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$[Ru^{III}(valen)(CN)_2]^-$: a New Building Block To Design 4d−4f Heterometallic Complexes

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Supporting Information

ABSTRACT: New 4d−4f heterometallic complexes with a one-dimensional structure, ${}^{1}_{\infty}[\{Ru(valen)(CN)_2KRu(valen)(CN)_2\}\{Ln(O_2NO)_2(CH_3OH)_3\}]\cdot 2CH_3OH$ (Ln = Gd, Tb, Dy), have been assembled from the reaction of $[K(H_2O)_2Ru^{III}(valen)(CN)_2]\cdot H_2O$ with lanthanide nitrates. The exchange interaction between Ru^{III} and Gd^{III} mediated by the cyanido ligand was determined for the first time and found to be weak and of antiferromagnetic nature.

The Schiff bases derived from *o*-vanillin and various diamines are very popular ligands for obtaining binuclear 3d−4f complexes.[1] Their deprotonated forms act as side-off compartmental ligands, with each compartment interacting with a specific metal ion: the inner compartment (N_2O_2) accommodates a 3d metal ion, while the large, outer one ($O_2O'_2$) hosts more easily a lanthanide (Ln) ion. This type of binuclear complex is an excellent model platform to probe the factors governing the nature and strength of the magnetic interactions between divalent 3d metal ions and trivalent lanthanides.[2] More recently, it has been shown that the open compartment, $O_2O'_2$, can also accommodate a second 3d metal ion as well.[3] In spite of the richness of the chemistry based on these ligands, binuclear complexes with a trivalent cation located within the N_2O_2 coordination site, $[M^{III}Ln^{III}]$, are unknown. A reason for that can be envisioned considering the stepwise synthesis of these heterometallic complexes. The mononuclear M^{III} species formed in the first step is cationic, and the interaction with the second metal cations is certainly not favored. A way to circumvent this difficulty could be to compensate for this positive charge by the addition of anionic ligands on the M^{III} ion within the mononuclear metalloligand. For example, these anions could coordinate to the apical positions of the M^{III} site. This idea is appealing, provided that the resulting anionic metalloligand is stable in solution toward dissociation of the ancillary ligands; otherwise, control over the reaction products would not be possible. In order to fulfill this condition, a metal ion that forms six very stable metal−ligand bonds must be employed. The best candidates to test this synthetic approach are thus 4d and 5d metal ions. Among these, Ru^{III} and Os^{III} ions are particularly important in molecular magnetism because they are both paramagnetic.[4] Herein we present the successful synthesis of $[K(H_2O)_2Ru^{III}(valen)(CN)_2]\cdot H_2O$ (**1**) as a useful precursor to design new heterometallic molecule-based magnetic materials (H_2valen is the Schiff base resulting from the condensation reaction between *o*-vanillin and ethylenediamine). It is important to mention that the related $[Ru^{III}(Rsalen)(CN)_2]^-$ complexes [$Rsalen^{2-}$ stands for substituted $salen^{2-}$ derivatives; $salen^{2-}$ = *N,N′*-ethylenebis(salicylideneiminate)] have been used recently to construct cyanido-bridged heterometallic magnetic complexes.[5] This anionic complex $[Ru^{III}(valen)(CN)_2]^-$ should be able to interact with a second metal ion through the cyanido groups or the $O_2O'_2$ compartment or both of them. The coordination properties of this new metalloligand toward Ln cations (Gd^{III}, Tb^{III}, and Dy^{III}) were checked, and it appears that $[Ru^{III}(valen)(CN)_2]^-$ coordinates to the Ln ion only through the cyanido groups. In the final isostructural heterometallic compounds ${}^{1}_{\infty}[\{Ru(valen)(CN)_2KRu(valen)(CN)_2\}\{Ln(O_2NO)_2(CH_3OH)_3\}]\cdot 2CH_3OH$ (Gd, **2**; Tb, **3**; Dy, **4**), the $O_2O'_2$ coordination site stays occupied by the K ion already present in the $[K(H_2O)_2Ru^{III}(valen)(CN)_2]$ precursor.

