Hydrogen-bridged Dimeric and Trimeric Copper(II) Triflate Compounds with Racemic and Optically Active Aminopropanols. Crystal and Molecular Structure of Hexakis(*R,S*-2-aminopropan-1-ol-*N,O*)-bis(*R,S*-2-aminopropan-1-olato-*N,O*)bis(trifluoromethanesulphonato-*O*)-tricopper(II) Bis(trifluoromethanesulphonate) †

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Isomers of aminopropanol react with $Cu[CF_3SO_3]_2$ to form compounds of the general formula $[Cu_2(RS\text{-ap})_2(RS\text{-Hap})_2][CF_3SO_3]_2$, $[Cu_2(S\text{-ap})_2(S\text{-Hap})_2][CF_3SO_3]_2$, $[Cu_3(RS\text{-pa})_2(RS\text{-Hap})_6][CF_3SO_3]_4$, and $[Cu_2(S\text{-pa})(S\text{-Hpa})_5][CF_3SO_3]_3$, where *RS*-Hap and *S*-Hap represent *R,S*- and *S*(+)-1-aminopropan-2-ol, respectively, and *RS*-Hpa and *S*-Hpa represent *R,S*- and *S*(+)-2-aminopropan-1-ol; *RS*-ap, *S*-ap, *RS*-pa, and *S*-pa are the respective anions formed by ionisation of the acidic alcohol proton of the isomers. The structure of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$ has been determined by *X*-ray crystallography. The compound crystallizes in space group *P*1 with unit-cell dimensions $a = 10.345(2)$, $b = 10.720(2)$, $c = 13.619(2)$ Å, $\alpha = 80.40(2)$, $\beta = 71.41(2)$, $\gamma = 85.14(2)°$, and $Z = 1$. The structure was solved by Patterson methods and least-squares refinement converged at *R* 0.046 and *R'* 0.046. The structure consists of unique O ··· H ··· O hydrogen-bonded trinuclear units. The central copper atom (C) has a tetragonal co-ordination and is linked to the other two copper atoms *via* two short oxygen–oxygen distances of 2.43(2) and 2.37(2) Å. Copper atoms A and B are octahedrally co-ordinated by three chelating ligands and have the configurations Δ(δλλ) [or Λ(λδδ)] and Λ(δδδ) [or Δ(λλλ)], respectively. The geometry of the CuN_3O_3 species for A and B is meridional. The magnetic behaviour of the four compounds is discussed. The magnitude of the magnetic exchange (*J*) is about −5 cm^{-1} for the dimeric 1-aminopropan-2-ol compounds. The *J* values for the trinuclear *R,S*-2-aminopropan-1-ol compound and the dimeric *S*(+)-2-aminopropan-1-ol compound are calculated to be +0.06 and −8.5 cm^{-1}, respectively. The magnitude of the magnetic exchange in these compounds has been related to the co-ordination geometry around the copper ions.

The co-ordination chemistry of optically active ligands is receiving increasing interest, but up to the present not much attention has been given to the differences in co-ordination chemistry between racemic and optically active isomers.[1] The present study is part of an investigation about the differences in co-ordination chemistry of racemic and optically active aminopropanol. Earlier work from this laboratory described compounds with *R,S*-1-aminopropan-2-ol (*RS*-Hap) and *S*(+)-1-aminopropan-2-ol (*S*-Hap).[2,3] Differences in composition and in lattice energy, depending upon the position of the ligands, were found for several compounds. Also, the crystal structures of $[Ni(NCS)_2(RS\text{-Hap})_2]$ and $[Ni(NCS)_2(S\text{-Hap})_2]$ were described and compared.[4] Small differences in the nickel geometry and in the conformation of the ligands were observed, but no differences in hydrogen bonding could be detected, in contrast with earlier studies on diamine ligands.[1] With the aim of preparing tris-chelate compounds, we have extended this investigation by using the weakly co-ordinating anion $CF_3SO_3^-$ ('triflate').[5] The present paper describes compounds of $Cu[CF_3SO_3]_2$ with the ligands *RS*-Hap, *S*-Hap, *R,S*-2-aminopropan-1-ol (*RS*-Hpa), and *S*(+)-2-aminopropan-1-ol (*S*-Hpa). All compounds contain deprotonated ligands, as deduced from the elemental analyses. This, together with the magnetic measurements of the compounds with *RS*-Hap, *S*-Hap, and *S*-Hpa showing these compounds to be binuclear, suggested the monomeric units in the compounds to be joined by hydrogen bonding, which is known to occur in compounds containing both hydrogen-bond donor groups and hydrogen-bond acceptor groups.[6-8] Only a few examples of such transition-metal compounds associated into polynuclear compounds through O ··· H ··· O hydrogen bonds have been reported so far. In these compounds direct magnetic exchange is unlikely, because of the large copper–copper distance (about 5.0 Å). The coupling most likely occurs *via* superexchange through the hydrogen bonds.[8] The magnetic behaviour of the compound with the ligand *RS*-Hpa, however, appeared to be totally different. Therefore, it was decided to investigate the crystal structure of this compound, which is presented in this paper.

In a future paper the i.r. and c.d. spectra of these compounds, together with the corresponding Zn^{II}, Ni^{II}, and Co^{III} triflate compounds of the four aminopropanol isomers, will be discussed.

Experimental

Starting Materials.—All ligands with the exception of *S*-Hap were commercially available. *S*-Hap was prepared as reported previously.[2] $Cu[CF_3SO_3]_2 \cdot xH_2O$ was prepared by addition of pure CF_3SO_3H to $CuCO_3$ in acetonitrile.[5] After concentrating the solution the compound precipitated. The salt was recrystallized from hot ethanol (yield 90%).

Synthesis of the Copper Compounds.—All compounds were prepared by dissolving $Cu[CF_3SO_3]_2 \cdot 2H_2O$ (5 mmol) and the ligand in the ratio 1 : 3 in absolute ethanol (20 cm^3). The ligands used were *RS*-Hap, *S*-Hap, *RS*-Hpa, and *S*-Hpa. In agreement with the Cu, C, H, N, and S elemental analyses, the compounds prepared had the following compositions:

† *Supplementary data available* (No. SUP 23471, 17 pp.): observed and calculated structure factors, isotropic and anisotropic thermal parameters, hydrogen atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: c.g.s. = e.m.u. = $4\pi \times 10^{-6}$ m^3.

