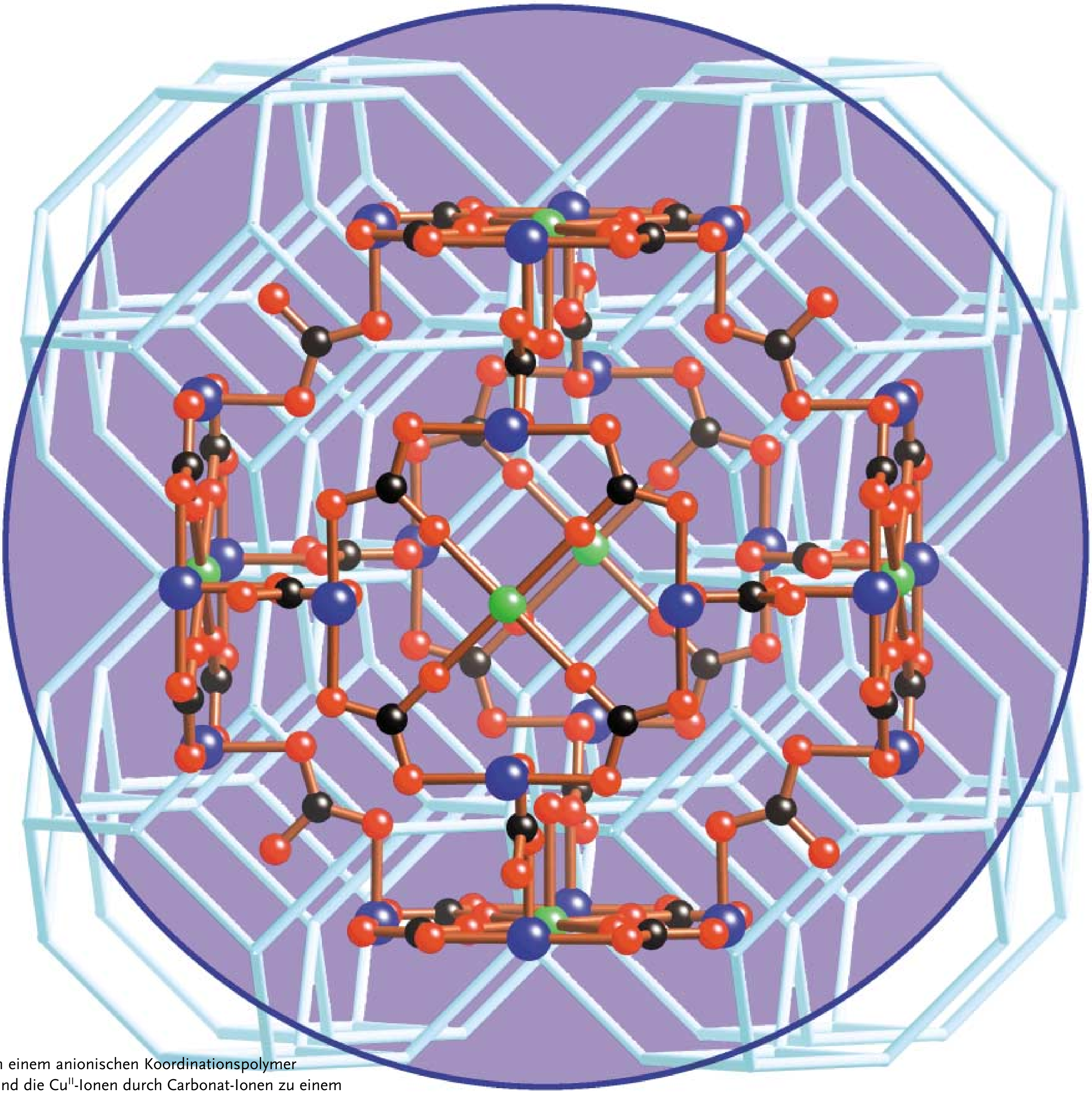
# Zuschriften



In einem anionischen Koordinationspolymer sind die $Cu^{II}$-Ionen durch Carbonat-Ionen zu einem kubischen Netzwerk verknüpft, das die Topologie des im Hintergrund dargestellten Sodalithnetzes hat. Paare von Guanidinium-Ionen in den hexagonalen Fenstern des Sodalithkäfigs (nicht gezeigt) dienen als H-Brücken-Template, während Alkalimetallionen (grün) gut in die quadratischen Fenster passen. Näheres erläutern R. Robson et al. auf den folgenden Seiten.

