

## Serendipity and Design in the Generation of New Coordination Polymers: An Extensive Series of Highly Symmetrical Guanidinium-Templated, Carbonate-Based Networks with the Sodalite Topology

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**Abstract:** The serendipitous discovery of a 3D  $[\text{Cu}(\text{CO}_3)_2]_n$  network with the topology of the  $4^26^4$  sodalite net in  $[\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\cdot\text{K}_4\cdot 8\text{H}_2\text{O}$  paved the way for the deliberate engineering of an extensive series of structurally related guanidinium-templated metal carbonates of composition  $[\text{M}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3\text{N}(\text{CH}_3)_4\cdot x\text{H}_2\text{O}$ , where the divalent metal M in the framework may be Mg, Mn, Fe, Co, Ni, Cu, Zn, or Cd. A closely related crystalline material with a  $[\text{Ca}(\text{CO}_3)_2]_n$  sodalite-like framework, but containing  $\text{K}^+$  rather than  $\text{Na}^+$ , of composition  $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4]\cdot 3\text{H}_2\text{O}$  was also isolated. All of these compounds were obtained under the simplest possible conditions from aqueous solution at room temperature, and their structures were determined by single-crystal X-ray diffraction. Pairs of guanidinium cations are associated with the hexagonal windows of the sodalite cages, alkali-metal cations are associated with their square windows, and  $\text{N}(\text{CH}_3)_4^+$  ions are located at their centers. Structures fall into two classes depending on the metal,  $\text{M}^{\text{II}}$ , in the framework. One type, the BC type ( $Im\bar{3}m$ ), comprising the compounds for which  $\text{M}^{2+} = \text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$ , has a body-centered cubic unit cell, while the second type, the FC type ( $Fd\bar{3}c$ ), for which  $\text{M}^{2+} = \text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ , has a face-centered cubic unit cell with edges on the order of twice those of the BC structural type. The metal M in the BC structures has four close carbonate oxygen donors and four other more distant ones, while M in the FC structures has an octahedral environment consisting of two bidentate chelating carbonate ligands and two *cis* monodentate carbonate ligands.

### Introduction

More than a decade ago a general strategy was proposed for the construction of coordination polymers with a range of deliberately intended 2D or 3D structures, each topologically related by design to a chosen one of a number of simple archetypes.<sup>1</sup> At the same time attention was drawn to the potential importance of coordination polymers as materials of the future with specifically tailored, useful properties. It was pointed out that, given the almost limitless range of connecting ligands that could be devised and given also the rich geometrical and electronic diversity of metallic elements, coordination polymers could afford microporous solids resembling zeolites but with a much wider range of architectures, functionalities, and properties. Also at the same time promising preliminary experimental support was presented for the general viability of the strategy. The simple notion underlying this *net-based* approach was that if molecular building blocks with a functionality and stereochemistry appropriate to a chosen target net

could be generated, merely allowing these preorganized, complementary components to react together under the correct conditions could conceivably lead to the spontaneous assembly of the intended network. The general approach can be illustrated by taking as the target the particular example of the  $4^28^4$  net conveniently referred to as the PtS net, the essence of which is equal numbers of tetrahedral and square planar nodes, each connected to four of the other type: it was shown, with deliberate intent, that square planar  $\text{Pt}(\text{CN})_4^{2-}$  and tetrahedral  $\text{Cu}^{\text{I}}$  do indeed assemble themselves into an anionic network with the topology of  $\text{PtS}^2$  and further that very much larger square planar porphyrin-derived building blocks bearing metal-binding groups at the four *meso* positions likewise spontaneously generate networks with the intended PtS topology when linked together by tetrahedral  $\text{Cu}^{\text{I}}$  or  $\text{Ag}^{\text{I}}$  centers.<sup>3</sup> Many coordination polymers with intended structures topologically related to simple target nets such as the 4-connected diamond net, the 6-connected  $\alpha$ -polonium net, the 3-connected (10,3)a net, and so on have now been generated,<sup>4</sup> and many further examples can confidently be expected in the future. These expanding capabilities

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in framework construction are leading to coordination polymers showing increasing promise as tailor-made materials with interesting or useful properties such as magnetic, electrical, storage, catalytic, chiral separation, optical, and mechanical properties; the range of such properties that coordination polymers exhibit has been reviewed very recently.<sup>4b</sup>

With regard to the general concept of *design*, it is important to draw a very clear distinction between on one hand obtaining, in a somewhat sporting manner, a structure that, while intended and hoped for, could not possibly have been guaranteed and, on the other hand, truly engineering a structure in such a way that the outcome was as absolutely certain as the translation of precise blueprints into a real office block. For our part the best we have achieved has been to obtain, from time to time, structures that were optimistically intended but by no means guaranteed. Often, however, the structures that have materialized have been totally unexpected (by us). We suspect other workers in the field of coordination polymers may have had similar experiences. In many cases we can see no way in which these unanticipated outcomes could possibly have been predicted. Such serendipitous results therefore provide important signposts for the future development of the coordination polymer area. The results presented in this paper arose out of yet another serendipitous observation as we indicate below.

One way of better controlling the architecture of coordination polymers is to use templates to secure ligands in appropriate arrangements. In this respect, hydrogen-bonding templates are particularly attractive. One only has to look to biology or to the fine achievements in supramolecular chemistry to appreciate the powerful structure-directing capabilities of hydrogen bonding. The difficulty is how one ensures that the hydrogen-bonding template associates with the coordination network. One solution is to use a cationic hydrogen-bonding template in combination with an anionic network. The guanidinium ion,  $[\text{C}(\text{NH}_2)_3]^+$ , is an outstanding candidate for this role. Not only does its high symmetry confer upon it the potential to impose correspondingly high symmetry upon the coordination network to which it is hydrogen bonded, but it is an extremely weak acid (unlike, for example, protonated amines), retaining its cationic character without proton loss even in strongly basic solution. The guanidinium cation plays a key role as a structure-determining template in the systems we report in this paper.

Bridging ligands of some complexity are often used to construct coordination polymers. In our view, common oxy-anions, despite the very extensive earlier exploration of their chemistry, still afford great opportunities as bridging units for the generation of new and interesting networks. In this paper we report some new, highly symmetrical carbonate-bridged coordination networks. There have been previous structural studies of 1D,<sup>5</sup> 2D,<sup>6</sup> and 3D<sup>7</sup> carbonate-bridged networks; one that particularly caught our attention and alerted us to the still untapped potentialities of the common carbonate ion was the

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**Table 1.** Crystallographic Data and Information

framework metal	Mg	Ca	Mn	Fe	Co	Ni	Cu <sup>II</sup>	Zn	Cd
empirical formula	$\text{C}_{24}\text{H}_{64}\text{Mg}_6\text{N}_{25}\text{O}_{39}$	$\text{C}_{24}\text{H}_{60}\text{Ca}_6\text{K}_3\text{N}_{25}\text{O}_{38}$	$\text{C}_{24}\text{H}_{66}\text{Mn}_6\text{N}_{25}\text{Na}_3\text{O}_{39}$	$\text{C}_{24}\text{H}_{64}\text{Fe}_6\text{N}_{25}\text{Na}_3\text{O}_{38}$	$\text{C}_{24}\text{H}_{64}\text{Co}_6\text{N}_{25}\text{Na}_3\text{O}_{38}$	$\text{C}_{24}\text{H}_{64}\text{Ni}_6\text{N}_{25}\text{Na}_3\text{O}_{38}$	$\text{C}_{24}\text{H}_{62}\text{Cu}_6\text{N}_{25}\text{Na}_3\text{O}_{37}$	$\text{C}_{24}\text{H}_{64}\text{N}_{25}\text{Na}_3\text{O}_{38}\text{Zn}_6$	$\text{C}_{24}\text{H}_{70}\text{Cd}_6\text{N}_{25}\text{Na}_3\text{O}_{41}$
fw	1525.83	1686.80	1727.63	1715.07	1733.55	1732.23	1743.2	1772.19	2108.42
cryst syst	cubic	cubic	cubic	cubic	cubic	cubic	cubic	cubic	cubic
space group	$Fd\bar{3}c$	$Im\bar{3}m$	$Im\bar{3}m$	$Fd\bar{3}c$	$Fd\bar{3}c$	$Fd\bar{3}c$	$Im\bar{3}m$	$Fd\bar{3}c$	$Im\bar{3}m$
color	colorless	colorless	colorless	colorless	pink	green	blue	colorless	colorless
$\alpha$ (Å)	28.9234(13)	14.8173(14)	14.5662(8)	29.0191(7)	28.9057(4)	28.7780(11)	14.411(2)	28.9736(12)	14.7493(4)
$V$ (Å <sup>3</sup> )	24196(2)	3253.2(5)	3090.6(3)	24437.2(10)	24151.9(6)	23833(2)	2993.0(6)	24323(2)	3208.6(2)
$T$ (K)	293	293	293	293	293	293	293	293	293
$Z$	16	2	2	16	16	16	2	16	2
$wR2$ ( $F^2$ , all data)	0.2538	0.1745	0.1668	0.1967	0.1048	0.1625	0.0991	0.1132	0.1196
$R1$ [ $I > 2\sigma(I)$ ]	0.0805	0.0544	0.0562	0.0511	0.0257	0.0644	0.0364	0.0306	0.0372
GOF	0.919	1.176	1.159	1.133	1.144	1.352	1.160	1.013	1.392

