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Preparation, Crystal and Molecular Structures, and Properties of Tetrabromo(1,5,9,13,17,21-hexaazacyclotetracosane)dicopper(II) and Bromo(1,5,9-triazacyclododecane)zinc(II) Bromide. Separation of Mono- and Binucleating Ligands by Selective Complexation

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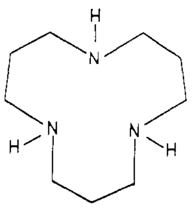
The preparation, spectroscopic properties, and crystal structure are reported for a mononuclear zinc(II) complex containing the 1,5,9-triazacyclododecane ligand ([12]aneN_3) and a binuclear copper(II) complex containing the hexaaza macrocyclic ligand 1,5,9,13,17,21-hexaazacyclotetracosane ([24]aneN_6). The synthesis of an approximately 10:1 [12]aneN_3:[24]aneN_6 mixture is described along with the separation of these species by selective complexation with zinc(II) and copper(II), respectively. The species Cu_2([24]aneN_6)Br_4 crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with $a = 9.622$ (2) Å, $b = 14.054$ (3) Å, $c = 20.558$ (3) Å, $\beta = 91.700$ (13)°, $V = 2778.9$ (8) Å^3, and $Z = 4$. The structure was solved (with difficulty, due to a large percentage of systematically weak reflections) and was refined to $R_F = 8.6\%$ for all 2469 independent data. The two copper(II) ions lie inside the macrocyclic ligand. Each has a square-pyramidal coordination environment, with two nitrogen atoms and two bromide ligands defining the square base and a third nitrogen atom defining the apical position. The basal planes of the copper(II) ions face each other in an eclipsed position with Cu(1)···Cu(2) = 5.432 (3) Å. The basal copper–bromine distances show significant variations (2.427 (3)–2.609 (3) Å), while the basal copper–nitrogen bond lengths (2.025 (11)–2.043 (12) Å) are equivalent and are systematically shorter than the apical copper–nitrogen bond lengths (2.201 (13)–2.224 (14) Å). The mononuclear zinc(II) complex [ZnBr([12]aneN_3)][Br] crystallizes in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with $a = 14.605$ (2) Å, $b = 12.974$ (2) Å, $c = 15.050$ (2) Å, $V = 2851.7$ (6) Å^3, and $Z = 8$. The structure was solved and refined to $R_F = 6.6\%$ for all 1701 independent reflections ($R_F = 3.8\%$ for those 1190 data with $|F_o| > 6\sigma(|F_o|)$). The crystal is composed of [ZnBr([12]aneN_3)]$^+$ cations and Br^- anions. The coordination environment about zinc is tetrahedral, with three nitrogen atoms of the macrocycle and a bromine being the bonded atoms (Zn–N = 2.018 (7)–2.055 (7) Å and Zn–Br = 2.359 (1) Å).

Introduction

Our interest in metalloproteins containing Cu(II) has led us previously to study selected coordination complexes that might mimic certain aspects of the active metal site.[1-3] Recently attention has been directed toward cyclic polyaza complexes.[4-6] Although tetraaza complexes associated with a 14-membered ring received most of the early attention, there has been developing interest in the synthesis and characterization of both triaza[2,7-10] and hexaaza complexes[9,11-16] of macrocyclic ligands. Over the past decade synthetic routes to triaza and hexaaza macrocycles have been well documented. Recently, we found that in preparing 1,5,9-triazacyclododecane ([12]aneN_3, **1**),[17] using Richman and Atkins' modification[18] of Koyama and Yoshino's procedure,[19] a substantial amount of the dimeric product 1,5,9,13,17,21-hexaazacyclotetracosane ([24]aneN_6, **2**) was produced as a byproduct.



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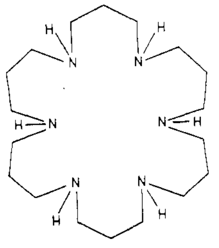
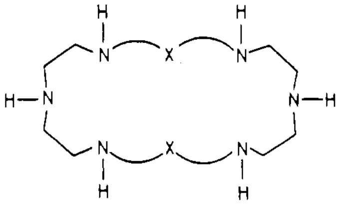


2

Ligand **2** is capable of behaving as a donor to two metal ions (i.e., is a potential binucleating ligand). Several reports of derivatives related to this have appeared previously.[12-15] Copper(II) derivatives of binucleating ligands are of importance as potential bimetallic catalysts and as possible models for the active site in metallobiomolecules.[20-25] To date, however, most monocyclic hexaaza ligands capable of binucleation have contained five-atom bridges between two sets of diethylenetriamine units[11-15] (i.e., **3** with X = $(CH_2)_5$ or $(CH_2CH_2)_2O$).



3

A few "large"[26] polyaza ligands have been described,[27-30] but these contain 7–10 potential nitrogen donor atoms. Little work

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has been reported on [24]aneN_6. We now describe the synthesis, structure, and properties of tetrabromo(1,5,9,13,17,21-hexaazacyclotetracosane)dicopper(II), $Cu_2([24]aneN_6)Br_4$.

The knowledge that "type I" copper(II) in proteins is associated with a pseudotetrahedral geometry or, at least, a C_3 axis[31-34] has led to our being interested also in triaza macrocyclic ligands. We report herewithin, in addition, the synthesis, structure, and properties of bromo(1,5,9-triazacyclododecane)zinc(II) bromide, $[ZnBr([12]aneN_3)]Br$; the [12]aneN_3 ligand is more flexible than [9]aneN_3, which has been found to be unsuitable for tetrahedral coordination.[2,35]

Experimental Section

Materials. All starting materials and solvents were of reagent grade and were used without further purification unless specifically indicated. Elemental analysis and vapor pressure osmometry data were obtained from Galbraith Laboratories, Knoxville, TN.

1,5,9-Triazacyclododecane Trihydrobromide ([12]aneN_3·3HBr). Richman's modification[18] of the procedure of Koyama and Yoshino[19] was employed for the preparation of this compound.

1,5,9,13,17,21-Hexaazacyclotetracosane Hexahydrobromide ([24]aneN_6·6HBr). This compound was synthesized as a byproduct in the synthesis of [12]aneN_3·3HBr. At this point, no attempt was made to separate the two macrocycles.[36] Separation–complexation procedures are described below.

