

A Novel Octupolar Metal–Organic NLO Material Based on a Chiral 2D Coordination Network

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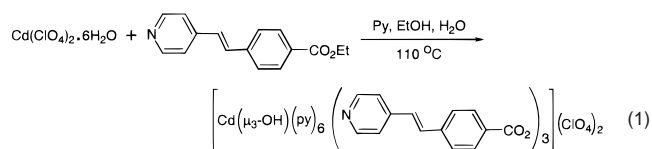
Received August 9, 1999

Recent interest in multipolar second-order nonlinear optical (NLO) materials has been motivated by theoretical calculations¹ and experimental results² which indicated that donor–acceptor-substituted molecules with 3-fold rotational symmetry (octupolar chromophores) can have an improved transparency/optical nonlinearity tradeoff when compared to traditional dipolar chromophores as a result of the presence of four significant components of molecular hyperpolarizability (β).³ Owing to the ease of building coordination complexes with 3-fold rotational symmetry around a metal center (e.g., tetrahedral, octahedral, or trigonal bipyramidal geometries), several octupolar metal–organic molecules have been synthesized and their β values evaluated using the hyper-Rayleigh scattering technique.⁴ However, assembly of octupolar molecules into an acentric bulk presents a significant challenge, and to date no NLO-active bulk materials based on octupolar metal–organic chromophores have been reported.⁵ On the other hand, there has been significant progress in the construction of coordination polymers with novel topologies and potentially exploitable functions via metal ligation-directed self-assembly processes.⁶ We have in particular demonstrated the utility of metal–ligand coordination in counteracting unfavorable centric interactions (such as dipole–dipole repulsions) and thereby facilitating the rational synthesis of acentric polymeric coordination networks with dipolar NLO chromophoric building blocks.⁷

Our synthetic approach to acentric octupolar NLO materials is based on “basic” trinuclear carboxylates.⁸ We have focused our attention on d¹⁰ metals (in particular, M = Zn^{II} and Cd^{II}) for

their favorable optical transparency despite that “basic” trinuclear carboxylates of group 12 metals have not yet been prepared. We hypothesized that if triangular M₃(μ_3 -OH) cores linked with pyridinecarboxylate groups could be made under basic conditions, the M^{II} center could coordinate to both pyridyl and carboxylate functionalities of the pyridinecarboxylate ligands to result in 2D polymeric sheets of [M₃(μ_3 -OH)(pyridinecarboxylate)₆]²⁺. Each [M₃(μ_3 -OH)(pyridinecarboxylate)₆]²⁺ building block would possess 3-fold rotational symmetry and would thus be octupolar. The conjugate pyridinecarboxylate ligands have been shown to have adequate electronic asymmetry (push–pull effects)⁷ so that the resulting coordination networks can exhibit high optical nonlinearity. Moreover, the unsymmetrical nature of pyridinecarboxylate ligands will ensure the absence of an inversion center in the 2D sheet of [M₃(μ_3 -OH)(pyridinecarboxylate)₆]²⁺ and therefore facilitate the synthesis of acentric solids. Herein we wish to report the synthesis, X-ray structure, and NLO activity of the octupolar 2D polymeric network [Cd₃(μ_3 -OH)L₃(py)₆](ClO₄)₂, **1**, where L is 4-[2-(4-pyridyl)ethenyl]benzoate.

Compound **1** was synthesized by a hydro(solvo)thermal reaction between Cd(ClO₄)₂·6H₂O and ethyl 4-[2-(4-pyridyl)ethenyl]benzoate (eq 1).⁹ The presence of two strong peaks at 1587 and



1388 cm⁻¹ in the IR spectrum of **1** suggests the formation of bridging carboxylate groups via the hydrolysis of the precursor ligand,⁷ while the very strong and broad peak at 1090 cm⁻¹ is consistent with the presence of perchlorate groups. The formulation of **1** has been supported by elemental analysis and thermogravimetric analysis (TGA) results.^{9,10}

A single-crystal X-ray diffraction study of **1** reveals an infinite 2D coordination network that crystallizes in the chiral space group R32.¹¹ The basic building block for **1** is an unprecedented “basic” tricadmium carboxylate. The μ_3 -OH group lies on the 3-fold axis, while the Cd atom sits on a 2-fold axis. The μ_3 -OH group, L ligands, and perchlorate anions are disordered around the 2-fold axis. Each Cd center adopts a slightly distorted octahedral geometry by coordinating to a μ_3 -OH group, two pyridine nitrogen atoms, and one pyridyl nitrogen atom of an L ligand in the equatorial plane and to two carboxylate oxygen atoms of two different L ligands in the axial positions (Figure 1). The Cd–O1 distance of 2.284 Å is consistent with a μ_3 -OH group (but not a μ_3 -O group),¹² which is further substantiated by elemental analysis, TGA, and density measurements.^{9,10} The C₃ symmetry operation generates the [Cd₃(μ_3 -OH)L₆(py)₆]²⁺ building block in which the

