the recognition species. Distortions such as the one noted here, which generate a pseudo-2-fold rotation axis, may arise in binding to DNA dyad structures.

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Supplementary Material Available: Figures showing ^{1}H NMR spectra and square-wave voltammetric scans of *cis*-[NCl(phen)$_2$Tc]Cl·H$_2$O and [NCl(phen)$_2$Tc]PF$_6$ in DMF, square-wave voltammetric scans of *cis*-[NCl(phen)$_2$Tc]$^+$ in DMF, an ORTEP diagram of [NCl(phen)$_2$Tc]PF$_6$, and infrared spectra and tables of complete crystallographic data, temperature factors for non-hydrogen atoms, complete bond distances and angles, and results of calculations of least squares planes (29 pages); listings of calculated and observed structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.[33–37]

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New 12-Membered and 24-Membered Macrocycles with Pendent Acetato Groups and X-ray Crystal Structures of the Copper(II) and Manganese(II) Complexes

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A condensation reaction between ethylenediaminetetraacetic dianhydride and ethylenediamine provided two new macrocyclic ligands: one is a 12-membered macrocycle with two pendent acetato groups, $C_8H_{14}N_4O_2(CH_2CO_2H)_2$ [represented as $L(12)H_2$], and the other is a 24-membered macrocycle with four pendent acetato groups, $C_{16}H_{28}N_8O_4(CH_2CO_2H)_4$ [represented as $L(24)H_4$], in which two ethylenediaminetetraacetato groups and two ethylenediamine groups are linked by amide bonds. The formation of the macrocycles was confirmed by X-ray crystal analyses of their metal complexes, $CuL(12)\cdot 4H_2O$ and $Mn_2L(24)\cdot 8H_2O$. The copper(II) complex crystallized in the orthorhombic space group $P2_12_12_1$ with a = 10.070 (1) Å, b = 18.832 (2) Å, c = 9.425 (1) Å, and Z = 4. Each copper atom has a distorted octahedral coordination geometry with two amine nitrogen atoms (Cu–N = 2.088 and 2.485 Å), an amide oxygen atom (Cu–O = 1.988 Å), two carboxylato oxygen atoms (Cu–O = 1.996 and 2.334 Å), and another carboxylato oxygen atom from a neighboring metal chelate (Cu–O = 1.936 Å); one of the amide groups is not coordinated to copper. One of the carboxylato groups is coordinated to two copper atoms, forming a one-dimensional –Cu–O–C–O–Cu– chain. The manganese complex crystallized in the hexagonal space group $P6_2$ (or $P6_4$) with a = 18.072 (3) Å, c = 10.195 (2) Å, and Z = 3. Each ligand coordinates two manganese ions, which are located outside the cavity of the macrocycle and are crystallographically equivalent to each other. Each manganese atom has a distorted seven-coordination geometry with two amine nitrogen atoms (Mn–N = 2.358 and 2.445 Å), two carboxylato oxygen atoms (Mn–O = 2.111 and 2.212 Å), a water molecule (Mn–O = 2.137 Å), and two amide oxygen atoms (Mn–O = 2.184 and 2.686 Å).

Introduction

The coordination chemistry of macrocyclic multidentate ligands is an established and important field.[2–4] Recently, a great deal of interest has been directed to metal complexes with functionalized macrocycles that have pendent functional groups such as amine, hydroxy, and carboxylato groups.[4–9] In attempts to synthesize new aliphatic macrocycles with pendent acetato groups, we have carried out a condensation reaction with ethylenediaminetetraacetic dianhydride and ethylenediamine. This reaction has resulted in the formation of two macrocycles as shown in Scheme I. One [represented as $L(12)H_2$] is a 12-membered macrocycle that has two pendent acetato groups, and the other [represented as $L(24)H_4$] is a 24-membered macrocycle with four pendent acetato groups. The formation of the macrocyclic rings

