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Synthesis, Characterization, Crystal Structures and Magnetic Exchange in Dinuclear Copper Complexes with 3-Amino-1-propanol as Terminal and Bridging Ligand*

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Abstract

The synthesis, X-ray structures and spectroscopic and magnetic properties are described for two groups of dinuclear Cu(II) compounds with the ligand 3-amino-1-propanol (Hap). The formulae of the compounds are for group A: $[Cu(ap)(anion)]_2$, in which ap is the dehydronated Hap and the anions are formate, nitrate, chloride and bromide and for group B: $[Cu(ap)(Hap)]_2(anion)_2$, with anion = iodide, bromide, chloride, nitrate and tetrafluoroborate. The structure of group A compounds consists of dinuclear units with the co-planar centrosymmetric chromophore ANCuOO′CuNA, in which the A ligands (anions) bridge to neighbouring units as axial ligands, thereby forming infinite chains. Dimer Cu...Cu distances are about 295 pm. The X-ray structure of $[Cu(ap)(NO_3)]_2$ (I) is described in detail. Dark blue crystals of I were studied with single crystal X-ray measurements and refined to a final R value of 0.025 for 1440 reflections. The compound crystallizes in the monoclinic space group $P2_1/c$ with two dimeric molecules in a cell of dimensions a = 886.56(5), b = 815.92(6), c = 928.71(3) pm and β = 104.671(4)°. The structure consists of centrosymmetric di-alkoxy bridged dimers in which the Cu...Cu distance is 293.91(3) pm. The dimers are polymerized along the c axis into chains via NH--O hydrogen bonds. These chains are joined together along the b axis by CuONOCu bridges and weak NH--O hydrogen bonds. This results in layers, which are held together by van der Waals forces. The copper(II) ions have a distorted square pyramidal geometry, which is close to a tetragonally distorted octahedral coordination sphere.

The structure of group B compounds consists of dinuclear units with the centrosymmetric chromophore [LNCuOO′CuNL] in which L is an N-coordinating Hap ligand. The alcoholic function of Hap coordinates as an axial ligand to neighbouring dimeric units, forming again an infinite chain structure. Dimeric Cu...Cu distances are 303 pm. The anions in structure B are not coordinated to copper, but are hydrogen bonded to the ligand N–H and O–H groups.

Ligand-field spectra agree with square-pyramidal (4 + 1) or distorted octahedral (4 + 1 + 1) coordination geometries for Cu(II) in all cases. Small differences in ligand-field spectra are ascribed to differences in anions and axial Cu–O distances.

The compounds are all very strongly magnetically coupled, as seen from the fact that they are diamagnetic at low temperatures. Both groups of compounds have been studied with magnetic susceptibility measurements in the 2–400 K region and the data could be fitted with the Bleaney–Bowers equation for dimers. Compounds of type A have much smaller values of $-2J$ than those of type B. This nicely agrees with the larger value of the Cu–O–Cu angles in the case of group B (99.5–7° in A, against 103.5°). EPR spectra of the compounds show mainly small paramagnetic impurities (below 1%) in agreement with the dimeric structure.

Introduction

The coordination chemistry of amino alcohols, abbreviated Haa, general formula R_2N-X-OH, with

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*Taken in part from the *Ph.D. Thesis* of T. Lindgren.

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X = alkylene fragment, has been the subject of investigation for many years [1–3]. These ligands, which are important as models for aminopolysaccharides, for example, are interesting because of the fact that:

(i) They can easily be substituted at nitrogen and at the carbons in the X group; the X group can easily be varied in length, allowing the study of chelate ring-size effects.

(ii) They can often be prepared as *R* and *S* isomers, allowing the study of enantiomers.

(iii) After dehydronation at the OH group, dimers and clusters are easily formed, allowing the study of magnetic exchange coupling between metal ions.

