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The Crystal Structures of 4,4′-Bipyridinium(+1) Tetranitratodiaqua(4,4′-bipyridyl)neodymiate(III) and Trinitratotetraaquaytterbium(III)-4,4′-Bipyridinium(+1) Nitrate (1/2)

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The structures of $(C_{10}H_9N_2)[Nd(NO_3)_4(H_2O)_2(C_{10}H_8N_2)]$ *[*$P2_12_12_1$, a = 7.214(4), b = 19.928(9), c = 18.515(9) Å, Z = 4; R = 0.066 *for 3481 reflections] and* $Yb(NO_3)_3(H_2O)_4\cdot 2(C_{10}H_9N_2)(NO_3)$ *[*$P\bar{1}$, a = 15.184(10), b = 12.755(12), c = 8.156(10) Å, α = 79.75(13), β = 78.49(5), γ = 95.09(5)°, Z = 2; R = 0.076 *for 3349 reflections] have been solved from, respectively, diffractometer and film data. In both compounds, ligand* NO_3 *groups are bidentate. In the Nd compound, one 4,4′-bipyridyl is protonated, and the other is a ligand; Nd is 11-coordinate, with bond lengths Nd–O(*NO_3*)(av.), 2.626; Nd–*OH_2 *(av.), 2.484; Nd–N, 2.767 Å. In the Yb compound, both bipyridyls are protonated and un-coordinated; Yb is 10-coordinate, with Yb–O(*NO_3*)(av.), 2.592; Yb–*OH_2*(av.) 2.471 Å. There is extensive hydrogen bonding in three dimensions in both compounds. The Nd compound has a Pr isomorph, and the Yb compound has a Nd isomorph.*

Introduction

Adducts of hydrated lanthanide nitrates with 4,4′-bipyridyl (4-bipy) of general formula $Ln(NO_3)_3(H_2O)_n(4\text{-bipy})_2$ have been reported. The values of n are variously stated to be 2 to 6, for all lanthanides and Y [1]; 2, for Ln = La, Nd, Sm, and Tb [2]; and 4 for Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, and Ho, 3 = for Ln = Yb, and 2 for Ln = Lu [3, 4]. The infra-red spectra [3, 4] have been interpreted as showing the presence of coordinated 4-bipy. We undertook a structural study of these compounds in order to ascertain (a) whether more than one compound exists for any lanthanide; (b) whether the structural type is dependent on the radius of Ln^{3+}; and (c) whether 4-bipy, which cannot act as a chelating ligand, is indeed coordinated, either to a single cation, or as a bridge between cations. The compounds whose structures are reported in this first paper prove to contain cationic 4-bipyH^+.

Results and Discussion

The compounds are $(4\text{-bipyH})[Nd(NO_3)_4(H_2O)_2(4\text{-bipy})]$ (I), space-group $P2_12_12_1$, which has an isomorph (II) containing Pr; and $[Yb(NO_3)_3(H_2O)_4]\cdot 2(4\text{-bipyH})(NO_3)$ (III), which has an isomorph (IV) containing Nd. The formulae are derived from X-ray determinations of the structures of I and III. The criteria of isomorphism are identity of space-group and a close similarity in cell dimensions and in the distributions of intensities in corresponding Weissenberg photographs. The Ln:4-bipy ratio is 2 in both pairs of compounds, but only in I and II is a 4-bipy molecule coordinated to Ln, and the non-coordinated 4-bipy molecules are protonated in all four compounds. The preparative procedure (Experimental section), from Ln_2O_3 *without* intermediate isolation of the crystalline nitrate, evidently results in the introduction of excess nitric acid.

Compounds I and II are isostructural with $(4\text{-bipyH})[Ce(NO_3)_4(H_2O)_2(4\text{-bipy})]$ whose composition was deduced [5] from the X-ray structural analysis (of which we were initially unaware) of a compound earlier thought to be $Ce(NO_3)_3(H_2O)_4(4\text{-bipy})_2$. The cell dimensions and space-group of '$La(NO_3)_3(H_2O)_4(4\text{-bipy})_2$' [6] strongly suggest that it is isostructural with I, II, and the Ce compound. Thus an isomorphous series $(4\text{-bipyH})[Ln(NO_3)_4(H_2O)_2(4\text{-bipy})]$ exists for Ln = La, Ce, Pr, and Nd. The Ce compound has been described in detail [5], so we give only the principal features of the structure of I (Fig. 1). The Nd atom is present in a complex anion with the relatively unusual coordination number of 11. The set of ligand atoms comprises eight oxygen atoms of four bidentate NO_3^- ligands, two water oxygens, and a 4-bipy nitrogen atom, N(6). The bond lengths (Table I) closely parallel those in the Ce isomorph but are *ca.* 0.06 Å shorter. Mean

