Binuclear Copper(II) Complexes of Bis(pentadentate) Ligands Derived from Alkyl-Bridged Bis(1,4,7-triazacyclonane) Macrocycles

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Three alkyl-bridged bis(pentadentate) ligands, 1,2-bis[*N*,*N*′-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]ethane (tmpdtne), 1,3-bis[*N*,*N*′-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]propane (tmpdtnp), and 1,4-bis[*N*,*N*′-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]butane (tmpdtnb), have been synthesized by reaction of the corresponding bis(tridentate) macrocycles with 2-picolyl chloride at pH $\sim$ 10. Copper(II) complexes of the three ligands have been prepared and were found to have the composition $[Cu_2L](ClO_4)_4 \cdot xH_2O$ where $x = 2$ for L = tmpdtne and $x = 0$ for L = tmpdtnp and tmpdtnb. Single-crystal X-ray diffraction studies established the molecular structure of the monomeric complex, $[Cu(dmptacn)](ClO_4)_2$ (**1**), where dmptacn = 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane, and the corresponding binuclear complex $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (**2**). The mononuclear complex **1** crystallizes in the orthorhombic space group *Pbcn* with $a = 19.467(4)$ Å, $b = 16.798(6)$ Å, $c = 14.204(4)$ Å, $V = 4644(1)$ Å^3, and $Z = 8$. The structure was refined to final $R = 0.066$ and $R_w = 0.056$ for 1806 observed reflections. The binuclear complex **2** crystallizes in the monoclinc space group $P2_1/c$ with $a = 13.885(1)$ Å, $b = 13.218(2)$ Å, $c = 13.531(3)$ Å, $\beta = 106.04(1)°$, $V = 2386(1)$ Å^3, and $Z = 2$ (dimers). Refinement gave final $R = 0.055$ and $R_w = 0.063$ for 3509 observed reflections. The binuclear unit is centrosymmetric about the ethane bridge, and the pentadentate compartments are orientated away from one another such that the complex adopts an *anti*-configuration. Both complexes **1** and **2** exhibit distorted square pyramidal geometries about the Cu(II) centers. The UV−vis spectra of the binuclear complexes $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (**2**), $[Cu_2(tmpdtnp)](ClO_4)_4$ (**3**), and $[Cu_2(tmpdtnb)](ClO_4)_4$ (**4**) show a band in the range 598−602-nm which, for five-coordinate Cu(II) complexes, is indicative of a square pyramidal geometry. The slightly higher λ_{max} value of 612 nm for the mononuclear complex **1** suggests more distortion toward trigonal bipyramidal geometry in solution. These data are in agreement with the solid state structures which show that **1** and **2** are 32% and 11% distorted from SP, respectively. Variable-temperature magnetic susceptibility measurements of **2**−**4** show no evidence of exchange coupling between the Cu(II) centers. ESR measurements in frozen DMF and nitromethane solutions indicate the presence of weak dipole−dipole interactions in **2** and **3**, which have ethane and propane linkages between the pentadentate compartments. Complex **4**, however, shows little evidence of coupling, with its ESR spectrum closely resembling that of **1**.

Introduction

The synthesis and complexation properties of ligands comprising linked 1,4,7-triazacyclononane (tacn) macrocycles have attracted considerable attention in recent years.[1−9] This interest has arisen because such ligands can accommodate two metal centers in close proximity and thus may provide the basis of models for the active sites of important biological systems such as those found in cytochrome *c* oxidase, hemocyanin, hemerythrin, and photosystem II.[10−12] Simplified model complexes of this type may help to elucidate the factors that determine the electronic properties and the type and strength of magnetic interactions in these polynuclear bio-sites.

Tacn macrocycles linked via ethane (dtne),[4] propane (dtnp),[4] and butane (dtnb)[1] bridges (Chart 1) have enabled the formation of a variety of binuclear complexes containing metals such as Mn(II/III), Fe(II/III), Co(II/III), Cu(II), and Zn(II). The three nitrogen donor atoms of the tacn macrocycle coordinate to each metal, leaving two or three sites available for either the attachment of additional ligands or bridge formation. Zompa and co-workers prepared hydrochloride salts of dtnp and dtnb and determined their acid dissociation constants.[7] The results were found to parallel those for tacn.[13] Equilibrium studies showed dtnp and dtnb to form extremely stable 1:1 and 2:1 Cu(II):L complexes. The structures of the binuclear copper(II) complexes, $[Cu_2(dtnp)Cl_4 \cdot 2H_2O]$ and $[Cu_2(dtnb)Cl_4]$, were determined by X-ray crystallography.

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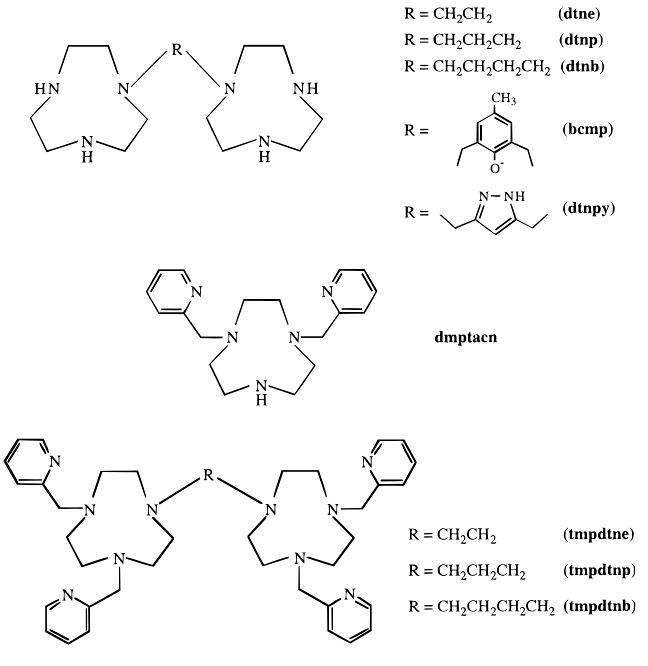
(1) Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1990**, *29*, 4143.
(2) Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 621.
(3) Sessler, J. L.; Sibert, J. W.; Burrell, A. K.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 4277.
(4) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.
(5) Hanke, D.; Wieghardt, K.; Nuber, B.; Lu, R.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *Inorg. Chem.* **1993**, *32*, 4300.
(6) Geilenkirchen, A.; Neubold, P.; Schneider, R.; Wieghardt, K.; Flörke, U.; Haupt, . H.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1994**, 457.
(7) Xiaoping, Z.; Hsieh, W.; Margulis, T. N.; Zompa, L. J. *Inorg. Chem.* **1995**, *34*, 2883.
(8) Diril, H.; Chang, H.; Nilges, M. J.; Zhang, X.; Potenza, J. A.; Schugar, H. J.; Isied, . S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 5102.
(9) Behle, L.; Neuburger, M.; Zehnder, M.; Kaden, T. A. *Helv. Chim. Acta* **1995**, *78*, 693.
(10) Lindoy, L. F. *The Chemistry of Macrocyclic Ligands*; Cambridge University Press: Cambridge, U.K., 1989.
(11) Zanello, P.; Tamburini, S.; Vigato, P. A.; Mazzocchin, G. A. *Coord. Chem. Rev.* **1987**, 165.
(12) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
(13) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

