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Formation of Polymeric Network Arrays by Complexes of Manganese(II) or Cobalt(II) with Alkane Chain Linked Bis(amide) Ligands of Biological Relevance

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Bis(amides) of the type $CH_3CONH(CH_2)_nNHCOCH_3$ ($n = 2$, 4, or 6) react with a range of manganese(II) and cobalt(II) salts to produce polymeric “framework” arrays, five of which have been studied by X-ray crystallography. Hexamethylenebis(acetamide) (HMBA) forms the compound $[Co(HMBA)_3](CoCl_4)\cdot 2EtOH$ in which the HMBA molecules bridge the metal centers, binding octahedrally via the oxygen atoms of the amide groups and forming cationic arrays of large rhomboidal “boxes” containing tetrahedral $CoCl_4^{2-}$ ions. The butylenebis(acetamide) (BBA) complex $[Co(BBA)_3]Br_2$ forms a sheet cationic network, but in this case, the counteranions are simple bromide ions. The ethylenebis(acetamide) (EBA) complex $[Co(EBA)_2(H_2O)_2]Br_2$ comprises *trans*-octahedral $[Co(O\text{-amide})_4(H_2O)_2]^{2+}$ units interlinked by the bridging action of the EBA ligands to form sheet arrays, with simple bromide counterions. From the reaction of HMBA with manganese(II) bromide two crystalline forms were obtained, $[Mn(HMBA)_3](MnBr_4)\cdot 2EtOH$, with a structure similar to $[Co(HMBA)_3](CoCl_4)\cdot 2EtOH$, and a solvent-free form, $[Mn(HMBA)_3](MnBr_4)$, comprising a cationic sheet array. The preparations of several other transition-metal complexes with these ligands are reported together with relevant spectroscopic data.

Introduction

The initial report on the effectiveness of the polymethylene bis(amides) $CH_3CONH(CH_2)_nNHCOCH_3$ ($n = 2-8$) as inducers of erythroid differentiation in murine erythroleukemia cells[1] has led to a continuing interest in their biological and pharmacological properties and particularly in the anticancer properties of hexamethylenebis(acetamide) (HMBA; *N*,*N′*-diacetyl-1,6-hexanediamine).[2−7] Because of this, one of us carried out a study of the interaction of HMBA with a number of metal ions, including some of biological relevance.[8] During that work some complexes of stoichiometry $M_2(HMBA)_3X_4$ (M = Mn, Co, or Ni; X = Cl or Br) were obtained that, from spectroscopic studies, appeared to contain both octahedral and tetrahedral coordination geometries.[8,9]

At that time,[8] no attempt was made to obtain crystals of these products for X-ray structural characterization. However, in view of the length of the hexamethylene linking unit in HMBA and in the light of subsequent observations from these laboratories on the ability of other “extended reach” O-donor ligands, such as bis(lactams)[10,11] and bis(pyridones)[12−14] to form complex polymeric structures, it appeared probable that these HMBA complexes also formed network structures. We report here the results of X-ray studies which confirm this and the extension to complexes with two other alkane-bridged bis(amides), ethylenebis(acetamide) (EBA) and butylenebis(acetamide) (BBA), to explore the generality of the network-forming ability of this type of ligand.

Experimental Section

Preparation of Compounds. The polymethylenebis(acetamide) ligands $CH_3CONH(CH_2)_nNHCOCH_3$ ($n = 2-6$) were prepared by a standard literature method[15] by reacting the respective diamine with acetic anhydride and recrystallizing the resulting solid from ethanol. The purity of the products was checked by comparison of the melting points with the literature values, but further confirmation of the nature of each of the ligands was obtained from the X-ray structural results on their metal complexes.

Metal Complexes. Complexes of $CH_3CONH(CH_2)_2NHCOCH_3$ (EBA). $Mn(EBA)_3Br_2\cdot H_2O$ and $M(EBA)_2Br_2\cdot 2H_2O$ (M = Co or Ni). These compounds were prepared by slow concentration of a solution of the respective metal(II) bromide (0.1 mmol) and EBA (0.2 mmol) in a mixture of acetonitrile (10 mL) and 2,2-dimethoxypropane (1 mL).

$Mn(EBA)_3Br_2\cdot H_2O$: White. Yield: 79%. Anal. Calcd for $C_{18}H_{38}Br_2MnN_6O_7$: C, 32.5; H, 5.8; N, 12.6. Found: C, 32.1; H, 5.9; N,

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Table 1. Crystal Data for $[Co(HMBA)_3](CoCl_4)\cdot 2EtOH$ (**1**), $[Mn(HMBA)_3](MnBr_4)\cdot 2EtOH$ (**2**), $[Mn(HMBA)_3](MnBr_4)$ (**3**), $[Co(BBA)_3]Br_2$ (**4**), and $[Co(EBA)_2(H_2O)_2]Br_2$ (**5**)

	1	**2**	**3**	**4**	**5**
formula	$C_{34}H_{72}Cl_4Co_2N_6O_8$	$C_{34}H_{72}Br_4Mn_2N_6O_8$	$C_{30}H_{60}Br_4Mn_2N_6O_6$	$C_{24}H_{48}Br_2CoN_6O_6$	$C_{12}H_{28}Br_2CoN_4O_6$
fw	952.6	1122.5	1030.4	735.4	543.1
space group	*C*2/c	*C*2/c	$P\bar{1}$	$P\bar{1}$	Pbca
a, Å	23.846(3)	24.404(3)	11.597(3)	8.0051(9)	13.285(5)
b, Å	11.301(1)	11.262(2)	12.652(2)	10.2210(13)	9.569(2)
c, Å	20.326(1)	21.160(3)	16.040(2)	10.8266(9)	16.460(3)
α, deg	90	90	72.018(10)	67.556(7)	90
β, deg	103.446(7)	102.334(11)	85.26(2)	83.640(8)	90
γ, deg	90	90	83.69(2)	85.830(11)	90
V, Å^3	5327.4(9)	5681.3(12)	2222.0(8)	813.2(2)	2092.6(9)
Z	4	4	2	1	4
ρ_{calcd}, g cm^{-3}	1.188	1.312	1.540	1.502	1.724
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ, mm^{-1}	0.867	3.299	4.207	3.028	4.671
T, °C	20	20	20	20	20
$R_1{}^a$	0.0800	0.0857	0.0657	0.0467	0.0433
$wR_2{}^b$	0.2149	0.2235	0.1456	0.0962	0.0959

