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Heterobinuclear Complexes as Building Blocks in Designing Extended Structures

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The heterobinuclear complex [CuPrL(NO_3)$_3$] has been used as a building block for the construction of a two-dimensional coordination polymer with the formula ${}^{2}_{\infty}[\mathrm{CuPrL(NO_3)_2(IN)}]$, **1** ($L^{2-}$ = the dianion of the compartmental Schiff-base ligand obtained from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,3-propanediamine; IN^- = the isonicotinate ion). The heterobinuclear units, $[\mathrm{CuPrL(NO_3)_2}]^+$, are connected through the unsymmetrical *exo*-bidentate ligands, IN^-, leading to a unique extended structure. Crystal data for compound **1**: FW, 790.94; monoclinic, space group $P2_1/n$, $a = 11.2837(3)$ Å, $b = 14.7785(4)$ Å, $c = 16.9745(4)$ Å, $\beta = 100.427(1)°$; $V = 2783.86(12)$ Å^3; $Z = 4$; R1 = 0.0210, wR2 = 0.0562 [$I > 2\sigma(I)$].

In the past decade or so, the construction of multidimensional arrays and networks containing metal ions as nodes and *exo*-bidentate ligands as spacers achieved considerable progress. The increasing interest in this field is justified by the potential utility of these compounds as zeolite-like materials,[1] catalysts,[2] or magnetic materials.[3] There is also an aesthetic perspective: chemists are attracted by the particular beauty and the intriguing diversity of the architectures which can be obtained by assembling metal ions and multifunctional ligands. Since the pioneering work of Robson et al., in 1990,[4] symmetrical divergent ligands such as pyrazine or bis(4-pyridyl) derivatives are widely used as tectons in constructing coordination polymers (the so-called "node-and-spacer" approach). The (divergent ligand):(metal ion) stoichiometry is a key factor in determining the dimensionality of the resulting systems. Usually, high ligand-to-metal ratios lead to 2-D and 3-D architectures.[5] The coordination geometry of the metal ion is crucial in these self-assembly processes, and it strongly influences the final solid-state architectures. Apart from metal coordination, there are two other important organizing forces in sustaining the supramolecular solid-state architectures: the hydrogen bonds and the $\pi-\pi$ stacking interactions. Their complex interplay leads to robust superstructures.[6]

A quite interesting tecton in constructing extended structures is the isonicotinate anion, IN^-, an unsymmetrical divergent ligand bearing, at one end, the nitrogen atom and, at the other one, the oxygen atoms from the carboxylato group. It can connect two metal ions by coordinating to a metal ion with the nitrogen atom and, to the other one, with one or two carboxylato oxygen atoms.[7] Very interesting extended structures have been obtained by combining the bridging ability of the isonicotinato ligand with that of other bridging ligands, e.g., 4,4′-bipyridine,[8] *trans*-1,2-bis(4-pyridyl)ethylene,[9] and 1,2-bis(4-pyridyl)ethane.[10] The isonicotinic acid itself, acting as a ligand, can generate extended structures: it coordinates with the nitrogen atom to the metal ion, the structure being further expanded on the base of the classical synthon.

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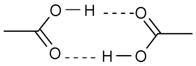

synthon

Following this strategy, Sekiya and Nishikiory have obtained an interesting 2-D network, which combines the dimer formation of isonicotinic acid by double hydrogen bonds with a 1-D thiocyanato-bridged Ni(II) complex.[11]

Recently we have started a research project on the use of homo- and heterobinuclear complexes as building blocks in designing high-dimensionality systems. As a heterobinuclear building block we have chosen to begin with a $[\mathrm{Cu^{II}Ln^{III}}]$ complex. Our synthetic strategy is based on the observation that 3d and 4f metal ions have different chemical behaviors: the rare-earth cations are hard acids and exhibit high coordination numbers, whereas copper(II) is a borderline acid with a strong tendency to form a more or less distorted square-pyramidal geometry. From this perspective, the use of the isonicotinato anion as a linker is very appealing: the rare-earth cations are extremely oxophilic and will therefore prefer to interact with the carboxylato group, while the copper(II) ion will bind to the nitrogen atom of the pyridyl group.