0020-1669/96/1335-1974$12.00/0

Chart 1



In an effort to synthesize a model complex for the respiratory enzyme hemerythrin, Sessler and co-workers attempted to form a μ-oxo-, μ-diacetato-bridged binuclear Fe(III) complex using dtnb as a ligand.[1] The tetranuclear complex, $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(dtnb)]_2^{4+}$, was formed rather than the target binuclear complex. Indeed, for these bis(tacn) ligands, examples of bridged binuclear complexes are few. Wieghardt and co-workers reported the synthesis and X-ray crystal structure of a dtne-based binuclear complex, $[Ru_2(dtne)(\mu\text{-}O)_2(\mu\text{-}CO_3)]PF_6\cdot 5H_2O$, in which the mixed-valent Ru(II/III) centers were bridged by two μ-oxo groups and one μ-carbonato group at a distance of 2.469 Å.[6]

In an attempt to promote bridge formation between the metal centers, potential donor atoms such as oxygen and nitrogen have been incorporated into the ligand backbone joining the two tacn compartments. Hendrickson and co-workers synthesized a methylphenol-linked bis(tacn) ligand, bcmp (Chart 1), and formed a mixed-valent binuclear Mn(II/III) complex, $[Mn_2(bcmp)(\mu\text{-}OAc)_2]^{2+}$, in which the metals were bridged by two μ-acetato groups and the oxygen from the phenolic linking group.[8] Recently, Kaden and co-workers synthesized a bis(tacn) ligand, dtnpy (Chart 1), containing a pyrazole moiety as an endogenous bridging unit.[9] A binuclear Cu(II) complex was formed in which two pentacoordinate Cu(II) centers in a distorted square pyramidal geometry were linked through the nitrogens on the pyrazole group and an end-on coordinated azido group.

The number of *functionalized* bis(tacn) ligands reported to date is relatively small. Schröder and co-workers recently reported the synthesis of a bis(pentadentate) ligand with alcohol pendant arms attached to each secondary nitrogen in dtne.[14] Binuclear complexes of this ligand incorporating Co(II), Ni(II), Zn(II), and Cu(II) were prepared. X-ray diffraction studies of the Cu(II) complex showed that the two pentadentate compartments are oriented toward one another in a *syn*-configuration. This orienation was a result of intramolecular H-bonding between protonated and deprotonated alcohol groups from different compartments of the ligand. In the Co(II), Ni(II), and Zn(II) complexes, all four alcohol groups remained protonated, and this led the complexes to adopt an open *anti*-configuration; i.e., the two compartments were oriented away from one another. This example illustrates how the addition of pendant arms to a bis-macrocycle can increase the coordination capabilities of the ligand and hence influence the type of compounds formed on complexation.

In this paper, we report the synthesis and characterization of a series of binucleating bis(pentadentate) ligands, tmpdtne, tmpdtnp, and tmpdtnb, which have been prepared by the addition of four 2-pyridylmethyl pendant arms to the bis(tacn) ligands, dtne, dtnp, and dtnb (Chart 1). The Cu(II) complexes of each new ligand have been prepared and their properties compared to those of the mononuclear analogue $[Cu(dmptacn)](ClO_4)_2$, which was reported previously[15] but not structurally characterized.

Experimental Section

Materials and Reagents. Reagent or analytical grade materials were used throughout the study. The ligands 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne),[4] 1,3-bis(1,4,7-triaza-1-cyclononyl)propane (dtnp),[4] 1,4-bis(1,4,7-triaza-1-cyclononyl)butane (dtnb),[1] and 1,4-bis(2-methylpyridyl)-1,4,7-triazacyclononane (dmptacn)[15] were all prepared by published methods. The copper complex, $[Cu(dmptacn)](ClO_4)_2$ (**1**), was also prepared by a literature method.[15] Dark blue crystals of **1** suitable for single-crystal X-ray analysis were grown by slow evaporation of a water/acetonitrile mixture of the complex.

Physical Measurements. Proton and carbon spectra were recorded on a Bruker AC200 spectrometer. Infrared spectra were measured on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Cary 3 spectrophotometer. Electron microprobe analyses were made with a JOEL JSM-1 scanning electron microscope through an NEC X-ray detector and pulse processing system connected to a Packard multichannel analyzer. Microanalyses were performed by Chemical and Micro-Analytical Services (CMAS), Melbourne, Australia. ESR spectra were measured on a Bruker ECS 106 spectrometer as frozen (99 K) DMF solutions using a concentration of 0.5 mM. Perchlorate analyses were determined gravimetrically as Ph_4AsClO_4. Copper analyses were carried out using EDTA titrations with fast sulphon black as an indicator. Conductivity measurements were made using a Crison 522 conductimeter with Pt black electrodes. Standard KCl (0.020 M) with a conductivity of 2.77 mS cm^{-1} was used as a calibrant. Room-temperature magnetic moments were determined by the Faraday method. Diamagnetic corrections were made using Pascal's constants. Low-temperature magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID magnetometer as described in ref 15.

