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A Noncentrosymmetric 3D Coordination Polymer of Metallocalix[4]arene

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Sequential reaction of a lower-rim functionalized calix[4]arene, 25,27-bis(hydroxycarbonylmethoxy)-26,28-dimethoxy-*p-tert*-butylcalix[4]arene (H_2L^{C4}), with K_2CO_3 and $CoCl_2 \cdot 6H_2O$ in ethanol afforded a 3D coordination polymer $[K_3Co_2(L^{C4})_3(EtOH)_6]Cl$ (**1**). X-ray crystal analysis revealed that **1** features a noninterpenetrated (10,3)-a net structure wherein octahedral Co^{2+} ions serve as the three-connecting nodes and $[K(L^{C4})]^-$ units function as the bridges between the Co^{2+} ions. The calixarene ligands in **1** adopt a 1,3-alternate conformation, and there are considerable cation−π interactions between the K^+ ion and the phenyl rings within each $[K(L^{C4})]^-$ unit.

Introduction

Noncentrosymmetric coordination polymers have been receiving considerable attention for their potential applications as nonlinear optical (NLO) materials,[1] catalysts for asymmetric catalysis, and materials for enantioselective separation.[2] In the literature, calixarenes have been reported to exhibit second-order NLO properties,[3] and some metallocalixarenes are known to be efficient catalysts for organic transformations.[4] Thus, noncentrosymmetric coordination polymers built from metallocalixarenes could be interesting and potentially useful materials; such metal-organic assemblies, to the best of our knowledge, remain unknown, despite previous reports on several 1D or 2D metallocalixarene coordination polymers.[5]

In our pursuit of new functional coordination polymers, we examined the coordination chemistry of lower-rim functionalized calix[4]arenes with metal ions and have obtained, from self-assembly reaction, a polymeric metallocalix[4]arene complex that features a chiral 3D network. Herein, we report the isolation, X-ray crystal structure, and second-order NLO properties of this metallocalix[4]arene complex, which contributes *the first example of a noncentrosymmetric 3D metallocalixarene coordination polymer.*

Results

The calix[4]arene ligand employed in this work is 25,27-bis(hydroxycarbonylmethoxy)-26,28-dimethoxy-*p-tert-*

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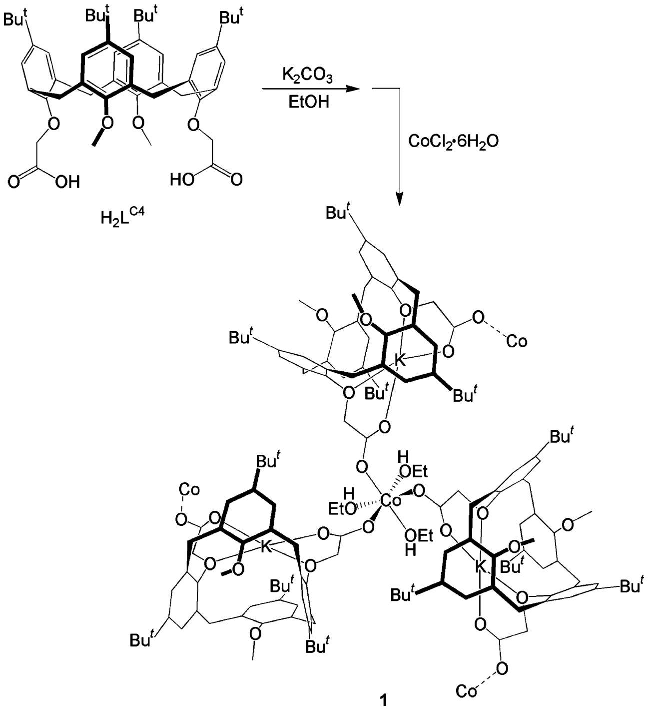
Scheme 1. Formation of **1** from H_2L^{C4}, K_2CO_3, and $CoCl_2{\cdot}6H_2O$[a]



