from the SHELXTL version 4 package (Nicolet Instruments, Madison, WI). The lattice was found to be monoclinic P by standard procedures using the $P2_1$ software. Quick scan of the reflections for space group determination gave the conditions $0k0$ ($k = 2n$) and $h0l$ ($l = 2n$), which are consistent with the space group $P2_1/c$ (No. 14). The positions of the platinum and rhodium atoms were determined from a Patterson map. The remaining non-hydrogen atoms were found on successive Fourier maps. Final refinement included all hydrogen atoms of the phenyl rings in calculated positions and fixed by a riding model in which the C–H distance is fixed at 0.96 Å and the U value for hydrogen is tied to 1.2 times the U value for the carbon atom to which it is bonded. Final refinement, which used anisotropic thermal motion for all atoms except hydrogen, resulted in a conventional R value of 0.0382. A final difference map was devoid of chemically significant features.

Physical Measurements. The ^{31}P NMR spectra were recorded at 81 MHz on a Nicolet NT-200 Fourier transform spectrometer. The ^{31}P NMR spectra were proton decoupled and referenced to external 85% phosphoric acid. The high-frequency-positive convention recommended by IUPAC was used to report chemical shifts. Infrared spectra were recorded from mineral oil mulls or dichloromethane solutions on a Perkin-Elmer 180 spectrometer.

Acknowledgment. We thank the National Science Foundation (Grant CHE82 17954) for support. F.E.W. was a University of California Regents Fellows.

Registry No. Pt(dapm)Cl_2, 88867-61-2; Pt(dapm)Br_2, 96211-61-9; Pt(dapm)I_2, 96211-62-0; *cis*-Pt$(dapm)_2Cl_2$, 89144-43-4; *cis*-Pt$(dapm)_2Br_2$, 96211-63-1; *cis*-Pt$(dapm)_2I_2$, 96227-23-5; *trans*-Pt$(dapm)_2I_2$, 96290-72-1; [Pt$(dapm)_2$Br]Br, 96227-24-6; [Pt$(dapm)_2$I]I, 96227-25-7; [*cis*-Pt$(dapm)_2$][PF_6]$_2$, 96211-65-3; [*trans*-Pt$(dapm)_2$][PF_6]$_2$, 96290-34-5; $Pt_2(\mu$-dapm$)_2Cl_2$ (HH), 89153-36-6; $Pt_2(\mu$-dapm$)_2Cl_2$ (HT), 89153-37-7; $Pt_2(\mu$-dapm$)_2(\mu$-CO)Cl_2 (HH), 96211-66-4; $Pt_2(\mu$-dapm$)_2(\mu$-CO)Cl_2 (HT), 96211-67-5; *trans*-Rh$(dapm)_2$(CO)Cl, 96211-68-6; $Rh_2(\mu$-dapm$)_2(CO)_2Cl_2$ (HH), 89144-46-7; $Rh_2(\mu$-dapm$)_2(CO)_2Cl_2$ (HT), 83153-27-9; *trans*-Rh(CO)Cl$(\mu$-dapm$)_2$-*cis*-PtCl_2, 88867-59-8; (1,5-COD)PtCl_2, 12080-32-9; (1,5-COD)PtBr_2, 12145-48-1; (1,5-COD)PtI_2, 12266-72-7; $Rh_2(CO)_4(\mu$-Cl$)_2$, 14523-22-9; $Pt_2(dba)_2$, 35915-79-8.

Supplementary Material Available: Tables of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom positions (42 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Victoria University of Wellington, Wellington, New Zealand,
and Simon Fraser University, Burnaby, B.C., Canada V5A 1S6

Structural and Magnetic Studies of Bis(μ-olato) Dinuclear Compounds of Copper(II) with Bicyclic Amine Alcohols

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Reaction of partially hydrolyzed quaternary hydroxyalkyl "hexaminium" salts with copper(II) results in the formation of compounds of bicyclic tetraamine alcohols coordinated as tridentate diamine olato ligands. X-ray structural studies for four compounds with the ligands (1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)ethanolato (eta), the 3-propanolato analogue (pta), and the 7-(methoxymethyl) derivative of the first compound (etam) are reported: $[\{Cu(eta)(ClO_4)\}_2]\cdot 2CH_3OH$, triclinic, $P\bar{1}$, $a = 8.970$ (4) Å, $b = 9.974$ (3) Å, $c = 10.123$ (5) Å, $\alpha = 101.09$ (3)°, $\beta = 128.57$ (3)°, $\gamma = 93.93$ (3)°, $Z = 2$ for $C_8H_{19}ClCuN_4O_6$, $R = 0.053$ for 2153 reflections; $[\{Cu(eta)(dmso)\}_2](ClO_4)_2$, monoclinic, $P2_1/c$, $a = 9.175$ (2) Å, $b = 13.511$ (3) Å, $c = 12.934$ (2) Å, $\beta = 99.86$ (1)°, $Z = 4$ for $C_9H_{21}ClCuN_4O_6S$, $R = 0.046$ for 1642 reflections; $[\{Cu(etam)(dmso)\}_2](ClO_4)_2$, monoclinic, $P2_1/n$, $a = 12.431$ (2) Å, $b = 14.251$ (3) Å, $c = 11.132$ (2) Å, $\beta = 108.01$ (2)° Å, $Z = 4$ for $C_{11}H_{25}ClCuN_4O_7S$, $R = 0.033$ for 2148 reflections; $[\{Cu(pta)(ClO_4)\}_2]$, triclinic, $P\bar{1}$, $a = 9.074$ (1) Å, $b = 9.971$ (1) Å, $c = 7.708$ (1) Å, $\alpha = 82.39$ (1)°, $\beta = 104.77$ (1)°, $\gamma = 107.02$ (1)°, $Z = 2$ for $C_8H_{17}ClCuN_4O_5$, $R = 0.025$ for 2135 reflections. These compounds have centrosymmetric dinuclear, bis(μ-olato)-bridged structures, with nitrogen atoms 3 and 7 and the deprotonated alcohol oxygen atoms approximately coplanar with the Cu(II) and with an oxygen atom of a perchlorate ion or of dimethyl sulfoxide weakly coordinated axially. Magnetic susceptibilities, 95–330 K, indicate no appreciable spin coupling for the eta compounds or for $[\{Cu(etam)(dmso)\}_2]$ and appreciable spin coupling ($J = -72$ cm^{-1}) for $[\{Cu(etam)(ClO_4)\}_2]$, while the pta compounds are highly spin coupled ($J =$ ca. -400 cm^{-1}).

Introduction

Preparations of quaternary "hexaminium" salts (salts of 1-alkyl-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane cations) by reaction of the substituted ammonium salt, formaldehyde, and ammonia have been described.[2] Hydroxyalkyl perchlorate salts of this type are formed by 2-aminoethanol,[2] [etad]ClO_4, and the analogue derived from 3-aminopropan-1-ol, [ptad]ClO_4 is now reported (Scheme I) (etad = 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane; ptad = 1-(3-hydroxypropyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane).