Earlier work from our laboratories [3–8] has dealt with transition metal complexes of amino ethanols and 2-amino-1-propanol and 1-amino-2-propanol, i.e. forming a five-membered chelate ring [3–6], and with 3-aminopropanols, i.e. forming a six-membered ring [7, 8]. We have now extended this study to the synthesis, structure and properties of copper complexes with the ligand 3-amino-1-propanol, abbreviated Hap (after loss of hydrogen abbreviated as ap). This ligand can form six-membered chelate rings, and also easily dehydronates at the alcoholic group, allowing possible bridging structures. As a matter of fact for compounds analysing as Cu(aa)(Haa)(anion), two different structural types have been reported. In type I, which was reported for the first time about a decade ago [9], an intermolecular dimer occurs, which can be best formulated as $Cu(aa)_2(\mu\text{-}H)_2(aa)_2Cu$. In this class of compounds the two hydrogen ions bridge between oxygens of two different $M(aa)_2$ units. The short O...O contacts of 230–250 pm in fact generate magnetic exchange between the Cu ions ($-2J$ values up to 70 cm^{-1}). In type II (called type B in this paper), the general formula can best be described as $[(Haa)Cu(aa)_2Cu(Haa)](anion)_2$, with bridging oxygen atoms of the dehydronated aa ligands. The present paper describes a number of new compounds which fall into two categories, i.e. with stoichiometry Cu(ap)(anion) and with stoichiometry Cu(ap)(Hap)(anion). To verify the structures and to understand the interesting magnetic properties, a few crystal structures were determined, some of which were communicated before [7, 8], the details of which are also included in the paper.

Experimental

Starting Materials

Ligands and metal salts were used as obtained commercially, without further purification.

Synthesis of the Compounds (cf. ref. 10)

Preparation of Cu(ap)NO₃

The synthesis was done according to the following reaction in methanol

$$2Cu(NO_3)_2 + 4Hap \xrightarrow{MeOH} [Cu(ap)(NO_3)]_2(s) + 2H_2ap^+ + 2NO_3^-$$

A quantity of 2.9 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) was dissolved in 50 ml of MeOH. To this solution was added 6.0 mmol of 3-amino-1-propanol (Hap) (Aldrich) in 100 ml of MeOH. The blue solution was allowed to stand at room temperature for 36 h. The dark blue crystalline product was filtered and washed with ethanol and acetone. A yield of 87% was obtained.

Preparation of Cu(ap)(HCOO)

The compound was prepared in ethanol according to ref. 8 except that the Cu concentration was 3 mmol/100 ml of ethanol. The yield was 80%.

Preparation of Cu(ap)(Hap)NO₃

In a flask 16 mmol $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 80 ml ethanol and 10 ml DME (1,2-dimethoxyethane) containing 16 mmol Hap, and 16 mmol triethylamine (Fluka) was added. Finally 42 mmol Hap was added resulting in a dark blue solution, which on standing overnight at room temperature yielded 4.35 g of blue crystals (99%). These were separated by filtration and washed with ethanol, acetonitrile and ether.

Preparation of Cu(ap)(Hap)Br

A 3.3 mmol solution of $Cu(ap)CF_3SO_3$ was prepared in 15 ml ethanol from a stoichiometric mixture (1:1:1) of $Cu(CF_3SO_3)_2$ (Aldrich), Hap and $N(Et)_3$. To the green solution was added 15 ml ethanol containing 30 mmol Hap. The blue solution was cooled in a freezer and a 10 ml ethanolic solution containing 3.6 mmol $N(Et)_4Br$ (Fluka) was added; 7 ml DME was also added. The bottle was kept in a freezer for a week. The blue crystals were filtered and washed with THF. The yield was 70%.

Preparation of Cu(ap)(Hap)I

A solution of 4.2 mmol of $Cu(ap)CF_3SO_3$ in 10 ml DME and 0.5 ml methanol was prepared from a stoichiometric mixture (1:1:1) of $Cu(CF_3SO_3)_2$, Hap and $N(Et)_3$. To the green solution was added 30 mmol Hap. To the blue solution was added 4 mmol $N(Bu)_4I$ in 15 ml DME and 2 ml methanol. The solution was kept overnight at room temperature (r.t.). The blue crystals were separated by filtration and washed with acetone and ether. The yield was 76%.