In this communication we report on the synthesis and crystal structure of a novel 2-D coordination polymer which has been obtained by reacting the heterobinuclear complex, $[\mathrm{LCuPr(NO_3)_3}]$, with lithium isonicotinate [L^{2-} = *N*,*N*′-propylenedi(3-methoxysalicylideneiminato), the dianion of the Schiff base obtained from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,3-propanediamine]. The heterobinuclear complexes belonging to the $[\mathrm{LCuLn(NO_3)_3}]$ family have some common features:[12] the copper(II) ion is hosted within the inner compartment (the $\mathrm{N_2O_2}$ site) of the organic ligand, leading to the [CuL] moiety, which is then coordinated through the empty outer $\mathrm{O_4}$ cavity to the Ln(III) ion (two oxygen atoms arise from the phenoxo groups, the two others from the methoxy ones). Three nitrato ions act as bidentate ligands toward the Ln(III) ion. We planned to replace one nitrato ligand with one isonicotinato group. Due to the oxophilicity of the rare-earth cations, we anticipated the coordination of the IN^- ion through the carboxylato group to the praseodymium ion. On the other hand, we expected that the IN^- group further coordinates through the nitrogen atom to the copper(II) ion, which achieves thereby a coordination number of 5 and a square-pyramidal geometry.

By reacting $[\mathrm{CuPrL(NO_3)_3}]$[13] (0.1 mmol; 10 mL of water) with lithium isonicotinate (0.1 mmol, 10 mL of water) we obtained, by slow evaporation of the resulting mixture, green crystals of a compound with the formula $[\mathrm{CuPrL(NO_3)_2(IN)}]$, **1**. The crystals were suitable for X-ray diffraction analysis.[14]

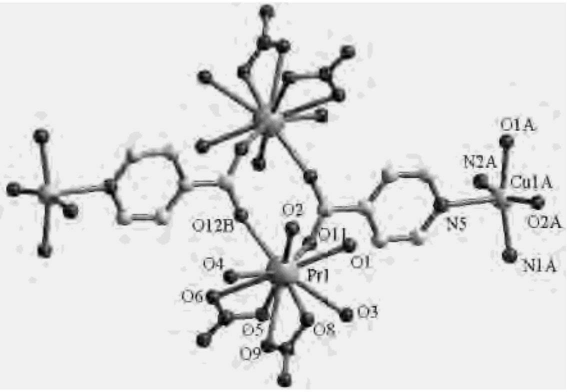

Figure 1. Connection of the Pr(III) and Cu(II) ions by the bridging isonicotinato ligand. For the sake of clarity, the carbon atoms from the compartmental Schiff-base ligands have been removed. Rhomboidal $[\mathrm{Pr_2O_4C_2}]$ rings result by bridging two Pr(III) ions with two carboxylato groups. Selected interatomic distances: Pr(1)−O(1) = 2.4402(12); Pr(1)−O(2) = 2.4931(13); Pr(1)−O(3) = 2.6816(13); Pr(1)−O(4) = 2.7062(13); Pr(1)−O(5) = 2.6182(14); Pr(1)−O(6) = 2.6196(14); Pr(1)−O(8) = 2.6963(15); Pr(1)−O(9) = 2.5790(14); Pr(1)−O(11) = 2.4478(13); Pr(1)−O(12B) = 2.3564(13); Cu(1A)−O(1A) = 1.9704(12); Cu(1A)−O(2A) = 1.9696(13); Cu(1A)−N(1A) = 1.9955(17); Cu(1A)−N(2A) = 1.9934(16). O(1) and O(2) are phenoxo oxygen atoms; O(3) and O(4) arise from the methoxy groups.

