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Synthetic Analogue Approach to Metallobleomycins. 4. New Halo-Bridged Dimeric and Polymeric (Infinite Zigzag Chain) Complexes of Copper(II) with Peptide Ligands Related to Bleomycins

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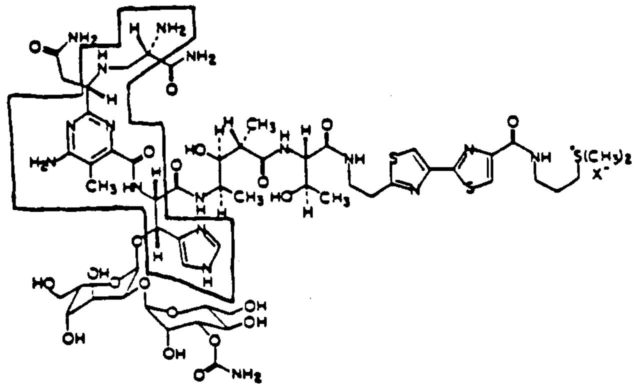
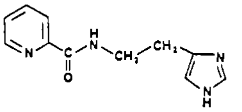
Reactions of CuX$_2$ (X = Cl, Br) with PypepH (**2**) or PmpepH (**3**), two peptide ligands that resemble part of the metal-chelating portion of the antitumor drug bleomycin (BLM), in methanol afford a new class of halo-bridged peptide complexes of bivalent copper (**4**–**7**). The structures of **4** and **7** have been determined by X-ray crystallography. [Cu(Pypep)Cl]$_2$·2H$_2$O (**4**) crystallizes in the monoclinic space group $P2_1/n$ with a = 10.134 (2) Å, b = 14.141 (4) Å, c = 9.198 (4) Å, β = 95.01 (3)°, V = 1313.1 (7) Å^3, and Z = 4. The structure was refined to R = 2.99% on the basis of 1581 unique data ($F_o^2 > 3\sigma(F_o^2)$). A centrosymmetric dimeric Cu$_2$Cl$_2$ core is present in **4**. [Cu(Pmpep)Br]$_\infty$ (**7**) crystallizes in the monoclinic space group $P2_1/c$ with a = 11.405 (3) Å, b = 16.821 (6) Å, c = 7.881 (2) Å, β = 108.06 (2)°, V = 1437.1 (8) Å^3, and Z = 4. On the basis of 1282 unique data, the structure of **7** was refined to R = 4.14%. In **7**, the repeating [Cu(Pmpep)Br] units bridge via single Br$^-$ ions to give rise to a novel zigzag chain structure. Both peptide ligands occupy three coordination sites in the basal plane of copper, and the coordination geometry around copper is approximately square-pyramidal in each of these complexes. In solutions, the halo-bridged complexes dissociate into monomeric tetragonal copper(II) complexes. The EPR parameters of such monomeric species are characteristic of the specific peptide ligand they contain. Preliminary magnetic susceptibility measurements have established an antiferromagnetically coupled ground state for **4** with an exchange coupling constant (J) value of -2.32 cm^{-1}. A weakly ferromagnetic ground state is indicated for **7**.

Introduction

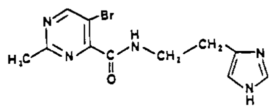
Though the structures and magnetic properties of halo-bridged dimeric and polymeric (chain structures) copper(II) complexes have been studied extensively,[1-3] no such complex with peptide ligands has been reported. The peptide complexes are mostly monomeric.[4] Recently, as part of a "synthetic analogue approach"[5] to the problem of metallobleomycins (M-BLMs),[6] we have undertaken the task of synthesizing transition-metal complexes of small peptide fragments related to the antitumor drug bleomycin (BLM, **1**). We have already reported[7] the synthesis of two such peptides, namely, *N*-(2-(4-imidazolyl)ethyl)pyridine-2-carboxamide (**2**) and *N*-(2-(4-imidazolyl)ethyl)-2-methyl-5-bromopyrimidine-4-carboxamide (**3**), which resemble part of the metal-chelating portion of BLM (boxed area in **1**).



Bleomycin A$_2$ (**1**)



PypepH (**2**)



PmpepH (**3**)

These two peptides mimic three of the five proposed donor centers in various M-BLMs and are abbreviated as PypepH and PmpepH, respectively (the dissociable H is the amide H). The Cu(II) complexes of **2** and **3** containing acetate ions as bridging or bidentate ligands[7] and "bis" complexes of low-spin Fe(III)[8] and Co(III)[9] with **2** have been reported by us. Since there is an appreciable amount of Cl$^-$ in cellular fluid as well as in the in vitro DNA cleavage experiments with M-BLMs,[6] we attempted to look into the possibility of Cl$^-$ ion coordination to Cu(II) centers of the synthetic analogues derived from PypepH and PmpepH. In this paper we report the syntheses and spectroscopic properties of two chloro- and two bromo-bridged complexes of copper(II) derived from PypepH and PmpepH. The structures of [Cu(Pypep)Cl]$_2$·2H$_2$O (**4**) and [Cu(Pmpep)Br]$_\infty$ (**7**) are also included. Two different types of halide ion bridges are observed in these two structures. Preliminary magnetic susceptibility data on **4** and **7** are also discussed.

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Experimental Section

Preparation of Compounds. Copper(II) chloride dihydrate and copper(II) bromide were purchased from Mallinckrodt, Inc. Triethylamine was procured from Aldrich Chemical Co. and was used without further purification. Ligands **2** and **3** were synthesized by following published procedures.[7]

[Cu(Pypep)Cl]$_2$·2H$_2$O (4). A solution of 170 mg (1 mmol) of copper chloride dihydrate in 10 mL of water was slowly added with stirring to 216 mg (1 mmol) of PypepH in 10 mL of methanol. A small amount of light blue precipitate appeared. The mixture was then heated (~60 °C) with slow addition of water (~8 mL was used) until the solution was clear. To this blue solution was added an amount of 140 μL (1 mmol) of triethylamine dissolved in 5 mL of methanol. Again, a light blue precipitate was formed. Addition of 5 mL of water and warming of the mixture resulted in a clear deep blue solution, which was filtered to remove trace amounts of suspended particles. Slow evaporation of the blue filtrate at room temperature afforded dark blue blocks within 24 h. The crystals were collected by filtration, washed with 5 mL of methanol, and dried in air; yield 180 mg (50%). Anal. Calcd for $C_{11}H_{13}N_4O_2CuCl$: C, 39.77; H, 3.94; N, 16.86; Cl, 10.67; Cu, 19.12. Found: C, 40.02; H, 3.86; N, 17.01; Cl, 10.61; Cu, 19.08. Selected IR bands (KBr pellet, cm^{-1}): 3440 (m, ν_{OH}), 3020 (m), 2840 (m), 1610 (s), 1600 (vs), 1400 (s), 1340 (m), 1230 (m), 1040 (m), 840 (m), 790 (m), 760 (m), 690 (s), 650 (m), 630 (m), 540 (m), 495 (w).