Caution! *Although no problems were encountered in this work, transition metal perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.*

Synthesis of 1,2-Bis[*N*,*N*′-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]ethane (tmpdtne). To a stirred solution of dtne·6HBr (1.60 g, 2.08 mmol) in H_2O (20 mL) was added 4 molar equiv of 2-picolyl chloride hydrochloride (1.36 g, 8.32 mmol). Sodium hydroxide (2 M) was added until pH 10 was reached. After daily readjustment of the pH to 10 (for 3 or 4 days) to ensure the reaction had gone to completion, the pH was increased to 14, whereupon an oil formed. On cooling of the mixture in ice, the oil could be more easily separated from the aqueous solution. It was collected and dissolved in chloroform, and the solution was dried over sodium sulfate. Evaporation of the solvent gave the ligand as a red oil (yield 1.30 g, 96%). To purify the product, the HBr salt of the ligand was formed. The oil was dissolved in the minimum amount of concentrated hydrobromic acid and the salt precipitated by the addition of ethanol and ether.

Characterization. Anal. Calc for $(C_{18}H_{24}N_5)_2C_2H_4\cdot 9HBr$: C, 33.1; H, 4.4; N, 10.2; Br, 52.3. Found: C, 33.1; H, 4.7; N, 10.2; Br, 51.9. ^1H NMR (D_2O): $\delta(CH_2)$ 2.82 s (8H), 3.19 t (8H), 3.44 t (8H), 3.71 s (4H); δ(Py CH_2) 4.37 s (8H); δ(Ar CH) 7.95 m, 8.04 m, 8.52 m, 8.72

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(14) Blake, A. J.; Donlevy, T. M.; England, P. A.; Fallis, I. A.; Parsons, S.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1981.

(15) McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254.

m (16H). ^{13}C NMR (D_2O): δ(ring CH_2) 48.77, 49.74, 51.24; δ(bridge CH_2) 49.92; δ(Py CH_2) 56.40; δ(Ar CH) 126.23, 127.41, 142.44, 146.45; δ(quaternary C) 151.51. Selected IR bands (cm^{-1}): 3386 s (H_2O); 2350−3050 s (C−H and protonated N−H groups); 1613 s, 1540 m, 1500 m (skeletal vibrations of pyridine rings).

Synthesis of 1,3-Bis[*N,N′*-bis(2-methylpyridyl)-1,4,7-triazacyclononyl]propane (tmpdtnp). The method outlined for the preparation of tmpdtne was employed except that dtnp·6HBr (6.0 g, 7.66 mmol) was used as the starting material. The product also separated as a red oil (yield 4.95 g, 98%). To further purify the oil and fully characterize the ligand, the HBr salt was formed as described above.

Characterization. Anal. Calc for $(C_{18}H_{24}N_5)_2C_3H_6{\cdot}7HBr{\cdot}3H_2O$: C, 36.5; H, 5.2; N, 10.9. Found: C, 36.7; H, 5.6; N, 10.6. ^1H NMR (D_2O): δ(CH_2) 2.52 m (2H), 2.81 s (8H), 3.27 m (8H), 3.64 m (4H), 3.68 s (8H); δ(Py CH_2) 4.42 s (8H); δ(Ar CH) 8.07 m, 8.15 m, 8.67 m, 8.78m (16H). ^{13}C NMR (D_2O): δ(ring CH_2) 47.65, 50.05, 51.68; δ(bridge CH_2) 51.98, 18.71; δ(Py CH_2) 56.15; δ(Ar CH) 126.42, 127.59, 141.59, 147.39; δ(quaternary C) 151.87. Selected IR bands (cm^{-1}): 3414 s (H_2O), 2350−3050 m (C−H and protonated N−H groups); 1617 s, 1538 m, 1500 w (skeletal vibrations of pyridine rings).

Synthesis of 1,4-Bis[*N,N′*-bis(2-methylpyridyl)-1,4,7-triazacyclononyl]butane (tmpdtnb). The method outlined for the preparation of tmpdtne was employed using dtnb·6HBr (6.00 g, 7.53 mmol) as the starting material. The product also appeared as a red oil (yield 4.95 g, 97%). The hydrated HBr salt of the ligand was formed as described above.

Characterization. Anal. Calc for $(C_{18}H_{24}N_5)_2C_4H_8{\cdot}10HBr{\cdot}5H_2O$ C, 30.3; H, 4.8; N, 8.8. Found: C, 30.1; H, 4.4; N, 8.6. ^1H NMR (D_2O): δ(CH_2) 1.98 m (4H), 2.75 (8H), 3.21 (8H), 3.54 (8H), 3.55 m (4H); δ(Py CH_2) 4.37 s (8H); δ(Ar CH) 8.02 m, 8.10 m, 8.62 m, 8.75 m (16H). ^{13}C NMR (D_2O): δ(ring CH_2) 47.54, 49.88, 51.69; δ(bridge CH_2) 55.02, 21.02; δ(Py CH_2) 56.01; δ(Ar CH) 126.39, 127.53, 141.49, 147.41; δ(quaternary C) 151.87. Selected IR bands (cm^{-1}): 3386 s (H_2O); 2350−3050 s (C−H and protonated N−H groups); 1616 s, 1540 m, 1502m (skeletal vibrations of pyridine ring).

Synthesis of $[Cu_2(tmpdtne)](ClO_4)_4{\cdot}2H_2O$ (2). Tmpdtne·9HBr (0.061 g, 4.5×10^{-5} mol) was dissolved in H_2O (5 mL) and the solution neutralized (pH 7) by adding sodium hydroxide (1 M). An excess of $Cu(NO_3)_2{\cdot}3H_2O$ (0.030 g, 1.2×10^{-4} mol) dissolved in H_2O (5 mL) was added, producing a dark blue solution. Addition of sodium perchlorate (0.2 g) produced a light blue solid, which was collected by filtration and washed with cold water (yield 0.041 g, 76%). Royal blue crystals suitable for X-ray crystallography were grown by slow evaporation of a water/acetonitrile mixture.

Characterization. Anal. Calc for $[Cu_2(C_{18}H_{24}N_5)_2C_2H_4](ClO_4)_4{\cdot}2H_2O$: C, 37.7; H, 4.7; N, 11.6; ClO_4^-, 32.9; Cu, 10.5. Found: C, 37.7; H, 4.6; N, 11.8; ClO_4^-, 32.6; Cu, 10.5. Electron microprobe: Cl:Cu ratio 2:1. Molar conductivity (CH_3CN): 450 S cm^2 mol^{-1}. Visible spectrum (CH_3CN): $\lambda_{max} = 598$ nm, $\epsilon_{max} = 398$ M^{-1} cm^{-1}. Selected IR bands (KBr, cm^{-1}): 3416 s (H_2O), 1614 s, 1486 m, 1450 m (skeletal vibrations of pyridine rings); 1088 vs, 626 s (ClO_4^-). Magnetic moment: μ_{eff} (296 K) = 1.89 μ_B per Cu(II).