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## Crystal Engineering

# New Tricks for an Old Dog: The Carbonate Ion as a Building Block for Networks Including Examples of Composition $[Cu_6(CO_3)_{12}\{C(NH_2)_3\}_8]^{4-}$ with the Sodalite Topology**

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*In memory of Bernard Hoskins*

Metal carbonates have been extensively studied and the carbonate ion has been widely used as a ligand in coordination chemistry since Werner's day.[1] Despite this, we are convinced that large tracts of unexplored carbonate-based chemistry still lay open for exploration. Here we describe some new, highly symmetrical metal–carbonate networks that have the topology of the $4^26^4$ sodalite net.[2] Structural studies of one-,[3] two-,[4] and three-dimensional[5] metal–carbonate polymers have been reported. In 1996 a beautiful network with cubic symmetry was described by Stucky et al. for the compound $Na_2Zn_3(CO_3)_4{\cdot}3H_2O$.[6] We recently reported metal derivatives of a nitrogen-containing close analog of carbonate in a triply chelating connecting unit constructed around a dianionic, guanidine-based $CN_3$ core.[7] Because of its potential threefold axial symmetry, the $CN_3$ moiety is an attractive unit for network building, and the guanidinium ion, $[C(NH_2)_3]^+$, is an essential component of all the structures described below. The structures of the guanidinium-containing carbonate compounds $(CH_6N_3)_2[Zn(CO_3)_2]$[8] and $(CH_6N_3)_6[M(CO_3)_5]{\cdot}4H_2O$, M = Ce,[9] Th,[10] have been reported previously.

$Cu(NO_3)_2$ dissolves readily in aqueous solutions containing $KHCO_3$ and $K_2CO_3$ in excess to give deep blue solutions. Upon treatment with a guanidinium salt in excess such solutions deposit crystals of royal blue **1**, which has according to X-ray diffraction studies[11] a diamond-like topology (Figure 1). It is interesting to note that the tetrahedral nodes required for the diamond net are here provided by seemingly incompatible square-planar $O_4$-coordinated copper centers: the pronounced bends in the carbonate connections between copper nodes make this possible. The guanidinium ion is secured within every cyclohexane-like $Cu_6(CO_3)_6$ "window" by multiple hydrogen bonds to carbonate oxygen atoms (Figure 1). This structure is surprisingly similar to that of $(CH_6N_3)_2[Zn(CO_3)_2]$,[8] which also has the diamond topology—surprising in our view because the zinc centers have an essentially tetrahedral $O_4$ environment in contrast to the square-planar $O_4$ environment of copper in **1**.

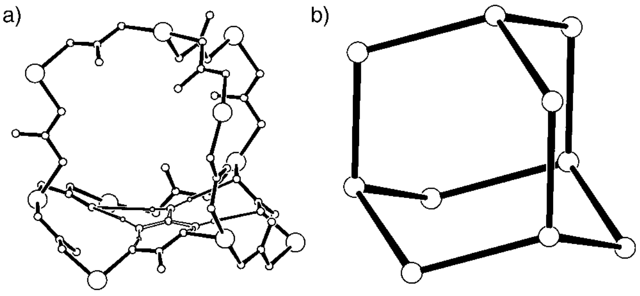

*Figure 1.* An adamantane unit in the diamond-like structure of **1**. a) Circles in order of decreasing radius represent Cu, O, N, C, and H. The Cu/$CO_3$ framework is indicated by heavy lines. For clarity, only the details of the hydrogen-bonded incorporation of the guanidinium ion into one of the cyclohexane-like windows is shown, represented by "open" connections. b) Only the Cu centers seen from the same angle as in (a).