Preparation of Cu(ap)(Hap)BF$_4$

Into a flask was measured 20 mmol $Cu(BF_4)_2 \cdot nH_2O$) (Ventron) (n was found to be 3.5), 50 ml ethanol and 80 mmol Hap. The solution was allowed to stand overnight at r.t. and the undissolved green solid was separated by decantation. To the blue solution was added 55 ml THF and the solution was kept for 2 weeks in a freezer. The blue solid which formed was separated by filtration and washed with THF. To the filtrate was added 20 ml THF and after keeping two weeks in a freezer an extra batch of blue crystals was obtained. The total yield was 67%.

Spectroscopy, Analyses and Magnetism

Metal analyses were carried out by standard complexometric titrations and atomic absorption spectroscopy; in addition a few C,H analyses were carried out by the Analytical Laboratories, Engelskirchen. Satisfactory agreement with the proposed formulae was obtained in all cases.

Infrared spectra were obtained as KBr pellets (4000–200 cm^{-1}) on a Perkin-Elmer 580B spectrophotometer, or on Nujol mulls on a Perkin-Elmer 180 spectrophotometer. Ligand field spectra were obtained by the diffuse-reflectance method on solid powders on a Perkin-Elmer 330 spectrophotometer and on Nujol mulls on a Cary 14D spectrophotometer. EPR spectra of the powdered compounds were recorded at room and liquid nitrogen temperatures with a Varian E-3 spectrometer operating at X-band frequencies (9 GHz).

Magnetic susceptibilities were measured routinely on a local Faraday balance (77–300 K). In all cases also a complete set of data (2–300 K) was collected on a squid magnetometer at the University of New Orleans (S.H.E. Corp. VTS-50 superconducting susceptometer; for operation and calibration procedures see ref. 11.), or on an automated Faraday balance (4–300 K) at Memorial University of Newfoundland*.

X-ray Data Collection and Structure Determination

Single-crystal X-ray measurements were done with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The data obtained were corrected for Lorentz and polarization effects. The experimental details and crystal data are as follows: $Cu[O(CH_2)_3NH_2]NO_3$; M_r = 199.65; space group $P2_1/c$; a = 886.56(5), b = 815.92(6), c = 928.71(3) pm; β = 104.671(4)°; Z = 4; V = 0.650 nm^3; D_c = 2.04 g/cm^3: μ(Mo Kα) = 33.2 cm^{-1}; $F(000)$ = 404; T = 296 K.

TABLE 1. Atomic positional parameters and equivalent isotropic temperature factors for $[Cu(ap)NO_3]_2$

Atom	x	y	z	B_{eq}/B_{iso}[a]
Cu	0.97143(2)	0.02315(3)	0.33841(2)	2.187(2)
O1	0.8695(2)	0.0575(2)	0.4956(1)	2.58(3)
O2	1.0985(2)	−0.0221(2)	0.1897(2)	2.76(3)
O3	1.1446(2)	0.2335(2)	0.2451(2)	3.52(3)
O4	1.2523(2)	0.1154(3)	0.0875(2)	4.25(4)
N1	0.7994(2)	0.1091(2)	0.1783(2)	2.66(3)
N2	1.1670(2)	0.1128(2)	0.1725(2)	2.49(3)
C1	0.7064(2)	0.0371(3)	0.4706(2)	2.60(4)
C2	0.6187(2)	0.1419(3)	0.3420(2)	2.98(4)
C3	0.6379(2)	0.0845(3)	0.1915(2)	2.97(4)
H(1C1)	0.675(4)	0.071(5)	0.556(4)	5.0
H(2C1)	0.679(4)	−0.068(5)	0.448(3)	5.0
H(1C2)	0.642(4)	0.265(5)	0.356(3)	5.0
H(2C2)	0.508(4)	0.143(5)	0.335(3)	5.0
H(1C3)	0.608(4)	−0.041(5)	0.176(3)	5.0
H(2C3)	0.565(3)	0.143(5)	0.118(3)	5.0
H(1N1)	0.817(4)	0.058(5)	0.100(4)	5.0
H(2N)	0.820(3)	0.207(5)	0.171(3)	5.0

[a] The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} a_i \cdot a_j$.