$[Cu_2(RS\text{-ap})_2(RS\text{-Hap})_2][CF_3SO_3]_2$ (1), $[Cu_2(S\text{-ap})_2(S\text{-Hap})_2][CF_3SO_3]_2$ (2), $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$ (3), and $[Cu_2(S\text{-pa})(S\text{-Hpa})_5][CF_3SO_3]_3$ (4), in which the anionic ligands are formed by deprotonation of the hydroxy group of the ligand.

The crystals of compound (3) were obtained by dissolving $Cu[CF_3SO_3]_2 \cdot 2H_2O$ and *RS*-Hpa (1 : 3) in absolute ethanol. After dilution with sodium-dried diethyl ether, compound (3) crystallized after standing at 4 °C for several days. All attempts to obtain suitable single crystals of compound (4) using *S*-Hpa have failed so far (the mosaic spread of the crystals was too large).

Analyses and Physical Measurements.—Metal analyses were carried out by complexometric titration.[9,10] Carbon, nitrogen, hydrogen, and sulphur analyses were performed by Dr. F. Pascher (Mikroanalytisches Laboratorium, Buschstrasse 54, D-5500. Bonn-1, BRD). Magnetic measurements (2—80 K) were carried out using a PAR vibrating-sample magnetometer. The *X*-band e.s.r. spectra of the powdered samples were recorded at room temperature with a Varian E3 apparatus (9.5 GHz). *X*-Ray powder diffraction patterns were recorded on a Philips diffractometer using Cu-K_α radiation. Diffuse reflectance spectra (35 000—5 000 cm^{-1}) were recorded on a Beckman DK-2A spectrophotometer using MgO as a reference.

Crystal Structure Determination of Compound (3).—*Collection and reduction of the intensity data.* Rotation photographs and zero-level Weissenberg photographs with Cu-K_α radiation showed no symmetry and no systematic absences, which implied that the space group was $P1$ or $P\bar{1}$. The unit-cell parameters were determined using a Nonius CAD-4 automatic four-circle diffractometer. The intensities were measured using the ω—θ scan mode. The observed data were corrected for Lorentz and polarisation effects. An absorption correction was not applied, because the difference in transmission was very small. All crystal data and experimental data are summarized in Table 1.

Solution and refinement of the structure. The positions of the copper and sulphur atoms were derived from a sharpened Patterson synthesis. Subsequent Fourier and difference-Fourier syntheses revealed the positions of all heavy atoms. The least-squares refinement, assuming the space group $P\bar{1}$ and using isotropic temperature parameters, resulted in $R = \Sigma||F_o| - |F_c||/|F_o| = 0.104$. The least-squares refinement, assuming space group $P1$ and using isotropic temperature parameters resulted in $R = 0.083$. Therefore, space group $P1$ was used during the following refinement with anisotropic temperature parameters. Most hydrogen atoms were located in difference-Fourier maps. The positions of the remaining hydrogen atoms, with the exception of six methyl protons and two hydroxy protons, were calculated with the bond lengths O–H = 0.90, N–H = 0.95, and C–H = 1.00 Å. The hydrogen atoms were not refined. Their overall *B* parameters were fixed at 4.0 $Å^2$. The scattering factors of all atoms were taken from international tables.[11] During the following refinement, with individual anisotropic temperature parameters for the heavy atoms, problems arose, caused by pseudo-symmetry in the structure and disorder in the non-co-ordinated CF_3SO_3 groups, numbered T2 and T4. The high correlations between the copper, nitrogen, and oxygen atoms of part A and B of the structure (Figure 1) and between most of the atoms of the co-ordinated CF_3SO_3 groups, numbered T1 and T3, indicated a pseudo-inversion centre on Cu(C). Those atoms were therefore coupled with respect to Cu(C). At the end of the refinement, however, these constraints were relaxed. The high degree of correlation required the introduction of Waser-Slack constraints [12] for the bond lengths C(1)–C(2) (1.51 Å) and C(2)–C(3) (1.53 Å) for all A and B rings, and N–C(2) (1.425 Å) for rings A1 and B3. These values were obtained from the average values of the disordered rings and the available crystal structures containing 1-aminopropan-2-ol.[4,13] The fluorine atoms of the CF_3SO_3 group T4 were refined with individual isotropic temperature parameters. Now, the refinement resulted in $R = 0.046$ and $R' = [\Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.046$ with reflections $I > \sigma(I)$. A refinement of the enantiomorphic structure gave

Table 1. Crystal data and experimental parameters for $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$

(*a*) Crystal data

Formula	$C_{28}H_{70}Cu_3F_{12}N_8O_{20}S_4$
M	1 385.77
a/Å	10.345(2)
b/Å	10.720(2)
c/Å	13.619(2)
α/°	80.40(2)
β/°	71.41(2)
γ/°	85.14(2)
U/$Å^3$	1 410.7
Z	1
D_m/g cm^{-3}	1.65(2)
D_c/g cm^{-3}	1.63
F(000)	644.51
Crystal system	Triclinic
Space group	*P*1
μ(Mo-K_α)/mm^{-1}	1.425
Crystal dimensions/mm	0.13 × 0.15 × 0.20
Calc. transmission factors	0.81—0.83

(*b*) Experimental parameters

λ(Mo-K_α)/Å	0.709 30
Monochromator	graphite
Take-off angle/°	3
$\theta_{max.}$/°	23
Data collected	3 928
Data with $I > \sigma(I)$	2 885

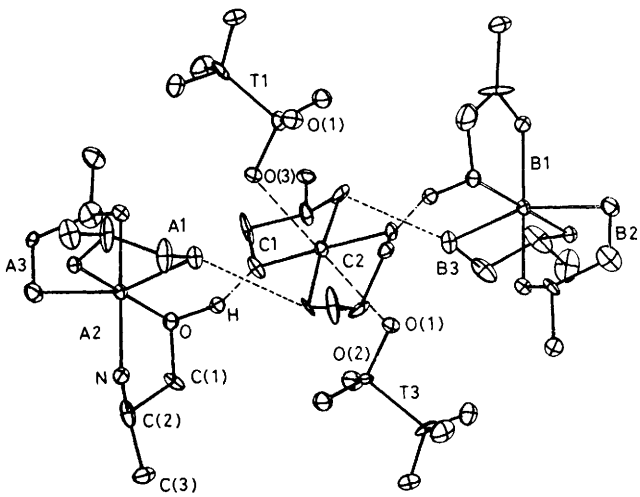

Figure 1. The trimeric unit of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6]^{4+}$ and the two semi-co-ordinating $CF_3SO_3^-$ anions. The atom labelling, the Cu(C)–triflate semi-co-ordination, and the intramolecular hydrogen bonds are indicated. All hydrogen atoms, except those of the strong O · · · H · · · O bonds, have been omitted for clarity