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(9) In a typical synthesis, a mixture of Cd(ClO₄)₂·6H₂O (0.25 mmol) and ethyl 4-[2-(4-pyridyl)ethenyl]benzoate (0.25 mmol) was mixed with pyridine (0.21 mL), ethanol (0.23 mL), and water (0.13 mL) in a heavy-walled Pyrex tube. After the solution was heated at 110 °C for several days, cubic crystals of **1** were obtained in 71% yield. *D*_{3h5} = 1.538(1) g/cm³. Anal. Calcd for C₂₇H₆₁N₉O₁₅Cl₂Cd₃: C, 50.9; H, 3.62; N, 7.41. Found: C, 50.4; H, 3.57; N, 7.33.

(10) **1** experienced a weight loss of 27.2% in the 160–275 °C range, which corresponds to the loss of all the coordinated pyridine molecules. If one had contained a μ_3 -O group, the EA, TGA, and density results would have been significantly different owing to the presence of only one perchlorate anion.

(11) Crystal data: trigonal, space group R32 (No. 155), with *a* = 19.173(3) Å, *c* = 17.416(4) Å, *U* = 5544.6(2) Å³, *Z* = 3, *D*_{calc} = 1.528 g/cm³, *T* = 293 K, Mo K α radiation (λ = 0.71073 Å). Least-squares refinements based on 2674 [1984 with *I* > 2 σ (*I*)] reflections, 254 parameters, and 21 restraints led to convergence, with a final value of *R*1 = 0.049 (0.027) and *wR*2 = 0.065 (0.060). The crystal is enantiomerically twinned with a BASF value of 0.57.

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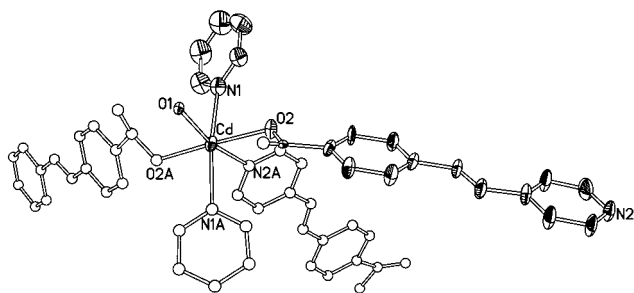


Figure 1. Coordination geometry around Cd. Only one of the two disordered orientations of the μ_3 -OH group and L ligands is shown. The asymmetric unit (without the perchlorate anion) is represented by thermal ellipsoids at 30% probability. Key bond distances: Cd–N1, 2.390(3) Å; Cd–N2A, 2.374(6) Å; Cd–O1, 2.284(1) Å; Cd–O2, 2.283(2) Å.

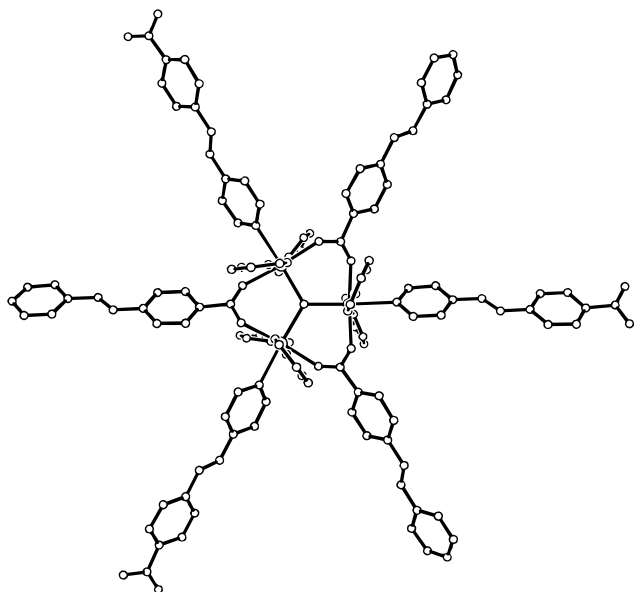


Figure 2. A view of the octupolar $[\text{Cd}_3(\mu_3\text{-OH})\text{L}_6(\text{py})_6]^{2+}$ building block down the c axis. Only one of the two disordered orientations of μ_3 -OH and L ligands is shown.

