The Crystal Structures of 4,4′-Bipyridinium μ-(4,4′-Bipyridine)bis[diaquatetranitratoneodymate(III)]-Tris(4,4′-bipyridine) and a Second Monoclinic Form of Triaquatrinitratoholmium(III) – Bis (4,4′-bipyridine)

TIMOTHY J. R. WEAKLEY

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

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The structures of $(4\text{-bipyH})_2[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]\cdot 3(4\text{-bipy})$ *(4-bipy = 4,4′-bipyridine;* $P2_1/c$, a = *18.723(10),* b = *10.720(6),* c = *18.027(10) Å, β = 94.43(5)°, Z = 2;* R = *0.066 for 4931 diffractometer data) and of a second monoclinic form of* $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$ *(*$P2_1/c$, a = *15.830(10),* b = *21.44(3),* c = *15.70(3) Å, β = 100.4(2)°, Z = 8;* R = *0.091 for 2335 film data) are reported. In the first compound pairs of Nd atoms are bridged across a crystal inversion centre by a 4-bipy ligand, and 10-coordination is completed by one monodentate* NO_3*, three bidentate* NO_3*, and two* H_2O *ligands, with bond lengths Nd–N 2.70, Nd–*OH_2 *(av.) 2.44, Nd–O(*NO_3*, av.) 2.56 Å. The second compound has a variant of the previously-reported monoclinic* $[Y(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$ *structure, with doubling of the unit cell on* a *but with essentially no change in the geometry and orientation of the nine-coordinate complex. In both compounds the non-coordinated, non-protonated 4-bipy N atoms form hydrogen bonds with ligand* H_2O*.*

Introduction

Adducts of 4,4′-bipyridine (4-bipy) with the hydrated nitrates of all lanthanide elements were originally formulated $Ln(NO_3)_3,nH_2O,2(4\text{-bipy})$ (n = 2 to 6) [1, 2]. Single-crystal diffraction studies have shown that several structurally-distinct series exist, in some of which a 4-bipy molecule is protonated. The nature of the product obtained is sensitive to the presence of traces of acid and to the solvent (EtOH/H_2O) composition, and a given mixture may [3] yield crystals of two compounds. The structures of the following have been published: (4-bipyH) $[Ce(NO_3)_4(H_2O)_2(4\text{-bipy})]$ [4] and its Nd isomorph [5]; $[Yb(NO_3)_3(H_2O)_4]\cdot 2(4\text{-bipyH})(NO_3)$ [5]; $[La_2(NO_3)_6(H_2O)_7]\cdot 4(4\text{-bipy})$ [3]; $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$ (orthorhombic) [3]; $[Y(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$ (I, monoclinic) [3]. Each of these is isomorphous with a derivative of at least one other lanthanide element (in the case of I, seven other elements including Nd and Ho). We now report the structures of two of the three other compounds whose formation was noted earlier [3]; a second monoclinic compound (II) containing Ho and a second monoclinic compound (III) containing Nd. The structural analysis of the third compound, of probable composition $[Pr(NO_3)_3(H_2O)_n]\cdot 2(4\text{-bipy})$ (IV, orthorhombic, n = 3 or 4), was abandoned when the emerging structure appeared to be severely disordered.

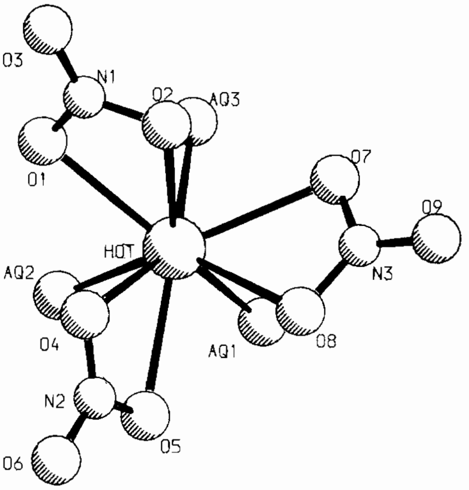

Fig. 1. The $Ho(NO_3)_3(H_2O)_3$ complex in II.