Scheme I

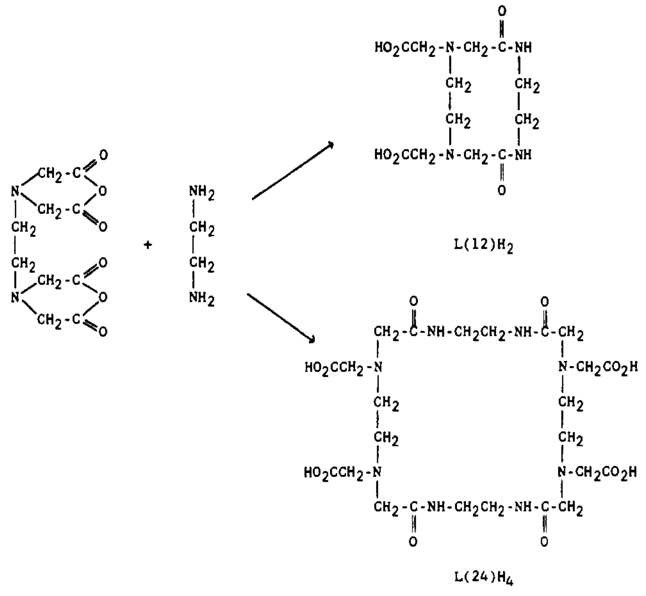

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Table I. Summary of Crystal Data for CuL(12)·4H_2O (I) and $Mn_2L(24)$·8H_2O (II)

	I	II
empirical formula	$CuC_{12}H_{26}N_4O_{10}$	$Mn_2C_{24}H_{52}N_8O_{20}$
f.w.	449.90	882.60
T/°C	23	23
λ/Å (monochromated Mo Kα)	0.71073	0.71073
F(000)	940	1386
cryst dimens/mm	0.30 × 0.18 × 0.17	0.48 × 0.37 × 0.25
space group	orthorhombic $P2_12_12_1$ (No. 19)	hexagonal $P6_2$ (No. 171)[a]
a/Å	10.070 (1)	18.072 (3)
b/Å	18.832 (2)	18.072 (3)
c/Å	9.425 (1)	10.195 (2)
V/Å^3	1787.3 (6)	2884 (2)
Z	4	3
d_{calcd}/g cm^{-3}	1.67	1.56
μ/cm^{-1}	12.8	7.2
R[b]	0.040	0.036
R_w[c]	0.050	0.055

[a] Represented by one of the space groups of a chiral pair ($P6_2$ and $P6_4$). [b] $R = \sum|F_o - F_c|/\sum F_o$. [c] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

has been confirmed by X-ray crystal analyses of the copper(II) and the manganese(II) complexes, CuL(12) and $Mn_2L(24)$.

Experimental Section

Synthesis of Macrocyclic Ligands. In a three-neck flask assembled with a condenser, a dropping funnel, and a nitrogen-inlet tube, 2.05 g (8.0 mmol) of ethylenediaminetetraacetic dianhydride (supplied from Aldrich Chemical Co.) was suspended in 350 mL of dry dimethylformamide (DMF) with stirring under a nitrogen atmosphere. To the suspension was added dropwise a DMF solution (50 mL) containing 0.48 g (8.0 mmol) of ethylenediamine (supplied from Aldrich Chemical Co.) through the dropping funnel in a period of 2 h. The resulting reaction mixture was heated at 60 °C for 3 h and left to stand at room temperature overnight. The precipitate formed was removed by filtration. The filtrate was concentrated by the use of a rotary evaporator at a temperature below 60 °C, and 10 mL of water was added to the resulting viscous liquid. The finely divided solid that was formed was separated from the mixture by filtration, washed with tetrahydrofuran (THF), and dried in vacuum; this product was L(12)H_2. Yield: 0.6 g. Anal. Calcd for $C_{12}H_{20}N_4O_6$: C, 45.56; H, 6.37; N, 17.71. Found: C, 45.23; H, 6.31; N, 16.97. The filtrate was concentrated in a rotary evaporator, and the resulting viscous solution was mixed with a large amount of THF. The colorless solid that precipitated was found to be L(24)H_4. The product was collected on a glass filter, washed with THF, and dried in vacuum overnight. Yield: 1.2 g. At a higher reaction temperature, the yield of the 24-membered ligand decreased and that of the 12-membered ligand increased. Anal. Calcd for $C_{24}H_{40}N_8O_{12}$·H_2O: C, 44.30; H, 6.51; N, 17.22. Found: C, 44.67; H, 6.89; N, 16.69.