[Cu(Pypep)Br]$_2$ (5). This compound was synthesized from copper bromide and PypepH by following the procedure described above. A 1-mmol amount of triethylamine was used. A batch of 226 mg (63%) of deep blue needles was obtained from a reaction mixture containing 1 mmol of each reactant. Anal. Calcd for $C_{11}H_{11}N_4OCuBr$: C, 36.85; H, 3.09; N, 15.62; Cu, 17.71. Found: C, 36.45; H, 3.14; N, 15.50; Cu, 17.69. Selected IR bands (KBr pellet, cm^{-1}): 3140 (m), 2920 (w), 1610 (s), 1600 (vs), 1400 (s), 1280 (m), 1240 (m), 1090 (m), 820 (w), 790 (m), 760 (m), 690 (m), 630 (m), 545 (w), 500 (w).

[Cu(Pmpep)Cl]$_\infty$ (6). A 310-mg (1-mmol) amount of PmpepH in 6 mL of methanol was added with stirring to a solution of 170 mg (1 mmol) of copper chloride dihydrate in 6 mL of methanol followed by 140 μL (1 mmol) of triethylamine. The resultant dark green solution was then allowed to stand at room temperature for 24 h. The green needles that were deposited during this period were collected by filtration, washed with 5 mL of cold (0 °C) ethanol, and dried in air: yield 200 mg (49%); mp 135–140 °C dec. Anal. Calcd for $C_{11}H_{11}N_5OCuClBr$: C, 32.37; H, 2.72; N, 17.16; Cu, 15.57. Found: C, 32.24; H, 2.84; N, 17.26; Cu, 15.17. Selected IR bands (KBr pellet, cm^{-1}): 3100 (m), 3050 (m), 2880 (m), 1620 (vs), 1540 (s), 1430 (m), 1390 (m), 1060 (m), 1030 (m), 830 (m), 720 (m), 700 (m), 620 (s), 540 (w).

[Cu(Pmpep)Br]$_\infty$ (7). A procedure similar to that described above and starting with 1 mmol of both copper bromide and PmpepH afforded 280 mg (62%) of dark green needles, mp 200–205 °C dec. Anal. Calcd for $C_{11}H_{11}N_5OCuBr_2$: C, 29.17; H, 2.43; N, 15.47; Cu, 14.04. Found: C, 29.28; H, 2.52; N, 15.43; Cu, 13.89. Selected IR bands (KBr pellet, cm^{-1}): 3280 (s), 2920 (w), 1630 (vs), 1560 (s), 1440 (m), 1400 (m), 1220 (m), 1170 (m), 1060 (m), 990 (m), 800 (br, m), 780 (m), 720 (m), 695 (m), 630 (s), 545 (m).

In the last two preparations, anhydrous methanol was used since **6** and **7** decompose in aqueous methanol.

X-ray Data Collection and Reduction. Deep blue blocks of **4** were grown from aqueous methanol solution. After several attempts, X-ray-quality green needles of **7** were obtained by very slow evaporation of the reaction mixture in methanol. Diffraction experiments were performed on a four-circle Syntex P2$_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 15 machine-centered reflections selected from rotation photographs. These data were used to determine the crystal systems. Partial rotation photographs around each axis were consistent with monoclinic crystal systems. For **4**, 30 high-angle reflections (22° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrix. In case of **7**, 20 such reflections were used. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P2_1/n$ and $P2_1/c$ for **4** and **7**, respectively. $\pm h,+k,+l$ data were collected over the range 4.5° < 2θ < 45.0° for both **4** and **7**. Three standard reflections were recorded every 197 reflections. Their intensities showed no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package.[10] The total number of reflections with $F_o^2 > 3\sigma(F_o^2)$ used in the refinements are listed in Table I. Analytical absorption corrections were applied to both data sets by employing the program ABSORB.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for [Cu(Pypep)Cl]$_2$·2H$_2$O (**4**) and [Cu(Pmpep)Br]$_\infty$ (**7**)

	4	**7**
formula (mol wt)	$C_{11}H_{13}N_4O_2CuCl$ (332.12)	$C_{11}H_{11}N_5OCuBr_2$ (452.47)
cryst color, form	blue prisms	green needles
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	10.134 (2)	11.405 (3)
b, Å	14.141 (4)	16.821 (6)
c, Å	9.198 (4)	7.881 (2)
β, deg	95.01 (3)	108.06 (2)
V, Å^3	1313.1 (7)	1437.1 (8)
Z	4	4
d_{calcd}, g/cm^3	1.68	2.09
d_{obsd},[a] g/cm^3	1.69 (1)	2.07 (1)
cryst dimens, mm	0.35 × 0.29 × 0.33	0.12 × 0.23 × 0.42
cryst faces	$(1\bar{1}0)$, $(\bar{1}10)$, (110), $(\bar{1}\bar{1}0)$, (101), $(10\bar{1})$	(100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001), $(00\bar{1})$
abs coeff (μ), cm^{-1}	17.88	69.14
radiation (λ, Å)[b]	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	24	24
scan speed, deg/min	2.0–5.0 (θ–2θ scan)	2.0–5.0 (θ–2θ scan)
scan range, deg	1.0 below Kα_1 to 1.0 above Kα_2	1.0 below Kα_1 to 1.0 above Kα_2
bkgd/scan time ratio	0.5	0.5
no. of data collcd	1929	2087
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	1581	1282
no. of variables	172	261
R, %	2.99	4.14
R_w, %	3.96	4.26
max Δ/σ in final least-squares cycle	0.008	0.002
largest residual electron density, e/Å^3	0.5	0.6
atom associated with residual density	Cu	Cu

[a] Determined by flotation in CCl$_4$/CHBr$_3$. [b] Graphite monochromator.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[11] The Cu atom position for **4** was determined by the heavy-atom (Patterson) method. In the case of **7**, positions for Cu and Br atoms were obtained by employing direct methods. The remaining non-hydrogen atoms in both cases were located from successive difference Fourier map calculations. Refinement was carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where the weight, *w*, is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In final cycles of refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were allowed to ride on the carbon to which they are bonded by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. In all cases, the hydrogen atom contributions were calculated but not refined. The final values of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ are given in Table I. The maximum Δ/σ values on any of the parameters in the final cycle of refinement are also included in Table I. Final difference Fourier map calculations showed no peak(s) of chemical significance; the magnitudes of the largest peaks in the final difference maps and the locations of these residuals are listed in Table I. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and values of $10|F_o|$ and $10|F_c|$ (Table S3) have been deposited as supplementary material.

