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Dinuclear Lanthanide(III) Complexes by Metal-Ion-Assisted Hydration of Di-2-pyridyl Ketone Azine

Nikolaos C. Anastasiadis,[†] Carlos M. Granadeiro,[‡] Nikolaos Klouras,[†] Luís Cunha-Silva,[‡] Catherine P. Raptopoulou,[§] Vassilis Psycharis,[§] Vlasoula Bekiari,[∥] Salete S. Balula,*[,‡] Albert Escuer,*[,⊥] and Spyros P. Perlepes*[,†]

[†]Department of Chemistry, University of Patras, 26504 Patras, Greece

[‡]REQUIMTE & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

[§]Department of Materials Science, Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, NCSR "Demokritos", 15310 Aghia Paraskevi Attikis, Greece

[∥]Department of Aquaculture, Technological Educational Institute of Messolonghi, 30200 Messolonghi, Greece

[⊥]Departament de Quimica Inorganica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

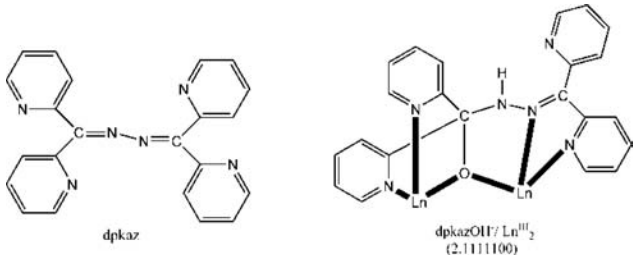
Supporting Information

ABSTRACT: The initial employment of di-2-pyridyl ketone azine in 4f metal chemistry has led to a unique ligand transformation; the resulting anionic ligand is able to bridge two Ln^{III} ions, affording neutral and cationic dinuclear complexes with interesting properties.

Molecular dinuclear and polynuclear lanthanide(III) (Ln^{III}) complexes currently attract intense interest of the inorganic chemistry community because they play a central role in diverse scientific fields/areas, such as (among others) single-molecule magnetism (SMM),[1] magnetic refrigeration,[2] quantum computing,[3] homogeneous[4] and heterogeneous[5] catalysis, optics,[6] and organic transformations,[7] and in the chemistry of multifunctional (or "hybrid") materials.[8] The choice of organic ligands is of paramount importance for the construction of Ln^{III}-based complexes with specific properties.

Over the past 15 years, the coordination chemistry of di-2-pyridylmethanone (common name: di-2-pyridyl ketone, dpk) has attracted broad attention[9] because this ligand can exist in its neat, alcoholated hemiketal and hydrated *gem*-diol forms (Figure S1 in the Supporting Information, SI) in either uncharged or deprotonated state(s) in coordination to metal ions. The anionic forms feature flexible coordination modes in the generation of dinuclear and polynuclear 3d, 4f, and 3d/4f metal complexes with fascinating structures and properties.[9,10] Much less attention has been devoted to the pair of ligands that derive from the 1:1 (hydrazone) and 2:1 (azine) condensation of dpk with hydrazine; the reactions of the latter (di-2-pyridyl ketone azine, dpkaz; Scheme 1) with lanthanide(III) nitrates are the focus of this Communication. Note that only the chemistry of dpkaz with Ag^{I},[11a,b] Ni^{II},[11c] and Cu^{II} [11a,c] has been investigated. The known[12] hydrolytic instability exhibited by the azomethine bond in the presence of metal ions makes dpkaz a serious candidate[11a,c] for Ln^{III}-assisted (promoted) reactivity chemistry. It is worth mentioning that the C═N bond has recently emerged as an extraordinarily diverse and useful one in the hands of synthetic inorganic chemists.[13]

Scheme 1. Structural Representation of the Initially Used Compound dpkaz and the Observed Coordination Mode (Harris Notation) of Its Ln^{III}-Promoted Reactivity Product $dpkazOH^-$