$(CH_6N_3)_2[Cu(CO_3)_2]$ **1**

In some reactions in which reduced proportions of guanidinium salt were added to the $Cu^{II}/KHCO_3/K_2CO_3$ solutions, we noticed that small quantities of a paler blue crystalline by-product, **2**, accompanied the predominant royal blue **1**. X-ray diffraction studies of **2**[11] revealed cubic symmetry and the topology of the $4^26^4$ net. A representation of the parent $4^26^4$ net, referred to here as the sodalite net is given in Figure 2; it can be visualized in terms of truncated octahedral sodalite cages sharing faces, both square and hexagonal. A representation of the copper and carbonate components of one such cage of **2** is shown in Figure 3a, and Figure 3b shows the truncated octahedron defined by the 24 copper centers associated with each cage. Again, as in the diamond-like structure of **1**, the essentially tetrahedral nodes of the sodalite net are provided by seemingly incompatible square-planar coordinated copper centers. Every $Cu_6(CO_3)_6$ hexagonal ring in the structure is occupied by a pair of

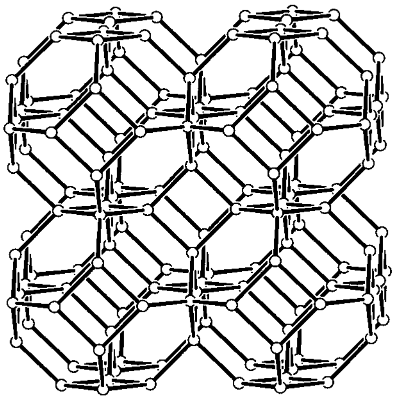

*Figure 2.* The $4^26^4$ sodalite net showing a central sodalite cage surrounded by eight others.

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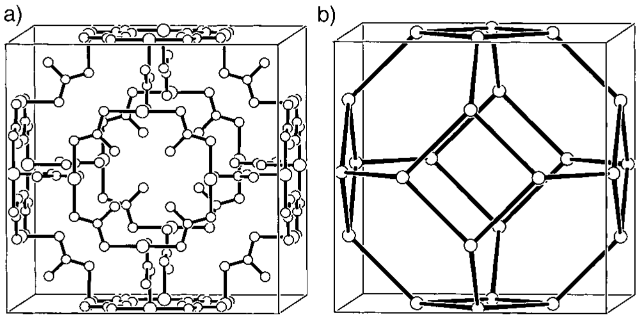

***Figure 3.*** a) A single sodalite cage in the structure of **2**. For clarity, only copper and carbonate are shown. b) The truncated octahedron defined by the 24 copper centers associated with each cage seen from the same angle as in (a).

guanidinium ions arranged around a $\bar{3}m$ site (Figure 4). The separation between the guanidinium ions (C···C 3.19 Å) is remarkably close for two like-charged species. The pair is held in place by a symmetrical array of twelve equivalent hydrogen bonds to the coordinated carbonate oxygen atoms of the surrounding $Cu_6(CO_3)_6$ ring.

$[Cu_6(CO_3)_{12}(CH_6N_3)_8] \cdot 4K \cdot 8H_2O$ **2**

All atoms within the $Cu_4(CO_3)_4$ units of **2** representing the square faces of the truncated octahedral cages are internally coplanar and the carbonate ions are so oriented that the four noncoordinated C=O groups point directly at the center of the square (see Figure 3a). We refer to the spaces at the centers of such quartets of noncoordinated oxygen atoms below as "the $O_4$ holes". The sodalite cages in **2** are larger than those in the aluminosilicate compounds sodalite and ultramarine and contain four $K^+$ ions and eight $H_2O$ molecules which are disordered, as are the contents of the cages in the other sodalite analogs we report below and as are the contents of the cages in many of the aluminosilicate analogs. The $K^+$ ions are located equidistant from the four oxygen atoms of an $O_4$ hole (K-O 2.7 Å, Figure 5). The four $K^+$ ions are disordered over all six such sites in the cage. The two sites of this type not occupied by $K^+$ are occupied by two of the water molecules which have not exactly the same distance from the $O_4$ set as have the $K^+$ ions. The remaining six water molecules form an inner shell located roughly at the corners of an octahedron (see Figure 5).

