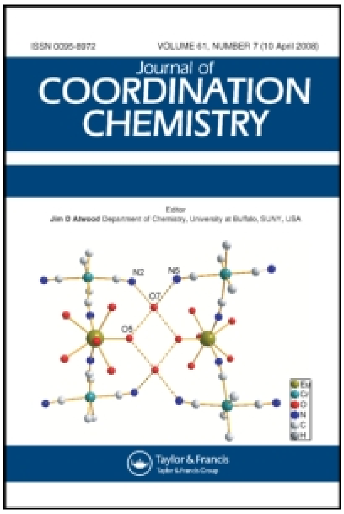

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CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDIES OF TRIS(2-AMINOETHYL)AMINE COPPER(II) COMPLEXES WITH 4-AMINOPYRIDINE

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A tris (2-aminoethyl)amine (tren) copper(II) complex with a coordinated 4-aminopyridine (4-APy) ligand was synthesized and characterized. Single crystal X-ray diffraction study reveals that there are two slightly different cations and four perchlorate anions present in an asymmetric unit. The coordination geometry of both Cu(II) centers are nearly identical and close to trigonal bipyramidal with three terminal amine nitrogen atoms forming the equatorial plane, while the tertiary nitrogen atom and the pyridine nitrogen atom from 4-APy occupy the apical positions. Of the two different cations, one shows an outer-sphere, bridged copper dimer with the nitrogen atom N(6) from 4-APy and the terminal amino nitrogen atom N(3) linked together by hydrogen bonds N(6)-H...N(3a) and N(3)..H-N(6a) (1 − x −y, 1 − z). Magnetic and spectroscopic data support the outer-sphere, bridged dimeric structure.

The title complex, Cu(tren)(4-Apy)}$(ClO_4)_2$, crystallizes in the monoclinic space group $P2_1/n$ with cell parameters a = 8.150(1), b = 33.854(2), c = 14.810(1) Å, β = 90.00(1)°, V = 3967(2) Å^3 and Z = 8. The structure was refined by full-matrix least-squares to R = 0.065 and Rw = 0.088 with 3880 reflections having $F > 6\sigma(F)$.

Keywords: Copper(II); Outer-sphere; bridged dimer; Tripodal complex

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INTRODUCTION

Investigation of the coordination chemistry of copper(II) complexes continues to be stimulated by interest in developing bioinorganic model systems for copper proteins and in understanding the factors which give rise to the seemingly infinite variety of distortions from regular stereochemistry observed in Cu(II) complexes.[1,2] Tripodal copper systems derived from tris(2-aminoethyl)amine are most interesting because of their implication in a wide variety of biochemical activities[3-5] and their magnetic properties as well as the variety of molecular and electronic structure.[6-10] It has been postulated that when the fifth coordinated donor is Cl^-, NCO^-, NCS^- or CN^-, the trencopper complexes always form an outer-sphere, bridged dimeric structure.[6-8] When the fifth coordination position is imidazolate or benzidines, the di-copper complexes formed are normal bridged dimerics.[9,10] We have worked to establish the factors controlling formation of the dicopper-tren systems.[11-13] Here we report the design and synthesis of the tris(2-aminoethyl)amine copper complex derived from 4-aminopyridine, its crystal structure, magnetic and spectroscopic properties.

EXPERIMENTAL

Materials and Reagents

All chemicals were reagent grade and used without further purification. The $[Cu(tren)](ClO_4)_2$ complex was synthesized according to the procedure described earlier,[11] using $Cu(OAc)_2 \cdot H_2O$ and $NaClO_4$ in place of $CuCl_2 \cdot 2H_2O$ and KSCN, respectively.

Preparation of the Title Complex

To a solution of $[Cu(tren)](ClO_4)_2$ (1.00 mmol, 0.408 g) in ethanol-acetonitrile (5:1) (30 mL) was added 4-aminopyridine (4-APy) (1.06 mmol, 0.100 g). The mixture was refluxed for 3 hours. After cooling to room temperature, the precipitate was filtered by suction and dried *in vacuo* over silica. Yield, 85%. IR data (KBr discs, cm^{-1}) 3485, 3435, 3355, 3290 (N-H, m), 1635 (C=N, s), 1091 (Cl-O, s), 929 (Cl-O, m), 624(Cl-O, s), 530, 460, 270 (Cu-N, s). Electronic spectra (CH_3CN) λmax (nm) (ϵ): 680 (203), 830 (230). Anal. Calcd. for $C_{11}H_{24}Cl_2CuN_6O_8$(%): C, 26.28; H, 4.81; N, 16.72. Found: C, 26.67; H, 5.10; N, 17.11. Crystals suitable for X-ray analysis were grown by slow evaporation of an ethanol-acetonitrile (5:1) solution in air.