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR_2 = [\sum(w|F_o{}^2 - F_c{}^2|)/\sum w|F_o{}^2|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Co(1)−Cl(1)	2.264(2)	Co(1)−Cl(2)	2.286(1)
Co(2)−O(2)	2.109(3)	Co(2)−O(8)	2.089(3)
Co(2)−O(14)	2.099(3)		
Cl(1)−Co(1)−Cl(1A)	111.81(10)	Cl(1)−Co(1)−Cl(2)	108.35(5)
Cl(1)−Co(1)−Cl(2A)	109.20(5)	Cl(2)−Co(1)−Cl(2A)	109.91(7)
O(2)−Co(2)−O(2A)	180.0	O(8)−Co(2)−O(8A)	180.0
O(14)−Co(2)−O(14A)	180.0	O(2)−Co(2)−O(8)	86.45(12)
O(2)−Co(2)−O(8A)	93.55(12)	O(2)−Co(2)−O(14)	88.14(12)
O(2)−Co(2)−O(14A)	91.86(12)	O(8)−Co(2)−O(14)	86.52(12)
O(8)−Co(2)−O(14A)	93.48(12)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Mn(1)−Br(1)	2.482(2)	Mn(1)−Br(2)	2.495(2)
Mn(2)−O(2)	2.185(6)	Mn(2)−O(8)	2.151(7)
Mn(2)−O(14)	2.145(7)		
Br(1)−Mn(1)−Br(1A)	112.16(12)	Br(1)−Mn(1)−Br(2)	108.40(5)
Br(1)−Mn(1)−Br(2A)	108.75(5)	Br(2)−Mn(1)−Br(2A)	110.38(11)
O(2)−Mn(2)−O(2A)	180.0	O(8)−Mn(2)−O(8A)	180.0
O(14)−Mn(2)−O(14A)	180.0	O(2)−Mn(2)−O(8)	86.5(3)
O(2)−Mn(2)−O(8A)	93.5(3)	O(2)−Mn(2)−O(14)	88.3(3)
O(2)−Mn(2)−O(14A)	91.7(3)	O(8)−Mn(2)−O(14)	85.5(3)
O(8)−Mn(2)−O(14A)	94.5(3)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**

Mn(1)−O(1)	2.174(9)	Mn(1)−O(2)	2.173(7)
Mn(1)−O(3)	2.152(9)	Mn(1)−O(4)	2.188(7)
Mn(1)−O(5)	2.169(9)	Mn(1)−O(6)	2.208(8)
Mn(2)−Br(1)	2.512(2)	Mn(2)−Br(2)	2.528(2)
Mn(2)−Br(3)	2.470(2)	Mn(2)−Br(4)	2.519(2)
O(1)−Mn(1)−O(2)	86.5(3)	O(1)−Mn(1)−O(3)	86.1(4)
O(1)−Mn(1)−O(4)	94.3(3)	O(1)−Mn(1)−O(5)	90.8(4)
O(1)−Mn(1)−O(6)	176.8(3)	O(2)−Mn(1)−O(3)	95.1(3)
O(2)−Mn(1)−O(4)	177.9(3)	O(2)−Mn(1)−O(5)	86.8(3)
O(2)−Mn(1)−O(6)	90.4(3)	O(3)−Mn(1)−O(4)	86.9(3)
O(3)−Mn(1)−O(5)	176.3(4)	O(3)−Mn(1)−O(6)	93.1(4)
O(4)−Mn(1)−O(5)	91.3(3)	O(4)−Mn(1)−O(6)	88.8(3)
O(5)−Mn(1)−O(6)	90.1(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**

Co−O(2)	2.080(3)	Co−O(7)	2.096(4)
Co−O(12)	2.106(4)		
O(2)−Co−O(2′)	180.0	O(2)−Co−O(7)	85.9(2)
O(2)−Co−O(7′)	94.1(2)	O(2)−Co−O(12)	86.0(2)
O(2)−Co−O(12′)	94.0(2)	O(7)−Co−O(7′)	180.0
O(7)−Co−O(12)	94.5(2)	O(7)−Co−O(12′)	85.5(2)
O(12)−Co−O(12′)	180.0		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Co−O(2)	2.095(4)	Co−O(6)	2.103(4)
Co−O(10)	2.078(5)		
O(2)−Co−O(2′)	180.0	O(2)−Co−O(6)	93.4(2)
O(2)−Co−O(10)	89.2(2)	O(2′)−Co−O(6)	86.6(2)
O(2)−Co−O(10′)	90.8(2)	O(6)−Co−O(6′)	180.0
O(6)−Co−O(10)	85.7(2)	O(6)−Co−O(10′)	94.3(2)
O(10)−Co−O(10′)	180.0		

12.5. IR (CsI, cm^{-1}): 3276vs br ν(NH) + ν(OH), 1631vs ν(C═O), 1565s, 1546s ν(amide II), 1299s ν(amide III).

$[Co(EBA)_2(H_2O)_2]Br_2$: Pink. Yield: 83%. Anal. Calcd for $C_{12}H_{28}Br_2CoN_4O_6$: C, 26.5; H, 5.2; N, 10.3. Found: C, 27.0; H, 5.2; N, 10.7. IR (CsI, cm^{-1}): 3322s, 3274s, 3216sh ν(NH) + ν(OH), 1629vs ν(C═O), 1562sh, 1542vs ν(amide II), 1297 s ν(amide III). Electronic spectrum (reflectance, cm^{-1}): 7500, 14 600, 19 300, 21 350sh.

