C(15)–C(14)	119.4(3)
C(11)–N–C(15)	121.1(3)	C(12)–C(13)–C(14)	116.2(3)
C(11)–C(3)–C(4)	120.0(3)	C(15)–C(10)–C(9)	120.0(3)
C(3)–C(4)–C(5)	121.5(3)	C(10)–C(9)–C(8)	121.0(3)
C(4)–C(5)–C(6)	119.2(3)	C(9)–C(8)–C(7)	119.8(3)
C(5)–C(6)–C(12)	121.0(3)	C(8)–C(7)–C(14)	120.7(3)
C(6)–C(12)–C(11)	119.8(3)	C(7)–C(14)–C(15)	119.0(3)
C(6)–C(12)–C(13)	119.2(3)	C(7)–C(14)–C(13)	120.0(3)
C(13)–C(12)–C(11)	121.0(3)	C(13)–C(14)–C(15)	121.0(3)
C(12)–C(13)–O(3)	120.3(3)	C(14)–C(13)–O(3)	123.5(3)
O(4)–H(41)···O(3^{v})	170(4)	O(4)–H(42)···O(2^{vi})	170(4)

^{a}Symmetry codes: (0) x, y, z; (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, y, 0.5-z$; (iv) $x, 1-y, 0.5+z$; (v) $1.5-x, 0.5+y, 0.5-z$; (vi) $x, 1-y, z-0.5$.

coordinates) and 3 (geometric informations). See also 'Supplementary Material'.

Results and discussion

Description of structure

The ligand geometry and crystal structure are shown in Figs. 1–3. The structure of Cu(CMA)$_2$(H$_2$O)$_2$ consists of one-dimensional polymers, which contain zigzag (Cu–O$_2$–Cu–O$_2$)$_\infty$ chains and stacks of acridone moieties. Each CMA$^-$ ion coordinates to two different copper ions, forming monooxygen, asymmetrical bridges (Cu–O = 1.921(2); 2.892(3) Å). Two water molecules coordinate to Cu at 1.947(2) Å and are connected via hydrogen bonds to the uncoordinated oxygen atoms from the acetate groups and to the 9-oxygen atoms from the acridones of a neighboring polymer chain. The interaction between the polymer chains is further strengthened by mutual insertion of the acridone stacks.

Coordinated to copper(II) are six oxygen atoms, in a strong tetragonally distorted octahedral geometry. The local symmetry of the coordination sphere and of the polymer unit is C_2. The short bond lengths are 1.921(2) Å for Cu–O(1) and 1.947(2) Å for Cu–O(4). These values of the Cu–O distance are in the normal range for compounds having monooxygen copper carboxylate bridges [22]. The remaining bonds between the copper ions and the axial oxygen atoms O(1) equal 2.892(3) Å, and are significantly longer than the corresponding ones in the other copper monooxygen carboxylate bridges [22]. Every O(1) acetate oxygen atom occupies the equatorial position in respect to one copper center and simultaneously the axial position in relation to the next copper ion. The bridgehead angle Cu–O(1)–Cu^{ii} equals 109.4(1)°, i.e. amongst the larger ones for these bridges [22]. The O(1), O(1^{iii}), O(4), O(4^{iii}) and Cu atoms are nearly coplanar. The subsequent [O1,O1^{iii}, O4,O4^{iii}, Cu] equatorial pseudoplanes in the polymer are parallel. The Cu...Cu^{i} distance is 3.967(3) Å, i.e. by far the largest one known for such bridges [22].

On the basis of the observed C–O(1) and C–O(2) bond lengths, 1.231(3) and 1.270(3) Å, respectively, coordination via the single-bonded oxygen in Cu(CMA)$_2$(H$_2$O)$_2$ has been assumed. Also the C–C–O angles in the carboxyl group are indicative of the manner of acetate group coordination. From the structural data available for the phenoxyacids and their complexes, the C–C–O carboxyl angle is always significantly greater than the C–C–O hydroxyl one [23]. The values of the carboxyl angles observed in the studied compound, 121.6(3)° (carbonyl) and 111.2(3)° (hydroxyl), are characteristic for monodentate hydroxo-bonding mode of the acetate group in copper(II) complexes [23].