Physical Measurements

Elemental analyses were performed using a Perkin-Elmer 240C analytical instrument. An IR spectrum was recorded on a Nicolet FT-IR-170SX instrument (KBr, discs) in the 4000-400 cm^{-1} region. The far-IR spectrum (500-100 cm^{-1}) was recorded as Nujol mulls between polyethylene sheets. A solid electronic reflectance spectrum was recorded on a Shimadzu 240 spectrophotometer. The solution electronic spectrum was recorded on a Shimadzu 3100 spectrophotometer in absolute DMF. The ESR spectrum was measured using a Bruker 200D-SRC spectrometer at 110 K in DMF. The magnetic measurement on a powder sample was carried out with a CAHN 2000 Faraday-type magnetometer in the temperature range 75-300 K. Diamagnetic correction for the constituent atoms was made using Pascal' constants.

Crystallography

The intensity data were collected by the $\omega/2\theta$ scan mode on a Rigaku AFC7R diffractometer using MoKα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max}$ = 55.2°) and corrected for Lorenz polarization effects. There were 3880 observed reflections with $F > 6\sigma(F)$ from 9100 independent reflections (*Rint* = 4%) used for further computation. The title complex crystallizes in the monoclinic space group $P2_1/n$ with cell parameters a = 8.150(1), b = 33.854(2), c = 14.810(1) Å, β = 90.00(1)°, V = 3967(2) $Å^3$ Z = 4, *Mw* = 1005.6, *D calcd* = 1.684 g/cm^{-3}, *F*(000) = 2072 and μ = 1.423 mm^{-1}.

All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were placed in their calculated positions with C-H = 0.96Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculation. All computations were carried out on a PC-486 using the SHELXTL-PLUS program package.[14,15] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] Final conventional $R(F)$ = 0.065 and wR = 0.088 for $F > 6\sigma(F)$ with the weighting scheme, $w = 1/[\sigma^2(F^2) + 0.0011F^2)]$. The maximum and minimum residual electron densities of the difference Fourier map are 0.91 and −0.80 $eÅ^{-3}$, respectively.

The atom coordinates and important bond lengths and angles are shown in Table I and Table II, respectively.

TABLE I Atomic coordinates and equivalent isotropic displacement parameters.

atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Cu(1)	0.8387(1)	0.0522(1)	0.2603(1)	3.9(1)
N(1)	1.0221(2)	0.0663(1)	0.3513(2)	4.0(1)
N(2)	0.9068(2)	0.1062(1)	0.1991(2)	5.5(1)
N(3)	0.9960(2)	0.0032(1)	0.2336(2)	6.3(1)
N(4)	0.6754(2)	0.0537(1)	0.3700(2)	5.5(1)
N(5)	0.6528(2)	0.0368(1)	0.1780(2)	4.4(1)
N(6)	0.2186(2)	0.0065(1)	0.0347(2)	5.9(1)
C(1)	1.0627(2)	0.1085(2)	0.3380(2)	5.4(1)
C(2)	1.0716(2)	0.1182(2)	0.2390(2)	5.5(1)
C(3)	1.1735(2)	0.0405(2)	0.3339(2)	5.6(1)
C(4)	1.1154(2)	0.0004(2)	0.3077(2)	5.6(1)
C(5)	0.9474(2)	0.0584(2)	0.4433(2)	5.2(1)
C(6)	0.7700(2)	0.0707(2)	0.4491(2)	5.6(1)
C(7)	0.5882(2)	0.0005(2)	0.1765(2)	5.2(1)
C(8)	0.4492(2)	−0.0118(2)	0.1329(2)	4.7(1)
C(9)	0.3622(2)	0.0158(2)	0.0817(2)	4.8(1)
C(10)	0.4259(2)	0.0545(2)	0.0806(2)	5.1(1)
C(11)	0.5656(2)	0.0627(2)	0.1279(2)	5.4(1)
Cu(2)	0.0314(1)	−0.2612(1)	0.5717(1)	4.3(1)
N(7)	0.0067(2)	−0.3158(1)	0.6315(2)	5.2(1)
N(8)	−0.1846(2)	−0.2476(2)	0.6468(2)	9.6(1)
N(9)	0.0318(2)	−0.2922(1)	0.4539(2)	6.1(1)
N(10)	0.2474(2)	−0.2583(2)	0.6524(2)	9.1(1)
N(11)	0.0584(2)	−0.2101(1)	0.5045(2)	5.3(1)
N(12)	0.1182(2)	−0.1107(2)	0.3440(2)	8.7(1)
C(12)	−0.1427(2)	−0.3153(2)	0.6877(2)	11.4(1)
C(13)	−0.2519(2)	−0.2827(2)	0.6862(2)	8.7(1)
C(14)	−0.0204(2)	−0.3427(2)	0.5589(2)	13.3(1)
C(15)	0.0316(2)	−0.3348(2)	0.4738(2)	8.2(1)
C(16)	0.1542(2)	−0.3236(2)	0.6818(2)	11.1(1)
C(17)	0.2661(2)	−0.2937(2)	0.7037(2)	7.4(1)
C(18)	−0.0760(2)	−0.1909(2)	0.4701(2)	6.4(1)
C(19)	−0.0627(2)	−0.1588(2)	0.4171(2)	7.6(1)
C(20)	0.0959(2)	−0.1436(2)	0.3935(2)	6.7(1)
C(21)	0.2358(2)	−0.1628(2)	0.4300(2)	6.3(1)
C(22)	0.2101(2)	−0.1962(2)	0.4813(2)	5.5(1)
Cl(1)	0.9840(2)	0.0927(1)	0.9200(1)	6.4(1)
Cl(2)	0.6145(2)	−0.0651(1)	0.3853(1)	6.4(1)
Cl(3)	−0.5139(2)	−0.1628(1)	0.6901(1)	5.4(1)
Cl(4)	0.9624(2)	0.2198(1)	0.0880(1)	6.4(1)
O(11)	1.1158(2)	0.0681(1)	0.8920(2)	13.5(1)
O(12)	0.8504(2)	0.0835(2)	0.8511(2)	8.7(1)
O(13)	0.9103(2)	0.0794(2)	1.0021(2)	9.0(1)
O(14)	1.0122(2)	0.1327(1)	0.9183(2)	9.2(1)
O(12′)	0.8294(2)	0.0759(2)	0.9354(2)	15.0(1)
O(13′)	1.0491(2)	0.1069(2)	1.0100(2)	12.5(1)

Table I *Continued*

atom	*x/a*	*y/b*	*z/c*	*B(eq)*
O(14′)	0.9756(2)	0.1277(1)	0.8674(2)	8.2(1)
O(31)	−0.6934(2)	−0.1664(1)	0.6837(2)	9.2(1)
O(32)	−0.4748(2)	−0.1239(1)	0.7175(2)	12.3(1)
O(33)	−0.4396(2)	−0.1709(2)	0.6048(2)	10.9(1)
O(34)	−0.4500(2)	−0.1908(1)	0.7524(2)	13.6(1)
O(21)	0.7753(2)	−0.0509(2)	0.3590(2)	7.8(1)
O(22)	0.5004(2)	−0.0330(1)	0.3937(2)	7.7(1)
O(24)	0.5498(2)	−0.0911(1)	0.3166(2)	11.6(1)
O(23)	0.6254(2)	−0.0873(1)	0.4658(2)	12.3(1)
O(21′)	0.7605(2)	−0.0691(2)	0.3315(2)	8.0(1)
O(22′)	0.5915(2)	−0.0246(1)	0.4103(2)	13.0(1)
O(24′)	0.4703(2)	−0.0771(2)	0.3347(2)	10.9(1)
O(42)	0.9159(2)	0.2577(1)	0.0560(2)	12.4(1)
O(43)	0.8235(2)	0.2004(2)	0.1270(2)	10.8(1)
O(44)	1.0249(2)	0.1969(2)	0.0129(2)	13.6(1)
O(41)	1.0976(2)	0.2232(1)	0.1495(2)	16.8(1)
O(42′)	0.8404(2)	0.2498(1)	0.1112(2)	13.8(1)
O(43′)	0.8795(2)	0.1827(1)	0.0934(2)	9.3(1)
O(44′)	1.0154(2)	0.2269(2)	−0.0021(2)	10.1(1)