$Ni(EBA)_2Br_2\cdot 2H_2O$: Green. Yield: 66%. Anal. Calcd for $C_{12}H_{28}Br_2N_4NiO_6$: C, 26.5; H, 5.2; N, 10.3. Found: C, 25.9; H, 5.2; N, 10.3. IR (CsI, cm^{-1}): 3312sh, 3270s, 3222sh ν(NH) + ν(OH), 1625vs ν(C═O), 1562s, 1532vs ν(amide II), 1297s ν(amide III). Electronic spectrum (reflectance, cm^{-1}): 8500, 13 700, 24 400.

$M(EBA)_2(NO_3)_2\cdot nH_2O$ (M = Co, *n* = 2; M = Ni, *n* = 3). Mixing a hot solution of the respective hydrated metal(II) nitrate (0.1 mmol) in methanol (1 mL) with a hot solution of EBA (0.2 mmol) in acetonitrile (32 mL) resulted in the formation of oily products which were converted to fine powders on trituration with diethyl ether.

Co: Pink. Yield: 76%. Anal. Calcd for $C_{12}H_{28}CoN_6O_{12}$: C, 28.4; H, 5.5; N, 16.6. Found: C, 28.5; H, 5.6; N, 16.6. IR (CsI, cm^{-1}): 3293s br ν(NH) + ν(OH), 1631s ν(C═O), 1565s ν(amide II), 1303s ν(amide III). Electronic spectrum (reflectance, cm^{-1}): 7850, 14 300w, 19 150, 21 050sh.

Ni: Green. Yield: 79%. Anal. Calcd for $C_{12}H_{30}N_6NiO_{13}$: C, 27.4; H, 5.7; N, 16.0. Found: C, 27.5; H, 5.8; N, 15.2. Electronic spectrum (reflectance, cm^{-1}): 8500, 13 700, 24 700.

Complexes of $CH_3CONH(CH_2)_4NHCOCH_3$ (BBA). $Mn(BBA)_3Br_2$: A warm solution of $MnBr_2\cdot 4H_2O$ (0.1 mmol) in a mixture of ethanol (5 mL) and 2,2-dimethoxypropane (1 mL) was added to a hot solution of BBA (0.3 mmol) in ethyl acetate. Storage of the resulting solution over concentrated sulfuric acid for 2 days gave a white microcrystalline solid. Yield: 72%. Anal. Calcd for $C_{24}H_{48}Br_2MnN_6O_6$: C, 39.4; H, 6.6; N, 11.5. Found: C, 39.4; H, 6.6; N, 11.4. IR (CsI, cm^{-1}): 3280s ν(NH), 1628vs ν(C═O), 1554s ν(amide II), 1305s ν(amide III).

$[Co(BBA)_3]Br_2$: A hot solution of hydrated cobalt(II) bromide (0.1 mmol) in a mixture of acetonitrile (2 mL) and 2,2-dimethoxypropane

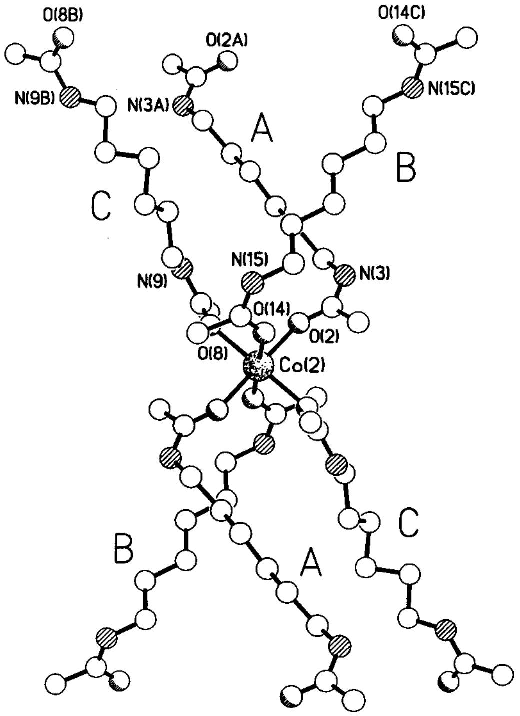

Figure 1. Part of the polymeric structure of **1** showing one of the octahedrally coordinated cobalt centers and its associated bridging HMBA ligands.

(2 mL) was added dropwise to a hot solution of BBA (0.3 mmol) in acetonitrile (3 mL). Purple crystals suitable for X-ray analysis formed overnight. Yield: 88%. Anal. Calcd for $C_{24}H_{48}Br_2CoN_6O_6$: C, 39.2; H, 6.6; N, 11.4. Found: C, 39.2; H, 6.8; N, 11.6. IR (CsI, cm^{-1}): 3228s, 3205sh ν(NH), 1621vs ν(C═O), 1563s ν(amide II), 1307s ν(amide III).

$M(BBA)_3(ClO_4)_2 \cdot 2H_2O$ (M = Mn or Ni), $Co(BBA)_3(ClO_4)_2$, and $Zn(BBA)_3(ClO_4)_2 \cdot H_2O$: CAUTION! *Although we did not observe any explosive behavior with any of the perchlorate compounds described below, all metal perchlorates must be regarded as potentially explosive and appropriate safety measures must be taken* (for example, see: *J. Chem. Educ.* **1973**, *50,* A355). A warm solution of BBA (0.3 mmol) in methanol (5 mL) was added to a solution of the respective hydrated metal perchlorate (0.1 mmol) also in methanol (5 mL). Slow concentration of the resulting solution under reduced pressure gave solid products which were washed with diethyl ether and dried in vacuo.