Synthesis of $[Cu_2(tmpdtnp)](ClO_4)_4$ (3). The method used to prepare compound **2** was followed except that 0.091 g (7.1×10^{-5} mol) of tmpdtnp·7HBr·3H_2O and 0.041 g (1.7×10^{-4} mol) of $Cu(NO_3)_2{\cdot}3H_2O$ were used (yield 0.062 g, 74%).

Characterization. Anal. Calc for $[Cu_2(C_{18}H_{24}N_5)_2C_3H_6](ClO_4)_4$: C, 39.4; H, 4.6; N, 11.8; ClO_4^-, 33.5; Cu, 10.7. Found: C, 39.2; H, 4.7; N, 11.6; ClO_4^-, 33.3; Cu, 10.4. Electron microprobe: Cl:Cu ratio 2:1. Visible spectrum (CH_3CN): $\lambda_{max} = 602$ nm, $\epsilon_{max} = 436$ M^{-1} cm^{-1}. Selected IR bands (KBr, cm^{-1}): 3423 s (H_2O); 1612 s, 1487 m, 1449 m (skeletal vibrations of pyridine rings); 1089 vs, 627 s (ClO_4^-). Magnetic moment: μ_{eff} (296 K) = 1.89 μ_B per Cu(II).

Synthesis of $[Cu_2(tmpdtnb)](ClO_4)_4$ (4). The method used to prepare compound **2** was followed except that 0.077 g (4.84×10^{-5} mol) of tmpdtnb·10HBr·5H_2O and 0.030 g (1.2×10^{-4} mol) of $Cu(NO_3)_2{\cdot}3H_2O$ were used (yield 0.043 g, 75%).

Characterization. Anal. Calc for $[Cu_2(C_{18}H_{24}N_5)_2C_4H_8](ClO_4)_4$: C, 40.0; H, 4.7; N, 11.7; ClO_4^-, 33.1; Cu, 10.6. Found: C, 39.9; H, 4.6; N, 11.9; ClO_4^-, 33.2; Cu, 10.6. Electron microprobe: Cl:Cu ratio 2:1. Visible spectrum (CH_3CN): $\lambda_{max} = 600$ nm, $\epsilon_{max} = 420$ M^{-1} cm^{-1}. Selected IR bands (KBr, cm^{-1}): 3430 s (H_2O); 1612 s, 1485 m, 1449 m (skeletal vibrations of pyridine rings); 1089 vs, 626 s (ClO_4^-). Magnetic moment: μ_{eff} (296K) = 1.84 μ_B per Cu(II).

Table 1. Crystal Data for $[Cu(dmptacn)](ClO_4)_2$ (**1**) and $[Cu_2(tmpdtne)](ClO_4)_4{\cdot}2H_2O$ (**2**)^a

	1	**2**
empirical formula	$C_{18}H_{25}Cl_2CuN_5O_8$	$C_{38}H_{56}Cl_4Cu_2N_{10}O_{18}$
fw	573.9	1209.8
space group	orthorhombic, *Pbcn*	monoclinic, $P2_1/c$
a, Å	19.467(4)	13.885(1)
b, Å	16.798(6)	13.218(2)
c, Å	14.204(4)	13.531(3)
β, deg	90	106.04(1)
V, Å^3	4644(1)	2386(1)
Z	8	2 (dimers)
T (°C)	20	20
λ (Å)	0.71703	0.71703
ρ_{calcd}, g cm^{-3}	1.641	1.683
h,k,l range collected	$0 \le h \le 18$	$0 \le h \le 18$
	$0 \le k \le 25$	$0 \le k \le 18$
	$0 \le l \le 18$	$-18 \le l \le 18$
max/min transm factors	0.915/1.044	0.930/1.044
F(000)	2360	1248
μ, cm^{-1}	12.25	12.00
no. of data measd	5319	6197
no. of unique data	5319	5957
no. of obsd data [$I \ge 3.0\sigma(I)$]	1806	3509
R	0.066	0.055
R_w	0.056	0.063

^{a} $R = \sum|F_o - F_c|)/\sum|F_o|$; $R_w = \sum(|F_o - F_c|)w^{1/2}/\sum|F_o|w^{1/2}$ and $w = [\sigma^2(F_o)]^{-1}$.

Crystal Structure Determination. Intensity data for blue crystal blocks of $[Cu(dmptacn)](ClO_4)_2$ (**1**) (0.23 × 0.24 × 0.36 mm) and $[Cu_2(tmpdtne)](ClO_4)_4{\cdot}2H_2O$ (**2**) (0.11 × 0.40 × 0.40 mm) were measured at 293 K on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å; the $\omega-2\theta$ scan technique was employed to measure data such that θ_{max} was 25.0° (27.5° for **2**). No significant decomposition of the crystals occurred during their respective data collections, and only absorption-corrected data[16] which satisfied the $I \ge 3.0\sigma(I)$ criterion were used in the subsequent analyses. An empirical absorption correction was applied in each case.[16] Crystal data are summarized in Table 1.

The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on *F*.[17] Generally, non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the models at their calculated positions (C−H, N−H 0.97 Å); the water-bound H atoms were not located in **2**. In both refinements some disorder was detected with some of the perchlorate O atom positions. Thus, in **1**, the O(7) and O(8) atoms were refined over two sites, each with 50% site occupancy, employing isotropic thermal parameters. In **2**, the O(8) site was refined over two positions, again each with 50% site occupancy. At convergence (σ weights) $R = 0.066$ and $R_w = 0.056$ for **1** and $R = 0.055$ and $R_w = 0.063$ for **2**; final refinement details are collected in Table 1. Scattering factors for all atoms were those incorporated in the teXsan program.[17] Fractional atomic coordinates are listed in Tables 2 and 3; the numbering schemes are shown in Figures 1 and 2, which were drawn with the ORTEP[18] program and shown at 30 and 20% probability ellipsoids, respectively.