[a] The double bonds of the aryl rings in **1** and the charge of the $[K_3Co_2(L^{C4})_3(EtOH)_6]^+$ unit are not shown.

butylcalix[4]arene (H_2L^{C4}, Scheme 1).[6] Treatment of H_2L^{C4} with K_2CO_3 in refluxing ethanol (containing 5% water) for 2 h, followed by reaction with $CoCl_2{\cdot}6H_2O$ at room temperature for 0.5 h, afforded coordination polymer $[K_3Co_2(L^{C4})_3(EtOH)_6]Cl$[7] (**1**, Scheme 1) as fine crystals in ~50% yield upon slow evaporation of the filtered reaction mixture. Energy dispersive X-ray microanalysis of **1** gave a K/Co/Cl atomic ratio of 3.2:2.1:1, close to that of its formulation.

Complex **1** is insoluble in common solvents. Thermal gravimetric analysis (TGA) showed a slight weight loss of 3.4% at 25−120 °C, probably due to the removal of water molecules occluded in the sample.[8] No further weight loss was observed before the temperature reached ~293 °C. After that, the weight dropped rapidly with increasing temperature, indicating a decomposition of the complex. The IR spectrum of **1** shows a strong band at 1610 cm^{-1}, together with two moderately strong bands at 1480 and 1417 cm^{-1}, consistent with the presence of coordinated carboxylate groups in **1**.

X-ray analysis revealed that **1** crystallized in a chiral space group of $I2_13$. The crystal structure of **1** (Flack parameter: 0.01(2)) features a 3D network of (10,3)-a net topology[9] (Figure 1), an inherently noncentrosymmetric network having three-connecting nodes and interconnected 4-fold helices of the same handedness. The (10,3)-a network in **1** is composed of three-connecting Co^{2+} ions linked by $[K(L^{C4})]^-$ bridges, with a nearest Co···Co distance of 9.727(1); no interpenetration of the (10,3)-a nets was observed.

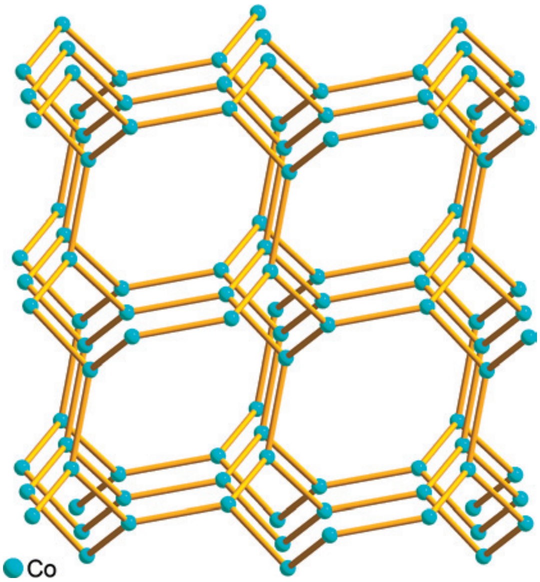


Figure 1. Diagram of the (10,3)-a net topology in the crystal structure of **1**. Co^{2+} ions occupy the three-connecting nodes, and each of the $[K(L^{C4})]^-$ bridges connecting the two nearest Co^{2+} ions is simplified as a rod. The EtOH molecules coordinated to Co^{2+} ions are not shown.