The coordinated water molecule forms two strong hydrogen bridges; one (intrachain) with O(2) of the acetate and the other (intermolecular) with O(3) of acridone. The bond length of the first is 2.800(3) Å while the second one is 2.657(4) Å. The acridone ring system in the present structure is significantly distorted from planarity as compared to other acridone and acridine crystalline compounds [24–33]. The deviation from the least-squares plane calculated for three rings is the largest for the following atoms: N 0.079(2), C(3) −0.062(3), C(9) −0.066(3), C(4) −0.058(3) and C(2) 0.311(3) Å. The acridone geometry in Cu(CMA)$_2$(H$_2$O)$_2$ is slightly different from that of normal acridine [24] and the differences in bond lengths and angles occur mainly in the central ring. These differences indicate that the oxo group at C(13) influences the π delocalization in the ring.

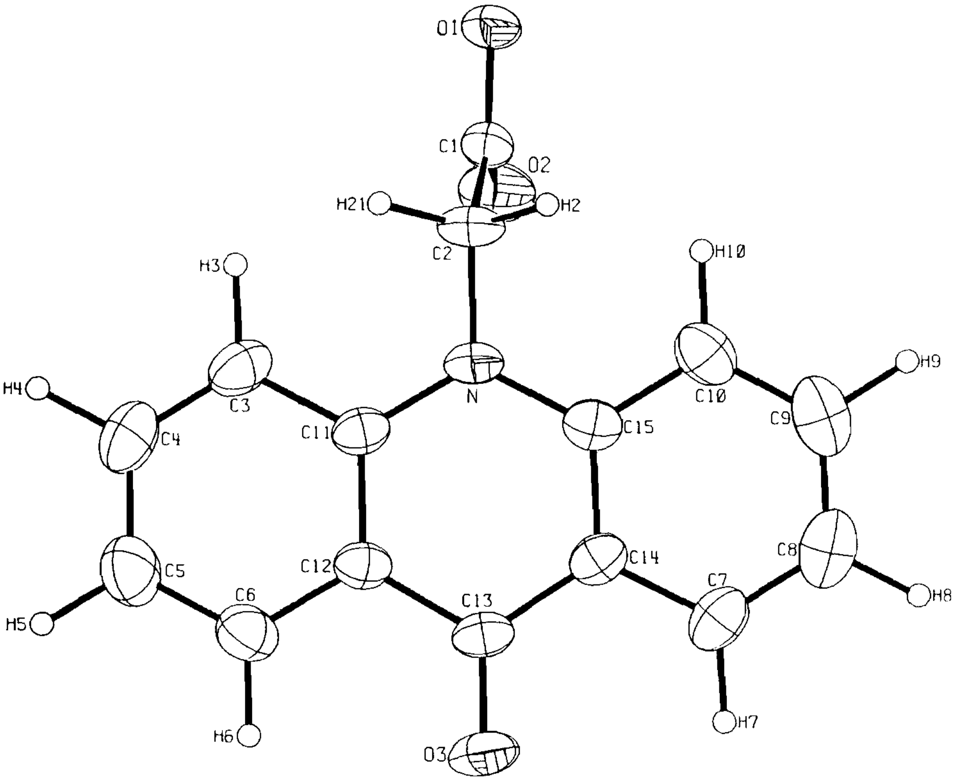


Fig. 1. Molecular geometry and numbering of the coordinated ligand.

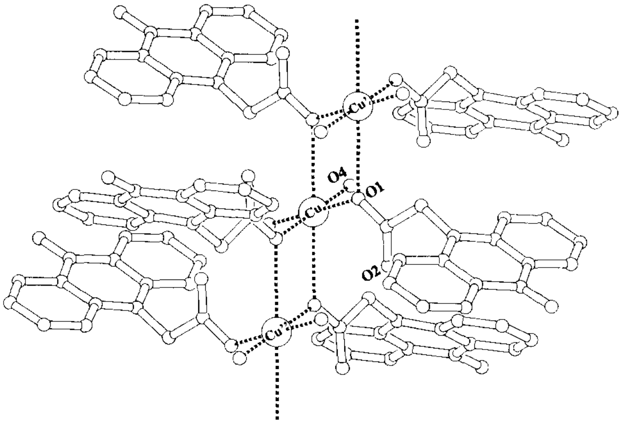


Fig. 2. View of the $Cu(CMA)_2(H_2O)_2$ chain.