Results and Discussion

Preparation of Ligands. The synthesis of tmpdtne, tmpdtnp, and tmpdtnb involved reaction of aqueous solutions of the hexahydrobromide salts of dtne, dtnp, and dtnb with 4 molar equiv of 2-picolyl chloride hydrochloride at pH 10 for 2−3 days (Scheme 1). After this time, the pH was increased to 14 and

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(16) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(17) teXsan: Structure Analysis Software. Molecular Structure Corp., The Woodlands, TX.

(18) Sheldrick, G. M. SHELXS86: Program for the Automatic Solution of Crystal Structure. University of Göttingen, Germany, 1986.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Cu(dmptacn)](ClO_4)_2$ (**1**)

Cu−N(1)	2.162(8)	Cu−N(2)	2.016(8)
Cu−N(3)	2.071(8)	Cu−N(4)	2.000(8)
Cu−N(5)	2.015(8)	N(1)−C(1)	1.51(1)
N(1)−C(6)	1.48(1)	N(2)−C(2)	1.49(1)
N(2)−C(3)	1.51(1)	N(2)−C(13)	1.47(1)
N(3)−C(4)	1.47(1)	N(3)−C(5)	1.49(1)
N(3)−C(7)	1.50(1)	N(4)−C(8)	1.33(1)
N(4)−C(12)	1.35(1)	N(5)−C(14)	1.36(1)
N(5)−C(18)	1.32(1)		

N(1)−Cu−N(2)	84.8(3)	N(1)−Cu−N(3)	85.4(3)
N(1)−Cu−N(4)	97.5(4)	N(1)−Cu−N(5)	122.1(4)
N(2)−Cu−N(3)	85.7(4)	N(2)−Cu−N(4)	168.1(4)
N(2)−Cu−N(5)	83.3(4)	N(3)−Cu−N(4)	82.9(4)
N(3)−Cu−N(5)	149.0(3)	N(4)−Cu−N(5)	105.0(4)
Cu−N(1)−C(1)	106.1(6)	Cu−N(1)−C(6)	101.7(6)
C(1)−N(1)−C(6)	115(1)	Cu−N(2)−C(2)	104.9(6)
Cu−N(2)−C(3)	109.1(6)	Cu−N(2)−C(13)	105.9(6)
C(2)−N(2)−C(3)	112.7(8)	C(2)−N(2)−C(13)	110.2(9)
C(3)−N(2)−C(13)	113.4(9)	Cu−N(3)−C(4)	102.7(7)
Cu−N(3)−C(5)	108.1(7)	Cu−N(3)−C(7)	103.7(6)
C(4)−N(3)−C(5)	113.6(9)	C(4)−N(3)−C(7)	113.5(9)
C(5)−N(3)−C(7)	113.9(9)	Cu−N(4)−C(8)	112.6(8)
Cu−N(4)−C(12)	126.3(8)	C(8)−N(4)−C(12)	121(1)
Cu−N(5)−C(14)	113.3(7)	Cu−N(5)−C(18)	126.7(9)
C(14)−N(5)−C(18)	120(1)		

Table 3. Selected Bond Distances (deg) and Angles (deg) for $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (**2**)

Cu−N(1)	2.205(4)	Cu−N(2)	1.993(4)
Cu−N(3)	2.009(4)	Cu−N(4)	1.978(4)
Cu−N(5)	2.001(4)	N(1)−C(1)	1.465(6)
N(1)−C(6)	1.465(6)	N(1)−C(19)	1.471(6)
N(2)−C(2)	1.473(7)	N(2)−C(3)	1.480(6)
N(2)−C(13)	1.474(7)	N(3)−C(4)	1.491(6)
N(3)−C(5)	1.476(7)	N(3)−C(7)	1.465(7)
N(4)−C(8)	1.330(6)	N(4)−C(12)	1.332(6)
N(5)−C(14)	1.334(7)	N(5)−C(18)	1.326(6)
C(19)−C(19′)	1.517(9)		

N(1)−Cu−N(2)	83.8(2)	N(1)−Cu−N(3)	85.4(2)
N(1)−Cu−N(4)	101.3(2)	N(1)−Cu−N(5)	106.7(2)
N(2)−Cu−N(3)	85.3(2)	N(2)−Cu−N(4)	167.0(2)
N(2)−Cu−N(5)	81.1(2)	N(3)−Cu−N(4)	83.2(2)
N(3)−Cu−N(5)	160.6(2)	N(4)−Cu−N(5)	108.3(2)
Cu−N(1)−C(1)	106.2(3)	Cu−N(1)−C(6)	99.5(3)
Cu−N(1)−C(19)	110.0(3)	C(1)−N(1)−C(6)	113.8(4)
C(1)−N(1)−C(19)	114.0(4)	C(6)−N(1)−C(19)	112.3(4)
Cu−N(2)−C(2)	106.7(3)	Cu−N(2)−C(3)	110.6(3)
Cu−N(2)−C(13)	104.3(3)	C(2)−N(2)−C(3)	111.6(4)
C(2)−N(2)−C(13)	110.7(4)	C(3)−N(2)−C(13)	112.6(4)
Cu−N(3)−C(4)	103.0(3)	Cu−N(3)−C(5)	108.8(3)
Cu−N(3)−C(7)	107.2(3)	C(4)−N(3)−C(5)	112.3(4)
C(4)−N(3)−C(7)	111.9(4)	C(5)−N(3)−C(7)	112.9(4)
Cu−N(4)−C(8)	113.3(4)	Cu−N(4)−C(12)	128.8(4)
C(8)−N(4)−C(12)	117.7(5)	Cu−N(5)−C(14)	111.0(3)
Cu−N(5)−C(18)	130.1(4)	C(14)−N(5)−C(18)	118.8(5)

the products precipitated from the aqueous medium in the form of red-brown oils. The free ligands were found to be hygroscopic, and satisfactory elemental and NMR spectroscopic characterization could not be obtained. In addition, the yields of complexes produced directly from these oils were much lower than expected on the basis of the amounts of ligands used.

Conversion of the ligands to the hydrobromide salts allowed detailed ^1H and ^{13}C NMR spectroscopic and elemental analyses to be carried out. Isolation of these salts was difficult because of their extremely hygroscopic nature and tendency to convert back to oils. Elemental analyses of the salts were consistent with the formulas tmpdtne·9HBr, tmpdtnp·7HBr·3H$_2$O, and tmpdtnb·10HBr·5H$_2$O. The KBr disk infrared spectra of these HBr salts show broad stretches in the 2350−3050 cm^{-1} region due to the protonated nitrogens. Bands corresponding to vibrations of the pyridyl rings were observed at 1615, 1540, and 1500 cm^{-1}. In the spectrum of the unprotonated ligand, tmpdtnb, these bands are shifted to lower frequency: 1593, 1475, and 1436 cm^{-1}.

