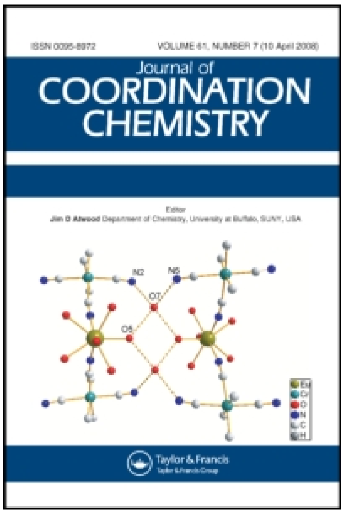

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PREPARATION AND PROPERTIES OF PYRIDINE DICARBOXYLIC ACID COMPLEXES OF THE LANTHANIDES

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PREPARATION AND PROPERTIES OF PYRIDINE DICARBOXYLIC ACID COMPLEXES OF THE LANTHANIDES

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The preparation and spectroscopic properties of eleven hydrated lanthanide (III) dipicolinate and quinolinate complexes are reported for the first time. The complexes are of three general types: $M(dipi)(dipiH)(H_2O)_4$, $M(dipiH)_3(H_2O)$ and $M(quin)(quinH)(H_2O)_3$ [where M = lanthanide (III); $dipiH_2$ = pyridine-2, 6-dicarboxylic acid (dipicolinic acid); $quinH_2$ = pyridine-2, 3-dicarboxylic acid (quinolinic acid)], and evidence is presented which indicates that they may be six-coordinate.

INTRODUCTION

We have previously reported the formation of pyridine-carboxylates with Co(II), Ni(II)[1] and lanthanides(III)[2] (M = La, Nd, Sm, Eu, Tb and Er), and analogous complexes have also been reported.[3–8]

We report here the preparation of hydrated picolinates and quinolinates of some lanthanides (III), together with their magnetic and spectroscopic properties.

EXPERIMENTAL

Starting Materials

These were obtained commercially (ex B.D.H. and Schurhardt München), and used without further purification.

Analyses

Lanthanides were estimated gravimetrically and carbon, hydrogen and nitrogen were determined at the microanalytical laboratory at Reading University.

PHYSICAL MEASUREMENTS

Infrared spectra were recorded upon a Perkin-Elmer 337 instrument. Magnetic moments were determined by the Gouy method. The vacuum thermograms were recorded using a model MF-FS Stanton Massflow Thermobalance, the temperature rise being programmed at 6°C/min.[9]

Preparation of Complexes

All the complexes were prepared by the following general method:

A solution of the pyridine dicarboxylic acid was prepared, and its pH was adjusted to about 5 by the careful addition of sodium hydroxide solution. The solution was then heated to 60° and was added to an aqueous solution of lanthanide(III) nitrate, also at 60°, (Metal:ligand mole ratio = 1:3). The mixture was allowed to cool and the solid was collected by filtration, washed with small amounts of water, ethanol and diethyl ether, and dried *in vacuo* over calcium chloride.

RESULTS AND DISCUSSION

The complexes were prepared by the reaction between the carboxylate and lanthanide(III) nitrate in aqueous solution. Table I lists the complexes isolated, their analytical figures and magnetic moments. The complexes are of three general types: $M(dipi)(dipiH)(H_2O)_4$, $M(dipiH)_3(H_2O)$ and $M(quin)(quinH)(H_2O)_3$ [where M = lanthanide(III)· $dipiH_2$ = pyridine-2, 6-dicarboxylic acid (dipicolinic acid); $quinH_2$ = pyridine-2, 3-dicarboxylic acid (quinolinic acid)]. The magnetic moments of the complexes are close to the theoretical values for the M^{3+} ion.[10, 11]

The infrared spectra of all the complexes showed two bands in the region 1600–1750 cm^{-1}. The bands occurring between 1690 and 1710 are due to $\nu(COO)$ of uncoordinated -COOH, and those between 1610