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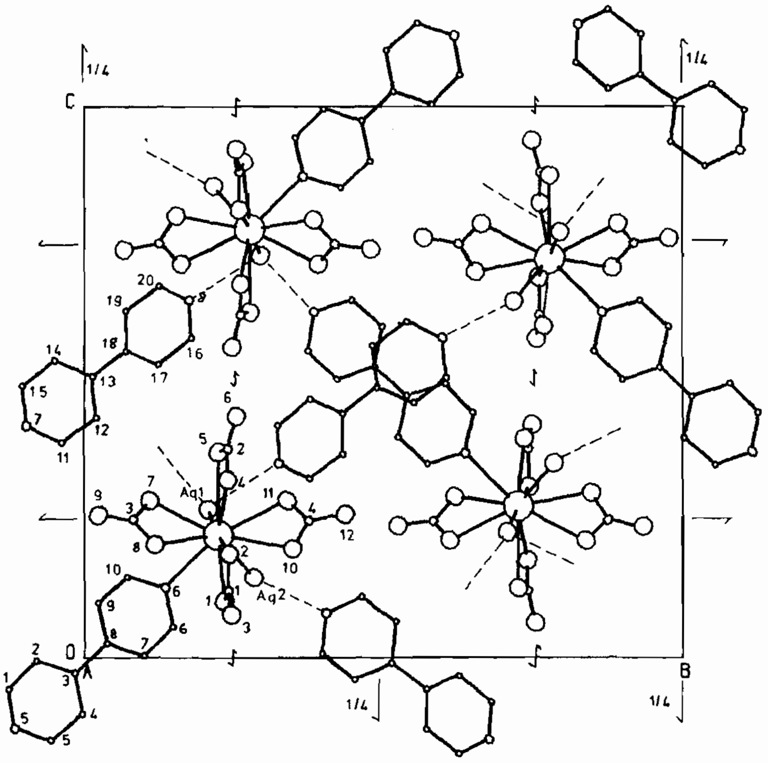


Fig. 1. I, (4-bipyH)[Nd$(NO_3)_4(H_2O)_2$(4-bipy)] : *a*-axis projection.

TABLE I. Selected Molecular Dimensions for I, $(C_{10}H_9N_2)Nd(NO_3)_4(H_2O)_2(C_{10}H_8N_2)$.

(i) Nd coordination sphere			
Nd–O(1)	2.551(10) Å	Nd–O(10)	2.654(11) Å
Nd–O(2)	2.698(13)	Nd–O(11)	2.616(13)
Nd–O(4)	2.498(13)	Nd–Aq(1)	2.533(10)
Nd–O(5)	2.780(11)	Nd–Aq(2)	2.434(11)
Nd–O(7)	2.561(10)	Nd–N(6)	2.767(12)
Nd–O(8)	2.606(13)		
O(1)–Nd–O(2)	48.3(3)°	O(7)–Nd–O(8)	49.1(4)°
O(4)–Nd–O(5)	46.6(4)	O(10)–Nd–O(11)	48.7(4)
(ii) Nitrate groups			
N(1)–O(1)	1.25(2) Å	N(3)–O(7)	1.25(2) Å
N(1)–O(2)	1.29(2)	N(3)–O(8)	1.25(2)
N(1)–O(3)	1.21(2)	N(3)–O(9)	1.22(2)
N(2)–O(4)	1.23(2)	N(4)–O(10)	1.32(2)
N(2)–O(5)	1.23(2)	N(4)–O(11)	1.23(2)
N(2)–O(6)	1.23(2)	N(4)–O(12)	1.20(2)
(iii) Hydrogen bonds			
Aq(1)··O(2)	2.83(3) Å	Aq(2)··N(7^{ii})	2.76(3) Å
Aq(2)··O(3)	2.81(3)	Aq(1)··N(8^{iii})	2.89(3)
Aq(1)··N(5^{i})	2.68(3)		

