

Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 80th anniversary

UNEXPECTED REPLACEMENT OF Gd(III) BY Hg(II) FROM AN OXYGEN BINDING SET LEADING TO A HETEROMETALLIC Cu(II)-Hg(II) 1-D COORDINATION POLYMER

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The reaction between [LCuLn(NO₃)₃] and K₂[Hg(SCN)₄] in a 1:1 molar ratio led to a new heterobimetallic system, $[\text{LCu}^{\text{II}}\text{Hg}^{\text{II}}(\text{SCN})_2]_{\infty}$ **1**, resulting from the unexpected replacement of Gd(III) by Hg(II) in the second compartment of the organic ligand (L is the dianion of the Schiff-base obtained by 2:1 condensation of 3-methoxysalicylaldehyde and 1,3-propanediamine). Compound **1** was also obtained directly, by reacting the neutral mononuclear complex [LCu] with mercury(II) acetate, in the presence of potassium thiocyanate. The crystallographic investigation of **1** reveals an alternating chain-like structure, made of dinuclear [LCu^{II}Hg^{II}] units linked by thiocyanate bridges. The copper(II) ions are pentacoordinated, with a square pyramidal geometry, the apical position being occupied by the nitrogen atom of the NCS⁻ bridge. The mercury(II) ions display a strongly distorted (4 + 2) octahedral geometry. The distance between the phenoxo-bridged metal ions is 3.491(15) Å. The Cu...Hg distance across the NCS⁻ bridge is equal to 6.480(6) Å.

INTRODUCTION

Coordination polymers have been much investigated in recent years due to their potential applications as molecular magnetic materials, conducting solids, luminescent materials, zeolite-like materials or catalysts.¹ Appropriate synthetic routes are needed to control the dimensionality and the network topology, which are crucial factors in determining the physical and chemical properties of the resulting materials. The careful study of the unexpectedly obtained compounds enriches crystal engineering with new connectivity rules and useful synthetic concepts.

The node and spacer approach is widely employed in designing coordination polymers with various dimensionalities and network topologies.² It relies upon the strong directionality of the coordination bonds established between the metal

ions (nodes, connectors) and the *exo*-dentate ligands (spacers, linkers). The desired network topology can be achieved by choosing the appropriate metal ion (coordination number and geometry, charge, HSAB behaviour) and the suitable designed bridging ligand (denticity, shape, size, HSAB behaviour). Coordination polymers can be constructed from oligonuclear nodes as well.³

In a series of papers we have shown that 3d-4f heterometallic complexes, based on a dissymmetric compartmental ligand derived from 3-methoxysalicylaldehyde and a diamine, can be successfully used as nodes in constructing novel solid-state architectures, by connecting them through a large variety of *exo*-dentate ligands (spacers).⁴ Moreover, the binuclear 3d-4f complexes are suitable starting materials in the attempt to design heterospin systems with three different spin carriers.⁵ We have recently reported that such dissymmetric ligands can generate

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3d-3d' heterometallic complexes that can act as nodes for new coordination polymers.⁶

In this paper, we present the result of our further investigations on the ability of such ligands to form new 3d-5d tectons, that is, the synthesis and crystal structure of a new 1-D heteropolymetallic polymer, $^1_\infty[\text{LCu}^{\text{II}}\text{Hg}^{\text{II}}(\text{SCN})_2]$, which is obtained by reacting [CuL] with mercury(II) acetate and potassium thiocyanate (L^{2-} is the dianion of the compartmental Schiff-base ligand obtained from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,3-diaminopropane).