The structure was solved by direct methods (MULTAN11/82) and refined by least-squares techniques to an R value of 0.025 (R_w = 0.037) for 1440 independent reflections having $I > 3\sigma(I)$. Hydrogen atoms were refined with isotropic parameter B = 5.00 Å^2. Scattering factors were taken from the International Tables [12]. All calculations were performed on an VAX II microcomputer using SDP-PLUS software [13]. Figures were drawn with PLUTO. The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table 1. See also 'Supplementary Material'.

Results and Discussion

Description of the Structure of [Cu(ap)(NO$_3$)]$_2$

The dimeric $[Cu(ap)NO_3]_2$ unit and atom numbering is shown in Fig. 1. Each copper atom has a square-pyramidal coordination (4 + 1), which is close to tetragonally distorted octahedral (4 + 1 +1) coordination. In the xy-plane around copper(II) ion there are two alkoxide oxygens, one amine nitrogen and one nitrate ion oxygen atom. The fifth coordination site is occupied by a nitrate ion oxygen atom, O(3), from the adjacent dimer unit, with a Cu–O distance of 261.6 pm. As a sixth ligand another oxygen atom, O(3), from a chelating nitrate is present, although the O(2)–Cu–O(3) angle is only 54.14(6)° (cf. Fig. 1). Similar coordination for didentate, chelating nitrates is known in the literature [14a, b]. Bond distances and angles are presented in Table 2.

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*Variable temperature magnetic susceptibilities were determined using an Oxford Instruments Superconducting Faraday Susceptometer. A main solenoid field of 1.5 T and a gradient field of 10 T.m^{-1} were employed. Molar susceptibility data (per copper) are corrected for diamagnetism.

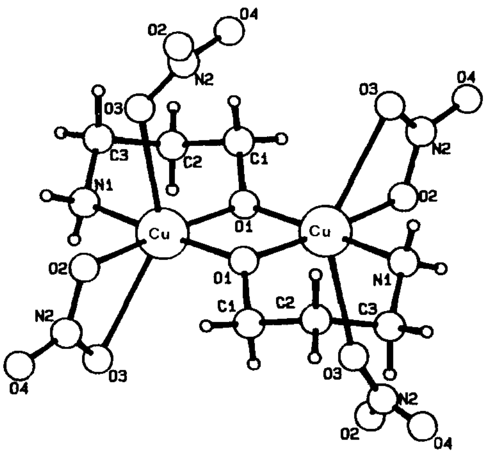

Fig. 1. PLUTO projection of $[Cu(ap)(NO_3)]_2$ (I).

TABLE 2. Bond distances (pm) and angles (°) with e.s.d.s in parentheses for $[Cu(ap)NO_3]_2$

Distances			
Cu–O1	192.2(2)	C1–O1	141.6(2)
Cu–O1^{i}	192.2(2)	C1–C2	151.4(3)
Cu–N1	197.0(2)	C2–C3	152.4(3)
Cu–O2	202.5(2)	C3–N1	148.2(3)
Cu–O3	259.4(2)	N2–O2	128.7(2)
Cu–O3^{ii}	261.6(2)	N2–O3	123.8(2)
Cu···Cu^{i}	293.91(3)	N2–O4	122.4(3)
Angles			
O1–Cu–N1	95.66(7)	O1–C1–C2	111.2(2)
O1–Cu–O2	173.87(5)	C1–C2–C3	113.3(2)
O1–Cu–O1^{i}	80.29(6)	C2–C3–N1	111.7(2)
O1–Cu–O3	126.10(6)	O2–N2–O3	117.8(2)
O1–Cu–O3^{ii}	97.57(6)	O2–N2–O4	118.9(2)
N1–Cu–O2	90.46(7)	O3–N2–O4	123.7(2)
N1–Cu–O3	85.56(6)		
N1–Cu–O1^{i}	175.95(7)		
N1–Cu–O3^{ii}	85.81(6)		
O2–Cu–O1^{i}	95.59(6)		
O2–Cu–O3	54.14(6)		
O2–Cu–O3^{ii}	82.99(6)		
O1^{i}–Cu–O3^{ii}	94.69(6)		
O3–Cu–O1^{i}	96.80(6)		
O3–Cu–O3^{ii}	136.09(5)		
Cu–O1–Cu^{i}	99.71(6)		

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $2 - x, y - 0.5, 0.5 - z$.