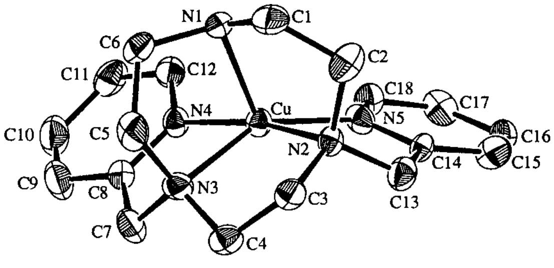


Figure 1. Molecular structure and crystallographic numbering scheme for the cation in $[Cu(dmptacn)](ClO_4)_2$ (**1**).

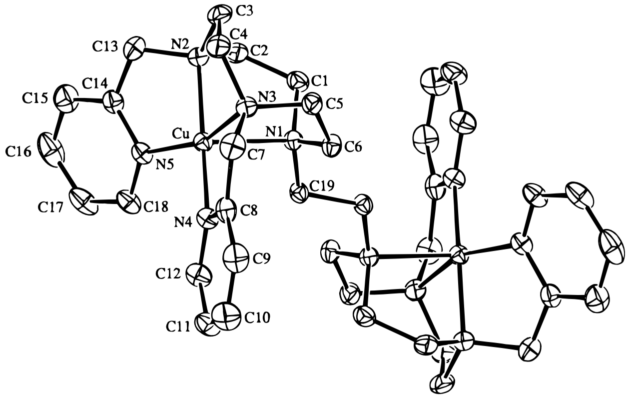
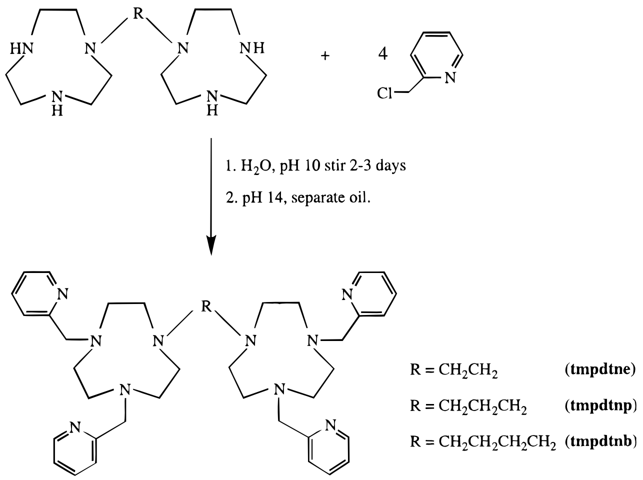


Figure 2. Molecular structure and crystallographic numbering scheme for the cation in $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (**2**).

Scheme 1



The ^{13}C NMR spectrum of tmpdtne·9HBr recorded in D$_2$O (Figure 3) clearly defines each unique carbon atom and confirms the symmetric nature of the ligand. The three signals labeled 1−3 at 48.77, 49.74, and 51.24 ppm, respectively, correspond to the three pairs of carbon atoms on each tacn ring. Peak 4 at 49.92 ppm is assigned to the two identical bridging carbons. These four signals appeared as one broad signal in the ^{13}C NMR spectrum of the free ligand and could not be resolved. The four equivalent carbon atoms connecting each of the pyridine rings to the bis(tacn) backbone are further downfield at 56.40 ppm (peak 5). Signals 7−10 correspond to the four CH carbons on each pyridine ring at 126.23, 127.41, 142.44, and 146.45 ppm, respectively, while the aromatic quaternary carbons are deshielded most and appear at 151.51 ppm (peak 6). The ^{13}C NMR spectra of the other two bis(pentadentate) ligands are

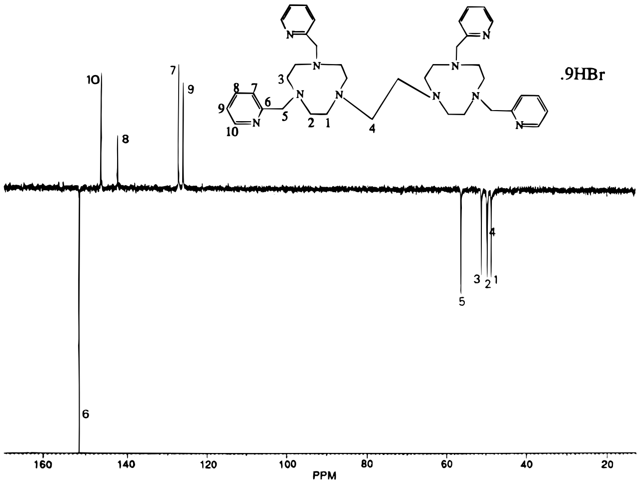


Figure 3. ^{13}C NMR spectrum of tmpdtne·9HBr run in D_2O.

similar except that they display an extra signal at 18.71 ppm for tmpdtnp·7HBr·$3H_2O$ and 21.02 ppm for tmpdtnb·10HBr·$5H_2O$ representing the extra carbon(s) in the bridging units.

Preparation of Copper(II) Complexes. The synthesis of $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (**2**), $[Cu_2(tmpdtnp)](ClO_4)_4$ (**3,**) and $[Cu_2(tmpdtnb)](ClO_4)_4$ (**4**) was achieved by reacting the hydrobromide salts of the ligands with $Cu(NO_3)_2 \cdot 3H_2O$ in aqueous solution at pH 7 followed by addition of $NaClO_4$. Elemental analyses of the three compounds are consistent with the composition $[Cu_2L](ClO_4)_4 \cdot xH_2O$ where $x = 2$ for L = tmpdtne and $x = 0$ for L = tmpdtnp and tmpdtnb. The IR spectra of the complexes show bands due to the pyridine ring skeletal vibrations in the 1400−1620 cm^{-1} region and bands at 1090 and 625 cm^{-1} due to the perchlorate counter-ions. The mononuclear complex $[Cu(dmptacn)](ClO_4)_2$ (**1**) is easily distinguished from the bridged complexes as it exhibits a strong band at 3336 cm^{-1} due to the NH stretch.