Other Physical Measurements. Infrared spectra were obtained with a Nicolet MX-S FT spectrophotometer. Absorption spectra were recorded on a Perkin-Elmer Lambda-9 spectrophotometer. EPR spectra were monitored with a Varian E-3 spectrometer connected to a Digital

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Table II. Positional Parameters[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			Compound **4**				
Cu	4888 (1)	5289 (1)	3035 (1)	Cl	6680 (1)	5377 (1)	4779 (1)
N1	5308 (3)	3958 (2)	2444 (3)	N2	3515 (3)	5145 (2)	1395 (3)
N3	4522 (3)	6655 (2)	3175 (3)	N4	4827 (3)	8188 (2)	3110 (3)
O1	3030 (2)	4240 (2)	−682 (3)	C1	6144 (3)	3326 (2)	3130 (4)
C2	6336 (3)	2448 (2)	2572 (4)	C3	5709 (3)	2205 (2)	1246 (4)
C4	4841 (3)	2848 (2)	533 (4)	C5	4653 (3)	3711 (2)	1164 (3)
C6	3658 (3)	4415 (2)	538 (3)	C7	2435 (3)	5804 (2)	916 (4)
C8	2174 (3)	6501 (2)	2141 (4)	C9	3346 (3)	7084 (2)	2614 (4)
C10	3541 (4)	8023 (2)	2557 (4)	C11	5375 (4)	7354 (2)	3467 (4)
O2	6102 (3)	9872 (2)	2602 (3)				
			Compound **7**				
Cu	3106 (1)	3039 (1)	1484 (1)	Br1	2474 (1)	1774 (1)	2481 (1)
Br2	911 (1)	5680 (1)	3838 (2)	O	3255 (7)	5311 (4)	3126 (10)
N1	1471 (6)	3618 (4)	1285 (9)	N2	3742 (6)	4095 (4)	2201 (10)
N3	4706 (6)	2648 (4)	1441 (9)	N4	6286 (7)	1886 (5)	1505 (11)
N5	−687 (7)	3741 (5)	900 (11)	C1	275 (8)	3366 (5)	619 (11)
C2	−10 (9)	2638 (6)	−521 (13)	C3	−435 (10)	4406 (7)	1846 (15)
C4	735 (10)	4727 (6)	2504 (12)	C5	1706 (8)	4322 (5)	2177 (11)
C6	3000 (8)	4619 (6)	2578 (12)	C7	5016 (9)	4363 (6)	2464 (13)
C8	5499 (9)	3993 (6)	1049 (13)	C9	5649 (8)	3128 (6)	1261 (12)
C10	6624 (8)	2648 (6)	1290 (12)	C11	5117 (8)	1906 (6)	1570 (12)

[a] Multiplied by 10^4.

PDP 11 computer for data manipulation. Samples were run at 9 GHz (X-band) in the temperature range 80–298 K. Room-temperature magnetic susceptibility measurements were performed on a Johnson Matthey magnetic susceptibility balance. Diamagnetic corrections were calculated from Pascal constants.[12] Variable-temperature magnetic susceptibility measurements in the polycrystalline state were carried out on an SHE Model 905 SQUID susceptometer. A Kel-F sample holder was used, and its moment was subtracted from the observed moment with the sample present at every temperature in order to obtain moment due to the sample alone. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA. The percent Cu was determined by EDTA titration using Fast Sulphon Black F as indicator.[13]

Results and Discussion

The halo-bridged complexes **4**–**7** have been synthesized from CuX_2 (X = Cl, Br) and PypepH (**2**) or PmpepH (**3**) in methanol. Addition of a base like triethylamine following initial mixing of the two reactants appears to be essential for successful coordination by these peptide ligands. This requirement is clearly evident in the case of complexes with PmpepH, where addition of triethylamine brings about a change in color from brown to dark green and precipitation of crystalline products within few hours. In the absence of triethylamine, no crystalline products are obtained[14] and the greenish brown reaction mixtures decompose to unknown products on long standing. Clearly, deprotonation of the peptide nitrogen with concomitant coordination to a copper(II) center is assisted by triethylamine. The weaker donor property of PmpepH[7] (vide infra) is reflected in the instability of **6** and **7** in water or even in aqueous methanol.

Structure of $[Cu(Pypep)Cl]_2 \cdot 2H_2O$ (4). The crystal structure is made up of unit cells containing four $Cu(Pypep)Cl \cdot H_2O$ units. These units pair up to result in centrosymmetric chloro-bridged dimers. The closest approach of two dimers is 2.335 Å ($O1_a \cdots HW_b$, where W is a water molecule and a and b refer to two different dimers). Within the asymmetric unit, hydrogen bonding between the water molecule and the amide oxygen is evidenced by the O2–HO2 distance of 1.727 Å. An ORTEP drawing of the dimer is shown in Figure 1, and selected bond distances and angles are listed in Table III.