<sup>a</sup> Previously reported structure.<sup>11</sup>

beautiful cubic net in the compound  $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot 3\text{H}_2\text{O}$  reported in 1996 by Stucky et al.<sup>8</sup>

A number of reports in the literature indicate that the combination of simple oxyanions as framework components together with the guanidinium ion as the templating counter-cation might be particularly fruitful. The structure of  $(\text{CH}_6\text{N}_3)_2\text{-Zn}(\text{SO}_4)_2$ , where  $\text{CH}_6\text{N}_3^+$  represents the guanidinium cation, was reported in 1970.<sup>9</sup> It consists of essentially tetrahedral zinc centers linked together by 2-connecting sulfate bridging ligands to form an infinite 3D network with the diamond topology. Each of the cyclohexane-like  $[\text{Zn}_6(\text{SO}_4)_6]$  windows in the net is occupied by a guanidinium cation multiply hydrogen bonded to oxygen centers of the surrounding sulfate ligands. Closely related diamond-like coordination networks with cationic guanidinium templates playing similar hydrogen-bonding roles have subsequently been discovered in which the bridging oxyanion may be carbonate,<sup>10,11</sup> phosphite,<sup>10</sup> or hydrogen phosphate,<sup>12</sup> and other guanidinium/metal/oxyanion networks unrelated to diamond have also been described.<sup>13</sup> In this paper we report a series of highly symmetrical carbonate-bridged anionic coordination networks with a range of different metal cations in which pairs of hydrogen-bonding guanidinium cations template the framework. The systems described are more or less deliberately crystal-engineered variants on an initial serendipitously discovered structure.

## Experimental Section

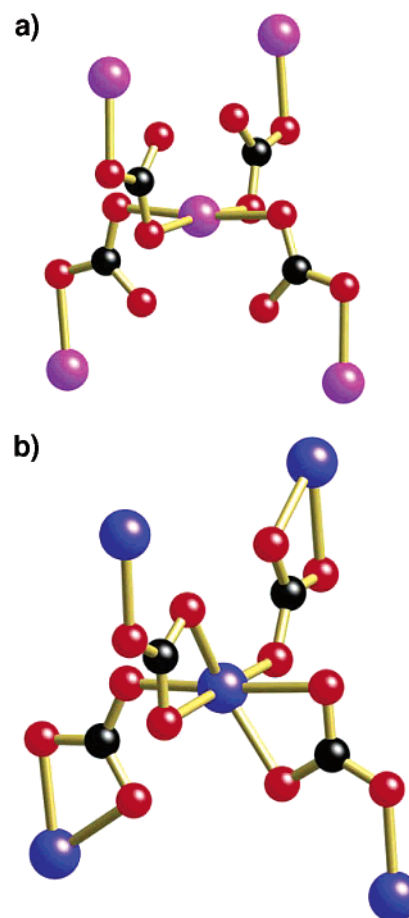
The potassium-containing stock solution used in some preparations below was 2.4 M in  $\text{K}_2\text{CO}_3$  and 1.25 M in  $\text{KHCO}_3$ , and the sodium-containing stock solution was 1 M in  $\text{Na}_2\text{CO}_3$  and 0.6 M in  $\text{NaHCO}_3$ .

In several of the preparations crystal growth and separation were moderated to optimize crystal quality by the trial and error addition of metal-binding agents (e.g.,  $\text{N}(\text{CH}_2\text{COO}^-)_3$ ,  $\text{NH}(\text{CH}_2\text{COO}^-)_2$ , or  $\text{OCN}^-$ , as indicated) which were intended to compete with carbonate in the reaction mixture but ultimately not to appear in the products.

**$[\text{Mg}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$ .** A solution of  $\text{Mg}(\text{CH}_3\text{-COO})_2 \cdot 4\text{H}_2\text{O}$  (200 mg, 0.83 mmol),  $\text{Me}_4\text{NCl}$  (455 mg, 8.3 mmol),  $\text{CH}_6\text{N}_3 \cdot \text{Cl}$  (790 mg, 8.3 mmol), and  $\text{NaOCN}$  (110 mg, 1.66 mmol) in  $\text{H}_2\text{O}$  (5 mL) was added to the  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  stock solution (10 mL). Colorless crystals of  $[\text{Mg}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$  were collected after 3 days, washed with water, and dried in air. Yield: 154 mg, 73%. Anal. Calcd: C, 18.9; H, 4.2; N, 22.9. Found: C, 18.9; H, 4.3; N, 22.7.

**$[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$ .** A solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (200 mg, 0.85 mmol),  $\text{Me}_4\text{NCl}$  (1.39 g, 12.7 mmol),  $\text{CH}_6\text{N}_3 \cdot \text{Cl}$  (1.21 g, 12.7 mmol), and  $\text{N}(\text{CH}_2\text{COOH})_3$  (160 mg, 0.85 mmol) in water (10 mL) was added to the  $\text{K}_2\text{CO}_3/\text{KHCO}_3$  stock solution (10 mL). Colorless crystals of  $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$  were collected, washed with water, and dried in air. Yield: 143 mg, 61%. Anal. Calcd: C, 17.1; H, 3.9; N, 20.8. Found: C, 17.9; H, 4.1; N, 20.3.

**$[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$ .** A solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (200 mg, 0.69 mmol),  $\text{Me}_4\text{NCl}$  (1.22 g, 11.2 mmol),  $\text{CH}_6\text{N}_3 \cdot \text{Cl}$  (1.1 g, 11.2 mmol), and  $\text{NH}(\text{CH}_2\text{COONa})_2$  (850 mg, 5.6 mmol) in  $\text{H}_2\text{O}$  (5 mL) was dissolved in the stock  $\text{K}_2\text{CO}_3/\text{KHCO}_3$

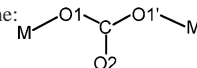


**Figure 1.** Environments of metal centers and carbonate ligands in (a)  $[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$ , which is representative of the BC structural class, and (b)  $[\text{Co}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$ , which is representative of the FC structural class.

**Table 2.** Selected Intermolecular Separations (Å) in the BC Structures<sup>a</sup>

	Cu	Mn	Cd	Ca
M–O(1) <sup>b</sup>	2.04	2.18	2.28	2.35
M–O(2) <sup>b</sup>	2.58	2.59	2.62	2.62
N···O <sup>c</sup>	2.94	2.88	2.88	2.85
C···C <sup>d</sup>	3.33	3.39	3.45	3.58
O···O <sup>e</sup>	4.28	4.57	4.80	5.02

<sup>a</sup> The column heads indicate the framework metal. <sup>b</sup> Refer to the following labeling scheme:



<sup>c</sup> Separation between nitrogen of guanidinium and hydrogen-bonded carbonate oxygen. <sup>d</sup> Separation between carbon centers in a guanidinium pair.

<sup>e</sup> Separation between diagonally opposed oxygen centers of the O<sub>4</sub> square.

solution (10 mL). Small almost colorless crystals of  $[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$  were collected after 3 days, washed with water, and dried in air. Yield: 118 mg, 37%. Anal. Calcd: C, 16.7; H, 3.8; N, 20.3. Found: C, 16.9; H, 3.8; N, 20.0.

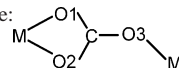
**$[\text{Fe}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$ .** Stock  $\text{K}_2\text{CO}_3/\text{KHCO}_3$  solution (10 mL) was added to a solution of  $\text{Fe}^{\text{II}}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (200 mg, 0.51 mmol) in  $\text{H}_2\text{O}$  (1 mL). A solution containing  $\text{Me}_4\text{NCl}$  (550 mg, 5.1 mmol),  $\text{NaNO}_3$  (430 mg, 5.1 mmol), and  $\text{CH}_6\text{N}_3 \cdot \text{Cl}$  (974 mg, 10.20 mmol) in  $\text{H}_2\text{O}$  (2 mL) was then added to the iron solution. Small almost colorless crystals of  $[\text{Fe}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$  separated rapidly. These crystals appeared to be perfectly stable in the presence of air while in contact with the mother liquor, but washing with water saturated in air caused them to discolor, passing

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**Table 3.** Selected Intermolecular Separations (Å) in the FC Structures<sup>a</sup>

	Mg	Fe	Co	Ni	Zn
M–O(1) <sup>b</sup>	2.15	2.21	2.20	2.11	2.21
M–O(2) <sup>b</sup>	2.15	2.21	2.12	2.10	2.11
M'–O(3) <sup>b</sup>	2.05	2.09	2.05	2.03	2.02
N···O <sup>c</sup>	2.88	3.00	2.84	2.96	2.85
	2.89	3.01	2.86	2.95	2.85
C···C <sup>d</sup>	3.32	3.32	3.33	3.32	3.28
O···O <sup>e</sup>	4.44	4.55	4.52	4.39	4.56

<sup>a</sup> The column heads indicate the framework metal. <sup>b</sup> Refer to the following labeling scheme:



<sup>c</sup> Separation between nitrogen of guanidium and hydrogen-bonded carbonate oxygen. <sup>d</sup> Separation between carbon centers in a guanidinium pair. <sup>e</sup> Separation between diagonally opposed oxygen centers of the O<sub>4</sub> square.

gradually through a very dark green, almost black stage and ultimately becoming dark brown. Therefore, in the isolation of the product, the crystals after the mother liquor had drained off were washed as rapidly as possible using a minimal amount of water and were rapidly dried in air. This procedure yielded a slightly yellowed product with a satisfactory elemental analysis. Yield: 110 mg, 75%. Anal. Calcd: C, 16.8; H, 3.8; N, 20.1. Found: C, 16.5; H, 3.7; N, 20.4.