Table 2. Atomic co-ordinates for $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$ *

Atom	x	y	z	Atom	x	y	z
Cu(A)	−0.001 0(1)	−0.000 9(1)	1.001 1(1)	O(C2)	0.251(2)	0.532(1)	0.754(1)
O(A1)	0.025 3(6)	0.210 0(5)	1.040 0(4)	N(C2)	0.280(2)	0.309(2)	0.863(1)
N(A1)	−0.125 2(6)	−0.003 5(5)	1.149 4(4)	C(1C2)	0.273(2)	0.532(2)	0.844(2)
C(1A1)	−0.027(3)	0.193(3)	1.149(2)	C(2C2)	0.349(1)	0.418(2)	0.882(1)
C(2A1)	−0.145(3)	0.116(2)	1.185(2)	C(3C2)	0.296(3)	0.415(2)	0.999(1)
C(3A1)	−0.204(4)	0.085(3)	1.304(2)	S(T1)	−0.117 5(8)	0.495 3(7)	0.888 9(7)
O(A2)	0.132 0(5)	0.010 3(5)	0.861 1(4)	O(1T1)	−0.111 3(6)	0.556 4(5)	0.972 9(5)
N(A2)	0.157 3(6)	−0.087 9(6)	1.043 9(5)	O(2T1)	−0.097 1(5)	0.571 5(5)	0.790 2(4)
C(1A2)	0.253(2)	−0.058(2)	0.862(1)	O(3T1)	−0.045 8(5)	0.372 6(4)	0.885 2(4)
C(2A2)	0.246(2)	−0.157(1)	0.955(1)	C(T1)	−0.291(3)	0.453(2)	0.926(2)
C(3A2)	0.385(8)	−0.196(8)	0.967(8)	F(1T1)	−0.328 6(5)	0.377 8(5)	1.018 1(5)
O(A3)	−0.109 6(6)	−0.187 0(4)	0.982 0(5)	F(2T1)	−0.376 4(4)	0.552 4(5)	0.935 8(4)
N(A3)	−0.146 5(6)	0.072 9(5)	0.934 6(4)	F(3T1)	−0.315 1(5)	0.391 6(5)	0.853 2(5)
C(1A3)	−0.210(2)	−0.140(2)	0.939(2)	S(T2)	0.440 1(2)	0.043 2(2)	0.157 7(2)
C(2A3)	−0.177(2)	−0.015(2)	0.874(2)	O(1T2)	0.395 3(8)	0.088 5(6)	0.071 3(5)
C(3A3)	−0.277(3)	0.042(3)	0.819(3)	O(2T2)	0.568(2)	0.021(3)	0.154(2)
Cu(B)	0.398 8(1)	0.728 9(1)	0.488 9(1)	O(3T2)	0.392(3)	−0.066(2)	0.218(2)
O(B1)	0.265 8(5)	0.717 7(5)	0.628 9(4)	C(T2)	0.373(6)	0.155(2)	0.267(2)
N(B1)	0.240 5(6)	0.815 9(5)	0.446 1(5)	F(1T2)	0.259(2)	0.197(3)	0.255(2)
C(1B1)	0.139(2)	0.784(2)	0.634(2)	F(2T2)	0.400(3)	0.125(2)	0.337(1)
C(2B1)	0.135(2)	0.837(2)	0.530(2)	F(3T2)	0.454(3)	0.261(2)	0.207(2)
C(3B1)	0.013 3(8)	0.924 2(8)	0.522 9(8)	S(T3)	0.515 1(6)	0.233 4(7)	0.600 1(6)
O(B2)	0.507 4(6)	0.915 1(5)	0.508 1(4)	O(1T3)	0.443 6(5)	0.355 4(4)	0.604 8(4)
N(B2)	0.544 3(6)	0.655 1(5)	0.555 4(4)	O(2T3)	0.509 1(6)	0.171 6(5)	0.517 1(5)
C(1B2)	0.600(4)	0.869(2)	0.567(2)	O(3T3)	0.494 9(6)	0.156 5(5)	0.699 8(4)
C(2B2)	0.576(2)	0.737(2)	0.620(1)	C(T3)	0.691(2)	0.280(2)	0.559(2)
C(3B2)	0.691(2)	0.684(2)	0.663(2)	F(1T3)	0.712 9(5)	0.336 4(6)	0.626 8(5)
O(B3)	0.372 5(6)	0.518 0(5)	0.450 0(4)	F(2T3)	0.726 4(5)	0.350 2(5)	0.471 9(5)
N(B3)	0.523 0(5)	0.731 5(5)	0.340 6(4)	F(3T3)	0.774 2(4)	0.175 6(5)	0.554 3(4)
C(1B3)	0.480(3)	0.516(2)	0.352(2)	S(T4)	0.957 7(2)	0.684 8(2)	0.332 4(2)
C(2B3)	0.497(3)	0.638(2)	0.280(2)	O(1T4)	1.002 5(8)	0.639 5(6)	0.418 7(5)
C(3B3)	0.595(4)	0.620(3)	0.171(2)	O(2T4)	1.037(2)	0.795(2)	0.277(2)
Cu(C)	0.195 9(5)	0.363 9(5)	0.746 5(5)	O(3T4)	0.812(2)	0.676(3)	0.363(2)
O(C1)	0.149(2)	0.204(2)	0.736(2)	C(T4)	1.024(2)	0.567(2)	0.252(1)
N(C1)	0.125(2)	0.426(2)	0.630(2)	F(1T4)	0.987(3)	0.464(3)	0.279(2)
C(1C1)	0.069(3)	0.206(2)	0.667(2)	F(2T4)	1.008(3)	0.615(2)	0.160(2)
C(2C1)	0.123(2)	0.313(2)	0.582(1)	F(3T4)	1.154(3)	0.553(3)	0.227(2)
C(3C1)	0.059(2)	0.326(2)	0.497(2)				

* Estimated standard deviations are in parentheses in Tables 2—6.

identical R values. The atomic positional parameters are presented in Table 2.