$Cu_2([24]aneN_6)Br_4$. An ethanolic slurry composed of 0.43 g of the [12]aneN_3·3HBr/[24]aneN_6·6HBr mixture and 20 mL of absolute ethanol was gently heated to boiling and neutralized via addition of 0.17 g of potassium hydroxide (3 mmol). The slurry was boiled continuously, with stirring, for 15 min. (Care must be taken to ensure that the solvent level remains constant.) It was then allowed to cool to room temperature and filtered. Dropwise addition to the filtrate of 0.22 g of anhydrous copper(II) bromide (1 mmol) dissolved in 20 mL of absolute ethanol gave initial precipitation of a bright "green" compound. The product was intermittently removed from solution by suction filtration. This process was continued until the appearance of a dark "brown" precipitate. The combined green product was subsequently dissolved in 100 mL of water, the mixture was filtered, and the filtrate was allowed to evaporate slowly in air. Crystals suitable for X-ray diffraction studies were obtained.

Anal. Calcd for $C_{18}H_{42}N_6Br_4Cu_2$: C, 27.39; H, 5.33; N, 10.65. Found: C, 27.36; H, 5.19; N, 10.65.

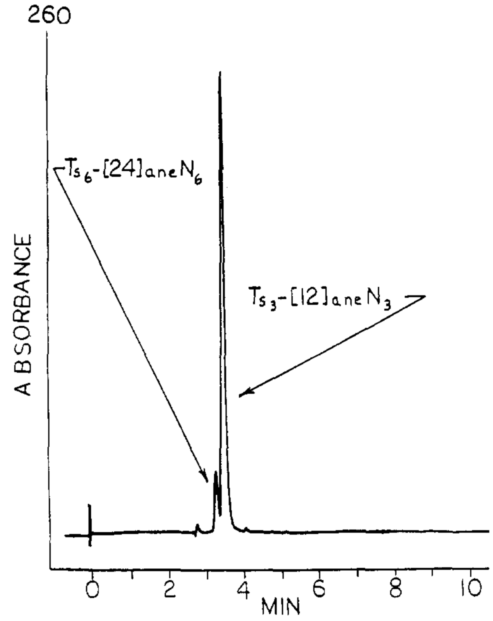

Figure 1. HPLC chromatogram of tosylated ligand precursors. The mobile phase consists of chloroform/hexane (90:10, v/v); flow rate was 1 mL/min, and detection was set at 260 nm.

$[ZnBr([12]aneN_3)]Br$. The neutral-ligand solution was obtained as above. Dropwise addition into 10 mL of an absolute ethanol solution containing 0.23 g (1 mmol) of anhydrous zinc(II) bromide resulted in immediate precipitation of a "white" product, which was subsequently isolated by suction filtration. Recrystallization from a minimal amount of water resulted in the isolation of well-formed colorless crystals suitable for X-ray diffraction studies.

Anal. Calcd for $C_9H_{21}N_3Br_2Zn$: C, 27.26; H, 5.30; N, 10.60. Found: C, 27.35; H, 5.28; N, 10.57.

High-Pressure Liquid Chromatography (HPLC). Tosylated Ligand Precursors.[18,19,36] Small amounts (~10 mg) of tosylated ligand precursor were dissolved in 10-mL portions of chloroform, and the mixtures were filtered through a 0.45 μm disposable-filter assembly (Acrodisc CR, Gelman Sciences, Ann Arbor, MI). These solutions were analyzed for purity with a modified Varian 5000 liquid chromatograph (Varian Associates, Inc., Walnut Creek, CA). This system was equipped with a pneumatic actuated automatic sample injector (Model ACV-6-HPAX, Valco Instruments, Houston, TX), fitted with a 10-μL loop. The detector was a variable-wavelength visible–ultraviolet detector (Model VUV-10, Vari-Chrom, Varian, Walnut Creek, CA). Wavelength was set at 260 nm to detect both tosylated ligand precursors. Chromatograms were recorded on an OmniScrib, dual-pen, strip chart X-Y recorder (Model B 5217-5 I; Houston Instruments, Austin, TX).

Prepacked stainless steel columns (30 × 0.4 cm) containing 5-μm silica were used (Micro Pak Si-5, Varian, Walnut Creek, CA). The mobile phase consisted of an isocratic mixture of HPLC grade chloroform and hexane (90:10, v/v). The column was operated at ambient temperature with a flow rate of 1 mL/min. Chart speed was set at 1 cm/min. Detector bandwidth was fixed at 8 nm and AUFS at 1.0 (see Figure 1).

Spectroscopic Measurements. Optical spectra were obtained as Nujol mulls and in dimethyl sulfoxide and aqueous solutions with a Cary 14 spectrophotometer. Matched quartz cells of 1-cm path length were used. Electron spin resonance (ESR) spectra were obtained on a Varian E-4 spectrophotometer, at 77 K in a 50:50 dimethyl formamide:chloroform frozen glass, by using procedures described previously.[37]

Determination of the Crystal Structure of $Cu_2([24]aneN_6)Br_4$. (A) Collection of X-ray Diffraction Data. A total of three distinct data sets were collected for this species. We describe only the last, which was collected at a slower rate. (It transpires that this species does not give rise to diffraction data of the normally desired quality, for reasons outlined below.)

The crystal selected for the X-ray diffraction study was emerald green, with approximate orthogonal dimensions 0.2 × 0.3 × 0.4 mm; the crystal was sealed into a thin-walled capillary and was mounted on a eucentric goniometer with its longest dimension almost coincident with the ϕ axis of a Syntex P2$_1$ four-circle diffractometer. Setup operations and data collection (coupled θ(crystal)–2θ(counter) scan) were performed essen-

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Table I. Experimental Data for the X-ray Diffraction Studies of $Cu_2([24]aneN_6)Br_4$ and $[ZnBr([12]aneN_3)]Br$

A. Crystal Parameters at 24 °C (297 K)

compd	Cu_2 complex	Zn complex
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a, Å	9.6220 (17)	14.6048 (18)
b, Å	14.0543 (23)	12.9744 (16)
c, Å	20.5581 (29)	15.0495 (22)
β, deg	91.700 (13)	(90)
V, Å^3	2778.9 (8)	2851.7 (6)
Z	4	8
formula	$C_{18}H_{42}Br_4Cu_2N_6$	$C_9H_{21}Br_2N_3Zn$
mol wt	789.4	396.5
D(calcd), g cm^{-3}	1.89	1.85
D(measd), g cm^{-3}	1.88 (2)[a]	1.84 (2)[a]