Crystal Structures of $[Cu(dmptacn)](ClO_4)_2$ (1) and $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ (2). The molecular structure of the cation in **1** is shown in Figure 1, and selected interatomic parameters are listed in Table 2. The mononuclear complex features an N_5 donor set derived from the pentadentate ligand which defines a distorted square pyramidal geometry about the Cu(II) cation; the secondary amine N(1) atom occupies the apical position in this description. The deviations of the N(2), N(3), N(4), and N(5) atoms from the least-squares plane through them are 0.228(9), −0.210(9), 0.202(9), and −0.182(9) Å, respectively, and the Cu atom lies 0.322(1) Å out of the plane in the direction of the N(1) atom. The greatest deviation from the ideal geometry is manifested in the N(1)−Cu−N(5) angle of 122.1(4)°, which can be traced to the restricted N(1)−Cu−N(3) bite angle of 85.4(3)°. The Cu−N(1) bond distance of 2.162(8) Å is significantly longer than the remaining Cu−N interactions, which range from 2.071(8) Å [N(3)] to 2.000(8) Å [N(4)]. These Cu−N distances compare well with those in the Cu(II) complex of 4,7-bis(2-methylpyridyl)-1-thia-4,7-diazacyclononane.[19] The pentadentate mode of coordination leads to the formation of five five-membered rings, three of which have ethyl backbones. The two rings incorporating the pyridine rings are puckered as seen in the values of the Cu/N(2)/C(13)/C(14) and Cu/N(3)/C(7)/C(8) torsion angles of 31(1) and −37(1)°, respectively. There are some important interionic associations in the lattice. Most notable is a hydrogen-bonding contact involving the N(1)H hydrogen atom and a perchlorate O(2) atom (symmetry operation: $0.5 - x$, $0.5 - y$, $0.5 + z$) of 2.46 Å (N(1)···O(2) is 3.14 Å). There is also a contact between the Cu center and one of the disordered O(8) atoms such that Cu···O(8′) is 2.99(2) Å. Given the relatively long distance of this interaction and the fact that the O(8′) atom has a site occupancy factor of 0.5, this interaction is not considered significant.

The dinuclear cation in **2** (Figure 2, Table 3) is centrosymmetric and features two pentadentate ligands linked via an ethane bridge that connects the N(1) atoms which are replaced by hydrogen in **1**. The two pentadentate compartments of the ligand are oriented away from each other in an *anti*-configuration as was found for the Co(II), Ni(II), and Zn(II) complexes of the corresponding ligand with alcohol pendant groups.[14] This open structure is probably favored by steric and electrostatic factors and results in an intramolecular Cu···Cu′ separation of 7.4809(6) Å while the shortest intermolecular Cu···Cu distance is 8.1168(8) Å. Each pentadentate half of the ligand defines a distorted square pyramidal geometry with the N(1) atom in the apical position as for **1**. The Cu−N(1) distance of 2.205(4) Å is longer than that in **1**, and concomitantly there has been a uniform contraction in the remaining Cu−N distances which range from 1.978(4) Å [N(4)] to 2.009(4) Å [N(3)]. This 0.043 Å elongation of the Cu−N(1) bond in the binuclear complex, **2**, is probably due to the greater electron-withdrawing power of the carbon atom C(19) from the ethylene bridge causing the tertiary N(1) nitrogen to draw the tacn ring outward a little. Such an effect is not seen with the secondary N(1) nitrogen in the mononuclear complex, **1**.

The distortions from the ideal geometry are less in **2**, with the maximum deviation being found in the N(4)−Cu−N(5) angle of 108.3(2)°. The atoms comprising the basal plane, i.e. N(2) to N(5), deviate 0.073(4), −0.065(4), 0.052(4), and −0.059(4) Å, respectively, from the least-squares plane through them, with the Cu atom lying 0.1931(6) Å above this plane in the direction of the N(1) atom. The lack of planarity found in the two five-membered rings involving the pyridine rings in **1** is not evident in **2**, as seen in the values of the Cu/N(4)/C(8)/C(7) and Cu/N(5)/C(14)/C(13) torsion angles of 7.3(6) and 4.1(6)°, respectively. Thus, even though one might expect the bridged complex to show more distortion, the degree of distortion from square pyramidal (SP) geometry toward trigonal bipyramidal (TB) geometry, calculated using the approach of Addison *et al.*,[20] is only 11% for the binuclear complex whereas it is 32% for the mononuclear complex. In other five-coordinate complexes of, for example, tmpa (tris(2-pyridylmethyl)amine)[21] and the pentadenate ligand trenpy, which is derived from tren (tris(2-aminoethyl)amine),[15] the geometry about the Cu(II) center is closer to TB. For the latter, however, the introduction of unsaturation gives rise to a geometry that is closer to SP. This is demonstrated by the structure of $[Cu(trenimpy)]^{2+}$, where the degree of distortion of the Cu(II) center from SP is similar to that in **1**.[15]

There are several intermolecular contacts in the crystallographic unit cell of **2** which comprises two dinuclear cations, eight perchlorate molecules, and four water molecules of crystallization. A close Cu···O(5) contact of 2.883(6) Å is noted; however, this is not regarded as significant (see above). The water molecule O(9) atom (H atoms were not located in the X-ray study) forms two close contacts with perchlorate O atoms, i.e. O(9)···O(1) 2.853(7) Å, O(9)···O(7) 3.17(2) Å, and O(9)···O(7′) 2.86(2) Å (the O(7) and O(7′) atoms each have 50% site occupancy factors).

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(19) Wasielewski, K; Mattes, R. *Acta Crystallogr. Sect. C* **1990**, *46*, 1826.

(20) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349.

(21) Jacobson, R. R.; Tyeklar, Z.; Karlin, K. D.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 2035.

Table 4. UV−Visible Spectral Data for Complexes **1**−**4**

complex	solvent	λ_{max}, nm (ϵ_{max})
[Cu(dmptacn)](ClO_4)$_2$ (**1**)	CH_3CN	612 (210); 613[a] (176)
	Nujol mull	619 br (600)[a]
[Cu_2(tmpdtne)](ClO_4)$_4$·$2H_2O$ (**2**)	CH_3CN	598 (398)
	Nujol mull	602 br
[Cu_2(tmpdtnp)](ClO_4)$_4$ (**3**)	CH_3CN	602 (436)
	Nujol mull	602 br
[Cu_2(tmpdtnb)](ClO_4)$_4$ (**4**)	CH_3CN	600 (420)
	Nujol mull	596 br

[a] Reference 15.

