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The Crystal Structures of Three Adducts of Lanthanide Nitrates, Water and 4,4′-Bipyridyl: $[La_2(H_2O)_7(NO_3)_6]\cdot 4C_{10}H_8N_2$, $[Ho(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$ and $[Y(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$

TIMOTHY J. R. WEAKLEY

Chemistry Department, Dundee University, Dundee DD1 4HN, U.K.

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Three classes of adducts of aqua-nitratolanthanide complexes and 4,4′-bipyridyl (4-bipy) have been structurally characterised: (1) $[Ln_2(H_2O)_7(NO_3)_6]\cdot 4(4\text{-bipy})$, Ln = La, Ce(III), Pr; (2) $[Ln(H_2O)_3(NO_3)_3]\cdot 2(4\text{-bipy})$, Ln = Y, Ho; (3) $[Ln(H_2O)_3(NO_3)_3]\cdot 2(4\text{-bipy})$, Ln = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho. In all cases, nitrate groups are bidentate, and 4-bipy molecules are un-protonated and un-coordinated and are hydrogen-bonded to ligand water molecules. In (1), a doubly-bidentate NO_3 group bridges two Ln atoms. Crystal data include: (1) (Ln = La). $Cmc2_1$, a = 24.52(2), b = 16.673(12), c = 13.245(8) Å, Z = 4, diffractometer data, R = 0.094 for 3241 reflections; (2) (Ln = Ho), Pbca, a = 7.731(7), b = 43.77(8), c = 15.67(3) Å, Z = 8, film data, R = 0.060 for 2124 reflections; (3) (Ln = Y), $P2_1/c$, a = 7.910(6), b = 20.81(2), c = 16.56(2) Å, β = 104.60(5)°, film data, R = 0.058 for 2820 reflections.

Introduction

Numerous compounds of the type $Ln(NO_3)_3\cdot nH_2O\cdot 2(4\text{-bipy})$ have been reported [1, 2] in which Ln is a trivalent lanthanide or yttrium, 4-bipy is 4,4′-bipyridyl, and n ranges from 2 to 6. It was inferred from the infra-red spectra that 4-bipy was coordinated to Ln [2]. However, the compounds of this type so far subjected to single-crystal X-ray structural analysis have proved to have NO_3:Ln ratios in excess of 3:1; in $(4\text{-bipyH})[Ln(H_2O)_2(NO_3)_4(4\text{-bipy})]$ (Ln = La, Ce, Pr, Nd) [3, 4] only one 4-bipy is coordinated and the other is protonated, while in $[Ln(H_2O)_4(NO_3)_3]\cdot 2(4\text{-bipyH})(NO_3)$ (Ln = Nd, Yb) [4] both 4-bipy are protonated and uncoordinated. We have now identified three more structural types, in all of which the NO_3:Ln ratio is 3:1; the 4-bipy molecules are unprotonated and

TABLE I. Crystal Data.

Compound	Space-group	a/Å	b/Å	c/Å	β/deg	Z	D_c/g cm^{-3}
$La_2C_{40}H_{46}N_{14}O_{25}$(I)[a]	$Cmc2_1$	24.52(2)	16.673(12)	13.245(8)	90	4	1.710
$Ce_2C_{40}H_{46}N_{14}O_{25}$	$Cmc2_1$	24.48(2)	16.62(2)	13.21(1)	90	4	1.754
$Pr_2C_{40}H_{46}N_{14}O_{25}$	$Cmc2_1$	24.45(2)	16.53(2)	13.20(1)	90	4	1.770
$HoC_{20}H_{22}N_7O_{12}$(II)[a]	Pbca	7.731(7)	43.47(8)	15.67(3)	90	8	1.797
$YC_{20}H_{22}N_7O_{12}$	Pbca	7.758(8)	43.65(10)	15.67(3)	90	8	1.605
$YC_{20}H_{22}N_7O_{12}$ (III)[a]	$P2_1/c$	7.910(6)	20.81(2)	16.555(19)	104.60(5)	4	1.614
$NdC_{20}H_{22}N_7O_{12}$	$P2_1/c$	8.08(1)	20.85(2)	$c\sin\beta$ = 16.02(1) Å		4	1.713
$SmC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.979(7)	20.73(2)	16.643(15)	105.7(1)	4	1.760
$EuC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.968(7)	20.81(2)	16.63(2)	105.7(1)	4	1.761
$GdC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.951(7)	20.76(2)	16.573(15)	105.2(1)	4	1.784
$TbC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.953(7)	20.81(2)	16.58(2)	105.05(10)	4	1.782
$DyC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.921(7)	20.75(2)	16.57(2)	104.9(1)	4	1.803
$HoC_{20}H_{22}N_7O_{12}$	$P2_1/c$	7.917(7)	20.79(3)	16.54(2)	104.8(1)	4	1.809

[a] Intensity data were collected. Values of λ and μ were 0.71069, 1.5418, 1.5418 Å; 16.2, 62.1, 37.6 cm^{-1}, for I, II, III.