The infrared spectrum of **1** shows the characteristic bands of both nitrato (1382 cm^{-1}) and carboxylato groups (ν_{as} = 1473 cm^{-1}, ν_{s} = 1308 cm^{-1}), indicating the partial substitution of the nitrato ligands by the isonicotinato ion. The crystal structure of **1** is in line with our expectations. Indeed, the binuclear [CuPr] units are connected by the isonicotinate ligand, which is coordinated through the carboxylato group to two Pr(III) ions and with the nitrogen atom to the copper(II) ion (Figure 1). So each IN^- is coordinated simultaneously to three metallic centers: two Pr(III) and one Cu(II). Two Pr(III) ions arising from two [CuPrL] units are bridged by two carboxylato groups from two isonicotinato bridges (syn−syn bridging mode). Each Pr(III) exhibits a coordination number of 10, the coordination sphere being formed by oxygen atoms. Four of them arise from the two chelating nitrato ligands, four others from the compartmental ligand (two phenoxo and two methoxy oxygen atoms), and two oxygen atoms from the bridging carboxylato groups. The Pr−O distances fall in the range 2.356(1)−2.706(1) Å. The distance between two praseodymium atoms bridged by the carboxylato groups is 5.525 Å. The copper(II) ion is pentacoordinated, with a square-pyramidal geometry. The basal position is occupied by the oxygen and nitrogen atoms from the compartmental ligand, while the apical position is occupied by the nitrogen atoms arising from the pyridyl group of the isonicotinato ligand [Cu(1A)−N(5) = 2.306(1) Å]. The Pr−Cu distance within the [PrCu] building block is 3.611(1) Å.

The extension of the structure can be described as follows: two praseodymium ions are bridged by two

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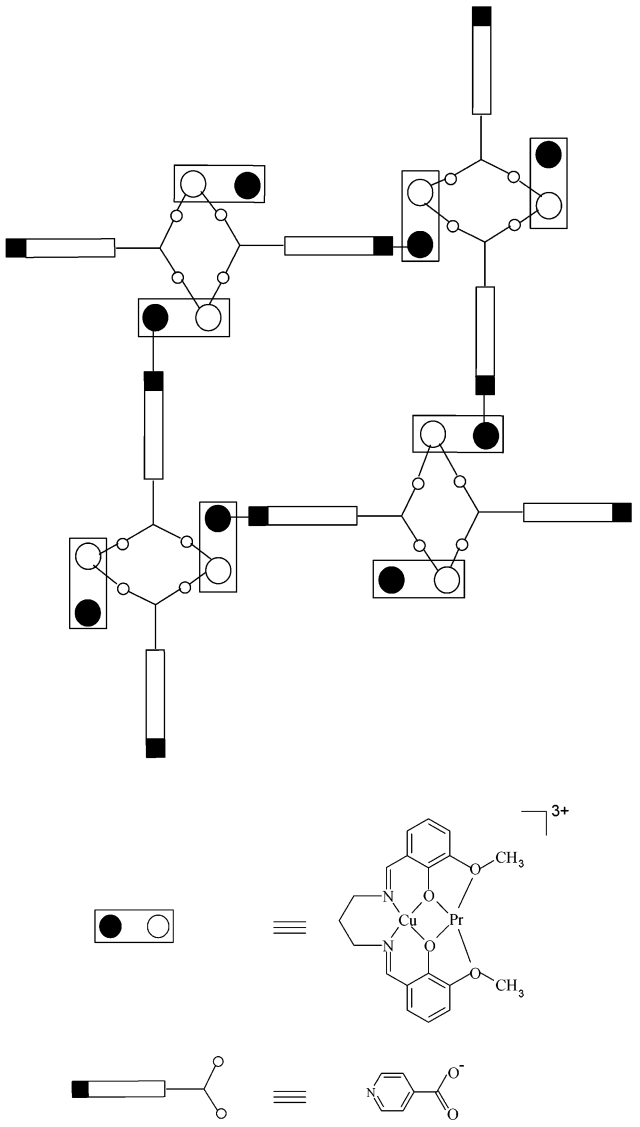
[14] Crystal data for **1**: FW, 790.94; monoclinic, space group $P2_1/n$. Unit cell dimensions a = 11.2837(3) Å, b = 14.7785(4) Å, c = 16.9745(4) Å, β = 100.427(1)°; cell volume, 2783.86(12) Å^3; Z = 4; D_{c} = 1.887 g/cm^3; μ = 2.568 mm^{-1}; T = 183(2) K. Reflections collected: 21607. Independent reflections: 7968 (R_{int} = 0.0213). Final R indices: R1 = 0.0210, wR2 = 0.0562 [$I > 2\sigma(I)$]; R1 = 0.0258, wR2 = 0.0586 (all data).

