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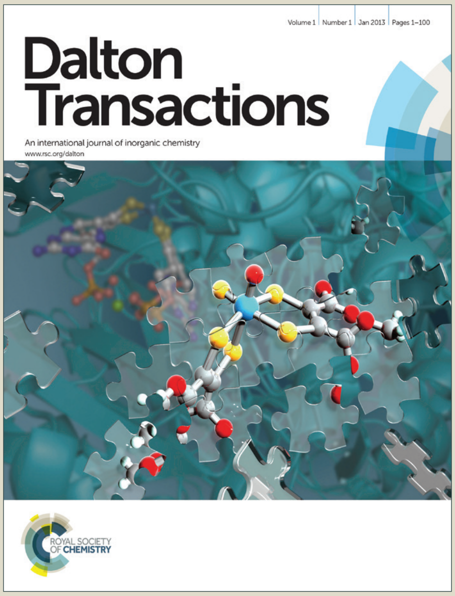

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ARTICLE TYPE

Ascorbic acid decomposition into oxalate ions: a simple synthetic route towards oxalato-bridged heterometallic 3d-4f clusters

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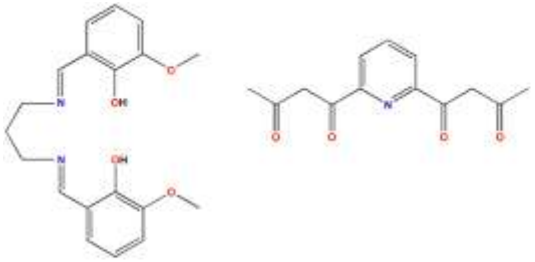
Two types of oxalato-bridged heterometallic 3d-4f dodeca- and hexanuclear compounds have been obtained by connecting six bi- and, respectively, trinuclear moieties through oxalato bridges arising from the slow decomposition of the *L*-ascorbic acid.

The interest in heterometallic 3d-4f assemblies is mainly due to their magnetic properties.[1] The association of various 3d and 4f metal ions within the same molecular entity leads to exciting physical properties, which arise from the electronic peculiarities of the two partners, as well as from their interaction. For example, trivalent lanthanide cations with a large magnetic moment and a strong uniaxial magnetic anisotropy (Tb^{III}, Dy^{III} and Ho^{III}) are chosen when envisaging the preparation of single molecule magnets (SMMs). For these cations, the exchange interaction with Cu^{II} and Ni^{II} was frequently found to be ferromagnetic, a feature that also favors the SMM behaviour. Conversely, because of its isotropic magnetic moment and big spin, Gd^{III} is an excellent ingredient for obtaining magnetic refrigerants (complexes with a strong magnetocaloric effect).[2] On the other hand, the combination of lanthanides with the diamagnetic Zn^{II} ion leads to luminescent materials, the {zinc-organic ligand} moiety acting as an efficient antenna.[3] The oxalato-bridged homometallic 4f and heterometallic 3d-4f complexes are not very numerous, since the interaction of the Ln^{III} ions with oxalate immediately affords insoluble amorphous compounds of general formula $Ln_2(C_2O_4)_3$. Most of the crystallographically characterized compounds have been obtained through the slow release of the oxalate ions by the decomposition of a reagent. One of the first oxalato-bridged Cu^{II}-Ln^{III} complexes was reported by Kahn *et al.*,[4] the oxalate ions resulting from the decomposition of a bis(oxamato) ligand. Several years ago, we described a 1-D coordination polymer constructed from binuclear $Cu^{II}Gd^{III}$ nodes connected by oxalato bridges which result from the decomposition of a bis(oxalato) complex, $[Cr(bipy)(C_2O_4)_2]^-$ (bipy = 2,2'bipyridine).[5] The structure of the gadolinium(III) oxalate itself was determined on single crystals obtained by reacting gadolinium nitrate with *L*-ascorbic acid, whose decomposition generates oxalate ions.[6] This work is the first one mentioning that the slow decomposition of the *L*-ascorbic acid into oxalate ions can be employed for growing single crystals of oxalato-complexes. However, this property was rarely applied to generate polynuclear complexes, the few known examples being homometallic.[7] We recall that the decomposition of the ascorbic acid in various conditions has been intensively investigated, especially in food chemistry.[8] The oxalic, formic, and acetic acids were identified in the mixtures resulting from the decomposition processes. Here we report on the first examples of heterometallic oxalato-bridged complexes obtained using *L*-ascorbic acid as a reagent.