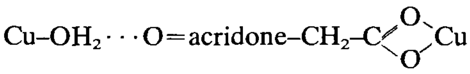
Inspection of the packing of the complex in the crystal shows a stacking of the acridone ligands. The infinite intermolecular ring overlap, involving a 3.35 Å interlayer separation is present, with minimum interaction separations of 3.401, 3.497 and 3.503 Å between C(11)···C(7), C(7)···N and C(13)···N, respectively.

Spectroscopic and magnetic results

The IR spectrum of $Cu(CMA)_2(H_2O)_2$ exhibits two medium-intensity broad bands at 3400 and 3180 cm^{-1}, due to the two types of O–H bridges formed by two coordinated water molecules. The first band, positioned at 3400 cm^{-1} results from the ν(OH) vibration in the O(4)–H(42)···O(2^{VI}) bridge. The stretching of the stronger hydrogen bond, i.e. between the water hydrogen atom and the oxo-O(3^{V}) atom gives rise to the band located at 3180 cm^{-1}. The positions of these two bands nicely agree with values calculated (3350 and 3150 cm^{-1}) from the relationship developed by Bellamy and Owen [34] between the distances O···O and the OH stretch.

The ν_{as}(COO) and ν_s(COO) bands of $Cu(CMA)_2(H_2O)_2$ are located at 1572 and 1395 cm^{-1}, respectively; the difference in frequencies (177 cm^{-1}) is almost equal to that found for NaCMA (163 cm^{-1}) [18], which indicates small changes in the carboxylate group upon complexation.

The broad maxima observed in the ligand field spectrum of $Cu(CMA)_2(H_2O)_2$ at 12 000 and 9700 cm^{-1} agree with the tetragonally distorted octahedral geometry of copper(II) [35].

Given the linear-chain structure with bridging oxygen atoms, one could expect some communication between the Cu(II) ions [36, 37]. Also the stacks of the acridones, intertwined from neighboring chains could perhaps lead to some cooperative behavior between the copper ions. Finally, exchange through the path  $Cu{-}OH_2\cdots O{=}acridone{-}CH_2{-}C\overset{O}{\underset{O}{\leqslant}}Cu$ would be a