TABLE II Selected bond distances (Å) and angles (°) for title complex

atom-atom	*distance*	*atom-atom*	*distance*
Cu(1)-N(1)	2.037(2)	Cu(2)-N(7)	2.057(4)
Cu(1)-N(2)	2.109(4)	Cu(2)-N(8)	2.091(2)
Cu(1)-N(3)	2.111(4)	Cu(2)-N(9)	2.037(3)
Cu(1)-N(4)	2.076(2)	Cu(2)-N(10)	2.087(2)
Cu(1)-N(5)	1.980(2)	Cu(2)-N(11)	2.008(4)
atom-atom-atom	*angle*	*atom-atom-atom*	*angles*
N(1)-Cu(1)-N(2)	84.2(1)	N(7)-Cu(2)-N(8)	83.8(2)
N(1)-Cu(1)-N(3)	83.5(1)	N(7)-Cu(2)-N(9)	84.6(1)
N(1)-Cu(1)-N(4)	85.4(1)	N(7)-Cu(2)-N(10)	82.8(1)
N(1)-Cu(1)-N(5)	176.4(1)	N(7)-Cu(2)-N(11)	175.6(1)
N(2)-Cu(1)-N(3)	116.7(1)	N(8)-Cu(2)-N(9)	124.8(1)
N(2)-Cu(1)-N(4)	118.4(2)	N(8)-Cu(2)-N(10)	110.8(1)
N(2)-Cu(1)-N(5)	98.8(1)	N(8)-Cu(2)-N(11)	99.2(2)
N(3)-Cu(1)-N(4)	122.2(2)	N(9)-Cu(2)-N(10)	120.9(1)
N(3)-Cu(1)-N(5)	96.7(1)	N(9)-Cu(2)-N(11)	91.0(2)
N(4)-Cu(1)-N(5)	91.5(1)	N(10)-Cu(2)-N(11)	99.0(1)

DISCUSSION

IR Spectrum

The infrared spectrum shows N-H stretching bands at 3485 cm^{-1} and 3435 cm^{-1} for the amino group in 4-APy, 3355 cm^{-1}, 3290 cm^{-1} for the amino group from tren and 1639 cm^{-1} for the $\nu_{C=N}$ of the pyridine group. The bands due to the ionic perchlorate groups are around 1092 cm^{-1} (strong), 930 cm^{-1} (weak) and 622 cm^{-1} (strong), which can be assigned as the IR-allowed ν_3 mode, IR-forbidden ν_1 mode and the nondegenerate ClO_3 symmetrical bending frequency, ν_3, respectively.[17] It is reasonable to assign the two bands around 418 cm^{-1} and 460 cm^{-1} as the $\nu_{Cu\text{-}N}$ (NH_2 of tren) stretching mode, corresponding to the in-plane and out-of-plane Cu-N stretching modes.[18] The Cu-N(3°) stretching mode is at 536 cm^{-1}. The band at 354 cm^{-1} can be assigned to the $\nu_{Cu\text{-}N}$ (pyridine) stretching mode.

Electronic Spectra

A solid spectrum shows a maximum at 12200 cm^{-1} and a high-energy shoulder at 14500 cm^{-1}. These agree with those previously reported for trigonal bipyramidal $[Cu(tren)L]^{2+}$ (where L is a monodentate ligand)[19-21] The intense band at higher energy can be assigned to the d_{xy}, $d_{x2-y2} \rightarrow d_{z2}$ transition which is allowed in C_3 and D_{3h}, symmetry. The less intense shoulder at lower energy can be assigned to the d_{xy}, $d_{yz} \rightarrow d_{z2}$ transition which, although allowed in C_3 symmetry, is forbidden in D_{3h}, but can occur weakly by a vibronic mechanism.