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

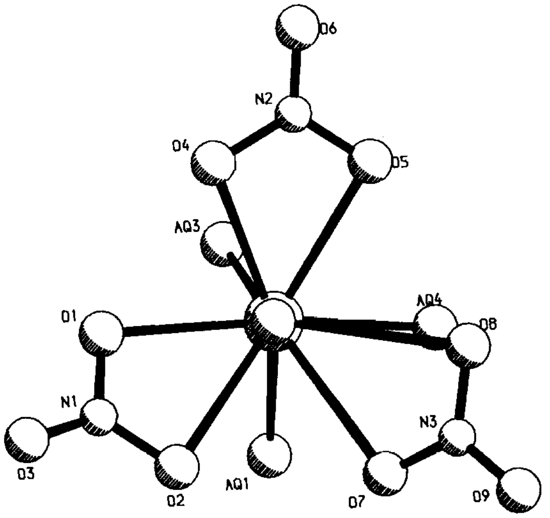


Fig. 2. III, $[Yb(NO_3)_3(H_2O)_4]\cdot2(4\text{-bipyH})(NO_3)$: coordination sphere viewed along Aq(2)–Yb bond.

values are 2.621 Å for Nd–O(NO_3) and 2.484 Å for Nd–OH_2. No hydrogen atoms were located, but the lengths and orientations of the N••O vectors strongly imply the existence of hydrogen bonds between ligand H_2O molecules and un-coordinated 4-bipy nitrogen atoms. The protonated nitrogen atom was identified in the Ce isomorph [5] as the one here designated N(8). The complex anions are also more directly linked, *via* NO_3••H_2O bonds, into chains along [100]. As a result of hydrogen bonding, two interpenetrating but unconnected networks are present.

In III and IV (Figs. 2 and 3) the lanthanide atom is 10-coordinate, and the ligand atoms are six oxygens of bidentate NO_3 groups and four water oxygen atoms. Bond lengths for III are given in Table II; average values are 2.592 Å for Yb–O(NO_3) and 2.471 Å for Yb–OH_2. Roughly, the NO_3 groups lie at the corners of one face of a distorted octahedron centred on Yb; this face is capped by a water molecule, Aq(2), and the other water molecules occupy the other three corners (Fig. 2). The Yb atom lies close to the mean planes of the NO_3 ligands, which are tilted up towards Aq(2) [the normals to these planes make angles of 144, 147, and 161° with the Yb–Aq(2) bond] and are also all tilted about the Yb••N directions so that their six ligand atoms lie alternately above and below the mean plane through them. As in I, the complexes are linked directly by NO_3••H_2O hydrogen bonds, across an inversion

TABLE II. Selected Molecular Dimensions for III, $[Yb(NO_3)_3(H_2O)_4]\cdot2(C_{10}H_9N_2)(NO_3)$.[a]

(i) Yb coordination sphere			
Yb–O(1)	2.563(12) Å	Yb–O(8)	2.798(14) Å
Yb–O(2)	2.599(10)	Yb–Aq(1)	2.440(11)
Yb–O(4)	2.582(13)	Yb–Aq(2)	2.507(11)
Yb–O(5)	2.514(10)	Yb–Aq(3)	2.480(10)
Yb–O(7)	2.494(9)	Yb–Aq(4)	2.455(10)
O(1)–Yb–O(2)	49.1(4)°	O(7)–Yb–O(8)	47.3(3)°
O(4)–Yb–O(5)	50.5(4)		
(ii) Nitrate groups			
N(1)–O(1)	1.287(14) Å	N(3)–O(9)	1.265(17) Å
N(1)–O(2)	1.255(17)	N(4)–O(10)	1.210(25)
N( )–O(3)	1.199(15)	N(4)–O(11)	1.244(20)
N(2)–O(4)	1.272(17)	N(4)–O(12)	1.245(21)
N(2)–O(5)	1.292(17)	N(5)–O(13)	1.239(18)
N(2)–O(6)	1.199(15)	N(5)–O(14)	1.210(20)
N(3)–O(7)	1.247(17)	N(5)–O(15)	1.260(19)
N(3)–O(8)	1.242(16)		
(iii) Hydrogen bonds			
N(6)••O(7′)	2.98(2) Å	O(3)••Aq(2′)	2.92(2) Å
N(6)••O(9′)	2.93(2)	O(9)••Aq(3′)	2.88(2)
N(7)••Aq(1)	2.76(2)	O(10)••Aq(2)	2.71(2)
N(8)••Aq(4′)	2.79(2)	O(11)••Aq(3)	2.70(2)
N(9)••O(13′)	2.73(2)	O(13)••Aq(4)	2.83(2)
N(9)••O(15′)	3.04(3)	O(14)••Aq(1′)	2.91(2)

[a] Primed and unprimed atoms are related by an inversion centre.