**[Co<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O.** A solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (503 mg, 1.73 mmol), NaOCN (3.7 g, 56.9 mmol), and CH<sub>6</sub>N<sub>3</sub>·NO<sub>3</sub> (3 g, 25 mmol) in water (45 mL) was added to a solution of (Me<sub>4</sub>N)<sub>2</sub>CO<sub>3</sub> (1.2 M, 3.5 mL). An initial amorphous pink precipitate was gradually replaced over a period of 5 days by deep pink crystals of [Co<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O which were collected, washed with ice cold water, and dried in air. Yield: 266 mg, 54%. Anal. Calcd: C, 16.6; H, 3.8; N, 20.2. Found: C, 16.6; H, 3.4; N, 20.2.

**[Ni<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O.** A solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (200 mg, 0.68 mmol), Me<sub>4</sub>NCl (740 mg, 6.8 mmol), CH<sub>6</sub>N<sub>3</sub>·NO<sub>3</sub> (830 mg, 6.8 mmol), and NaOCN (440 mg, 6.8 mmol) in H<sub>2</sub>O (5 mL) was added to the stock K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> solution (5 mL). Green crystals of [Ni<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O that separated were collected, washed with water, and dried in air. Yield: 54.1 mg, 28%. Anal. Calcd: C, 16.6; H, 3.7; N, 20.2. Found: C, 16.7; H, 3.6; N, 20.1.

**[Cu<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·H<sub>2</sub>O.** A solution containing NaNO<sub>3</sub> (316 mg, 3.72 mmol), (CH<sub>6</sub>N<sub>3</sub>)<sub>2</sub>CO<sub>3</sub> (330 mg, 1.86 mmol), and Me<sub>4</sub>NCl (680 mg, 6.2 mmol) in water (2 mL) was added to a solution containing K<sub>2</sub>CO<sub>3</sub> + KHCO<sub>3</sub> + Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (2.4, 1.25, and 0.34 M, respectively, 3 mL). The pale blue crystals of [Cu<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·H<sub>2</sub>O that formed were collected after 15 min, washed with water, and dried in air. Yield: 186 mg, 45%. Anal. Calcd: C, 16.5; H, 3.6; N, 20.1; Cu, 21.9; Na, 4.0. Found: C, 16.3; H, 3.5; N, 19.8; Cu, 22.0; Na, 4.5.

**[Zn<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O.** A solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (200 mg, 0.67 mmol), Me<sub>4</sub>NCl (2.2 g, 20.2 mmol), CH<sub>6</sub>N<sub>3</sub>·Cl (640 mg, 6.7 mmol), and NaOCN (430 mg, 6.7 mmol) in H<sub>2</sub>O (10 mL) was added to a solution containing Na<sub>2</sub>CO<sub>3</sub> (1.1 g, 10.1 mmol), K<sub>2</sub>CO<sub>3</sub> (800 mg, 5.8 mmol), and KHCO<sub>3</sub> (300 mg, 3 mmol) in H<sub>2</sub>O (8 mL). Colorless crystals of [Zn<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O were collected after 3 days, washed with water, and dried in air. Yield: 87 mg, 44%. Anal. Calcd: C, 15.6; H, 3.4; N, 18.8. Found: C, 16.3; H, 3.6; N, 19.7. The X-ray powder diffraction pattern of the product was in excellent agreement with that calculated on the basis of the single-crystal X-ray diffraction results and showed no signs of crystalline impurities.

**[Cd<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·5H<sub>2</sub>O.** A solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (200 mg, 0.65 mmol), Me<sub>4</sub>NCl (710 mg, 6.5 mmol), NaNO<sub>3</sub> (550 mg, 6.5 mmol), CH<sub>6</sub>N<sub>3</sub>·Cl (620 mg, 5.6 mmol), and NH(CH<sub>2</sub>-COOH)<sub>2</sub> (430 mg, 3.24 mmol) in H<sub>2</sub>O (5 mL) was added to 10 mL of the K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> stock solution. The colorless crystals of [Cd<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·5H<sub>2</sub>O that separated were collected, washed with water, and dried in air. Yield: 160 mg, 72.4%. Anal. Calcd: C, 13.7; H, 3.3; N, 16.6. Found: C, 14.3; H, 3.4; N, 17.0.

**X-ray Crystallography.** Diffraction data for all crystals were measured on a Bruker CCD diffractometer fitted with Mo K $\alpha$  radiation. Structures were solved using direct methods and refined using a full-matrix least-squares procedure based on  $F^2$ .<sup>15</sup> Crystallographic data and information are presented in Table 1.

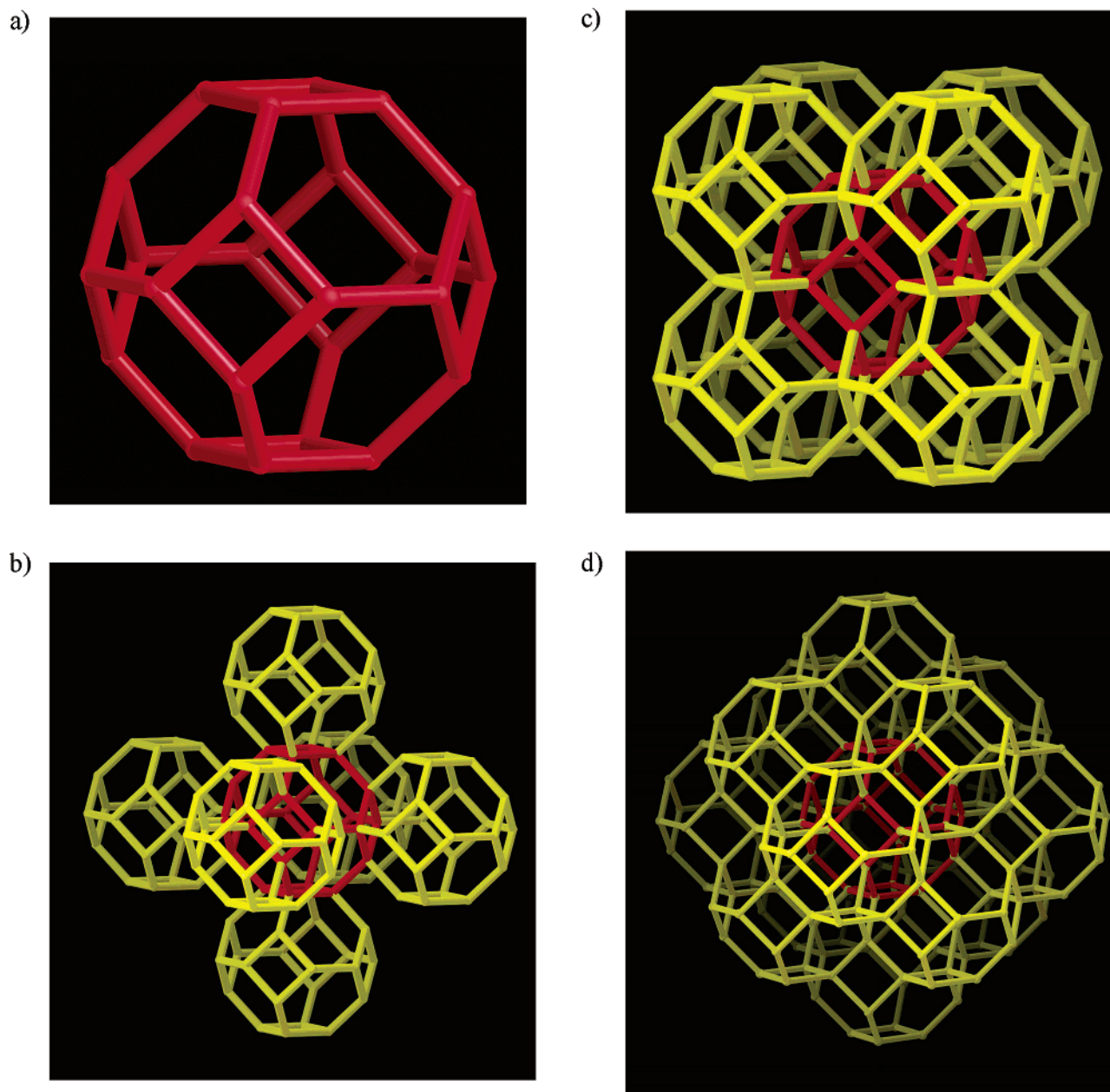
## Results

Compounds of composition [M<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]M'<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·xH<sub>2</sub>O {where M<sup>2+</sup> = Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Cd<sup>2+</sup>, where CH<sub>6</sub>N<sub>3</sub><sup>+</sup> = the guanidinium cation, where M'<sup>+</sup> = Na<sup>+</sup> for all compounds except when the divalent metal ion is Ca<sup>2+</sup>, in which case M'<sup>+</sup> = K<sup>+</sup>, and where x = 1 (M<sup>2+</sup> = Cu<sup>2+</sup>), 2 (M<sup>2+</sup> = Mg<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>), 3 (M<sup>2+</sup> = Ca<sup>2+</sup>, Mn<sup>2+</sup>), or 5 (M<sup>2+</sup> = Cd<sup>2+</sup>)} are obtained in crystalline form extremely simply from aqueous mixtures at room temperature containing the various components. The copper compound was described in a recent preliminary communication.<sup>11</sup>