The partially hydrolyzed compounds coordinate to copper(II) as tridentate diamine alcohols. Compounds of copper(II) with a variety of amine alcohols have been described,[3] including a number of diamine alcohols, which form compounds structurally similar to those reported here. These commonly have dinuclear structures, with the deprotonated alcohol (olato) oxygen atoms acting as bridging groups and with other donor atoms completing square-planar coordination about the copper ions. One, or less commonly two, additional donor atoms are often weakly coordinated axially to give tetragonal coordination environments. These additional donor atoms are often the bridging oxygens of other dinuclear groups to form tetranuclear (cubanelike) clusters, or higher order polymers. Aggregation of the dinuclear units is uncommon for bulkier amine alcohol ligands, including in general those with 3-(amino olato) bridging groups. Spin coupling between the copper(II) ions, mediated by the bridging oxygen atoms, is usually present; antiferromagnetic coupling within the basic dinuclear unit and weaker antiferromagnetic, or occasionally ferromagnetic, coupling between the dinuclear units may occur. Many attempts have been made to establish correlations between magnetic coupling and structural parameters, but these are generally valid only within groups of compounds that are structurally closely related.

In this paper the preparations and magnetic and spectroscopic properties of some copper(II) compounds with tridentate bicyclic ligands formed by partial hydrolysis of the 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane (hexamine) cage of etad and ptad are reported. The structures of four of the compounds, with three different amine alcohol ligands, have been determined by X-ray diffraction. Magnetic susceptibilities (95–330 K) have been determined, and the relationship between the spin coupling pa-

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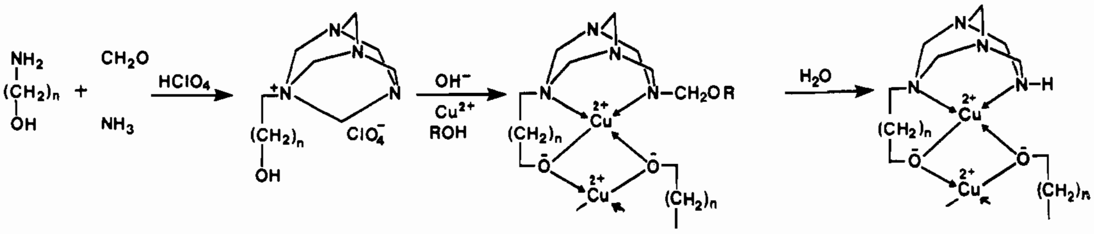
(1) (a) Victoria University of Wellington. (b) Simon Fraser University.
(2) Morgan, K. R.; Curtis, N. F. *Aust. J. Chem.* **1980**, *33*, 1157.
(3) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259.

0020-1669/85/1324-2026$01.50/0

Scheme I



[etad]ClO$_4$: $n = 2$
[ptad]ClO$_4$: $n = 3$

$[\{Cu(etam)\}_2]^{2+}$: $n = 2$, R = Me
$[\{Cu(etae)\}_2]^{2+}$: $n = 2$, R = Et

$[\{Cu(eta)\}_2]^{2+}$: $n = 2$
$[\{Cu(pta)\}_2]^{2+}$: $n = 3$

rameters J and structural parameters is discussed.

Experimental Section

Preparations. The preparation of [etad]ClO$_4$ has been reported.[2]

1-(3-Hydroxypropyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1^{3,7}]decane Perchlorate, [ptad]ClO$_4$. This was prepared as for [etad]ClO$_4$, substituting 3-aminopropan-1-ol for the 2-aminoethanol. The reaction mixture was rotary evaporated to a thick gum, which was stirred with propan-2-ol, when the *product* crystallized. This was filtered off and washed with propan-2-ol; yield ca. 80%. Anal. Calcd for $C_9H_{19}ClN_4O_5$: C, 36.2; H, 6.4; N, 18.8. Found: C, 36.4; H, 6.5; N, 18.6.

The reaction of the hexaminium salts [etad]ClO$_4$ and [ptad]ClO$_4$ with copper(II) to form the olato compounds should require 2 mol of base. Yields were generally higher for the etad derivatives when 1 mol of base, as sodium hydroxide, was used, the additional base required apparently being generated by hydrolysis of some of the hexaminium compound.

Bis{(perchlorato-*O*)-*μ*-[2-[7-(methoxymethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl]ethanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)}, [{Cu(etam)(ClO$_4$)}$_2$]. Sodium hydroxide (6 mmol) dissolved in methanol (10 mL) was added slowly to a boiling solution containing copper(II) perchlorate tetrahydrate (6 mmol) and [H(etad)]ClO$_4$ (6 mmol) in methanol (20 mL). The dark blue-green *product* commenced to precipitate when about 80% of the sodium hydroxide had been added. This was filtered off from the cold solution and recrystallized from hot acetonitrile/methanol. Anal. Calcd for $C_{18}H_{38}Cl_2Cu_2N_8O_{12}$: C, 28.6, H, 5.1; Cu, 16.9; N, 14.8. Found: C, 28.6; H, 5.1; Cu, 16.8; N, 14.8.

Bis{(dimethyl sulfoxide-*O*)-*μ*-[2-[7-(methoxymethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl]ethanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)} Perchlorate, [{Cu(etam)(dmso)}$_2$](ClO$_4$)$_2$. [{Cu(etam)(ClO$_4$)}$_2$] was recrystallized from warm (100 °C), dry dimethyl sulfoxide. The blue-green *product*, which crystallized slowly from the cold solution, was filtered off and washed with propan-2-ol. Anal. Calcd for $C_{22}H_{50}Cl_2Cu_2N_4O_{14}S_2$: C, 28.9; H, 5.5, Cu, 13.9; N, 12.3. Found: C, 29.2; H, 5.5; Cu, 13.9; N, 12.4.

Bis{(perchlorato-*O*)-*μ*-[2-[7-(ethoxymethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl]ethanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)}, [{Cu(etae)(ClO$_4$)}$_2$]. Powdered sodium hydroxide (6 mmol) and [H(etad)]ClO$_4$ were heated in ethanol (20 mL) until they dissolved. Copper(II) perchlorate tetrahydrate (6 mmol) in ethanol (20 mL) was added slowly to the hot solution. The dark blue-green product, which commenced to crystallize after about 60% of the copper perchlorate had been added, was filtered off from the cold solution and recrystallized from hot acetonitrile/ethanol. Anal. Calcd for $C_{20}H_{42}Cl_2CuN_8O_{12}$ C, 30.6; H, 5.4; Cu, 16.2; N, 14.3. Found: C, 30.0; H, 5.4; Cu, 16.7; N, 14.3.

Bis{(dimethyl sulfoxide-*O*)-*μ*-[2-(1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)ethanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)} Perchlorate, [{Cu(eta)(dmso)}$_2$](ClO$_4$)$_2$. A solution of [{Cu(etam)(ClO$_4$)}$_2$] in dimethyl sulfoxide was heated at 100 °C for 15 min. Dark blue crystals of the *product*, which crystallized when propan-2-ol was added, were filtered off and recrystallized from warm dimethyl sulfoxide/propan-2-ol. Anal. Calcd for $C_{18}H_{42}Cl_2Cu_2N_2O_{12}S_2$: C, 26.2; H, 5.1; Cu, 15.4; N, 13.6. Found: C, 26.9; H, 5.2; Cu, 15.2; N, 13.4.

Bis{(perchlorato-*O*)-*μ*-[2-(1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)ethanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)} Dimethanol, [{Cu(eta)(ClO$_4$)}$_2$]·2CH$_3$OH. Purple crystals of the *product* were formed by recrystallizing the previous compound from hot acetonitrile/methanol. The compound was also formed by reaction of equimolar quantities of copper(II) perchlorate tetrahydrate, [H(etad)]ClO$_4$, and sodium hydroxide in water. The solution was rotary evaporated to leave a gum, which was stirred with methanol, when the *product* crystallized. Anal. Calcd for $C_{16}H_{38}Cl_2CuN_8O_{12}$: C, 26.2; H, 5.2; Cu, 17.4; N, 15.3. Found: C, 26.2; H, 5.2; Cu, 17.9; N, 15.8.