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TABLE II. Selected Molecular Dimensions for I, $[La_2(H_2O)_7(NO_3)_6]\cdot 4C_{10}H_8N_2$.

(i) La Coordination sphere			
La(1)–O(4)	2.603(11) Å	La(2)–O(1)	2.659(12) Å
La(1)–O(5)	2.613(12)	La(2)–O(2)	2.660(11)
La(1)–O(7)	2.649(16)	La(2)–O(8)	2.658(16)
La(1)–O(8)	2.815(17)	La(2)–O(9)	2.743(15)
La(1)–Aq(1)	2.577(12)	La(2)–O(10)	2.651(14)
La(1)–Aq(2)	2.520(15)	La(2)–O(11)	2.887(16)
La(1)–Aq(3)	2.578(13)	La(2)–Aq(4)	2.458(13)
		La(2)–Aq(5)	2.505(10)
O(4)–La(1)–O(5)	48.3(4)°	O(1)–La(2)–O(2)	47.7(3)°
O(7)–La(1)–O(8)	46.4(4)	O(8)–La(2)–O(9)	45.1(5)
La(1)–O(8)–La(2)	169.2(6)	O(10)–La(2)–O(11)	45.1(5)
(ii) Nitrate groups			
N(1)–O(1)	1.263(19) Å	N(3)–O(7)	1.159(23) Å
N(1)–O(2)	1.259(18)	N(3)–O(8)	1.276(21)
N(1)–O(3)	1.206(20)	N(3)–O(9)	1.205(24)
N(2)–O(4)	1.250(18)	N(4)–O(10)	1.275(25)
N(2)–O(5)	1.262(18)	N(4)–O(11)	1.236(25)
N(2)–O(6)	1.257(18)	N(4)–O(12)	1.223(24)
(iii) Hydrogen bonds			
O(10)··Aq(1^{i})	2.72(3) Å	N(6)··Aq(4^{iii})	2.76(3) Å
O(11)··Aq(1)	2.83(3)	N(7)··Aq(3^{iv})	2.67(3)
O(12)··Aq(5^{ii})	2.96(3)	N(8)··Aq(2^{i})	2.72(3)
N(5)··Aq(5^{ii})	2.66(3)		

Symmetry code: (i) x, 1 – y, –½ + z; (ii) x, 1 – y, ½ + z; (iii) ½ + x, ½ – y, ½ + z; (iv) ½ – x, ½ – y, –½ + z

uncoordinated, as they also are in $[Ln(H_2O)_8]Cl_3\cdot 2$(4-bipy) (Ln = Y, Gd) [5].

Results and Discussion

The compounds whose structures have been determined are $[La_2(H_2O)_7(NO_3)_6]\cdot 4$(4-bipy) (I), space-group $Cmc2_1$, which has isomorphs containing Ce and Pr; $[Ho(H_2O)_3(NO_3)_3]\cdot 2$(4-bipy) (II), space-group Pbca, which has an isomorph containing Y; and $[Y(H_2O)_3(NO_3)_3]\cdot 2$(4-bipy) (III), space-group $P2_1/c$, which has isomorphs containing Nd, Sm, Eu, Gd, Tb, Dy, and Ho. As previously [4], the criteria for isomorphism are identity of space-group and close similarities in cell dimensions and in the distribution of intensities in corresponding Weissenberg photographs. Crystal data are given in Table I. When Ln was Er, Tm, Yb or Lu the only products obtainable were aggregates of small crystals (from 95:5 EtOH: H_2O). No homogeneous crystals or fragments large enough for diffraction photography were found, but the crystal symmetry appeared to be low and the products were isomorphous with one another (powder diffractometry) but not with I, II, or III. Analysis of the Yb compound indicated a composition close to $Yb(NO_3)_3\cdot 3\text{-}4H_2O\cdot 2$(4-bipy).

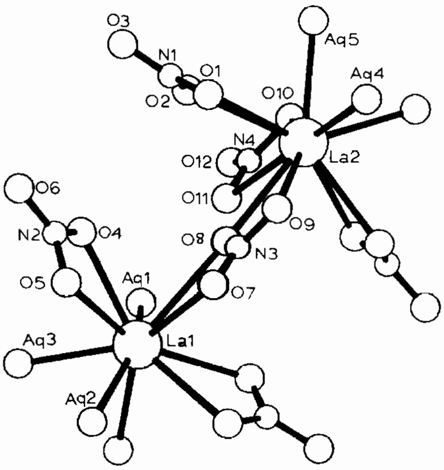


Fig. 1. I, $[La_2(H_2O)_7(NO_3)_6]\cdot 4C_{10}H_8N_2$: the binuclear complex. The viewpoint is close to the crystal mirror plane.