Structures, determined by single-crystal X-ray diffraction, fall into two classes depending on the metal, M<sup>II</sup>, in the framework. One type, comprising the compounds for which M<sup>2+</sup> = Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, has a body-centered cubic unit cell of edge 14.41–14.82 Å (see Table 1); we shall refer to this structural type as the “BC structure”. The second type (M<sup>2+</sup> = Mg<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>) has a face-centered cubic unit cell with edges on the order of twice those of the BC structural type (see Table 1); we shall refer to this structural type as the “FC structure”.

We shall focus on the structures of the manganese and cobalt compounds as representative of the BC and FC structural types, respectively. The environments of the manganese and carbonate units in [Mn<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·3H<sub>2</sub>O are shown in Figure 1a, and some internuclear separations for all the BC structures are presented in Table 2. As can be seen in Figure 1a the manganese environment consists of a square planar set of carbonate oxygen donors (Mn–O = 2.18 Å), but four other more distant carbonate oxygen centers interact significantly with the metal (Mn–O = 2.59 Å). The carbonate units (all of which are equivalent) in the BC structures act as  $\mu_2$ -bridges as can be seen in Figure 1a. The bond distances and angles associated with these  $\mu_2$  carbonate units are unexceptional.

In the FC structures the divalent metal centers, all of which are equivalent, are 6-coordinate with two chelating carbonate ligands and two monodentate *cis* carbonate ligands as is shown for the representative cobalt case in Figure 1b. Some interatomic separations for the FC structures are given in Table 3. Individual cobalt centers are chiral, each being attached as in Figure 1b to four others of the opposite hand. In the FC structure the



**Figure 2.** (a) A truncated octahedron or sodalite cage. (b) A central (red) sodalite cage sharing its square faces with six others. (c) A central sodalite cage sharing its hexagonal faces with eight others. (d)  $4^2 6^4$  sodalite net showing a central sodalite cage surrounded by 14 others.

carbonate units, all of which are equivalent, act as monodentate ligands through one oxygen to one metal and as bidentate chelating ligands through the other two oxygen donors to a second metal, as can be seen in Figure 1b. Bond distances and angles associated with these bridging and chelating carbonate units are unexceptional.

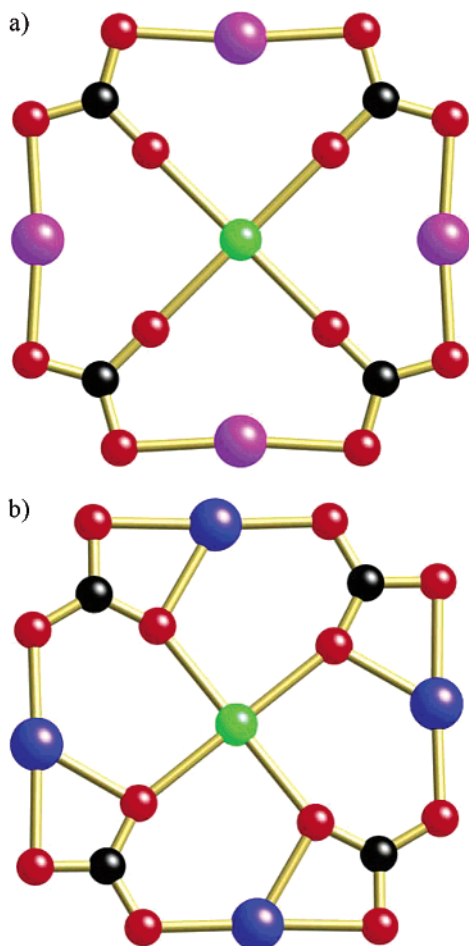
Both the FC and the BC structures have topologies based on that of the  $4^2 6^4$  net shown in Figure 2d. In all cases, if metal centers are linked to nearest neighbor metal centers by imaginary linear connections, the topology shown in Figure 2d is generated. This is precisely the topology generated if the tetrahedral centers (Si or Al) in the mineral sodalite are linked together by imaginary linear connections; it is convenient therefore to refer to this net, as we do below, as the “sodalite net”. Structural motifs characteristic of the net are cages with the shape of a truncated octahedron shown in Figure 2a, which we shall refer to as “sodalite cages”. The truncated octahedron is one of the

solid figures capable of tessellating 3D space. One way to visualize the sodalite net is in terms of truncated octahedral cages each sharing a square face with six neighboring cages and sharing a hexagonal face with eight others as illustrated in Figure 2b–d. There is a report in the literature of the structures of some metal squarates,  $M(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)$  ( $M^{2+} = \text{Co}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ ;  $\text{C}_4\text{O}_4^{2-} = \text{squarate}$ ), which are described as sodalite networks, incorrectly we believe.<sup>16</sup>

In both the BC and FC structures  $\text{M}_4(\text{CO}_3)_4$  rings correspond to the square faces of the sodalite cages. In all the sodium-containing compounds reported here the sodium cation is located at the center of each of these rings.  $\text{Mn}_4(\text{CO}_3)_4 \cdot \text{Na}^+$  and  $\text{Co}_4(\text{CO}_3)_4 \cdot \text{Na}^+$  units are shown in parts a and b, respectively,

(14) Hudson, T.; Robson, R. Unpublished results.

(15) Sheldrick, G. M. *SHELX97—Programs for Crystal Structure Analysis*; Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.



**Figure 3.**  $M_4(\text{CO}_3)_4 \cdot \text{Na}^+$  units in (a)  $[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$  and (b)  $[\text{Co}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$ .

of Figure 3; in both cases all atoms are coplanar. In the BC structures the Na—O—C system is linear at oxygen. The square arrangement of four carbonate oxygen centers which surrounds the sodium ions in both the BC and FC structures (see Figure 3) will be referred to below as the “ $\text{O}_4$  hole”. In the FC structures the carbonate bridges acquire a directionality; i.e., they possess a head and a tail. The  $M_4(\text{CO}_3)_4$  rings in all the FC structures have a circulatory character, apparent in Figure 3b, whereby every metal center in the ring is attached to a head and a tail; we return to this circulatory theme below. The  $\text{K}^+$  in  $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$  appears to be too large to fit in-plane into the  $\text{O}_4$  hole, being disordered over two sites 0.93 Å on either side of the center of the hole. Other aspects of this somewhat exceptional potassium-containing structure are discussed below. In all the sodium-containing compounds disordered water molecules are associated with some of the sodium ions at sites perpendicular to the  $\text{NaO}_4$  plane, each site being only partially occupied as is considered further below.

(16) Neeraj, S.; Noy, M. L.; Rao, C. N. R.; Cheetham, A. K. *Solid State Sci.* **2002**, 1231. We make reference to this paper here only because one of the reviewers recommended that we should. In our opinion the structures of  $M(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)$  ( $M^{2+} = \text{Co}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ ;  $\text{C}_4\text{O}_4^{2-} = \text{squarate}$ ) that are described there are not related to sodalite. In the sodalite net the four nodes that form a square are all 4-connecting as can be seen in Figure 2, whereas the four nodes forming a square in  $M(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)$  are only 3-connecting. Each  $\text{C}_4\text{O}_4^{2-}$  unit is attached to four  $M(\text{H}_2\text{O})_2^{2+}$  units, and each  $M(\text{H}_2\text{O})_2^{2+}$  unit in turn is attached to four  $\text{C}_4\text{O}_4^{2-}$  units; both  $\text{C}_4\text{O}_4^{2-}$  and  $M(\text{H}_2\text{O})_2^{2+}$  therefore act as 4-connecting nodes in the net, which in fact has the  $6^48^2$  topology of NbO.