Bis{(perchlorato-*O*)-*μ*-[3-(1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)propanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)}, [{Cu(pta)(ClO$_4$)}$_2$. Sodium hydroxide and [H(ptad)]ClO$_4$ were dissolved in a small volume of warm methanol, and copper(II) perchlorate tetrahydrate was added in small portions, followed by triethylamine (equimolar amounts of all reagents). The deep purple *product* was filtered off from the cold solution and recrystallized from hot acetonitrile/methanol. Anal. Calcd for $C_{16}H_{34}Cl_2Cu_2N_8O_{10}$: C, 27.6; H, 4.9; Cu, 18.3; N, 16.0. Found: C, 27.7; H, 5.0; Cu, 18.1; N, 15.7.

Bis{(dimethyl sulfoxide-*O*)-*μ*-[3-(1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)propanolato-*N*^{3},*N*^{7},*μ*-*O*]copper(II)} Perchlorate, [{Cu(pta)(dmso)}$_2$](ClO$_4$)$_2$. The previous compound was recrystallized from warm dimethyl sulfoxide/propan-2-ol. The dark blue *product* was filtered off and washed with propan-2-ol. Anal. Calcd for $C_{20}H_{46}N_8Cl_2Cu_2O_{12}S_2$: C, 28.2; H, 5.4; N, 13.1. Found: C, 28.5; H, 6.1; N, 12.8.

Possible 7-(Hydroxyethyl) Compound. When [etad]ClO$_4$ was warmed with NaOH in methanol, and subsequently reacted with copper(II) perchlorate, a blue product with an infrared different from those of the etam or eta compounds was obtained. The same material was obtained when methanol was added to a solution of [{Cu(etam)(ClO$_4$)}$_2$] in acetonitrile/water. When this material was dissolved in a small volume of dimethyl sulfoxide and methanol added, [{Cu(etam)(dmso)}$_2$](ClO$_4$)$_2$ crystallized. If this dmso solution was heated before adding the methanol, [{Cu(eta)(dmso)}$_2$](ClO$_4$)$_2$ crystallized.

This material could be formulated as the 7-(hydroxyethyl) derivative of the eta cage, etah, with the methoxy group of etam hydrolyzed, but additional CH$_3$OH is required to fit the analytical data, i.e. [{Cu(etah)(ClO$_4$)}$_2$]·2CH$_3$OH. Methanol is shown to be present in [{Cu(etam)(ClO$_4$)}$_2$]·2CH$_3$OH by the crystallographic study, below. The hydroxyethyl-substituted ligand would be expected to be very easily hydrolyzed. Unfortunately, although the material looked superficially well crystalline, we were unable to obtain a single crystal suitable for an X-ray diffraction study and are unable to exclude the possibility that this material is a mixture, possibly stoichiometric, of the etam and eta series. However, the magnetic susceptibility of the material shows a low 298 susceptibility, and the 100–300 K data fit the parameters J −35 cm^{-1}, $g = 1.99$, and $N\alpha = 750 \times 10^{-12}$ m^3 mol^{-1}. The material shows a singlet $\nu_3(ClO_4^-)$ band at 1091 cm^{-1}, which suggests that the material is not a simple mixture of the etam and eta complexes.

Structure Determination. The structures of the compounds [{Cu(eta)(ClO$_4$)}$_2$]·2CH$_3$OH (**1**), [{Cu(eta)(dmso)}$_2$](ClO$_4$)$_2$ (**2**), [{Cu(etam)(dmso)}$_2$] (**3**), and [{Cu(pta)(ClO$_4$)}$_2$] (**4**) were determined by X-ray diffraction, using a Picker FACS-1 four-circle diffractometer and graphite-monochromatized Mo Kα radiation ($\lambda(K\alpha_1) = 0.70930$ Å). Crystal data are shown in Table I. The structures were solved by conventional heavy-atom (**1** and **3**) or MULTAN (**2** and **4**) methods. Refinement was by least-squares methods. For **1**–**3** hydrogen atoms were included in structure factor calculations, but their parameters were not refined; for **4** the hydrogen atom parameters were refined. Table II lists details of data collection and refinement, and further information is included in the supplementary material.

The coordinates of the non-hydrogen atoms for each compound are listed in Table III, and selected bond lengths and bond angles are given in Table IV. Observed and calculated structure factors, thermal parameters, bond lengths and angles involving the H atoms of **4**, and selected least-squares planes are included in the supplementary material. Figures 1–4 show a view of each compound, with the atom-labeling scheme.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured by the Faraday method, with HgCo(CNS)$_4$ as calibrant and using apparatus described elsewhere.[4]

The pta compounds have very small diamagnetic susceptibilities over the range 100–330 K. Under these conditions, uncertainties in the absolute values of the susceptibilities are appreciable, leading to unreasonable values for $N\alpha$, but relative uncertainties are smaller, and permit

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(4) Martin, J. W. L.; Curtis, N. F. *Aust. J. Chem.* **1980**, *33*, 1219.

Table I. Crystal Data

	compd[a]			
	1	**2**	**3**	**4**
formula	$C_8H_{19}ClCuN_4O_6$	$C_9H_{21}ClCuN_4O_6S$	$C_{11}H_{25}ClCuN_4O_7S$	$C_8H_{17}ClCuN_4O_5$
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space gp	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	8.970 (4)	9.175 (2)	12.431 (2)	9.074 (1)
b, Å	9.974 (2)	13.511 (3)	14.251 (3)	9.971 (1)
c, Å	10.123 (5)	12.934 (2)	11.132 (2)	7.708 (1)
α, deg	101.09 (3)	90.0	90.0	82.39 (1)
β, deg	128.57 (3)	99.86 (1)	108.01 (2)	104.77 (1)
γ, deg	93.93 (3)	90.0	90.0	107.02 (1)
V, Å^3	673.6	1579.6	1875.5	643.5
Z[b]	2	4	4	2
fw	366.26	412.35	456.40	348.24
μ, cm^{-1}	19.2	17.7	15.0	19.9
ρ_{obsd},[c] g cm^{-3}	1.80	1.72	1.61	1.79
ρ_{calcd}, g cm^{-3}	1.806	1.734	1.616	1.797
cryst size, mm	0.29 × 0.23 × 0.45	0.40 × 0.22 × 0.20	0.35 × 0.23 × 0.20	0.35 × 0.21 × 0.40

[a] **1** = $[\{Cu(eta)(ClO_4)\}_2]\cdot 2CH_3OH$, **2** = $[\{Cu(eta)(dmso)\}_2](ClO_4)_2$, **3** = $[\{Cu(etam)(dmso)\}_2](ClO_4)_2$, **4** = $[\{Cu(pta)(ClO_4)\}_2]$. [b] Based on formula above. [c] Flotation in CH_2I_2/CCl_4.