Synthesis of Metal Complexes. L(12)H_2 was suspended in water and was reacted with a large excess of copper(II) hydroxycarbonate (supplied from J. T. Baker Chemical Co.) at ca. 45 °C with stirring overnight. Unreacted solids were removed by filtration. Evaporation of the solvent at ca. 40 °C yielded a vitreous solid, which was repeatedly purified by crystallization from water. Light blue needlelike crystals suitable for an X-ray crystal analysis were grown from an aqueous solution by slow evaporation.

L(24)H_4 suspended in water was reacted with manganese(II) carbonate (supplied from J. T. Baker Chemical Co.) in the mole ratio 1:2 at 45 °C with stirring overnight. Unreacted solids were removed by filtration. The filtrate was concentrated at 45 °C. When the resulting solution was mixed with a large amount of ethanol, a colorless solid was obtained. Repeated recrystallization of the product from water by slow evaporation yielded needlelike colorless crystals.

A copper(II) complex with L(24)H_4 and a manganese(II) complex with L(12)H_2 were obtained by reactions between the appropriate carbonates and the ligands. Single crystals of these compounds have not yet been obtained.

Table II. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of CuL(12)·4H_2O

atom	x	y	z	B_{eq}[a]/Å^2
Cu	0.49178 (5)	0.23571 (3)	0.57602 (6)	1.557 (8)
O1	0.4096 (3)	0.2862 (2)	0.4202 (4)	2.26 (7)
O2	0.2060 (3)	0.2777 (2)	0.5147 (4)	2.05 (7)
O3	0.0711 (4)	0.1746 (2)	0.3494 (4)	2.17 (7)
O4	0.0181 (4)	0.0660 (2)	0.2751 (5)	3.42 (9)
O5	−0.0955 (4)	0.3526 (2)	0.4923 (4)	2.17 (7)
O6	−0.3238 (5)	0.3716 (3)	0.0667 (5)	4.6 (1)
N1	0.0861 (4)	0.3346 (2)	0.2854 (4)	1.51 (7)
N2	−0.1333 (4)	0.2370 (2)	0.2034 (5)	1.84 (7)
N3	−0.1356 (5)	0.4626 (2)	0.4059 (5)	2.67 (9)
N4	−0.3233 (4)	0.3571 (3)	0.3047 (5)	2.54 (9)
C1	0.0183 (5)	0.3370 (3)	0.1451 (5)	2.2 (1)
C2	−0.0338 (5)	0.2642 (3)	0.1021 (5)	2.22 (9)
C3	0.2282 (4)	0.3136 (3)	0.2722 (6)	1.85 (9)
C4	0.2831 (5)	0.2911 (3)	0.4166 (6)	1.97 (9)
C5	−0.1271 (6)	0.1585 (3)	0.2108 (6)	2.6 (1)
C6	−0.0028 (6)	0.1312 (3)	0.2823 (5)	2.27 (9)
C7	0.0767 (5)	0.4048 (3)	0.3569 (6)	2.1 (1)
C8	−0.0598 (5)	0.4067 (3)	0.4248 (6)	2.09 (9)
C9	−0.2713 (5)	0.2556 (3)	0.1593 (6)	2.4 (1)
C10	−0.3075 (5)	0.3344 (3)	0.1749 (6)	2.5 (1)
C11	−0.2743 (6)	0.4621 (3)	0.4549 (7)	3.1 (1)
C12	−0.3621 (6)	0.4301 (3)	0.3404 (8)	3.4 (1)
OW1	0.6732 (7)	0.6359 (3)	0.3121 (6)	6.6 (2)
OW2	0.3457 (7)	0.5026 (3)	0.5139 (8)	7.5 (2)
OW3	0.5991 (7)	0.9556 (4)	0.4053 (8)	7.9 (2)
OW4	0.5758 (6)	0.0684 (3)	0.2318 (8)	7.9 (2)