The electronic spectrum of the complex in solution is comparable with that of the solid state, which suggests that no dissociation of the ligand occurs in solution. The spectrum features a broad band at 12400 cm^{-1} ($\epsilon = 203$ dm^3 mol^{-1} cm^{-1}) and an apparent flanking higher energy shoulder at 14700 cm^{-1} ($\epsilon = 230$ dm^3 mol^{-1} cm^{-1}). The assignments are the same as above. The difference in relative intensities of the two observed bands is larger in solution than in the solid state. This may indicate that the solution electronic spectrum of the complex should be assigned to a higher symmetry than the solid state.

Electronic Spin Resonance Spectra and Magnetic Data

The 110K ESR spectrum of the complex in absolute DMF is shown in Figure 1. The spectrum shows an intense signal with clear resolution of the four copper hyperfine lines, $g_{\perp} = 2.198$, $A_{\perp} = 11.94 \times 10^{-3}$ cm^{-1} and $g_{\|} = 2.000$, $A = 5.97 \times 10^{-3}$ cm^{-1}. The fact that $g_{\|} \approx 2.00$ is in agreement with the trigonal

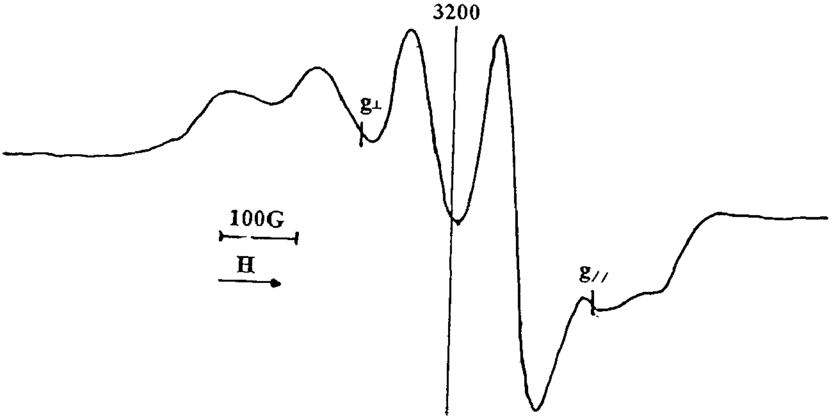

FIGURE 1 110 K ESR in the absolute DMF for the complex.

bipyramidal stereochemistry established for $[Cu(tren)L]^{2+}$ systems with a d_{z2} ground state.

The room temperature magnetic moment of the complex (2.14B M) is a little larger than that of a trigonal-bipyramidal $3d^9$ ion,[22] which should be associated with some orbital contribution and dependent on temperature.[23] Variable-temperature magnetic susceptibility measurements are more helpful in this respect. The magnetic behavior of the complex was studied over the temperature range 300-75K. Correction for the diamagnetism of the complex were estimated from Pascal' constants to be 346×10^{-6} cm^3 mol^{-1}. The magnetic susceptibility data for the complex may be interpreted in terms of the Currie-Weiss law:

$$\chi_M^{coor} = Ng^2\beta^2/[4K(T - \theta)] + N_\alpha$$

where χ_M^{coor} is the molar susceptibility corrected for diamagnetism, N_α is the corrected value of temperature-independent paramagnetism and the remaining symbols have their usual meanings. The plot (Figure 2) of the reciprocal of the molar susceptibility corrected for both diamagnetism and temperature-independent paramagnetic *vs.* temperature afforded the value of $\theta = -18.0$ K and $g = 2.232$. The g value is a little larger than that measured by ESR. From the θ value, it might suggest that there exists slight copper(II)-copper(II) magnetic interactions, indicating some dimeric structure. However, the small θ value also indicates that no "normal" bridged dicopper(II) system is likely to be present.