Mn: White. Yield: 68%. Anal. Calcd for $C_{24}H_{52}Cl_2MnN_6O_{16}$: C, 35.7; H, 6.5; N, 10.4. Found: C, 36.0; H, 6.6; N, 10.4. IR (CsI, cm^{-1}): 3370vs ν(NH), 1629vs ν(C═O), 1563s ν(amide II), 1305m ν(amide III), 1134sh, 1086vs $\nu_3(ClO_4)$, 622s $\nu_4(ClO_4)$.

Co: Pink. Yield: 79%. Anal. Calcd for $C_{24}H_{48}Cl_2CoN_6O_{14}$: C, 37.2; H, 6.3; N, 10.9. Found: C, 37.9; H, 6.5; N, 10.8. Electronic spectrum (reflectance, cm^{-1}): 7200, 14 300w, 18 900, 20 800sh. IR (CsI, cm^{-1}): 3369vs ν(NH), 1627vs ν(C═O), 1562s ν(amide II), 1305m ν(amide III), 1137s, 1068vs $\nu_3(ClO_4)$, 622s $\nu_4(ClO_4)$.

Ni: Green. Yield: 84%. Anal. Calcd for $C_{24}H_{52}Cl_2N_6NiO_{16}$: C, 35.6; H, 6.5; N, 10.4. Found: C, 35.4; H, 6.1; N, 11.0. Electronic spectrum (reflectance, cm^{-1}): 8200, 13 250, 24 100. IR (CsI, cm^{-1}): 3367vs ν(NH), 1625vs ν(C═O), 1562s ν(amide II), 1307m ν(amide III), 1137s, 1068vs $\nu_3(ClO_4)$, 622s $\nu_4(ClO_4)$.

Zn: White. Yield: 60%. Anal. Calcd for $C_{24}H_{50}Cl_2N_6O_{15}Zn$: C, 36.1; H, 6.3; N, 10.5. Found: C, 36.0; H, 6.1; N, 10.8. IR (CsI, cm^{-1}): 3365vs ν(NH), 1627vs ν(C═O), 1562s ν(amide II), 1305m ν(amide III), 1137s, 1068vs $\nu_3(ClO_4)$, 622s $\nu_4(ClO_4)$.

Complexes of $CH_3CONH(CH_2)_6NHCOCH_3$ (HMBA). $[Co(HMBA)_3](CoCl_4) \cdot 2EtOH$: A warm solution of HMBA (3 mmol) in ethyl acetate (30 mL) was added to a solution of $CoCl_2 \cdot 6H_2O$ (1 mmol) in a mixture of ethanol (6 mL) and 2,2-dimethoxypropane (3 mL). On standing overnight, blue crystals of appropriate quality for X-ray characterization had formed. After separation of a sample for X-ray analysis, the rest of the solid was filtered off, washed with a little ethyl acetate and dried in vacuo. Anal. Calcd for $C_{15}H_{30}Cl_2CoN_3O_3$: C, 41.9; H, 7.0; N, 9.8. Found: C, 41.7; H, 7.0; N, 9.7. μ_{eff} (per metal ion) 4.74 μ_B. IR (CsI, cm^{-1}): 1620vs ν(C═O), 1564s ν(amide II), 1303m ν(amide III).

$[Mn(HMBA)_3](MnBr_4) \cdot 2EtOH$: This was prepared as for the previous complex but using hydrated manganese(II) bromide. Colorless blocky crystals separated overnight, and after removal of a sample for X-ray analysis, the remainder was collected, washed with ethyl acetate, and dried in vacuo. Anal. Calcd for $C_{15}H_{30}Br_2MnN_3O_3$: C, 35.0; H, 5.9; N, 8.2. Found: C, 35.3; H, 5.9; N, 8.2. μ_{eff} (per metal ion) 5.96 μ_B. IR (CsI, cm^{-1}): 1625vs ν(C═O), 1564s ν(amide II), 1303m ν(amide III).

$[Mn(HMBA)_3](MnBr_4)$: When the solution was allowed to stand in a refrigerator for ca. 2 months, crystals of a different habit were gradually formed. These were collected and characterized by X-ray analysis (see below).

Microanalyses and Physical Measurements. Elemental analyses were performed by the Scientific Analysis and Consultancy Service, University of North London, magnetic measurements were made on powdered samples at room temperature using an Evans balance calibrated with $HgCo(NCS)_4$, and the spectroscopic measurements were made as described previously.[16]

Crystallographic Analyses. Table 1 provides a summary of the crystal data, data collection, and refinement parameters for complexes **1**−**5**. The data were collected on a Siemens P4/PC diffractometer with Mo Kα radiation using ω-scans. Data for compounds **1** and **3**−**5** were corrected for absorption. The structures of **1** and **2** were solved by the Patterson method, those of **3**−**5** were solved by direct methods, and they were all refined by full matrix least-squares based on F^2. In both **1** and **2**, the included solvent ethanol molecule was found to be disordered over two partial occupancy sites, whereas in **3**, parts of two of the bridging hexyl chains were found to be disordered and were resolved into two partial occupancy orientations. In each case, only the major occupancy nonhydrogen atoms were refined anisotropically. The remaining nonhydrogen atoms throughout all five structures were refined anisotropically. The C−H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{equiv}(C)$ [$U(H) = 1.5U_{equiv}(C{-}Me)$], and allowed to ride on their parent atoms. The N−H hydrogen atoms in **1**, **2**, **4**, and **5** were found from ΔF maps, idealized, assigned isotropic thermal parameters, $U(H) = 1.2U_{equiv}(N)$, and allowed to ride on their parent atoms. In **3**, they were again found from a ΔF map, but they were then refined isotropically subject to an N−H distance constraint. Although the O−H hydrogen atoms of the ethanol solvent molecule in **1** and **2** could not be located, those of the aqua molecules in **5** were found from a ΔF map and refined isotropically subject to an O−H distance constraint. Computations were carried out using the SHELXTL PC program system.[17] Selected bond lengths and angles are given in Tables 2−6.