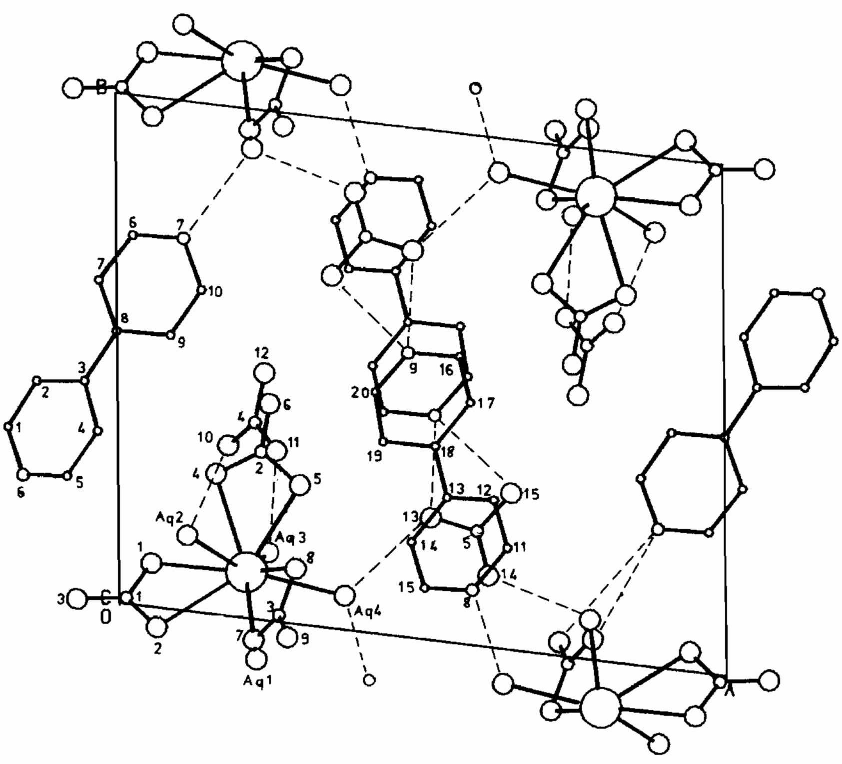
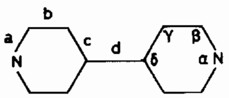


Fig. 3. III, $[Yb(NO_3)_3(H_2O)_4]\cdot2(4\text{-bipyH})(NO_3)$: *c*-axis projection.

TABLE III. Summary of Dimensions of 4,4'-Bipyridyl Molecules. Standard Deviations are *ca.* 0.02 Å and 1.5°.

 Bond or angle type	Pyridine rings		Pyridinium rings	
	Range	Mean	Range	Mean
a	1.32–1.38 Å	1.35 Å	1.30–1.38 Å	1.35 Å
b	1.36–1.44	1.40	1.36–1.45	1.40
c	1.37–1.43	1.40	1.36–1.45	1.40
α	115–121°	118°	120–125°	122°
β	121–125	123	116–124	120
γ	118–120	119	115–122	119
δ	117–119	118	116–122	119
		d	Dihedral angle	
	4,4'-bipyridyl	1.49 Å	1.4°	
	4,4'-bipyridinium(+1)	1.46	14.9	
		1.47	18.1	
		1.48	3.4	

centre and along [001]. The lengths and orientations of the other short N··O vectors imply, firstly, that the non-coordinated NO_3 anions form hydrogen bonds to ligand water molecules and secondly, that the 4-bipy nitrogen atoms also participate in hydrogen bonds. Atoms N(6) and N(9) are deduced to be protonated as they each make two close contacts with nitrate O atoms (bifurcated hydrogen bonds), while N(7) and N(8) form N••H-OH bonds.

