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Unprecedent Isolation of a Mixture of Conformational and Linkage Isomers in a Thiosemicarbazone Cobalt Mesocate

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A cobalt(II) thiosemicarbazonate mesocate has been structurally characterized as an unexpected mixture of conformational and linkage isomers. Moreover, we have shown that the absence of a nitrogen atom in the spacer of the helicand ligand H_2L^a, enables the assembly of an achiral mesohelical complex in the case of Co(II) ions.

Over the last two decades, a great deal of effort in metallosupramolecular chemistry has been dedicated to controlling the shape and arrangement of the various possible metallic species, e.g., helicates, grids, polygons, or polyhedrons.[1,2] Among the great variety of supramolecular species reported to date, helicates are considered the most simple and fundamental architectures.[3] The most extensively used strategy for the assembly of these chiral species is based on the design of suitable ligands, which usually contain two binding domains and are capable of wrapping around a spine of central metal ions in a helical mode.[4,5] The intrinsic chirality of helicates arises from the homochiral mechanical coupling of Δ or Λ chiral metal centers,[6] i.e. $\Delta\Delta$ or $\Lambda\Lambda$ configurations, respectively, whereas heterochiral coupling ($\Delta\Lambda$) results in the assembly of achiral species named mesocates or box diastereoisomers. Mesohelical structures have been studied far less than the related helicates, despite their proven technological interest. For example, copper(II) meso-helicates have been employed as basic building blocks for the construction of molecule-based nanomagnets.[7] In terms of the nature of the metal, the majority of published cases concern manganese, silver, zinc, and copper mesocates.[8] In contrast, very few cobalt mesocates have been reported to date.[9]

As a part of a general research program directed at the assembly of novel supramolecular topologies using

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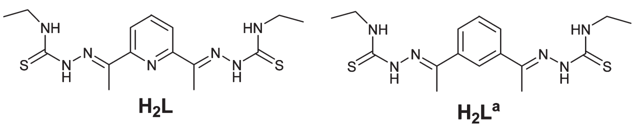
Chart 1. Pentadentate and Tetradentate Thiosemicarbazone Ligands H_2L and H_2L^a



thiosemicarbazones, we recently reported a general route for the construction of multimetallic helicates using pentadentate and tetradentate thiosemicarbazone ligands of the type H_2L^x (Chart 1).[10] The proposed strategy demonstrated that the self-assembly process can be perfectly controlled using a dianionic helicand thiosemicarbazone ligand, equipped with two soft donor atoms, by introducing a donor atom into the aromatic spacer and by selection of the oxidation state of the metal center.[11]

Bearing these results in mind, and with the aim of checking whether the Zn(II) behavior patterns could be extended to other M(II) metal ions, we decided to study the reactivity of the thiosemicarbazone ligand H_2L^a toward another M^{II} metal ion. We report here the results obtained on studying the electrochemical interaction of a cobalt plate with the tetradentate thiosemicarbazone ligand H_2L^a.

The ligand H_2L^a was synthesized according to the procedure reported by us.[11] Electrochemical oxidation of a cobalt anode in the presence of an acetonitrile solution of H_2L^a gave rise to a solid, which was readily characterized.[12] The ESI+ mass data, combined with the analytical and magnetic information, led us to propose a $Co^{II}_2(L^a)_2$ formulation for the complex. Recrystallization of the solid by slow evaporation of a solution in acetonitrile at room temperature afforded green crystals suitable for X-ray analysis. The structural data revealed that the self-assembly process involving Co^{2+} metal ions yields the dinuclear complex $[Co_2(L^a)_2]\cdot CH_3CN$ (Figure 1).[13]

The complex crystallizes in the triclinic space group P-1, and to our surprise, the crystal cell contains four different $[Co_2(L^a)_2]$ isomers (Figure 2). In all of them, the cobalt(II) ions are tetracoordinated by two dianionic ligands $(L^a)^{2-}$, both using their two pairs of imine/hydrazide-thiolate donor atoms in the coordination to the metal centers (Figure 1). The final Co(II) geometry can be described as $[N_2S_2]$ distorted tetrahedral and heteroquiral (Δ and Λ). Therefore, this complex can be termed as mesohelical or mesocate. Despite the cases of mesocates that we have found in the recent literature, we must stress that the herein reported complex $[Co_2(L^a)_2]\cdot CH_3CN$ constitutes one of the rare examples of cobalt mesohelicates.[9]

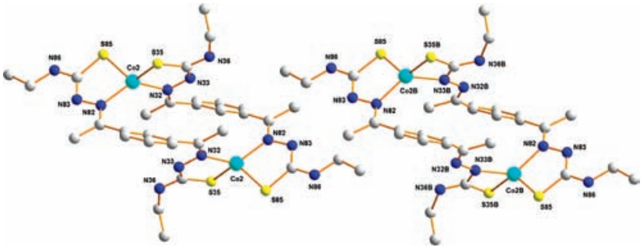


Figure 1. Ball-and-stick representation of the meso-helical linkage isomers in complex $[Co_2(L^a)_2]\cdot CH_3CN$.