Results and Discussion

Description of the Structure of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$.—Intramolecular bond lengths, bond angles, and torsion angles are listed in Tables 3, 4, and 5. The trinuclear unit is shown in Figure 1, together with the atomic labelling. The packing of the structure and the numbering of the triflate groups is shown in Figure 2. The structure consists of layers of unique O · · · H · · · O hydrogen-bonded trinuclear units. The trinuclear units are coupled *via* hydrogen bonds to triflate groups to form the layers. The triflate groups connect the trinuclear units by hydrogen bonding and semi-co-ordination to Cu(C). The copper atoms A and B are each co-ordinated by three bidentate 2-aminopropan-1-ol ligands and have a relatively large distortion of the ideal octahedral bond angles, with *trans* angles of 160.3—174.4° and *cis* angles of 76.9—99.5°. The central atom Cu(C) has a smaller distortion with *trans*-angles of 175.8—179.8 Å and *cis* angles of 83.1—97.0 Å. Cu(C) is tetragonally co-ordinated by two bidentate ligands and semi-co-ordinated by two of the triflate groups [Cu–O 2.615(7) and 2.678(7) Å]. The term 'semi-co-ordination' indicates that in tetragonal-octahedral copper(II) compounds the unidentate axial fifth and sixth

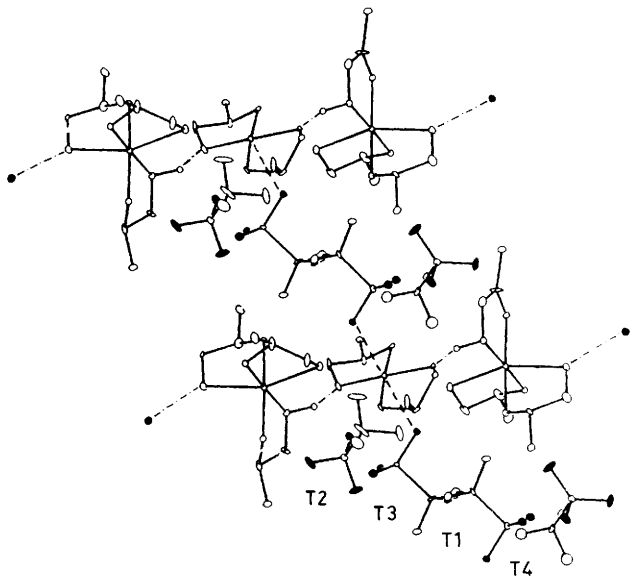

Figure 2. Crystal packing in the structure of (3). The numbering of the triflate groups is indicated and the oxygen atoms of the triflate groups are marked in black

Table 3. Intramolecular bond lengths (Å) and bond angles (°) of the co-ordination octahedra * of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$

(*a*)		(*b*)			
Cu(A)–O(A1)	2.462(5)	Cu(B)–O(B3)		Cu(C)–O(C1)	1.862(2)
Cu(A)–N(A1)	2.016(6)	Cu(B)–N(B3)		Cu(C)–N(C1)	1.957(2)
Cu(A)–O(A2)	1.956(5)	Cu(B)–O(B1)		Cu(C)–O(C2)	1.967(2)
Cu(A)–N(A2)	2.015(6)	Cu(B)–N(B1)		Cu(C)–N(C2)	2.023(2)
Cu(A)–O(A3)	2.460(5)	Cu(B)–O(B2)		Cu(C)–O(C3T1)	2.615(7)
Cu(A)–N(A3)	2.035(6)	Cu(B)–N(B3)		Cu(C)–O(C1T3)	2.678(7)
O(A1)–Cu(A)–N(A1)	76.9(2)	O(B3)–Cu(B)–N(B3)		O(C1)–Cu(C)–N(C1)	86.5(9)
O(A1)–Cu(A)–O(A2)	98.8(2)	O(B1)–Cu(B)–O(B3)		O(C1)–Cu(C)–O(C2)	178(1)
O(A1)–Cu(A)–N(A2)	96.9(2)	N(B1)–Cu(B)–O(B3)		O(C1)–Cu(C)–N(C2)	97.0(8)
O(A1)–Cu(A)–O(A3)	160.3(2)	O(B2)–Cu(B)–O(B3)		O(C1)–Cu(C)–O(C3T1)	85.1(8)
O(A1)–Cu(A)–N(A3)	89.7(2)	N(B2)–Cu(B)–O(B3)		O(C1)–Cu(C)–O(C1T3)	95.0(8)
N(A1)–Cu(A)–O(A2)	174.4(2)	O(B1)–Cu(B)–N(B3)		N(C1)–Cu(C)–O(C2)	93.4(8)
N(A1)–Cu(A)–N(A2)	94.3(2)	N(B1)–Cu(B)–N(B3)		N(C1)–Cu(C)–N(C2)	175.8(9)
N(A1)–Cu(A)–O(A3)	91.1(2)	O(B2)–Cu(B)–N(B3)		N(C1)–Cu(C)–O(C3T1)	92.8(6)
N(A1)–Cu(A)–N(A3)	94.6(2)	N(B2)–Cu(B)–N(B3)		N(C1)–Cu(C)–O(C1T3)	87.4(6)
O(A2)–Cu(A)–N(A2)	82.6(2)	O(B1)–Cu(B)–N(B1)		O(C2)–Cu(C)–N(C2)	83.1(7)
O(A2)–Cu(A)–O(A3)	94.0(2)	O(B1)–Cu(B)–O(B2)		O(C2)–Cu(C)–O(C3T1)	96.9(6)
O(A2)–Cu(A)–N(A3)	88.9(2)	O(B1)–Cu(B)–N(B2)		O(C2)–Cu(C)–O(C1T3)	83.0(6)
N(A2)–Cu(A)–O(A3)	99.5(2)	N(B1)–Cu(B)–O(B2)		N(C2)–Cu(C)–O(C3T1)	90.0(5)
N(A2)–Cu(A)–N(A3)	169.9(2)	N(B1)–Cu(B)–N(B2)		N(C2)–Cu(C)–O(C1T3)	89.9(5)
O(A3)–Cu(A)–N(A3)	75.6(2)	O(B2)–Cu(B)–N(B2)		O(C3T1)–Cu(C)–O(C1T3)	179.8(1)

