Lanthanide Complexes with Pyridine-2,6-dicarboxylic and Thiophene-2,5-dicarboxylic Acids*

P. GUERRIERO, U. CASELLATO, S. SITRAN,
P. A. VIGATO**

Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Corso Stati Uniti 4, 35020 Padua, Italy

and R. GRAZIANI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell' Università, 35100 Padua, Italy

We report here some results on the interaction of pyridine-2,6-dicarboxylic acid (H_2pdc) and thiophene-2,5-dicarboxylic acid (H_2tdc) with lanthanide ions {Ln (lanthanide) = La, Dy, Gd} and the crystal structure of $La(pdc)(Hpdc)(H_2O)_2 \cdot 4H_2O$.

Interest in the study of these systems, especially in aqueous solution, comes from the possible usefulness of the lanthanide complexes in bioinorganic chemistry as aqueous shift reagents, particularly in the study of the transport of alkali metal ions (and alkaline earth ions) across model and real biological membranes [1].

Results and Discussion

Complexes with Pyridine-2,6-dicarboxylic Acid

It has been reported that in aqueous solution lanthanide ions form $[Ln(pdc)_3]^{3-}$, $[Ln(pdc)_2(H_2O)_3]^-$ and $[Ln(pdc)(H_2O)_2]^+$ species [2]. For the Ln(III)-bisdipicolinate complexes (Ln = Ce–Dy), NMR studies in aqueous solution have shown a structure with three water molecules bonded to the central metal ions, and with two dipicolinate anions acting as tridentate.

By reacting $Ln(NO_3)_3 \cdot nH_2O$ (Ln = La, Dy, Gd; n = 6, 5, 4 respectively) with H_2pdc in water in the presence of NaOH (in a Ln/H_2pdc/NaOH molar ratio of 1:3:6 and 1:2:4 respectively), $Na_3[Ln(pdc)_3] \cdot nH_2O$ and $Ln(pdc)(Hpdc) \cdot mH_2O$ have been synthesized. The tris complexes are soluble in cold water, while the bis complexes are solubilized only by hot water. All the bis and tris complexes prepared behave as electrolytes in water solution, suggesting that a dissociation occurs also for $Ln(pdc)(Hpdc) \cdot nH_2O$. A comparison of the IR spectra of the bis and tris complexes does not show significant differences except for an additional shoulder, for the bis complexes, at about 1660 to *ca.* 1670 cm^{-1} which makes the peaks due to ν(asym COO^-) broader.

The thermal behaviour of crystals of $La(pdc)(Hpdc) \cdot 6H_2O$, grown from water, has shown the loss of the water molecules in three distinct, well detectable steps. Two H_2O molecules are lost at about 87 °C, another two in the 120 to *ca.* 200 °C temperature range and the last two molecules at about 300 °C. Above 300 °C there is decomposition of the sample.

$Dy(pdc)(Hpdc) \cdot 6H_2O$ loses water molecules in three distinct steps. The first loss of three H_2O molecules is observed also at room temperature on maintaining the sample in a dry gas flux. On heating, this loss was observed at about 90 °C. Two additional water molecules are lost at 150 °C and the remaining sixth molecule is lost at 211 °C. The anhydrous complex obtained is stable in the 245 to *ca.* 420 °C temperature range.

Thermal analysis of $Gd(pdc)(Hpdc) \cdot 8H_2O$ shows that the water molecules are lost in one step with a maximum at 120 °C. The anhydrous complex obtained is stable in the 200 to *ca.* 435 °C temperature range.

The crystal structure determination shows the complex $La(pdc)(Hpdc) \cdot 6H_2O$ to be $[La(pdc)(Hpdc)(H_2O)_2] \cdot 4H_2O$, the lanthanum atom being nine-coordinate.

Figure 1 shows the asymmetric unit with the atom numbering scheme. In each unit two dipicolinate ions are chelated to the metal atom through the nitrogen and two carboxylate oxygens, and one of them links a further La atom by a multidentate bridging bond with one remaining carboxylate oxygen (the O(8) atom). Thus the repeating units are linked to form a

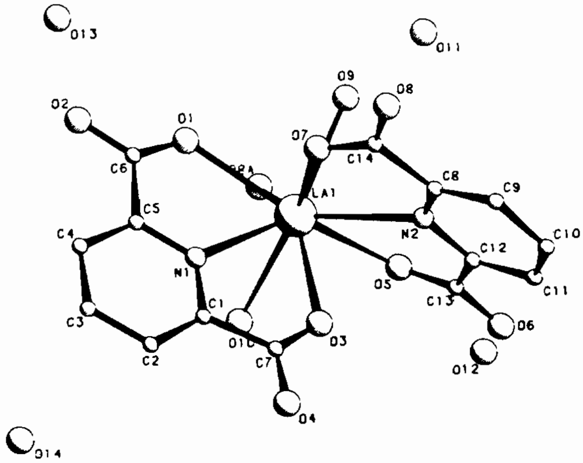

Fig. 1. The crystal structure of $[La(pdc)(Hpdc)(H_2O)_2] \cdot 4H_2O$.