[a] $B_{eq} = (4/3)[a^2(\beta(1,1)) + b^2(\beta(2,2)) + c^2(\beta(3,3)) + ab(\cos\gamma)(\beta(1,2)) + ac(\cos\beta)(\beta(1,3)) + bc(\cos\alpha)(\beta(2,3))]$.

Table III. Selected Bond Distances (Å) in CuL(12)·4H_2O

Cu–O1	1.936 (4)	O1–C4	1.277 (6)
Cu–O2	2.334 (3)	O2–C4	1.233 (6)
Cu–O3	1.996 (4)	O3–C6	1.274 (6)
Cu–O5	1.988 (4)	O4–C6	1.248 (6)
Cu–N1	2.088 (4)	O5–C8	1.254 (6)
Cu–N2	2.485 (4)	O6–C10	1.249 (8)

X-ray Crystal Analyses. The data collection for each crystal was performed on a Syntex P2$_1$ diffractometer with the Crystal Logic automatic system. The cell parameters were determined using 25 reflections in the range of 20° < 2θ < 30°. Crystal data are summarized in Table I. The θ–2θ scan method was used. For CuL(12)·4H_2O, 2368 reflections were collected in the scan range $0 < 2\theta \leq 55°$; 2343 reflections were unique. The 1807 reflections with $I > 3\sigma_I$ were used in the refinements. For $Mn_2L(24)$·8H_2O, 5592 reflections were collected in the range $0 < 2\theta \leq 50°$; 1804 were unique. The 1510 reflections with $I > 3\sigma_I$ were used for the refinement. Metal atoms were located by direct methods, and the remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed at calculated positions and were included in the refinement. All calculations were performed on a VAX computer with an SPD/VAX program.

Results and Discussion

The reaction between ethylenediamine and ethylenediaminetetraacetic dianhydride was carried out at high dilution to prevent polymerization. The macrocycles, L(12)H_2 and L(24)H_4, shown in Scheme I were obtained as finely divided colorless solids. The 24-membered macrocycle was obtained as an amorphous material; its X-ray powder diffraction pattern showed a single broad peak with a maximum at 2θ ≈ 21°. The IR spectrum of L(24)H_4 exhibited broad bands probably due to the amorphous nature of the compound. On the other hand, L(12)H_2 showed well-defined X-ray powder diffraction peaks and sharp IR bands. One of the significant differences in the IR spectra of the two macrocycles was observed for the NH stretch; L(12)H_2 showed a very sharp strong band at 3300 cm^{-1}, whereas L(24)H_4 exhibited a broad band with a maximum at 3400 cm^{-1}. These bands were used as a diagnostic test in the separation of the two compounds. Both ligands readily reacted with metal carbonates and yielded the corresponding metal complexes as vitreous solids. When recrystallization was repeated, needlelike crystals suitable for X-ray analyses were obtained for CuL(12)·4H_2O and $Mn_2L(24)$·8H_2O.

Structure of CuL(12)·4H$_2$O. Table II shows the positional parameters of the non-hydrogen atoms for CuL(12)·4H_2O. Tables III and IV show the selected bond distances and the bond angles, respectively. Figure 1 displays the coordination geometry around copper. The ligand consists of a 12-membered ring with amide bonds and contains two pendent acetato groups. Each copper atom is coordinated to an amine nitrogen atom N1 (Cu–N = 2.088 Å), an amide oxygen atom O5 (Cu–O = 1.988 Å), a carboxylato oxygen atom O3 (Cu–O = 1.996 Å), and another carboxylato