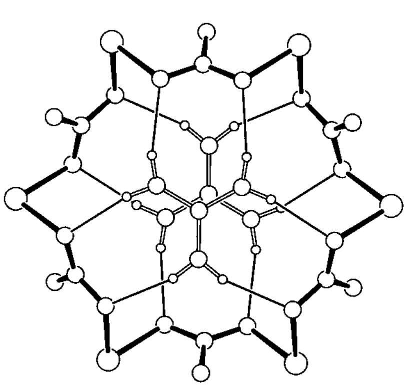

***Figure 4.*** Representation of the pair of guanidinium ions hydrogen-bonded (thin lines) inside a $Cu_6(CO_3)_6$ hexagonal face in the structure of **2**.

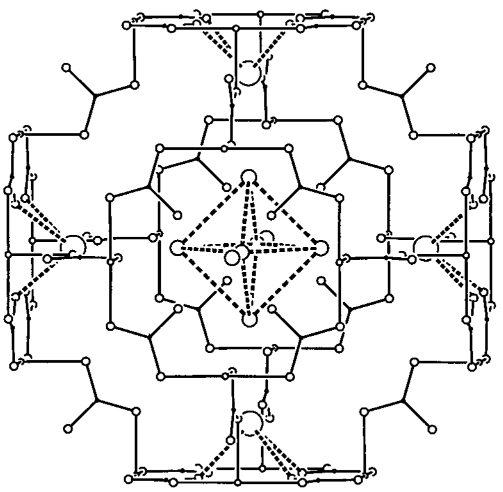

***Figure 5.*** Representation of one possible arrangement of the disordered four $K^+$ ions and eight $H_2O$ molecules within a sodalite cage of **2**. Circles in order of decreasing radius represent K, $O_{H_2O}$, $O_{CO_3^{2-}}$, and Cu.

We noticed that the $O_4$ square holes, with an O···O diagonal of 4.16 Å, although far too small to accomodate $K^+$ within the $O_4$ plane (as we saw above), might possibly accomodate an in-plane $Li^+$ ion very satisfactorily. If it were possible to incorporate $Li^+$ into every $O_4$ hole the composition and charge per cage would be $[\{Cu_6(CO_3)_{12}(CH_6N_3)_8\}Li_3]^-$ and we wondered if a tetramethylammonium ion might then be nicely accomodated inside the mononegative cage so formed. We discovered that crystals of **3**[11] with the intended composition and with the intended sodalite structure were indeed formed when aqueous solutions of $NMe_4HCO_3$ and $(NMe_4)_2CO_3$ in excess, $Cu(NO_3)_2$, $LiNO_3$, and guanidinium nitrate were brought together at room temperature. This constitutes the assembly of five components under extremely simple conditions into a deliberately intended extended three-dimensional structure—true crystal engineering.

$[Cu_6(CO_3)_{12}(CH_6N_3)_8] \cdot 3Li \cdot NMe_4 \cdot 5H_2O$ **3**

Subsequently we discovered that **3** could also be obtained by adding $LiNO_3$, guanidinium nitrate, and $NMe_4Cl$ to the Cu/$KHCO_3$/$K_2CO_3$ solutions referred to above; it is significant in this procedure that the crystallizing system incorporates $Li^+$ in preference to $K^+$ that is available in large excess. X-ray diffraction analysis[11] indicates that the $[Cu_6(CO_3)_{12}(CH_6N_3)_8]^{4-}$ components adopt a sodalite-like topology essentially identical to that seen in **2**, with $Li^+$ located at the center of every $O_4$ hole. The $(NMe_4^+)(H_2O)_5$ contents of the cages are disordered. The five water molecules are located 2.01 Å from $Li^+$ on the normal to the $O_4$ plane and are disordered over the six available sites of this type. The $NMe_4^+$ ions are orientationally disordered in compliance with the particular distribution of the five water molecules.