$\text{Cd}_3(\mu_3\text{-OH})$ core coordinates to the carboxylate groups of three L ligands in bridging fashion and to the pyridyl groups of three other L ligands (Figure 2). The $[\text{Cd}_3(\mu_3\text{-OH})\text{L}_6(\text{py})_6]^{2+}$ building block thus possesses 3-fold rotational symmetry and constitutes the octupolar NLO chromophoric unit of **1**. The most striking feature of **1**, however, is the connection of all $[\text{Cd}_3(\mu_3\text{-OH})\text{L}_6(\text{py})_6]^{2+}$ building blocks via linking ligands L to form an infinite 2D sheet with the formula $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ (Figure 3). The Cd center has a C_2 local symmetry, and is inherently chiral. The linking ligands (L) do not introduce an inversion center owing to their unsymmetrical nature, and each 2D sheet of $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ is therefore chiral. Stacking of 2D sheets of $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ along the c axis is also noteworthy. The coordinated pyridines above and below the $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ plane serve as pillars that direct the stacking of 2D sheets.¹³ The pyridine pillars from different 2D sheets adopt a highly interdigitated structure probably to avoid the formation of large open cavities in **1** (Figure 4). In this pillared structure, adjacent 2D sheets of $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ are related only

(12) The μ_3 -OH group is not coplanar with the Cd atoms in the $\text{Cd}_3(\mu_3\text{-OH})$ core. The O1 atom displaced 0.32 Å out of the Cd_3 plane. Also see: (a) Konno, T.; Kageyama, Y.; Okamoto, K.-i. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1957–1960. (b) Weidenbruch, M.; Herrndorf, M.; Schäfer, A.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139–145.

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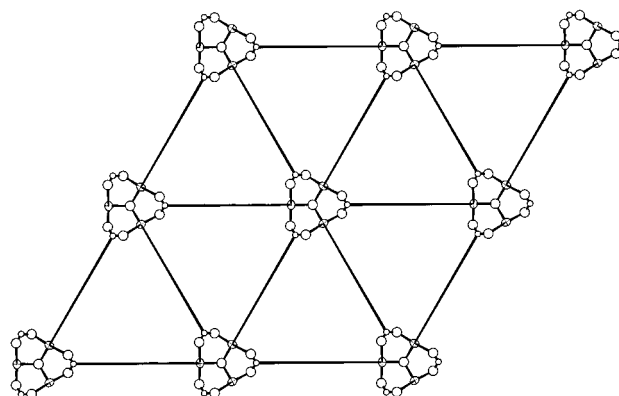


Figure 3. A view of the 2D $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ sheet down the c axis. For clarity, aromatic rings of L ligands are represented with straight lines and coordinated pyridines are omitted. Only one of the two disordered orientations of μ_3 -OH and L ligands is shown.

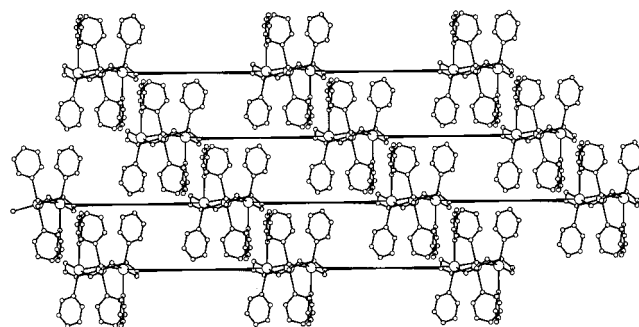


Figure 4. Stacking of 2D $\{[\text{Cd}_3(\mu_3\text{-OH})\text{L}_3(\text{py})_6]^{2+}\}_\infty$ sheets via interdigitation of coordinated pyridines along the c axis as viewed down the a axis. Void spaces are occupied by disordered perchlorate anions. Aromatic rings of ligands L are represented with straight lines. Only one of the two disordered orientations of the μ_3 -OH group and L ligands is shown.

by translational symmetry, to result in a bulk chiral solid. The void space left after interdigitation of coordinated pyridines in Figure 4 is occupied by disordered perchlorate anions (not shown).

We have performed Kurtz powder second harmonic generation (SHG) measurements¹⁴ on **1** to confirm its acentricity as well as to evaluate its potential as second-order NLO material. Compound **1** has a powder SHG efficiency approximately 10 times higher than that of technologically useful potassium dihydrogen phosphate (KDP),^{15,16} and represents the first NLO-active bulk solid based on octupolar metal–organic chromophoric units. This new solid is totally transparent in the visible region, and insoluble in common solvents as a result of its polymeric structure. All the above attributes make **1** an attractive candidate for future practical applications. More significantly, given that mononuclear metal coordination spheres and multinuclear systems with 3-fold rotational symmetry are readily obtainable, we believe that the present work will open the door for further exploration of other NLO-active octupolar coordination networks.

Acknowledgment. We acknowledge NSF (CHE-9727900 and CHE-9875544) for financial support. We also thank Dr. Bruce M. Foxman for X-ray data collection, Dr. I. Y. Chan for access to his laser setup, and Dr. Gregory S. Girolami for help with disorder modeling.

Supporting Information Available: Crystallographic data for **1**, figures of the X-ray structure of **1**, and TGA data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Compound **1** has an $I^{2\omega}$ of 130 vs. α -quartz, while KDP has an $I^{2\omega}$ of ca. 10 vs. α -quartz.

(16) We believe that charge transfer from the carboxylate end to the pyridine end in L is the origin of second-order optical nonlinearity in **1** since the replacement of L in **1** with isonicotinate groups results in the diminishment of SHG efficiency. Unpublished results.