Table IV. Selected Bond Angles (deg) in CuL(12)·4H_2O

O1–Cu–O2	99.8 (1)	O2–Cu–N2	142.9 (1)
O1–Cu–O3	91.3 (2)	O3–Cu–O5	177.1 (2)
O1–Cu–O5	88.6 (2)	O3–Cu–N1	97.7 (2)
O1–Cu–N1	168.7 (2)	O3–Cu–N2	74.5 (1)
O1–Cu–N2	108.5 (1)	O5–Cu–N1	82.7 (2)
O2–Cu–O3	81.4 (1)	O5–Cu–N2	102.7 (1)
O2–Cu–O5	101.5 (1)	N1–Cu–N2	80.7 (1)
O2–Cu–N1	75.0 (1)		

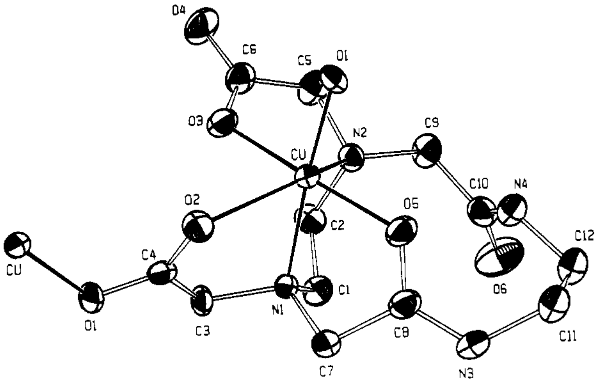

Figure 1. Coordination geometry around a copper atom in CuL(12). Atoms are shown at the 50% probability level.

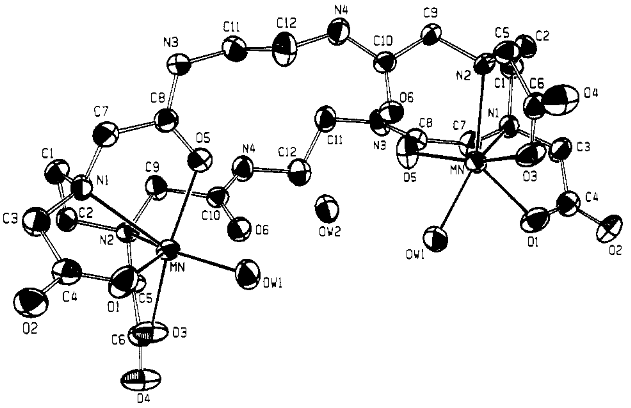

Figure 2. Molecular structure of $Mn_2L(24)\cdot 2H_2O$. Atoms are shown at the 50% probability level.

oxygen atom O1 that belongs to the neighboring metal chelate (Cu–O = 1.936 Å). In addition to these four atoms which form a plane around copper, an amine nitrogen atom N2 and a carboxylato oxygen atom O2 are weakly coordinated to copper, with Cu–N = 2.485 Å and Cu–O = 2.334 Å, and form an elongated octahedron around the copper. One of the amide groups is not coordinated to the metal ion. The 12-membered ring is too small to involve the metal ion inside its macrocyclic cavity. Water molecules are hydrogen-bonded to each other and are not coordinated to copper. One of the features of the structure is that one of the acetato groups is coordinated to two copper atoms, forming a one-dimensional –Cu–O–C–O–Cu– chain.

Table V. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of $Mn_2L(24)\cdot 8H_2O$

