Crystal Engineering of Acentric Diamondoid Metal – Organic Coordination Networks**

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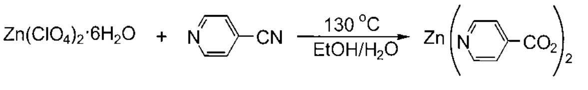
Many bulk properties of solid materials including second-order nonlinear optical (NLO) effects require the absence of a center of symmetry.[1] The rational synthesis of such acentric solids presents a formidable challenge to synthetic chemists.[2] Diamondoid networks have been recognized as potential structural motifs for the construction of acentric solids since the pioneering work of Ermer et al. on hydrogen-bonded networks of adamantane-1,3,5,7-tetracarboxylic acid and methanetetraacetic acid.[3] Diamondoid networks are not predisposed to pack in centric space groups owing to the lack of inversion centers on each tetrahedral connecting point. Moreover, diamondoid networks are generally robust.[4] Over the past decade, many metal – organic diamondoid networks have been synthesized.[5] To date, however, a low-temperature polymorph of potassium dideuterophosphate (KDP) remains as the only NLO-active diamondoid network.[6] Herein we report the first rational crystal engineering of acentric, NLO-active metal – organic coordination networks based on diamondoid structures.

Our strategy for the construction of acentric diamondoid metal – organic coordination networks lies in the recognition that an acentric diamond net will arise if unsymmetrical bridging ligands are used to link tetrahedrally connected metal centers. The use of unsymmetrical, bifunctional bridging ligands (e.g., pyridinecarboxylates) also introduces the electronic asymmetry (push – pull effects) that is essential for second-order optical nonlinearity. On the other hand, it is well established that diamondoid networks tend to interpenetrate to fill the voids generated within a single diamond net.[5a, 7] Such interpenetration could potentially introduce an inversion center, which will complicate the crystal engineering of acentric solids based on diamondoid networks. We demonstrate in this communication that, by using unsymmetrical bridging ligands of suitable length, diamondoid networks with an *odd* number of interpenetrating nets can be constructed, thereby avoiding the potential undesirable introduction of inversion centers through interpenetration. We describe here the synthesis, X-ray single-crystal structures, preliminary NLO properties, and high thermal stabilities of the acentric diamondoid networks bis(isonicotinato)zinc (**1**) and bis(4-pyridylacrylato)cadmium · H_2O (**2**).

Compound **1** was synthesized hydro(solvo)thermally by treating $Zn(ClO_4)_2 \cdot 6H_2O$ and 4-cyanopyridine at 130 °C [Eq. (1)], while compound **2** was obtained by treating $Cd(ClO_4)_2 \cdot 6H_2O$ and *trans*-4-pyridylacrylic acid at 130 °C [Eq. (2)]. The isonicotinate group in **1** evidently results from the hydrolysis of 4-cyanopyridine under the reaction conditions.[8] The large difference between the antisymmetric and symmetric C=O stretching frequencies (1560 and 1365 cm^{-1}, respectively) for **1** suggests monodentate coordination of the carboxylate group, while the antisymmetric and symmetric C=O stretches at 1545 and 1400 cm^{-1} in **2** are consistent with chelation of the carboxylate group.[9] The formulations of **1** and **2** are supported by elemental analysis and thermogravimetric analysis results.



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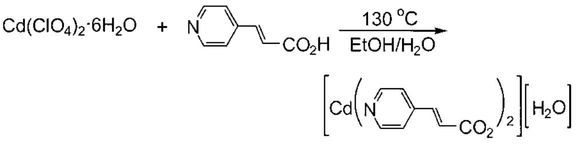

(2)