Results and Discussion

As our initial aim was to determine whether representative members of the previously studied HMBA complexes had network structures, we discuss first the results of the X-ray structural studies on $[Co(HMBA)_3](CoCl_4) \cdot 2EtOH$ (**1**), $[Mn(HMBA)_3](MnBr_4) \cdot 2EtOH$ (**2**), and $[Mn(HMBA)_3](MnBr_4)$ (**3**).

Structure of $[Co(HMBA)_3](CoCl_4) \cdot 2EtOH$ (1). The X-ray study of crystals of **1** reveals that in the structure of the cation of this compound each Co atom is positioned on an inversion center and binds to six amide oxygen atoms, one from each of three pairs of crystallographically independent HMBA ligands (Figure 1). The geometry at Co is slightly distorted octahedral, with cis angles at Co ranging between 86.5(1)° and 93.6(1)° and Co−O bond lengths of 2.089(3)−2.109(3) Å.

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(17) SHELXTL PC, version 5.03; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

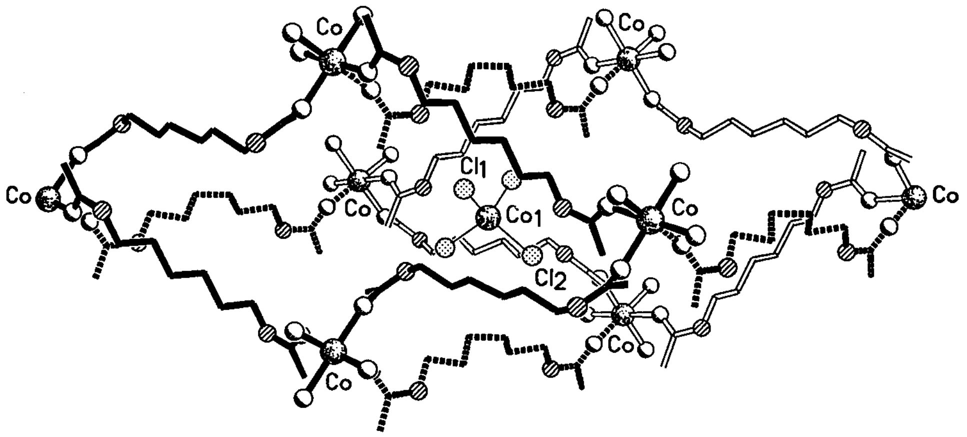

Figure 2. One of the distorted rhomboidal "boxes" in the structure of **1** showing also the position of one of the encapsulated $CoCl_4^{2-}$ ions.

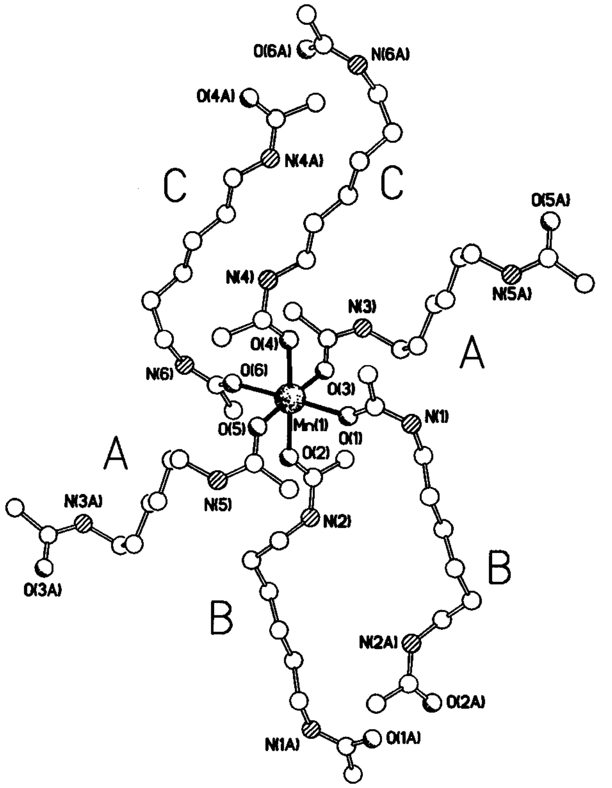

Figure 3. Part of the polymeric structure of **3** showing one of the octahedrally coordinated manganese centers and its associated bridging HMBA ligands. The letters A–C refer to the independent ligand types.

The HMBA ligands all have extended geometries. In two instances, the aliphatic chain and its attached nitrogen atoms adopt a near-planar, all anti geometry, the amide groups being oriented essentially orthogonally (91° in the ligand shown as A in Figure 1 and 98° in the ligand shown as B) to the plane of the backbone. Both of these ligands have crystallographic inversion symmetry. In contrast, the third, independent ligand (shown as C in Figure 1) has C_2 symmetry but is disordered, with several different conformations being observed for the aliphatic linkages. Here the planes of the two amide groups are inclined by ca. 50°, the oxygen atoms being syn with respect to each other (cf. anti geometries in the other two ligands). The ligand lengths, O···O, range between 10.2 and 10.4 Å.

A consequence of the extended HMBA geometries is that the ligands adopt a bridging rather than a chelating role, thus leading to the formation of an extended three-dimensional network comprising contiguous arrays of somewhat distorted rhomboidal "boxes", one of which is illustrated in Figure 2. The three independent, linked Co···Co separations are 13.2, 13.2 and 13.8 Å, respectively. The longest intervertex Co···Co distance is 34.8 Å, and the angles between the three acute Co···Co vectors are 50.7, 51.1, and 51.1°.