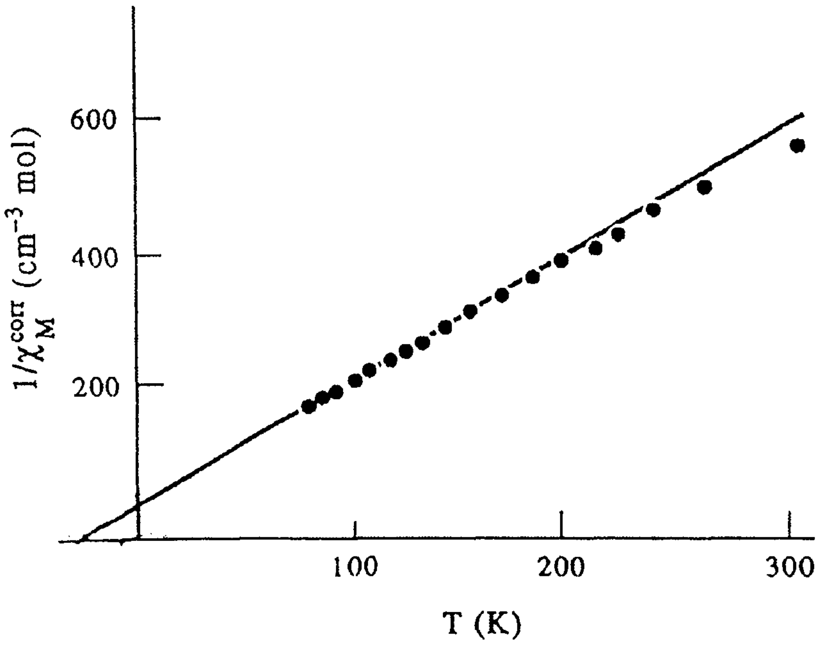

FIGURE 2 Plot of inverse magnetic susceptibility *vs.* temperature for the complex.

Descriptions of the Structure

Figure 3 shows an ORTEP plot of the title complex with the atom-numbering scheme. There are two slightly different five-coordinate Cu(II) cations. Both are trigonal bipyramidal with three primary amine nitrogen atoms from tren forming the equatorial plane, the tertiary amine nitrogen atom and the nitrogen atom from pyridine occupying the apical positions. The value of the geometric parameter τ is 0.84.[24] In both cations the angles around the tripodal nitrogens, N(3°)-Cu-N (amine) are acute (average at 84° in Table II). Consequently, the Cu(II) centers lie 0.18 Å below the plane defined by the three primary amine nitrogen atoms toward the pyridyl nitrogen atom. These values are comparable to those found in the related complexes Cu(tren)(Py)$(ClO_4)_2$[12] and Cu(tren)(DMP)$(ClO_4)_2$.[11] The axial Cu-N (pyridinyl) [1.980(2) and 2.008(4) Å] bonds are the shortest the Cu-N bond distances, which can be attributed to a single electron in the d_{z2} orbital.

The presence of two unsymmetric cations in an asymmetric unit is due to hydrogen bonding and crystal packing effects (Figure 4). Detailed intermolecular hydrogen bond analysis shows that a pair of the cations crystallize in an outer-sphere dimer structure, in which the amine nitrogen of 4-Apy and the amino nitrogen N(3) are linked together by the N(3)...N(6a) and N(6)...N(3a) (1 − x,

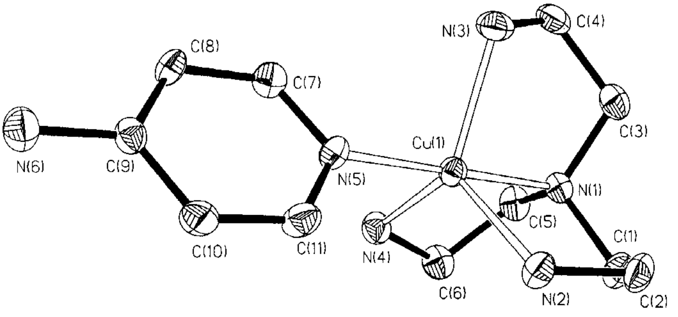

FIGURE 3 An ORTEP drawing of the title complex $[Cu(tren)(4\text{-}APy)]^{2+}$ with atomicnumber scheme. Thermal ellipsoids are drawn at the 30% probability level.