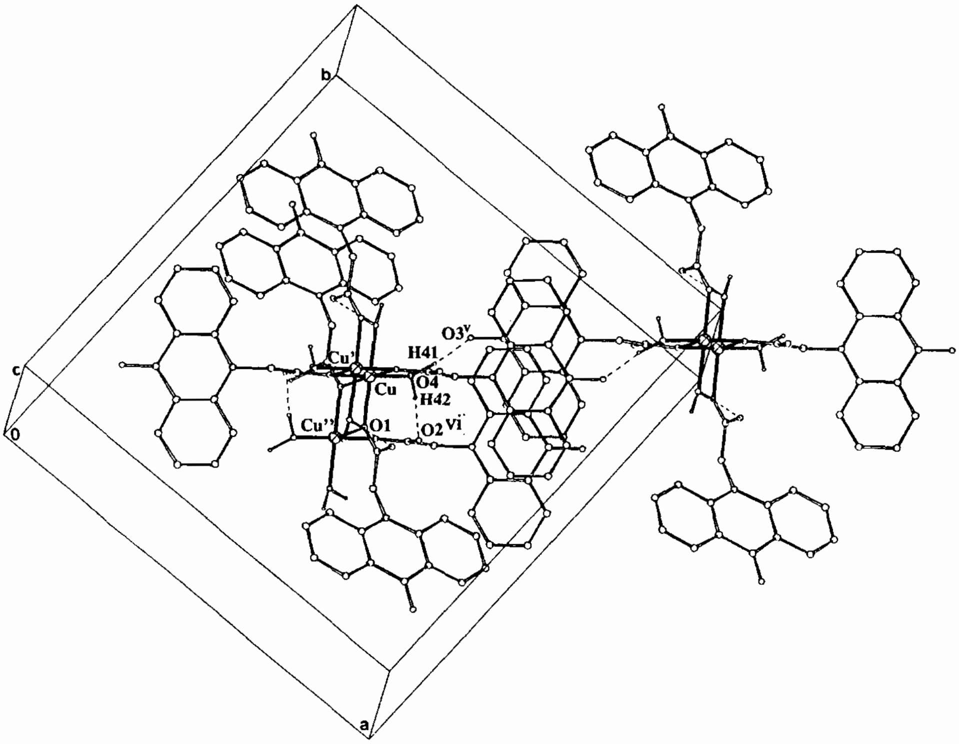


Fig. 3. The packing of the complex in the crystal.

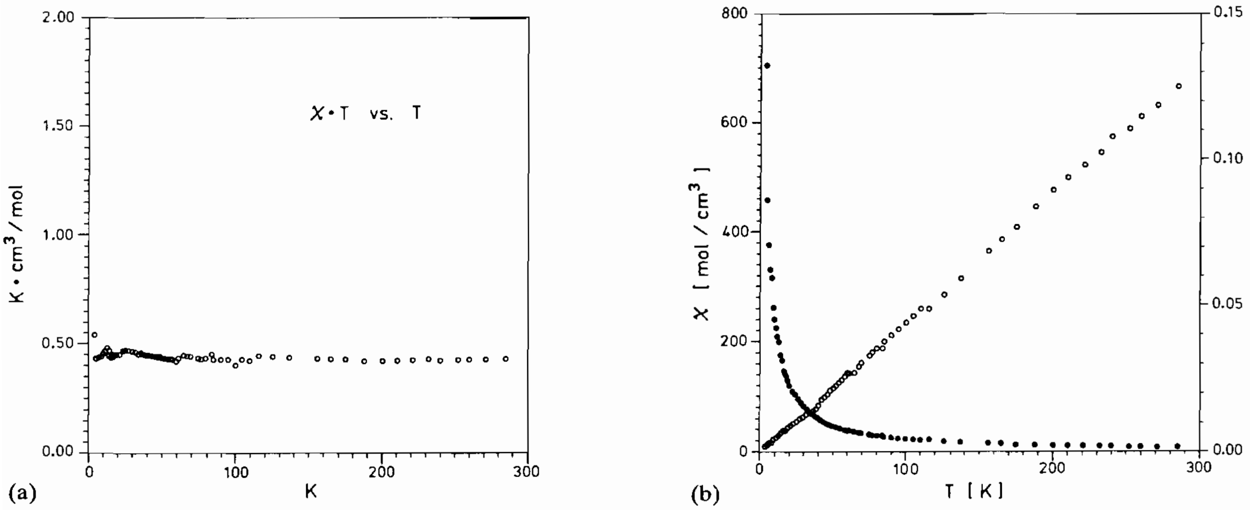


Fig. 4. (a) Temperature dependence of $\chi_{Cu}T$ for $Cu(CMA)_2(H_2O)_2$. (b) Magnetic susceptibility (●) and reciprocal susceptibility (○) data for $Cu(CMA)_2(H_2O)_2$ from 4.2 to 300 K.

possibility for magnetic exchange. Therefore, a study of the magnetic susceptibility was undertaken down to 4.2 K and also the EPR of the title compound spectrum was recorded in the solid state.

The magnetic behavior of $Cu(CMA)_2(H_2O)_2$ in the form of $\chi_{Cu}T$ versus the temperature is given in Fig. 4(a), χ_{Cu} and $\chi_{Cu}{}^{-1}$ versus the temperature in Fig. 4(b).

These data clearly indicate that the compound $Cu(CMA)_2(H_2O)_2$ behaves as an $S=1/2$ paramagnet down to 4.2 K. $\chi_{Cu}T$ is nearly constant and equals 0.45 ± 0.03 cm^3 mol^{-1} K in the whole temperature range. This Curie constant is slightly higher than the value typical for the isolated copper(II) ion, and gives an average g factor of 2.15 ($\chi_{Cu}T = N\beta^2 g^2 S(S+1/2)/3k$, $S=1/2$).