* The positions of the atoms Cu(A) and Cu(B) and the corresponding oxygen and nitrogen atoms were coupled during the refinement; therefore columns (*a*) and (*b*) share the same set of bond lengths and angles.

ligands are weakly bonded at a definite distance which is about 0.6 Å longer than the in-plane distance.[14] Inspection of the equatorial co-ordination planes of the copper atoms shows the planes of A and B to be mutually parallel and plane C to be almost perpendicular to planes A and B (91.0°). The average distance of the ligand donor atoms from the least-squares planes is 0.07, 0.07, and 0.01 Å for A, B, and C respectively. The copper atoms are 0.01, 0.01, and 0.03 Å removed from the respective planes. The O · · · H · · · O hydrogen bonds (see Figure 1 and Table 6), between a protonated and a deprotonated ligand in the trinuclear unit, are extremely short, *i.e.* 2.43(2) and 2.37(2) Å. The Cu(A)–Cu(C) and Cu(B)–Cu(C) distances are 4.91(1) and 4.88(1) Å respectively. The length of the hydrogen bonds and the copper–copper distances are similar to some related O · · · H · · · O hydrogen-bonded structures.[6-8] The distance of the oxygen atoms O(A2) and O(B1), which participate in the O · · · H · · · O hydrogen bonds, to plane C is 0.47 Å. In addition to the strong O · · · H · · · O hydrogen bonds, two much weaker O · · · H–N hydrogen bonds (3.02 and 3.07 Å) are present within each trinuclear unit, as also indicated in Figure 1. The two co-ordinated triflate groups have strong O · · ·H–O hydrogen bonds (both 2.78 Å) to ligand hydroxy groups of neighbouring trimers, as indicated in Figure 2. Because of the semi-co-ordination and the hydrogen bonding, no disorder is present in groups T1 and T3, contrary to the non-co-ordinated triflate groups T2 and T4, which only possess weak O · · · H–N hydrogen bonds (see Table 5). Thus, the triflate groups act as additional cross-links between the trimeric units. Relevant hydrogen-bond distances and angles are listed in Table 6.

Conformation of the Ligands.—The trinuclear unit contains eight bidentate chelating ligand rings. Four of these ligand rings contain ' long ' Cu–O distances. The bite distances of these rings are therefore larger than the bite distances of the four rings with ' short ' Cu–O distances. As a result, the N–Cu–O angles are smaller to compensate for the long Cu–O distance (about 76° compared with 84°). The Cu–O distances to the oxygen atoms involved in the strong O · · · H · · · O

Table 4. Intramolecular bond lengths (Å) and bond angles (°) of the triflate groups (T) of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$

	Group			
	T1	T2	T3	T4
(*a*) Bond lengths				
S–C	1.78(3)	1.98(3)	1.81(2)	1.75(2)
S–O(1)	1.43(1)	1.40(1)	1.44(1)	1.40(1)
S–O(2)	1.41(1)	1.31(2)	1.42(1)	1.45(1)
S–O(3)	1.45(1)	1.34(2)	1.43(1)	1.44(1)
C–F(1)	1.33(3)	1.27(5)	1.26(2)	1.17(3)
C–F(2)	1.32(2)	1.07(4)	1.26(2)	1.33(3)
C–F(3)	1.38(3)	1.44(5)	1.35(2)	1.28(3)
(*b*) Bond angles				
C–S–O(1)	104(1)	111(1)	101(1)	102(1)
C–S–O(2)	103(1)	102(2)	103.5(8)	104(1)
C–S–O(3)	102.4(8)	98(2)	104.9(9)	105(1)
O(1)–S–O(2)	116.8(6)	125(1)	114.4(5)	107(1)
O(1)–S–O(3)	113.3(6)	119(1)	114.2(6)	109(1)
O(2)–S–O(3)	114.6(6)	97(2)	116.2(6)	127(2)
S–C–F(1)	112(2)	102(2)	111(1)	121(1)
S–C–F(2)	113(1)	116(2)	113(2)	105(2)
S–C–F(3)	111(2)	96(3)	109(2)	114(2)
F(1)–C–F(2)	106(2)	130(5)	109(2)	111(2)
F(1)–C–F(3)	108(1)	98(3)	106(2)	103(3)
F(2)–C–F(3)	106(2)	109(4)	109(1)	101(2)

hydrogen bonding are short (in the equatorial plane of the copper octahedron). The most stable conformation of a bidentate 2-aminopropan-1-ol ring is known to have a O–C(1)–C(2)–N torsion angle of about 55°, as found for free and co-ordinated 1-aminopropan-2-ol,[4,13,15] free 2-aminopropan-1-ol,[16] as well as for co-ordinated propane-1,2-diol [17] and propane-1,2-diamine.[1,18] The OCCN torsion angle of ring B1 indicates that this ring is almost planar, which is known as a very unfavourable conformation.[19] Atom C(1B1) has a relatively short van der Waals distance of 3.40 Å to an oxygen atom of T1, whereas C(2B1) has a distance of 3.40 Å to an oxygen atom of T4. The distance of 3.40 Å is equal to

Table 5. Intramolecular bond lengths (Å), bond angles, and torsion angles (°) of the ligand rings of $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$

(*a*) Bond lengths

	Ring							
	A1	A2	A3	B1	B2	B3	C1	C2
C(1)-O	1.40(2)	1.40(2)	1.37(2)	1.43(2)	1.44(3)	1.45(3)	1.44(1)	1.32(3)
C(2)-N	1.42(2)	1.52(2)	1.46(2)	1.34(2)	1.46(2)	1.49(2)	1.47(3)	1.51(1)
C(1)-C(2)	1.44(2)	1.50(1)	1.47(1)	1.45(2)	1.48(2)	1.48(2)	1.49(1)	1.51(2)
C(2)-C(3)	1.52(2)	1.51(2)	1.50(2)	1.52(1)	1.52(2)	1.54(1)	1.50(2)	1.50(2)