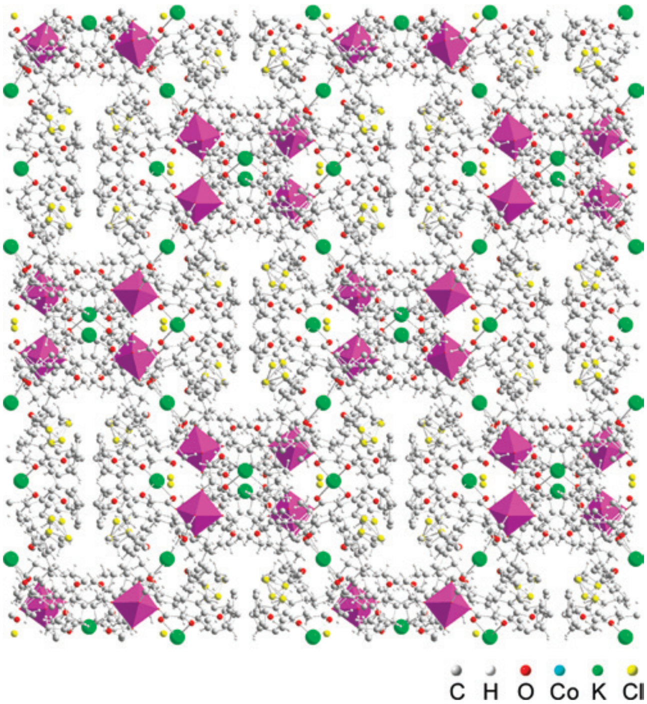


Figure 2. Packing diagram for the crystal structure of **1** viewed along the *c* axis. The octahedra represent the coordination geometry of Co^{2+} ions.

Each three-connecting Co^{2+} ion in **1** is six-coordinate and situated in the center of an octahedron constituted by six O atoms, as depicted in Figures 2 and 3. Of the six O atoms, three belong to three $[K(L^{C4})]^-$ units (Co−O(carboxylate): 2.047(4) Å), and the others belong to three-coordinated EtOH molecules (Co−O(EtOH): 2.087(4) Å). The coordination

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(7) This formulation only represents the coordination network and does not include any solvent molecules occluded in the voids.

(8) The occlusion of water in the sample of **1** was also suggested by elemental analysis, which gave satisfactory results for the formulation of $\mathbf{1}{\cdot}4.5H_2O$, with the calculated content of occluded water being 2.7%, comparable to that from TGA measurements.

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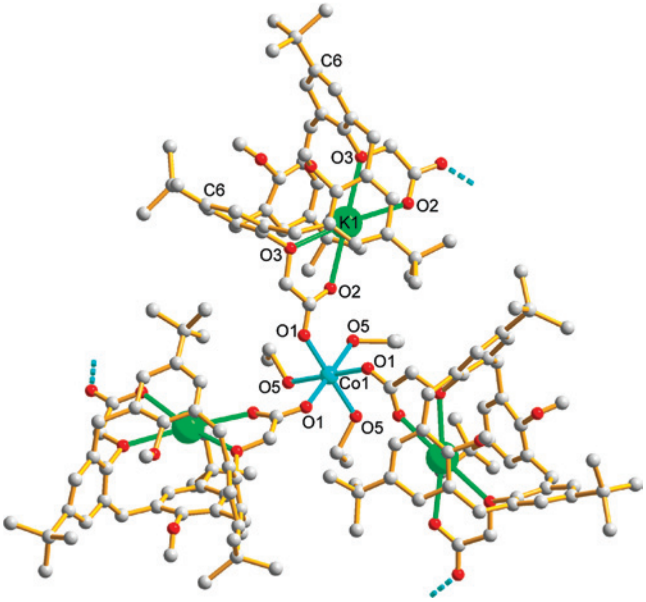

Figure 3. Ball-and-stick representation of part of the crystal structure of **1** showing the coordination geometry of a three-connecting Co^{2+} ion along with the three [K(L^{C4})]$^-$ units coordinated to it (hydrogen atoms and Cl$^-$ anions are not shown). The ^{t}Bu groups bonded to the C6 atoms are disordered.

bonds connecting the Co^{2+} ion and three [K(L^{C4})]$^-$ units are nonplanar and have an angle of 89.81(17)° (O1−Co−O1′), much smaller than the interbond angle of 120° in the most regular (10,3)-a net.[9]