Results and Discussion

Crystals of II, $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$, like those of the yttrium isomorph [3], were of poor quality but afforded intensity data adequate for the resolution of the structure. The main point of interest is that II is structurally related to I [3]; in II, heavy atoms related in the parent structure by the *a* translation have undergone small relative displacements so that the cell is doubled in the *a* direction compared with that of I and there are now two formulae in the asymmetric unit. The space-group, however, remains $P2_1/c$. The $Ln(NO_3)_3(H_2O)_3$ complexes in the two

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TABLE I. Bond Lengths and Angles for II, $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$.

Ho(1)–O(1)	2.47(2) Å	N(2)–O(4)	1.24(3) Å	Ho(2)–Aq(4)	2.28(2) Å
Ho(1)–O(2)	2.42(2)	N(2)–O(5)	1.25(3)	Ho(2)–Aq(5)	2.32(3)
Ho(1)–O(4)	2.63(2)	N(2)–O(6)	1.22(4)	Ho(2)–Aq(6)	2.34(2)
Ho(1)–O(5)	2.49(2)	N(3)–O(7)	1.26(3)	N(4)–O(10)	1.28(3)
Ho(1)–O(7)	2.52(3)	N(3)–O(8)	1.28(3)	N(4)–O(11)	1.29(4)
Ho(1)–O(8)	2.42(2)	N(3)–O(9)	1.27(4)	N(4)–O(12)	1.22(3)
Ho(1)–Aq(1)	2.30(2)	Ho(2)–O(10)	2.46(2)	N(5)–O(13)	1.30(4)
Ho(1)–Aq(2)	2.33(2)	Ho(2)–O(11)	2.43(2)	N(5)–O(14)	1.25(4)
Ho(1)–Aq(3)	2.35(2)	Ho(2)–O(13)	2.51(2)	N(5)–O(15)	1.20(3)
N(1)–O(1)	1.25(3)	Ho(2)–O(14)	2.44(2)	N(6)–O(16)	1.26(3)
N(1)–O(2)	1.28(3)	Ho(2)–O(16)	2.42(2)	N(6)–O(17)	1.27(3)
N(1)–O(3)	1.22(3)	Ho(2)–O(17)	2.47(2)	N(6)–O(18)	1.23(4)

O(1)–Ho(1)–O(2)	51.9(7)°	O(10)–Ho(2)–O(11)	53.0(8)°
O(4)–Ho(1)–O(5)	51.3(6)	O(13)–Ho(2)–O(14)	51.5(7)
O(7)–Ho(1)–O(8)	52.1(7)	O(16)–Ho(2)–O(17)	51.7(6)

4,4′-bipyridine

Bond type		Ring angles	
N–C(α)	1.27–144(5), av. 1.34 Å	N	113–121(3), av. 118°
C(α)–C(β)	1.33–1.45(5), av. 1.38	C(α)	115–128(3), av. 123
C(β)–C(γ)	1.36–1.43(5), av. 1.39	C(β)	114–122(3), av. 119
C(γ)–C(γ′)	1.45–1.54(5), av. 1.51	C(γ)	114–121(5), av. 118

Probable hydrogen bonds

Aq(1)···O(3^{i})	2.94(4)	Aq(4)···O(12^{i})	2.93(4)
Aq(1)···N(8^{ii})	2.65(4)	Aq(4)···N(9^{i})	2.73(4)
Aq(2)···O(15^{iii})	2.78(4)	Aq(5)···O(9)	2.91(4)
Aq(2)···N(11^{iv})	2.67(4)	Aq(5)···N(13)	2.67(4)
Aq(3)···N(14^{iv})	2.76(4)	Aq(6)···N(12)	2.72(4)
Aq(3)···N(10^{ii})	2.81(4)	Aq(6)···N(7^{i})	2.92(4)