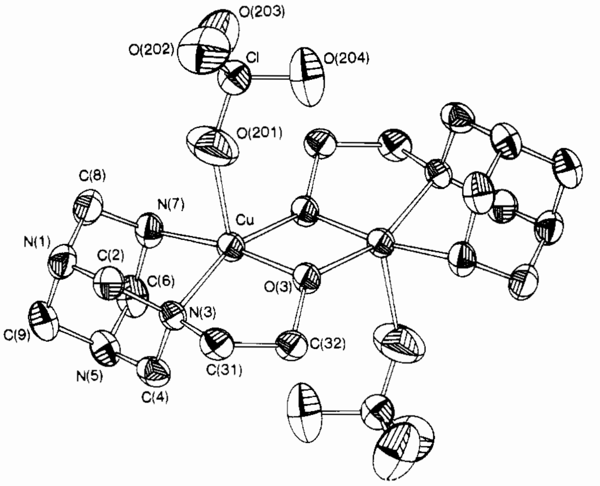

Figure 1. ORTEP projection of one $[\{Cu(eta)(ClO_4)\}_2]$ molecule of **1** showing atomic labeling. Here, and in Figures 2–4, thermal ellipsoids show 50% probability levels and hydrogen atoms have been deleted.

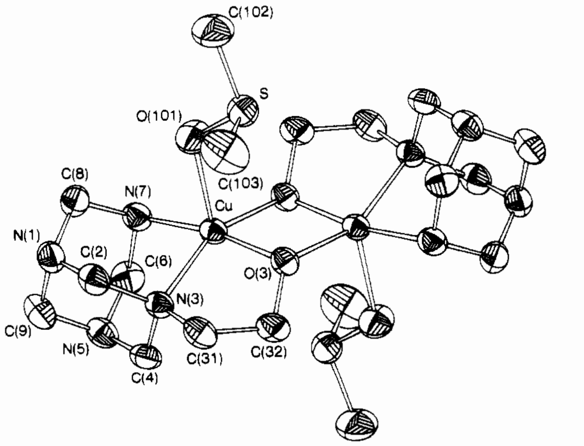

Figure 2. ORTEP projection of the $[\{Cu(eta)(dmso)\}_2]^{2+}$ cation of **2**.

satisfactory calculation of J values, albeit with large (±25 cm^{-1}) uncertainties.

Results

The hydroxyalkyl hexaminium salts [etad]ClO$_4$ and [ptad]ClO$_4$ undergo base hydrolysis of the hexamine cage, as for hexaminium salts in general (the Sommelet reaction). When this hydrolysis occurs under mild conditions, it is possible to prepare copper(II) complexes of partially hydrolyzed bicyclic ligands, formed by the opening of one nitrogen–nitrogen methylene bridge. The copper(II) ion is coordinated by these two nitrogen atoms and by the deprotonated hydroxyalkyl (olato) oxygen atom. The compounds thus have structures that can be considered to have the copper ion replacing one methylene group of the hexamine cage. The compounds have dinuclear diolato-bridged structures similar to those observed for the copper(II) derivatives of other diamine alcohol ligands.[3]

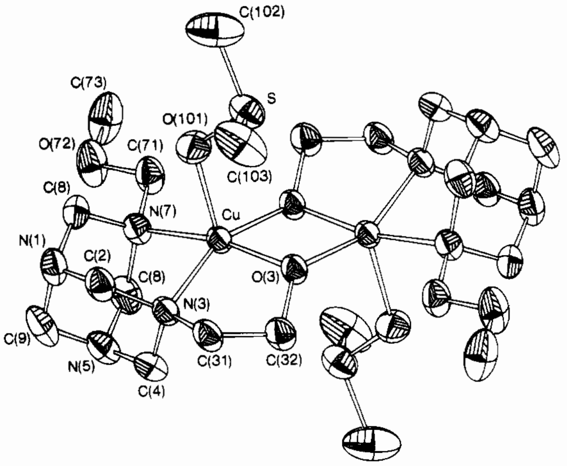

Figure 3. ORTEP projection of the $[\{Cu(etam)(dmso)\}_2]^{2+}$ cation of **3**.

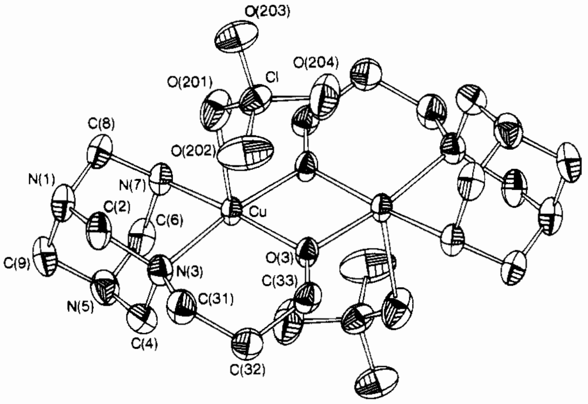

Figure 4. ORTEP projection of the $[\{Cu(pta)(ClO_4)\}_2]$ molecule, **4**.

For [etad]ClO$_4$, the product formed in methanol has the opened bridge methylene group present as a (noncoordinated) 7-(methoxymethylamine) function, etam, while an analogous 7-(ethoxymethylamine) derivative, etae, may be formed in ethanol. These alkoxymethylamine groups can be hydrolyzed off to yield the 7-amino compound, eta (Scheme I). For [ptad]ClO$_4$, only the

Table II. Data Collection and Refinement (θ–2θ Scan, 2° min^{-1})

	1	**2**	**3**	**4**
2θ range, deg	3–50	3–45	3–45	3–50
scan width,[a] deg (2θ range)	1.8 (3–30), 1.6 (30–50)	1.7 (3–30), 1.4 (30–45)	1.6 (3–30), 1.4 (30–45)	1.6 (3–20), 1.4 (20–50)
bkgd fraction[b]	0.1	0.4	0.4	0.1
line profile anal.[c]	yes	no	no	yes
no. of unique reflcns	2385	2076	2466	2274
no. of reflcns with $I > 2.3\sigma_I$	2153	1642	2148	2135
abs cor (T range)	(0.590–0.673)	no	no	(0.597–0.692)
no. of variables	182	200	227	223
final R[d]	0.053	0.046	0.033	0.025
final R_w[e]	0.069	0.054	0.043	0.038

[a] A dispersion correction is added to the base scan width. [b] Stationary-crystal, stationary-counter background counts at each side of scan expressed as fraction of scan time. [c] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114. [d] $R = \sum||F_o| - |F_c||/|F_o|$. [e] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Table III. Final Atomic Coordinates