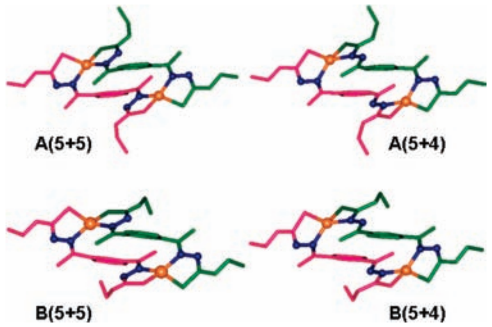


Figure 2. Mixture of conformational [A/B] and linkage isomers [(5+5)/(5+4)] in the crystal cell of the cobalt(II) mesocate $[Co_2(L^a)_2]\cdot CH_3CN$.

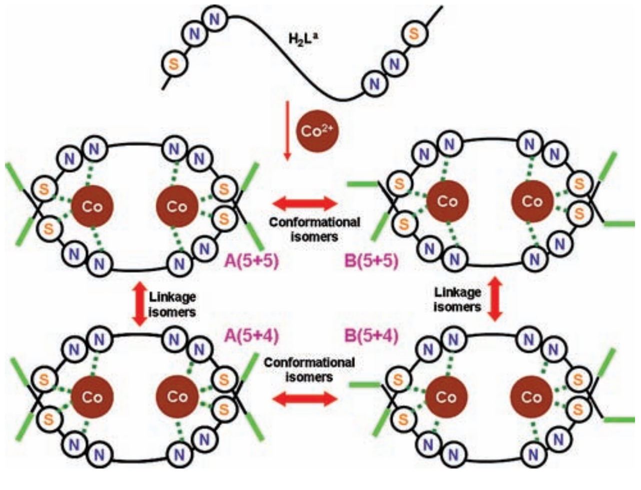


Figure 3. Schematic representation of conformational and linkage isomer mesocates cocrystallized in $[Co_2(L^a)_2]\cdot CH_3CN$.

The unexpected mixture of four meso-helical molecules that appears in the crystal cell (Figures 2 and 3) can be described as a pair of conformational isomers, each of which cocrystallizes with a different linkage isomer. The pair of conformational isomers, denoted as A/B, arises from the different spatial orientation adopted by one of the terminal thioamide ethyl chains in each ligand strand (Figures 2 and 3).

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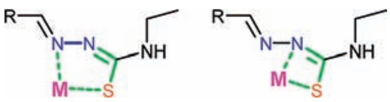
(12) Experimental data for $[Co_2(L^a)_2]$: The complex was obtained by means of an electrochemical method. The cell can be represented as Pt(−) | H_2L^a + MeCN | Co(+). To a solution of H_2L^a (0.1 g, 0.27 mmol) in acetonitrile (80 cm^3) was added a small amount of tetraethylammonium perchlorate as supporting electrolyte. The resulting mixture was electrolysed at 10 mA and 12 V for 1 h 28 min. The green powder obtained was washed with diethyl ether and dried under vacuum. ***Caution!*** *Perchlorate salts are potentially explosive and should be handled with care*. Yield: 0.1 g (91%). MS (ESI+): m/z 421.9 $\{CoL^a{+}H^+\}$, 843.0. $\{Co_2L^a{}_2{+}H^+\}$. Elemental anal. Found: C, 45.5; H, 5.1; N, 19.8; S, 15.0. $C_{32}Co_2H_{44}N_{12}S_4$ requires: C, 45.6; H, 5.3; N, 19.9; S, 15.2%. IR (KBr, cm^{-1}): ν(NH) 3345, 3265, ν(C=N)+ν(C-N) 1531, 1493, ν(N-N) 1051, ν(C=S) 748. μ = 4.0 B. M. $\Lambda_M = 4.5\ \mu S\ cm^{-1}$.

(13) $[Co_2(L^a)_2]\cdot CH_3CN$: $(Co_2C_{34}H_{47}N_{13}S_4)$, M_w = 883.95, crystal dimensions: 0.30 × 0.27 × 0.09 mm^3, triclinic, $P\bar{1}$, a = 11.6780(2) Å, b = 12.6479(2) Å, c = 14.2948(3) Å, α = 86.6190(10)°, β = 84.3870(10)°, γ = 74.3150(10)°, V = 2021.84(6) Å^3, Z = 2, μ = 1.071 mm^{-1}, $F(000)$ = 920. Radiation λ(Mo Kα) = 0.71073 Å, T = 100(2) K, reflns collected/unique 72704/15393 (R_{int} = 0.0328), R = 0.0455, wR = 0.1092, GOF = 1.075, max/min residual density 0.615/−0.486 e.Å^{-3}. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms positions (H26 H36 H66 H86) were located in a difference map and refined isotropically [$U_{iso}(H) = 1.2U_{eq}(N)$]. All other H atoms were placed in geometrically idealized positions. The distance (N26−H36) has been restrained. CCDC 735362.