It was clear from the structure of **2** that the $K^+$ ion, constrained by its size to a location well out of the plane of the $O_4$ hole, together with its associated water molecule, would occupy too much space to allow the simultaneous incorporation of $NMe_4^+$ in the cage, and not surprisingly, all attempts to generate a $K^+/NMe_4^+$ sodalite structure have failed. However it was of interest to explore the combination of $NMe_4^+$ with $Na^+$ the size of which is intermediate between those of $K^+$ and $Li^+$. Crystals of **4**[11] were obtained by the addition of $NaNO_3$ and guanidinium nitrate to solutions of copper nitrate and $NMe_4HCO_3$ and $(NMe_4)_2CO_3$ in excess. The sodalite structure is again observed.[11]

$[Cu_6(CO_3)_{12}(CH_6N_3)_8]\cdot 3\,Na\cdot NMe_4\cdot H_2O$ **4**

Subsequently we discovered that **4** could also be obtained by adding $NaNO_3$ and guanidinium nitrate to the $Cu/KHCO_3/K_2CO_3$ solution—again, the $K^+$ ions present in large excess are not incorporated. It is significant that whilst the $Li^+$ ions in **3** allow the incorporation of five water molecules the larger $Na^+$ ions allow only one water molecule per cage. The cage contents are again disordered. The nitrogen atom of $NMe_4^+$ lies on a $m\bar{3}m$ position and the methyl groups are disordered over a number of positions. It appears that, as a consequence of the fact that the single "coordinated" water molecule per cage projects further into the cage towards the $NMe_4^+$ ion than in the $Li^+$ case, the water molecule can be accomodated only when a methyl group is pointing directly away from it.

The presence of $Gd^{3+}$ has a profound effect on the course of reactions between $Cu^{2+}$, $CO_3^{2-}$, and $CH_6N_3^+$ that would otherwise have given **1**. Two side-by-side aqueous reaction mixtures containing the same reactants in the same concentrations (i.e. $KHCO_3$ and $K_2CO_3$ in excess, $Cu(NO_3)_2$, and guanidinium nitrate), differing only in that $Gd(NO_3)_3$ is present in one, follow visibly very different courses: royal blue crystals of **1** are formed in the Gd-free mixture and pale blue crystals of **5** separate from the other. Somehow $Gd^{3+}$ redirects the assembly of the components away from diamond-like **1** towards **5** which according to diffraction studies has the sodalite structure.[11] The contents of the cages are highly disordered.

$[Cu_6(CO_3)_{12}(CH_6N_3)_8]\cdot 2\,Gd\cdot 2\,K\cdot 4\,OH\cdot H_2O$ **5**

Preliminary experiments indicate that it is possible to incorporate divalent cations such as $Mg^{2+}$ into the $O_4$ holes and that sodalite networks can be generated with cobalt(II) or zinc(II) in place of copper(II). The results presented here point to rich opportunities for truly deliberate crystal engineering of a wide range of related networks in which a variety of paramagnetic and/or redox-active metal centers could conceivably be organized in close proximity, the properties of which could be unusual and useful. The prospects for future developments in this area are enhanced by the extreme simplicity of the preparative procedures and the ready availability and cheapness of the components.

## Experimental Section

**1** and **2**: A solution of $CH_6N_3Cl$ (595 mg, 4.9 mmol) in water (1 mL) was added to a solution of $K_2(CO_3)_2$ and $KHCO_3$ (2.4 and 1.25 M, respectively, 2 mL) in which $Cu(NO_3)_2\cdot 3\,H_2O$ (196 mg, 0.81 mmol) had been dissolved. Royal blue crystals of **1** were collected after four days, washed with water, and dried in air. Yield: 235 mg, 95%. Elemental analysis: found: C 16.0, H 4.1, N 27.6, Cu 20.6; calc.: C 15.8, H 4.0, N 27.7, Cu 20.9. A reaction conducted as above, except that a smaller amount of $CH_6N_3Cl$ (303 mg, 2.45 mmol) was used, yielded pale blue crystals of **2** together with the predominant deeper blue crystals of **1**. Crystals of **1** were separated from crystals of **2** by hand under the microscope for elemental analysis. Found (%): C 12.7, H 3.2, N 17.0, Cu 20.3, K 8.3; calcd: C 12.8, H 3.4, N 17.9, Cu 20.3, K 8.3. The crystals of **2** were insoluble in water.