The dimensions of the 4-bipy molecules in I and III are summarised in Table III. At the level of resolution achieved in the present work, there is no ***significant*** difference in dimensions between the protonated and unprotonated rings, although the apparent increase in the ring angle at N upon protonation and associated decrease in the angle at the adjacent carbon agree with the observations [5] for the Ce isomorph of I. All pyridyl rings are effectively planar but in each 4-bipy molecule the plane of one ring is rotated with respect to the other about the central C–C bond; although the range of observed dihedral angles is appreciable (Table III), the values do not correlate significantly with the length of the central bond, and it seems that the different dihedral angles merely reflect the requirements of molecular packing.

Our continuing work indicates that the above are only two of the several structural types exhibited by hydrated adducts of 4-bipy and lanthanide nitrates. The nature of the product isolated is evidently sensitive to the presence of small amounts of excess HNO_3 and possibly also to the solvent EtOH: H_2O ratio. For each of the elements Ho and Y, we have obtained not only an orthorhombic (Pbca) compound in which the Ln:NO_3 ratio is 1:3 and only neutral 4-bipy is present, but also two monoclinic compounds of currently-uncertain composition. We also note that an orthorhombic compound containing Nd has been stated [6] to have a space-group (Pcm2_1, Pc2m, or Pcmm) and cell dimensions which imply that it is not identical with compound I. We hope that structural studies now in progress will make matters clearer.

Experimental

The compounds were prepared essentially as described in ref. [1], by mixing warm solutions of $Ln(NO_3)_3$•aq and 4-bipy in 95:5 EtOH:H_2O (I, II) or 75:25 EtOH:H_2O (III, IV). We noted that clear solutions obtained by adding 4 *M* HNO_3 to suspensions of Ln_2O_3 in warm water became turbid on evaporation at 95 °C unless excess acid was present. In the case of III and IV, the product initially deposited was microcrystalline, but when the mixtures were left for up to four weeks in polyethylene-capped vials, with partial evaporation, larger crystals appeared although unfortunately not in amounts permitting satisfactory chemical analysis.

Crystal data: I, $C_{20}H_{21}N_8NdO_{14}$: orthorhombic, $P2_12_12_1$, a = 7.214(4), b = 19.928(9), c = 18.515(9) Å, Z = 4, d_{calc} = 1.849 g cm^{-3}; Mo Kα radiation (λ = 0.71069 Å), μ = 20.0 cm^{-1}.

TABLE IV. Atomic Coordinates and Thermal Parameters (all × 10^4) for I, $(C_{10}H_9N_2)[Nd(NO_3)_4(H_2O)_2(C_{10}H_8N_2)]$.

Atom	x	y	z	U
Nd	1783(1)	2236(1)	2240(1)	320(3)*
O(1)	3410(17)	2341(6)	1021(5)	445(57)*
O(2)	5378(18)	2420(6)	1891(5)	548(68)*
O(3)	6321(16)	2460(6)	776(6)	558(71)*
O(4)	4087(20)	2392(6)	3233(6)	615(77)*
O(5)	1511(17)	2234(7)	3738(6)	562(68)*
O(6)	3844(23)	2532(8)	4376(6)	845(104)*
O(7)	1705(21)	1089(5)	2862(5)	507(61)*
O(8)	3852(21)	1176(6)	2065(6)	643(81)*
O(9)	3402(26)	231(6)	2599(8)	839(97)*
O(10)	3006(22)	3471(5)	1994(6)	580(70)*
O(11)	998(24)	3379(6)	2863(7)	786(95)*
O(12)	2059(30)	4343(5)	2612(7)	896(103)*
Aq(1)	−1479(14)	2063(4)	2709(5)	377(48)*
Aq(2)	−369(17)	2836(5)	1460(5)	492(60)*
N(1)	5069(22)	2405(6)	1207(6)	462(75)*
N(2)	3155(24)	2390(6)	3790(6)	439(67)*
N(3)	2996(20)	822(6)	2512(7)	422(66)*
N(4)	1962(24)	3750(6)	2493(7)	468(69)*
N(5)	−2551(20)	−1170(6)	−1273(7)	469(32)
N(6)	172(18)	1347(6)	1279(6)	397(27)
N(7)	544(22)	−974(7)	4207(8)	538(35)
N(8)	2499(22)	1751(7)	6482(8)	571(38)
C(1)	−2580(25)	−1272(8)	−569(9)	512(40)
C(2)	−2076(23)	−800(7)	−46(8)	437(34)
C(3)	−1440(21)	−161(7)	−272(8)	385(82)
C(4)	−1409(24)	−34(8)	−1013(8)	468(36)
C(5)	−2016(26)	−552(8)	−1493(8)	503(38)
C(6)	175(22)	1479(7)	563(3)	402(31)
C(7)	−452(22)	1010(7)	40(7)	369(30)
C(8)	−975(20)	374(7)	257(7)	315(26)
C(9)	−1002(23)	233(7)	1002(8)	429(33)
C(10)	−454(25)	720(8)	1477(8)	472(36)
C(11)	1094(25)	−384(8)	3910(9)	492(38)
C(12)	1488(25)	191(8)	4353(8)	480(37)
C(13)	1280(20)	125(7)	5108(7)	355(30)
C(14)	764(24)	−498(8)	5393(8)	449(37)
C(15)	327(30)	−1035(9)	4929(10)	603(47)
C(16)	3188(34)	1783(9)	5794(10)	646(45)
C(17)	2694(23)	1235(8)	5318(8)	466(37)
C(18)	1708(25)	704(7)	5571(7)	412(29)
C(19)	966(29)	696(9)	6298(10)	592(46)
C(20)	1498(32)	1246(10)	6741(10)	668(50)