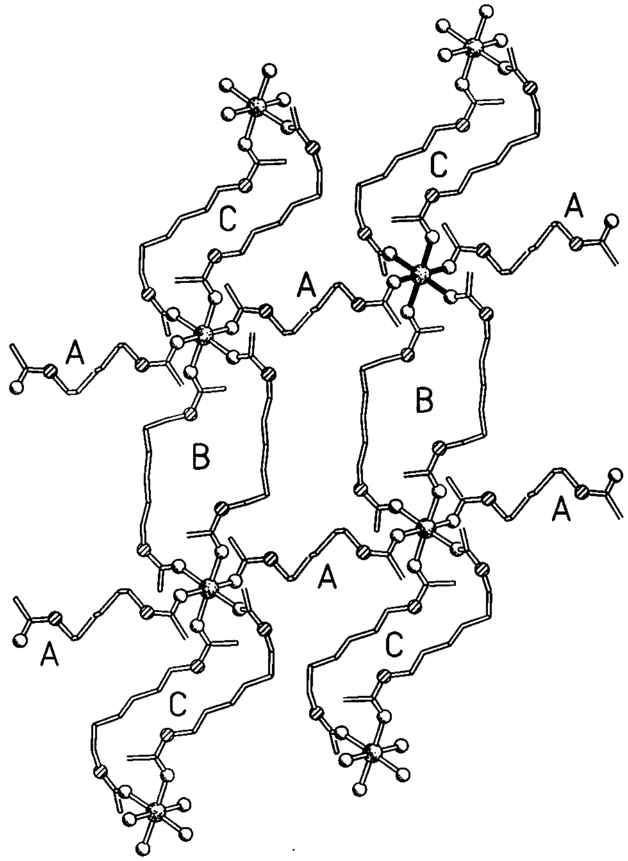

Figure 4. Part of the polymeric sheet structure of **3** showing the two types of 26-membered rings formed by ligands B and C and cross-linked by ligands of type A.

Each rhomboidal box has a significant internal free volume, the central region of which is occupied by the tetrahedral $CoCl_4^{2-}$ anion, and the "narrow" regions toward the ends are populated by included ethanol solvent molecules. Surprisingly there are no significant hydrogen-bonding interactions involving the amide groups, the shortest contacts from the N–H protons being 2.45 Å, which are directed toward chlorine atoms in the anion.

Structures of $[Mn(HMBA)_3](MnBr_4)\cdot 2EtOH$ (2) and $[Mn(HMBA)_3](MnBr_4)$ (3). The reaction between HMBA and

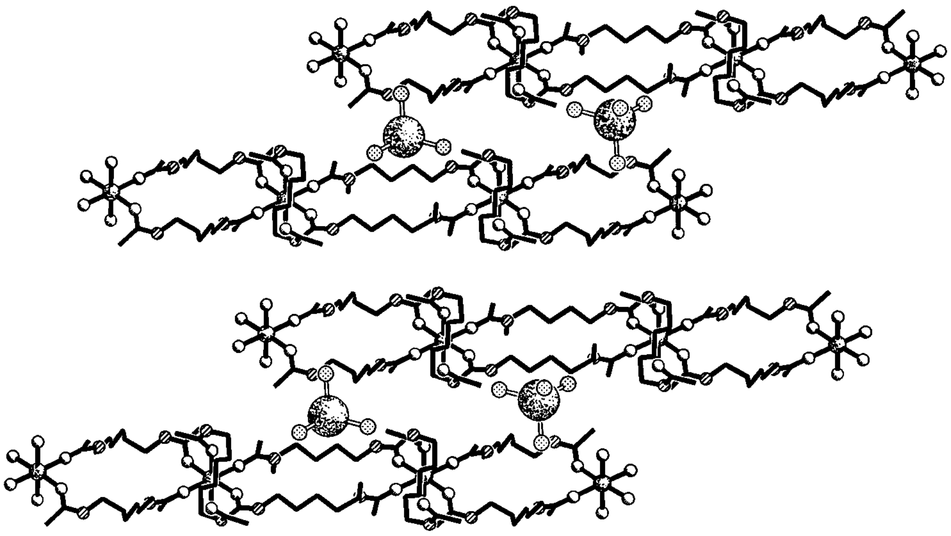

Figure 5. View of the stacked sheets in **3** showing the positions of the $MnBr_4^{2-}$ ions.

hydrated manganese(II) bromide in 3:1 mole ratio in a mixture of ethyl acetate, ethanol, and 2,2-dimethoxypropane gave two types of crystal. The initial product, which separated on standing overnight, formed monoclinic crystals of **2** which are isostructural with the cobalt chloride complex (**1**). Storage of the solution in a refrigerator for an extended period (ca. 2 months) resulted in the formation of triclinic crystals, which X-ray analysis showed to be the nonsolvated complex **3**.

In the case of **2**, there are only very minor differences in its structure from that discussed above for **1**, with Mn−O ranging between 2.145(7) and 2.185(6) Å and cis angles at Mn of between 85.5(3) and 94.5(3)°. The ligand lengths, O···O, range between 10.3 and 10.7 Å, the three independent linked Mn···Mn separations are 13.3, 13.4, and 13.4 Å and there is a slight lengthening of the longest intervertex Mn···Mn separation to 35.9 Å.