Chart 2. Ambidentate Behavior of the Hydrazide N−N Group in a Thiosemicarbazone Binding Domain



Each of these conformers cocrystallizes with a different linkage isomer, generating the pairs denoted as A(5 + 5)/A(5 + 4) and B(5 + 5)/B(5 + 4), depending on the size of the chelate rings formed for each cobalt atom (Chart 2).

The crystalline compound $[Co_2(L^a)_2]\cdot CH_3CN$ constitutes a clear example of this phenomenon because every pair of linkage isomers differs in the nitrogen atom employed to coordinate to the cobalt atoms. Thus, every [NS] thiosemicarbazone domain can coordinate either the imine or the hydrazide nitrogen atoms and we can therefore consider that these domains can behave in an $[(N_{im}/N_{hy})S]$ ambidentate manner. Conformers A(5 + 5)/B(5 + 5) exhibit behavior normally observed in thiosemicarbazonate complexes, with the metal bound to the imine nitrogen atoms and the thioamide sulfur atoms of two binding domains belonging to different ligand strands. In this case, four five-membered chelate rings are formed (two per cobalt atom), together with a central 19-membered metallacycle. However, in the pair of conformational isomers A(5 + 4)/B(5 + 4), both thiosemicarbazone strands employ different nitrogen atoms for coordination: one of them uses the imine nitrogen atom in a similar manner to the isomers A(5 + 5)/B(5 + 5), but the second domain is bound to the cobalt atom by the hydrazide nitrogen atom instead. This alternative coordination mode is less frequently observed in the coordination chemistry of thiosemicarbazones and gives rise to the formation of two five-membered and two four-membered chelate rings (one of each type per cobalt atom) and a smaller sized 17-membered central metallaring.

The ratio of the linkage isomers in the crystal cell was determined to be different for the two conformers: (5 + 5):(5 + 4) 79:21(%) for the conformer A and (5 + 5):(5 + 4) 59:41(%) for the conformer B. The lower percentage of the (5 + 4) isomers, containing the four-membered metallarings, can be attributed to the less-favorable energetic contribution of the smaller-sized metallacycle, a consequence of the thermodynamically unfavorable ring tension. The energy difference between four- and five-membered chelate rings in thiosemicarbazonate complexes was estimated to be ~20 KJ by Chattopadhyay and co-workers, who used DFT calculations.[15] This small barrier could explain the coexistence of the conformational and linkage isomers and suggests that the simultaneous control of the numerous factors involved in the crystallization process is complicated. We remark that the crystallization result herein reported is reproducible. In this respect, the different attempts to modify the ratio of isomers in the crystalline mixture by controlling the temperature or the recrystallization time gave rise to identical results.

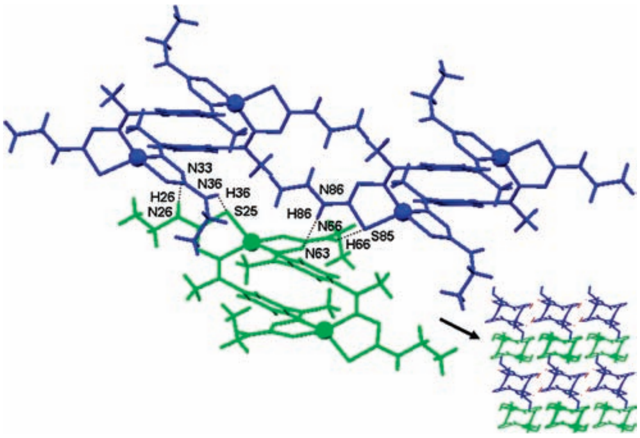


Figure 4. Hydrogen bond interactions between conformational isomers (blue and green) and crystal packing in $[Co_2(L^a)_2]\cdot CH_3CN$.

The Co···Co intermetallic distance is shorter in the (5 + 5) conformational isomers [6.745(1) Å] than in the (5 + 4) isomers that contain the four-membered cycles [7.476(5) Å]. The intermetallic bond distance is similar in the stereoisomeric pairs [e.g., 6.745(1) Å in A(5 + 5) and 6.780(2) Å in B(5 + 5)]. Finally, the distances clearly indicate that an interaction between the cobalt centers does not occur in any of the isomers.

The conformational isomers are linked by means of intermolecular hydrogen bond interactions involving the thioamide NH groups (see Table S1 in the Supporting Information). These contacts give rise to alternate layers of conformers in the mesocate crystal packing (Figure 4).

In summary, we report a unique example of a meso-helical complex that consists of a mixture of conformational and linkage isomers. Moreover, we have shown that the application of the principles established in our reported route to obtain helicates, using thiosemicarbazone ligands and the absence of a nitrogen atom in the spacer of the helicand ligand H_2L^a, enables the assembly of an achiral mesohelical complex in the case of Co(II) ions.

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Supporting Information Available: CIF file for complex $[Co_2(L^a)_2]\cdot CH_3CN$; table of hydrogen bond parameters and additional figure (PDF); structural drawings (CDX). This material is available free of charge via the Internet at http://pubs.acs.org.

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