The N–O bond parameters of the nitrate ion (N2)–O(2) = 128.7(2), N(2)–O(3) = 123.8(2) and N(2)–O(4) = 122.7(3) pm are in good agreement with the parameters of N–O bonds in coordinated nitrate ions [14c]. The asymmetry of N–O bonds of the nitrate ion can be a result of asymmetry in Cu–O(2) and Cu–O(3) bonds.

TABLE 3. Distances (pm) and angles (°) associated with the possible hydrogen bonds of $[Cu(ap)NO_3]_2$[a]

X–H···Y	X–H	H···Y	X···Y	X–H···Y
N1–H(1N1)···O(4^{iii})	88(4)	221(4)	301.5(2)	151(3)
N1–H(2N1)···O(1^{iv})	83(4)	262(4)	334.7(2)	147(3)
N1–H(2N1)···O(2^{v})	83(4)	257(4)	328.9(2)	146(3)

[a] e.s.d.s in parentheses. Symmetry codes: (iii) $2 - x, -y, -z$; (iv) $x, 0.5 - y, z - 0.5$; (v) $2 - x, 0.5 - y, 0.5 - z$.

The bond distances and angles are normal in the amino propanol ligand (Table 2). The C–H bond distances are from 90(4) to 106(4) pm. Upon coordination the 3-amino-1-propanolato ion adopts a chelated conformation with O–C–C–C and C–C–C–N torsion angles of 69.2(2)° and −68.1(3)°, respectively.

In the dimeric $[Cu(ap)NO_3]_2$ units the shortest Cu–Cu vectors are nearly along the *c* axis. The NH...O(4) hydrogen bonds (Table 3) bind the dimers in that direction. The CuONOCu bridge joins the dimers along the *b* axis (see Fig. 2). There are also weak bifurcated hydrogen bonds from another NH-hydrogen to O(1) and O(2) in the direction of the same axis.

Between the polymeric $[Cu(ap)NO_3]_2$ layers there are only weak van der Waals connections in the direction of the *a* axis. Given this structure and the coordination geometry one would expect only a weak interdimer magnetic interaction through nitrate ions. A projection showing the extended interactions is presented in Fig. 2.

Summary of the Structures of $[Cu(ap)(HCOO)]_2$ and $[Cu(ap)(Hap)]_2I_2$

The structure of the formate can be described as a chain of dinuclear units, just as for the nitrate described above. In fact the coordination geometries for Cu(II) and the Cu...Cu contact are almost the same as those for the nitrate, and especially the Cu–O–Cu angles are equal (99.5 versus 99.7°), which is important for the discussion of the magnetic properties (see below).

The structure of $[Cu(ap)(Hap)]_2I_2$ consists of alkoxo-bridged $[Cu(ap)(Hap)]_2^{2+}$ dimers and I^- ions. The halves of the dinuclear units are related by a crystallographic inversion symmetry. Each copper(II) ion shows a distorted (4 + 1) square pyramidal coordination. The nearest sixth ligand is a non-bonding iodide at 474.6 pm. The four short bonds are formed by two nitrogens (Cu–N(1) 197.5(11) pm and Cu–N2 = 200.1(8) pm) and by two oxygens (Cu–O1 = 192.8(6) pm and Cu–O1^{i} = 193.5(6) pm). The long apical bond (Cu–O2^{ii} = 246.1(9) pm) is due to the bridging aminoalcohol molecule which binds the dimers to polymers. This