atom	x	y	z
	[{Cu(eta)(ClO$_4$)}$_2$]·2CH$_3$OH (**1**)		
Cu	0.55497 (7)	0.61424 (6)	0.64738 (7)
N(1)	0.6149 (6)	0.8891 (4)	0.9338 (6)
C(2)	0.4451 (7)	0.8557 (5)	0.7477 (7)
N(3)	0.3674 (5)	0.6994 (4)	0.6596 (5)
C(4)	0.3352 (7)	0.6306 (5)	0.7618 (7)
N(5)	0.5078 (6)	0.6702 (4)	0.9489 (6)
C(6)	0.6738 (8)	0.6228 (6)	0.9838 (7)
N(7)	0.7516 (6)	0.6899 (4)	0.9112 (5)
C(8)	0.7873 (8)	0.8478 (6)	0.9722 (7)
C(9)	0.5635 (8)	0.8236 (6)	1.0220 (7)
C(31)	0.1797 (7)	0.6677 (3)	0.4725 (6)
C(32)	0.1559 (6)	0.5255 (5)	0.3652 (6)
O(3)	0.3332 (4)	0.5319 (3)	0.3944 (4)
Cl	0.8036 (2)	0.8350 (1)	0.5581 (2)
O(201)	0.6799 (9)	0.8031 (6)	0.5939 (8)
O(202)	0.7951 (8)	0.9673 (5)	0.5295 (7)
O(203)	0.9983 (7)	0.8348 (6)	0.7021 (7)
O(204)	0.7387 (8)	0.7287 (6)	0.4058 (6)
O(301)	0.1652 (7)	0.6667 (5)	0.1176 (6)
C(302)	0.2678 (10)	0.7972 (8)	0.1535 (11)
	[{Cu(eta)(dmso)}$_2$](ClO$_4$)$_2$ (**2**)		
Cu	0.36517 (7)	0.55675 (5)	0.49127 (5)
N(1)	0.0840 (5)	0.7164 (4)	0.4607 (4)
C(2)	0.1968 (7)	0.7269 (4)	0.3963 (5)
N(3)	0.3491 (5)	0.7017 (3)	0.4533 (3)
C(4)	0.3769 (7)	0.7614 (4)	0.5533 (5)
N(5)	0.2615 (5)	0.7500 (3)	0.6151 (4)
C(6)	0.2444 (7)	0.6508 (5)	0.6543 (4)
N(7)	0.1969 (5)	0.5794 (3)	0.5672 (4)
C(8)	0.0628 (7)	0.6175 (5)	0.4958 (5)
C(9)	0.1206 (7)	0.7801 (5)	0.5519 (8)
C(31)	0.4639 (7)	0.7207 (4)	0.3893 (5)
C(32)	0.5960 (7)	0.6538 (4)	0.4241 (5)
O(3)	0.5416 (4)	0.5563 (3)	0.4292 (3)
S	0.29458 (18)	0.41513 (11)	0.28156 (12)
O(101)	0.2246 (5)	0.4709 (3)	0.3617 (3)
C(102)	0.1486 (8)	0.3446 (6)	0.2107 (6)
C(103)	0.3137 (10)	0.5012 (6)	0.1842 (6)
Cl	0.22314 (21)	0.06279 (14)	0.35481 (14)
O(201)	0.1424 (10)	0.0679 (6)	0.2563 (6)
O(202)	0.2536 (9)	0.1479 (5)	0.4060 (7)
O(203)	0.3357 (11)	0.0046 (12)	0.3595 (11)
O(204)	0.1379 (17)	0.0101 (10)	0.4098 (8)
	[{Cu(etam)(dmso)}$_2$](ClO$_4$)$_2$ (**3**)		
Cu	0.43569 (3)	0.54856 (3)	0.38177 (3)
N(1)	0.2788 (3)	0.6198 (2)	0.0914 (3)
C(2)	0.2641 (3)	0.5259 (3)	0.1335 (3)
N(3)	0.3745 (2)	0.4840 (2)	0.2133 (2)
C(4)	0.4595 (3)	0.4923 (3)	0.1439 (3)
N(5)	0.4697 (3)	0.5863 (2)	0.1014 (3)
C(6)	0.5122 (3)	0.6541 (3)	0.2010 (3)
N(7)	0.4347 (2)	0.6693 (2)	0.2792 (2)
C(8)	0.3161 (3)	0.6876 (3)	0.1922 (3)
C(9)	0.3600 (4)	0.6170 (3)	0.0211 (3)
C(31)	0.3570 (3)	0.3846 (2)	0.2416 (3)
C(32)	0.4481 (3)	0.3552 (2)	0.3613 (3)
O(3)	0.4510 (2)	0.4227 (2)	0.4555 (2)
C(71)	0.4719 (3)	0.7477 (3)	0.3653 (3)
O(72)	0.4622 (3)	0.8322 (2)	0.2964 (2)
C(73)	0.5099 (4)	0.9063 (3)	0.3750 (4)
S	0.25430 (8)	0.54779 (8)	0.53576 (9)
O(101)	0.2812 (2)	0.5912 (2)	0.4248 (2)
C(102)	0.1525 (5)	0.6221 (4)	0.5665 (5)
C(103)	0.1655 (5)	0.4517 (4)	0.4738 (5)
Cl	0.84817 (22)	0.64526 (8)	0.20122 (10)
O(201)	0.7911 (5)	0.5622 (3)	0.2096 (4)
O(202)	0.8249 (5)	0.7155 (3)	0.2753 (4)
O(203)	0.9613 (4)	0.6284 (4)	0.2438 (6)
O(204)	0.8187 (5)	0.6729 (3)	0.0762 (4)
	[{Cu(pta)(ClO$_4$)}$_2$] (**4**)		
Cu	0.59530 (2)	0.61294 (2)	0.62540 (3)
N(1)	0.8088 (2)	0.8490 (2)	0.9347 (3)
C(2)	0.8888 (3)	0.7787 (2)	0.8531 (3)
N(3)	0.8120 (2)	0.7520 (2)	0.6579 (2)
C(4)	0.7797 (3)	0.8860 (3)	0.5599 (3)
N(5)	0.7013 (3)	0.9529 (2)	0.6507 (3)
C(6)	0.5423 (3)	0.8731 (2)	0.6622 (3)
N(7)	0.5435 (2)	0.7371 (2)	0.7711 (2)
C(8)	0.6534 (3)	0.7654 (2)	0.9510 (3)
C(9)	0.7974 (3)	0.9810 (2)	0.8326 (4)
C(31)	0.9289 (3)	0.7078 (3)	0.5880 (3)
C(32)	0.8683 (3)	0.6600 (3)	0.3984 (3)
C(33)	0.7516 (2)	0.5158 (2)	0.3850 (3)
O(3)	0.6146 (2)	0.5117 (1)	0.4419 (2)
Cl	0.70774 (7)	0.32460 (6)	0.88596 (7)
O(201)	0.6612 (2)	0.4488 (2)	0.8973 (2)
O(202)	0.8509 (3)	0.3607 (3)	0.8288 (3)
O(203)	0.7268 (2)	0.2522 (2)	1.0604 (2)
O(204)	0.5843 (3)	0.2359 (2)	0.7617 (3)

7-amino compound, pta, was prepared.

The compounds all form stable dimethyl sulfoxide adducts, e.g. [{Cu(eta)(dmso)}$_2$](ClO$_4$)$_2$, and somewhat less stable dimethylformamide adducts.

Description of the Structures. The structures of the four compounds are essentially similar. All are discrete dimers with a crystallographically imposed center of symmetry. Each copper atom is coordinated by two nitrogen atoms, the deprotonated oxygen atom of one ligand, and the oxygen atom of the symmetry-related ligand, with the four nitrogen atoms, two bridging oxygen atoms, and two copper atoms of each dimer approximately coplanar.