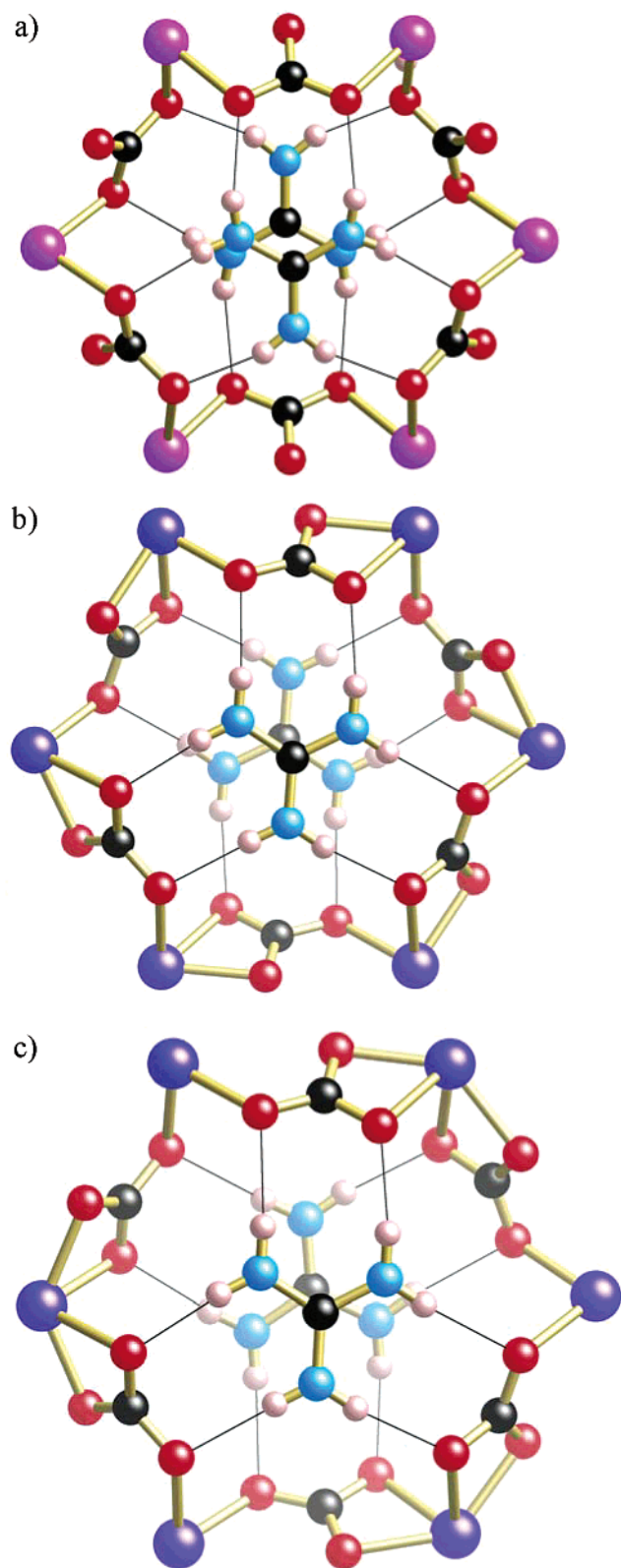
$M_6(\text{CO}_3)_6$  rings correspond to the hexagonal faces of the sodalite cage. In the BC structures each  $M_6(\text{CO}_3)_6$  ring contains a closely spaced face-to-face pair of guanidinium ions arranged around a site of  $\bar{3}m$  symmetry. Each pair is secured by 12 equivalent hydrogen bonds to the surrounding oxygen atoms from carbonate as can be seen for the  $\text{Mn}_6(\text{CO}_3)_6 \cdot (\text{CH}_6\text{N}_3)_2^{2+}$  unit shown in Figure 4a.  $\text{N} \cdots \text{O}$  separations in the  $\text{N}-\text{H} \cdots \text{O}$  associations are given in Table 2. Two distinct types of  $M_6(\text{CO}_3)_6$  rings are present in the FC structures, illustrated for  $[\text{Co}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$  in Figure 4b,c. The origin of the two distinguishable types of  $M_6(\text{CO}_3)_6$  rings is shown in Figure 5. When the connections between nodes have an element of directionality, as the carbonate units do in the FC structure, and when all the  $M_4(\text{CO}_3)_4$  rings within a given sodalite cage unit have a circulatory character of the same clock direction, it is inevitable that more than one type of  $M_6(\text{CO}_3)_6$  ring be present as can be seen by tracing the arrows in Figure 5. The circulatory type of  $\text{Co}_6(\text{CO}_3)_6$  ring is seen in Figure 4b and the noncirculatory type in Figure 4c. The guanidinium cations associated with these two types of  $\text{Co}_6(\text{CO}_3)_6$  rings are therefore intrinsically inequivalent. In addition the two hydrogen bonds between a particular guanidinium and a particular carbonate in the FC structures are intrinsically inequivalent because all three oxygen atoms of the carbonate units are inequivalent. C—N and N—H distances and angles are all unexceptional. The two guanidinium cations within a pair make contact which is surprisingly close for two like-charged species (C $\cdots$ C separation  $\sim 3.3$ – $3.6$  Å; see Tables 2 and 3).

Entire sodalite cages for the BC and FC structures are shown in parts a and b, respectively, of Figure 6, from which the guanidinium and alkali-metal cations have been omitted for clarity. Figure 6c shows the cage generated by linking the metal centers in part a or b of Figure 6 by imaginary linear connections, which is readily recognizable as sodalite-like. As will be apparent upon inspection of Figure 6b, the isolated sodalite cage in the FC class of compounds, as exemplified by the Co compound in the figure, is chiral because, when it is viewed from outside the cage, all six of the  $M_4(\text{CO}_3)_4$  rings “circulate” in the same direction of the clock. The FC net as a whole however is achiral because adjacent cages sharing a common  $M_4(\text{CO}_3)_4$  face are necessarily of the opposite hand. As will be appreciated upon inspection of Figure 7, the alternation through the structure of cages of opposite hand is responsible for the FC compounds having unit cell dimensions roughly twice those of the BC compounds.

In both the BC and the FC structures a tetramethylammonium cation, orientationally disordered, is located with its nitrogen atom at the center of each cage.

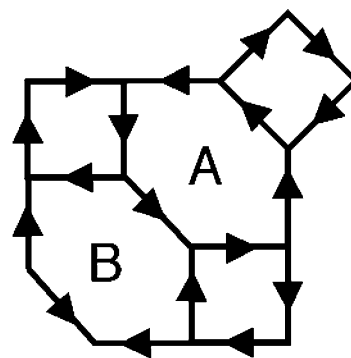
## Discussion

As has been reported previously, the addition of a guanidinium salt to the deep blue solution obtained by dissolving  $\text{Cu}(\text{NO}_3)_2$  in excess aqueous  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$  produces royal blue crystals of  $(\text{CH}_6\text{N}_3)_2[\text{Cu}(\text{CO}_3)_2]$ .<sup>11</sup> This contains a diamond-like anionic  $[\text{Cu}(\text{CO}_3)_2]_n$  framework in which the carbonate units act as  $\mu_2$ -bridges. Each of the cyclohexane-like  $[\text{Cu}_6(\text{CO}_3)_6]$  windows in the net is occupied by a single guanidinium cation multiply hydrogen bonded to oxygen centers of the surrounding carbonate ligands. This structure is similar to that of  $(\text{CH}_6\text{N}_3)_2[\text{Zn}(\text{CO}_3)_2]$ ,<sup>10</sup> which is very surprising in view of the fact that



**Figure 4.** Binding of the pair of guanidinium ions at the center of the  $M_6(\text{CO}_3)_6$  rings by 12 hydrogen bonds in  $[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4]\cdot 3\text{H}_2\text{O}$  (a) and in  $[\text{Co}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4]\cdot 2\text{H}_2\text{O}$  (b, c). The directional aspect of the carbonate bridges in the FC structures generates a circulatory  $\text{Co}_6(\text{CO}_3)_6$  ring in (b) but a noncirculatory one in (c).

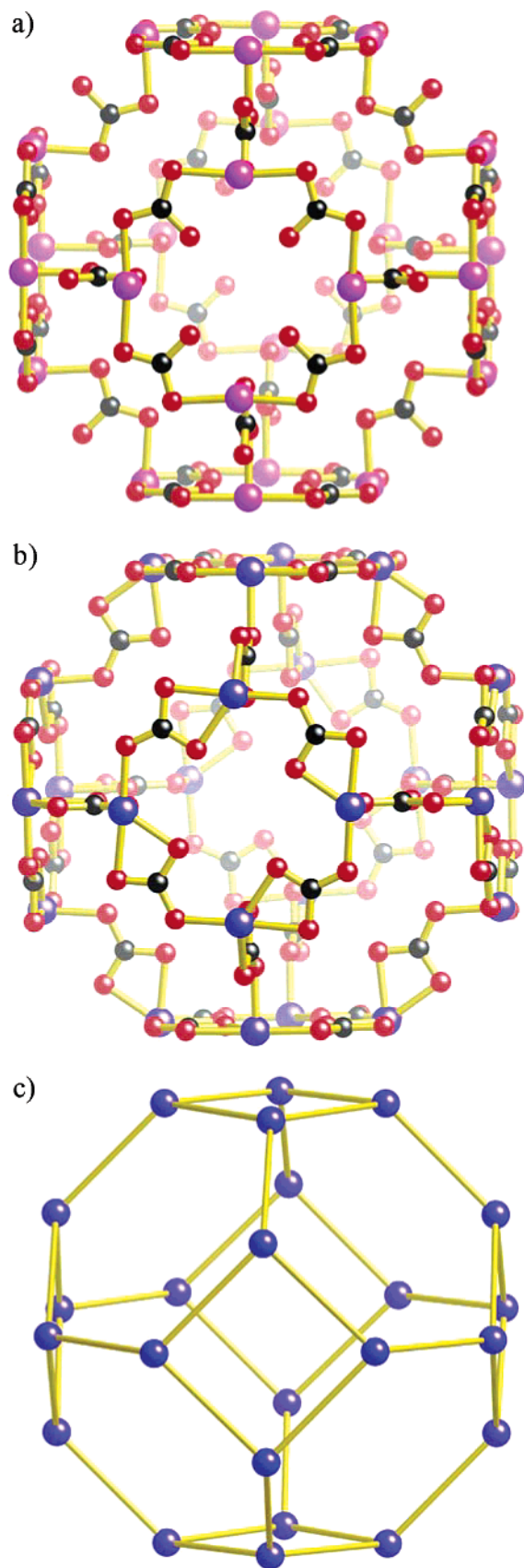
the Cu center, which acts as the pseudotetrahedral node of the diamond net, has an immediate environment consisting of a square planar set of four carbonate oxygen donors. In compari-