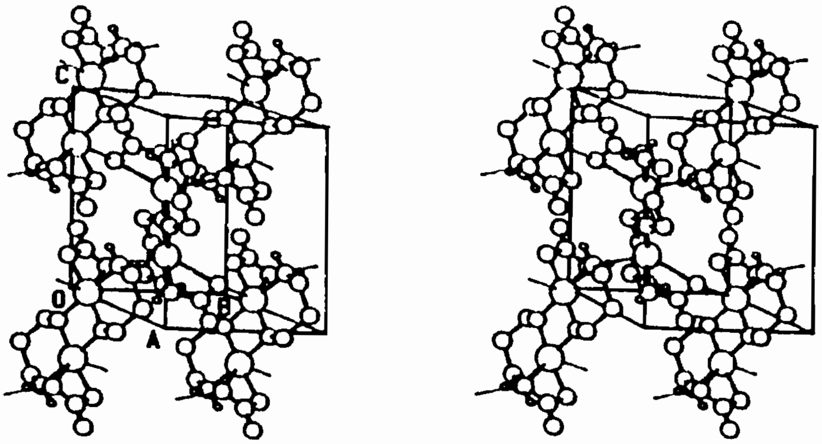

Fig. 2. Packing of the structure of $[Cu(ap)(NO_3)]_2$ (I).

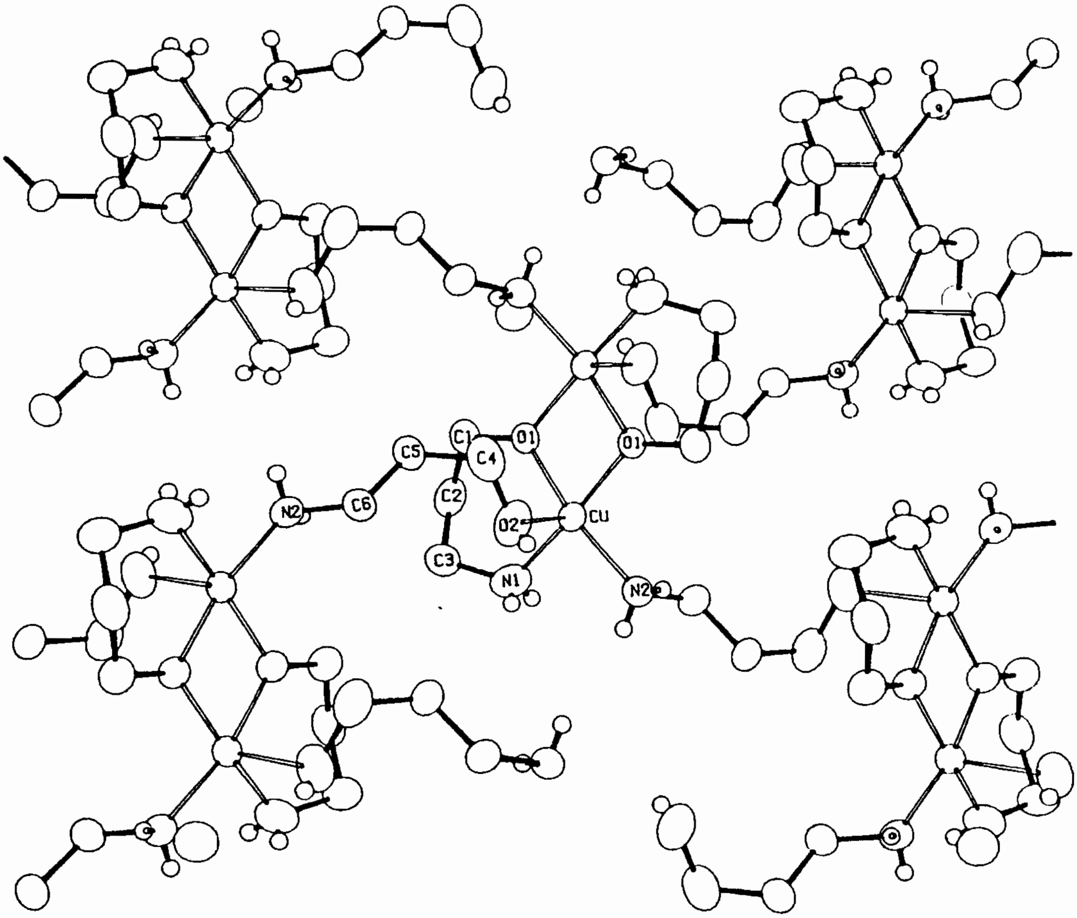

Fig. 3. ORTEP projection of $[Cu(ap)(Hap)]_2I_2$ and its molecular network.

is depicted in Fig. 3. The intramolecular Cu...Cu distance is 303.4(1) pm and the bridge angle Cu–O–Cu is 103.5(3)°. The distances and angles within the Cu_2O_2 core of $[Cu(ap)(Hap)]_2$ unit are longer and larger than the relevant parameters of Cu_2O_2 core of $[Cu(ap)A]_2$ unit (*vide supra*).