An X-ray single-crystal structure determination reveals that Zn^{II} centers are four-coordinate in **1** (Figure 1 a).[10] Each Zn^{II} center coordinates to two pyridine atoms of two isonicotinate groups, and to two carboxylate groups of two other isonicotinate groups in a monodentate fashion. The Zn^{II} centers thus have a tetrahedral geometry and extend three-dimensionally to form a diamondoid network (Figure 1 a). With Zn – Zn separations of 8.74 and 8.81 Å, a large void is generated within a single diamondoid cage. The void space in **1** is filled by the formation of a threefold diamondoid structure, in which three independent diamond nets mutually interpenetrate (Figure 2 a).[11] As a result of the unsymmetrical nature of isonicotinate groups and the threefold interpenetration, **1** crystallizes in the chiral space group $P2_12_12_1$. In contrast to the tetrahedral coordination of Zn^{II} centers in **1**, the Cd^{II} centers in **2** adopt a distorted octahedral geometry by coordinating to two pyridyl nitrogen atoms and chelating to two carboxylate groups of *trans*-(4-pyridyl)acrylate groups (Figure 1 b). If the chelating carboxylates are treated as one connecting point, the Cd^{II} centers in **2** have a pseudo-tetrahedral geometry. Each Cd^{II} center in **2** is thus connected to four other Cd^{II} centers to result in a diamondoid network (Figure 1 b). Owing to the larger length of the *trans*-(4-pyridyl)acrylate group versus the isonicotinate group (the Cd – Cd separations are 11.52 and 11.53 Å), **2** adopts a fivefold diamondoid structure and crystallizes in the acentric space group *Cc* (Figure 2 b). Interestingly, **2** also includes a water guest molecule, evidently to occupy the extra space within the interpenetrated diamondoid network. We have thus demonstrated that acentric polymeric networks based on diamondoid structures can be readily constructed with judicious choice of unsymmetrical bridging ligands.

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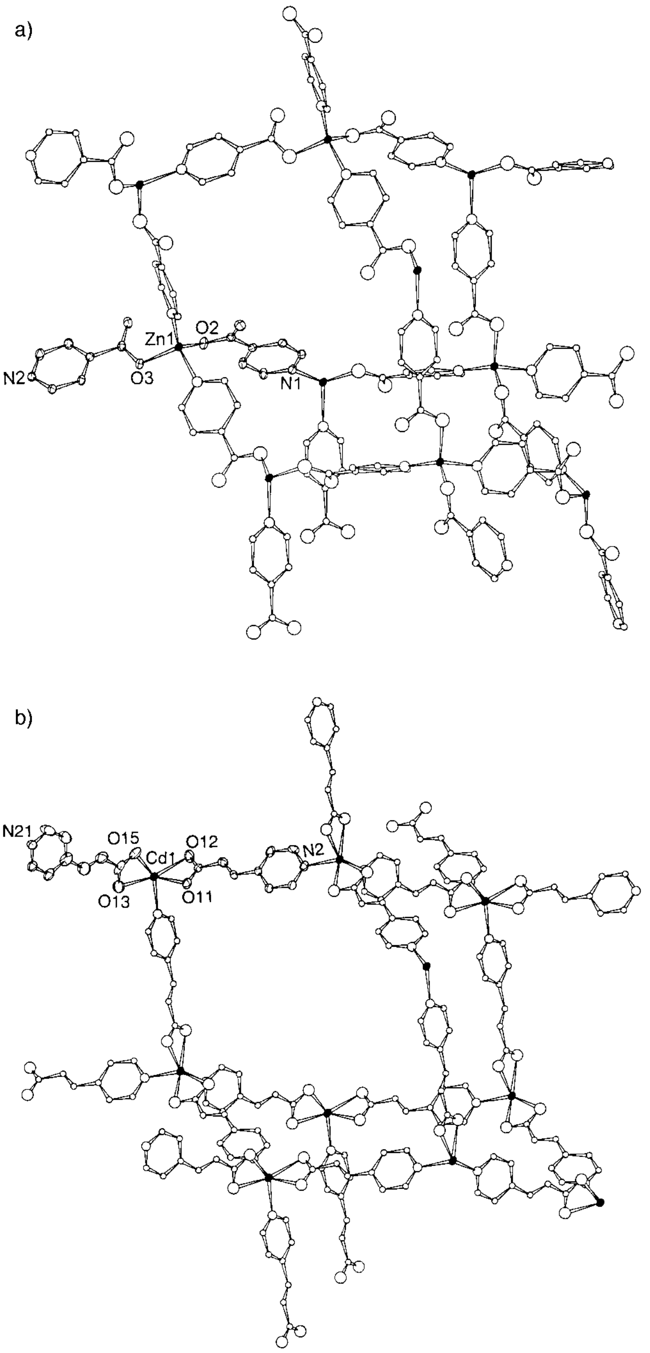

Figure 1. Diagrams showing the diamondoid cages in a) **1** and b) **2**. The solid ellipsoids represent metal centers, while open circles with increasing sizes represent C, N, and O, respectively. The asymmetric units are shown in ellipsoids at 50 % and 40 % probability for **1** and **2**, respectively. The guest water molecules have been omitted in **2**. Selected bond lengths [Å]: **1**: Zn1–O2 1.928(1), Zn1–O3 1.944(2), Zn1–N1 2.046(2), Zn1–N2 2.018(2); **2**: Cd1–N2 2.276(6), Cd1–N21 2.282(6), Cd1–O11 2.340(5), Cd1–O12 2.348(5) Å, Cd1–O13 2.433(6), Cd1–O15 2.348 (5).