B. Measurement of Intensity Data

diffractometer: Syntex $P2_1$

radiation: Mo K$\bar{\alpha}$ (λ = 0.710730 Å)

monochromator: pyrolytic graphite ($2\theta_m$ = 12.2°), equatorial mode; assumed 50% perfect/50% ideally mosaic for polarization cor

reflcns measd: $+h,+k,\pm l$ for 2θ = 4.5–40.0° (Cu_2 complex); $+h,+k,+l$ for 2θ = 4.5–45.0° (Zn complex)

scan type: coupled θ(crystal)–2θ(counter)

scan range: $[2\theta(K\alpha_1) - 0.8] \rightarrow [2\theta(K\alpha_2) + 0.8]°$ (Cu_2 complex); $[2\theta(K\alpha_1) - 1.0] \rightarrow [2\theta(K\alpha_2) + 1.0]°$ (Zn complex)

scan speed (2θ): variable; I(net) < 3000 counts, 1°/min; I(net) = 3000–10 000, interpolated; I(net) > 10 000, 4.0°/min (Cu_2 complex); 3.5°/min in 2θ (Zn complex)

bkgd: stationary cryst and counter at each end of 2θ scan, each for one-fourth of total scan time

total no. of measmts: 3065 reflcns, yielding 2469 unique data with I(net) > 0 (Cu_2 complex); 2226 reflcns, yielding 1701 unique data with I(net) > 0 (Zn complex)

std reflcns: 3 approximately mutually orthogonal reflcns collcd before every 97 data points; no decay obsd

abs coeff: μ = 77.0 cm^{-1}, corrected empirically by interpolation (in 2θ and ϕ) between three close-to-axial ψ scans (Cu_2 complex); μ = 76.9 cm^{-1}, corrected empirically by interpolation (in 2θ and ϕ) between four close-to-axial ψ scans (Zn complex)

[a] Neutral buoyancy in hexane/1,2-$C_2H_4Br_2$.

Table II. Final Atomic Parameters for $Cu_2([24]aneN_6)Br_4$

atom	x	y	z	B, Å$^{2\,a}$
Cu(1)	0.23069 (18)	0.23394 (14)	0.50054 (9)	1.678
Cu(2)	0.26225 (18)	0.52033 (14)	0.32416 (9)	1.941
Br(1)	0.22510 (20)	0.12450 (15)	0.40515 (9)	3.99
Br(2)	0.23846 (19)	0.37937 (14)	0.57706 (9)	3.76
Br(3)	0.25337 (24)	0.38472 (18)	0.25106 (11)	5.94
Br(4)	0.26871 (20)	0.62517 (15)	0.42892 (9)	4.04
N(1)	0.4422 (12)	0.24185 (88)	0.50188 (55)	1.73 (25)
C(2)	0.5148 (18)	0.1513 (13)	0.51865 (80)	3.28 (39)
C(3)	0.4769 (18)	0.1111 (14)	0.58456 (83)	3.59 (41)
C(4)	0.3367 (17)	0.0631 (13)	0.58417 (78)	2.87 (36)
N(5)	0.2190 (13)	0.1291 (10)	0.57972 (59)	2.57 (29)
C(6)	0.0899 (18)	0.0733 (14)	0.57973 (84)	3.64 (41)
C(7)	−0.0435 (19)	0.1366 (14)	0.57251 (88)	3.97 (42)
C(8)	−0.0665 (17)	0.1744 (13)	0.50649 (80)	3.06 (37)
N(9)	0.0218 (12)	0.25814 (90)	0.49052 (57)	1.88 (26)
C(10)	−0.0276 (16)	0.3015 (12)	0.42962 (74)	2.33 (34)
C(11)	0.0413 (16)	0.3965 (12)	0.41356 (73)	2.28 (33)
C(12)	−0.0150 (15)	0.4334 (12)	0.34837 (73)	2.21 (33)
N(13)	0.0512 (12)	0.52515 (92)	0.32863 (55)	1.94 (25)
C(14)	−0.0235 (16)	0.5653 (12)	0.27295 (76)	2.65 (36)
C(15)	0.0191 (18)	0.6675 (14)	0.25717 (84)	3.33 (39)
C(16)	0.1520 (18)	0.6773 (14)	0.22507 (84)	3.55 (40)
N(17)	0.2766 (13)	0.6505 (10)	0.26313 (62)	2.62 (29)
C(18)	0.4040 (18)	0.6625 (14)	0.22656 (85)	3.66 (41)
C(19)	0.5369 (18)	0.6381 (13)	0.26353 (83)	3.30 (39)
C(20)	0.5543 (16)	0.5359 (13)	0.28117 (76)	2.66 (35)
N(21)	0.4708 (12)	0.50817 (90)	0.33788 (54)	1.73 (25)
C(22)	0.5225 (16)	0.4114 (13)	0.36149 (76)	2.72 (36)
C(23)	0.4491 (16)	0.3786 (12)	0.42305 (75)	2.46 (34)
C(24)	0.4992 (16)	0.2786 (12)	0.43910 (75)	2.40 (33)

[a] The "isotropic" thermal parameters given for copper and bromine atoms are equivalent isotropic thermal parameters derived from the anisotropic thermal parameters (supplementary material, Table S2) as one-third of the sum of the diagonal terms in the $\mathbf{B}_{ij}$ tensor.

tially as described previously[38] (see Table I) except that a variable scan speed of 1 → 4°/min (in 2θ) was used in order to obtain more accurate measurements on the large number of systematically weak data. Unit cell parameters were based on a least-squares analysis of the optimized setting angles (2θ, ω, χ) of the unresolved Mo K$\bar{\alpha}$ components of 25 automatically centered reflections with 2θ = 20–29°. The diffraction data showed $2/m$ (C_{2h}) symmetry; the systematic absences ($h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$) uniquely define the space group $P2_1/c$.