EXPERIMENTAL

Synthesis

Chemicals were purchased from commercial sources and all manipulations were performed using materials as received. [CuL] was obtained according to ref. 7. For the synthesis of $\text{K}_2[\text{Hg}(\text{SCN})_4]$, we used a procedure already described in the literature.⁸

$^1_\infty[\text{LCu}^{\text{II}}\text{Hg}^{\text{II}}(\text{SCN})_2]$ **1** was obtained as follows: an acetonitrile-methanol (1/1) solution (10 mL) of $[\text{LCu}^{\text{II}}\text{Gd}^{\text{III}}(\text{NO}_3)_3]$ (0.1 mmol, 0.074 g) was added to a 1/1 acetonitrile-ethanol solution (10 mL) of $\text{K}_2[\text{Hg}(\text{SCN})_4]$ (0.1 mmol, 0.055 g). The green solution was stirred for about 15 minutes. After 24 hrs of slow evaporation, green single crystals appeared which were filtered off. IR data (KBr, cm^{-1}): 2928vw, 2831vw, 2128m, 1620vs, 1554w, 1470s, 1454s, 1411w, 1358vw, 1300m, 1245s, 1224s, 1193w, 1168vw, 1077m, 951w, 850w, 779vw, 738m, 634vw, 569vw, 436vw. Calcd. for $\text{C}_{21}\text{H}_{20}\text{CuHgN}_4\text{O}_4\text{S}_2$: C, 35.0 H, 2.8; N, 7.8%; Found: C, 35.2; H, 2.9; N, 8.1%.

A larger scale of the complex was obtained by addition of mercury(II) acetate (0.1 mmol, 0.032 g) and potassium

thiocyanate (0.1 mmol, 0.02 g) to a methanol suspension of [CuL] (0.1 mmol, 0.04 g). After stirring for 1 h, the resulting precipitate was filtered off, washed with methanol, diethyl ether and dried.

Physical measurements

The IR spectrum (KBr) pellets was recorded on a Bio-Rad FTS 135 spectrophotometer in the 4000 - 400 cm^{-1} region. The UV-Vis spectrum (diffuse reflectance technique) was recorded with a UV4 Unicam spectrophotometer.

Crystal structure determination

Crystallographic measurements for $^1_\infty[\text{LCu}^{\text{II}}\text{Hg}^{\text{II}}(\text{SCN})_2]$ **1** were carried out at 293 K with an Oxford-Diffraction XCALIBUR CCD diffractometer using graphite-monochromated Mo-K_α radiation. The crystals were placed 60 mm from the CCD detector. More than the hemisphere of reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ -angle (0, 90 and 180°). Coverage of the unique set is 99.8% complete up to $2\theta = 52^\circ$. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.^{9a} Intensity data were corrected for Lorentz and polarization effects.

All structures were solved by direct methods using SHELXS-97^{9b} and refined by full-matrix least-squares on Fo^2 with SHELXL-97^{9c} with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in idealized positions ($d_{\text{CH}} = 0.96 \text{ \AA}$) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom.

Relevant crystallographic data together with refinement details are summarized in Table 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 655276. Copies of this information may be obtained for free from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Table 1

Crystallographic data, details of datacollection and structure refinement parameters for compound **1**

| | |
|---|--|
| Empirical formula | $\text{C}_{21}\text{H}_{20}\text{CuHgN}_4\text{O}_4\text{S}_2$ |
| Formula weight | 720.66 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Temperature (K) | 293(2) |
| <i>a</i> (Å) | 11.254(2) |
| <i>b</i> (Å) | 15.418(3) |
| <i>c</i> (Å) | 14.782(3) |
| β (°) | 112.23(3) |
| <i>V</i> (Å ³) | 2374.2(8) |
| <i>Z</i> , D_{calc} , g/cm^{-3} | 4, 2.016 |
| $\mu(\text{Mo K}\alpha)$, mm^{-1} | 7.566 |
| Theta range (°) | 3.03 – 26.00 |

RESULTS AND DISCUSSION

The present work is a follow-up of our synthetic strategy leading to 3d-3d'-4f heterotrimetallic

systems that is based on a self-assembly process involving 3d-4f heterobinuclear cationic complexes and linkers carrying the third metal ion. As a starting cationic 3d-4f complex, we chose