The calixarene ligands in **1** adopt a 1,3-alternate conformation (rather than a cone or partial cone conformation observed in common metallocalix[4]arenes), with the two methoxy groups in each calixarene unit remaining uncoordinated (Figure 3). Each K$^+$ ion is bound to four of the six O atoms of the two deprotonated hydroxycarbonylmethoxy groups, with K−O distances of 2.677(4) and 2.689(4) Å falling within the range of 2.561(8)−3.013(2) Å in related mononuclear K$^+$ complexes of calix[4]arene cone conformers.[10] There are considerable cation−π interactions between the K$^+$ ion and two phenyl rings bearing the uncoordinated methoxy groups (Figure 4), with a distance of 3.166(1) Å from the K$^+$ ion to the center of the phenyl ring (K−C: 3.391(8)−3.521(9) Å). Such cation−π interactions are absent in the reported mononuclear K$^+$ complexes of calix[4]arene cone conformers.[10]

The self-assembly reaction for **1** could be extended to its Rb$^+$ counterpart [Rb$_3$Co$_2$(L^{C4})$_3$(EtOH)$_6$]Cl (**2**) by replacing K$_2$CO$_3$ with Rb$_2$CO$_3$. The structure of a racemically twinned crystal of **2** has been determined (Flack parameter 0.501(12), nearest Co···Co distance 9.754(2) Å, Co−O(carboxylate) 2.039(5) Å, Co−O(EtOH) 2.112(4) Å, O1−Co−O1′ 89.43(18)°), which is similar to that of **1**. The Rb−O distances of 2.742(4) and 2.800(5) Å in **2** are significantly shorter than those of 2.944(8)−3.124(2) Å in the reported mononuclear Rb$^+$ complexes of the calix[4]arene cone or partial-cone conformers.[11] Like the case of **1**, there are considerable cation−π interactions between the Rb$^+$ ion and two phenyl rings bearing the uncoordinated methoxy groups, with a distance of 3.194(1) Å from the Rb$^+$ ion to the center of the phenyl ring (Rb−C: 3.413(6)−3.569(8) Å). The nearest Co···Co distance in both **1** and **2** is shorter than that of 10.602 Å in the 1D coordination polymer [{Co(L)(NO$_3$)(dmso)$_2$}$_n$]$^{n+}$ (L = di(benzimidazole)-1,4-phenylene).[12]

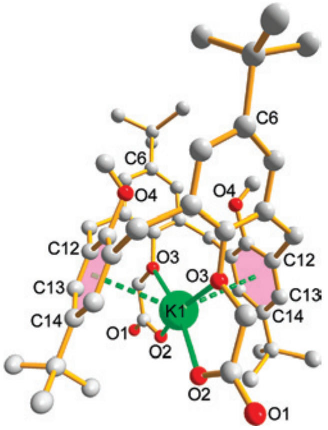

Figure 4. Ball-and-stick representation of the [K(L^{C4})]$^-$ moiety in the crystal structure of **1** with omission of the hydrogen atoms.

Complexes **1** and **2** show second-order NLO properties. The second harmonic generation (SHG) responses of **1** and **2** estimated using the Kurtz powder method[13] according to the literature procedure[14] are ~0.8 and ~1.0 times that of urea, respectively. In contrast, a powder SHG response of only about 10% of that for urea was found for H$_2$L^{C4}. Evidently, both the 3D metallocalixarene coordination polymers **1** and **2** exhibit considerably higher SHG efficiency than the free calix[4]arene ligand H$_2$L^{C4}.