The precursor, **1**, has been obtained by adapting the synthetic protocol reported for the salen derivative (see the Supporting Information, SI).[6] Subsequently, compounds **2**−**4** have been synthesized following a similar synthetic route by heating to 50 °C for 45 min a stoichiometric mixture of **1** and $Ln(NO_3)_3\cdot 6H_2O$ in methanol (see the SI). The green solution was then cooled to room temperature and filtered. Crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into the green filtrate (see the SI). The single-crystal X-ray diffraction investigation of **1** reveals the formation of a binuclear complex, with a Ru^{III} ion located in the N_2O_2 coordination site (Figure 1). The two N and two O atoms from the Schiff base ligand occupy the equatorial plane of the Ru^{III} octahedral coordination sphere [Ru1−N1 = 1.982(9) Å; Ru1−N2 = 2.000(8) Å; Ru1−O1 = 2.018(6) Å; Ru1−O4 = 2.025(7) Å], while the cyanido ligands are positioned in apical positions [Ru−C18 = 2.064(13) Å; Ru−C19 = 2.094(13) Å]. The K ion is located in the open compartment, being coordinated by two phenoxo bridging O atoms and by two aqua ligands. Coordination of the K ion by the O atoms from the open

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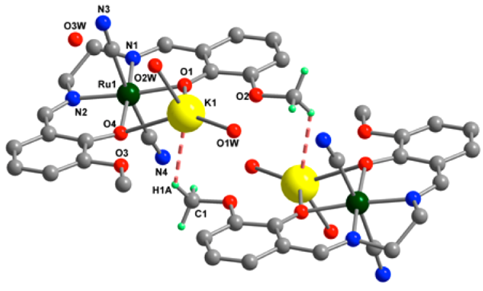

Figure 1. View of the supramolecular $\{[K(H_2O)_2Ru^{III}(valen)(CN)_2]\}_2$ pairs observed in **1** (the K⋯H distance is 2.831 Å).

compartment of the valen ligand is not surprising because the $O_2O'_2$ cavity has a marked crown ether-like ability to encapsulate alkali-metal ions.[7] The K−O distances vary between 2.676(7) and 2.795(8) Å. Interestingly, analysis of the packing diagram for **1** reveals the formation of supramolecular dimers, $\{[K(H_2O)_2Ru^{III}(valen)(CN)_2]\}_2$, through anagostic interactions established between one H atom belonging to a CH_3 group from one [KRu] dimer and the K ion from another one (Figure 1). The intermolecular K⋯H distance is 2.831 Å, and the C−H−K angle is 133.3°, with both values falling within the limits for such interactions.[8] Remarkably, only the anagostic interactions are responsible for the formation of supramolecular dimers in **1**. This complex shows a very rare case of anagostic interactions involving a K ion.[9]

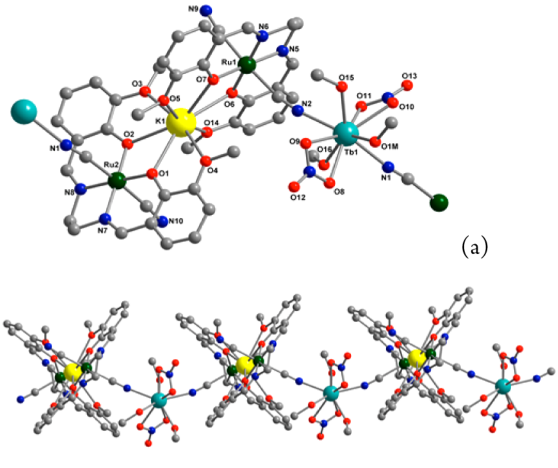

Figure 2. (a) View of the asymmetric unit in **3**, along with the atom numbering scheme. (b) View of the coordination polymer formed in **3**.