All data were corrected for absorption (via interpolation in 2θ and ϕ between a series of normalized ψ scans of close-to-axial reflections) and for Lorentz and polarization factors. Symmetry-equivalent reflections were averaged ($R(I)$ = 3.4%), and any reflection with I(net) < 0 was expunged from the data set. Data were converted to $|F_o|$ values, and the (approximate) absolute scale and overall isotropic thermal parameter ($\bar{B}$ = 2.59 Å^2) were determined from a Wilson plot.

(B) Solution and Refinement of the Structure. All calculations were performed by use of our locally modified version of the Syntex XTL system of interactive crystallographic programs.[39] The structure was solved (with considerable difficulty) by direct methods using MULTAN.[40] It proved necessary to renormalize data by parity group because of a very uneven intensity distribution (e.g. $\langle E^2 \rangle$ for eee was 1.68, compared to $\langle E^2 \rangle$ = 0.41 for oee) and to delete all automatically chosen starting reflections from the convergence map. An "E map" now revealed the Cu_2Br_4 core of the molecule. All six of these atoms lie close to $x = {}^1/_4$, causing half of the data to be systematically weak.

All remaining non-hydrogen atoms were located from a series of three difference-Fourier maps. Least-squares refinement of positional and thermal parameters (anisotropic for the Cu_2Br_4 moiety only) with all hydrogen atoms included in idealized positions (d(C–H) = 0.95 Å and d(N–H) = 0.87 Å)[41] led to convergence with[42] R_F = 8.6%, R_{wF} = 9.1%, and GOF = 2.95 for all 2469 data (R_F = 7.0% and R_{wF} = 8.9% for those 1950 data with $I > 3\sigma(I)$). A final difference-Fourier map showed residual peaks of height ~1 e/Å^3 in the vicinity of the copper atoms, but no other significant features. The final atomic parameters are collected in Table II.

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \{[\sigma(|F_o|)]^2 + [0.05|F_o|]^2\}^{-1}$. Values for F_c were calculated from the analytical expressions for the neutral-atom scattering factors and were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[43]

Determination of the Crystal Structure of $[ZnBr([12]aneN_3)]Br$. (A) Collection of X-ray Diffraction Data. A clear, colorless crystal of approximate dimensions 0.2 × 0.3 × 0.5 mm was selected. Data were collected and processed as described for the previous structure; details appear in Table I. The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$) define the centrosymmetric orthorhombic space group *Pbca*.

(B) Solution and Refinement of the Structure. The structure was solved by direct methods (MULTAN). An "E map" revealed the location of a ZnBr moiety and an isolated Br$^-$ anion. All remaining non-hydrogen atoms were located from a difference-Fourier map.

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, with $w = \{[\sigma(|F_o|)^2] + [0.015|F_o|]^2\}^{-1}$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (with all hydrogen atoms included in idealized locations) converged with R_F = 6.6%, R_{wF} = 4.3%, and GOF = 1.297 for all 1701 reflections (R_F = 3.8%, R_{wF} = 3.6%, and GOF = 1.320 for those 1190 data with $I > 3\sigma(I)$). A final difference-Fourier map, based on all data, showed a peak of height 0.97 e/Å^3 close to the position of Br(1), but no other significant features. Final positional parameters are collected in Table III.

A minor correction for secondary extinction was necessary; here g = 8.95 × 10^{-8} where $|F_{o,cor}| = |F_{o,uncor}|(1.0 + gI_o)$.

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(42) $R_F = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

(43) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

Table III. Final Atomic Parameters for $[Zn([12]aneN_3)]Br$

atom	*x*	*y*	*z*
Zn	0.139 80 (7)	0.333 78 (7)	0.085 83 (6)
Br(1)	0.236 32 (7)	0.409 33 (7)	−0.021 65 (6)
Br(2)	0.437 77 (7)	0.200 88 (7)	0.164 73 (6)
N(1)	0.076 24 (50)	0.434 22 (52)	0.171 51 (46)
C(2)	−0.025 95 (66)	0.431 56 (67)	0.168 07 (64)
C(3)	−0.066 42 (65)	0.385 94 (68)	0.083 93 (58)
C(4)	−0.052 13 (66)	0.269 84 (68)	0.075 31 (59)
N(5)	0.037 39 (50)	0.245 03 (54)	0.033 92 (43)
C(6)	0.060 23 (73)	0.132 76 (65)	0.036 11 (63)
C(7)	0.096 22 (73)	0.095 48 (67)	0.125 23 (71)
C(8)	0.195 11 (77)	0.124 72 (70)	0.143 25 (70)
N(9)	0.210 25 (47)	0.235 90 (52)	0.164 51 (45)
C(10)	0.195 89 (62)	0.258 48 (69)	0.260 43 (63)
C(11)	0.199 31 (69)	0.375 49 (75)	0.276 88 (58)
C(12)	0.110 99 (69)	0.431 58 (68)	0.264 91 (62)

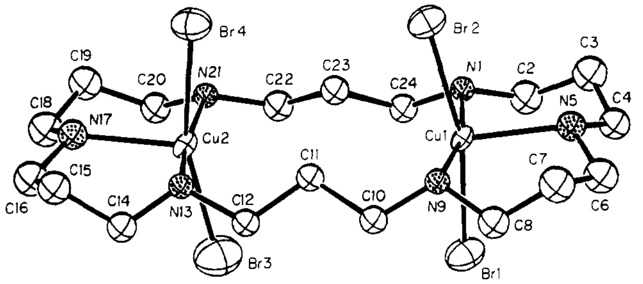

Figure 2. Molecular geometry and labeling of non-hydrogen atoms for $Cu_2([24]aneN_6)Br_4$ (ORTEP, 30% probability ellipsoids, all hydrogen atoms omitted).

Results and Discussion

Synthesis of Macrocycles. The two macrocycles $[12]aneN_3$ and $[24]aneN_6$ were synthesized simultaneously and isolated as their hydrobromide salts by using a modification of the procedure described by Richman and Atkins.[18] Vapor pressure osmometric and HPLC data collected on the tosylated ligand precursors indicate an approximate 10:1 relative distribution ratio between Ts_3-$[12]aneN_3$ and Ts_6-$[24]aneN_6$ in the mixture (see Figure 1). There is no reason to believe this distribution ratio is altered significantly during the detosylation procedure. No attempt was made to further purify the precursor mixture beyond recrystallization from excess ethanol.