TABLE III. Selected Molecular Dimensions for II, $[Ho(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$.

(i) Ho coordination sphere			
Ho–O(1)	2.391(8) Å	Ho–O(8)	2.514(10) Å
Ho–O(2)	2.475(8)	Ho-Aq(1)	2.333(7)
Ho–O(4)	2.416(9)	Ho–Aq(2)	2.296(7)
Ho–O(5)	2.451(9)	Ho–Aq(3)	2.343(8)
Ho–O(7)	2.434(9)		
O(1)–Ho–O(2)	52.7(3)°	O(7)–Ho–O(8)	50.4(3)°
O(4)–Ho–O(5)	51.6(3)		
(ii) Nitrate groups			
N(1)–O(1)	1.267(13) Å	N(2)–O(6)	1.228(13) Å
N(1)–O(2)	1.274(13)	N(3)–O(7)	1.238(16)
N(1)–O(3)	1.240(12)	N(3)–O(8)	1.231(15)
N(2)–O(4)	1.248(17)	N(3)–O(9)	1.214(18)
N(2)–O(5)	1.252(16)		
(iii) Hydrogen bonds			
O(9)••Aq(2^{i})	2.94(3) Å	N(5)••Aq(1^{iii})	2.80(2) Å
O(9)••Aq(3^{i})	2.97(3)	N(6)••Aq(1^{iv})	2.75(2)
N(4)••Aq(2^{ii})	2.71(2)	N(7)••Aq(3^{v})	2.69(2)

Symmetry code: (i) 1 + x, y, z; (ii) ½ + x, y, ½ – z; (iii) –½ + x, ½ + y, –z; (iv) x, ½ – y, ½ + z; (v) –½ – x, ½ +, y, z

Compound I contains a binuclear neutral complex, $La_2(H_2O)_7(NO_3)_6$ (Fig. 1). Dimensions are given in Table II. Bond lengths are similar to those in $[La(NO_3)_3(H_2O)_5]\cdot H_2O$ [7]. The chief feature of interest is the doubly-bidentate bridging NO_3 group. This has not, as far as we know, been reported previously in lanthanide complexes although it is known elsewhere, for instance in $AgNO_3$ [6]. This group is asymmetrically bidentate towards both La atoms, especially La(1), but the asymmetry is not necessarily a consequence of the bridging role as it is also found for non-bridging bidentate NO_3 in this compound [N(4), O(10, 11, 12)] and in others, *e.g.* $[Y(H_2O)_4(NO_3)_3]\cdot 2H_2O$ [9]. The La atoms, the bridging NO_3 and one non-bridging group, and two water ligands lie on a crystal mirror plane; apart from this imposed symmetry, the coordination geometry is irregular for both La(1) and La(2) which are respectively ten- and eleven-coordinate. The NO_3 groups on general positions are virtually planar and the La atoms bonded to them are near their mean planes [greatest deviation, 0.32 Å for La(2) and N(1), O(1,2,3)]. Short interatomic contacts which probably indicate hydrogen bonds (Table II) include: (i) an intra-complex contact (2.83 Å) between O(11), bonded to La(2), and Aq(1), bonded to La(1); (ii) $NO_3\cdot\cdot H_2O$ contacts between complexes related by the operation x, 1 – y, +½ + z; and (iii) a contact between each 4-bipy N atom and a water molecule near the extended N••N axis of that 4-bipy molecule. The 4-bipy molecules all lie nearly parallel to (001); they appear nearly superimposed in the *c* direction but are separated by a minimum of *ca.* 6.5 Å.

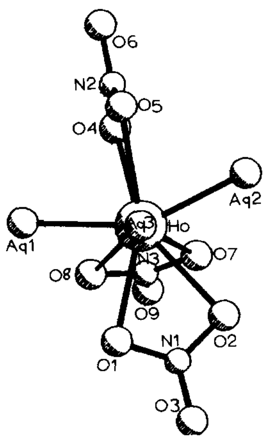


Fig. 2. II, $[Ho(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$: the coordination about Ho viewed along the Aq(3)–Ho bond.

In II, $[Ho(H_2O)_3(NO_3)_3]\cdot 2$(4-bipy), the NO_3 ligands are again bidentate so that the Ho atom is

TABLE IV. Selected Molecular Dimensions for III, $[Y(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$.