The structure of the nonsolvated crystalline compound, **3**, is, however, quite different. In **3**, the manganese atoms in the cationic array are again octahedrally coordinated by amide oxygen atoms from three different HMBA ligands (designated types A, B, and C) but in a pseudocentrosymmetric related arrangement (the Mn atom lies in a crystallographic general position) (Figure 3) with Mn−O distances of 2.152(9)−2.208(8) Å and cis angles at Mn of 86.1(3)−95.1(3)°. The conformations of the three independent ligands not only differ from each other but also from those observed in **1** and **2**. The HMBA ligand lengths (O···O) range between 9.4 Å (for ligand type C) and 13.0 Å (for ligand B). As in **1** and **2**, the HMBA ligands bridge adjacent metal centers, but the resulting supramolecular structure no longer comprises contiguous rhomboidal boxes. Instead, the network takes the form of chains of 26-membered, centrosymmetric macrocycles (employing ligands of types B and C in Figure 4) cross-linked by ligands of type A (where the HMBA ligand itself has inversion symmetry) to produce sheets. In this network, the sheets are stacked in a face-to-face/back-to-back arrangement (Figure 5).

The $MnBr_4^{2-}$ anions lie only between "face-to-face" pairs of sheets, with one of the faces of the anion tetrahedron positioned over the B-type rings and the remaining, apical Mn−Br bond directed toward the C-type rings.

The observation of two very different structures for essentially the same compound $[Mn(HMBA)_3](MnBr_4)$, both from the same solvent system, suggests that there is a very delicate energy balance between the two types. The geometry of the network formed must, in some way, be influenced by the need either to include or exclude solvent molecules and, indeed, this factor may control the crystallization process. The lower temperature at which **3** was formed could also be a factor.

Complexes with BBA and EBA. In view of the interesting network structures formed by HMBA, we explored the effects of reducing the length of the polymethylene bridge linking the amide units and, to this end, prepared a range of first row transition-metal complexes with butylenebis(acetamide) and ethylenebis(acetamide). The compounds listed in the Experimental Section simply reflect those isolated during our attempts to obtain crystals of suitable quality for X-ray determination of the linking modes of these shorter chain ligands and not an attempt at a comprehensive survey.

Structure of $[Co(BBA)_3]Br_2$ (4). The structure of **4** shows that shortening the alkyl chain between the amide centers does not inhibit network formation. In this case, a ruckled sheet structure of linked octahedral Co centers results (Figure 6) [Co−O, 2.080(3)−2.106(4) Å; cis angles at Co, 85.5(2)−94.5(2)°]. The resulting connectivity produces a set of approximately C_3 symmetric contiguous triads with Co···Co distances of 10.2, 10.8, and 11.7 Å. A bromide ion is located at the center of each triad, with the anion hydrogen bonded to an amide nitrogen atom from each of the three BBA ligand arms (N−H···Br in the range 3.35−3.48 Å). The bromide ions lie very close (<0.1 Å) to the mean plane of each sheet. Adjacent sheets are close-packed and offset with respect to each other, so that there are no significant residual voids in the structure.

Structure of $[Co(EBA)_2(H_2O)_2]Br_2$ (5). The effect of still further reduction in the bis(amide) ligand length is revealed in the modified network structure found for **5** and depicted in Figure 7. The geometry at Co is octahedral and C_i symmetric but with the EBA ligand oxygen atoms occupying only the four equatorial coordination sites; the axial sites are filled by aqua ligands. The Co−O(EBA) distances are 2.095(4) and 2.103(4) Å and the $Co-O(OH_2)$ distances are 2.078(5) Å; the cis angles at Co are between 85.7(2) and 94.3(2)°.

In the structure of **5**, there is only one unique EBA ligand geometry, and this links adjacent Co centers to form a ruckled sheet of fused 36-membered, approximately rhombic rings in which the Co···Co distance is 9.52 Å.

The bromide ions lie above and below the sheets and form pairs of N−H···Br and O−H···Br hydrogen bonds with the amide groups and aqua ligands, respectively; the N···Br

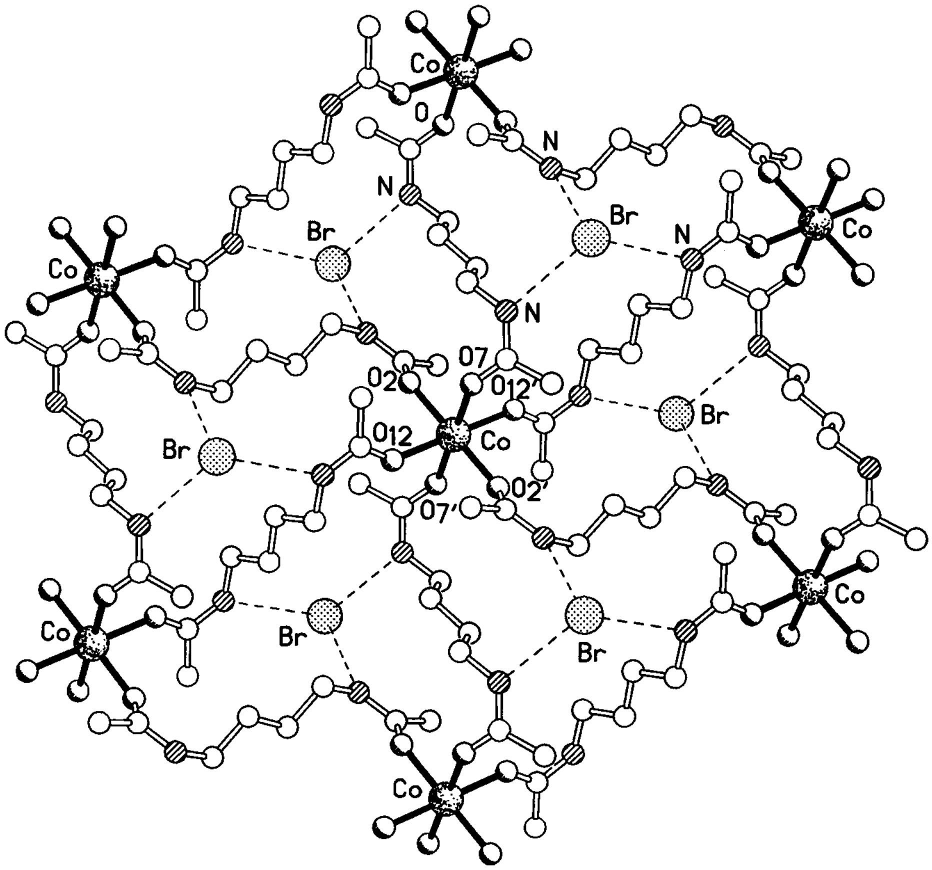

Figure 6. Part of the polymeric sheet structure of **4** showing also the N−H···Br hydrogen bonds.

