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# Dinuclear lanthanide(III) complexes from the use of di-2-pyridyl ketone: Preparation, structural characterization and spectroscopic studies

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## Abstract

The use of di-2-pyridyl ketone ($(py)_2CO$) in lanthanide(III) chemistry has yielded neutral dinuclear complexes. The 1:1:1 $Ln(NO_3)_3 \cdot xH_2O/(py)_2CO/LiOH \cdot H_2O$ reaction mixtures in MeOH–EtOH afford the complexes $[Ln_2(NO_3)_3\{(py)_2C(OMe)O\}_2\{(py)_2C(OH)O\}]$ (Ln = Pr, **1**; Ln = Eu, **2**; Ln = Tb, **3**; Ln = Er, **4**). The monoanionic derivatives of the hemiacetal and the *gem*-diol forms of di-2-pyridyl ketone have been derived from the Ln(III)-mediated addition of solvent (MeOH, $H_2O$ involved in the alcohols and in the starting materials) on the carbonyl group of $(py)_2CO$. The crystal structure of the representative complex **4** · 0.8EtOH · 0.4MeOH has been solved by single-crystal X-ray crystallography. The two $Er^{III}$ atoms are doubly bridged by the deprotonated oxygen atoms of the $\eta^1{:}\eta^2{:}\eta^1{:}\mu_2$ $(py)_2C(OH)O^-$ ligand and one $\eta^1{:}\eta^2{:}\eta^1{:}\mu_2$ $(py)_2C(OMe)O^-$ ion. One $Er^{III}$ atom is in a nine-coordinate tricapped trigonal prismatic ligand environment comprising the two bridging hydroxyl oxygen atoms, four oxygen atoms from two chelating nitrato ligands and three 2-pyridyl nitrogen atoms, while dodecahedral, eight-coordination at the other $Er^{III}$ atom is completed by two oxygen atoms of the third chelating nitrato ligand, one nitrogen atom of the bridging $(py)_2C(OMe)O^-$ ligand and the $N,N,O_{deprotonated}$ triad from one tridentate chelating $(py)_2C(Me)O^-$ ion. The complexes were characterized by room-temperature effective magnetic moments and spectroscopic (IR, solid-state f–f) techniques. All data are discussed in terms of the nature of bonding and known (**4**) or assigned (**1**–**3**) structures. The Eu(III) and Tb(III) complexes **2** and **3** display in the solid state and at room temperature an intense red and green emission, respectively; this photoluminescence is achieved by an indirect process (antenna effect).

*Keywords:* Antenna effect; Dinuclear lanthanide(III) nitrate complexes; Di-2-pyridyl ketone-based ligands; Photoluminescence studies of europium(III) and terbium(III) complexes; Single-crystal X-ray crystallography

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## 1. Introduction

The intense, long-lived emission from the lanthanide ions $Eu^{III}$ and $Tb^{III}$ has made their complexes of intense interest for a wide range of applications such as display devices, luminescent sensors and probes for clinical use (e.g., fluoroimmunoassay) [1]. Therefore, the photophysical properties of Eu(III) and Tb(III) complexes have received a huge amount of attention [2]. Luminescence from trivalent lanthanides ($Ln^{III}$) arises from electronic transitions between the 4f orbitals. These transitions are forbidden on symmetry grounds, leading to poor absorption cross-sections and relatively long-lived excited states [3]. Consequently, population of the emitting levels of the $Ln^{III}$ ion is best achieved by employing light-harvesting ligands (antenna chromophores) that normally absorb strongly UV light and can sensitize the metal ion by intramolecular

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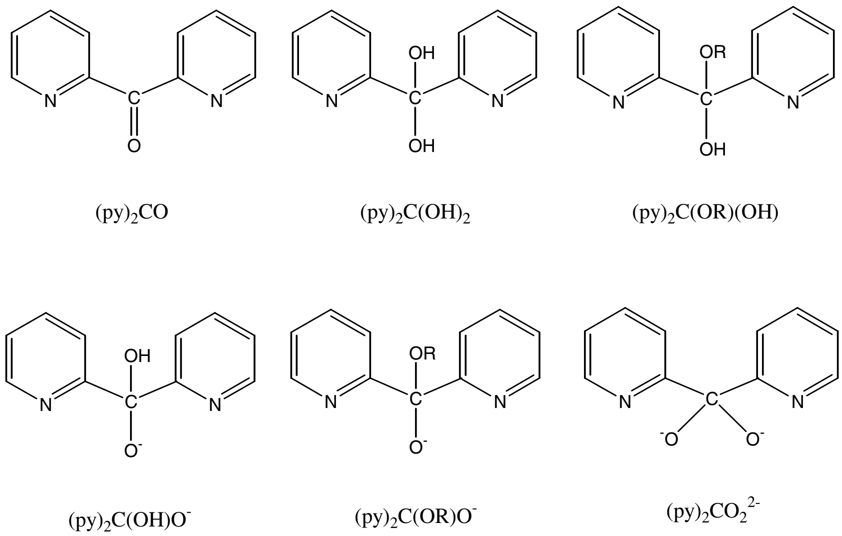
energy transfer from the resulting ligand-based triplet state [2i,3]. This is the usual basis for achieving sensitized emission from Eu(III) and Tb(III) [2]. Recently there have been intense efforts directed at attaching chromophores with relatively long wavelength absorption maxima (in the visible region), e.g., suitably functionalized organic dyes that have particularly low-energy π–π transitions [4] or d-metal complexes that have very strong charge-transfer absorptions at a range of wavelengths that span the visible region [5], to near-IR-emissive $Ln^{III}$ ions, such as Yb(III), Nd(III), Pr(III) and Er(III).