(i) Y coordination sphere			
Y–O(1)	2.395(6) Å	Y–O(8)	2.479(6) Å
Y–O(2)	2.475(5)	Y–Aq(1)	2.304(5)
Y–O(4)	2.467(6)	Y–Aq(2)	2.312(5)
Y–O(5)	2.432(6)	Y–Aq(3)	2.333(5)
Y–O(7)	2.433(5)		
O(1)–Y–O(2)	51.9(2)°	O(7)–Y–O(8)	51.8(2)°
O(4)–Y–O(5)	51.7(2)		
(ii) Nitrate groups			
N(1)–O(1)	1.261(8) Å	N(2)–O(6)	1.197(10) Å
N(1)–O(2)	1.264(9)	N(3)–O(7)	1.280(9)
N(1)–O(3)	1.216(9)	N(3)–O(8)	1.259(8)
N(2)–O(4)	1.261(9)	N(3)–O(9)	1.209(8)
N(2)–O(5)	1.269(9)		
(iii) Hydrogen bonds			
$O(6)\cdot\cdot Aq(2^{i})$	2.86(2) Å	$N(5)\cdot\cdot Aq(1^{iii})$	2.74(2)
$O(9)\cdot\cdot Aq(3^{ii})$	3.01(3)	$N(6)\cdot\cdot Aq(1)$	2.77(2)
$N(4)\cdot\cdot Aq(2)$	2.70(2)	$N(7)\cdot\cdot Aq(3)$	2.66(2)

Symmetry code: (i) −1 + x, y, z; (ii) x, ½ − y, −½ + z; (iii) 1 − x, 1 − y, 1 − z

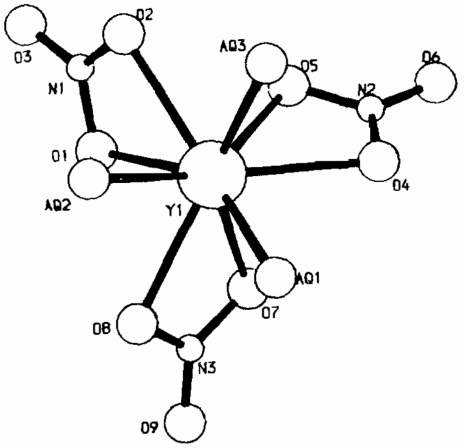


Fig. 3. III, $[Y(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$: the coordination about Y.

9-coordinate (Fig. 2). Average bond lengths are: Ho–O(nitrate), 2.447; Ho–OH$_2$, 2.324 Å. The coordination geometry can be described as follows. Atoms O(1), Aq(3), O(4), O(5) and O(8) define a puckered pentagon, the maximum deviations from the mean plane being +0.13 Å for O(5) and −0.14 Å for O(4). The Ho atom lies 0.46 Å below this plane, and a triangle of atoms O(2), Aq(2), O(7) are respectively 2.06, 2.43, 1.94 Å below the plane. The ninth ligand atom, Aq(1), is 1.86 Å above the plane with the Ho–Aq(1) inclined at 5.3° to the normal to the plane. The dihedral angles between the planes of the three NO$_3$ groups are 83.9, 86.5, 86.8°. Bond lengths and angles are given in Table III. The shorter Aq··N(bipy) distances and the near-collinearity of the Aq··N vectors with the 4-bipy N··N axes strongly imply the presence of hydrogen bonds. The resulting three-dimensional net is reinforced by $NO_3\cdot\cdot H_2O$ bonds parallel to *a*.

Compounds II and III both contain neutral, 9-coordinate $Ln(H_2O)_3(NO_3)_3$ complexes. However, in III the H_2O ligands all lie on the same side of the yttrium atom, and the complex has approximate three-fold symmetry (Fig. 3). The three chelate NO$_3$ groups are again steeply inclined to one another to minimise repulsions between non-bonded atoms (dihedral angles 79.4, 84.4, 88.8°). Bond lengths are given in Table IV. The average bond lengths are 2.316 Å for Y–OH$_2$ and 2.447 Å for Y–O(nitrate), to be compared with the average values 2.384 and 2.506 Å respectively in the 10-coordinate complex in $[Y(H_2O)_4(NO_3)_3]\cdot 2H_2O$ [8], and 2.352 and 2.549 Å in $[Y(H_2O)_4(NO_3)_3]\cdot 2H_2O$ [9] (also 10-coordinate, but with one long Y–O(nitrate) bond). In I and II both independent 4-bipy molecules are on general positions, but in