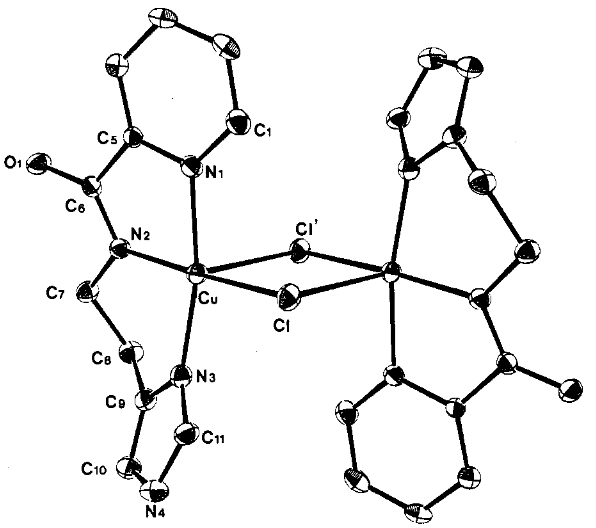

Figure 1. ORTEP drawing of $[Cu(Pypep)Cl]_2$ showing 50% probability ellipsoids and the atom-labeling scheme. Hydrogen atoms and the lattice water molecules have been omitted for clarity.

The coordination geometry around each copper atom in the dimer is distorted square-pyramidal with the three nitrogen atoms of the peptide ligand in the basal plane. The pyridine and the imidazole N atoms are trans to one another. The deprotonated amido nitrogen is trans to a bridging chlorine atom in the square plane, while the second bridging chlorine atom (Cl') occupies the apical position of the pyramid. An essentially similar type of binding of **2** to copper(II) as a monoanionic and tridentate ligand has been observed previously.[7] The Cu–N(peptide) and Cu–N(imidazole) distances in copper complexes of glycyl-L-histidine[15] and glycyl-L-histidylglycine[16] fall in the narrow ranges of 1.93–1.98 and 1.93–1.99 Å, respectively. The Cu–N(pyridine) bond is usually 2.00–2.05 Å long.[2d,17] Thus, the Cu–N bond lengths in

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(14) This statement is true except for **4**. A lower yield of **4** has also been obtained in the absence of triethylamine. Formation of the desired complex in this case might be due to the lower pK_a of PypepH.

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Table III. Selected Bond Distances and Angles

	Compound **4**		
	Distances (Å)		
Cu–Cl	2.319 (1)	Cu–Cl′	2.831 (1)
Cu–N1	2.014 (3)	Cu–N2	1.972 (3)
Cu–N3	1.973 (3)	N1–C1	1.350 (4)
N1–C5	1.346 (5)	C1–C2	1.365 (5)
C2–C3	1.369 (6)	C3–C4	1.390 (5)
C4–C5	1.372 (5)	C5–C6	1.496 (5)
C6–O1	1.265 (4)	N2–C6	1.315 (5)
N2–C7	1.475 (4)	C7–O8	1.537 (5)
C8–C9	1.479 (5)	N3–C9	1.396 (5)
N3–C11	1.325 (5)	N4–C11	1.332 (5)
N4–C10	1.377 (5)	C9–C10	1.345 (5)
Cu–Cu′	3.693 (1)		
	Angles (deg)		
Cl–Cu–N1	93.8 (1)	Cl–Cu–N2	173.0 (1)
Cl–Cu–N3	92.4 (1)	Cl′–Cu–N1	91.5 (1)
Cl′–Cu–N2	96.1 (1)	Cl′–Cu–N3	99.2 (1)
N1–Cu–N2	81.3 (1)	N1–Cu–N3	167.8 (1)
Cl–Cu–Cl′	88.9 (1)	Cu–Cl–Cu′	91.1 (1)
N2–Cu–N3	91.5 (1)	Cu–N1–C1	129.1 (3)
Cu–N1–C5	112.3 (2)	C1–N1–C5	118.6 (3)
N1–C1–C2	122.1 (4)	C1–C2–C3	119.6 (3)
C2–C3–C4	118.8 (3)	C3–C4–C5	119.2 (4)
C4–C5–C6	122.9 (3)	C4–C5–N1	121.7 (3)
N1–C5–C6	115.4 (3)	C5–C6–O1	118.8 (3)
O1–C6–N2	127.7 (3)	C5–C6–N2	113.4 (3)
C6–N2–Cu	115.6 (2)	C6–N2–C7	115.8 (3)
Cu–N2–C7	128.2 (2)	N2–C7–C8	110.9 (3)
C7–C8–C9	112.8 (3)	C8–C9–C10	131.0 (4)
C8–C9–N3	120.3 (3)	N3–C9–C10	108.6 (3)
C9–C10–N4	106.9 (3)	C10–N4–C11	107.6 (3)
N4–C11–N3	111.1 (3)	C11–N3–C9	105.7 (3)
C11–N3–Cu	128.4 (3)	C9–N3–Cu	124.1 (2)
	Compound **7**		
	Distances (Å)		
Cu–Br1	2.452 (1)	Cu–Br1′	3.027 (1)
Cu–N1	2.066 (7)	Cu–N2	1.936 (7)
Cu–N3	1.950 (7)	N1–C1	1.368 (10)
N1–C5	1.360 (11)	C1–C2	1.494 (13)
C1–N5	1.341 (11)	N5–C3	1.326 (14)
C3–C4	1.383 (15)	C4–Br2	1.892 (10)
C4–C5	1.391 (12)	C5–C6	1.496 (13)
C6–O	1.245 (11)	N2–C6	1.318 (12)
N2–C7	1.473 (11)	C7–C8	1.522 (13)
C8–C9	1.469 (12)	N3–C9	1.386 (11)
N3–C11	1.326 (11)	N4–C11	1.350 (11)
N4–C10	1.364 (12)	C9–C10	1.369 (12)
Cu–Cu′	4.338 (1)		
	Angles (deg)		
Br1–Cu–N1	94.2 (2)	Br1–Cu–N2	145.4 (2)
Br1–Cu–N3	94.7 (2)	Br1′–Cu–N1	87.4 (2)
Br1′–Cu–N2	99.0 (2)	Br1′–Cu–N3	86.5 (2)
N1–Cu–N2	80.6 (3)	N1–Cu–N3	170.1 (3)
Br1–Cu–Br1′	115.2 (2)	Cu–Br1–Cu′	104.2 (2)
N2–Cu–N3	92.6 (3)	Cu–N1–C1	130.7 (6)
Cu–N1–C5	110.0 (5)	C1–N1–C5	118.8 (7)
N1–C1–C2	119.3 (8)	C2–C1–N5	116.6 (8)
N1–C1–N5	124.1 (8)	C1–N5–C3	116.3 (9)
C3–C4–C5	118.0 (9)	C3–C4–Br2	117.6 (8)
Br2–C4–C5	124.4 (8)	C4–C5–C6	125.9 (8)
C4–C5–N1	118.8 (8)	N1–C5–C6	115.1 (7)
C5–C6–O	119.7 (9)	O–C6–N2	127.3 (9)
C5–C6–N2	112.9 (8)	C6–N2–Cu	118.0 (6)
C6–N2–C7	116.0 (7)	Cu–N2–C7	125.9 (6)
N2–C7–C8	109.7 (7)	C7–C8–C9	112.2 (8)
C8–C9–C10	130.6 (9)	C8–C9–N3	121.5 (8)
N3–C9–C10	107.9 (8)	C9–C10–N4	107.3 (8)
C10–N4–C11	107.6 (3)	N4–C11–N3	110.5 (9)
C11–N3–C9	106.8 (7)	C11–N3–Cu	128.8 (6)
C9–N3–Cu	124.4 (5)		