The chances of identifying new 4f-metal complexes with interesting photophysical properties will benefit from the development of new reaction systems with suitable organic ligands. With this in mind we have started a systematic study of the coordination properties of complexing agents capable of efficiently sensitizing Eu(III) and Tb(III) emission. Our ligand design will employ simple units, based on strong binding sites for $Ln^{III}$ coordination and bulky aromatic groups, to play the dual role of antenna and solvent shield, and to thus form – if possible – a hydrophobic shell around the metal ion. It should be mentioned at this point that species containing high-energy oscillators, such as C–H and O–H bonds (typically found in the ligand, coordinated solvent and moisture), are able to quench the metal excited states non-radiatively, leading to decreased luminescence intensities and shorter excited-state lifetimes [6]. In the ligands we plan to use, the binding and antenna domains may be or may not be independent of each other; in the former case this will allow the sensitizing group to be energetically optimized for a particular $Ln^{III}$ ion without changing the binding characteristics of the ligand [2a].

In this paper, we describe our initial studies in this area based on the ligand di-2-pyridyl ketone, $(py)_2CO$ (Fig. 1). Our groups [7,8] and others [9] have been exploring reaction systems involving Mn, Fe, Co, Ni, Cu and Zn ions, and either (i) the monoanion, $(py)_2C(OH)O^-$, or the dianion, $(py)_2CO_2^{2-}$, of the *gem*-diol form (derivative), $(py)_2C(OH)_2$, of di-2-pyridyl ketone, $(py)_2CO$, or (ii) the monoanion, $(py)_2C(OR)O^-$ (R = Me, Et, etc.) of the hemiacetal form (derivative), $(py)_2C(OR)(OH)$, of di-2-pyridyl ketone. The formulae of these ligands and their abbreviations are shown in Fig. 1. The general goal of these efforts is the isolation of polynuclear complexes with interesting magnetic and optical properties. There is a chemical characteristic of $(py)_2CO$ that makes this molecule special as ligand; this is its carbonyl group. Water and alcohols (ROH) have been shown to add to the carbonyl group *upon coordination of the carbonyl oxygen and/or the 2-pyridyl rings* forming the ligands $(py)_2C(OH)_2$ (the *gem*-diol form of $(py)_2CO$) and $(py)_2C(OR)(OH)$ (the hemiacetal form of $(py)_2CO$), respectively [7]. Interesting coordination modes are seen when the ligands $(py)_2C(OH)_2$ and $(py)_2C(OR)(OH)$ are deprotonated. The presence of deprotonated hydroxyl group(s) leads to a great coordinative flexibility, due to the well known ability of the negatively charged oxygen atom to bridge two or three ($\mu_3$) metal ions, while the dianionic form can bridge as many as five metal sites ($\mu_5$). The immense structural diversity displayed by the 3d-metal complexes reported stems in part from the ability of $(py)_2C(OH)O^-$, $(py)_2CO_2^{2-}$ and $(py)_2C(OR)O^-$ to exhibit no less than ten distinct bridging coordination modes [7].Employment of carboxylates, β-diketonates or inorganic anions ($NO_3^-, SO_4^{2-}, N_3^-, N(CN)_2^-$, etc.) as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the preparation of a variety of 3d-metal clusters with nuclearities ranging from 3 to 26 [7], and with interesting physical properties including single-molecule magnetism [8d].



$(py)_2CO$ $(py)_2C(OH)_2$ $(py)_2C(OR)(OH)$

$(py)_2C(OH)O^-$ $(py)_2C(OR)O^-$ $(py)_2CO_2^{2-}$

Fig. 1. The formulae of the ligands discussed in the text; note that $(py)_2C(OH)_2$, $(py)_2C(OR)(OH)$ and all four anions do not exist as free species but exist only in their respective metal complexes (R = Me, Et, etc.).