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Salen-Based Infinite Coordination Polymers of Nickel and Copper

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The reaction of *N,N′*-bis(4-carboxysalicylidene)ethylenediamine featuring carboxylate groups in the meta position to the OH groups, with nickel and copper acetate in the presence of a base, results in metal-functionalized, two-dimensional coordination polymers.

Infinite coordination polymers (ICPs) are an area of growing interest in chemistry. In materials science, ICP particles with micro- or nanostructural dimensions were recently reported.[1,2] In contrast to metal−organic frameworks (MOFs)[3−7] ICPs were reported to show a higher level of structural tailorability including size- and morphology-dependent properties.[2] The compounds having these structures were usually synthesized from the appropriate metal salts and bifunctional ligands. Among others, one successful strategy in the synthesis of ICPs and MOFs was the use of metalloligands[2,8−12] such as $[(\eta^6\text{-1,4-benzenedicarboxylate})\text{Cr(CO)}_3]$,[13] carboxylate-functionalized salphen [*N,N′*-phenylenebis(salicylideneimine)] templates,[14] and functionalized salen [*N,N′*-bis(salicylidene)ethylenediamine] ligands.[15] In this "metalloligand" approach, functionalized salen ligands (L) coordinate to a metal center (M), forming a "metalloligand" (ML), which is suitable for the construction of higher dimensional homo- or heterometallic ICPs or MOFs by reaction with further metal centers. Interest in such "metalloligands" comes from the fact that metals can have an unsaturated environment of the M center, which might be useful for hydrogen storage.[8] Another potential application could be homogeneous catalytic transformations such as the epoxidation of olefins, lactide polymerization, asymmetric ring opening of epoxides, and Michael reactions.[16,17] Until now, various ICPs and MOFs with an additional functional group such as carboxylates,[14] *p*-pyridyl groups,[17] and *p*-benzoic acid groups[18,19] in the para position to the OH group have been reported. Additionally, it has been theoretically investigated and proposed that the capability for hydrogen storage of ICPs or MOFs can be increased by including unsaturated Na^+ or Li^+.[20,21]

Having all these in mind, we report here our initial results using *N,N′*-bis(4-carboxysalicylidene)ethylenediamine ($\mathbf{H_4L}$) as a salen ligand,[22] which has carboxylate groups in the meta position to the OH groups. As a result of the different stereochemistries compared to those of the established systems and thus the resulting different angles, we expected a significant influence on the shape of the ICP. Surprisingly, no polymeric structures using $\mathbf{H_4L}$ as the ligand have been reported so far. The reaction of $\mathbf{H_4L}$ with nickel and copper acetate in the presence of sodium hydroxide in *N,N*-dimethylformamide resulted after crystallization in the ICP $[\text{Na}_4(\text{LM})_2\cdot 9\text{H}_2\text{O}]_n$ [M = Ni (**1**), Cu (**2**); Scheme 1].

Compounds **1** and **2** were obtained as red crystals. Both compounds were characterized by standard analytical/spectroscopic techniques, and the solid-state structures were determined by single-crystal X-ray diffraction (Figure 1). The transition metal in both compounds is coordinated by the salen ligand, resulting in a distorted square-planar geometry. As a result of this coordination mode, the d^8 nickel

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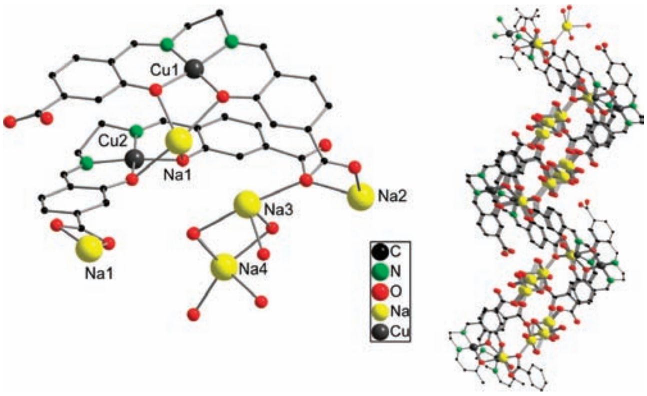


Figure 1. Solid-state structure of **2**, omitting hydrogen atoms. Left: asymmetric unit. Right: cutout of the polymeric structure. Compound **1** is isostructural.