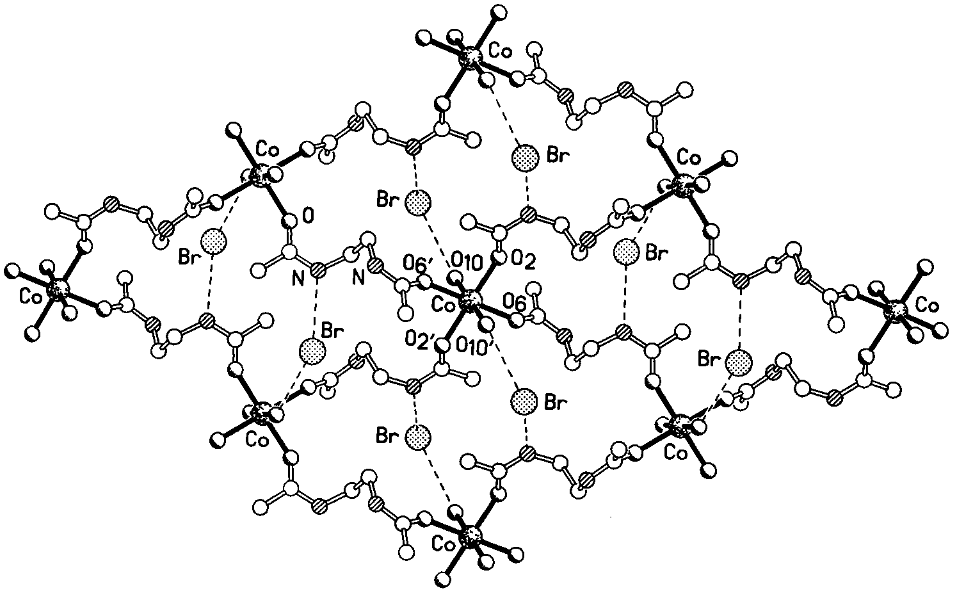

Figure 7. Part of the polymeric sheet structure of **5** showing also the N−H···Br and O−H···Br hydrogen bonds.

distances are 3.49 and 3.52 Å, and the O···Br distances are 3.30 and 3.33 Å, respectively. This pattern of hydrogen bonding serves to cross-link adjacent sheets.

It is interesting to note that there is a closer similarity between the network structures of **4** and **5** than might initially be apparent. The Co centers in **5** could also be viewed as forming a triangular array but with only two sides of each triangle being linked by EBA ligands. The Co···Co distance (9.57 Å) of the third, nonlinked side is very similar to those that are linked. It appears that the formation of a third EBA linkage would be hindered by the bulky, inwardly directed methyl groups of the amide units in this more contracted network.

Other Complexes of EBA and BBA. As stated earlier, several other complexes of EBA and BBA were obtained. Although they were not isolated in the form of crystals of sufficient quality for full X-ray characterization the solid-state electronic spectra of the cobalt(II) and nickel(II) compounds (the data are listed in the Experimental Section) are typical of an octahedral coordination geometry at the metal centers. The X-band electron paramagnetic resonance (EPR) spectra of the solid manganese(II) complexes $Mn(EBA)_3Br_2{\cdot}H_2O$, $Mn(BBA)_3Br_2$, and $Mn(BBA)_3(ClO_4)_2{\cdot}2H_2O$ are also consistent with this geometry (strong band at $g = 2.00$). When taken in conjunction with the representative X-ray results described above, these observations strongly suggest that the EBA and BBA ligands also adopt a bridging role in these other complexes, although X-ray characterization would be needed to confirm this.

Conclusions

From the X-ray structural results on the examples reported here, it appears that the alkane linked bis(amide)s have appreciable propensity for linking metal ions into network arrays. Moreover, the very extensive capacity for variations in both the type of link between the amide units and the substituent(s) within each of the amide groups should lead to a potentially rich and diverse range of framework complexes, particularly when taken into conjunction with differing favored modes of metal coordination geometry and the possible influences of changes in accompanying counteranions.

The observations reported here also prompt a complementary consideration as to the possible relevance of the results to those biological systems in which relatively weak but cooperative interactions between sets of metal ions and linked amide groups may be important but difficult to detect experimentally. The amide group, a key component of proteins, would normally be regarded as a relatively weak donor group toward metal ions in contrast to the more strongly binding, biologically relevant donor groups such as primary amines, imidazole, carboxylate anions, or thiolate groups. Although this may be the case for an individual amide group, the ease with which the linked amide systems form the array structures of the type reported here suggests that the consequences of a possible cooperative influence of *linked* amide groups in binding to *sets* of metal ions should be borne in mind in assessing the kinetic and mechanistic factors that may operate in relevant biological processes. Weak cooperative effects of this type may be sufficient to influence catalytic action or to provide key transient steps in recognition and control processes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[Co(HMBA)_3](CoCl_4){\cdot}2EtOH$ (**1**), $[Mn(HMBA)_3](MnBr_4){\cdot}2EtOH$ (**2**), $[Mn(HMBA)_3](MnBr_4)$ (**3**), $[Co(BBA)_3]Br_2$ (**4**), and $[Co(EBA)_2(H_2O)_2]Br_2$ (**5**) are available on the Internet only. Access information is given on any current masthead page.

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