With all of the above in mind and given the long-standing interest of our group in the reactivity of coordinated ligands,[9,14] we have decided to employ dpkaz in Ln^{III} chemistry. The reactions of $Ln(NO_3)_3 \cdot xH_2O$ ($x = 5$ or 6) and dpkaz in 2:1 or 1.5:1 molar ratios in MeCN gave a clear solution that upon storage at room temperature gave complexes $[Ln_2(NO_3)_4(dpkazOH)_2]$ [Ln = Pr (**1**), Nd (**2**)] and $[Ln_2(NO_3)_3(dpkazOH)_2(H_2O)](NO_3)$ [Ln = Eu (**3**), Gd (**4**), Tb (**5**), Dy (**6**)] in moderate yields, where $dpkazOH^-$ is the monoanionic ligand that derives from the addition of one H_2O molecule across one of the two C═N linkages of dpkaz and subsequent deprotonation of the −OH group. The difference between regular (dpkaz is very stable in MeCN solutions containing 2−5% H_2O at room temperature, as evidenced by ^1H NMR spectroscopy) and metal-mediated conditions leads us to believe that the hydration step is Ln^{III}-assisted. Without any detailed mechanistic implication, we suggest that one azomethine carbon center is electrophilically activated by coordination of its imino nitrogen atom in solution and becomes susceptible to nucleophilic attack by one H_2O molecule. This is a novel transformation of dpkaz[11a,c] (Figure S2 in the SI).

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Complexes **1**$\cdot$1.5MeCN$\cdot$0.2H_2O (see the SI) and **2**$\cdot$1.5MeCN$\cdot$0.2H_2O (Figure 1) are isomorphous. The two Nd^{III} atoms in **2** are bridged by the deprotonated oxygen atoms (O1 and O2) of two "head-to-head" $\eta^1:\eta^1:\eta^2:\eta^1:\eta^1:\mu_2$ (or 2.1111100 using Harris notation;[15] Scheme 1) dpkazOH$^-$ ligands, with the Nd1$\cdots$Nd2 distance being 3.985(1) Å. Four pyridyl nitrogen atoms (N5, N6, N11, and N12) from the halves of the ligands that contain the single C–N bonds [C12–N4 = 1.452(7) Å and C34–N10 = 1.455(8) Å] and two chelating nitrato groups complete sphenocoronal 10-coordination at Nd1 (Figure S3 in the SI). Nd2 is also 10-coordinate with a bicapped square-antiprismatic geometry (Figure S4 in the SI); its coordination sphere is completed by two pyridyl nitrogen atoms (N1 and N7) from the two dpkazOH$^-$ ligands, two Schiff base-type nitrogen atoms [N3 and N9; C6–N3 = 1.288(8) Å and C28–N9 = 1.313(8) Å] and two chelating nitrato groups.

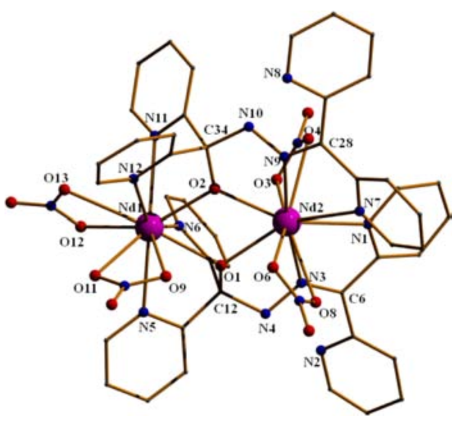

Figure 1. Partially labeled molecular structure of **2**. Color code: Nd^{III}, purple; O, red; N, blue; C, gray.

Complexes **3**$\cdot$2MeCN, **4**$\cdot$2MeCN, **5**$\cdot$2MeCN, and **6**$\cdot$2MeCN are isomorphous, as revealed by powder X-ray diffraction (XRD; Figures S5 and S6 in the SI); the crystal structure of **3**$\cdot$2MeCN has been solved by single-crystal XRD; its structure consists of $[Eu_2(NO_3)_3(dpkazOH)_2(H_2O)]^+$ cations, NO_3^- counterions, and solvate MeCN molecules in an 1:1:2 ratio. The molecular structure of the cation (Figure 2) resembles that of the molecule of **2**. The coordination sphere of Eu1 in **3** is similar to that of Nd2 in **2**, whereas Eu2 is 9-coordinate; the decreased coordination number of Eu2 is probably due to lanthanide contraction. Eu2 is bound to an EuO_5N_4 set of donor atoms. The 9-coordinate Eu2 center exhibits what has been described as a muffinlike geometry,[16] and the 10-coordinate Eu1 center has a coordination environment close to tetradecahedral and bicapped square antiprismatic (Figures S7 and S8 in the SI). The Eu1$\cdots$Eu2 distance is 3.900(1) Å. The crystal structures of **2** and **3** are stabilized by intermolecular $\pi-\pi$ stacking interactions that create 3D networks (Figures S9 and S10 in the SI).