The two nitrogen atoms are part of a tetraaza bicyclic group coordinated by a tertiary nitrogen (crystallographic N(3)) and for the eta (**1**, **2**) and pta (**4**) compounds by a secondary nitrogen at N(7). For the etam compound (**3**) this nitrogen is tertiary, with an attached –CH$_2$OCH$_3$ group. The Cu–N distances are all about 2.01 Å, apart from N(7) of **3** where Cu–N = 2.063 (3) Å. Bond lengths and angles within the bicyclic part of the ligand do not differ significantly between the structures. The C–N

Table IV. Interatomic Distances (Å) and Angles (deg)[a]

	1	2	3	4
Distances				
Cu–N(3)	1.996 (4)	2.018 (5)	2.015 (3)	2.024 (2)
Cu–N(7)	1.996 (4)	1.990 (5)	2.063 (3)	1.999 (2)
Cu–O(3)	1.951 (3)	1.927 (4)	1.957 (2)	1.913 (1)
Cu–O(3)^{i}	1.950 (3)	1.955 (4)	1.964 (2)	1.929 (1)
Cu–O(101)		2.254 (4)	2.204 (2)	
Cu–O(201)	2.441 (5)			2.540 (2)
N(1)–C(2)	1.446 (7)	1.443 (8)	1.448 (5)	1.436 (3)
C(2)–N(3)	1.501 (6)	1.503 (8)	1.509 (4)	1.511 (3)
N(3)–C(4)	1.498 (6)	1.510 (8)	1.495 (4)	1.513 (3)
C(4)–N(5)	1.454 (7)	1.439 (8)	1.440 (5)	1.447 (3)
N(5)–C(6)	1.439 (7)	1.451 (8)	1.442 (5)	1.449 (3)
C(6)–N(7)	1.497 (7)	1.491 (8)	1.502 (4)	1.498 (3)
N(7)–C(8)	1.509 (7)	1.498 (8)	1.515 (4)	1.493 (3)
C(8)–N(1)	1.453 (7)	1.435 (8)	1.445 (5)	1.440 (3)
N(1)–C(9)	1.461 (7)	1.452 (8)	1.457 (5)	1.459 (3)
C(9)–N(5)	1.462 (7)	1.465 (8)	1.448 (5)	1.463 (3)
N(3)–C(31)	1.497 (6)	1.469 (8)	1.482 (4)	1.496 (3)
C(31)–C(32)	1.521 (7)	1.517 (9)	1.516 (5)	1.512 (3)
C(32)–C(33)				1.513 (3)
C(32)/C(33)–O(3)	1.419 (5)	1.415 (7)	1.415 (4)	1.408 (2)
N(7)–C(71)			1.451 (4)	
C(71)–O(72)			1.413 (4)	
O(72)–C(73)			1.382 (5)	
O(101)–S		1.511 (5)	1.508 (3)	
S–C(102)		1.767 (8)	1.763 (5)	
S–C(103)		1.745 (8)	1.760 (5)	
Cu···Cu^{i}	2.9114 (20)	2.8865 (15)	2.9662 (10)	2.9949 (6)
Cl–O(201)	1.400 (5)	1.362 (7)	1.398 (4)	1.440 (2)
Cl–O(202)	1.401 (4)	1.333 (7)	1.383 (4)	1.410 (2)
Cl–O(203)	1.416 (5)	1.292 (10)	1.360 (5)	1.434 (2)
Cl–O(204)	1.417 (5)	1.347 (11)	1.382 (4)	1.432 (2)
O(301)–C(302)	1.382 (9)			
Angles				
N(3)–Cu–N(7)	87.14 (16)	86.60 (20)	85.98 (11)	86.22 (7)
N(3)–Cu–O(3)	86.17 (14)	86.17 (18)	86.05 (10)	97.35 (6)
N(3)–Cu–O(3)^{i}	158.56 (15)	153.30 (18)	155.61 (11)	171.76 (7)
N(3)–Cu–O(101)/O(201)	99.56 (16)	108.05 (18)	102.96 (10)	97.01 (7)
N(7)–Cu–O(3)	170.95 (14)	169.90 (19)	168.41 (10)	167.05 (7)
N(7)–Cu–O(3)^{i}	100.81 (15)	99.59 (18)	102.51 (10)	97.34 (6)
N(7)–Cu–O(101)/O(201)	95.81 (20)	93.02 (19)	91.93 (10)	92.42 (7)
O(3)–Cu–O(3)^{i}	83.46 (14)	83.91 (17)	81.69 (10)	77.59 (6)
O(3)–Cu–O(101)/O(201)	91.31 (19)	95.91 (17)	98.05 (10)	99.45 (6)
O(3)^{i}–Cu–O(101)/O(201)	99.39 (16)	97.61 (17)	99.59 (10)	90.28 (6)
C(2)–N(1)–C(8)	115.3 (4)	115.0 (5)	114.1 (3)	113.4 (2)
C(2)–N(1)–C(9)	109.8 (4)	108.7 (5)	109.1 (3)	109.9 (2)
C(8)–N(1)–C(9)	108.4 (4)	108.7 (5)	109.0 (3)	109.6 (2)
N(1)–C(2)–N(3)	111.5 (4)	113.2 (5)	112.0 (3)	113.6 (2)
Cu–N(3)–C(2)	111.5 (3)	111.2 (4)	112.3 (2)	112.4 (1)
Cu–N(3)–C(4)	108.0 (3)	108.4 (3)	108.7 (2)	104.0 (1)
Cu–N(3)–C(31)	106.6 (3)	106.1 (4)	106.1 (2)	114.4 (1)
C(2)–N(3)–C(4)	109.9 (3)	107.8 (5)	108.9 (3)	109.1 (2)
C(2)–N(3)–C(31)	110.3 (3)	112.3 (5)	109.7 (3)	105.3 (2)
C(4)–N(3)–C(31)	110.4 (4)	110.9 (5)	111.0 (3)	111.6 (2)
N(3)–C(4)–N(5)	112.6 (4)	112.8 (5)	113.0 (3)	113.7 (2)
C(4)–N(5)–C(6)	113.8 (4)	115.2 (5)	114.8 (3)	114.9 (2)
C(4)–N(5)–C(9)	108.8 (4)	108.8 (5)	108.8 (3)	108.9 (2)
C(6)–N(5)–C(9)	109.2 (4)	108.3 (5)	108.9 (3)	108.8 (2)
N(5)–C(6)–N(7)	112.8 (4)	111.7 (5)	113.2 (3)	110.8 (2)
Cu–N(7)–C(6)	108.2 (3)	108.7 (4)	107.8 (2)	107.4 (1)
Cu–N(7)–C(8)	111.1 (3)	111.9 (4)	109.6 (2)	115.1 (1)
Cu–N(7)–C(71)			109.3 (2)	
C(6)–N(7)–C(8)	109.5 (4)	110.3 (5)	109.1 (3)	109.7 (2)
C(6)–N(7)–C(71)			111.3 (3)	
C(8)–N(7)–C(71)			109.8 (3)	
N(7)–C(8)–N(1)	111.8 (4)	111.9 (5)	113.4 (3)	111.6 (2)
N(1)–C(9)–N(5)	110.1 (4)	110.4 (5)	110.7 (3)	109.9 (2)
N(3)–C(31)–C(32)	108.5 (3)	110.0 (5)	109.4 (3)	114.3 (2)
C(31)–C(32)–O(3)/C(33)	106.6 (4)	107.4 (5)	107.7 (3)	113.6 (2)
C(32)–C(33)–O(3)				112.0 (2)
C(32)/C(33)–O(3)–Cu	108.8 (3)	110.1 (4)	109.6 (2)	128.6 (1)
C(32)/C(33)–O(3)–Cu^{i}	132.1 (3)	128.8 (4)	132.3 (2)	128.6 (1)
Cu–O(3)–Cu^{i}	96.54 (14)	96.09 (17)	98.31 (10)	102.41 (6)
N(7)–C(71)–O(72)			110.0 (3)	
C(71)–O(72)–C(73)			111.1 (3)	

Table IV (Continued)

	1	2	3	4
Cu–O(101)–S		120.7 (3)	119.6 (1)	
O(101)–S–C(102)		104.5 (3)	105.5 (2)	
O(101)–S–C(103)		105.7 (4)	105.6 (2)	
C(102)–S–C(103)		98.4 (5)	98.2 (3)	
Cu–O(201)–Cl	141.2 (3)			122.7 (1)
O(201)–Cl–O(202)	108.9 (3)	117.1 (6)	111.7 (3)	110.5 (2)
O(201)–Cl–O(203)	109.7 (4)	112.1 (7)	108.6 (4)	108.3 (1)
O(201)–Cl–O(204)	108.3 (4)	104.4 (7)	109.1 (3)	108.6 (1)
O(202)–Cl–O(203)	110.7 (3)	113.8 (7)	107.7 (4)	110.0 (1)
O(202)–Cl–O(204)	110.9 (3)	106.6 (8)	110.8 (3)	110.3 (2)
O(203)–Cl–O(204)	108.3 (3)	100.7 (12)	109.0 (4)	109.2 (1)

[a] Atoms denoted by i are related to those given in Table III by the transformation $1 - x, 1 - y, 1 - z$.