atom	*x*	*y*	*z*	$B_{eq}{}^a/\text{Å}^2$
Mn	0.41960 (5)	0.15747 (4)	0.311	2.16 (1)
O1	0.3105 (2)	0.1395 (3)	0.1896 (4)	3.5 (1)
O2	0.2128 (2)	0.1761 (3)	0.1542 (5)	3.39 (9)
O3	0.4970 (3)	0.2705 (2)	0.2046 (4)	3.2 (1)
O4	0.6163 (3)	0.3950 (3)	0.1965 (5)	4.2 (1)
O5	0.3787 (2)	0.0524 (2)	0.4508 (5)	3.28 (9)
O6	0.5609 (2)	0.1619 (2)	0.4042 (4)	2.73 (8)
N1	0.3103 (3)	0.1572 (2)	0.4530 (5)	2.30 (9)
N2	0.4974 (2)	0.2622 (2)	0.4714 (5)	2.12 (9)
N3	0.3031 (3)	−0.0148 (2)	0.6286 (5)	2.7 (1)
N4	0.6172 (3)	0.1702 (3)	0.6056 (5)	2.8 (1)
C1	0.3528 (3)	0.2167 (3)	0.5630 (6)	2.6 (1)
C2	0.4390 (3)	0.2911 (3)	0.5200 (6)	2.6 (1)
C3	0.2592 (3)	0.1830 (3)	0.3730 (6)	3.0 (1)
C4	0.2608 (3)	0.1639 (3)	0.2278 (6)	2.7 (1)
C5	0.5708 (3)	0.3337 (3)	0.4047 (6)	2.6 (1)
C6	0.5599 (3)	0.3341 (3)	0.2583 (6)	2.6 (1)
C7	0.2590 (3)	0.0681 (3)	0.4981 (6)	2.7 (1)
C8	0.3185 (3)	0.0342 (3)	0.5249 (6)	2.2 (1)
C9	0.5280 (3)	0.2297 (3)	0.5779 (6)	2.5 (1)
C10	0.5717 (3)	0.1843 (3)	0.5205 (5)	2.1 (1)
C11	0.3559 (3)	−0.0532 (3)	0.6582 (7)	3.0 (1)
C12	0.6679 (4)	0.1299 (3)	0.5726 (8)	3.4 (1)
OW1	0.4231 (3)	0.0717 (2)	0.1705 (4)	3.8 (1)
OW2	0.000	0.500	0.9678 (7)	3.1 (1)
OW3	0.1784 (3)	0.3009 (3)	0.2365 (6)	5.1 (1)
OW4	0.3423 (4)	0.4387 (4)	0.2455 (6)	5.8 (2)
OW5[b]	0.0416 (7)	0.0803 (7)	0.052 (1)	5.0

[a] $B_{eq} = (4/3)[a^2(\beta(1,1)) + b^2(\beta(2,2)) + c^2(\beta(3,3)) + ab(\cos\gamma)(\beta(1,2)) + ac(\cos\beta)(\beta(1,3)) + bc(\cos\alpha)(\beta(2,3))]$. [b] When OW5 was refined by assuming a fixed isotropic thermal parameter, an occupancy of approximately 0.5 was obtained.

Table VI. Selected Bond Distances (Å) in $Mn_2L(24)\cdot 8H_2O$

Mn–O1	2.212 (5)	O1–C4	1.244 (9)
Mn–O3	2.111 (4)	O2–C4	1.248 (8)
Mn–O5	2.184 (4)	O3–C6	1.268 (6)
Mn–O6	2.686 (4)	O4–C6	1.235 (6)
Mn–OW1	2.137 (5)	O5–C8	1.226 (7)
Mn–N1	2.445 (5)	O6–C10	1.237 (7)
Mn–N2	2.358 (4)	OW2–O6	2.767 (5)
		OW1–OW2	2.680 (6)

Table VII. Selected Bond Angles (deg) in $Mn_2L(24)\cdot 8H_2O$

O1–Mn–O3	87.9 (2)	O5–Mn–O6	72.6 (1)
O1–Mn–O5	110.4 (1)	O5–Mn–OW1	85.8 (2)
O1–Mn–O6	165.0 (2)	O5–Mn–N1	72.1 (2)
O1–Mn–OW1	82.2 (2)	O5–Mn–N2	93.1 (2)
O1–Mn–N1	70.8 (2)	O6–Mn–OW1	83.4 (2)
O1–Mn–N2	129.5 (2)	O6–Mn–N1	123.2 (2)
O3–Mn–O5	161.7 (2)	O6–Mn–N2	63.7 (2)
O3–Mn–O6	89.6 (2)	OW1–Mn–N1	135.4 (1)
O3–Mn–OW1	96.3 (2)	OW1–Mn–N2	145.6 (2)
O3–Mn–N1	116.8 (2)	N1–Mn–N2	75.5 (1)
O3–Mn–N2	74.9 (2)		