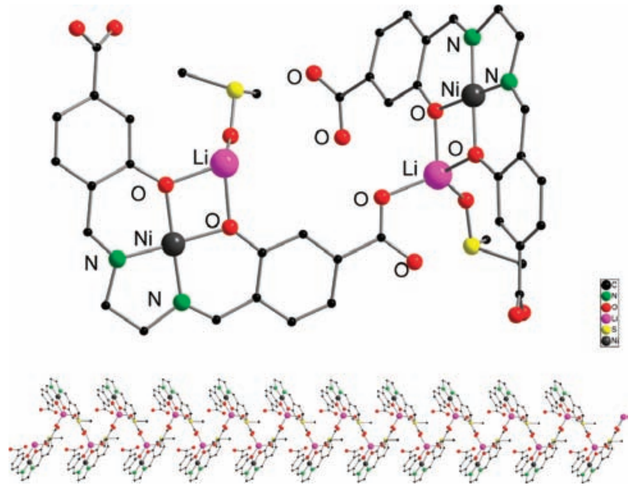
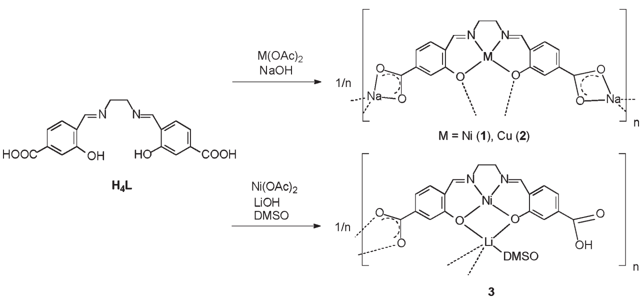


Figure 2. Solid-state structure of **3**, omitting hydrogen atoms. Top: asymmetric unit. Bottom: cutout of the polymeric structure.

Scheme 1



compound **1** is diamagnetic and thus could also be characterized by NMR. The NMR signals are in the expected range. $^{13}C\{^{1}H\}$ NMR clearly showed, compared to the free ligand, a significant downfield shift of the carboxyl group [δ 175.25 ppm (**1**) vs 167.86 ppm in **H$_4$L**], indicating that the Ni-salen unit is also deprotonted at the acid function. To balance the charge, two sodium cations are bound to the Ni-salen framework. These cations bridge the salen units by forming infinite structures. Four differently coordinated sodium atoms are localized in the solid-state structure.

Compounds **1** and **2** crystallize in the triclinic space group $P\bar{1}$ and form a neutral two-dimensional (2D) framework (Figure 1). The compounds are isostructural. The asymmetric unit comprises two different kinds of metalloligands, which are bridged via the phenol oxygen atoms and Na1, three additional sodium cations, and nine water molecules. All sodium atoms are six-coordinated. Vacant coordination sites are filled with water molecules; e.g., Na4 is surrounded by five molecules of water and one carboxylate group. The structures of **1** and **2** build into one-dimensional (1D) zigzag chains along the *c* axis, through ML and Na1, while Na2 incorporates to extend the structure along the *a* axis, forming a 2D layer, which possesses the very common **sql** ($4^4.6^2$) topology.

In contrast to the results described above, the reaction of compound **H$_4$L** with nickel acetate in the presence of lithium hydroxide in dimethyl sulfoxide (DMSO) resulted after crystallization in the polymeric compounds [(DMSO)Li{(HL)}Ni)]$_n$ (**3**; Scheme 1). Compound **3** was fully characterized by standard analytical techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 2). Compound **3** was almost insoluble in any solvent we tried; thus, no useful NMR data could be acquired. In contrast to compounds **1** and **2**, only one alkaline metal cation is found in the position equivalent to that of Na1, indicating that the ligand is not fully deprotonated. As a result of the bent ligand geometry and the deprotonation of only one carboxylate group, the [(DMSO)Li{(HL)}Ni)] units assemble into a helical-structured chain. The nickel atoms are, as expected, coordinated in the center of the salen ligand in a distorted square-planar mode, e.g., N1−Ni−N2 86.77(11)° and N1−Ni−O1 95.28(10)°. The lithium atom is coordinated in a chelating fashion by the two phenol oxygen atoms of a Ni-salen subunit having Li−O bond distances of Li−O1 1.986(5) Å and Li−O2 1.992(5) Å. Moreover, the lithium atom is coordinated by 1 equiv of DMSO and one carboxylate group of a neighboring [(DMSO)Li{(HL)}Ni)] unit. Thus, the lithium atom is in the center of a distorted tetrahedral-coordination polyhedron. The latter coordination is the reason for the formation of the helical structural setup. Overall, the structure is based on 1D chains that interact with each other through hydrogen bonding and $\pi-\pi$-stacking interactions, resulting in a three-dimensional supramolecular structure.