The EPR spectrum of the title compound shown in Fig. 5 is typical for a very weakly coupled copper(II) ion in an axially elongated tetragonal surrounding with $g_{\perp}=2.30$ and $g_{\parallel}=2.05$. The A value is unresolved as

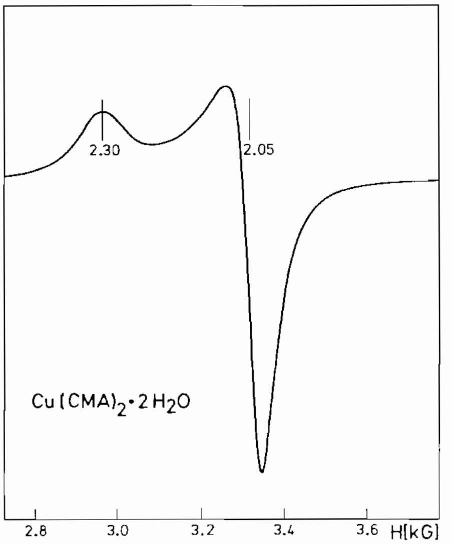


Fig. 5. X-band EPR spectrum of powdered $Cu(CMA)_2(H_2O)_2$, 300 K.

a result of so-called exchange narrowing [37]. The average g value (taken as $g_{av}^2=(g_\perp^2+2g_\parallel^2)/3$) is 2.135, which agrees with the value calculated from the magnetic data (within experimental error).

The geometry of the coordination sphere in the $Cu(CMA)_2(H_2O)_2$ polymer is such that the magnetic orbitals on the two most neighboring copper ions, consisting mainly of the $d_{x^2-y^2}$ orbital, are parallel to each other within two different planes and do not overlap. The exchange via the oxygen bridge and d_{z^2} orbital under this condition is expected to be very small [36, 37]. The indirect exchange interactions in the other directions are also very small; they are usually observed only below 4 K [9, 38]. Similar magnetic properties were found in fluoro-bridged [39], diamine-bridged [40] and acetate-oxamidate bridged [10] copper(II) polymers. However, chloride-bridged species often exhibit significant exchange [41].

Conclusions

In the results described above we have shown that $Cu(CMA)_2(H_2O)_2$ is an unusual chain compound, consisting only of (carboxylato–μ-O) bridges. The chains are separated by the acridone ring systems, which are stacked in one direction and connected to each other in the other direction by hydrogen bonds to coordinated water. The magnetic exchange in the compound is very small and cannot be detected down to 4.2 K.

Supplementary material

Tables with hydrogen coordinates, anisotropic thermal parameters and structure factors (14 pages) are available from the authors on request.

Acknowledgement

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References

1 R. J. Butcher, J. W. Overman and E. J. Sinn, *J. Am. Chem. Soc., 102* (1980) 3276.

2 Y. Boukari, A. Busnot, F. Busnot, A. Leclaire and M. A. Bernard, *Acta Crystallogr., Sect. B, 38* (1982) 2458.

3 B. Chiari, W. E, Hatfield, O. Piovesana, T. Tarantelli, L. W. Ter Haar and P. F. Zanazzi, *Inorg. Chem., 22* (1983) 1468.