Scheme 1



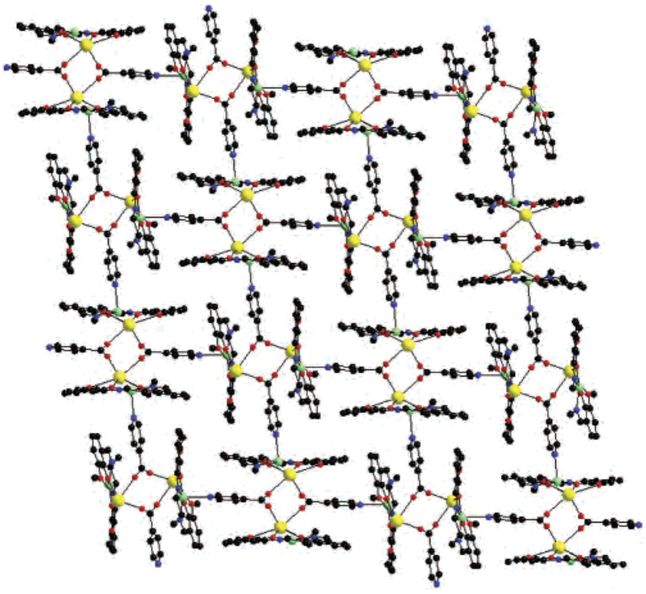


Figure 2. View of the 2-D network in **1**. For the sake of clarity, the nitrato groups coordinated to Pr have been omitted. Color code: praseodymium, yellow; copper, green; nitrogen, blue; oxygen, red; carbon, black.

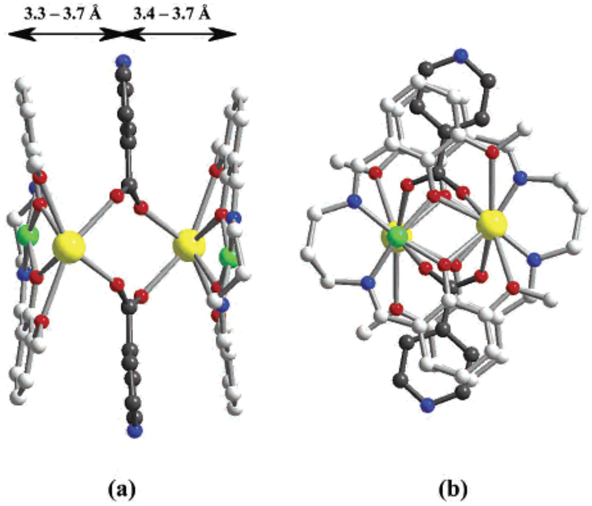


Figure 3. Views of a $[Pr_2Cu_2]$ moiety, showing the stacking interactions: (a) side view; (b) front view.

carboxylato groups, resulting in rhomboidal $[Pr_2(O_2C)_2]$ rings. These rings are interconnected through the pyridyl moieties of the isonicotinato bridges, which coordinate to the copper(II) ions. Large polygons containing four Pr(III) and four Cu(II) ions are formed (Scheme 1). Each [CuPr] unit is connected through three isonicotinato bridges to five other [CuPr] units, resulting in two-dimensional layers (Figure 2). The distances between the copper atom and the two praseodymium atoms bridged by the same IN$^-$ ion are slightly different: 8.75 and 9.30 Å. The solid-state architecture is sustained also by the graphitic-like $\pi-\pi$ stacking interactions established between the aromatic ring belonging to the organic ligand and the pyridyl ring of the isonicotinato ligand (the distances associated with the aromatic interactions are in the range 3.3−3.7 Å, Figure 3).

The room-temperature value of the $\chi_M T$ product (χ_M is the paramagnetic susceptibility) is 2.11 cm^3 mol^{-1} K, which corresponds to the expected one, calculated using the equation $\chi_M T = (Ng_{Cu}{}^2\beta^2/3k)[S_{Cu}(S_{Cu} + 1)] + (Ng_{Pr}{}^2\beta^2/3k)[J_{Pr}(J_{Pr} + 1)]$.[15] Further work on similar compounds, especially on those containing the Gd(III) ion, with no orbital contribution to the magnetic moment, is in progress, in order to emphasize the exchange interactions between the metallic centers.

In conclusion, we have shown that novel extended networks can be obtained by using heterobinuclear complexes as building blocks and appropriate spacers. These are unsymmetrical bridging ligands, which are able to coordinate with one side to a metal ion and, with the other one, to the second metal ion. To the best of our knowledge, compound **1** represents the first heterobimetallic system constructed by using the isonicotinate ion as a linker.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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