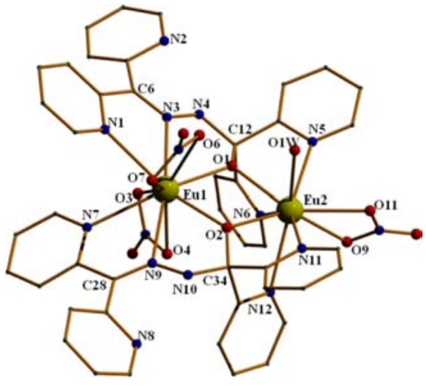

Figure 2. Partially labeled molecular structure of the cation of **3**. Color code: Eu^{III}, yellow; O, red; N, blue; C, gray.

Compounds **2** and **3** are the first structurally characterized metal complexes containing dpkazOH$^-$ or its neutral form as ligands.

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data on **4**–**6** were collected in 0.3 T (300–30 K) and 0.02 T (30–2.0 K) fields and are plotted as $\chi_M T$ versus T in Figure 3 (left). Complex **4** was selected for study because the isotropic nature of Gd^{III} (a 4f^7 system) would allow the quantitative determination of the Gd$^{III}\cdots$Gd^{III} exchange interaction. Compounds **5** and **6** were chosen because the strongly anisotropic character of Tb^{III} and Dy^{III} might give rise to interesting magnetic phenomena. The room temperature $\chi_M T$ value for **4** is 16.25 cm^3 K mol^{-1}, essentially equal to the spin-only value (15.75 cm^3 K mol^{-1}) expected for two noninteracting Gd^{III} ($S = {}^7/_2$, $L = 0$) centers. The $\chi_M T$ product remains almost constant down to ~20 K and then rapidly decreases to 11.89 cm^3 K mol^{-1} at 2.0 K, suggesting a very weak antiferromagnetic exchange interaction. Fit of the experimental data was performed by means of the conventional analytical expression derived from the isotropic spin Hamiltonian $H = -J(\hat{S}_{Gd1}\cdot\hat{S}_{Gd2})$. The best-fit parameters were $J = -0.08(1)$ cm^{-1} and $g = 2.032(1)$.

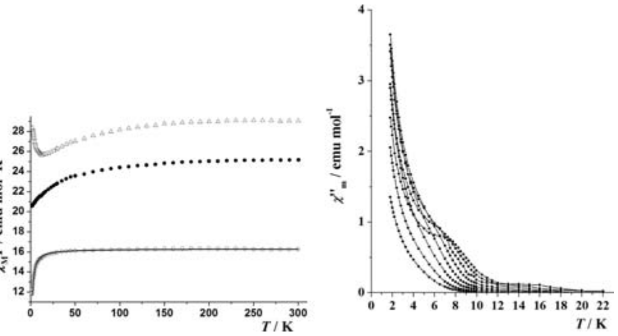

Figure 3. Left: $\chi_M T$ versus T plots for complexes **4** (open circles), **5** (solid circles), and **6** (triangles); the solid line is the fit of the data to the theoretical model for **4** (see the text for the fit parameters). Right: Out-of-phase (χ''_M) versus T ac susceptibility signals for **6** in a 4.0 G ac field oscillating between 1488 and 10 Hz; solid lines are guides for the eye.