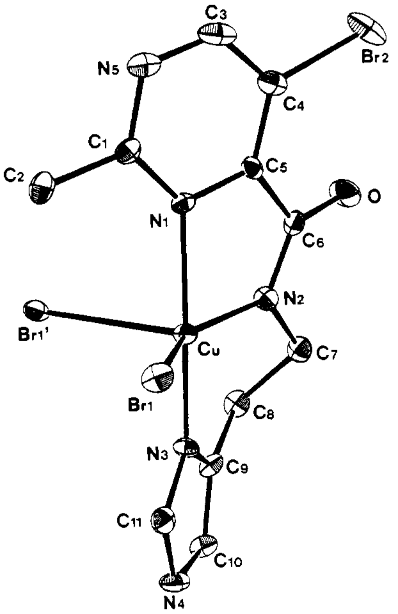

Figure 2. ORTEP drawing of the repeating unit [Cu(Pmpep)Br] in **7** showing 50% probability ellipsoids and the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. The bridging bromine atom Br′ belongs to the adjacent [Cu(Pmpep)Br] unit.

4 (Table III) are quite comparable to those found in other related compounds. The geometry and dimensions of the coordinated ligand are rather regular except for the peptide junction where, compared to those of free ligands, the C–N and the C–O bonds are respectively shorter and longer as a result of coordination of the deprotonated amido nitrogen to copper(II).[4a]

Two different Cu–Cl bond distances in the Cu_2Cl_2 unit appear to be the common feature among the chloro-bridged dimeric complexes of copper(II).[1] The difference varies from 0.16 Å in $[Cu(guaninium)Cl_3]_2 \cdot 2H_2O$ to 1.07 Å in $[Cu(2\text{-}Mepy)_2Cl_2]_2$.[3c] In **4**, the Cu–Cl apical bond is 0.51 Å, longer than the basal one (Table III). The Cu–Cl–Cu′ bridging angle is 91.1 (1)°. These two characteristic numbers are practically identical with those for $[Cu(terpy)Cl]_2(PF_6)_2$.[2a] The Cu–Cu′ distance in **4** (3.693 (1) Å) is also comparable to those observed in analogous compounds.[2c]

Structure of $[Cu(Pmpep)Br]_\infty$ (7). The crystal structure of **7** consists of unit cells each containing four Cu(Pmpep)Br units. These units bridge through Br^- ions to give rise to a novel zigzag polymeric chain structure in the lattice. An ORTEP drawing of the repeat unit is shown in Figure 2, and selected interatomic dimensions are given in Table III. The mono(μ-bromo)-bridged chain structure is shown in Figure 3.

The disposition of donor atoms around copper in **7** can be described as distorted square-pyramidal. The basal sites are occupied by three nitrogen atoms of the deprotonated peptide ligand and the bromine atom, while the bromine atom of the next repeating unit occupies the apical position (Figure 3). The copper atom sits slightly above the basal plane, toward the apical ligand. The mode of binding of the Pmpep moiety to copper in **7** is identical with that found in $[Cu(Pmpep)(CH_3COO)(H_2O)]$.[7] Also, the three Cu–N distances are quite comparable in these two complexes. The Cu–Br distance (2.452 (1) Å) in **7** is close to that observed with $[Cu(py)Br_2]_2$[18] (2.412 (4) Å) as well as $[Cu(2\text{-}Mepy)_2Br_2]$ (2.413 (3) Å).[19]

The most unusual feature of the crystal structure of **7** is the occurrence of the polymeric zigzag chain structure as a result of the apical Cu–Br interaction among the repeating units. The Cu(Pmpep) moieties are located on alternate sides of the chain presumably to minimize steric crowding. Steric requirements might also be responsible for the formation of the novel mono(μ-bromo)-bridged chain structure (Figure 3) since the centrosymmetric $[Cu(Pmpep)Br]_2$ complex with the Cu_2Br_2 core would have been an unfavorably crowded molecule due to two bulky

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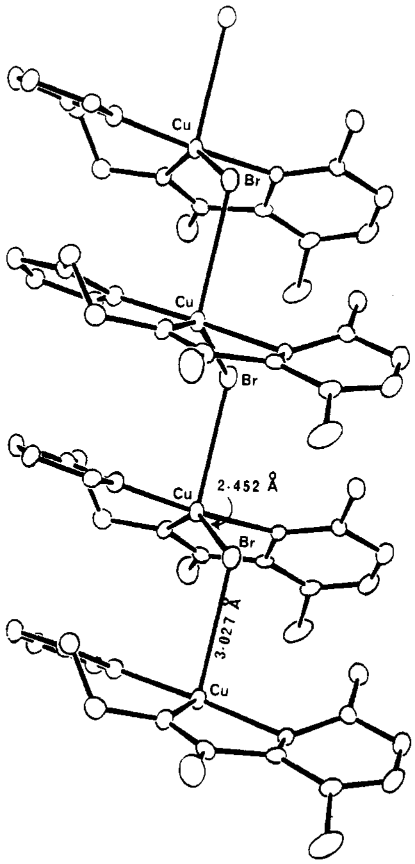

Figure 3. ORTEP drawing of the chain structure in the crystal lattice of 7. Alternate disposition of the organic framework along the zigzag chain minimizes steric crowding in such structures.

substituents on the pyrimidine ring of the Pmpep moiety.[20] Though mono(μ-chloro)-bridged copper(II) chain compounds are known,[1a,21] compounds with the mono(μ-bromo)-bridged chain structure are scarce. The structure of **7** is unique in this respect. In copper(II) complexes containing a centrosymmetric Cu_2Br_2 unit, the two types of bridging Cu–Br distances lie in the ranges of 2.38–2.56 and 2.46–3.87 Å.[1a] In **7**, the apical Cu–Br distance is 3.027 (1) Å. Clearly, the apical Cu–Br interaction, which holds the repeating Cu(Pmpep)Br units in the chain, is quite strong. The Cu–Cu′ distance (4.338 (1) Å) in the chain structure of **7** is considerably longer than that in a typical bis(μ-bromo)-bridged structure like $[Cu(py)Br_2]_2$ (3.643 (9) Å)[18] but is comparable to Cu–Cu′ distances found in the mono(μ-chloro)-bridged copper(II) chain compounds.[21] The $Cu–Br_b–Cu'$ angle (104.2 (2)°, b = bridging) in **7** is however smaller than the $Cu–Cl_b–Cu'$ angles (114–144°) reported for such chain complexes.