(*b*) Bond angles

	Ring							
	A1	A2	A3	B1	B2	B3	C1	C2
Cu-O-C(1)	102(1)	111.7(6)	105.5(8)	115(1)	107(1)	101(1)	113(2)	110(1)
Cu-N-C(2)	114.1(7)	108.4(8)	111.5(9)	111.3(8)	113.9(7)	117(1)	104(1)	111(1)
O-C(1)-C(2)	111(2)	117(1)	112(1)	110(2)	113(2)	114(2)	104(2)	117(2)
N-C(2)-C(1)	115(2)	101(1)	110(1)	120(1)	113(2)	105(2)	109(2)	103(1)
N-C(2)-C(3)	105(1)	112(1)	112(2)	123(2)	113(2)	122(2)	117(2)	104(2)
C(1)-C(2)-C(3)	114(2)	113(1)	116(2)	117(2)	112(2)	110(2)	113(2)	102(2)

(*c*) Torsion angles

	Ring							
	A1	A2	A3	B1	B2	B3	C1	C2
Cu-O-C(1)-C(2)	−39(3)	19(2)	28(2)	5(2)	−15(3)	−39(3)	36(3)	42(2)
Cu-N-C(2)-C(1)	−37(3)	44(2)	53(2)	−8(3)	−48(2)	−46(2)	44(2)	26(2)
Cu-N-C(2)-C(3)	−164(2)	165(1)	−176(2)	167(2)	−177(1)	−173(2)	173(2)	132(2)
O-Cu-N-C(2)	9(2)	−32(1)	−27(1)	8(1)	28(1)	20(1)	−19(1)	−6(1)
N-Cu-O-C(1)	17(1)	8(1)	−1(1)	−7(1)	−7(2)	10(1)	−10(2)	−19(1)
O-C(1)-C(2)-C(3)	177(2)	−162(2)	177(2)	−173(2)	169(2)	−169(2)	176(2)	−153(2)
O-C(1)-C(2)-N	55(3)	−42(2)	−54(3)	3(4)	40(3)	57(3)	−52(3)	−45(2)

Table 6. Intra- and inter-molecular hydrogen-bond lengths (Å) and angles (°) in $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$

	Distance	Corresponding angle O(N) · · · H-O
O(A2) · · · O(C1)	2.43(2)	156(1)
O(B1) · · · O(C2)	2.37(2)	160(1)
O(B2) · · · O(2T3) [a]	2.775(7)	*b*
O(A3) · · · C(1T1) [c]	2.776(7)	*b*
N(B3) · · · O(3T2) [a]	3.01(2)	158(1)
N(C1) · · · O(B3)	3.02(2)	138(1)
N(C2) · · · O(A1)	3.07(2)	166(1)
N(A2) · · · O(2T4) [d]	3.11(2)	134(1)
N(A1) · · · O(2T2) [e]	3.14(2)	159(1)

[a] Symmetry: x, $1 + y$, z. [b] The hydrogen atoms were not found in the difference-Fourier map. [c] Symmetry: x, $-1 + y$, z. [d] Symmetry: $-1 + x$, $-1 + y$, $1 + z$. [e] Symmetry: $-1 + x$, y, $1 + z$.

the sum of the van der Waals radii of these atoms.[20] Thus, ring B1 is very tightly packed in the lattice. This, together with the oxygen atom O(B1) being a part of a strong O · · · H · · · O hydrogen bond (Table 6), probably forces this ring to adopt the present flattened conformation rather than a more favourable one. However, the pronounced thermal anisotropy of atom C(2B1) could indicate some disorder in the position of this atom, which is related to the disorder of T4, the group with the short van der Waals distances to ring B1. Ligand ring A2, of which the N and O atoms were coupled to the corresponding atoms of B1 during the refinement, is less sterically hindered and the conformation is closer to normal (torsion angle 42°).

Three ligand rings have conformations with an OCCN torsion angle of about 42° (A2, B2, and C2). The rings resemble a disordered envelope.[19] They are all involved in hydrogen bonding. The deviations from 55° (see above) are in agreement with deviations found for other hydrogen-bonded structures in related compounds.[4,13,17] Rings A1, A3, B3, and C1 have the 'ideal' OCCN torsion angle of about 55°. The conformation of rings A1, B3, and C1 is twist-chair, which is known to be most favourable in energy.[19] The same symmetry is found for the most stable conformations of the 1-aminopropan-2-ol structures.[4,13] Ring A3 is present in a pure envelope conformation. The absolute configuration of Cu(A) is determined as $\Delta(\delta\lambda\lambda)[= \Lambda(\lambda\delta\delta)]$, that of Cu(B) as $\Lambda(\delta\delta\delta)[= \Delta(\lambda\lambda\lambda)]$. The refinement of the two enantiomorphic forms gave identical results, thus we cannot distinguish the two configurations of the copper atoms. It must be noted that the geometrical isomerism of octahedrons $Cu(A)N_3O_3$ and $Cu(B)N_3O_3$ is meridional, *i.e.* the three nitrogen atoms are located in the copper equatorial plane. Usually, meridional isomers of compounds with tris(bidentate ligand)metal groups result in amorphous glasses, or orientational disorder of the complex ion in the crystal lattice.[1] This is the first example of a crystal structure of a meridional isomer. The occurrence of the meridional isomer in our compound most likely results from the Jahn–Teller deformation of the copper ions, forcing the axial positions to be occupied by two weakly bonding oxygens. Further, it is noted that the conformation of the ligands aroung Cu(C) is $\delta\delta$ $[= \lambda\lambda]$ and not the centrosymmetric conformation $\delta\lambda$. The origin for this may be that the acentric $\delta\delta$ (or $\lambda\lambda$) conformation has a more favourable hydrogen-bonding network or less steric hindrance in the crystal packing compared with the $\delta\lambda$ conformation.

Spectroscopic and Magnetic Behaviour of the Compounds.— The presence of protonated and deprotonated ligands suggests these compounds to be magnetically interesting.[8] For further

Table 7. Ligand-field spectra, e.s.r. maxima, and powder diffraction type of the copper(II) aminopropanol compounds

Compound	Ligand-field band maxima (cm^{-1})	Powder e.s.r. g value	X-Ray type *
(1) $[Cu_2(RS\text{-ap})_2(RS\text{-Hap})_2][CF_3SO_3]_2$	17 240	2.12	A
(2) $[Cu_2(S\text{-ap})_2(S\text{-Hap})_2][CF_3SO_3]_2$	17 160	2.12	A
(3) $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$	15 430	2 05	B
(4) $[Cu_2(S\text{-pa})(S\text{-Hpa})_5][CF_3SO_3]_3$	15 340	2.09	C

* Types A, B, and C refer to a typical powder diffraction pattern, and they are mutually different.