The room temperature $\chi_M T$ values for **5** and **6** (25.16 and 29.06 cm^3 K mol^{-1}, respectively) are in agreement with the expected values of 23.64 and 28.34 cm^3 K mol^{-1} for two noninteracting Tb^{III} ($^7F_6$ free ion; $S = 3$; $L = 3$; $g_J = {}^3/_2$) and Dy^{III} ($^6H_{15/2}$ free ion; $S = {}^5/_2$; $L = 5$; $g_J = {}^4/_3$) centers, respectively. Upon cooling, the $\chi_M T$ products decrease monotonically to 2.0 K for **5** and to a well-defined minimum of 25.64 cm^3 K mol^{-1} at 12 K for **6**. This decrease is mainly due to the progressive depopulation of the Tb^{III} and Dy^{III} excited-state Stark sublevels.[1a,8a,b] Below 12 K, the $\chi_M T$ value of **6** increases to a maximum of 28.37 cm^3 K mol^{-1} at 2.0 K, which suggests[1a,17] the presence of intramolecular ferromagnetic interactions between the metal centers. The relatively high $\chi_M T$ value of 20.56 cm^3 K mol^{-1} at 2.0 K for **5**, larger than the usual values for two isolated Tb^{III} ions, as well as the rapid increase of its magnetization at low magnetic fields (Figure S11 in the SI), may also suggest weak ferromagnetic coupling. In light of the susceptibility responses, alternating-current (ac) magnetic susceptibility measurements were performed on polycrystalline samples of **5** and **6** in the 2.0−22 K range in a zero applied dc field and a 4.0 G ac field oscillating at 10−1500 Hz. Frequency-dependent out-of-phase (χ''_M) signals are observed at low temperatures only for **6**, but no peaks are seen (Figure 3, right), indicating the possibility of SMM behavior,[8b] below 2 K.

An identical room temperature photoluminescence behavior (Figures S12−S15 in the SI) is observed for solid **3** and **5**. Upon maximum excitation at 423 nm, a broad green emission at 498 nm was recorded; no significant Ln^{III} emission was detected. An identical behavior is also observed for solid **4**, revealing that the broad green emission at ~500 nm is $dpkazOH^-$-centered.[18]

The catalytic activity of **4** for the oxidation of styrene (Figures 4 and S16 in the SI) was examined using two different oxidants (H_2O_2 and *t*-BuOOH) and MeCN as the solvent. In the absence of the catalyst, no conversion was verified for both oxidants under conditions similar to those of the catalytic reaction. The selectivity and nature of the main product are influenced by the oxidant used. In the presence of H_2O_2, the selectivity obtained was 100% and only benzaldehyde was formed. When *t*-BuOOH was used, a similar yield was obtained for benzaldehyde and styrene oxide, with the latter being the first oxidation product of styrene.[19] Reports on the use of Ln^{III} complexes for the homogeneous oxidation catalysis of alkenes are extremely rare.[4]

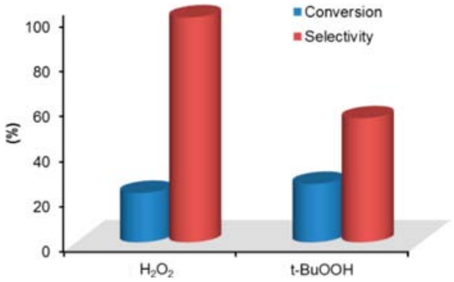

Figure 4. Selectivity and conversion data for the oxidation of styrene catalyzed homogeneously (MeCN) by **4** after 24 h, using H_2O_2 and *t*-BuOOH as oxidants (see the SI for experimental details).

In conclusion, the first use of dpkaz in Ln^{III} chemistry has resulted in a unique ligand transformation and provided access to neutral and cationic dinuclear complexes with interesting structures and properties. We are currently investigating other metal-ion-promoted transformations of dpkaz (and related azine-type ligands) and studying the properties of all of the Ln^{III} analogues of **1**−**6**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for complexes **2** and **3**, experimental details, various structural plots, as well as photoluminescence data for most of the reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sbalula@fc.up.pt (S.S.B.), albert.escuer@ub.edu (A.E.), perlepes@patreas.upatras.gr (S.P.P.).

Notes

The authors declare no competing financial interest.

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