Table V. Some Structural Correlations

compd[a]	$\sum\angle$O,[b] deg	τ,[c] deg	Cu–O–Cu, deg	Cu–O(3), Å	Cu–O(3)′, Å	Cu–O_{ax},[d] Å	Δ(Cu),[e] Å	Cu–Cu, Å
1	337	12	96.5 (1)	1.951 (3)	1.950 (3)	2.441 (5)	0.2267 (7)	2.911 (2)
2	335	16	96.1 (2)	1.927 (4)	1.955 (4)	2.254 (4)	0.2902 (6)	2.887 (2)
3	340	13	98.3 (1)	1.957 (2)	1.964 (2)	2.204 (2)	0.2752 (4)	2.966 (1)
4	360	7	102.4 (1)	1.913 (1)	1.929 (1)	2.540 (2)	0.1642 (2)	2.995 (1)

[a] **1** = [{Cu(eta)(ClO_4)}$_2$]·2CH_3OH, **2** = [{Cu(eta)(dmso)}$_2$](ClO_4)$_2$, **3** = [{Cu(etam)(dmso)}$_2$](ClO_4)$_2$, **4** = [{Cu(pta)(ClO_4)}$_2$]. [b] Sum of angles about bridging oxygen atom O(3). [c] Dihedral angle between Cu_2N_4 and Cu_2O_2 least-squares planes. [d] Distance Cu–O of axial ClO_4^- or dmso. [e] Displacement of Cu from N_2O_2 plane toward apical group.

distances to N(3) and N(7) average[5] 1.503 [8] Å, those to the bridged C(9) average 1.458 [8] Å, and the remainder average 1.444 [8] Å. N(3) and N(7) are the atoms bonded to the Cu atoms so this trend is consistent with a reduction in the electron density at the donor atom upon coordination. Angles C(2)–N(1)–C(8) and C(4)–N(5)–C(6) average 114.6 [7]°, which is sufficiently removed from tetrahedral to suggest that the ligand is slightly stretched to allow N(3) and N(7) to reach the appropriate bite.

In many respects structures **1–3** of the eta and etam compounds are similar, but there are significant differences between these and structure **4** of the pta compound. These differences arise essentially from the opening of the N(3)–Cu–O(3) chelate angle from ca. 86° for **1–3** where N(3)–O(3) forms a gauche conformation five-membered chelate ring to 97.4° for **4** where a chair conformation six-membered chelate ring is present. Significant structural parameters for the four compounds are shown in Table V.

For each of the compounds an oxygen atom is weakly coordinated axially: a perchlorate oxygen for **1** and **4** and a dimethyl sulfoxide oxygen for **2** and **3**. The copper atom is displaced from the N_2O_2 plane toward the apical oxygen atom.

The methanol molecule of **1** is hydrogen bonded to adjacent [{Cu(eta)(ClO_4)}$_2$] molecules: O(301) ($x + 1, y, z + 1$)···H(7)–N(7) [O···H = 2.13 Å; O···N = 2.970 (6) Å] and O(3)···H(301)–O(301) [O···H = 2.13 Å; O···O = 2.897(6) Å]. Hydrogen bonding in **2** and **4** is limited to weak interactions between H(7) and perchlorate ions: O(201) ($x, ^1/_2 - y, ^1/_2 + z$)···H(7)–N(7) [O···H = 2.60 Å; O···N = 3.26 (1) Å] in **2** and O(202) ($1 - x, 1 - y, 1 - z$)···H(7)–N(7) [O···H = 2.41 (2) Å; O···N = 3.086 (2) Å] in **4**. In **3** the distances between perchlorate oxygen atoms and hydrogen atoms are all >2.68 Å.

Magnetic Properties. The effective magnetic moments at 298 K of [{Cu(etam)(dmso)}$_2$](ClO_4)$_2$ (1.80 μ_B), [{Cu(eta)(ClO_4)$_2$}] (1.80 μ_B), and [{Cu(eta)(dmso)}$_2$] (1.83 μ_B) are "normal" for non spin-coupled copper(II). Measurements over the range 95–330 K for the dmso adducts showed susceptibilities obeying the Curie–Weiss relationship, with μ_{eff} = 1.80 μ_B, Θ = 4 K for the etam compound and μ_{eff} = 1.79 μ_B, Θ = −16.8 K for the eta compound.

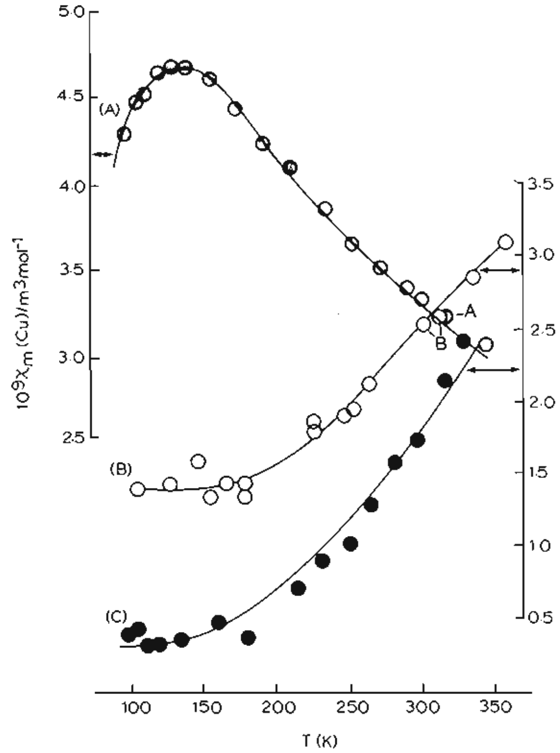

Figure 5. Magnetic susceptibility (per mol of Cu), corrected for diamagnetism, against temperature: A, [{Cu(etam)(dmso)}$_2$](ClO_4)$_2$; B, [{Cu(pta)(dmso)}$_2$](ClO_4)$_2$; C, [{Cu(pta)(ClO_4)}$_2$]. The curves represent the calculated values.