^{i}x, ½ − y, −½ + z. ^{ii}−x, ½ + y, ½ − z. ^{iii}−1 + x, y, z. ^{iv}−x, 1 − y, 1 − z.

structures are very similar both in geometry (approximate three-fold symmetry, Fig. 1) and in orientation. Details are given in Table I. As in I, the lengths and directions of $O(NO_3)\cdots H_2O$ and $N(4\text{-bipy})\cdots H_2O$ vectors imply that each H_2O ligand is a donor in two hydrogen bonds (Fig. 2). Bonds of the first type link the complexes along *a* and also link complexes related by the *c* glide. The 4-bipy molecules, as in I, are all un-coordinated. Those containing N(11,12) and N(13,14) correspond in position and connections to the one independent 4-bipy molecule of I which is not on a crystal inversion centre, while the molecules N(7,8) and N(9,10) correspond roughly in position to the two centrosymmetric 4-bipy molecules of I but have formed new $N\cdots H_2O$ connections as the result of the loss of half the inversion centres consequent on cell doubling. The dihedral angles between the ring mean planes in the four independent 4-bipy molecules are now 33 to 36(2)°, compared with 0° and 7.2° in I, and are all larger than the dihedral angles in other compounds of this type [3–5]. At the resolution here obtained, the pyridyl rings are essentially planar and have normal dimensions.

The second compound, III, has proved to be of more interest. Whereas compounds so far studied have had Ln:4-bipy ratios of 1:2, the ratio in III, $(4\text{-bipyH})_2[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]\cdot 3(4\text{-bipy})$, is 1:3. The four independent 4-bipy molecules are of three types. One molecule, on a general position, is protonated. Two are unprotonated lattice molecules, one lying on a general position and one on a crystal inversion centre. The remaining 4-bipy molecule, also on an inversion centre, is coordinated to an Nd atom at each end (Fig. 3). To the best of our knowledge a bridging role for 4-bipy has not previously been observed. The Nd atom is in irregular ten-coordination, with bond lengths (Table II) similar to those about the eleven-coordinate Nd atom in the $[Nd(NO_3)_4(H_2O)_2(4\text{-bipy})]^-$ anion [5]. In the latter all NO_3 ligands were symmetrically bidentate, but in III one is monodentate. All non-coordinated 4-bipy nitrogen atoms participate in hydrogen bonds (lengths in Table II). In particular, the co-linearity of

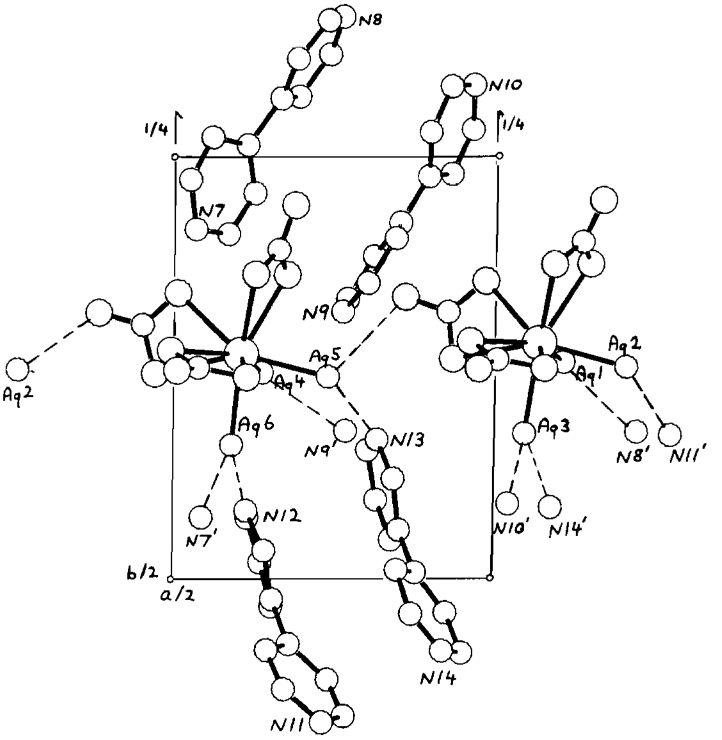

Fig. 2. Hydrogen bonds in II, $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$; *c*-axis projection.