Since we have determined the crystal structures of two complexes (**4** and **7**) out of a total of four, it must be pointed out that assignment of distinct dimeric (**4** and **5**) vs polymeric chain (**6** and **7**) structure is based, at least in part, on steric requirements of the ligands.

EPR Spectra. At liquid-N_2 temperature, the EPR spectrum of a polycrystalline sample of **4** appears to be approximately axial with the low-field absorption in the $g_\parallel$ region barely visible as a shoulder. Under the same conditions, broad and isotropic EPR spectra are recorded for the other three complexes (**5**–**7**). The observed spectral parameters are listed in Table IV. EPR spectra of **4** and **5** in water, methanol, or DMF glasses are, however, typical of a monomeric tetragonal copper(II) complex with a $d_{x^2-y^2}$ ground-state doublet. The spectrum of **4** in a 7:3 water:glycerol (v/v) glass and that of **6** in frozen DMF solution (80 K) are displayed in Figure 4. The bis(μ-halo)-bridged structures are dissociated in such solutions presumably due to additional coordination by the solvent molecules. Similar behavior has been observed with the acetate-bridged copper(II) complex of PypepH.[7] The mono(μ-halo)-bridged structures in **6** and **7** also appear to dissociate into monomeric units, since both complexes exhibit monomeric copper(II) spectra in frozen methanol or DMF solution. Thus, the EPR data (Table IV) indicate that the halide bridges observed in crystalline **4**–**7** are weak and readily dissociable. It is quite possible that, in solution, an equilibrium between monomeric and bridged species exists for each of these peptide complexes.[22] Slow crystallization from methanol, however, allows isolation of the bridged structures only.

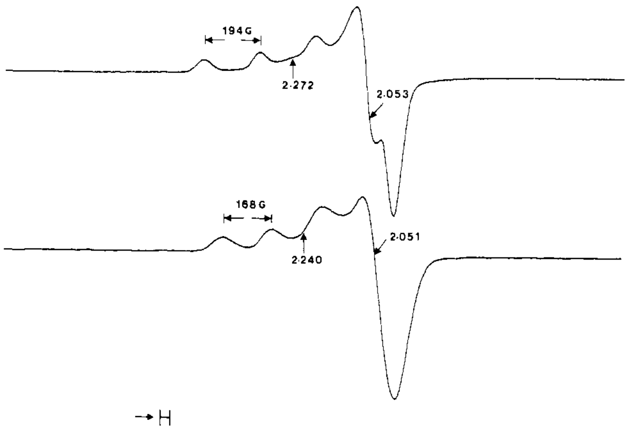

Figure 4. X-band EPR spectra (80 K) of **4** in 7:3 water:glycerol (v/v) glass (top) and **6** in frozen DMF solution (bottom). Selected g and $A_\parallel$ values are indicated. Spectrometer settings: microwave frequency, 9.19 GHz; microwave power, 10 mW; modulation frequency, 100 kHz; modulation amplitude, 2.0 G.

Table IV. EPR Parameters at 80 K

complex	$g_\parallel$	$g_\perp$	$A_\parallel$, G
$[Cu(Pypep)Cl]_2 \cdot 2H_2O$ (**4**)			
solid	2.198	2.070	
aq glass[a]	2.272	2.053	194
MeOH glass	2.240	2.043	194
$[Cu(Pypep)Br]_2$ (**5**)			
solid[b]	2.102		
aq glass[a]	2.266	2.054	194
MeOH glass	2.239	2.051	194
DMF glass	2.230	2.043	194
$[Cu(Pmpep)Cl]_\infty$ (**6**)[c]			
solid[b]	2.134		
MeOH glass	2.257	2.053	168
DMF glass	2.240	2.051	168
$[Cu(Pmpep)Br]_\infty$ (**7**)[c]			
solid[b]	2.151		
MeOH glass	2.245	2.046	168
DMF glass	2.244	2.041	168

[a] Spectrum obtained in 7:3 water:glycerol (v/v) mixture. [b] Only broad isotropic signal recorded. [c] Complex decomposes in water.

The EPR parameters collected in Table IV afford additional features of the coordination structures of the complexes. In tetragonal copper(II) complexes, increase in the strength of the basal ligand field brings about a reduction in the value of $g_\parallel$ with concomitant increase in the $A_\parallel$ value.[23] Since the $A_\parallel$ values observed with **4** and **5** are significantly larger than those recorded for **6** and **7** (Table IV), PypepH is the stronger ligand. Also, the higher $g_\parallel$ and smaller $A_\parallel$ values noted for complexes derived from PmpepH (**6** and **7**) are indicative of off-planar distortion in the coordination sphere of copper in such complexes.[7,24] Both these

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(20) In previous attempts with PmpepH,[7] only the mononuclear complex $[Cu(Pmpep)(CH_3COO)(H_2O)]$ has been isolated. The formation of the acetate-bridged dimer is presumably prohibited on steric grounds.

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(22) The EPR data also suggest that, in aqueous solution, this equilibrium lies to the dimer side for both **4** and **5**.

(23) Brill, A. S. *Mol. Biol. Biochem. Biophys* **1977**, *26*, 43.

(24) Miyoshi, K.; Tanaka, H.; Kimura, E.; Tsuboyama, S.; Murata, S.; Shimizu, H.; Ishizu, K. *Inorg. Chim. Acta* **1983**, *78*, 23.