Discussion

As an important type of chiral 3D networks, (10,3)-a nets have attracted considerable interest in recent years,[15−17] particularly for the construction of 3D coordination polymers of transition metals.[16,17] The most common method of building (10,3)-a nets employs tritopic ligands as three-connecting nodes.[16] Another method involves the use of metal ions as the three-connecting nodes without the need of a tritopic ligand;[17] in these cases, the metal ions either adopt a three-coordinate geometry (Figure 5a)[17c,d] or otherwise coordinate with chelating ligands to achieve a tritopic

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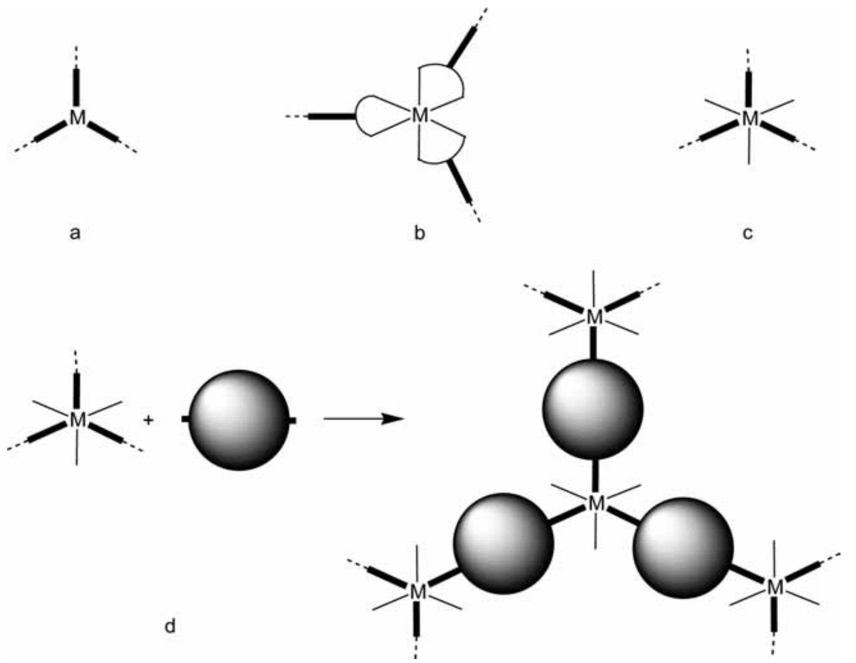

Figure 5. (a) Three-coordinate metal ion, (b) tris-chelated octahedral metal ion, and (c) simple octahedral metal ion as the three-connecting nodes in (10,3)-a nets. (d) Construction of a (10,3)-a net from simple octahedral metal ions and sterically encumbered bridges.

coordination, as depicted in Figure 5b for an octahedral metal ion chelated by three ligands.[17a,b]

Interestingly, neither a tritopic ligand, a three-coordinate metal ion, nor a chelated metal ion is required to act as the three-connecting nodes in the (10,3)-a nets of **1** and **2**. This is rather surprising, as the corresponding building block $CoCl_2 \cdot 6H_2O$ in EtOH is expected to be a simple six-coordinate species that has not been prefunctionalized to favor a three-connected network and may react with the multidentate calix[4]arene ligand to generate a complicated mixture of products.

The generation of **1** is likely to involve the formation of $[K(L^{C4})]^-$ as an initial step, since the H_2L^{C4} ligand was first treated with K_2CO_3 before reacting with $CoCl_2 \cdot 6H_2O$ and EtOH to afford the polymeric complex. Indeed, upon treatment of H_2L^{C4} with K_2CO_3 in refluxing ethanol for 2 h, the negative-ion electrospray mass spectrum of the reaction mixture showed a prominent peak at *m*/*z* 829.6, which can be assigned to $[K(L^{C4})]^-$ according to the *m*/*z* value and the isotope distribution. A similar phenomenon was found for the reaction of H_2L^{C4} with Rb_2CO_3.