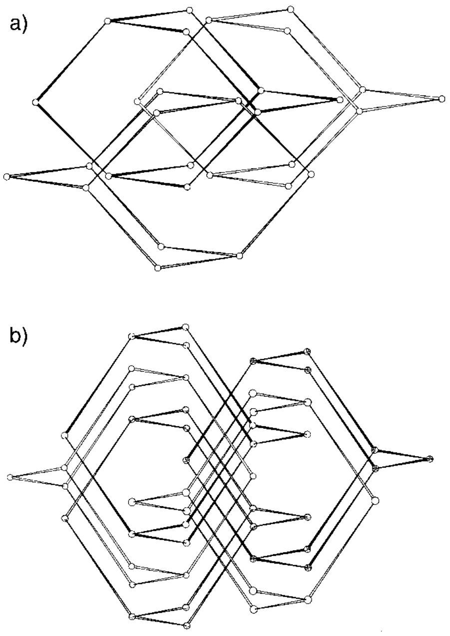

Figure 2. Diagrams showing a) threefold interpenetrating diamondoid network in **1** and b) fivefold interpenetrating diamondoid network in **2**. The bridging ligands are omitted for clarity, and the guest water molecules have been omitted in **2**.

Preliminary second harmonic generation measurements show that **1** possesses an effective *d* coefficient of 1.2 ± 0.6 $\mathrm{pm\,V^{-1}}$, a value about three times that of KDP. A Kurtz powder test indicates that **2** exhibits a second-order coefficient equivalent to that of KDP. The nonlinear optical activities of **1** and **2** are consistent with their acentric structures. Compounds **1** and **2** also exhibit remarkable thermal stability. Thermogravimetric analyses reveal that **1** has an onset temperature for decomposition of 420 °C. Compound **2** loses the guest water molecule by 70 °C, but maintains its diamondoid network structure up to 400 °C.[12] Additionally, both **1** and **2** are insoluble in common solvents because of their neutral three-dimensional polymeric structures. The above attributes make **1** and **2** excellent candidates for practical NLO applications. This work represents a significant advance in the field of supramolecular engineering of functional solids. We are currently further evaluating the optical properties of these new materials as well as extending this novel approach to the synthesis of other acentric polymeric networks.

Experimental Section

1: A heavy-walled Pyrex tube containing a mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.186 g, 0.5 mmol) and 4-cyanopyridine (0.104 g, 1 mmol) in ethanol (0.4 mL) and water (0.1 mL) was frozen and sealed under vacuum, and placed inside an oven at 130 °C. Colorless prismatic crystals were obtained after 48 h of heating. Yield: (0.136 g, 88 %); elemental analysis calcd (found) for $ZnC_{12}H_8O_4N_2$ (%): C 46.2 (46.5), H 2.61 (2.59), N 9.01 (9.05).

2: The reaction was carried out exactly in the same fashion as for **1** except that $Cd(ClO_4)_2 \cdot 6H_2O$ (0.22 g, 0.5 mmol) and *trans*-4-pyridylacrylic acid (0.15 g, 1 mmol) in ethanol (0.4 mL) were used. Yield: (0.11 g, 53 %); elemental analysis calcd (found) for $CdC_{16}H_{14}O_5N_2$ (%): C 45.0 (44.6), H 2.83 (3.16), N 6.56 (6.49).

Second harmonic generation was performed on a single crystal of **1** with dimensions of $\sim 1 \times 1 \times 0.4$ mm using Maker fringe technique. The fundamental wavelength of 1064 nm from a Nd:YAG laser was used. The second harmonic signal was compared to that of α-quartz, and a d_{eff} of 1.2 ± 0.6 $\mathrm{pm\,V^{-1}}$ was estimated. A Kurtz powder test was performed on **2** with a particle size of 76 ± 13 μm. A relative second harmonic intensity of 0.1 versus urea was obtained. This powder test can severely underestimate the second-order optical nonlinearity of **2** owing to the potentially smaller coherence length of **2**.