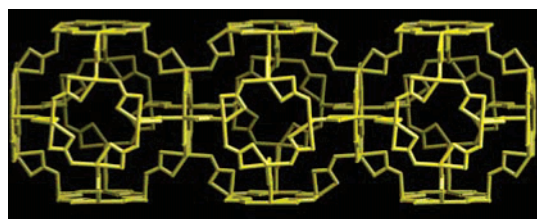
**Figure 5.** Schematic representation of three four-membered rings with clockwise character fused to a central six-membered ring (ring A) in the sodalite net. If ring A has circulatory character, it must be counterclockwise and the adjacent ring B inevitably is noncirculatory.

son, the zinc has a tetrahedral  $\text{O}_4$  environment more naturally compatible with the diamond connectivity. Square planar copper is able to play the role of tetrahedral node because of the moderately strain-free bending that is possible around the 2-connecting carbonate units.

The serendipitous observation out of which developed the highly symmetrical networks we describe in the Results was that in some reactions in which reduced proportions of guanidinium salt were added to the  $\text{Cu}^{\text{II}}/\text{KHCO}_3/\text{K}_2\text{CO}_3$  solutions a very small proportion of well-formed pale blue crystals accompanied the vastly predominant royal blue  $(\text{CH}_6\text{N}_3)_2\text{[Cu}(\text{CO}_3)_2]$  crystals.<sup>11</sup> This very minor byproduct was shown to have the composition  $[\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\cdot \text{K}_4\cdot 8\text{H}_2\text{O}$  and to contain an infinite 3D  $[\text{Cu}(\text{CO}_3)_2]_n$  network with a sodalite-like structure very similar to that of the  $[\text{Mn}(\text{CO}_3)_2]_n$  network shown in Figure 6a. The  $\text{K}^+$  ions are much too large to fit within the plane of the  $\text{O}_4$  holes in the network, and four of them, together with eight water molecules, are found trapped within each sodalite cage. It seemed to us that the  $\text{O}_4$  holes in this structure, with an  $\text{O}\cdots\text{O}$  diagonal of 4.16 Å, although too small to accommodate  $\text{K}^+$ , might well be able to bind  $\text{Li}^+$  or  $\text{Na}^+$  within the  $\text{O}_4$  plane. If it were to prove possible to incorporate either of these two monocations in this way, the composition and charge per cage would be  $[\{\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8\}\text{M}'_3]^-$  ( $\text{M}'^+ = \text{Li}^+$  or  $\text{Na}^+$ ) and an additional cation would be required for charge neutrality. Consideration of the space available inside the sodalite cages suggested that the tetramethylammonium cation might fit snugly and might be able therefore to serve as the required additional cation. Crystals of composition  $[\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4]\cdot \text{H}_2\text{O}$  were indeed obtained by the addition of  $\text{NaNO}_3$  and guanidinium nitrate to aqueous solutions of copper nitrate in excess tetramethylammonium bicarbonate and carbonate. In this experiment five components spontaneously assemble themselves under extremely simple conditions (aqueous solution at room temperature) into a 3D sodalite structure, almost all aspects of which are as deliberately intended; possibly therefore it qualifies as an example of true crystal engineering, but it has to be said that the outcome, though intended, could not possibly have been guaranteed. The combination of cations—copper, sodium, guanidinium, and tetramethylammonium—appears to be working in concert with the carbonate anion. Complementarity—a central theme in the broader area of supramolecular chemistry—is manifest here: the copper(II) and the carbonate form a sodalite network in which the central cavities, the square windows, and the hexagonal



**Figure 6.** Sodalite cages viewed in isolation for (a)  $[\text{Mn}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$  and (b)  $[\text{Co}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$ . The guanidinium and alkali-metal cations have been omitted for clarity. (c) shows the sodalite-like cage generated by linking the metal centers in (a) or (b) by imaginary linear connections.



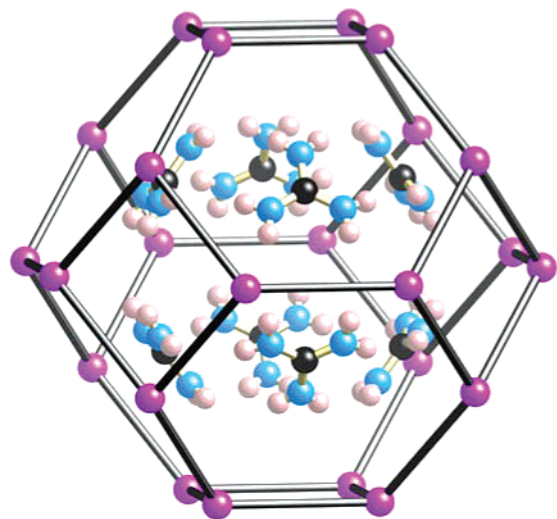
**Figure 7.** A central chiral sodalite cage of the FC structure sharing four-membered ring faces with two cages of the opposite hand, illustrating the doubling of the cell dimensions compared with those of the BC structure.

windows are geometrically and chemically complemented by tetramethylammonium ions, sodium ions, and *pairs* of guanidinium ions, respectively. With regard to complementarity, it is interesting to note that the infinite  $[\text{Cu}(\text{CO}_3)_2]_n$  network adopts a diamond-like connectivity when the countercation is either  $\text{K}^+$  alone<sup>7b</sup> or  $\text{CH}_6\text{N}_3^+$  alone, but the two cations in combination dispose the network to adopt the sodalite connectivity.

The first metal cation for which we observed the FC sodalite structure was  $\text{Co}^{2+}$ ; this again was serendipitous. We had been somewhat surprised to discover that  $\text{Cu}^{2+}$  in an essentially square planar environment was able to play the role of tetrahedral node first in the diamond net in  $(\text{CH}_6\text{N}_3)_2[\text{Cu}(\text{CO}_3)_2]$  and then in the sodalite net in  $[\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{K}_4 \cdot 8\text{H}_2\text{O}$ , but in the FC cobalt example the role of tetrahedral node was being played by an octahedral metal center! This seemed to open up many possibilities. In light of the knowledge that  $\text{Co}^{2+}$  generated the FC structure, it was no surprise to find that  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mg}^{2+}$  did likewise, but the adoption of the BC structure by  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  was not anticipated. Another BC structure that was not expected (but, given the result with  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$ , neither was it very surprising) was that of the potassium-containing  $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{K}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$ . Numerous attempts to obtain the sodium-containing analogue,  $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot x\text{H}_2\text{O}$ , in crystalline form, were not successful; possibly the  $\text{O}_4$  hole in the “expanded” network derived from the larger  $\text{Ca}^{2+}$  ( $\text{O} \cdots \text{O}$  diagonal 5.02 Å to be compared with the corresponding  $\text{O} \cdots \text{O}$  diagonal in  $[\text{Cu}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8] \cdot \text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot \text{H}_2\text{O}$  of 4.28 Å) is too large for the comfortable incorporation of  $\text{Na}^+$ .