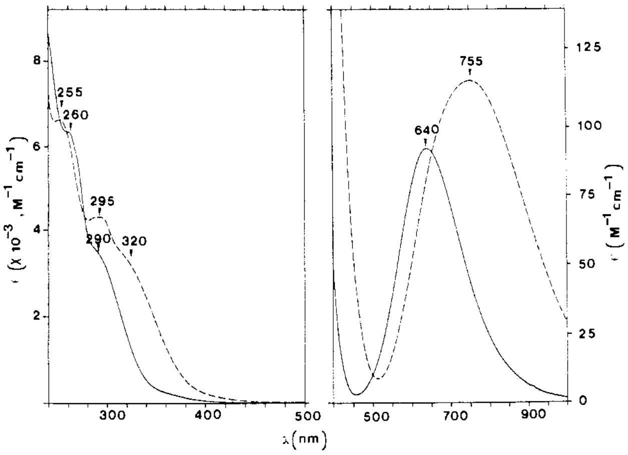

Figure 5. Absorption spectra of **4** (solid line) and **6** (broken line) in methanol solutions.

Table V. Electronic Spectral Data

complex	solvent	λ_{max}, nm (ϵ,[a] M^{-1} cm^{-1})
4[b]	H_2O	620 (65), 280 sh (4200), 260 (sh) (6000)
	MeOH	640 (90), 290 sh (3700), 260 sh (6300)
5	H_2O	620 (63), 280 sh (4000), 260 sh (5600)
	MeOH	650 (92), 290 sh (3500), 260 sh (5800)
	DMF	640 (95), 300 sh (3500)
6[c]	MeOH	755 (115), 320 sh (3600), 295 sh (4500), 255 sh (6500)
	DMF	740 (110), 320 sh (3400)
7[c]	MeOH	790 (125), 320 sh (3900), 295 sh (4700), 255 sh (7300)
	DMF	815 (155), 320 sh (3400)

[a] Values quoted per Cu atom. [b] Complex insoluble in DMF. [c] Complex decomposes in water.

features are supported by the absorption spectra of the complexes (vide infra).

As one goes through Table IV, it becomes evident that the EPR parameters of the complexes change only when the peptide ligand is changed. Hardly any variation is observed with change in the halide ligand. This is somewhat surprising since the replacement of Cl^- with Br^- in the basal plane of copper is expected to alter the in-plane ligand field to some extent. When parameters from Table IV are compared with those of $[Cu(Pypep)(CH_3COO)]_2 \cdot 1.46H_2O$ and $[Cu(Pmpep)(CH_3COO)(H_2O)]$,[7] it becomes evident that replacement of halide ions with acetate does not bring about noticeable changes in the EPR parameters either. Taken together, the EPR data suggest that PypepH and PmpepH each give rise to complexes whose EPR parameters are characteristic of the particular peptide ligand they contain. Since both these peptide ligands occupy three of the four basal coordination sites around copper(II) ion in all these complexes, it is quite possible that the spectral characteristics are determined almost exclusively by them. The remaining donor atoms exert significantly smaller influence on the EPR parameters of the resulting complexes. These results indicate that extra caution must be taken in assigning the various donor centers around the metal in Cu(II)-BLM[6] and the analogues[25] on the basis of solution spectral parameters.

Absorption Spectra. Shown in Figure 5 are the absorption spectra of **4** and **6** in methanol; the peak positions and extinction coefficients of the four complexes are collected in Table V. In each case, the characteristic blue or green color arises from one broad d-d band in the visible region. The blue shift of the band maximum in the case of **4** and **5** indicates that PypepH is the stronger of the two peptide ligands. That the pyrimidine N provides a weaker ligand field in the basal plane of the otherwise similar copper(II) chromophore has been noted previously.[7] Both the intensity and the width of the d-d band are enhanced in the case of **6** and **7** (Figure 5, Table V) presumably due to distortion of the coordination geometry.[24] Off-plane distortion in the coordination sphere of copper(II) in complexes of PmpepH is believed to arise from steric constraints in the ligand framework. Such distortion appears to be severe in **7** since, in methanol or DMF solution, a shoulder around 700 nm is observed in its electronic spectrum. With any particular species, shift of the visible band maximum with change in solvent (Table V) is indicative of axial coordination by solvent molecule(s).[27]

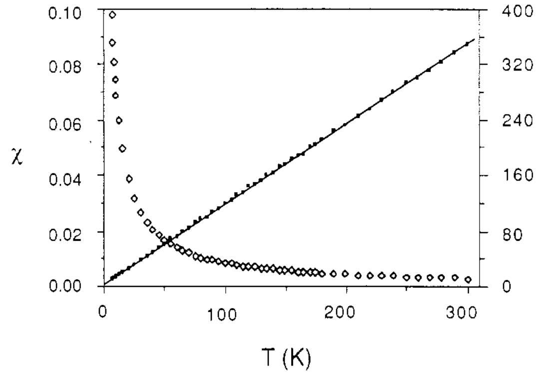

Figure 6. Temperature dependence of the molar magnetic susceptibility χ (emu/mol) and the inverse susceptibility of $[Cu(Pypep)Cl]_2 \cdot 2H_2O$ (**4**). The solid line is a fit to the Curie-Weiss law.

The features in the 350-250-nm range of the electronic spectra of **4**-**7** are associated with metal-to-ligand and intraligand transitions. The spectral parameters (Table V) are very similar to those reported for $[Cu(Pypep)(CH_3COO)]_2 \cdot 1.46H_2O$ and $[Cu(Pmpep)(CH_3COO)(H_2O)]$. The various absorptions have already been assigned, and pertinent discussion can be found in ref 7.

Magnetic Susceptibility. Initially, our interest in the set of complexes **4**-**7** was focused on the possibility of chloride (and bromide) ion coordination to copper(II) centers bonded to specific N-donor ligands that mimic part of the metal-chelating portion of BLM. However, the discovery of the novel halo-bridged structures of these peptide complexes prompted us to carry out a preliminary magnetic susceptibility study on **4** and **7**, for which the structures have been determined. It must be emphasized here that neither elaborate susceptibility measurements nor rigorous theoretical fittings of the data have been completed at the present time. Such studies are in progress, and the results will be reported elsewhere.