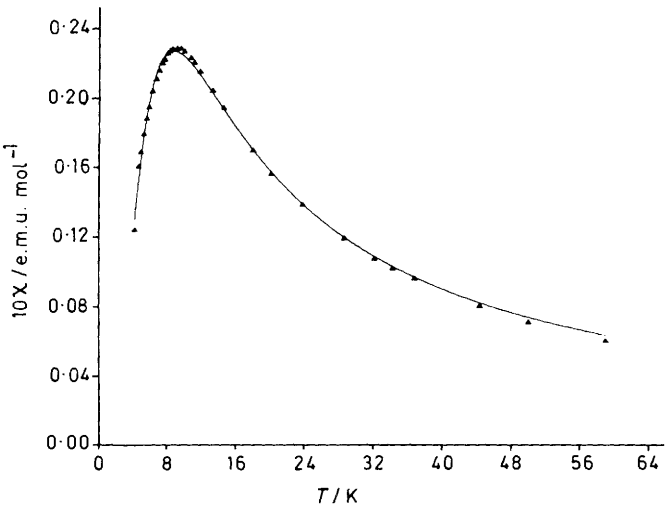

Figure 3. Observed (▲) and calculated (—) magnetic susceptibility data for $[Cu_2(RS\text{-ap})_2(RS\text{-Hap})_2][CF_3SO_3]_2$ (1), with $g = 2.05$ and $J = -5.0\ cm^{-1}$, using temperature-independent paramagnetism (t.i.p.) = 60×10^{-6} c.g.s./Cu atom and $\chi_{dia.} = 153 \times 10^{-6}$ c.g.s./Cu atom

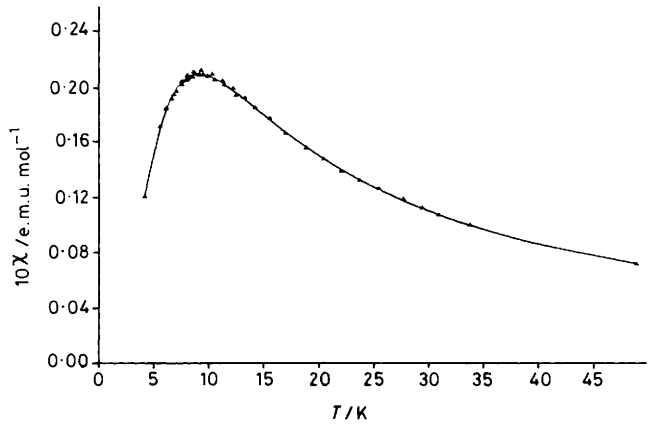

Figure 4. Observed (▲) and calculated (——) magnetic susceptibility data for $[Cu_2(S\text{-ap})_2(S\text{-Hap})_2][CF_3SO_3]_2$ (2), with $g = 2.01$ and $J = -5.3\ cm^{-1}$ using t.i.p. = 60×10^{-6} c.g.s./Cu atom and $\chi_{dia.} = 153 \times 10^{-6}$ c.g.s./Cu atom

characterisation it was, therefore, useful to measure the temperature-dependent magnetic susceptibility, in connection with e.s.r. and ligand-field spectra. The experimental and calculated magnetic susceptibility data are depicted in Figures 3—6. The magnetic susceptibility data are indicative of a binuclear structure in compounds (1), (2), and (4). Compound (3) is trinuclear, as seen from the crystal structure analysis. The magnetic measurements of compounds (1), (2), and (4) are fitted according to the Bleaney–Bowers equation for binuclear compounds [21] whereas (3) is fitted using the Heisenberg equation for linear trinuclear compounds.[22] The g values of the e.s.r. powder spectra, the absorption maxima of the diffuse reflectance spectra, and the X-ray powder diffraction types are listed in Table 7. All e.s.r. spectra at room temperature show a single isotropic line, with some asymmetry for compounds (3) and (4). So-called ' half-field ' e.s.r. lines are only observed for (3) and (4). The ligand-field maxima of (1) and (2) are indicative of a square-planar co-ordination with at best weak axial ligands. The co-ordination in compound (3) is tetragonally distorted, as is seen from the crystal structure. The absorption band of the ligand-field spectrum of compound (3) is broad, most likely resulting from the presence of two different copper geometries. The absorption maximum in the ligand-field spectrum of (3) is similar to (4). The copper ion in compound (4) will have a Jahn–Teller distorted tris-chelate co-ordination. The square-planar co-ordination and the binuclear structure proposed for compounds (1) and (2) suggest these to be very similar to $[Cu_2(NH_2CH_2CH_2OH)_2(NH_2CH_2CH_2O)_2][NO_3]_2$.[8] This compound has a *cis* arrangement of the ligands and an O · · · H · · · O hydrogen bond between a protonated and a deprotonated ligand. An analogous structure for compounds (1) and (2) seems likely, although they have a much smaller value of the antiferromagnetic exchange ($2J = -10.0$ and $-10.6\ cm^{-1}$) than has $[Cu_2(NH_2CH_2CH_2OH)_2(NH_2CH_2CH_2O)_2][NO_3]_2$ ($2J = -56\ cm^{-1}$). In similar hydrogen-bonded compounds [6-8] no correlation was found between the strength of the exchange and the copper–copper distances or the separation of the co-ordination planes, thus the decrease in exchange constants has to be attributed to the changes in the structure caused by the substitution of the methyl groups in our compounds. The methyl group normally occupies equatorial positions in compounds with bidentate co-ordinating ligands. The equatorial substitution of the methyl group usually does not alter the conformation of the five-membered ring.[18,23] However, the very short hydrogen bonds in the present compounds (*ca.* 2.40 Å) would induce significant steric interaction between the methyl groups as indicated in Figure 7. Assuming the O · · · O distance to be 2.4 Å, the methyl · · · methyl contacts would be 2.9 Å compared to the sum of the van der Waals radii (4.0 Å). The methyl groups will have to move into the axial direction, but influence, in this way, the torsion angles of the ligand ring, resulting in deviations from the co-ordination plane. The two co-ordination planes of the binuclear compound now cannot be parallel as in the corresponding aminoethanol compound. Such a different co-ordination plane will influence the relative orientation of the magnetic orbitals of Cu^{II} and as a result the magnetic exchange is expected to decrease.[24] The positions of the methyl groups in compounds (1) and (2) must be