Structure of $Mn_2L(24)\cdot 8H_2O$. Table V shows the positional parameters of the non-hydrogen atoms. The bond distances and the bond angles are collected in Tables VI and VII, respectively. The ligand has a 24-membered ring and four pendent acetato groups, as shown in Figure 2. Each ligand is coordinated to two manganese ions. The resulting manganese chelate molecule has C_2 symmetry, the symmetry axis of which coincides with the crystal C_2 axis and passes perpendicular to the averaged molecular plane of the macrocyclic ring. Two manganese atoms within a chelate molecule are, therefore, crystallographically equivalent to each other. Each metal atom is coordinated to four oxygen atoms and two nitrogen atoms with bond distances of 2.111–2.445 Å: two oxygen atoms O1 and O3 from two carboxylato groups (Mn–O1 = 2.212 and Mn–O3 = 2.111 Å), an amide oxygen atom O5 (Mn–O = 2.184 Å), a water molecule (denoted OW1 in Figure 2; Mn–O = 2.137 Å) and two amine nitrogen atoms N1 and N2 (Mn–N1 = 2.445 and Mn–N2 = 2.358 Å). The Mn–O distances of 2.111–2.212 Å are significantly shorter than the Mn–N distance of 2.358–2.445 Å. An additional weak bond is formed between a Mn atom and an amide oxygen atom O6 with a distance of 2.686 Å. Thus, a distorted seven-coordination geometry is established around the metal atom. This coordination geometry resembles that reported for $[Mn(H_2O)(EDTA)]^{2-}$ (EDTA = ethylenediaminetetraacetato), in which each Mn atom is coordinated to four carboxylato oxygen atoms, two nitrogen atoms, and a water molecule.[10]

The 24-membered macrocyclic ligand was obtained as an amorphous powder, as shown by its X-ray powder diffraction

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pattern, whereas its Mn(II) complex was obtained in a crystalline form. The framework of the 24-membered ring is probably too flexible to maintain a well-defined ring conformation. Chelate formation with metal ions makes the ring rigid and results in a well-defined configuration of the chelate ring. The structural integrity of the metal chelate rings leads to the formation of crystals of the metal chelate. Extensive hydrogen bonding occurs in the crystal lattice and defines the arrangement of the metal chelate molecules in the crystal. A water molecule (denoted OW2 in Figure 2) occupies a special position on the crystal C_2 axis that coincides with the C_2 axis of a metal chelate ring. This water molecule forms strong hydrogen bonds with two water molecules (denoted OW1 in Figure 2) coordinated to Mn and also with two amide oxygen atoms (O6) that are weakly bonded to Mn. These hydrogen bonds firmly link the two Mn ions within a chelate ring and define the molecular structure of the metal chelate.

In conclusion, the X-ray crystal analyses of the metal complexes have confirmed the formation of the new 12-membered and the 24-membered macrocycles. The new macrocyclic ligands are expected to form stable chelates with a variety of metal ions. One of the features of the synthetic method for the ligands is that the macrocyclic ring can be prepared in one step in a high yield without using template metal ions. The same method is expected to be useful for the synthesis of a series of macrocycles having different ring sizes and different numbers of pendent acetato groups.