Synthesis of Metal Complexes. Solutions of anhydrous metal bromide salts were added to neutralized solutions of the ligand mixture in absolute ethanol. The method of "selective differential solubility" was used to isolate individual metal complexes. This method is based on the observation that the binuclear transition-metal complexes of $[24]aneN_6$ exhibit appreciably different solubility properties than those of the mononuclear complexes of $[12]aneN_3$.[44] Metal–ligand complexes were thus isolated selectively as they precipitated from solution. The $Cu_2([24]aneN_6)Br_4$ and $[ZnBr([12]aneN_3)]Br$ species were isolated in analytically pure form, via slow recrystallization from saturated aqueous solutions, and are the subject of this report. The corresponding dibromo(1,5,9,13,17,21-hexaazacyclotetracosane)dizinc(II) dibromide ($[Zn_2Br_2([24]aneN_6]Br_2$) and dibromo(1,5,9-triazacyclododecane)copper(II) ($Cu([12]aneN_3)Br_2$) complexes have also been isolated, but not yet in a form suitable for X-ray diffraction studies.

Table IV. Interatomic Distances (Å) for $Cu_2([24]aneN_6)Br_4$

	(A) Copper–Ligand Distances		
Cu(1)–Br(1)	2.492 (3)	Cu(2)–Br(3)	2.427 (3)
Cu(1)–Br(2)	2.579 (3)	Cu(2)–Br(4)	2.609 (3)
Cu(1)–N(1)	2.038 (11)	Cu(2)–N(13)	2.036 (12)
Cu(1)–N(5)	2.201 (13)	Cu(2)–N(17)	2.224 (14)
Cu(1)–N(9)	2.043 (12)	Cu(2)–N(21)	2.025 (11)
Cu(1)···H(1)	2.45	Cu(2)···H(13)	2.41
Cu(1)···H(5)	2.55	Cu(2)···H(17)	2.53
Cu(1)···H(9)	2.41	Cu(2)···H(21)	2.38
Cu(1)···Cu(2)	5.432 (3)		
	(B) Carbon–Carbon Distances		
C(2)–C(3)	1.522 (24)	C(14)–C(15)	1.532 (26)
C(3)–C(4)	1.508 (24)	C(15)–C(16)	1.462 (24)
C(6)–C(7)	1.565 (26)	C(18)–C(19)	1.507 (25)
C(7)–C(8)	1.468 (25)	C(19)–C(20)	1.489 (25)
C(10)–C(11)	1.530 (23)	C(22)–C(23)	1.538 (22)
C(11)–C(12)	1.522 (22)	C(23)–C(24)	1.519 (24)
			av 1.514 ± 0.029
C(11)···C(23)	3.931 (22)		
	(C) Nitrogen–Carbon Distances		
N(1)–C(2)	1.487 (22)	N(13)–C(12)	1.499 (21)
N(1)–C(24)	1.509 (19)	N(13)–C(14)	1.448 (20)
N(5)–C(4)	1.464 (21)	N(17)–C(16)	1.462 (22)
N(5)–C(6)	1.468 (22)	N(17)–C(18)	1.466 (22)
N(9)–C(8)	1.494 (21)	N(21)–C(20)	1.487 (19)
N(9)–C(10)	1.459 (20)	N(21)–C(22)	1.522 (21)
			av 1.480 ± 0.023

Table V. Interatomic Angles (deg) for $Cu_2([24]aneN_6)Br_4$

	(A) Angles about the Copper Atoms		
Br(1)–Cu(1)–Br(2)	165.67 (10)	Br(3)–Cu(2)–Br(4)	162.60 (11)
Br(1)–Cu(1)–N(1)	92.44 (34)	Br(3)–Cu(2)–N(13)	92.13 (35)
Br(1)–Cu(1)–N(5)	99.70 (34)	Br(3)–Cu(2)–N(17)	107.34 (35)
Br(1)–Cu(1)–N(9)	91.44 (34)	Br(3)–Cu(2)–N(21)	92.09 (34)
Br(2)–Cu(1)–N(1)	86.42 (34)	Br(4)–Cu(2)–N(13)	86.75 (34)
Br(2)–Cu(1)–N(5)	94.63 (34)	Br(4)–Cu(2)–N(17)	90.05 (34)
Br(2)–Cu(1)–N(9)	86.57 (34)	Br(4)–Cu(2)–N(21)	86.18 (34)
N(1)–Cu(1)–N(5)	95.71 (47)	N(13)–Cu(2)–N(17)	94.40 (48)
N(1)–Cu(1)–N(9)	166.31 (48)	N(13)–Cu(2)–N(21)	169.00 (48)
N(5)–Cu(1)–N(9)	96.57 (48)	N(17)–Cu(2)–N(21)	94.02 (48)
	(B) Copper–Nitrogen–Carbon Angles		
Cu(1)–N(1)–C(24)	113.3 (9)	Cu(2)–N(13)–C(12)	114.6 (9)
Cu(1)–N(1)–C(2)	114.7 (9)	Cu(2)–N(13)–C(14)	116.7 (9)
Cu(1)–N(5)–C(4)	114.4 (10)	Cu(2)–N(17)–C(16)	116.8 (10)
Cu(1)–N(5)–C(6)	114.8 (10)	Cu(2)–N(17)–C(18)	116.8 (10)
Cu(1)–N(9)–C(8)	114.3 (9)	Cu(2)–N(21)–C(20)	115.2 (9)
Cu(1)–N(9)–C(10)	116.8 (9)	Cu(2)–N(21)–C(22)	115.6 (9)
			av 115.3 ± 1.2
	(C) C–N–C Angles		
C(24)–N(1)–C(2)	108.1 (12)	C(12)–N(13)–C(14)	110.1 (12)
C(4)–N(5)–C(6)	108.3 (13)	C(16)–N(17)–C(18)	112.4 (13)
C(8)–N(9)–C(10)	110.2 (12)	C(20)–N(21)–C(22)	107.8 (11)
			av 109.5 ± 1.8
	(D) C–C–N Angles		
C(23)–C(24)–N(1)	112.5 (13)	C(11)–C(12)–N(13)	112.9 (12)
C(3)–C(2)–N(1)	113.6 (14)	C(15)–C(14)–N(13)	113.8 (13)
C(3)–C(4)–N(5)	114.1 (14)	C(15)–C(16)–N(17)	116.6 (15)
C(7)–C(6)–N(5)	112.8 (14)	C(19)–C(18)–N(17)	115.1 (15)
C(7)–C(8)–N(9)	114.6 (14)	C(19)–C(20)–N(21)	112.6 (13)
C(11)–C(10)–N(9)	114.7 (13)	C(23)–C(22)–N(21)	112.1 (13)
			av 113.8 ± 1.3
	(E) C–C–C Angles		
C(2)–C(3)–C(4)	113.5 (15)	C(14)–C(15)–C(16)	115.3 (15)
C(6)–C(7)–C(8)	113.2 (15)	C(18)–C(19)–C(20)	115.5 (15)
C(10)–C(11)–C(12)	110.0 (13)	C(22)–C(23)–C(24)	107.8 (13)
			av 112.6 ± 3.1