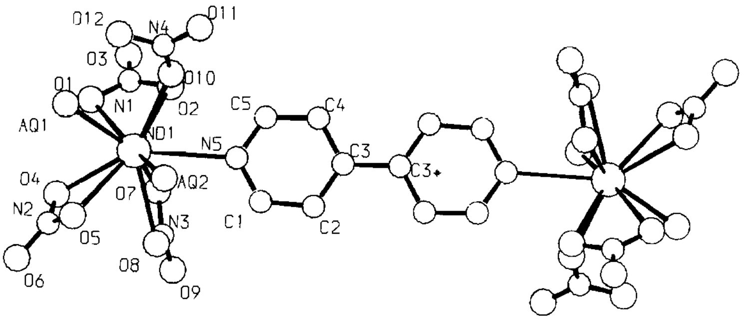

Fig. 3. The binuclear $[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]^{2-}$ complex in III.

TABLE II. Bond Lengths and Angles for III $(4\text{-bipyH})_2[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]\cdot 3(4\text{-bipy})$.

Nd–O(1)	2.556(6)	Nd–Aq(2)	2.460(6)	N(2)–O(6)	1.237(10)
Nd–O(2)	2.611(6)	Nd–N(5)	2.701(6)	N(3)–O(7)	1.242(10)
Nd–O(4)	2.535(6)	N(1)–O(1)	1.248(10)	N(3)–O(8)	1.279(11)
Nd–O(5)	2.575(6)	N(1)–O(2)	1.264(9)	N(3)–O(9)	1.220(11)
Nd–O(7)	2.529(6)	N(1)–O(3)	1.241(10)	N(4)–O(10)	1.234(10)
Nd–O(8)	2.589(6)	N(2)–O(4)	1.251(10)	N(4)–O(11)	1.241(9)
Nd–O(10)	2.531(6)	N(2)–O(5)	1.263(10)	N(4)–O(12)	1.249(9)
Nd–Aq(1)	2.429(7)				
O(1)–Nd–O(2)	48.6(2)		O(5)–N(2)–O(6)	121.2(8)	
O(4)–Nd–O(5)	49.8(2)		O(7)–N(3)–O(8)	116.7(8)	
O(7)–Nd–O(8)	49.6(2)		O(7)–N(3)–O(9)	122.5(8)	
O(1)–N(1)–O(2)	115.8(7)		O(8)–N(3)–O(9)	120.8(8)	

(continued overleaf)

TABLE II. *(continued)*

O(1)–N(1)–O(3)	123.6(7)	O(10)–N(4)–O(11)	120.1(7)
O(2)–N(1)–O(3)	120.6(7)	O(10)–N(4)–O(12)	121.6(7)
O(4)–N(2)–O(5)	117.8(7)	O(11)–N(4)–O(12)	118.4(8)
O(4)–N(2)–O(6)	120.9(8)		

4,4′-bipyridine

Bond type		Ring angles	
N–C(α)	1.324–1.371(13), av. 1.348 Å	N	117.1–118.9(7)^{a}, av. 118.0°
C(α)–C(β)	1.362–1.410(13), av. 1.391	C(α)	121.8–123.6(8)^{b}, av. 123.2
C(β)–C(γ)	1.378–1.430(12), av. 1.406	C(β)	116.1–119.6(8), av. 118.6
C(γ)–C(γ′)	1.494–1.500(14), av. 1.496	C(γ)	117.0–119.6(8), av. 118.7

^{a}121.9(7) Å at N(9). ^{b}120.6, 120.7(8)° at C(21), C(25).