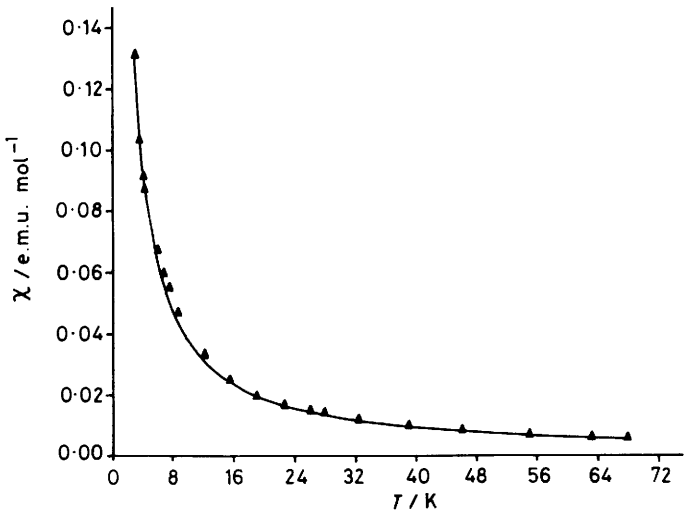

Figure 5. Observed (▲) and calculated (——) magnetic susceptibility data for $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$ (3), with $g = 2.0$ and $J = +0.06$ cm^{-1}, using t.i.p. $= 60 \times 10^{-6}$ c.g.s./Cu atom and $\chi_{dia.} = 222 \times 10^{-6}$ c.g.s/Cu atom

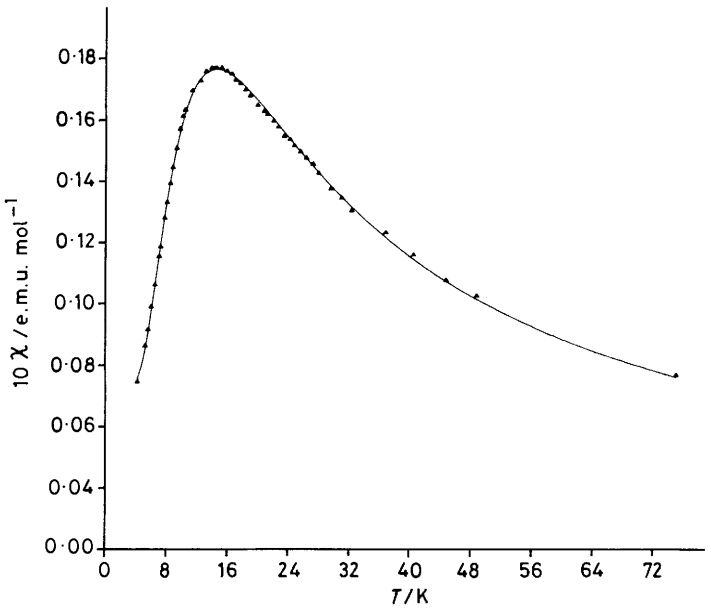

Figure 6. Observed (▲) and calculated (——) magnetic susceptibility data for $[Cu_2(S\text{-pa})(S\text{-Hpa})_5][CF_3SO_3]_3$ (4), with $g = 2.21$ and $J = -8.5$ cm^{-1}; using t.i.p. $= 60 \times 10^{-6}$ c.g.s./Cu atom and $\chi_{dia.} = 248 \times 10^{-6}$ c.g.s./Cu atom

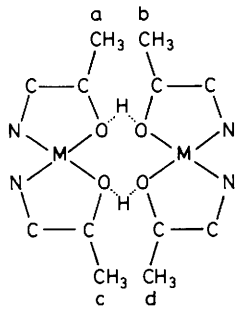

Figure 7. Possible schematic structure for $[Cu_2(RS\text{-ap})_2(RS\text{-Hap})_2][CF_3SO_3]_2$ (1) and $[Cu_2(S\text{-ap})_2(S\text{-Hap})_2][CF_3SO_3]_2$ (2). The position of the methyl groups a, b, c, and d with respect to the co-ordination plane is supposed to +, −, +, − for compound (1) and +, −, −, + for compound (2)

similar (see Figure 7) as the exchange constants are also similar ($J = -5.0$ and -5.3 cm^{-1} respectively).

The trinuclear compound (3) has a very small ferromagnetic exchange ($J = +0.06$ cm^{-1}). Inspection of the structure (see above) shows that the equatorial co-ordination planes containing the copper ions are almost perpendicular, resulting in a less favourable orientation of the magnetic orbitals of Cu and a very small exchange energy.[24,25] The magnetic susceptibility data show compound (4) to be binuclear ($J = -8.5$ cm^{-1}). Compound (4) has only one deprotonated ligand and, as a result, only one O · · · H · · · O hydrogen bond. The methyl group is now on the amine side of the ligand ring and cannot cause steric hindrance with respect to the O · · · H · · · O hydrogen bond. The exchange in compound (4) is therefore greater compared with the exchange in compounds (1) and (2), though (1) and (2) have two O · · · H · · · O hydrogen bonds. This is indicative of the more favourable

orientation for exchange of the magnetic orbitals of Cu in compound (4) compared with (1) and (2), because in (4) the methyl groups do not cause steric hindrance.

The square-planar co-ordination of the 1-aminopropan-2-ol compounds compared with the (distorted) octahedral 2-aminopropan-1-ol compounds is in agreement with the apparent resistance of the 1-aminopropan-2-ol compounds to form tris-chelate species. Compounds with one bidentate and two unidentate ligands have been obtained [2,3] with 1-aminopropan-2-ol, where the analogous 2-aminopropanol compounds form tris-chelate species.[26]

Conclusions

The results of these investigations have shown that interesting compounds containing several isomers of aminopropanol can be obtained with Cu^{II} triflate. Only in the case of *R,S*-1-aminopropan-2-ol and *S*(+)-1-aminopropan-2-ol were mutually isomorphous compounds obtained. For the isomers *R,S*-2-aminopropan-1-ol and *S*(+)-2-aminopropan-1-ol, different compositions were obtained. The structure of these compounds most likely contain pairs (or in one case trimers) of Cu polyhedra held together *via* strong O · · · H · · · O hydrogen bonds. Magnetic exchange through such an O · · · H · · · O bond can be significant. The strength of the magnetic exchange in these compounds has been related to the magnetic orbitals of copper.

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