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**Author to whom correspondence should be addressed.

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polymeric chain which extends along the *c* axis of the cell, as shown in Fig. 2. Two of the six formula water molecules are directly bonded to La. The coordination polyhedron around La can be considered to be a monocapped square-antiprism with $O(8^I)$ in the apical position. Selected bond distances are: La–N, 2.67 Å; La–O(water), 2.51 Å (mean); La–O(pdc), 2.55 Å (mean).

One of the two pdc ligands, bridged through the O(8) atom, is bianionic, while the other is monoanionic, having one protonated –COOH and one ionized $-COO^-$ group. This feature, which provides the electroneutrality of the compound, is directly supported by the fact that the presence and the position of the carboxylic hydrogen atom H(4) were determined with sufficient confidence and confirmed during the structure refinement, and indirectly supported by structural details. In fact, the C–O bond lengths in the anionic carboxylates are in the range 1.24–1.26 Å, showing delocalization of the negative charge with formation of partial double C–O bonds; on the contrary, these distances are 1.23 and 1.29 Å in the carboxylic group, which is coordinated to La through O(3), the ketonic oxygen atom.

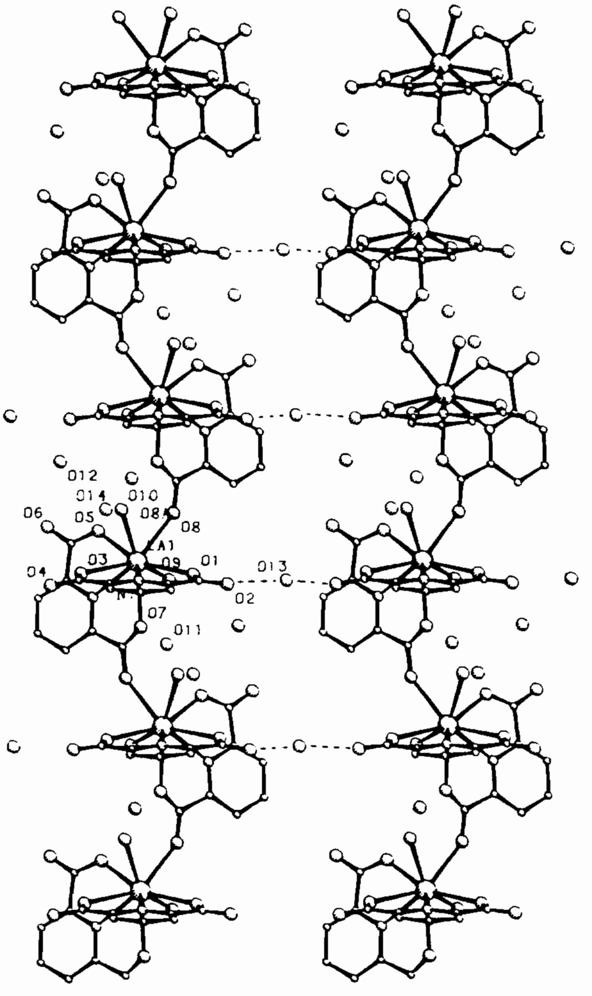

Fig. 2. The polymeric chain of $[La(pdc)(Hpdc)(H_2O)_2]\cdot 4H_2O$: projection along the *a* axis.

The two coordinated and the four clathrate water molecules are involved in a rather complicated network of hydrogen bonds which link together adjacent polymeric chains of the complex and provide compactness and stability to the crystal packing.

Complexes with Thiophene-2,5-dicarboxylic Acid

The interaction of thiophene-2,5-dicarboxylic acid with lanthanide(III) nitrate gives rise to a different system. Complexes, formulable on the basis of elemental analyses as $Ln_2(tdc)_3\cdot nH_2O$ (Ln = La, Gd, Dy) have been found by reaction of H_2tdc, NaOH and the appropriate lanthanide nitrate hydrate in water. White powders or microcrystalline compounds have been obtained. With samarium(III) nitrate, under similar conditions, only $Sm(tdc)OH\cdot H_2O$ was obtained. Both compounds have been synthesized with gadolinium.

The compounds obtained are insoluble in common organic solvents, thus preventing any correct assignment of their structural configuration. The infrared spectrum of H_2tdc shows $\nu(C{=}O)$ at 1764 cm^{-1} as a shoulder and at 1666 cm^{-1} as a strong band, and $\nu(C{-}O)$ at 1279 cm^{-1}. In the spectrum of Na_2tdc, ν(asym COO) lies at 1569 cm^{-1} and ν(symm COO) at 1386 cm^{-1}; ν(asym COO) is at lower field at 1558 to *ca.* 1547 cm^{-1}, while ν(symm COO) is unchanged by coordination to lanthanide ions.

In contrast to the lanthanide compounds synthesized with pyridine-2,6-dicarboxylic acid, we were not successful in the preparation of bis or tris lanthanide thiophene-2,5-dicarboxylate complexes.

References

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