In the polycrystalline state and at room temperature, complexes **4**-**7** exhibit effective magnetic moment values in the range 1.76-1.87 μ_B/Cu atom. For **4** and **7**, magnetic susceptibility measurements were carried out over the temperature range 6-300 K by using a SQUID susceptometer. For **4**, an amount of 13.70 mg of powdered sample was used and a field of 20 kG was employed. For **7**, the weight of the sample used was 34.20 mg and two sets of data were collected at two different field strengths (5 and 40 kG). No temperature-independent paramagnetism (TIP) term was included in any calculation. A plot of molar susceptibility (χ) vs temperature (T) for **4** is given in Figure 6. Analysis of the temperature variation of the inverse susceptibility (Figure 6) with the use of Curie-Weiss law yields a g value of 2.137 and a Θ value of -2.07 (4), an indication of a small antiferromagnetic coupling constant. EPR measurement in the polycrystalline state (80 K) affords a g_{av} value of 2.113 (Table IV). As an approximation to the susceptibility behavior,[28,29] the Bleany-Bowers

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(26) Reference deleted in revision.

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Inorg. Chem. **1988**, *27*, 1587-1592 1587

expression[30] was employed. With the value of g fixed at 2.137, use of 52 data points in the temperature range 6.7–299.7 K leads to a value of -2.316 (5) cm^{-1} (correlation coefficient 0.999 983) for the exchange coupling constant J of the antiferromagnetically coupled dimer **4**.[31]

When the $1/\chi$ vs T data for **7** is fitted to Curie–Weiss law, a small positive value is obtained for the constant Θ. For example, the set of data collected at 5-kG field yields a Θ value of $+1.085$. This indicates a ferromagnetically coupled ground state for **7**. Weak ferromagnetic interaction between adjacent copper(II) centers has been reported for mono(μ-chloro)-bridged copper(II) chain complexes of caffeine and 2-(2-(methylamino)ethyl)pyridine.[1c,21] Ferromagnetic ground states have also been observed in bis(μ-chloro)-bridged dimeric[32] and chain complexes[33] of divalent copper. A complete report on the magnetic properties of **7** will be reported later, following the acquisition of a good data set at extremely low temperatures.

Summary. The following are the principal results and conclusions of this investigation:

(1) A set of novel halo-bridged copper(II) complexes (**4**–**7**) of two peptide ligands, PypepH and PmpepH, have been synthesized, and the crystal structures of **4** and **7** have been determined. These complexes constitute a rare class of halo-bridged peptide complexes of bivalent copper.

(2) In **4**, two copper centers are bridged by two Cl$^-$ ions, giving rise to a centrosymmetric dimer. A similar structure is predicted for **5**. In **7**, two adjacent Cu(Pmpep)Br units are bridged by a single Br$^-$ ion and the pattern continues to give rise to a novel mono(μ-bromo)-bridged chain compound. A mono(μ-chloro)-bridged structure is assumed for **6**. Steric constraints, imposed by PmpepH, are responsible for the formation of the unusual mono(μ-halo)-bridged structures.

(3) When dissolved in water, methanol, or DMF, the halo-bridged complexes readily dissociate into monomeric tetragonal copper(II) species.

(4) The EPR parameters for each of the monomeric copper(II) species are characteristic of the particular peptide ligand it is derived of. The coordinated halide ion has minor influence on these values.

(5) Variable-temperature magnetic susceptibility studies demonstrate that the two copper(II) centers in **4** are antiferromagnetically coupled with an exchange coupling constant (J) value of -2.32 cm^{-1}. Similar measurements suggest a ferromagnetic ground state for **7**.

Acknowledgment. This research was supported by a Faculty Research Grant and the donors of the Petroleum Research Fund, administered by the American Chemical Society, at the University of California, Santa Cruz, CA, and by the NSERC of Canada at the University of Windsor, Ontario, Canada. We thank Drs. William Armstrong, Angelica Stacy, and Karl Hagen for help with susceptibility measurements.

Registry No. 4, 113403-58-0; 5, 113403-59-1; 6, 113403-60-4; 7, 113403-61-5.

Supplementary Material Available: Crystal structure data for [Cu(Pypep)Cl]$_2$·2H$_2$O (**4**) and [Cu(Pmpep)Br]$_\infty$ (**7**) including thermal parameters for non-hydrogen atoms (Table S1) and hydrogen atom parameters (Table S2) (3 pages); observed and calculated structure factors (Table S3) for **4** and **7** (12 pages). Ordering information is given on any current masthead page.

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(28) We are aware of the use of the more general magnetization expression[2b,2c,29] for a pair of $S = {}^1/_2$ ions in cases where the singlet–triplet splitting is comparable to (or smaller than) the Zeeman energy $g\mu_BB$ (B = magnetic field strength). As mentioned in the text, theoretical treatment of the susceptibility data will be reported in detail at a later date.

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Effectiveness of the Cadmium(II) Ion in Promoting Sulfonamide Nitrogen Deprotonation. ^{113}Cd NMR, Polarographic, and pH-Metric Investigations on the Cadmium(II)–*N*-Tosylglycinate and Cadmium(II)–*N*-Dansylglycinate Systems in Aqueous and Methanolic Solutions

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^{113}Cd NMR, polarographic, and pH-metric investigations reveal the ability of the Cd^{2+} ion in substituting for the nitrogen-bound hydrogen of the amino acids N-protected by a sulfonic group. In aqueous and methanolic solution, *N*-tosylglycine and *N*-dansylglycine interacting with the Cd^{2+} ion show a pH-dependent binding mode, at increasing pH changing from simple carboxylate to N,O-bidentate ligands. The overall equilibria involving the prevailing complexes are similar to those previously found with the Cu^{2+} ion, but the stability of the cadmium complexes is lower by factors ranging from 10 to 10^4. Two binary complexes of formula [CdL$_2$(H$_2$O)$_4$] (L = *N*-tosylglycinate, *N*-dansylglycinate) were separated in the solid state. X-ray powder spectra and IR data for the complex of *N*-tosylglycine show that it is isomorphous and isostructural with the analogous complexes with Zn^{2+}, Co^{2+}, and Ni^{2+}, in which the ligand is monodentate through the carboxylate group.

Introduction

Metal coordination of a peptide or sulfonamide nitrogen may only occur upon the substitution of the metal ion for the bound hydrogen.[1,2] The transition-metal ions exhibit different abilities in such a displacement: the order Pd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} has been found in peptide hydrogen substitution,[1] while

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(1) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385 and references cited therein.

(2) Sigel, H. *Angew. Chem.* **1968**, *80*, 124.

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