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

II, $C_{20}H_{21}N_8O_{14}Pr$: orthorhombic, $P2_12_12_1$, a = 7.264(8), b = 19.92(2), c = 18.52(2) Å, Z = 4, d_{calc} = 1.829 g cm^{-3}.

III, $C_{20}H_{26}N_9O_{19}Yb$; triclinic, P$\bar{1}$, a = 15.184(10), b = 12.755(12), c = 8.156(10) Å, α = 79.75(13), β = 78.49(5), γ = 95.09(5)°, Z = 2, d_{calc} = 1.911 g cm^{-3}. Cu Kα radiation (λ = 1.5418 Å), μ = 66.0 cm^{-1}.

TABLE V. Atomic Coordinates and Thermal Parameters (all × 10^4) for III, $[Yb(NO_3)_3(H_2O)_4]\cdot 2(C_{10}H_9N_2)(NO_3)$.

Atom	x	y	z	U
Yb	2093(1)	918(1)	1663(1)	59(3)*
O(1)	528(7)	869(10)	924(15)	321(65)*
O(2)	605(7)	−381(8)	3014(13)	254(56)*
O(3)	−705(7)	−9(11)	2587(16)	351(66)*
O(4)	1611(7)	2783(11)	725(14)	324(64)*
O(5)	2983(7)	2750(8)	1131(14)	308(55)*
O(6)	2497(9)	4272(9)	358(15)	361(63)*
O(7)	2204(7)	−401(8)	4245(12)	207(49)*
O(8)	2908(8)	1095(10)	4408(16)	365(66)*
O(9)	2760(9)	−272(10)	6494(13)	395(67)*
Aq(1)	2245(7)	−775(8)	697(13)	227(53)*
Aq(2)	1124(7)	1498(9)	4124(13)	251(57)*
Aq(3)	2455(9)	1364(9)	−1504(13)	356(63)*
Aq(4)	3703(6)	679(9)	997(14)	247(57)*
O(10)	1822(12)	3391(16)	4720(22)	677(47)
O(11)	2614(10)	3367(12)	6604(17)	441(32)
O(12)	2418(10)	4866(13)	5040(18)	479(35)
O(13)	5124(8)	2406(10)	237(14)	305(26)
O(14)	6095(10)	1407(12)	1104(18)	463(34)
O(15)	6475(10)	3073(12)	−57(17)	454(33)
N(1)	107(8)	129(10)	2197(14)	162(57)*
N(2)	2360(8)	3310(9)	736(15)	191(58)*
N(3)	2627(8)	136(10)	5046(15)	218(61)*
N(4)	2268(9)	3870(11)	5493(16)	234(27)
N(5)	5893(8)	2250(11)	435(16)	215(26)
N(6)	−1586(10)	2312(12)	2930(17)	294(30)
N(7)	1109(9)	7310(12)	1821(17)	278(29)
N(8)	5813(9)	1068(12)	6931(17)	265(28)
N(9)	4799(10)	5607(13)	1734(18)	328(32)
C(1)	−1828(11)	3196(14)	2094(21)	283(34)
C(2)	−1318(10)	4189(12)	1862(18)	197(29)
C(3)	−549(9)	4285(11)	2591(16)	140(26)
C(4)	−341(11)	3337(13)	3493(19)	244(32)
C(5)	−850(11)	2374(14)	3673(20	279(34)
C(6)	266(11)	7246(15)	1503(21)	294(35)
C(7)	−301(11)	6286(14)	1744(20)	256(33)
C(8)	−13(8)	5333(10)	2347(15)	89(23)
C(9)	886(9)	5377(12)	2647(17)	179(28)
C(10)	1383(12)	6354(15)	2410(21)	302(36)
C(11)	6396(11)	1984(14)	6437(20)	271(33)
C(12)	6186(16)	2896(20)	5499(29)	530(55)
C(13)	5407(9)	2855(11)	4828(16)	121(25)
C(14)	4818(14)	1909(18)	5321(25)	432(46)
C(15)	5027(13)	1023(16)	6377(23)	361(40)
C(16)	5609(11)	5634(15)	2217(21)	295(35)
C(17)	5801(10)	4741(13)	3188(19)	224(31)
C(18)	5203(9)	3793(11)	3674(17)	149(27)
C(19)	4375(11)	3785(14)	3187(20)	257(33)
C(20)	4223(13)	4733(16)	2186(23)	366(41)