We attribute the self-assembly of **1** and **2** from $CoCl_2 \cdot 6H_2O$ in EtOH to the following causes: (i) the pregeneration of a 1,3-alternate conformation of the calix[4]arene ligand upon binding K^+ or Rb^+ ions, which renders the calix[4]arene to be a suitable bridge for the three-connecting nodes, and (ii) the large steric hindrance imposed by the $[K(L^{C4})]^-$ and $[Rb(L^{C4})]^-$ bridges, which forces the octahedral Co ions to function as three-connecting nodes.

The large steric hindrance of $[K(L^{C4})]^-$ or $[Rb(L^{C4})]^-$ could also be responsible for the absence of interpenetration of the (10,3)-a nets in **1** and **2**, both featuring rather long $[K(L^{C4})]^-$ or $[Rb(L^{C4})]^-$ bridges (∼9 Å) between the three-connecting nodes. Examination of the packing diagram of **1** (Figure 2) shows that the $[K(L^{C4})]^-$ bridges occupy most of the space in the 3D network, revealing the importance of steric hindrance of the $[K(L^{C4})]^-$ bridges in preventing interpenetration of the (10,3)-a nets. Note that interpenetration of (10,3)-a nets has often been observed in the known non-metallocalixarene coordination polymers featuring this net topology,[15a,16b,d,f−h] except for those built from short bridging units (none of which contain calixarenes).[14,16c,i−k,17d]

From the self-assembly of **1** and **2** described in this work, a new approach to (10,3)-a nets of coordination polymers could be suggested, which employs a simple octahedral metal complex as building blocks for the three-connecting nodes, coupled with the use of sterically encumbered bridges to link such three-connecting nodes (Figure 5c,d). One more feature for the 3D nets assembled in this manner is that the simple octahedral metal centers (Figure 5c) are not inherently chiral, therefore eliminating complication that arises from the

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(16) Selected examples for (10,3)-a nets with tritopic ligands as three-connecting nodes: (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 12861. (b) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1996**, 1313. (c) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861. (d) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1998**, 31. (e) Abrahams, B. F.; Jackson, P. A.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2656. (f) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158. (g) Prior, T. J.; Rosseinsky, M. J. *Inorg. Chem.* **2003**, *42*, 1564. (h) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106. (i) Eubank, J. F.; Walsh, R. D.; Eddaoudi, M. *Chem. Commun.* **2005**, 2095. (j) Ke, Y.; Collins, D. J.; Sun, D.; Zhou, H.-C. *Inorg. Chem.* **2006**, *45*, 1897. (k) Sun, D.; Ke, Y.; Collins, D. J.; Lorigan, G. A.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 2725.

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presence of enantiomers (Δ and Λ) for the chelated octahedral metal ions depicted in Figure 5b.[15c,17a,b] The new approach reported herein not only makes it feasible to isolate a 3D coordination polymer of metallocalixarenes but also has potential application in constructing various three-connected nets, including (10,3)-a nets, for the coordination polymers of both metallocalixarenes and other types of metal complexes.

Conclusion

We have isolated a noncentrosymmetric 3D coordination polymer of metallocalixarene by treating an achiral lower-rim functionalized calix[4]arene with simple inorganic salts. Polymer **1** adopts a noninterpenetrated (10,3)-a net structure and, to the best of our knowledge, is the first example of a (10,3)-a net composed of metallocalixarenes, exhibiting second-order NLO properties (SHG) comparable to those of urea and considerably higher than those of the free calix[4]arene ligand H_2L^{C4}. The present work demonstrates that sterically encumbered bridges (such as $[K(L^{C4})]^-$) can be used to connect simple octahedral metal ions, not necessarily chelated ones, into (10,3)-a nets, an interesting type of inherently noncentrosymmetric network.

Experimental Section

Preparation of Complexes 1 and 2. A mixture of H_2L^{C4} (40 mg, 0.05 mmol) and M_2CO_3 (M = K, Rb; 0.05 mmol) in 95% ethanol (4 mL) was refluxed for 2 h. The mixture was cooled to room temperature (about 20 °C), treated with $CoCl_2 \cdot 6H_2O$ (12 mg, 0.05 mmol) in 95% ethanol (2 mL), and stirred for 0.5 h. Upon filtration, the filtrate was slowly evaporated at room temperature to give fine crystals, which were collected by filtration and washed with 95% ethanol. Yield: ~50% (based on the amount of H_2L^{C4} used).