[LCuLn(NO₃)₃] [where L²⁻ is the *N,N*-propylenedi(3-methoxysalicylideneiminato) anion]. This strategy was successful when the metalloligand we used was a hexacyanometallate anion [M(CN)₆]³⁻ [M(III) = Cr, Fe, Co] and a family of isomorphous heterotrimetallic chains, [LCuLn(H₂O)₄{M(CN)₆}]·3H₂O, was obtained.^{4d,5b} The X-ray structure of the product resulted from the reaction between a [Cu^{II}Gd^{III}] binuclear complex and a bis-oxalato anionic chromium(III) complex, [Cr^{III}(bipy)(ox)₂], confirmed the presence of the three different metal ions. However, that was not a genuine heteropolynuclear complex: the [Cr(bipy)(C₂O₄)₂]⁻ species are not coordinated neither to Cu^{II}, nor to Gd^{III}. The binuclear [LCuGd]³⁺ entities are connected by bis-bidentate oxalato ions, which result from the partial decomposition of the [Cr(bipy)(C₂O₄)₂]⁻ ions. Cationic zigzag chains are thus formed, whose charge is counterbalanced by uncoordinated [Cr(bipy)(C₂O₄)₂]⁻ anions.^{5b} Aiming to diversify the structural type, as well as the magnetic properties of the new heterotrimetallics, we employed another anionic building-block, namely the tetrakisothiocyanato cobaltate(II) ion, [Co(NCS)₄]²⁻. The reaction between [LCuGd(NO₃)₃] and (Et₄N)₂[Co(NCS)₄] led to the isolation of a product, whose crystallographic investigation revealed the formation of a novel [CuCo] complex, ¹_∞[LCu^{II}Co^{II}(NCS)₂], where the gadolinium(III) ions were substituted by the cobalt(II) ones.⁶ As that was a rather surprising outcome, we decided to extend our study with

another tetraconnective building-block, containing this time a bulkier 5d metal ion, namely the [Hg(SCN)₄]²⁻ anion.

The reaction between [LCuLn(NO₃)₃] and K₂[Hg(SCN)₄] in a 1:1 molar ratio led to a new heterobimetallic system, ¹_∞[LCu^{II}Hg^{II}(SCN)₂] **1**. The gadolinium ions were replaced by the mercury ones. Compound **1** can also be obtained in a rational way, as follows: the first step consists in the reaction of 3-methoxysalicylaldehyde and 1,3-diaminopropane (2:1 molar ratio) in methanol, followed by addition of copper(II) acetate which yields the “compartmental complex ligand” [LCu]. The reaction of [LCu] with mercury(II) acetate in presence of potassium thiocyanate yields a very well-defined product analysed as ¹_∞[LCu^{II}Hg^{II}(SCN)₂] **1**.

The IR spectrum of compound **1** clearly shows, apart from the characteristic bands of the organic compartmental ligand [ν(C=N), 1620 cm⁻¹; ν(C=C), 1470 cm⁻¹; ν(C-O), 1300 cm⁻¹; ν_{as}(C-O-C), 1224 cm⁻¹; ν_s(C-O-C), 1077 cm⁻¹], a band generated by the thiocyanato group at 2128 cm⁻¹.¹⁰

The solid state electronic spectrum of **1** exhibits a large band located at 650 nm, that is due to the overlapping *d*_{z²}→*d*_{x²-y²}, *d*_{xy}→*d*_{x²-y²}, *d*_{xz,yz}→*d*_{x²-y²} transitions for a [Cu^{II}N₂O₂O'] square pyramidal chromophore.

The structure of **1** is constructed from binuclear [LCuHg] entities connected through thiocyanato ligands, resulting in infinite chains (Fig. 1).