*U is given as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i a_j a_i^* \cdot a_j^*$.

IV, $C_{20}H_{26}N_9NdO_{19}$; triclinic, $P\bar{1}$, a = 15.17(2), b = 12.79(2), c = 8.126(13) Å, α = 80.1(1), β = 78.6(1), γ = 95.1(1)°, Z = 2, d_{calc} = 1.848 g cm^{-3}.

Intensity data for I were collected by use of a Stoe STADI-2 two-circle diffractometer, from a crystal mounted on a (layers 0–8); 3481 independent reflections with $|F| > 4\sigma(F)$ were recorded. Because of the limited availability of the diffractometer, data for III were collected via equi-inclination multi-film Weissenberg photographs (layers 0–5kl and hk0–3) which were scanned by the Science Research Council Microdensitometer Service, Daresbury Laboratory, England; 3349 independent reflections were above background. Both structures were solved in a straightforward manner by location of the heavy atom from a Patterson synthesis followed by cycles of least-squares refinement alternating with difference syntheses. No attempt was made to locate hydrogen atoms. In the later stages, the lanthanide atoms and the N and O atoms of ligand NO_3 groups and water molecules were assigned anisotropic thermal parameters, and the parameters were refined in blocks grouped by atoms. Refinement terminated at R 0.066 for I (268 parameters, unit weights for all reflections) and at R 0.076, R_w 0.080 for III (241 parameters, weighting factor w = $[1 + 0.00037F^2]^{-1}$ in last cycle). The use of a weighting scheme for I did not lead to a significant decrease in the residual or in standard deviations, nor did the use of absorption-corrected data for either compound. The SHELX-76 program [7] was used in all calculations. Values of the atomic coordinates and U_{iso} or U_{eq} are given in Table IV for I and in Table V for III.

References

1 N. I. Lobanov and A. I. Vlasov, *Zh. Neorg. Khim., 13,* 395 (1968).

2 A. Anagnastopoulos, *J. Inorg. Nucl. Chem., 35,* 3611 (1973).

3 M. D. Czakis-Sulikowska and J. Radwanska-Doczekalskaya, *Roczniki Chem., 49,* 197 (1975).

4 M. D. Czakis-Sulikowska and J. Radwanska-Doczekalskaya, *Roczniki Chem. 50,* 2181 (1976).

5 M. Bukowska-Strzyzewska and A. Tosik, *Inorg. Chim. Acta, 30,* 189 (1978).

6 M. Bukowska-Strzyzewska and A. Tosik, *Roczniki Chem., 51,* 193 (1977).

7 G. M. Sheldrick, SHELX-76 Program for Crystal Structure Determination, Cambridge University, 1975.