Complex 1. IR (KBr, cm^{-1}): 3422s, 2963vs, 1610vs, 1480s, 1417m, 1362m, 1320m, 1245w, 1201s, 1123s, 1047s, 993w, 948vw, 871m, 692w, 634w, 581w. Anal. calcd for $C_{162}H_{222}ClCo_2K_3O_{30} \cdot 4.5H_2O$: C, 64.83; H, 7.76. Found: C, 65.33; H, 7.78.

Complex 2. IR (KBr, cm^{-1}): 3420m, 2961vs, 1604vs, 1480s, 1415m, 1362m, 1320m, 1245w, 1202s, 1122s, 1043s, 991w, 949w, 871m, 691w, 634w, 551w. Satisfactory elemental analysis was not obtained for this complex.

X-Ray Crystal Structure Determination. Diffraction-quality crystals of **1** (0.4 × 0.3 × 0.25 mm^3) and **2** (0.1 × 0.1 × 0.1 mm^3) were obtained by slow evaporation of the filtrates of the reaction mixtures for the preparation of the two complexes. The data were collected at 293(2) K on a Bruker SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 package. Two of the ^{t}Bu groups in each $(L^{C4})^{2-}$ unit are disordered. The crystal structure contains solvent-accessible voids of ~2536 $Å^3$ for **1** and ~2500 $Å^3$ for **2**, which are probably occupied by completely disordered H_2O and EtOH molecules. The number of electrons in these voids per unit cell estimated by the PLATON SQUEEZE method is ~510 for **1** and ~320 for **2**, corresponding to ~128 and ~80 electrons, respectively, per $[M_3Co_2(L^{C4})_3(EtOH)_6]Cl$ unit. A lower content of occluded solvent molecules was deduced by elemental analysis and TGA measurement (both used an opaque crystalline sample); this may be attributed to a partial loss of the occluded solvent molecules (presumably EtOH molecules), as crystals of **1** and **2** became opaque upon exposure to the air. A list of the crystallographic data of **1** and **2** is shown in Table 1.

Table 1. Crystallographic Data of **1** and **2**

	1	**2**
formula	$C_{162}H_{222}ClCo_2K_3O_{30}$	$C_{162}H_{222}ClCo_2O_{30}Rb_3$
cryst syst	cubic	cubic
fw	2919.71	3058.61
space group	$I2_13$	$I2_13$
a, Å	27.046(2)	27.083(5)
b, Å	27.046(2)	27.083(5)
c, Å	27.046(2)	27.083(5)
α, deg	90.00	90.00
β, deg	90.00	90.00
γ, deg	90.00	90.00
V, $Å^3$	19783(3)	19865(6)
Z	4	4
ρ_{calcd}, g cm^{-3}	0.962	1.005
2θ range, deg	56.60	56.56
GOF	0.95	1.11
R1/wR2	0.074/0.089	0.069/0.149

Measurement of SHG Responses. Powders of samples were graded by using standard sieves to particle sizes with diameters of 80−150 μm (checked by standard optical microscopy technique) and were placed on a microscope slide and held in place with transparent tape. The second-order NLO intensities were estimated by the method previously reported by Kurtz and Perry,[13] with the use of a pulsed Q-switched Nd:YAG laser (λ = 1064 nm) to generate the SHG signal. The backward scattered SHG light was collected by employing a spherical concave mirror and passed through a filter that transmits only 532-nm radiation. The SHG efficiencies of the samples were estimated by comparison with that obtained for urea.[14]

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Supporting Information Available: Positional and thermal parameters and bond lengths and angles in CIF format for the crystal structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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