Scheme 1. The organic proligands 1,3-propanedyil-bis(2-iminomethylene-6-methoxyphenol) (H_2valpn) (a) and 2,6-di(acetoacetyl)pyridine (H_2L^1) (b).

As precursors we employed complexes belonging to two families: the dinuclear complex $[(valpn)M^{II}Ln^{III}(CH_3COO)_3]$ and the trinuclear species $[L^1Ni^{II}{}_2Ln^{III}(NO_3)_3]$, which contain the dideprotonated forms of the assembling ligands H_2L^1 and H_2L^1 (Scheme 1). The new compounds have been obtained in a similar way, namely by reacting a solution containing *L*-ascorbic acid and triethylamine with a solution containing the oligonuclear 3d-4f precursors (See Supplementary Information).

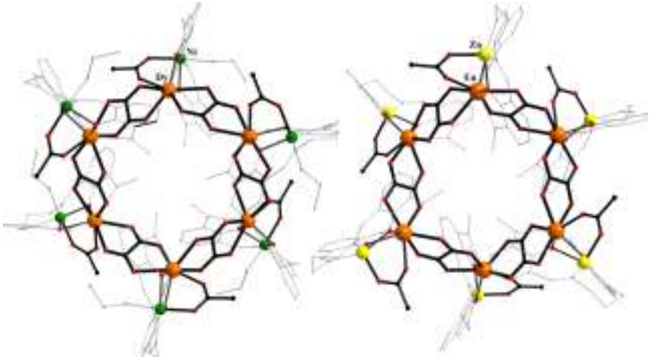


Figure 1. Perspective views of the dodecanuclear structures of **1** (left) and **5** (right).

The crystal structures of six compounds have been solved (ESI): $[\{(valpn)Ni^{II}Dy^{III}(CH_3COO)\}_6(CH_3CH_2OH)_5\,H_2O(C_2O_4)_6]\cdot 2.7H_2O\cdot CH_3CN$ **1**, $[\{(valpn)Cu^{II}Eu^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 2H_2O$ **2**, $[\{(valpn)Cu^{II}Gd^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 9H_2O\cdot 0.7DMF$ **3**, $[\{(valpn)Cu^{II}Dy^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 5H_2O$ **4**, $[\{(valpn)Zn^{II}Eu^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 10.3H_2O\cdot DMF$ **5**, $[\{(valpn)Zn^{II}Dy^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 6H_2O\cdot 5.5CH_3OH$ **6** and $[\{L^1Ni^{II}{}_2Gd^{III}(H_2O)_4\}_2(C_2O_4)_3]\cdot 12H_2O$ **7**.

The structures of four of them are described here: **1, 4**, and **7**. Compound **6** was found to be isomorphous with compound **5**. Complexes **1**-**6** are constructed in the same way (Figure 1). First of all, we notice that the 3d and 4f metal ions are hosted into the two compartments of the organic ligand ($valpn^{2-}$) like in all the binuclear 3d-4f complexes with side-off compartmental ligands derived from *o*-vanillin (the 3d metal ion occupies the inner N_2O_2 compartment, and the 4f ion the open large $O_2O'_2$ compartment).[5,9] The acetato groups bridge the 3d and 4f metal ions within the same binuclear moiety, while the oxalato ligands connect the 4f ions from different binuclear units (bis-chelating bridging mode), resulting in a neutral, cyclic dodecanuclear complex. Within the $[Zn_6Ln_6]$ and $[Cu_6Ln_6]$ clusters, the 3d metal ions are five-coordinate with a square-pyramidal geometry (two nitrogen and two oxygen atoms from the inner compartment of the organic ligand, forming the basal plane, and one acetato oxygen atom into the apical position). In the case of the $[Ni_6Ln_6]$ complex, the nickel(II) ions show an octahedral stereochemistry: two nitrogen and two oxygen atoms from the Schiff-base define the equatorial plane and the apical positions are occupied by one acetato oxygen and one ethanol molecule at four of the six Ni(II) ions. For the two other nickel(II) ions, the sixth position is occupied by either an ethanol molecule or an aqua ligand (each one with the occupation factor 0.5).