**3**: A mixture of $LiNO_3$ (51 mg, 0.74 mmol), $Me_4NCl$ (182 mg, 1.65 mmol), and $(CH_6N_3)_2CO_3$ (74 mg, 0.41 mmol) in water (1 mL) was added to a solution containing $K_2CO_3$, $KHCO_3$, and $Cu(NO_3)_2$ (2.41, 1.25, and 0.34 M, respectively, 2 mL). The pale blue-green crystals of **3** which separated were collected after 5 h, washed with water, and dried in air. Yield: 35 mg, 38%. Elemental analysis: found (%): C 16.8, H 3.7, N 19.8, Cu 22.4, Li 1.3; calcd: C 16.3, H 4.0, N 19.8, Cu 21.6, Li 1.2. The crystals were insoluble in water.

**4**: A solution containing $NaNO_3$ (316 mg, 3.72 mmol), $(CH_6N_3)_2CO_3$ (330 mg, 1.86 mmol), and $Me_4Cl$ (680 mg, 6.2 mmol) in water (2 mL) was added to a solution containing $K_2CO_3$, $KHCO_3$, and $Cu(NO_3)_2$ (2.4, 1.25, and 0.34 M, respectively, 3 mL). The pale blue crystals of **4** that formed were collected after 15 min, washed with water, and dried in air. Yield: 186 mg, 45%. Elemental analysis: found (%): C 16.3, H 3.5, N 19.8, Cu 22.0, Na 4.5; calcd: C 16.5, H 3.6, N 20.1, Cu 21.9, Na 4.0. The crystals were insoluble in water.

**5**: A solution containing $CH_6N_3Cl$ (119 mg, 1.25 mmol) in water (0.5 mL) was added to a solution (1 mL) containing $K_2CO_3$ (2.4 M), $KHCO_3$ (1.25 M), $Cu(NO_3)_2$ (0.17 M), and $Gd(NO_3)_3$ (0.092 M). Blue crystals began to form after 1 h and were collected after 1 day, washed with water, and dried in air. Yield: 60 mg, 63%. Elemental analysis: found (%): C 11.8, H 3.2, N 16.3, Cu 17.8, K 4.8, Gd 15.0; calcd: C 11.7, H 2.6, N 16.3, Cu 18.5, K 3.8, Gd 15.3. The crystals were insoluble in water.

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**Keywords:** cage compounds · carbonates · coordination polymers · guanidinium ion · sodalite

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[11] Crystal data for compounds **1–5**: **1**: Tetragonal, $P\bar{4}n2$, $a = 9.0368(6)$, $c = 12.5364(16)$ Å, $V = 1023.77(16)$ Å$^3$, $\rho_{calcd} = 1.971\ g\,cm^{-3}$, 1187 unique reflections out of 6089 reflections measured, $R_1 = 0.0206$, $wR_2 = 0.0582$. Compounds **2–5** are all

cubic, space group $Im\bar{3}m$. **2**: $a = 14.3828(4)$ Å, $V = 2975.30(14)$ Å$^3$, $\rho_{calcd} = 2.101$ g cm$^{-3}$, 374 unique reflections out of 9423 reflections measured, $R_1 = 0.0482$, $wR_2 = 0.1425$. **3**: $a = 14.3228(5)$ Å, $V = 2938.22(18)$ Å$^3$, $\rho_{calcd} = 1.997$ g cm$^{-3}$, 374 unique reflections out of 9328 reflections measured, $R_1 = 0.0552$, $wR_2 = 0.1503$. **4**: $a = 14.4113(18)$ Å, $V = 2993.0(6)$ Å$^3$, $\rho_{calcd} = 1.934$ g cm$^{-3}$, 378 unique reflections out of 9427 reflections measured, $R_1 = 0.0362$, $wR_2 = 0.0991$. **5**: $a = 14.5275(6)$ Å, $V = 3066.0(2)$ Å$^3$, $\rho_{calcd} = 2.232$ g cm$^{-3}$, 389 unique reflections out of 9770 reflections measured, $R_1 = 0.0776$, $wR_2 = 0.2123$. The data for **1**–**5** were measured on a Siemens SMART/CCD diffractometer fitted with $Mo_{K\alpha}$ radiation. For all structures data were measured in the range $2° < \theta < 27.5°$ at 293 K. Empirical absorption corrections were applied using the SADABS program. Structures were solved using direct methods (SHELXTL[12]) and refined using a full-matrix least squares procedure based on $F^2$ (SHELX97[13]). CCDC194983–CCDC194987 (**1**–**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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