The Structure of $Cu_2([24]aneN_6)Br_4$. Optical spectral features [$cm^{-1} \times 10^3$ (molar absorptivities): Nujol mull, 9.45, 15.4, 23.7, 33.1; water, 9.13 (65.0), 14.9 (108), 37.0 (3010), 38.8 (2760); dimethyl sulfoxide, 8.67 (44.6), 14.1 (159), 35.5 (4370)] and observed ESR parameters in a 50:50 dimethyl sulfoxide:chloroform mixture ($A_\parallel$ = 107 G, $A_\perp$ = 40 G, $\langle a \rangle$ = 62 G, $g_\parallel$ = 2.239, $g_\perp$ = 2.050, $\langle g \rangle$ = 2.113) do not allow a clear differentiation between the various coordination possibilities for this complex. Features of the optical spectra are consistent with the expected 5-coordinate[45,46] binuclear complex. However, the ESR data, with the low $A_\parallel$ value, are indicative of an unusual geometry[47] and/or the presence of very polarizable ligand atoms (Br).[48] An X-ray

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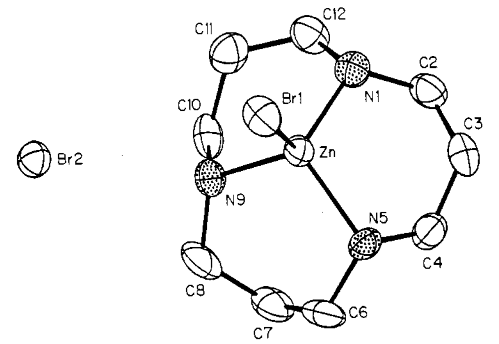

Figure 3. Geometry and labeling of atoms for [ZnBr([12]aneN$_3$)]Br (ORTEP, 30% probability ellipsoids, all hydrogen atoms omitted).

diffraction study of this complex was therefore undertaken in order to determine the actual coordination geometry.

Interatomic distances and angles are collected in Tables IV and V. An ORTEP diagram of the molecule, showing the atomic labeling scheme, appears as Figure 2.

Each of the two Cu(II) atoms has a square-pyramidal coordination environment; the basal plane is defined by two nitrogen atoms and two bromide ligands, and a further nitrogen atom acts as the apical ligand. Copper–bromide distances show some variations (Cu(1)–Br(1) = 2.492 (3) Å, Cu(1)–Br(2) = 2.579 (3) Å, Cu(2)–Br(3) = 2.427 (3) Å, Cu(2)–Br(4) = 2.609 (3) Å); the basal copper–nitrogen distances are equivalent (Cu(1)–N(1) = 2.038 (11) Å, Cu(1)–N(9) = 2.043 (12) Å, Cu(2)–N(13) = 2.036 (12) Å, Cu(2)–N(21) = 2.025 (11) Å) and are systematically shorter than the axial copper–nitrogen distances (Cu(1)–N(5) = 2.201 (13) Å and Cu(2)–N(17) = 2.224 (14) Å). The basal planes of the two square-pyramidal CuN$_3$Br$_2$ moieties face each other in an eclipsed configuration with Cu(1)···Cu(2) = 5.432 (3) Å.

The basal Br–Cu–Br angles are Br(1)–Cu(1)–Br(2) = 165.67 (10)° and Br(3)–Cu(2)–Br(4) = 162.60 (11)°; the corresponding N–Cu–N angles are N(1)–Cu(1)–N(9) = 166.31 (48)° and N(13)–Cu(2)–N(21) = 169.00 (48)°. N(axial)–Cu–Br angles are rather irregular (N(5)–Cu(1)–Br(1) = 99.70 (34)°, N(5)–Cu(1)–Br(2) = 94.63 (34)°, N(17)–Cu(2)–Br(3) = 107.34 (35)°, N(17)–Cu(2)–Br(4) = 90.05 (34)°, with the largest angle being associated with shortest Cu–Br bond length and vice versa. The N(axial)–Cu–N(basal) angles are much more regular (N(5)–Cu(1)–N(1) = 95.71 (47)°, N(5)–Cu(1)–N(9) = 96.57 (48)°, N(17)–Cu(2)–N(13) = 94.40 (48)°, N(17)–Cu(2)–N(21) = 94.02 (48)°), presumably as a result of their involvement in six-membered chelate rings.

Other distances and angles in the 24-membered C$_{18}$N$_6$ ring are normal with the following average values and rms deviations: C–C = 1.514 ± 0.029 Å, N–C = 1.480 ± 0.023 Å, C–N–C = 109.5 ± 1.8°, C–C–N = 113.8 ± 1.3°, C–C–C = 112.6 ± 3.1°.

The [24]aneN$_6$ ligand and the two Cu(II) centers define five fused, closed rings, four 6-membered rings, and a central 12-membered ring. The area of the cavity within the 12-membered ring is ~21 Å^2, as defined by the Cu(1)···Cu(2) distance of 5.432 (3) Å and the C(11)···C(23) distance of 3.925 (24) Å.

Mononuclear Zinc(II) Complex. [ZnBr([12]aneN$_3$)]Br was synthesized specifically to compare physically and structurally with the copper(II) complexes Cu([12]aneN$_3$)Br$_2$ (vide supra) and Cu([9]aneN$_3$)Br$_2$.[2] There are several possible structures for this zinc(II) complex; since spectroscopic data are of little aid in differentiating between these possibilities,[49] a single-crystal X-ray structural investigation was deemed appropriate.