4 J. P. Costes, F. Dahan and J. P. Laurent, *Inorg. Chem., 24* (1985) 1018.

5 N. A. Bailey, D. Fenton, J. R. Tate and P. M. Thomas, *J. Chem. Soc., Dalton Trans.,* (1985) 1371.

6 S. J. Brown, X. Tao, D. W. Stephan and P. K. Masharak, *Inorg. Chem., 25* (1986) 3377.

7 B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem., 24* (1985) 4615.

8 R. Hämäläinen, M. Ahlgrén and U. Turpeinen, *Acta Crystallogr., Sect. B, 38* (1982) 1577.

9 B. Chiari, J. H. Helms, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem., 25* (1986) 870.

10 A. Bencini, C. Benelli, A. C. Fabretti, G. Franchini and D. Gatteschi, *Inorg. Chem., 25* (1986) 1963.

11 B. Chiari, J. H. Helms, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem., 25* (1986) 2408.

12 B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem., 27* (1988) 3246.

13 G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb and D. N. Hendrickson, *Inorg. Chem., 29* (1990) 3657.

14 J. N. Brown and L. M. Trefonas, *Inorg. Chem., 12* (1973) 1730.

15 D. B. W. Yawney, J. A. Moreland and R. J. Deodens, *J. Am. Chem. Soc., 95* (1973) 1164.

16 A. M. Greenway, C. J. O'Connor, J. W. Overman and E. Sinn, *Inorg. Chem., 20* (1981) 64.

17 R. Österberg and S. Sjöberg, *J. Chem. Soc., Chem. Commun.,* (1972) 983.

18 D. Miernik, M. Cieślak-Golonka and Z. Szulc, *J. Coord. Chem., 20* (1989) 203.

19 A. D. Inglot, J. Młochowski, Z. Szulc, O. Inglot and M. Albin, *Arch. Immun. Ther. Exp., 33* (1985) 275.

20 *Syntex XTL/XTLE Structure Determination System,* Syntex Analytical Instruments, Cupertino, CA, 1976.

21 *International Tables for X-Ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1986.

22 G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb and D. N. Hendrickson, *Inorg. Chem., 29* (1990) Table V.

23 G. Smith, E. J. O'Reilly, C. H. L. Kennard, K. Stadnicka and B. Oleksyn, *Inorg. Chim. Acta, 47* (1981) 111.

24 D. C. Philips, F. R. Ahmed and W. H. Barnes, *Acta Crystallogr., 13* (1960) 365.

25 Z. H. L. Abraham and S. Neidle, *Acta Crystallogr., Sect. C, 43* (1987) 1992.

26 W. E. Zawodnik, L. A. Czetkina and G. A. Wałkowa, *Kristallografiya, 24* (1979) 592.

27 W. A. Dziawczenko, W. E. Zawodnik and W. K. Bielskij, *Kristallografiya, 25* (1980) 72.

28 W. E. Zawodnik, L. A. Czetkina and G. A. Wałkowa, *Kristallografiya, 26* (1981) 392.

29 D. M. Goodgame, Ch. J. Page and D. J. Williams, *Inorg. Chim. Acta, 153* (1988) 219.

30 D. M. Goodgame, C. A. O'Mahoney, Ch. J. Page and D. J. Williams, *Inorg. Chim. Acta, 175* (1990) 141.

31 R. Talacki, H. L. Carrell and J. P. Glusker, *Acta Crystallogr., Sect. B, 30* (1974) 1044.

32 H. M. Berman and J. P. Glusker, *Acta Crystallogr. Sect. B, 28* (1972) 590.

33 J. P. Glusker, B. Gallen and H. L. Carrell, *Acta Crystallogr., Sect. B, 29* (1973) 2000.

34 L. J. Bellamy and A. J. Owen, *Spectrochim. Acta, Part A, 25* (1969) 329.

35 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.

36 (a) W. E. Hatfield, *Inorg. Chem., 22* (1983) 833; (b) R. L. Carlin, R. Burriel, R. M. Corneliesse and J. A. Van Duyneveldt, *Inorg. Chem., 22* (1983) 831; (c) O. Kahn, J. Morgenstern-Baradau and R. Block, *Chem. Phys Lett., 108* (1984) 457.

37 B. J. Hataway, *Struct. Bonding (Berlin), 57* (1984) 55.

38 R. L. Carlin and R. Block, *Proc. Ind. Acad. Sci., 98* (1987) 79.

39 A. J. Oosterling, R. A. G. De Graaff, J. G. Haasnoot, S. F. Keij, J. Reedijk and E. Pedersen, *Inorg. Chim. Acta, 163* (1989) 63.

40 H. W. Richardson, J. R. Wasson and W. E. Hatfield, *Inorg. Chem., 16* (1977) 484.

41 J. A. C. Van Doijen and J. Reedijk, *Inorg. Chim. Acta, 25* (1977) 131.