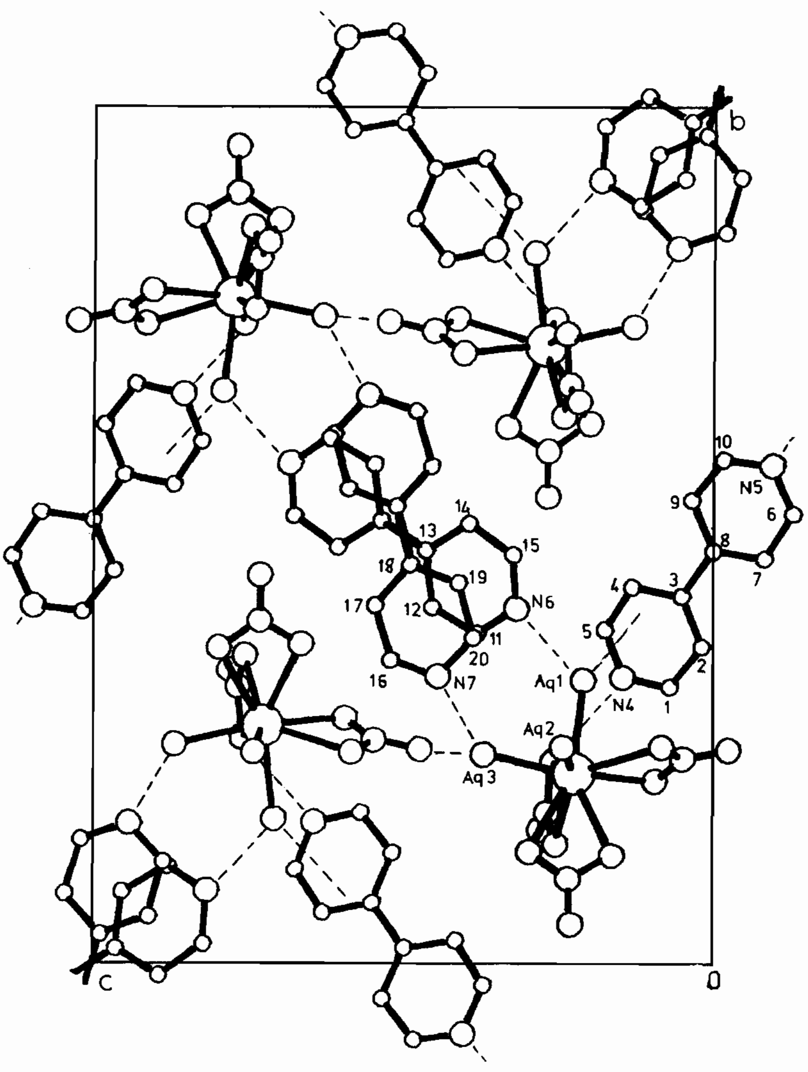


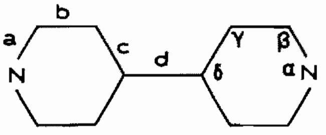
Fig. 4. III, $[Y(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$: *a*-axis projection.

III there are three independent 4-bipy molecules of which one lies on a general position and two lie on crystal inversion centres (Fig. 4). The mean planes of the 4-bipy molecules are slightly inclined to the (100) plane; stacks of 4-bipy molecules occur parallel to *a* with separations of 3.38 and 4.53 Å for molecules in general positions and 3.96 Å for molecules on inversion centres. As in I and II, each 4-bipy molecule enters into hydrogen bonds with ligand water molecules close to the extended N••N axis, and there are also intermolecular $NO_3\cdot\cdot H_2O$ bonds.

The dimensions of the 4-bipy molecules in I, II, and III are summarized in Table V. They are in general agreement with previous measurements [3, 4], in particular as regards the decrease in the ring angle at N from the 'hexagonal' value of 120° and the enhanced ring angle at the adjacent carbon atom. Here too, the different dihedral angles between the pyridyl rings appear merely to reflect the requirements of crystal packing, and are not correlated with the central C–C bond length. In compound III the dihedral angle is constrained to be zero for the 4-bipy molecules on inversion centres. However, the ring atoms (especially those off the N••C–C••N axis) have highly anisotropic thermal parameters indicating high apparent vibrational amplitudes normal to the ring planes, and these may in fact represent static disorder of the 4-bipy molecules over two conformations each with small but non-zero dihedral angles.

It is not clear which, if any, of the present compounds are identical with the $Ln(NO_3)_3\cdot nH_2O\cdot 2$(4-bipy) adducts whose infra-red spectra were regarded [2] as showing that the 4-bipy molecules were in

TABLE V. Summary of Dimensions of 4,4′-bipyridyl Molecules. Standard deviations of individual values range from 0.014 to 0.026 Å, and from 0.7 to 1.6°.