The 3-amino-1-propanolato ion adopts a chelated conformation with O–C–C–C and C–C–C–N torsion angles of 57(1)° and −73(1)°, respectively. These differ from those of the formate referred to above, which are −67.4(1)° and 71.5(2)°, respectively. On the contrary the neutral 3-amino-1-propanol

TABLE 4. Spectroscopic data of copper(II) 3-amino-1-propanol compounds[a]

Compound	Colour	LF and CT maxima ($cm^{-1} \times 10^3$)		Typical infrared bands[b] (cm^{-1})			
$[Cu(ap)(HCOO)]_2$	blue	15.7	29.9	3270	3245		3160
$[Cu(ap)(NO_3)]_2$	blue	16.6	29.0	3310	3260		3130
$[Cu(ap)Cl]_2$	green	16.0	25.6	3280	3240		3145
$[Cu(ap)Br]_2$	green	16.0	25.2	3230	3160	3120	
$[Cu(ap)(Hap)]_2Cl_2$	blue	17.2	28.2	3310	3230		3130
$[Cu(ap)(Hap)]_2Br_2$	blue	17.2	29.0	3340	3245	3220	3135
$[Cu(ap)(Hap)]_2(NO_3)_2$	blue	17.2	29.4	3390	3285	3240	3180
$[Cu(ap)(Hap)]_2(BF_4)_2$	blue	17.3	29.4	3560	3345	3290	3170
$[Cu(ap)(Hap)]_2I_2$	blue	17.2	28.6	3390	3240	3200	3140

[a] Ligand-field spectra were recorded on Nujol mull or on powders in the diffuse reflectance mode in the range 30 000–5000 cm^{-1}; all compounds show a charge-transfer band. [b] Infrared bands above 3000 cm^{-1} (NH and OH stretches mainly), recorded as Nujol mulls.

TABLE 5. Magnetic susceptibility data of a few selected aminopropanol compounds of type A and type B

Compound	Magnetic parameters[a]			
	$-2J$ (cm^{-1})	g value	TIP (in cgs $\times 10^6$)	Impurity (x) (%)
$[Cu(ap)(HCOO)]_2$ (type A)	282	2.06	36	0.15
$[Cu(ap)(NO_3)]_2$ (type A)	387	2.09	45	0.06
$[Cu(ap)(Hap)]_2Br_2$ (type B)	956	2.10	45	0.29
$[Cu(ap)(Hap)]_2(NO_3)_2$ (type B)	997	2.08	28	0.32
$[Cu(ap)(Hap)]_2(BF_4)_2$ (type B)	978	2.07	48	0.18
$[Cu(ap)(Hap)]_2I_2$	926	2.28	145	0.15

[a] Obtained from measurements between 4 and 300 K and least-squares analysis of the data. The used equation, according to the classical Bleaney–Bowers equation was:

$$\chi = (1-x)\frac{Ng^2\beta^2}{3kT}\{1 + 1/3\exp(-2J/kT)\}^{-1} + x.Ng^2\beta^2/4kT + \mathrm{TIP}$$

e.s.d. values in J are estimated to be about 5%; g values are accurate to less than 1%.

molecule, which bridges the dimers to polymers, has a half linear conformation with O–C–C–C and C–C–C–N torsion angles 70(1) and −166(1)°, respectively. The iodides are hydrogen bonded by OH and NH protons. Full details and drawings for both structures are given in refs. 7 and 8.

Spectroscopic Characterizations and Magnetic Measurements

Relevant spectral data for all compounds studied in this work are listed in Table 4 (ligand-field spectra and infrared spectra). The magnetic measurement data are given in Table 5.