Electronic Spectra and Magnetic Properties. The UV−visible spectral data for the complexes are shown in Table 4. The three binuclear complexes **2**−**4** have absorbance maxima in the 598−602 nm range. For five-coordinate Cu(II) complexes, this spectral feature is typical of Cu(II) complexes with SP or distorted SP geometries which generally exhibit a band in the 550−660 nm range (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$).[15] The mononuclear complex **1** displays a slightly higher λ_{max} of 612 nm, suggesting that, in solution, its geometry is distorted more toward trigonal bipyramidal than that of the binuclear complexes. The solid state spectra of the complexes recorded as Nujol mulls are similar to the solution spectra, indicating little change in stereochemistry on dissolution. The spectra of **1** and **2** are entirely consistent with the degree of distortion from SP geometry found in the X-ray structure.

The effective magnetic moments, μ_{eff}(per Cu), of complexes **2**−**4** are typical of Cu(II) complexes, ranging between 1.84 and 1.89 μ_B at 296 K. Variable-temperature magnetic susceptibility measurements (4.5−296 K) showed little deviation from the room-temperature magnetic moment values, indicating the absence of exchange coupling between the Cu(II) centers. This is a reflection of the large Cu···Cu separations which, for compound **2**, are ≥7.48 Å.

Electron Spin Resonance Spectra. The ESR spectra of complexes **1**−**4** were recorded for frozen DMF solutions at 99 K and are shown in Figure 4. Complex **1** shows an ESR spectrum typical of a mononuclear Cu(II) complex with nuclear spin $^3/_2$; three of the four expected hyperfine signals are displayed, with the fourth being hidden under the $g_\perp$ line. The parameters obtained from this ESR spectrum ($g_{||} = 2.23$, $A_{||} = 170 \times 10^4$ cm^{-1}, and $g_\perp = 2.049$) are typical of SP Cu(II) complexes.[15] For the three binuclear complexes, there is a clear relationship between the length of the alkyl bridge linking the two pentadentate compartments and the ESR spectrum. For both **2** and **3**, there are clearly more than four hyperfine signals, although the signals are weaker for **3**. In contrast, the ESR spectrum and associated parameters for **4** ($g_{||} = 2.22$, $A_{||} = 170 \times 10^4$ cm^{-1}, and $g_\perp = 2.045$) closely match those found for **1.**

As discussed earlier, the crystal structure of **2** shows it to be centrosymmetric about the ethane bridge. Hence, the additional hyperfine lines in the ESR spectra are not thought to be due to the Cu(II) centers residing in different environments. To check on the possibility that this behavior was due to coordination of DMF to one of the Cu(II) centers, thereby creating two different environments, the spectra were also run in nitromethane, a noncoordinating solvent, but were found to be the same as those obtained from frozen DMF solutions. Dissociation of the complex is unlikely to be responsible for the extra hyperfine lines since the Cu(II) complexes of the parent bis(macrocycles) have extremely high stability constants. For example, the stability constant for the binuclear Cu(II) complex of dtnb is ca. 10^{30}.[7]

These considerations point to the existence of weak dipole−dipole coupling between the Cu centers in the binuclear complexes, with the extent of this coupling depending on the Cu···Cu separation, which is governed by the length of the alkyl bridge. Thus, ESR spectroscopy suggests that dipole−dipole coupling exists in the ethane- and propane-bridged complexes, **2** and **3**, but not in the butane-bridged complex, **4**. The behavior of extremely weakly exchange-coupled systems is well documented.[22,23] In such systems, the presence of, for example, magnetic dipolar interactions with strengths in fractions of a wavenumber, can give rise to spectra that are very different from those of the uncoupled systems. Murase and co-workers[24] have observed such behavior for the binuclear Cu(II) complexes of a series of alkyl-bridged unsaturated bis(tetradentate) macrocycles. The room-temperature magnetic moments were all larger than the spin-only value, and these decreased only slightly at low temperatures. ESR measurements revealed that intramolecular coupling existed within these complexes and the degree of interaction decreased as the bridging chain length increased.

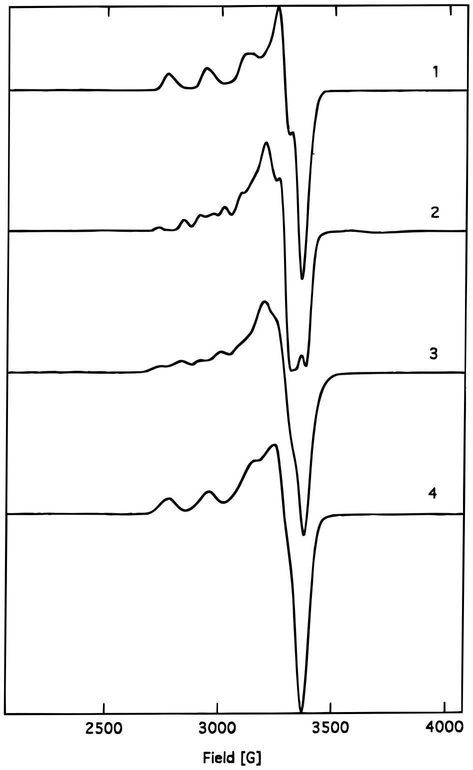

Figure 4. Frozen-solution (99 K) ESR spectra of Cu(II) complexes **1**−**4** determined in DMF at X-band frequency.

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Supporting Information Available: Tables of fractional atomic coordinates, H atom parameters, anisotropic thermal parameters, and all bond distances and angles for [Cu(dmptacn)](ClO_4)$_2$ and [Cu(tmpdtne)](ClO_4)$_4$·$2H_2O$ (13 pages). Ordering information is given on any current masthead page.

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(22) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173.
(23) Bencini, A.; Gatteschi, D. *EPR of exchange coupled systems*; Springer-Verlag: Berlin, Heidelberg, 1990.
(24) Murase, I.; Hamada, S.; Ueno, S.; Kida, S. *Synth. React. Inorg. Met.-Org. Chem.* **1983**, *13*, 191.