Description of the Structure of [ZnBr([12]aneN$_3$)]Br. The crystal consists of an ordered 1:1 arrangement of [ZnBr([12]aneN$_3$)]$^+$ cations and bromide anions. The labeling of atoms within the cation is shown in Figure 3. Interatomic distances and angles are collected in Tables VI and VII.

Table VI. Interatomic Distances (Å) for [ZnBr([12]aneN$_3$)]Br

	(A) Zn–Ligand Distances		
Zn–Br(1)	2.359 (1)	Zn–N(5)	2.043 (7)
Zn–N(1)	2.055 (7)	Zn–N(9)	2.018 (7)
Zn···H(1)	2.40	Zn···H(9)	2.40
Zn···H(5)	2.45		
	(B) Nitrogen–Carbon Distances		
N(1)–C(12)	1.495 (12)	N(5)–C(6)	1.495 (11)
N(1)–C(2)	1.494 (12)	N(9)–C(8)	1.494 (11)
N(5)–C(4)	1.484 (12)	N(9)–C(10)	1.488 (12)
			av 1.492 ± 0.005
	(C) Carbon–Carbon Distances		
C(2)–C(3)	1.518 (13)	C(7)–C(8)	1.518 (15)
C(3)–C(4)	1.526 (12)	C(10)–C(11)	1.539 (13)
C(6)–C(7)	1.519 (14)	C(11)–C(12)	1.492 (14)
			av 1.519 ± 0.015

(D) Bromide Ion···Cation Distances (<2.8 Å)	
Br(2)···H(1) ($^1/_2 - x$, $-^1/_2 + y$, z)	2.73
Br(2)···H(5) ($^1/_2 + x$, $^1/_2 - y$, $-z$)	2.60
Br(2)···H(9) (x, y, z)	2.56

Table VII. Interatomic Angles (deg) for [ZnBr([12]aneN$_3$)]Br

	(A) Angles about the Zn Atom		
Br(1)–Zn–N(1)	115.89 (20)	N(1)–Zn–N(5)	105.47 (28)
Br(1)–Zn–N(5)	114.17 (20)	N(1)–Zn–N(9)	105.15 (28)
Br(1)–Zn–N(9)	111.05 (20)	N(5)–Zn–N(9)	104.06 (28)
	(B) Zn–N–C Angles		
Zn–N(1)–C(2)	114.52 (53)	Zn–N(5)–C(6)	112.17 (53)
Zn–N(1)–C(12)	114.97 (53)	Zn–N(9)–C(8)	113.99 (55)
Zn–N(5)–C(4)	111.24 (52)	Zn–N(9)–C(10)	111.93 (52)
	(C) C–N–C, N–C–C, and C–C–C Angles		
C(2)–N(1)–C(12)	111.8 (7)	C(2)–C(3)–C(4)	113.7 (8)
C(4)–N(5)–C(6)	113.5 (7)	C(6)–C(7)–C(8)	114.0 (8)
C(8)–N(9)–C(10)	112.2 (7)	C(10)–C(11)–C(12)	115.7 (8)
N(1)–C(12)–C(11)	114.7 (8)	N(5)–C(6)–C(7)	114.0 (8)
N(1)–C(2)–C(3)	115.3 (7)	N(9)–C(8)–C(7)	114.9 (8)
N(5)–C(4)–C(3)	111.7 (7)	N(9)–C(10)–C(11)	110.2 (7)

The zinc atom has a slightly distorted tetrahedral coordination environment, with the nitrogen atoms of the macrocyclic ligand defining three of the ligating positions and a bromide ligand the fourth. Individual zinc–nitrogen distances are Zn–N(1) = 2.055 (7) Å, Zn–N(5) = 2.043 (7) Å, and Zn–N(9) = 2.018 (7) Å, with the lone zinc–bromide bond length being Zn–Br(1) = 2.359 (1) Å. Br–Zn–N angles are all greater than the regular tetrahedral value of 109.47° and are Br(1)–Zn–N(1) = 115.89 (2)°, Br(1)–Zn–N(5) = 114.17 (20)°, and Br(1)–Zn–N(9) = 111.05 (20)°, while the N–Zn–N angles are all reduced from the ideal tetrahedral angle with values of N(1)–Zn–N(5) = 105.47 (28)°, N(1)–Zn–N(9) = 105.15 (28)°, and N(5)–Zn–N(9) = 104.06 (28)°.

Individual distances within the macrocyclic ring are normal; nitrogen–carbon bond lengths range 1.484 (12)–1.495 (12) Å (average 1.492 ± 0.005 Å), while carbon–carbon bond lengths are 1.492 (14)–1.539 (13) Å (average 1.519 ± 0.015 Å). Angles within the ring are self-consistent and uniformly greater than the accepted tetrahedral value of 109.47°; they range from N(9)–C(10)–C(11) = 110.2 (7)° through C(10)–C(11)–C(12) = 115.7 (8)° (average 113.43 ± 1.67°).

Conclusions

The two macrocyclic ligands [24]aneN$_6$ and [12]aneN$_3$ were synthesized simultaneously and isolated as a mixture of hydrobromide salts in a "one-pot" procedure. Selective precipitation was used to separate and isolate the zinc(II) and copper(II) complexes of [12]aneN$_3$ and [24]aneN$_6$, respectively. Cu$_2$([24]aneN$_6$)Br$_4$ is a binuclear complex that contains two square-pyramidal copper(II) centers separated by 5.432 (3) Å. Although similar "large" binucleating macrocycles have been reported,[27-30] to the best of our knowledge, this is the first reported dicopper(II) complex of a symmetrical hexaaza macrocycle that

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(49) Optical spectra investigations of [ZnBr([12]aneN$_3$)]Br recorded in both water and dimethyl sulfoxide reveal no identifiable structural features between 6.7 × 10^3 and 47.6 × 10^3 cm^{-1}.

is *not* stabilized by bridging ligands.[12-15] The molecular structure of this complex is unique. In addition, the rather large "empty" cavity within the central ring of the molecule (of area approximately 21 Å^2) possesses dimensions appropriate for the insertion of small molecules. There is much potential for binuclear catalytic activity.