The infrared spectra of the compounds are as one would expect, showing the anions as coordinated (deduced from low-symmetry splittings) in compounds of class A, and as free anions in class B. All ligand peaks can be easily recognized, although there are differences from compound to compound, depending upon the anion, for the N–H and O–H vibrations (OH group present only for class B). Clear correlations are observed in the IR spectra between the H bond accepting properties of the anion and the N–H and O–H stretching frequencies. Especially the ν(OH) band for the BF_4 salt is amazingly high, in agreement with its weak accepting possibilities. Such correlations are well known [15, 16].

The ligand-field spectra show broad bands with shoulders, all in agreement with a 4 + 1 and a 4 + 1 + 1 tetragonal-based coordination geometry [17]. EPR powder spectra show only very weak signals, which have been ascribed to paramagnetic impurities (below 1%) and they will not be discussed in detail.

The magnetic susceptibilities were studied in quite some detail, especially because the two different groups A and B, have quite different structures, whith in one case a Cu–O–Cu angle of 99.5 (formate) or 99.7° (nitrate), and in the other case (type B) an angle of 103.5° (so far only the iodide has been studied). Figure 4 presents the susceptibility versus T for the nitrate of type A, whereas Fig. 5 presents the susceptibility for the nitrate of type B.

As can be seen from Table 5 the relatively small values of $-2J$ nicely agree with type A, whereas the

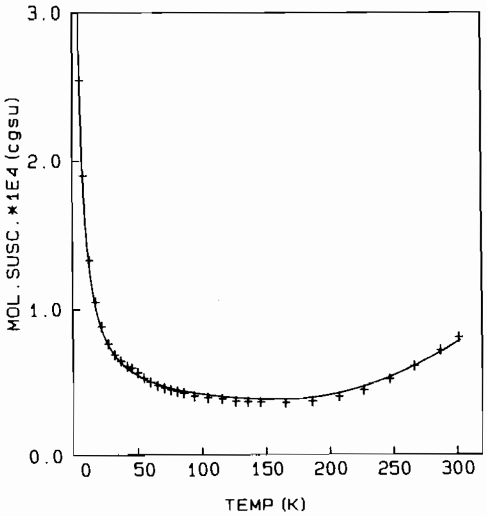

Fig. 4. Magnetic susceptibility of $[Cu(ap)(NO_3)]_2$ as a function of temperature with the best fit against the parameter set from Table 5.

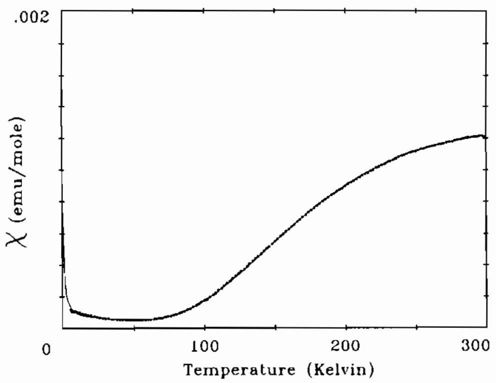

Fig. 5. Magnetic susceptibility of $[Cu(ap)(Hap)]_2(NO_3)_2$ as a function of temperature with the best fit against the parameter set from Table 5.

larger values of $-2J$ agree with type B. This is just as one would expect, based on the early research of Hatfield *et al.* [18] for dinuclear $Cu(OH)_2Cu$ species with a square-planar based geometry, where a linear relationship was found between the Cu–O–Cu angle and the value of $-2J$. The somewhat smaller value for the iodide in Table 5 might originate from the fact that this compound is difficult to obtain pure and that it easily decomposes upon heating.

Conclusions

The results described above have once again shown that dinuclear, square-planar based Cu(II) compounds with oxygen-bridging ligands show a magnetic coupling which is largely determined by the bridging angle Cu–O–Cu. The larger the angle, the stronger the antiferromagnetic coupling between the Cu(II) ions. For such compounds the axial ligands for Cu(II) have hardly any influence on the exchange coupling, as long as the unpaired (magnetic) orbital remain more or less co-planar with the plane of the $L_2CuO_2CuL_2$ unit, i.e. a $d_{x^2-y^2}$ orbital.

Supplementary Material

The authors can be contacted for supplementary information about anisotropic thermal parameters, hydrogen parameters and a table of observed and calculated F values.

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