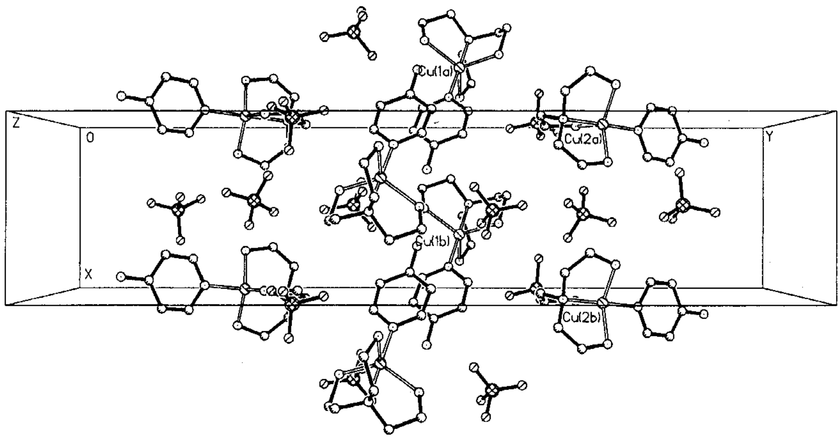

FIGURE 4 Packing diagram viewed down the *a* axis of $[(tren)Cu(4\text{-}Apy)](ClO_4)_2$.

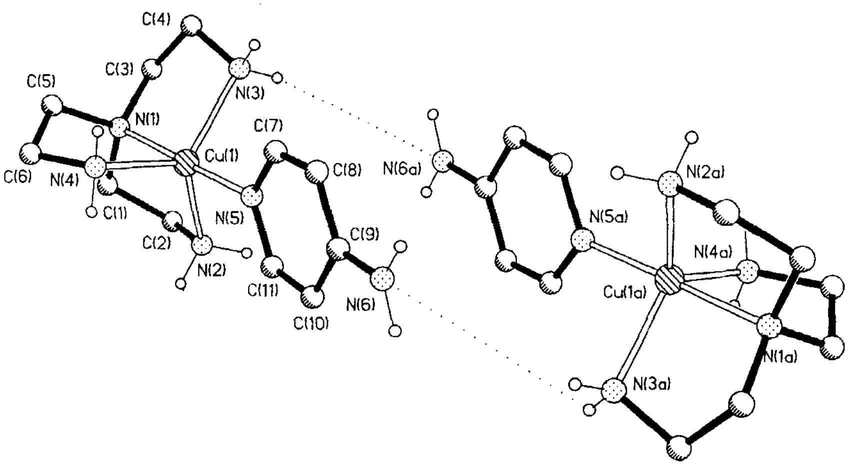

FIGURE 5 Hydrogen-bonding scheme showing an outer-sphere bridged dimeric structure. symmetry code: a, $-x$, $-y$, $1 - z$.

$-y$, $1 - z$). The two metal-containing moieties are bridged in a more remote fashion by two of the perchlorate counter ions through hydrogen bonds (Figure 5). Because the perchlorate oxygens are disordered, it is difficult to ascertain accurate contact distances. However, the best values obtained are indicated in Figure 5.

It is interesting to compare the outer-sphere, bridged dicopper(II)-tren complexes and normal, bridged dicopper(II)-tren complexes. The ability of the ligand to form hydrogen-bonds is the main factor which controls formation of the outer-sphere bridged dicopper complexes. Since the NH_2 groups from tren have the ability to form donor hydrogen-bonds, if the other ligand has the potential to accept hydrogen bonds a possible outer-sphere bridging dicopper system may be formed. If, on the other hand, the ligand does not have the ability to accept a hydrogen bond, only a normal bridged dicopper-tren system or monocopper-tren will be formed. Secondly, the coordinating ability of the bridged ligand also plays a factor in control of the bridge type in the dicopper-tren system. So, it can be expected that, when the bridged ligand is Cl^-, SCN^- or CN^-,[6,7,8] outer-sphere bridged dicopper complexes exist, but when the bridged ligand is benzidine, or imidazolate anione,[9,10] normal bridging dicopper(II)-tren complexes form. This expectation is supported by the crystal structure of the related complexes. The title complex should form an outer-sphere, bridged dicopper-tren system, since the NH_2 group of the 4-Apy does not participate in the coordination of the metal complex and has the potential to form donor or accept hydrogen-bonds. This expectation is supported by the structure. The two hydrogen atoms attached to the nitrogen atom in 4-Apy may weaken the accepting hydrogen bond making a weak bridge. In fact, only part of the title complex forms in the outer-sphere dicopper system.

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