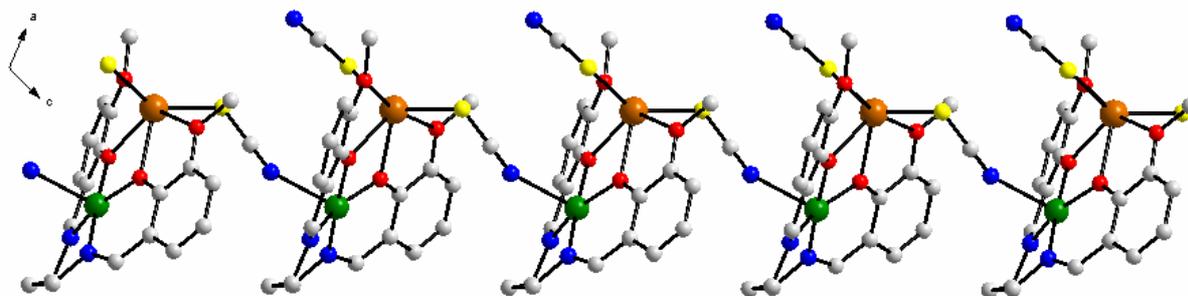


Fig. 1 – 1D coordination polymer {CuLHg(SCN)₂}_n in the crystal structure **1**.

A view of the heterobinuclear node in **1** is depicted in Fig. 2, whereas the relevant interatomic bonds are collected in Table 2. The copper and mercury ions are linked to the deprotonated compartmental ligand L²⁻, within the N₂O₂ and O₂O₂ coordination sites, respectively. The separation Cu(1)⋯Hg(1) is of 3.491(2) Å, and the dihedral angle between the Cu(1)O(1)O(2) and Hg(1)O(1)O(2) planes is 5.7°. The copper ion adopts a slightly distorted square pyramid geometry, being coordinated to the N₂O₂ donor set

of L²⁻ in the basal plane, whereas the nitrogen atom of the NCS⁻ ligand is axially bonded. Cu(II) is pulled out the equatorial plane by 0.168 Å toward the nitrogen atom of the bridging isothiocyanate which is linked by its sulfur atom to the mercury ion of a neighbouring {LCuHg} unit. The bond lengths to Cu(II) are within the usual range observed for copper coordinated to Schiff bases: Cu-O(3) = 1.933(8), Cu-O(2) = 1.958(9), Cu-N(1) = 2.001(10), Cu-N(2) = 1.973(12). The axial Cu-N bond length is larger, 2.431(13) Å.

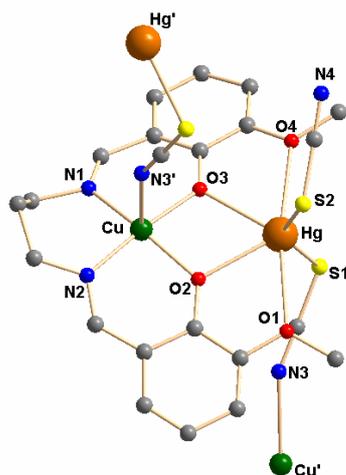


Fig. 2 – Molecular structure of dinuclear LCuHg(SCN)₂ unit.

Table 2

Selected bond lengths (Å) and angles (°)

| | | | |
|--------------|----------|---------------------------|-----------|
| Hg-S(2) | 2.387(4) | Cu-O(3) | 1.933(8) |
| Hg-O(2) | 2.402(9) | Cu-O(2) | 1.958(9) |
| Hg-O(3) | 2.425(8) | Cu-N(2) | 1.973(12) |
| Hg-O(4) | 2.694(8) | Cu-N(1) | 2.001(10) |
| Hg-S(1) | 2.432(4) | Cu-N(3) ¹ | 2.431(13) |
| Hg-O(1) | 2.652(9) | N(3)-Cu ² | 2.431(13) |
| <hr/> | | | |
| S(2)-Hg-O(2) | 99.4(2) | O(4)-Hg-O(1) | 168.5(3) |
| S(2)-Hg-O(3) | 108.3(3) | S(1)-Hg-O(1) | 89.3(2) |
| S(2)-Hg-O(4) | 97.1(3) | O(3)-Cu-O(2) | 82.7(3) |
| O(2)-Hg-O(3) | 64.3(3) | O(3)-Cu-N(2) | 174.4(4) |
| O(4)-Hg-O(3) | 62.5(3) | O(2)-Cu-N(2) | 91.7(4) |
| S(2)-Hg-S(1) | 142.2(2) | O(3)-Cu-N(1) | 91.1(4) |
| O(2)-Hg-S(1) | 111.6(2) | O(2)-Cu-N(1) | 160.3(4) |
| O(3)-Hg-S(1) | 104.4(2) | N(2)-Cu-N(1) | 94.3(5) |
| O(4)-Hg-S(1) | 81.6(2) | O(3)-Cu-N(3) ¹ | 90.6(4) |
| S(2)-Hg-O(1) | 86.2(2) | O(2)-Cu-N(3) ¹ | 100.6(4) |
| O(2)-Hg-O(1) | 62.6(3) | N(2)-Cu-N(3) ¹ | 90.4(5) |
| O(3)-Hg-O(1) | 126.5(3) | N(1)-Cu-N(3) ¹ | 98.0(5) |