The coordination numbers of the Ln^{III} ions in the whole series of compounds is nine: four oxygen atoms from the Schiff-base ligand, four from two oxalato bridges, and one from the bridging acetato ligand. Within all these structures, the six oxalate-bridged Ln^{III} ions are describe a cyclohexane-like chair conformation (Figure 2). The distances between the 3d and 4f metal ions within the binuclear fragments vary as follows: 3.336 - 3.380 Å for **1**, and 3.377 - 3.406 Å for **4**. The distances between the oxalato-bridged lanthanide ions range between 6.121 and 6.150 in **1**, and between 6.110 and 6.144 Å in **4.** The asymmetric units for compounds **1** and **4** are presented in Figure S2 and selected bond distances and angles for compounds **1**-**5** and **7** are gathered in Table S2.

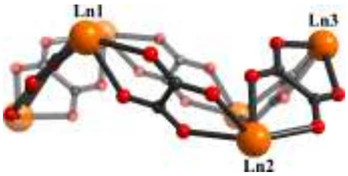


Figure 2. Detail showing the topology of the lanthanide ions within the dodecanuclear entities.

In order to check the generality of this synthetic approach, we have employed a second type of precursor, namely a trinuclear $[Ni^{II}Gd^{III}Ni^{II}]$ complex, which is assembled using the ligand depicted in Scheme 1b. Its reaction with *L*-ascorbic acid leads to a neutral hexanuclear cluster, $[\{L^1Ni^{II}{}_2Gd^{III}(H_2O)_4\}_2(C_2O_4)_3]\cdot 12H_2O$ **7** which is built from two $\{Ni^{II}Ln^{III}Ni^{II}\}$ moieties, the oxalato ligand connecting the lanthanide ions (Figure 3). The nickel(II) ions are hosted into the 1,3-diketonate compartments of two ligand molecules, showing an octahedral geometry with four oxygen atoms arising from the organic ligands forming the equatorial plane and two *trans*-positioned aqua ligands achieving the six-coordination. The gadolinium(III) ion is coordinated by the inner pockets of the two L^1 ligands and two oxalate groups, one being terminal and the other bridging, showing a coordination number of ten. The distance between the oxalato-bridged gadolinium(III) ions is 6.410 Å. The values of the Ni···Gd separation across the diphenoxo bridge vary in the range 3.664 - 3.670 Å.

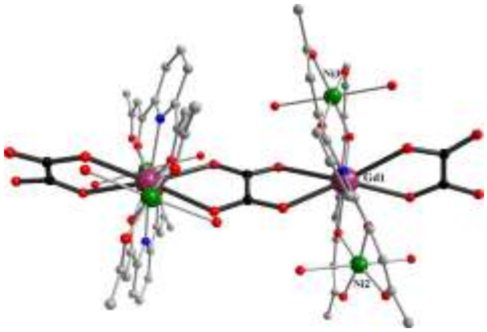


Figure 3. X-ray molecular structure of $\{L^1Ni^{II}{}_2Gd^{III}(H_2O)_4\}_2(C_2O_4)_3]\cdot 12H_2O$ **7** .

We started the investigation of the magnetic properties of these systems, the preliminary results for **1**, **4**, and **6** being presented here. The temperature dependence of their $\chi_M T$ products is shown in Figure 4 (χ_M is the paramagnetic susceptibility per dinuclear 3d-4f unit). The room temperature values [15.39 (**1**), 14.60 (**4**) and 14.18 $cm^3\ mol^{-1}\ K$ (**6**)] agree with the calculated values for the non-interacting set of spin carriers, 15.25 (**1**), 14.53 (**4**) and 14.15 $cm^3\ mol^{-1}\ K$ (**6**) [$S_{Ni} = 1$, $g_{Ni} = 2.10$, $S_{Cu} = ½$ and $g_{Cu} = 2.0$; Dy(III): $4f^9$ electronic configuration, $^6H_{15/2}$ low-lying state, $J = 15/2$ and $g_J = 4/3$].