Probable hydrogen bonds

N(6)•••Aq(2)	2.843(13)	N(10^{ii})••Aq(2)	2.847(13)
N(7)•••N(9)	2.696(4)	Aq(1)••O(12)	2.703(14)
N(8^{i})•••Aq(1)	2.701(15)		

^{i}1 – x, 1 – y, 1 – z. ^{ii}–x, 1 – y, –z.

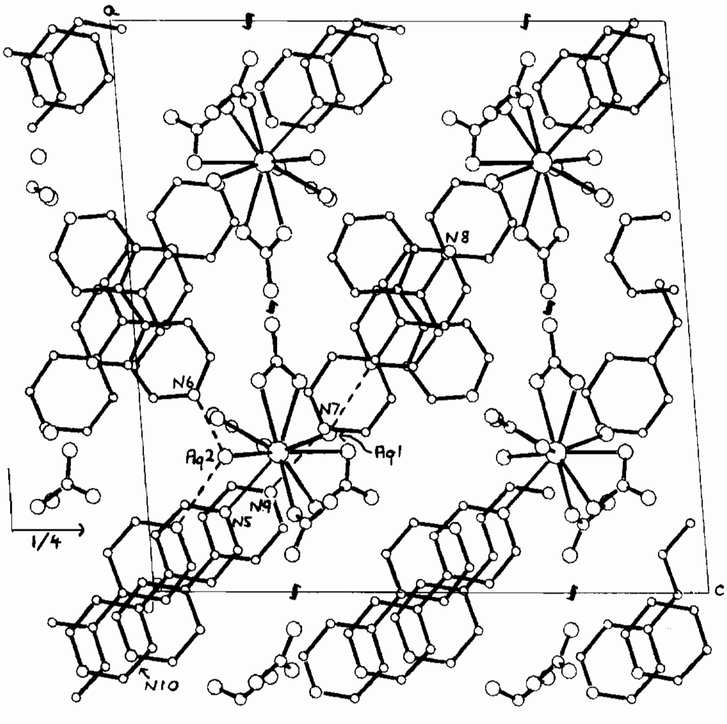

Fig. 4. III, $(4\text{-bipyH})_2[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]\cdot 3(4\text{-bipy})$: *b*-axis projection.

the molecules containing N(7) and N(9) and the separation between these atoms imply that one of them is the site of protonation. We believe it to be N(9), as the enhanced ring angle at N(9) and the reduced angles at the adjacent atoms C(21,25) (Table II) agree with observations for a related compound [4] where the H(N) atom was directly located. Other dimensions of the 4-bipy molecules are normal Table II). The appreciable dihedral angles (16.4, 23.8°) between the mean planes of the rings for the two molecules on general positions appear merely to reflect the requirements of crystal packing. The mean

TABLE III. Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for II, $[Ho(NO_3)_3(H_2O)_3]\cdot 2(4\text{-bipy})$.