Symmetry transformations for equivalent atoms: ¹ $x+1/2, -y+1/2, z+1/2$; ² $x-1/2, -y+1/2, z-1/2$

The hexacoordinated mercury ion is in a strongly distorted (4+2) octahedral geometry, formed by four oxygen atoms of the polydentate ligand L²⁻ and two sulphur atoms of the thiocyanate bridging ligand. Its coordination mode is more delicate to state precisely. The bond lengths Hg - O_{phenoxo} (2.402(9) and 2.425(8) Å) are shorter than the Hg - O_{methoxy} ones (2.652(8) and 2.694(8) Å). The Hg-S1 and Hg-S2 bond lengths are respectively equal to 2.432(4) and 2.387(4) Å.

Within the infinite {CuLHg(SCN)₂}_n chains (Fig. 1), one over the two thiocyanate groups participates to the bridging, the other one being only linked to the mercury ion by its sulfur atom. The Cu...Hg distance for the SCN⁻ bridged ions is equal to 6.480(6) Å.

The supramolecular solid-state architecture is further stabilized by π - π intermolecular stacking

interactions established between the aromatic rings of the compartmental L ligand belonging to neighbouring chains (Fig. 3a). These interactions run along the *c* crystallographic axis, and they are quite offset (Fig. 3b), the shortest intermolecular distances ranging from 3.22 to 3.72 Å.

Although the structures of compounds **1** and ¹_∞[LCu^{II}Co^{II}(NCS)₂] reported elsewhere⁶ (Fig. 4) have the same stoichiometry and dimensionality, they are built differently. This might be accounted on the difference of volume and chemistry between the Co(II) and Hg(II) ions, translated into a geometrical and coordinative difference of the role played by the SCN⁻ in both compounds. Mercury(II), as a typical soft acid, binds the SCN⁻ ligand through S, while cobalt(II), a borderline acid, binds the SCN⁻ through N, thus obeying the symbiotic influence of the O₄ environment given

by the compartmental ligand. Another difference comes from the orientation of the bridging SCN^- ligands: in the case of the $[\text{Cu}^{\text{II}}\text{Co}^{\text{II}}]$ system, they are disposed on the same side of the $\{\text{LCuCo}\}$ mean plane, contrary to their *trans* disposition in the case of the compound **1**.

The fact that both the cobalt(II) and mercury(II) ions were able to replace the oxophilic

gadolinium(III) ion from an O_4 donor site of the compartmental ligand remains surprising so that further investigation is needed in order to explain the exchange phenomenon.