Compounds **2**−**4** are isomorphous (Table S1 in the SI), and thus only the structure of **3** is discussed here. As shown in Figure 2, trinuclear cyanido-bridged units, {Ru−CN−Tb−NC−Ru}, are connected by the K ions, trapped by two $O_2O'_2$ compartments of two different valen ligands, to form an infinite one-dimensional coordination polymer. Each $[Ru(valen)(CN)_2]^-$ metalloligand is coordinated to a Tb^{III} ion through one cyanido group, with the other one being terminal. The Tb ion is nine-coordinated by two cyanido bridging ligands, four O atoms from two chelating nitrato groups, and three methanol molecules. The two Tb−N distances are 2.436(7) and 2.458(6)Å, and the Tb−O distances vary between 2.415(7) and 2.522(6) Å. Regarding the cyanido bridges, the values of the Tb−C−N angles are 165.36(68) (Tb1−N1−C4) and 170.03(69)° (Tb1−N2−C3). On the other hand, the K ion is eight-coordinated by the two $O_2O'_2$ sets, with bond distances varying between 2.780(6) and 2.951(6) Å, which are in the range observed for similar compounds.[10] The longest K−O bond distances correspond to the methoxy groups. The intramolecular Tb⋯Ru distances across the cyanido bridges are 5.590 and 5.636 Å, and the shortest intramolecular Ru⋯Ru distance is 7.607 Å. Selected bond distances and angles for compounds **1** and **3** are gathered in Table S2 in the SI.

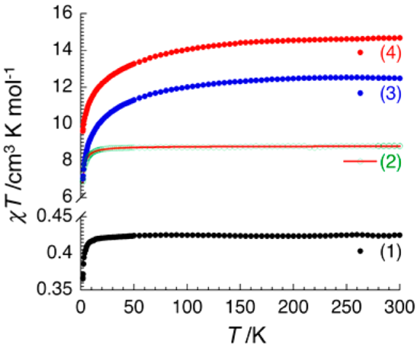

Figure 3. Temperature dependence of the χT product at 1000 Oe (where χ is the molar magnetic susceptibility equal to the ratio between the magnetization and applied magnetic field, M/H, per mole of complex) between 1.85 and 300 K for a polycrystalline sample of **1** (black symbols), **2** (green symbols), **3** (blue symbols), and **4** (red symbols). The solid red line is the best fit to the model described in the text for **2**.

The magnetic properties of the four complexes have been investigated. The temperature dependence of the χT product for compounds **1**−**4** is shown in Figure 3. The room temperature values, 0.42, 8.8, 12.5, and 14.7 cm^3 K mol^{-1} for **1**−**4**, respectively, correspond well to those expected (i) for an $S = {}^1/_2$ system [$\chi T = 0.42$ cm^3 K mol^{-1} with $g = 2.12(5)$] in the case of **1** or for heterometallic units with noninteracting magnetic centers: (ii) two Ru^{III} ($S = {}^1/_2$, $C = 0.42$ cm^3 K mol^{-1}) and one Gd^{III} ($S = {}^7/_2$, $C = 7.875$ cm^3 K mol^{-1}) metal ions in **2** ($\chi T = 8.715$ cm^3 K mol^{-1}); (iii) two Ru^{III} and one Tb^{III} ($S = 3$, $L = 3$, $g = {}^3/_2$, $C = 11.8125$ cm^3 K mol^{-1}) metal ions in **3** ($\chi T = 12.65$ cm^3 K mol^{-1}) and two Ru^{III} and one Dy^{III} ($S = {}^5/_2$, $L = 5$, $g = {}^4/_3$, $C = 14.17$ cm^3 K mol^{-1}) metal ions in **4** ($\chi T = 15.01$ cm^3 K mol^{-1}). For **1**, the χT product remains quasi-constant down to 20 K, and then it decreases, reaching 0.37 cm^3 K mol^{-1} at 1.8 K. This thermal behavior can be due to either a small magnetic anisotropy of the Ru^{III} metal ion or weak antiferromagnetic interactions between the Ru^{III} ions (a Curie−Weiss fit gives a θ value of −0.27 K and thus $zJ/k_B = -0.54$ K) or to a combination of these two factors. The magnetization (M) versus field (H) data (Figures S1 and S2 in the SI) follow the expected Brillouin function for an $S = {}^1/_2$ spin with $g = 2.16(5)$ in good agreement with the χT versus T measurements. This result, the saturation of the magnetization (1.09 μ_B at 1.8 K and 7 T), and the superposition of the M versus H/T data (Figure S2 in the SI) suggest the absence of significant magnetic anisotropy for the ruthenium(III) precursor. For **2**, the decrease of the χT product when the temperature is lowered indicates the occurrence of a weak antiferromagnetic interaction (J) between Ru^{III} and Gd^{III} ions across the cyanido bridge. For this system, the theoretical magnetic susceptibility in the weak-field approximation can be easily calculated (see the SI) from the following Heisenberg spin Hamiltonian: $H = -2J(S_{Ru1}\cdot S_{Gd} + S_{Gd}\cdot S_{Ru2})$. This simple model is able to fit the experimental data almost perfectly down to 1.8 K