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Supplementary Material Available: Tables of crystallographic experimental details, thermal parameters, positional parameters of hydrogen, and additional bond lengths and angles and ORTEP diagrams of the unit cells for CuL(12)$\cdot$4H_2O and Mn_2L(24)$\cdot$8H_2O and a table of least-squares planes for CuL(12)$\cdot$4H_2O (14 pages); listings of observed and calculated structure factors for the two compounds (23 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Pseudo-1-D Mixed-Valence $(Et_{4-n}Me_nN)Cu_2X_4$ Salts: Pinned Charge Density Wave Systems Exhibiting Intervalence Charge Transfer

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A series of mixed-valence Cu(I)/Cu(II) linear chain compounds exhibiting pinned charge density waves have been synthesized. The compounds have stoichiometry $ACu^ICu^{II}X_4$ with X = Cl or Br and A = tetraethylammonium (TEA), triethylmethylammonium (TEM), or diethyldimethylammonium (DEM). The crystal structures of the bromide analogues have been determined. The $(TEM)Cu_2Br_4$ salt is tetragonal, with space group $P4_2/ncm$, $a = 10.812$ (1) Å, $c = 13.234$ (2) Å, $V = 1546.9$ (4) Å^3, $Z = 4$, $d_x = 2.42$ g/cm^3, and $R = 0.0647$. The $(DEM)Cu_2Br_4$ salt is also tetragonal, with space group $P4_2/ncm$, $a = 10.523$ (1) Å, $c = 13.1630$ (9) Å, $V = 1457.5$ (4) Å^3, $Z = 4$, $d_x = 2.50$ g/cm^3, and $R = 0.0974$. The $(TEA)Cu_2Br_4$ salt is orthorhombic, with space group $P2_12_12_1$, $a = 11.084$ (2) Å, $b = 19.696$ (3) Å, $c = 21.847$ (2) Å, $V = 4770$ (1) Å^3, $Z = 12$, $d_x = 2.41$ g/cm^3, and $R = 0.0358$. These structures reveal infinite chains of alternating $Cu^IX_4{}^{3-}$ and $Cu^{II}X_4{}^{2-}$ tetrahedra (distorted) sharing edges, the chains being effectively isolated by bulky tetraalkylammonium cations. Although the valence states appear to be localized, with a 0.1 Å difference in the Cu(I)–X and Cu(II)–X bond lengths, several characterization techniques indicate Robin and Day class II behavior. The data also support a Peierls $4k_f$ distorted charge density wave state for these chains. All salts show an intervalence charge-transfer band in the visible region of the spectrum. Conductivity measurements indicate semiconductive behavior. Temperature-dependent magnetic susceptibility measurements on $(TEA)Cu_2Br_4$ reveal weak antiferromagnetic coupling, which is attributed to short Br$\cdots$Br contacts between $Cu^{II}X_4{}^{2-}$ species within the chains. The above physical properties are rationalized in light of previous EHMO band calculations.

Introduction

A recent endeavor in this laboratory has focused on the design, synthesis, and characterization of low-dimensional, mixed-valence copper halide systems.[1] The main goal behind this research is to discover new systems which exhibit intervalence charge transfer and conductivity. The advent of the copper oxide superconductors, which show copper in different oxidation states and low-dimensional networks, have given this work added significance.[2] There has also been speculation that the trigonal-planar copper species present in the record T_c organic superconductors is of mixed-valence character; it is true that the superconduction is taking place in the organic stacks in these systems, but the role of the cocrystallite copper species is not fully understood.[3] The structural instabilities that low-dimensional materials often exhibit is another factor which adds interest to these compounds.[4]

The mixed-valence chemistry of copper(II)–copper(I) halide compounds is very rich. These compounds fall into two classes; one class containing isolated copper(I) and copper(II) species, the other containing bridging halide ions between the copper(II) and copper(I) centers. The latter class of compounds may, or may not, exhibit intervalence charge transfer, depending on the nature of the Cu(II)–X–Cu(I) bridge. These classes correspond to the Robin and Day classes I and II.[5] The former class contains compounds such as $(Bu_4N)_3Cu_3Cl_8(L)$ (where L = CH_3NO_2, CH_3CN, etc.), which is currently being characterized in this laboratory. This mixed-valence salt contains isolated $Cu_2Cl_6{}^{2-}$ and $CuCl_2L^-$ anions, and thus no pathway for intervalence charge transfer.[6] The latter class contains a myriad of interesting compounds. The classic example of this is the $Co(NH_3)_6Cu$-

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