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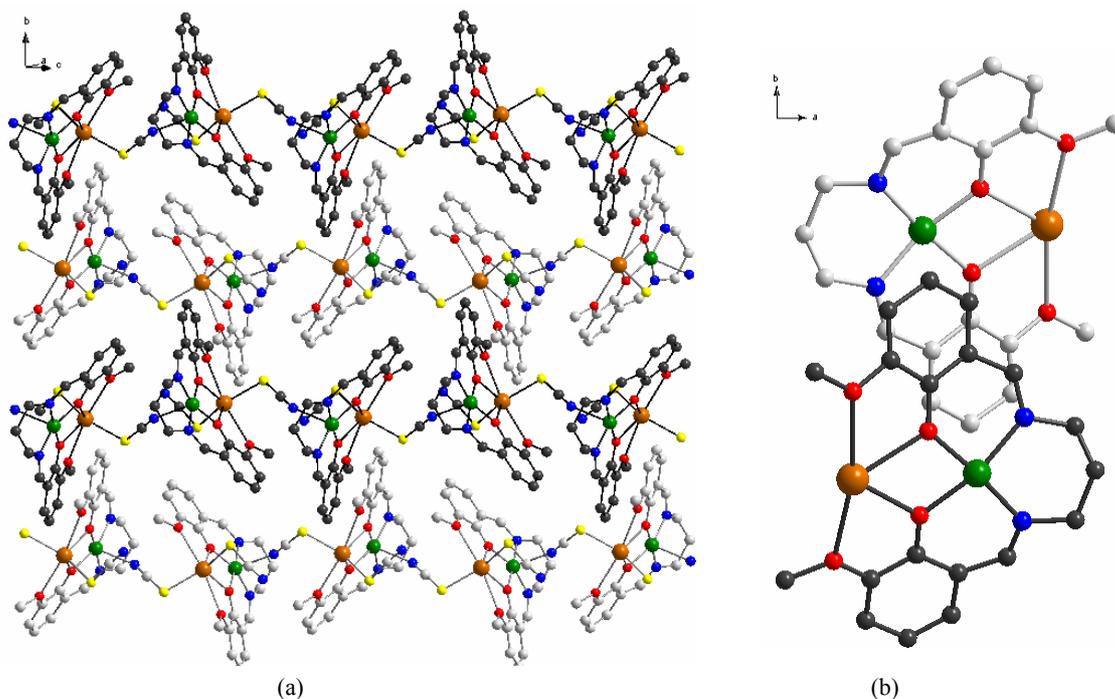


Fig. 3 – (a) Packing diagram for crystal **1**; (b) Superposition of two aromatic rings of the compartmental ligands through π - π interactions.

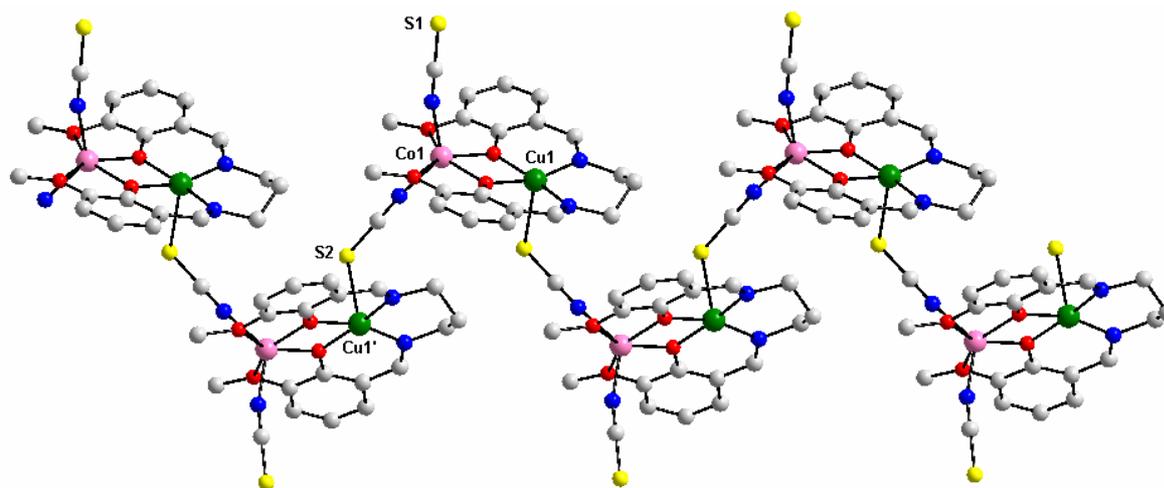


Fig. 4 – Crystal structure of $[\text{LCu}^{\text{II}}\text{Co}^{\text{II}}(\text{NCS})_2]_6$

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