TABLE I
Analyses and i.r. spectra of the isolated complexes

Compound	Colour	Found% C	H	N	M	Calc.% C	H	N	M	μ eff RT (BM)	i.r. spectra (1.800–1500 cm^{-1})^a
$Nd(dipi)(dipiH)(H_2O)_4$	pale violet	29.60	3.33	4.73	26.00	30.71	2.76	5.11	26.35	3.53	1690s; 1610vs†; 1570vs
$Sm(dipiH)_3.H_2O$	white	37.27	2.14	6.1	22.77	37.83	2.17	6.30	22.55	2.65	1690s; 1650s.br† 1585vs
$Tb(dipiH)_3.H_2O$	white	36.54	2.04	6.1	23.50	37.35	2.09	6.22	23.53	9.47	1690s; 1635s.br† 1585vs
$La(dipi)(dipiH)(H_2O)_4$	white	30.03	3.25	5.01	24.98	31.00	2.79	5.17	25.62	b	1690s; 1610vs†; 1585vs
$Er(dipiH)_3.H_2O$	pink	36.85	2.11	5.91	24.36	36.89	2.06	6.15	24.45	9.5	1690s; 1660s.br†; 1640vs
$Eu(dipiH)_3.H_2O$	white	37.01	2.13	6.12	22.50	37.74	2.11	6.29	22.74	3.48	1690s; 1655s.br†; 1585vs
$Nd(quin)(quinH)(H_2O)_3$	pale violet	32.80	2.22	5.71	27.50	31.68	2.66	5.28	27.18	3.35	1722s; 1650sh†; 1560br.
$Sm(quin)(quinH)(H_2O)_3$	white	31.64	2.30	5.57	28.70	31.32	2.63	5.22	28.01	1.65	1720s; 1650sh†; 1550br.
$Tb(quin)(quinH)(H_2O)_3$	white	31.86	1.92	5.51	29.50	30.83	2.59	5.14	29.14	9.30	1715s; 1650sh†; 1560vs.br.
$La(quin)(quinH)(H_2O)_3$	white	32.51	2.37	6.02	26.85	32.01	2.69	5.33	26.44	b	1710m; 1650sh†; 1560vs.br.
$Er(quin)(quinH)(H_2O)_3$	pink	31.22	2.31	6.24	30.52	30.37	2.55	5.06	30.21	9.38	1700m; 1652sh†; 1560vs.br.

a = Bands marked† are assigned to asym (COO). i.r. spectra of dipicolinic (1690 s.br†; 1570s) and quinolinic acids (1710sh†; 1570 s.br) are given for comparison.
b = diamagnetic

TABLE II
Vacuum T.G.A. results

Stable phase or thermal reaction	%wt. loss Found	Theory
$M(dipi)(dipiH)(H_2O)_4$ 30–95°C	–	—
$M(dipi)(dipiH)(H_2O)_3$ 95–320°C	3.47	3.28
$M(dipi)(dipiH)(H_2O)$ 320–420°C	9.88	9.85
$M(dipi)(dipiH)$	13.17	13.14
$M(dipiH)_3.H_2O$ 183–285°C	–	–
$M(dipiH)_3$	3.07	2.73
$M(quin)(quinH)(H_2O)_3$ 180–268°C	–	–
$M(quin)(quinH)(H_2O)$ 268–322°C	7.32	6.76
$M(quin)(quinH)$	11.09	10.15

and 1660 are due to ν(COO) of coordinated carboxylate (see Table I). The vacuum T.G.A. data for typical compounds of each type are listed in Table II. The complexes were found to contain two types of water: lattice water being evolved at a low temperature, and coordinated water being evolved at a higher temperature. Similar results have previously been reported for the Co(II) and Ni(II) complexes[1]. The complexes of the general form $M(dipi)(dipiH)(H_2O)_4$ contain three lattice waters and one coordinated water. Infrared data revealed that –COOH was uncomplexed. The complexes were accordingly formulated as having a six-coordinate structure (see Figure 1). The complexes of the general form $M(dipiH)_3(H_2O)$ were found to contain no coordinated water, and free –COOH groups, and so were formulated as shown in Figure 2. Finally complexes of the general form M(quin)(quinH)

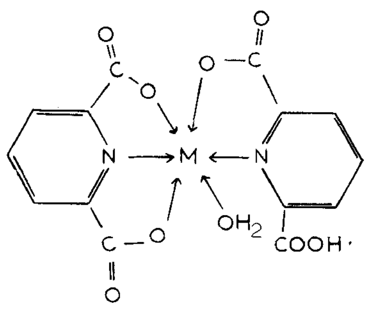

FIGURE 1 Structure of $M(dipi)(dipiH)(H_2O)_4$.

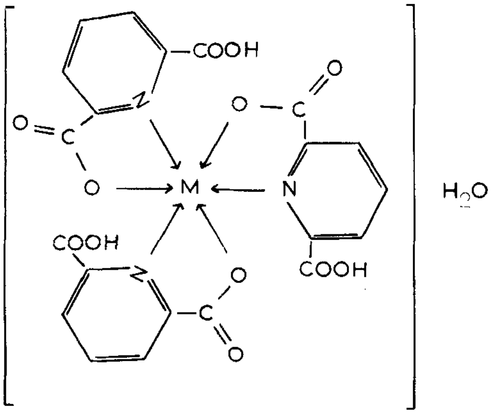

FIGURE 2 Structure of M(dipiH)$_3$.H_2O.

$(H_2O)_3$ contain two molecules of lattice-held water and one molecule of coordinated water. These must be formulated as being polymeric species, with each pyridine dicarboxylate bridging between two metal ions.

Although it is unusual to find the lanthanides with the low coordination number of six, it is not entirely unexpected in this case, in view of the bulk of the ligands.

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