The complex $[\mathrm{ZnBr}([12]\mathrm{aneN}_3)]\mathrm{Br}$ is mononuclear with a slightly distorted tetrahedral coordination environment about zinc. Our data indicate that the macrocycle $[12]\mathrm{aneN}_3$ is sufficiently flexible to conform to the normal coordination requirements of the zinc(II) ion and does not have the same rigid steric requirements as the smaller symmetrical triaza species, $[9]\mathrm{aneN}_3$.[2,7,8,50,51]

Addendum. A reviewer drew our attention to a communication by Margulis and Zompa[52] in which the synthesis of $[20]\mathrm{aneN}_6$ (as a byproduct of synthesizing $[10]\mathrm{aneN}_3$) is reported along with a structural study of the mononuclear nickel(II) complex $[\mathrm{Ni}([20]\mathrm{aneN}_6)][\mathrm{ClO}_4]_2\cdot\mathrm{DMF}$.

Acknowledgment. We thank Professor R. D. Bereman and P. J. Hochgesang (North Carolina State University) and Professor R. D. Allendoerfer (University at Buffalo, SUNY) for their assistance in obtaining ESR spectra.

Registry No. **2**·6HBr, 113380-64-6; [ZnBr(**1**)]Br, 113380-63-5; Cu_2(**2**)Br_4, 113380-62-4.

Supplementary Material Available: Tables S1 and S2, listing hydrogen atom coordinates and anisotropic thermal parameters for $\mathrm{Cu}_2([24]\mathrm{aneN}_6)\mathrm{Br}_4$, and Tables S3 and S4, with similar information for $[\mathrm{ZnBr}([12]\mathrm{aneN}_3)]\mathrm{Br}$ (5 pages); tables of calculated and observed structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of $\mathrm{V}_2(\mathrm{VO})(\mathrm{P}_2\mathrm{O}_7)_2$. A Mixed-Valence Vanadium(III,III,IV) Pyrophosphate

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A new pyrophosphate of mixed-valent vanadium, $\mathrm{V}_2(\mathrm{VO})(\mathrm{P}_2\mathrm{O}_7)_2$, has been synthesized by the reaction of $\mathrm{VO}(\mathrm{PO}_3)_2$ with VPO_4. Single crystals were formed as a minor phase during high-temperature annealing of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$. The new compound is orthorhombic, space group *Pnma*, with $a = 17.459$ (3) Å, $b = 12.185$ (2) Å, $c = 5.2431$ (7) Å, $V = 1115.4$ (3) Å^3, and $Z = 4$. The structure was determined by single-crystal X-ray diffraction with final residuals $R = 0.0350$ and $R_w = 0.0339$. $\mathrm{V}_2(\mathrm{VO})(\mathrm{P}_2\mathrm{O}_7)_2$ consists of linear vanadium trimers containing two octahedrally coordinated V^{3+} cations joined through edges to a central V^{4+} square pyramid. These trimers are linked in three dimensions through the pyrophosphate groups. The magnetic susceptibility, measured from 1 to 300 K, shows that the vanadium(III) ions in the trimer are antiferromagnetically coupled to the central vanadium(IV) ion with $J = -22$ cm^{-1}. Longer range interactions lead to bulk antiferromagnetic order below 5 K.

Introduction

Vanadyl(IV) pyrophosphate, $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$, has been the subject of recent studies due to its efficacy as catalyst for the oxidation of butane to maleic anhydride as well as for its interesting magnetic properties. Ladders of antiferromagnetically coupled V^{4+} ions run throughout the structure, giving rise to magnetic behavior similar to that of linear-chain compounds.[1] In order to study the antiferromagnetic ordering in more detail at temperatures below 4 K, better crystals than those available by prior techniques were needed to minimize the effect of paramagnetic defects. While attempting to grow crystals of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ from the melt at 1000 °C, we observed formation of a minor phase by X-ray powder diffraction. Single-crystal analysis of a few small well-formed crystals gave unit cell constants that did not correspond to any known phase of vanadium phosphate, so a structure determination was undertaken. Successful solution of the structure showed that a new phase of vanadium phosphate had been formed with a formula $\mathrm{V}_3\mathrm{P}_4\mathrm{O}_{15}$.

The structure consists of vanadium trimers composed of two trivalent vanadium atoms and one tetravalent vanadyl group. The trimers are linked together by $\mathrm{P}_2\mathrm{O}_7{}^{4-}$ groups. The compound can be synthesized in bulk microcrystalline form by the reaction of $\mathrm{VO}(\mathrm{PO}_3)_2$ with VPO_4. Investigation of the magnetic susceptibility shows that the V^{3+} ions are antiferromagnetically coupled to the V^{4+} ion and that intertrimer interactions lead to antiferromagnetic ordering below 5 K.

Experimental Section

Materials. $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ was prepared by heating $\mathrm{VO}(\mathrm{HPO}_4)\cdot0.5\mathrm{H}_2\mathrm{O}$ for 20 h at 700 °C in flowing helium.[2] VPO_4 was prepared by decomposition of $(\mathrm{NH}_4)_2[(\mathrm{VO})_2(\mathrm{HPO}_4)_2(\mathrm{C}_2\mathrm{O}_4)]\cdot5\mathrm{H}_2\mathrm{O}$ at 980 °C.[3] $\mathrm{VO}(\mathrm{PO}_3)_2$ was prepared by dehydration of $\mathrm{VO}(\mathrm{H}_2\mathrm{PO}_4)_2$ at 700 °C under flowing helium.[4]

Preparation of $\mathrm{V}_3\mathrm{P}_4\mathrm{O}_{15}$. A sample of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ was placed in a crimped platinum tube, which was sealed in an evacuated silica tube, heated to 1030 °C to melt the charge, and slowly cooled to 800 °C. Upon air quenching and examination of the crystalline product by X-ray powder diffraction, it was apparent that, in addition to $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$, a small amount of an additional phase was present. A single-crystal diffraction study showed this second phase to be the new compound $\mathrm{V}_3\mathrm{P}_4\mathrm{O}_{15}$. Subsequently, this new compound was prepared in pure form by reaction of VPO_4 and $\mathrm{VO}(\mathrm{PO}_3)_2$ in a 2:1 molar ratio at 850 °C for 4 days in an evacuated silica tube. The observed X-ray powder diffraction pattern corresponded well with that calculated from the single crystal data.

Magnetic susceptibility $\chi(T)$ data were obtained in a magnetic field $H = 6.3$ kG by using a George Associates Faraday magnetometer and sweeping the temperature at less than 1 K/min. The contribution of

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