Although we certainly would not have been able to predict whether a particular metal would yield the BC structure or the FC structure, it is possible nevertheless, with hindsight, to rationalize the observations. The octahedral metal geometries adopted in the FC structures of the  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  compounds are those very commonly seen for these cations and are not surprising. The coordination environment in the BC structure of the  $\text{Cu}^{2+}$  compound can best be regarded as the essentially square planar geometry generally preferred by this cation. The four secondary interactions ( $\text{Cu}-\text{O} = 2.58$  Å) are substantially weaker than the four primary bonds ( $\text{Cu}-\text{O} = 2.04$  Å). It is common for  $\text{Cu}^{2+}$  to have four close square planar ligands together with a variable number of more weakly attached ligands. By coincidence we recently discovered<sup>14</sup> an almost identical copper environment in the nitrite-derived complex ion  $\text{Cu}(\text{ONO})_4^{2-}$  (four almost square planar oxygen donors at  $\text{Cu}-\text{O}$  distances of 2.00 and 1.99 Å and four more distant ones at  $\text{Cu}-\text{O}$  distances of 2.55 and 2.66 Å). The coordination geometries adopted in the BC structures of the  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cd}^{2+}$  compounds are better regarded as





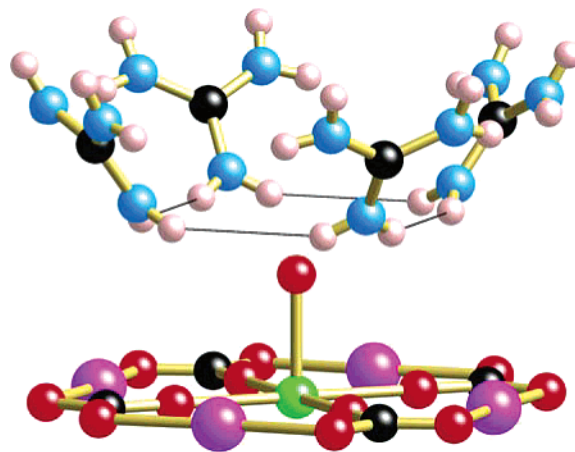
**Figure 8.** An  $M_{24}$  sodalite cage containing eight guanidinium cations “face-on” to the cage center.

approximating the 8-coordinate arrangement often seen for  $Ca^{2+}$  and  $Cd^{2+}$  and occasionally seen for  $Mn^{2+}$ . In the cases of these three larger cations the difference between the four primary bonds and the four secondary bonds is much less marked than in the copper case (2.35 and 2.62 Å for Ca, 2.18 and 2.59 Å for Mn, and 2.28 and 2.62 Å for Cd, which are to be compared with 2.04 and 2.58 Å for Cu); in other words, the longer interactions in the case of the larger cations are relatively more important than in the copper case.

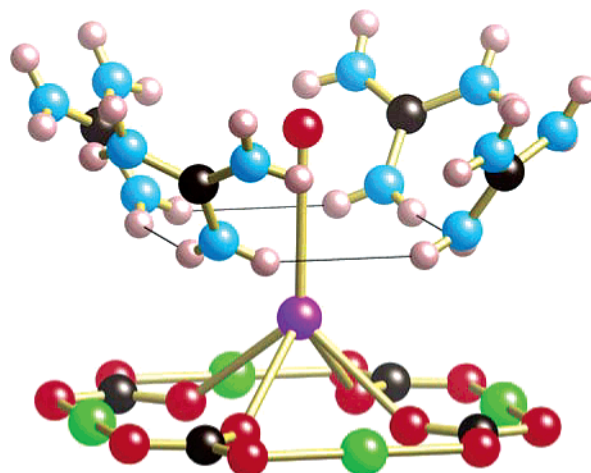
The two guanidinium cations within a pair make contact which is surprisingly close for two like-charged species (Figure 4,  $C\cdots C$  separation  $\sim 3.3\text{--}3.6$  Å; see Tables 2 and 3), which perhaps reflects the pronounced stabilization provided by the very favorable interaction each cation makes with six highly complementary oxy anionic centers. This is yet another crucial structural feature which is difficult to imagine could ever have been predicted prior to its first accidental observation.

One member of the pair of guanidinium cations associated with each  $M_6(CO_3)_6$  face is located  $\sim 1.5\text{--}1.8$  Å inside the imaginary surface of the truncated octahedron defined by the 24 metal centers as shown in Figure 8. When the “van der Waals space” occupied by the guanidinium units and the hydrogen bonds to the surrounding carbonate components are taken into account, it is apparent that the eight guanidinium cations within an  $M_{24}$  cage effectively seal off the interior except for six somewhat constricted “access ports” located to the inner side of each of the  $M_4(CO_3)_4$  units. In these constricted regions pairs of hydrogen atoms from four separate guanidinium cations are arranged around the 4-fold axis, as shown in Figure 9, generating a rather tight  $H_8$  “belt” which imposes restrictions upon the environments that are possible for counteranions and water molecules.

In the case of  $[Cu_6(CO_3)_{12}(CH_6N_3)_8]\cdot K_4\cdot 8H_2O$ <sup>11</sup> the four  $K^+$  ions, which are too large to be accommodated in the  $O_4$  plane, are disordered over six sites on the 4-fold axes 1.64 Å from the centers of the  $O_4$  holes, as shown in Figure 10. Two of the eight water molecules per cage occupy the two sites not occupied by  $K^+$ . The remaining six water molecules are located roughly at the corners of an octahedron inside the region bounded by the six  $H_8$  belts. The positions occupied by the other two water molecules are close to but not exactly coincident with



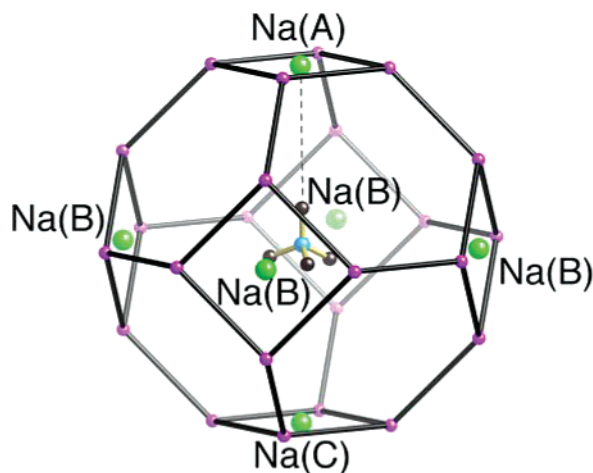
**Figure 9.**  $H_8$  belt (represented by fine lines) formed by pairs of hydrogen atoms from four separate guanidinium ions. The proximity of the  $H_8$  belt to the water molecule associated with the  $Na^+$  center in the  $O_4$  hole can be seen; for the particular case of  $[Mn_6(CO_3)_{12}(CH_6N_3)_8]Na_3[N(CH_3)_4]\cdot 3H_2O$  represented here the water oxygen atom is 2.89 Å from the hydrogen atoms of the belt.



**Figure 10.** Environment of the  $K^+$  center in  $[Cu_6(CO_3)_{12}(CH_6N_3)_8]\cdot K_4\cdot 8H_2O$ . The  $K^+$  interacts with a water molecule through the  $H_8$  belt.

those occupied by  $K^+$ . Each  $K^+$  ion interacts with a single water molecule ( $K\text{--}OH_2 = 3.23$  Å) located on the opposite side of the  $H_8$  belt as can be seen in Figure 10. This 5-coordinate, square pyramidal environment, a consequence of the restrictions imposed by the guanidinium units, is unusual for  $K^+$ .

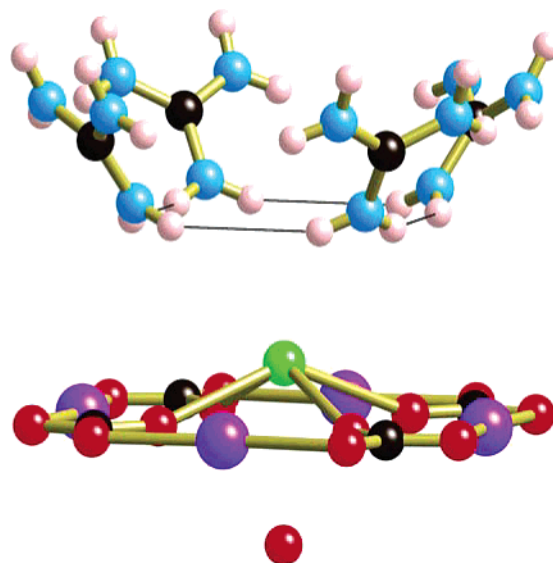
It appears that the eight guanidinium units within a cage place restrictions on the orientations that are possible for the disordered tetramethylammonium cation at the center. The crystallographic analyses clearly show that one  $N\text{--}CH_3$  group of each tetramethylammonium cation points directly toward one of the six sodium ions. Figure 11 is a schematic representation of one of these six possible  $N\text{--}C$  orientations in which the methyl group is directed vertically upward toward the sodium ion at the top of the figure,  $Na(A)$ . However, there is additional disorder in that the other three methyl groups are rotationally disordered around the axis along which the first  $N\text{--}C$  is directed (i.e., the vertical axis in Figure 11). The sodium site ( $Na(C)$  in Figure 11) diametrically opposite the one toward which the first methyl group is directed is the least sterically constrained; in the sodium-containing compounds described here this site is *always* occupied by a water molecule. The remaining four sites ( $Na(B)$  in Figure 11) are significantly constrained by the methyl groups



**Figure 11.** Schematic representation of one of six possible N–C orientations for the disordered central tetramethylammonium cation. One of the methyl groups points directly at one sodium center (Na(A) here) and directly away from another (Na(C) here), while the other three methyl groups are rotationally disordered around the Na(A)···Na(C) axis. Na(A) is strongly constrained, Na(C) is minimally constrained, and the four Na(B) sites are constrained to an intermediate extent.

but less so than the Na(A) site. Depending on how “tight” the metal–carbonate sodalite framework is, these four Na(B) sites may be completely occupied, completely unoccupied, or partially occupied. Among the sodium-containing compounds the least tight network is that in the cadmium compound which is sufficiently expanded to allow all the sodium sites except the most constrained Na(A) in Figure 11 to take on water molecules. Fewer water molecules per cage are seen in the tighter structures, with numbers being roughly in line with the size of the framework cation. In the Cu, Mg, Fe, Co, Ni, and Zn compounds some of the sodium ions have a 5-coordinate environment that is not exceptional, but it is inevitable that other sodium ions must be present with an unusual square planar O<sub>4</sub> environment—one of several examples here of unusual alkali-metal environments arising from the steric constraints imposed by the combination of guanidinium and tetramethylammonium cations.