Bond or angle	Range (mean value in parentheses)						
	I			II		III	
a	1.328–1.390(1.347) Å			1.309–1.359(1.338) Å		1.272–1.344(1.315) Å	
b	1.353–1.405(1.392)			1.361–1.405(1.390)		1.383–1.403(1.393)	
c	1.361–1.414(1.390)			1.355–1.432(1.396)		1.350–1.426(1.382)	
α	116.4–122.0(118.9)°			116.0–119.2(117.7)°		116.2–118.8(117.4)°	
β	119.0–123.9(122.0)			120.9–125.6(123.0)		120.8–125.7(123.3)	
γ	115.0–122.9(119.3)			117.1–122.6(119.3)		118.1–122.5(119.6)	
δ	116.2–122.3(118.9)			115.3–118.6(117.3)		115.1–118.3(116.4)	
Bond d	1.530	1.477	1.486	1.488	1.493	1.444	1.462 Å
Dihedral angle	5.3	14.6	5.2	28.8	7.2	0	0°

the coordination sphere. Although the preparative procedure is simple, the yield, rate of crystallization, homogeneity, and identity of the products are all sensitive to the solvent (ethanol + water) composition and apparently also to the presence of traces of acid from the preparation of the lanthanide nitrate. Thus, in addition to the structural types represented by I, II, and III we have obtained the following products:

(i) Isomorphous compounds containing yttrium and holmium were deposited from 75% EtOH in poor yield on long standing. The space-group was also $P2_1/c$ but the approximate cell dimensions, for Y, were a = 15.80(2), b = 21.45(3), c = 15.65(2) Å, β = 99.8(1)°. The crystals gave streaked or blurred diffraction spots, and intensity data were not collected.

(ii) The neodymium isomorph of III crystallized first as a minor product; the bulk of the material obtained was another monoclinic compound, *also* with space-group $P2_1/c$ but with cell dimensions a = 18.70(3), b = 10.72(2), c = 18.02(2) Å, β = 94.2(1)°.

(iii) The crystallization of the praseodymium isomorph of I was preceded by the deposition of small amounts of another orthorhombic compound, space-group $Pm2_1b$, P2mb, or Pmmb. Its cell dimensions [a = 24.73(3), b = 16.22(2), c = 7.123(8) Å] are close to those given [10] for a neodymium compound whose space-group was, however, stated to be $Pcm2_1$ or Pc2m.

Experimental

The compounds were prepared by mixing hot solutions of $Ln(NO_3)_3 \cdot 6H_2O$ (2.0 mmol) and 4-bipy·H_2O (4.0 mmol), total volume 10 cm^3, and allowing the filtered mixtures to stand at room temperature. The solvent was 95:5 EtOH:H_2O (I, III, and their isomorphs) or 75:25 EtOH:H_2O (II and its Y isomorph). In the latter case the yield of product, after several days, was too low to permit satisfactory analysis. The analytical data for I suggested that a disordered molecule of lattice water, not revealed by the structure analysis, might be present (calculated for $2La(NO_3)_3 \cdot nH_2O \cdot 4C_{10}H_8N_2$, n = 7, La 19.89, C 34.36, H, 3.32, N 14.03%; for n = 8, 19.59, 33.86, 3.39, 13.82%; found, 19.3, 33.9, 3.41, 13.8%). Analyses of III and its Ho isomorph agreed with the formulae based on structural analysis.

Crystal data have been given in Table I. Cell dimensions for all compounds were obtained from NaCl-calibrated Weissenberg photographs. All crystals were stable in air. Intensity data for I were collected by use of a Stoe STADI-2 diffractometer and Mo radiation from a crystal mounted on c (layers hk0–11); 3250 unique data were obtained with $|F| > 3\sigma(F)$. Data for II and III were collected via equi-inclination multi-film Weissenberg photographs (Cu radiation) which were scanned by the Science and Engineering Research Council Microdensitometer Service, Daresbury Laboratory, England. The layers recorded were 0–5kl and hk0–3 for II and 0–7kl and h0–71 for III; there were respectively 2134 and 2820 unique reflections above background. Data for II were corrected for absorption. The heavy-atom positions were obtained from Patterson syntheses. The Patterson synthesis for I could be interpreted for the acentric space-group $Cmc2_1$, with two

TABLE VI. Atomic Coordinates and Thermal Parameters (all × 10^4) for I, $[La_2(H_2O)_7(NO_3)_6]\cdot 4C_{10}H_8N_2$.