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[10] X-ray single crystal diffraction data for both **1** and **2** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: crystal size $0.16 \times 0.22 \times 0.34$ mm, orthorhombic, space group $P2_12_12_1$, $a = 8.2149(1)$, $b = 11.6635(2)$, $c = 12.7420(1)$ Å, $U = 1220.9(1)$, $Z = 4$, $\rho_{calcd} = 1.68\,g\,cm^{-3}$, $\rho_{obs} = 1.65(1)\,g\,cm^{-3}$, $T = 123$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Least-squares refinement based on 2755 reflections with $I > 3\sigma(I)$ and 173 parameters led to convergence, with a final value of $R = 0.026$ and $R_w = 0.031$. Crystal data for **2**: crystal size $0.14 \times 0.40 \times 0.40$ mm, monoclinic, space group Cc, $a = 12.0137(2)$, $b = 22.3435(4)$, $c = 7.7738(1)$ Å, $\beta = 123.509(1)°$, $U = 1739.9(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.63\,g\,cm^{-3}$, $\rho_{obs} = 1.63(1)\,g\,cm^{-3}$, $T = 198$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Least-squares refinement based on 2034 reflections with $I > 3\sigma(I)$ and 226 parameters led to convergence, with a final value of $R = 0.039$ and $R_w = 0.043$. – Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-391070 and CSD-391071.

[11] Interestingly, when attempts were made to synthesize the Cd^{II} analogue of **1**, a twofold diamondoid structure with a formula [Cd(isonicotinate)$_2$(EtOH)][EtOH] was obtained. The formation of twofold (but not threefold) diamondoid structure is presumably a consequence of the larger size of Cd^{II} versus Zn^{II}. [Cd(isonicotinate)$_2$(EtOH)][EtOH] adopts a centrosymmetric structure (space group *Pbca*, SHG-inactive) due to the twofold interpenetration: W. Lin, R. Xiong, O. Evans, Z. Wang, unpublished results.

[12] Identical X-ray powder diffraction patterns were obtained for samples of **2** before and after the removal of water guest molecules.

Highly Efficient Ruthenium-Based Catalytic Systems for the Controlled Free-Radical Polymerization of Vinyl Monomers[**]

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The ability to control molecular architecture constitutes a major challenge for synthetic polymer chemists.[1] Controlled free-radical polymerization (also referred to as "living" or "pseudoliving") has in recent years revitalized the rather mature field of radical olefin polymerization in an unprecedented way, and has provided access to well-defined polymers and copolymers. Stable free radicals, such as nitroxides, have been introduced for control of radical polymerization.[1] Recently, the groups of Matyjaszewski, Sawamoto, Jérôme, and others have replaced the stable nitroxide free radical with transition metal species to obtain inter alia a variety of copper-,[2] iron-,[3] nickel-,[4] palladium-,[5] or rhodium-mediated[6] controlled free-radical polymerization systems, a methodology which goes by the name of atom transfer radical polymerization (ATRP).

Ruthenium was introduced by Sawamoto et al. for the polymerization reaction,[7] but $[RuCl_2(PPh_3)_3]$ (the most widely used ruthenium complex) requires the presence of a Lewis acid activator. We now report on the exceptional efficacy of new catalytic systems based on well-defined and fully characterized $[RuCl_2(p\text{-cymene})(PR_3)]$ complexes (*p*-cymene = 4-isopropyltoluene) for promotion of the controlled free-radical polymerization of vinyl monomers *without* cocatalyst activation. These readily prepared and air-stable catalysts compare favorably with the most active ATRP catalysts reported to date.

Methyl methacrylate (MMA) was chosen as a model substrate, and polymerization was initiated by ethyl 2-bromo-2-methylpropionate in the presence of various $[RuCl_2(p\text{-cymene})(PR_3)]$ complexes at 85 °C. From the results summarized in Table 1, it appears that only phosphanes which are both strongly basic (the pK_a being taken as a reasonable measure of the σ-donating ability of the ligand) and which possess a well-defined steric bulk ($160° < \theta < 170°$, θ = cone angle of the phosphane) present both high catalytic activity and high control of the polymerization process (high initiation efficiency *f*, and molecular weight distribution $M_w/M_n = 1.1$). A polydispersity as narrow as $M_w/M_n = 1.07$ is observed when the catalyst is prepared in situ from the ruthenium dimer $[\{RuCl_2(p\text{-cymene})\}_2]$ and tricyclohexylphosphane in the ratio $Ru{:}PCy_3 = 2{:}1$.

Under these experimental conditions, all the criteria of living polymerization are fulfilled. Indeed, the plots of

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