The potassium ions in the Ca/K compound are too large to fit within the plane of the O<sub>4</sub> holes and are disordered over two sites 0.93 Å on either side of the midpoint of the holes as shown in Figure 12. Each cage contains three such K<sup>+</sup> ions, disordered over the six available sites, together with three disordered H<sub>2</sub>O molecules which occupy the three sites not occupied by K<sup>+</sup>. The positions occupied by water (2.67 Å from the center of the O<sub>4</sub> hole) are close to but not exactly coincident with those occupied by K<sup>+</sup>. Every O<sub>4</sub> hole therefore has K<sup>+</sup> on one side and H<sub>2</sub>O on the other. When the K<sup>+</sup> is displaced in this way away from the O<sub>4</sub> hole toward the central tetramethylammonium ion, there simply is not enough room for a water molecule to associate with it. A trihydrate therefore is a completely logical outcome. The fact that the alkali-metal component in the Ca-derived compound, with the most expanded network in the entire series reported here, is K<sup>+</sup> rather than Na<sup>+</sup> explains why it accommodates fewer water molecules than the Cd-derived compound whose framework is in fact tighter. The 4-coordinate environment of the K<sup>+</sup> ion in this case, with a square arrangement of four carbonate-derived oxygen centers off to one side, is even more unusual than the square pyramidal environment seen in [Cu<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]·K<sub>4</sub>·8H<sub>2</sub>O—yet another consequence of the constraints imposed by the combination



**Figure 12.** Environment of the 4-coordinate K<sup>+</sup> and the water molecule in [Ca<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]K<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·3H<sub>2</sub>O. The K<sup>+</sup> is 0.93 Å out of the O<sub>4</sub> plane, and the water molecule is 2.67 Å out on the opposite side.

of guanidinium and tetramethylammonium cations within the cage. This unusual asymmetrical environment of the K<sup>+</sup> possibly resembles what might be found for a potassium cation at the very surface of certain crystals.

When sodium nitrate and guanidinium nitrate are added to Cu<sup>II</sup>/KHCO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> solutions in which K<sup>+</sup> is present in great excess relative to Na<sup>+</sup>, the compound that crystallizes is [Cu<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]Na<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]·H<sub>2</sub>O and not [Cu<sub>6</sub>(CO<sub>3</sub>)<sub>12</sub>(CH<sub>6</sub>N<sub>3</sub>)<sub>8</sub>]·K<sub>4</sub>·8H<sub>2</sub>O; on the other hand all our attempts to generate a Cu<sup>II</sup>/K<sup>+</sup>/N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> sodalite have failed. It appears therefore that there is sufficient room inside the tight Cu-based sodalite cage to accommodate the tetramethylammonium cation only if the monovalent alkali-metal cation is small enough to fit into the plane of the O<sub>4</sub> holes. As mentioned above, in the Cu<sup>II</sup>/Na<sup>+</sup>/N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> compound there is room for only one water molecule per cage, and it is found directed toward the least restricted “rear end” of the tetramethylammonium cation (Na(C) in Figure 11), while the remaining sodium cations (corresponding to Na(A) and the four Na(B) sites in Figure 11) must be only 4-coordinate. A Cu<sup>II</sup>/K<sup>+</sup>/N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> sodalite structure, if it were capable of existence, could possibly tolerate one “out-of-plane” K<sup>+</sup> at the least constricted site corresponding to Na(C) in Figure 11, but the other two K<sup>+</sup> ions in the Na(B) sites would clash unacceptably with the methyl groups. This steric stress would be exacerbated by the fact that the tight Cu-based framework and the correspondingly tight O<sub>4</sub> hole would require the K<sup>+</sup> to be excessively pyramidal (similar to that in Figure 10 but minus the associated water molecule). This preference for Na<sup>+</sup> over K<sup>+</sup> in the Cu<sup>II</sup>/N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> system is to be contrasted with the reversed preference seen when the larger Ca<sup>2+</sup> is the metal component of the sodalite framework; the expanded Ca-containing framework generates O<sub>4</sub> holes too large to suit Na<sup>+</sup>, but K<sup>+</sup> can be accommodated despite its unusual environment. These preferences exhibited by macrocyclic rings involving oxygen donors are somewhat reminiscent of those seen with crown ether macrocycles.

It is interesting to compare the systems described in this paper with the aluminosilicate sodalites and ultramarines. Because of the planarity and relative orientations of the carbonate units,

the BC networks have higher symmetry ( $Im\bar{3}m$ ) than the aluminosilicates ( $I\bar{4}3m$ ); indeed they have the same symmetry as the parent  $4^26^4$  net! The carbonate nets described above share with the aluminosilicates a marked tendency for the contents of the sodalite cages to be disordered.

### Concluding Remarks and Prospects

On the basis of the exploratory work described here, scores if not hundreds of crystalline compounds with deliberately engineered sodalite-related structures promise to be readily accessible using the simplest of procedures. Three aspects of the structure and composition are amenable in principle to wide, deliberate variation, namely, (1) the framework metal, (2) the species, if any, occupying the  $O_4$  holes, and (3) the species occupying the central cavity. Considering first the metal component of the framework, it is difficult to see why oxidation states other than II could not be incorporated. Frameworks involving mixed metals as well as mixed oxidation states of the same metal are realistic possibilities (indeed mixed  $Fe^{II/III}$  frameworks are probably responsible for the dark colors seen in the case of  $[Fe_6(CO_3)_{12}(CH_6N_3)_8]Na_3[N(CH_3)_4]\cdot 2H_2O$  as described in the Experimental Section). Modification of the charge on the framework would of course require appropriate change in the occupants of the  $O_4$  holes and/or the central cavity to maintain charge balance. Turning now to the contents of the  $O_4$  holes, preliminary work suggests that sodalite structures can be obtained in which the alkali-metal cations are replaced by protons. Moreover, the possibility of introducing divalent metal ions into the  $O_4$  holes appears to be an eminently realistic prospect; if these were themselves paramagnetic or redox active, the close contact with the metal centers of the framework would suggest many opportunities for interesting cooperative magnetic or electronic behavior. The possible composition  $\{[(^aM^{II})_6(CO_3)_{12}(CH_6N_3)_8](^bM^{II})_3\}^{2+}$ , in which  $^aM^{II}$  and  $^bM^{II}$  are the divalent metals in the framework and those proposed to occupy the  $O_4$  holes, respectively, would require a species of the correct size and shape and carrying a 2- charge to occupy the central cavity. The introduction in this way of a dianion into the space immediately surrounded by eight guanidinium cations may prove to be strongly favored (contrast this with the close juxtaposition

of the tetramethylammonium cation and the eight repellent guanidinium cations in the compounds described above, which nonetheless form readily). With regard to the contents of the central cavity, preliminary work suggests that sodalite networks can be obtained in which  $K^+$ ,  $Na^+$ ,  $NH_4^+$ , and  $Me_3NH^+$  in various combinations are found there. Clearly, there is great scope for variation. A very persuasive demonstration has previously been presented of the profound effect exerted by  $Gd^{3+}$  upon the course of reactions among  $Cu^{2+}$ ,  $CO_3^{2-}$ , and  $CH_6N_3^+$  that would otherwise have generated royal blue crystals of the diamond-related  $(CH_6N_3)_2[Cu(CO_3)_2]$ .<sup>11</sup> Two side-by-side aqueous reaction mixtures, both containing  $Cu(NO_3)_2$ , guanidinium nitrate,  $KHCO_3$ , and  $K_2(CO_3)_2$  in the same concentrations, differing only in that  $Gd(NO_3)_3$  is present in one, follow visibly very different courses: the Gd-free mixture deposits royal blue crystals of  $(CH_6N_3)_2[Cu(CO_3)_2]$ , while pale blue crystals of composition  $[Cu_6(CO_3)_{12}(CH_6N_3)_8]\cdot Gd_2\cdot K_2\cdot (OH)_4\cdot H_2O$  containing a sodalite-related network structure separate from the other. The contents of the sodalite cages, in common with the cage contents in many aluminosilicate sodalites and ultramarines, are again highly disordered, and their arrangement, at this stage, remains something of a mystery, but it is clear that the  $Gd^{3+}$  is somehow redirecting the assembly of the copper, carbonate, and guanidinium components. It remains to be seen whether many other trivalent cations, including all the other lanthanide cations, when introduced in place of  $Gd^{3+}$  into the  $Cu^{II}/CO_3^{2-}/CH_6N_3^+$  reaction mixture likewise produce sodalite-related networks; the enormous scope for new engineered sodalite-related compounds can be appreciated when all of these possibilities are combined with the range of different cations that the results presented above demonstrate can be incorporated into the framework itself.

**Acknowledgment.** We are grateful to the Australian Research Council for support.

**Supporting Information Available:** Details of the crystallographic studies in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA038904I