Atom	x	y	z	U
La(1)	0	2319(1)	3818(1)	231(4)*
La(2)	0	3536(1)	0	289(5)*
O(1)	965(5)	2831(6)	227(10)	633(78)*
O(2)	945(4)	4054(6)	740(8)	516(66)*
O(3)	1708(5)	3407(7)	681(10)	631(77)*
O(4)	952(4)	2774(7)	3162(10)	635(77)*
O(5)	917(5)	1540(7)	3588(10)	680(80)*
O(6)	1696(5)	2031(8)	3086(11)	781(92)*
O(7)	0	1530(9)	2082(13)	552(112)*
O(8)	0	2801(8)	1781(13)	470(99)*
O(9)	0	1966(9)	621(14)	559(110)*
O(10)	0	5107(9)	305(11)	464(99)*
O(11)	0	4556(10)	1761(11)	561(112)*
O(12)	0	5847(8)	1654(12)	576(103)*
Aq(1)	0	3862(7)	3711(12)	533(88)*
Aq(2)	0	1044(9)	4841(13)	540(91)*
Aq(3)	566(5)	2695(7)	5388(10)	682(79)*
Aq(4)	0	2595(7)	−1429(10)	391(79)*
Aq(5)	575(4)	4117(7)	−1381(8)	585(72)*
N(1)	1221(7)	3431(9)	567(11)	560(91)*
N(2)	1198(5)	2123(8)	3274(10)	454(77)*
N(3)	0	2064(10)	1523(12)	264(92)*
N(4)	0	5183(12)	1263(15)	481(134)*
N(5)	1582(6)	5335(9)	3352(10)	561(37)
N(6)	4095(6)	3295(9)	3057(11)	627(41)
N(7)	3431(6)	1708(8)	596(11)	610(37)
N(8)	913(5)	−369(8)	637(10)	492(32)
C(1)	2058(7)	5713(10)	3447(12)	512(41)
C(2)	2572(6)	5351(9)	3339(12)	431(36)
C(3)	2561(6)	4521(8)	3163(11)	377(33)
C(4)	2079(7)	4100(10)	3054(12)	499(41)
C(5)	1593(7)	4544(11)	3133(13)	577(45)
C(6)	4091(8)	4094(12)	3139(15)	696(53)
C(7)	3590(7)	4494(10)	3178(13)	568(44)
C(8)	3102(6)	4066(9)	3106(11)	417(35)
C(9)	3109(8)	3254(11)	2995(13)	628(50)
C(10)	3627(8)	2863(12)	2967(14)	659(52)
C(11)	3427(7)	883(10)	744(12)	516(40)
C(12)	2947(6)	487(8)	806(11)	409(34)
C(13)	2442(5)	871(7)	740(10)	309(29)
C(14)	2456(7)	1714(10)	625(14)	582(45)
C(15)	2959(9)	2094(12)	534(17)	795(57)
C(16)	934(6)	432(9)	746(12)	486(39)
C(17)	1423(6)	847(8)	841(11)	386(33)
C(18)	1913(5)	449(7)	745(9)	262(27)
C(19)	1887(5)	−376(8)	612(11)	353(30)
C(20)	1394(6)	−753(8)	586(11)	430(35)

*U is given as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i\cdot a_j$, the thermal factor being $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

TABLE VII. Atomic Coordinates and Thermal Parameters (all × 10^4) for II, $[Ho(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$.

Atom	x	y	z	U
Ho	862(1)	1239(1)	478(1)	367(4)*
O(1)	1580(13)	716(2)	223(5)	503(56)*
O(2)	504(12)	804(2)	1471(5)	515(53)*
O(3)	1280(13)	338(2)	1131(6)	571(57)*
O(4)	1741(14)	1766(2)	338(6)	479(56)*
O(5)	−860(12)	1677(2)	−3(6)	479(53)*
O(6)	114(16)	2141(2)	−73(6)	679(61)*
O(7)	3085(13)	1283(2)	1570(5)	447(53)*
O(8)	4099(13)	1223(2)	333(6)	565(61)*
O(9)	5830(16)	1302(3)	1362(10)	847(93)*
Aq(1)	1505(11)	1255(2)	−976(4)	360(43)*
Aq(2)	−493(9)	1432(2)	1665(5)	309(43)*
Aq(3)	−1802(10)	1038(2)	40(5)	353(46)*
N(1)	1148(14)	613(2)	948(6)	409(61)*
N(2)	327(20)	1869(2)	82(6)	516(71)*
N(3)	4365(17)	1272(2)	1096(8)	439(67)
N(4)	2717(13)	1952(3)	3031(7)	473(27)
N(5)	−895(13)	3356(2)	1587(7)	472(25)
N(6)	335(13)	4149(2)	2807(7)	403(25)
N(7)	−2107(14)	5487(2)	578(7)	452(25)
C(1)	2137(19)	2166(3)	3593(10)	574(36)
C(2)	1380(17)	2437(3)	3306(9)	490(33)
C(3)	1326(15)	2616(2)	2469(8)	321(23)
C(4)	1931(17)	2293(3)	1902(9)	452(31)
C(5)	2642(16)	2028(3)	2224(8)	420(30)
C(6)	−116(19)	3170(3)	1042(10)	564(36)
C(7)	630(17)	2888(3)	1304(9)	502(33)
C(8)	560(14)	2809(2)	2178(7)	324(25)
C(9)	−137(16)	3026(3)	2726(8)	337(25)
C(10)	−914(18)	3283(3)	2422(8)	443(29)
C(11)	314(17)	4147(3)	1952(8)	430(30)
C(12)	−203(15)	4402(3)	1471(8)	370(26)
C(13)	−576(14)	4674(2)	1890(7)	311(24)
C(14)	−510(15)	4679(3)	2792(8)	367(28)
C(15)	−45(18)	4413(3)	3214(9)	455(31)
C(16)	−2379(17)	5210(3)	241(8)	469(33)
C(17)	−1929(16)	4939(3)	653(7)	368(26)
C(18)	−1099(14)	4955(2)	1425(7)	296(22)
C(19)	−731(16)	5250(3)	1774(9)	474(31)
C(20)	−1339(17)	5499(3)	1334(9)	467(31)

$^*U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i\cdot a_j$.