The effective magnetic moments at 298 K of [{Cu(etam)(ClO_4)}$_2$]·2CH_3OH, [{Cu(pta)(ClO_4)}$_2$], and [{Cu(pta)(dmso)}$_2$](ClO_4)$_2$ are appreciably lower than the spin-only value for copper(II). Measurements were made over the range 95–330 K for these compounds, and the results were fitted to the Bleaney–Bowers relationship for spin-coupled dinuclear copper(II) systems

$$\chi_m = (g^2\beta^2N/3k_BT)[1 + \tfrac{1}{3}\exp(-2J/k_BT)]^{-1} + N\alpha$$

where $2J$ is the singlet–triplet separation and the other symbols have their usual meanings. Satisfactory fits of the data were

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[5] The esd's [in brackets] quoted with the averages were calculated by the equation

$$\sigma = [\sum_m (X_m - X_0)^2/(m - 1)]^{1/2}$$

where

$$X_0 = (\sum_m X_m)/m$$

When this number is less than the esd in the individual measurements, the largest $\sigma(X_m)$ is quoted.

obtained with the following parameters: $[\{Cu(etam)(ClO_4)\}_2]\cdot 2CH_3OH$, $J = -72 \pm 5$ cm^{-1}, $g = 1.99$, $N\alpha$ fixed at 750×10^{-12} m^3 mol^{-1}; $[\{Cu(pta)(ClO_4)\}_2]$, $J = -380 \pm 25$ cm^{-1}, $g = 2.10$, $N\alpha = 330 \times 10^{-12}$ m^3 mol^{-1}; $[\{Cu(pta)(dmso)\}_2](ClO_4)_2$, $J = -430 \pm 25$ cm^{-1}, $g = 2.15$, $N\alpha = 1400 \times 10^{-12}$ m^3 mol^{-1}. See Figure 5.

Spectroscopic Properties. The perchlorate compounds in acetonitrile all have a single broad asymmetric d–d band, plus a more intense band in the near-UV that is characteristic of dinuclear copper(II) compounds. The intensity of this band is notably greater for the pta compounds, which have the largest spin-coupling constant, J (λ, nm (ϵ, mol^{-1} m^2): eta, 617 (16), 386 (25); etam, 633 (14), 391 (33); etae, 625 (16), 388 (33); pta, 595 (13), 373 (160). The d–d bands for the solids are broad and asymmetric, the maxima for the perchlorate compounds shifting from 570 nm for the purple pta compound through 617 nm for the blue eta compound to 625 nm for the blue-green etam/eta compounds. The band shifts to lower energy for the dmso adducts.

The compounds shown to have weakly coordinated perchlorate groups show doublet $\nu_3(ClO_4^-)$ bands in the infrared spectra (cm^{-1}): eta, 1098, 1063; pta, 1095, ca. 1073; etam, 1095, ca. 1073; etae, broad with poorly resolved detail. The dmso adducts show a singlet $\nu_3(ClO_4^-)$ band (pta, 1085 cm^{-1}) or closer doublets, the splitting attributed to hydrogen-bonding interactions (eta, 1094, 1082 cm^{-1}; etam, 1096, 1081 cm^{-1}).

The compounds of eta and pta show a strong ν(NH) band near 3270 cm^{-1}.

Discussion. The structures of a number of dinuclear diamine olato compounds of Cu(II) have been determined and attempts made to correlate the antiferromagnetic spin-coupling parameter J with various structural parameters.[3] As a general observation, for similar ligands, the coupling is much larger when the chelate link to the oxygen, $N-(CH_2)_n-O^-$, contains three or more members ($n > 2$) than when $n = 2$. Correlations of J with the O–Cu–O angle, planarity about the bridging oxygen atom (as evidenced by the sum of the bond angles at the oxygen), Cu–Cu distance, tetrahedral distortion of the N_2CuO_2 plane (τ = dihedral angle between N_4Cu_2 and Cu_2O_2 least-squares planes), magnitude of axial interactions (displacement of Cu from the N_2O_2 plane and the distance of Cu to the axial donor atom), Cu–O and Cu–O′ distances, etc., have been reported and are often satisfactory for closely similar groups of compounds. These parameters are interrelated, and all may have some relevance to the extent to which electron spins on the copper atoms can be coupled via the orbitals of the bridging oxygen atom.

The values of these parameters (Table V) for the highly spin-coupled pta compound, relative to the non-spin-coupled or very weakly spin-coupled eta compounds all shift in the directions expected.

For the ligand etam, with the 7-(methoxymethyl) substituent on the cage, the perchlorato compound shows an intermediate level of spin coupling ($J = -72$ cm^{-1}), but unfortunately a crystal suitable for a structural study could not be found. The dmso adduct of the compound, which obeys the Curie–Weiss relationship down to 95 K ($\Theta = 4$ K), indicating very little spin coupling, was structurally investigated, and the relevant structural parameters are closer to the values for the eta compounds. The Cu–O (apical) distances are shorter; the displacement of the Cu from the mean equatorial plane, Δ(Cu), and the tetrahedral distortion of the equatorial donor atoms τ are larger for the dmso adducts **2** and **3** than for the perchlorato compounds **1** and **4**. The smaller spin coupling for the etam–dmso adduct than for the perchlorato compound thus arises essentially from the stronger axial interaction of the dmso oxygen, but unfortunately the way this interaction affects the structural parameters is unknown.

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Supplementary Material Available: Details of diffraction data collection and structure solution and listings of anisotropic thermal parameters (Table VI), hydrogen atom coordinates (Table VII), bond lengths and angles involving hydrogen atoms for $[\{Cu(pta)(ClO_4)\}_2]$ (Table VIII), selected least-squares planes (Table IX), and observed and calculated structure factors (Table X) (77 pages). Ordering information is given on any current masthead page.

Registry No. **1**, 96165-68-3; **2**, 96165-70-7; **3**, 96193-95-2; **4**, 96165-71-8; $\{Cu(etam)(ClO_4)\}_2$, 96165-72-9; $\{Cu(etae)(ClO_4)\}_2$, 96165-73-0; $[\{Cu(pta)(dmso)\}](ClO_4)_2$, 96193-97-4; $\{Cu(etah)(ClO_4)\}_2$, 96165-74-1; $[ptad]ClO_4$, 96165-76-3; $[H(etad)]ClO_4$, 96165-77-4.

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Five- vs. Four-Coordination in Platinum(II)–Olefin Complexes with Bidentate Nitrogen Ligands

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Bidentate nitrogen ligands (N–N) can bind the fragment $PtCl_2$(olefin) to give five- or four-coordinate species. In the latter case N–N acts as a monodentate or a bridging ligand. The ^{1}H NMR spectra of $[PtCl_2(N{-}N)(olefin)]$ complexes provide information on the metal coordination number through the chemical shift of the olefin protons. The crystal and molecular structures of the two complexes $[PtCl_2(C_2H_4)(Me_2CHN{=}CHCH{=}NNMe_2)]$ (**1d**) (monoclinic, space group $P2_1/c$; $a = 8.710$ (1) Å, $b = 15.400$ (1) Å, $c = 10.753$ (1) Å, $\beta = 99.16$ (1)°; $Z = 4$; $R_w = 3.8\%$) and $[PtCl_2(E\text{-}CH_3CH{=}CHCH_3)(Me_3CN{=}CHCH{=}NCMe_3)]$ (**4g**) (orthorhombic, space group $P2_12_12_1$; $a = 6.969$ (5) Å, $b = 10.675$ (7) Å, $c = 26.009$ (15) Å; $Z = 4$; $R_w = 4.6\%$) have been determined by single-crystal X-ray diffraction. An attempt to correlate the geometry of the complexes with the electronic and steric properties of the nitrogen ligands and of the coordinated olefins is presented.

Introduction

Five-coordinate species have been postulated for a long time[1] as intermediates in substitution reactions involving platinum(II) complexes, but theoretical speculations[2] seemed to exclude the possibility that stable complexes with such a coordination number could be isolated. The few five-coordinate platinum(II) complexes described until 1973 seemed to be very unusual species that could only be obtained with a particular choice of ligands.[3] However,

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(1) See e.g.: Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1967.

(2) Nyholm, R. S.; Tobe, M. L. "Essay in Coordination Chemistry"; Birkhausen Verlag: Basel, Switzerland, 1964; p 112.