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with $J/k_B = -0.24(5)$ K and $g = 2.02(5)$. This J value represents the first estimation of an exchange coupling constant for a cyanido-bridged Ru^{III}/Gd^{III} system.

In the absence of the magnetic data for other cyanide-based Ru^{III}/Gd^{III} complexes, no comparison or magnetostructural correlations can be made at this stage. Nevertheless, a comparison with the exchange interaction of related systems based on Gd^{III} and another low-spin d^5 ion, like Fe^{III}, is possible. For example, in the binuclear complex $[(H_2O)_8Gd\text{-}NC\text{-}Fe(CN)_5]$,[11] the coupling is slightly larger, $J/k_B = -0.36$ K (with $H = -2JS_{Gd}\cdot S_{Fe}$), but of the same order of magnitude. Obviously, new cyanide-based $M^{III}(d^5)/Gd^{III}$ complexes are necessary in order to emphasize the role of the bridging angle, Gd−N−C, and the role of the d metal ion (3d and 4d) on the magnitude of the $M^{III}-Gd^{III}$ interaction. The field dependence of the magnetization for **2** (Figures S1 and S2 in the SI) has been measured below 8 K. The magnetization reaches 9.1 μ_B at 1.85 K and 7 T. Thus, at this applied field, the weak antiferromagnetic interactions (as it is also highlighted by the nonsuperposition of the M versus H/T data; Figure S2 in the SI) are easily compensated by the Zeeman effect. The discussion of the magnetic properties for compounds **3** and **4** is less straightforward. The observed decrease of the χT product is due to the superposition of two effects: depopulation of the Stark levels for both Tb^{III} and Dy^{III} ions and likely weak intramolecular $Ru^{III}-Ln^{III}$ antiferromagnetic interactions. Nevertheless, weak ferromagnetic $Ru^{III}-Ln^{III}$ interactions cannot be ruled out completely, but in these two cases, if they are present, they are overwhelmed by the intrinsic magnetic behavior of the Ln^{III} ions. The 1.8 K M versus H data for **3** and **4** (Figure S1 in the SI) show that the saturation of the magnetization is not reached at 7 T likely because of the strong magnetic anisotropy present in these two systems, as it is also confirmed by the nonsuperposition of the M versus H/T curves (Figure S2 in the SI). The alternating-current measurements for all of the reported compounds did not show any sign of slow relaxation of the magnetization above 1.8 K and up to 1.5 kHz.

In conclusion, we succeeded in synthesizing a new heteroleptic cyanido-Schiff base complex, $[Ru^{III}(valen)(CN)_2]^-$, which proved to have excellent potential as a building block for constructing heterometallic coordination assemblies of interest in molecular magnetism. It can act as a versatile metalloligand, through cyanido groups and/or its $O_2O'_2$ coordination site. Further work on heterometallic systems assembled from the $[Ru^{III}(valen)(CN)_2]^-$ tecton and various metal ions (as aqua complexes or carrying blocking ligands) is in progress in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format [CCDC 1057815 (**1**) and 1057816 (**3**)], full experimental details, Figures S1 and S2, and crystallographic Tables S1 and S2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00889.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday.

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