All of the compounds are very robust. At room temperature, they retain their crystalline behavior for a couple of months. Thermogravimetric analysis (TGA) measurements were performed for all compounds. The TGA curve of compound **1** shows that seven water molecules are lost in the temperature range of 70−115 °C (obsd 12.14%, calcd 11.71%). Then the compound is stable up to 330 °C. At higher temperature, decomposition starts and two weight losses are observed, one from 300 to 570 °C (obsd 37.67%) and another in the range from 830 to 1130 °C. As the final product, we suggest a mixture of NiO and Na_2O (obsd 24.97%, calcd 25.40%). Compound **2** shows a similar TGA curve. Eight water molecules are lost in the temperature range of 60−128 °C (obsd 12.87%, calcd 13.26%). Then the dehydrated product is stable up to 260 °C, after which decomposition of the organic ligands starts. This results in a weight loss in the range of 260−560 °C (obsd 39.98%) and another weight loss in the range of 850−990 °C (obsd 25.49%, calcd 26.06%), leading to a suggested formation of CuO and Na_2O. The TGA curve of compound **3** is different. A gradual decomposition occurs up to 520 °C, resulting in an observed weight loss of 74%. We suggest the

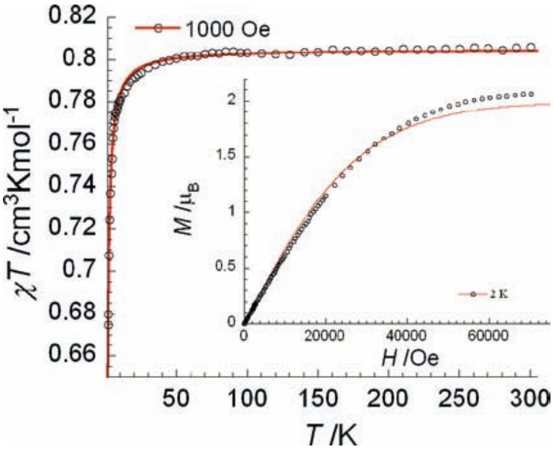


Figure 3. Magnetic susceptibility product (χT vs T plot) at 1000 Oe. Inset: field dependence of magnetization (M vs H plot) at 2 K for compound **2**. Open circles are experimental data; red solid lines indicate the calculated curves discussed in the text.

formation of LiOH and $Ni(OH)_2$ (calcd 76.53%). Finally, there is a slight weight loss up to 1230 °C, which leads to a suggested mixture of NiO and Li_2O (2:1) (obsd 20.18%, calcd 18.03%).

Magnetic susceptibility measurements were performed in the temperature range of 1.8−300 K only for paramagnetic compound **2**. The evolution of $\chi_M T$ with temperature is shown in Figure 3. The magnetic superexchange interaction between the two Cu^{II} centers within each repeating unit is mediated by the phenol oxygen atoms from each ligand strand through one sodium atom. However, no interaction could be possible between each unit, which is connected by three double sodium atoms along with the 1D chain. At room temperature, the $\chi_M T$ product is 0.81 cm^3·K/mol. This value is in very good agreement with the presence of two Cu^{II} metal ions ($S = {}^1/_2$). The g value can thus be estimated at 2.07. Upon decreasing temperature, the $\chi_M T$ product at 1000 Oe stays almost constant until 40 K and then continuously decreases to reach 0.67 cm^3·K/mol at 1.8 K, indicating the presence of weak antiferromagnetic interactions. The data have been analyzed using the isotropic spin Hamiltonian $H = -2JS_1S_2$ with quantum numbers $S_1 = S_2 = {}^1/_2$. Using the Bleaney−Bowers equation,[23] the fit to the magnetic susceptibility data leads to the best set of parameters as $J = -0.53(1)$ K and $g = 2.07(1)$ (Figure 3). The sign and magnitude of the magnetic interactions imply that the two Cu^{II} ions are weakly interacting through the oxygen and sodium atoms. Furthermore, the field dependence of the magnetization of compound **2** almost saturates to 2.1 μ_B at 2 K above 6 T (Figure 3, inset), corresponding to two uncoupled $S = {}^1/_2$ spins. This is also confirmed by simulation of the Brillouin function with $g = 2.06$ for two noninteracting $S = {}^1/_2$ spins, further suggesting weak antiferromagnetic interactions present in each dinuclear motif.

In conclusion, we have shown that the *N*,*N*′-bis(4-carboxysalicylidene)ethylenediamine ligand, which is a salen-type compound that has carboxylate groups in the meta position to the OH groups, is suitable to build new kinds of coordination polymers. Two isostructural 2D ICPs [$Na_4(LM)_2 \cdot 9H_2O$] [M = Ni (**1**), Cu (**2**)] and one 1D ICP [(DMSO)-Li{(HL)}Ni)] (**3**) were built. The shape of the coordination polymers depends on the alkaline metal that is coordinated to the carboxylate function. Efforts to increase the dimensionality of the final product, in order to produce compounds that will be suitable for hydrogen storage, are in progress, while catalytic studies are also under investigation. A thermal study shows that **1** and **2** are very robust. Additionally, for the copper compound, a weak antiferromagnetic interaction was observed.

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Supporting Information Available: Experimental details and X-ray crystallographic files in CIF format for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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