TABLE VIII. Atomic Coordinates and Thermal Parameters (all × 10^4) for III, $[Y(H_2O)_3(NO_3)_3]\cdot 2C_{10}H_8N_2$.

Atom	x	y	z	U_{eq}*
Y	1657(1)	2222(1)	2261(1)	287(3)
O(1)	2487(7)	1266(2)	1654(3)	465(30)
O(2)	3410(7)	1307(2)	2980(3)	424(30)
O(3)	3911(10)	455(3)	2309(4)	720(44)
O(4)	−1185(7)	2355(2)	2602(4)	452(31)
O(5)	−269(7)	1393(3)	2559(5)	641(41)
O(6)	−2789(8)	1564(4)	2805(6)	929(56)

(continued overleaf)

TABLE VIII. *(continued)*

Atom	x	y	z	U_{eq}*
O(7)	–564(7)	2132(3)	948(3)	528(33)
O(8)	1880(6)	2525(3)	844(3)	452(30)
O(9)	–284(9)	2495(4)	–250(4)	659(44)
Aq(1)	1134(7)	3308(3)	2088(3)	471(30)
Aq(2)	4534(6)	2523(2)	2416(3)	419(30)
Aq(3)	2295(7)	2438(3)	3689(3)	445(29)
N(1)	3286(9)	989(3)	2318(4)	458(38)
N(2)	–1472(8)	1763(4)	2665(5)	520(42)
N(3)	321(8)	2390(3)	484(4)	430(36)
N(4)	5788(9)	3346(4)	1449(5)	640(48)
N(5)	8225(9)	5822(4)	–958(5)	566(45)
N(6)	68(13)	4150(5)	3162(5)	844(60)
N(7)	4491(11)	3360(4)	4417(5)	650(47)
C(1)	5937(21)	3230(6)	688(10)	1157(113)
C(2)	6417(21)	3703(5)	185(8)	1022(95)
C(3)	6886(9)	4293(3)	502(5)	388(38)
C(4)	6782(16)	4404(6)	1302(6)	893(75)
C(5)	6260(18)	3901(7)	1739(6)	965(88)
C(6)	7692(19)	5250(6)	–1289(7)	871(83)
C(7)	7275(15)	4733(5)	–834(6)	756(70)
C(8)	7387(8)	4822(3)	–1(4)	341(35)
C(9)	7925(16)	5410(5)	343(6)	688(62)
C(10)	8321(5)	5809(5)	–167(7)	794(73)
C(11)	–331(18)	3858(5)	3792(7)	849(76)
C(12)	–442(19)	4166(5)	4516(7)	892(81)
C(13)	25(11)	4828(4)	4624(5)	551(49)
C(14)	385(13)	5132(5)	3926(6)	659(58)
C(15)	408(17)	4771(6)	3220(7)	891(83)
C(16)	4569(18)	3546(5)	5188(8)	923(84)
C(17)	4743(18)	4186(3)	5435(7)	871(76)
C(18)	4904(10)	4663(4)	4872(5)	499(46)
C(19)	4927(17)	4449(5)	4093(6)	806(69)
C(20)	4676(16)	3808(5)	3862(6)	769(66)

*$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

independent La atoms on a mirror plane at Oyz, but not for the centric Cmcm. Other atoms were located in difference Fourier syntheses. In the later stages of refinement some reflections judged to be affected by extinction or to have been badly measured were omitted (9 for I and 10 for II). Block-matrix least-squares refinement with anisotropic thermal parameters for atoms of the coordination complexes, and for 4-bipy also in the case of III, converged as follows: I, R = 0.094, R_w = 0.074, 3241 data, 253 parameters, w = $[\sigma^2(F) + 0.00052F^2]^{-1}$ in last cycle; II, R = 0.060, R_w = 0.067, 2124 data, 231 parameters, w = $[1 + 0.00052F^2]^{-1}$ in last cycle; III, R = 0.058, R_w = 0.061, 2820 data, 351 parameters, w = $[1 + 0.00499F^2]^{-1}$ in last cycle. No attempt was made to locate H atoms or include them in the calculations. The SHELX 76 program [11] was used in all calculations. Atomic coordinates are given in Tables VI, VII and VIII for I, II, and III respectively.

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