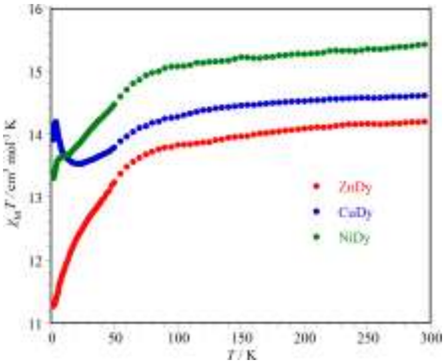


Figure 4. Temperature dependence of the $\chi_M T$ product for **1**, **4**, and **6**.

The magnetic properties of **6** are due only to the Dy^{III} ions. Upon cooling down, $\chi_M T$ of **6** decreases slowly, then more and more, reaching 11.23 $cm^3\ mol^{-1}$ K at 1.9 K, as a result of the depopulation of M_J states, the possible magnetic interaction between de Dy^{III} ions through the oxalato-bridge being masked by this decrease. $\chi_M T$ vs. T curve for **4** unambiguously shows the occurrence a ferromagnetic interaction between the Cu^{II} and Dy^{III} ions within the binuclear moieties: the $\chi_M T$ product first decreases to 13.48 cm^3 mol^{-1} K at 22.5 K (this part is solely due to the Dy^{III} ions), then increases to a value of 14.20 cm^3 mol^{-1} K at 3.7 K. For compound **1**, the decrease of the $\chi_M T$ product due to the Dy^{III} ions is also observed between 300 and 9.5 K. After a small plateau (9.5 and 6.0 K), $\chi_M T$ drops to 13.28 cm^3 mol^{-1} K at 1.9 K).

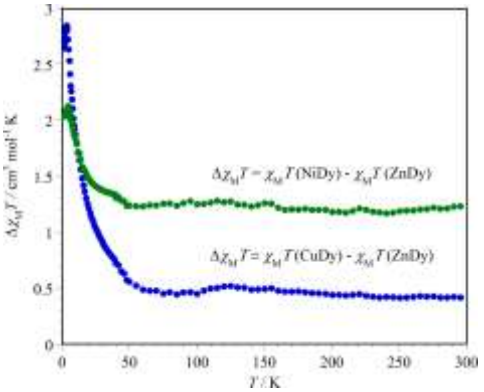


Figure 5. Temerature dependence of the the difference $\Delta\chi_M T = \chi_M T$(MLn) - $\chi_M T$(ZnLn) (M = Cu; M = Ni).

In order to identify the nature of the exchange interaction between Ni^{II} and Dy^{III} in compound **1**, we used a general procedure that consists of representing the temperature dependence of the difference $\Delta\chi_M T = \chi_M T$(NiLn) - $\chi_M T$(ZnLn), where the intrinsic magnetic behaviour of the lanthanide ions, as found within the dinuclear [Zn^{II}Ln^{III}] complex, is subtracted from the one measured for the [Ni^{II}Ln^{III}] complex. We applied the same procedure for **4**. The results for the two compounds are illustrated in Figure 5 and clearly show that the Cu^{II}-Dy^{III} and N^{iII}-Dy^{III} exchange interactions are ferromagnetic, as in many other diphenoxo-bridged Cu^{II}Dy^{III} and Ni^{II}Dy^{III} complexes.[10] As far as the Dy^{III}-Dy^{III} interaction through the bridging oxalate is concerned, a ferromagnetic interaction was reported in the dinuclear compound [$Dy_2(HBpz_3)_2(\mu\text{-ox})$]·$2CH_3CN$·$CH_2Cl_2$ [Hpz_3^- = hydrotris(pyrazolyl)borate].[11]

The results presented herein show that the potential of this synthetic approach towards oxalato-bridged heterometallic complexes deserves to be further exploited. A rich library of oligonuclear heterometallic complexes, which can be used as precursors, is available in literature, opening the door towards unprecedented oxalato-bridged structures. A systematic investigation of several families of such heterometallic complexes and of their magnetic properties is underway in our laboratories and will be published in subsequent papers.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, X-ray collecting data, spectroscopic and elemental analysis details. CCDC: 1049546; 1049497; 1049498; 1049499; 1049500; 1049932, 1049501. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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SYNOPSIS TOC

Ascorbic acid decomposition into oxalate ions: a simple synthetic route towards oxalato-bridged heterometallic 3d-4f clusters

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Dodecanuclear and hexanuclear heterometallic 3d-4f clusters have been obtained by connecting the lantahanide ions through oxalato bridges arising from the slow decomposition of the *L*-ascorbic acid.