Atom	x	y	z	U_{iso}
Ho(1)	−783(2)	2192(1)	2763(1)	19(1)[a]
O(1)	−854(14)	2495(9)	4264(11)	9(4)
O(2)	351(14)	2159(10)	4020(11)	14(5)
O(3)	224(15)	2489(10)	5311(13)	19(5)
N(1)	−85(17)	2382(10)	4558(14)	8(6)
O(4)	−1058(15)	1258(10)	3542(12)	13(5)
O(5)	−1651(15)	1259(10)	2212(12)	15(5)
O(6)	−1876(18)	498(12)	3036(15)	30(6)
N(2)	−1532(17)	993(11)	2933(14)	5(5)
O(7)	646(16)	2368(10)	2316(13)	23(6)
O(8)	78(14)	1446(9)	2139(11)	6(4)
O(9)	1403(15)	1623(9)	1881(12)	11(5)
N(3)	705(17)	1809(11)	2081(14)	6(5)
Aq(1)	−1173(17)	2427(8)	1313(10)	3(4)
Aq(2)	−2204(14)	2496(9)	2693(12)	11(5)
Aq(3)	−507(16)	3270(10)	2835(13)	18(6)
Ho(2)	4124(2)	2284(1)	2465(1)	22(1)[a]
O(10)	4404(14)	2559(9)	3968(11)	10(5)
O(11)	5279(15)	2224(12)	3716(12)	24(5)
O(12)	5181(19)	2466(13)	5021(17)	45(8)
N(4)	4837(18)	2436(12)	4264(15)	14(6)
O(13)	5545(15)	2499(9)	2031(12)	11(5)
O(14)	5138(15)	1543(10)	2039(12)	14(5)
O(15)	6441(19)	1761(12)	1889(15)	34(7)
N(5)	5728(22)	1914(13)	1959(17)	20(7)
O(16)	3860(14)	1335(10)	3203(12)	13(5)
O(17)	3341(15)	1344(10)	1853(12)	15(5)
O(18)	3186(18)	510(12)	2586(14)	30(6)
N(6)	3472(17)	1041(11)	2558(14)	8(6)
Aq(4)	3789(15)	2506(10)	1024(12)	17(5)
Aq(5)	2705(16)	2565(10)	2446(13)	24(6)
Aq(6)	4312(15)	3364(9)	2579(12)	8(5)
N(7)	4827(22)	781(14)	6322(18)	24(8)
C(1)	4905(25)	189(16)	6586(21)	21(9)
C(2)	4529(22)	−314(13)	6186(18)	7(7)
C(3)	3955(23)	−215(14)	5421(19)	8(7)
C(4)	3854(26)	363(16)	5072(21)	16(8)
C(5)	4292(30)	845(20)	5568(25)	36(11)
N(8)	2351(20)	−1729(12)	4294(17)	18(7)
C(6)	2592(28)	−1689(18)	5149(24)	27(10)
C(7)	3107(28)	−1237(18)	5519(23)	27(9)
C(8)	3390(24)	−767(15)	5035(20)	12(8)
C(9)	3095(24)	−785(15)	4131(19)	13(7)
C(10)	2579(25)	−1285(16)	3806(21)	22(8)
N(9)	2434(19)	1790(13)	5231(16)	17(7)
C(11)	2353(23)	1639(14)	4411(19)	12(7)
C(12)	1904(23)	1134(14)	4032(19)	8(7)
C(13)	1462(23)	732(14)	4536(19)	8(7)
C(14)	1539(24)	919(15)	5419(19)	14(8)
C(15)	2013(27)	1453(18)	5746(23)	30(9)
N(10)	216(20)	−897(13)	3461(16)	17(7)
C(16)	585(22)	−884(13)	4284(18)	6(7)
C(17)	942(25)	−345(15)	4679(20)	14(8)
C(18)	981(22)	187(13)	4188(18)	3(7)
C(19)	604(22)	162(13)	3331(17)	7(7)
C(20)	250(23)	−372(14)	2970(18)	11(7)
N(11)	2905(21)	6684(13)	6357(17)	23(7)
C(21)	3519(24)	6286(16)	6673(20)	18(8)
C(22)	3790(23)	5816(14)	6216(18)	12(7)
C(23)	3427(24)	5745(14)	5324(19)	10(7)
C(24)	2798(23)	6178(14)	4945(18)	9(7)
C(25)	2544(22)	6614(13)	5452(17)	8(7)
N(12)	4077(20)	4228(13)	3787(17)	20(7)
C(26)	4091(24)	4147(16)	4649(20)	16(8)
C(27)	3806(26)	4625(15)	5163(21)	18(8)
C(28)	3691(21)	5206(12)	4799(17)	0(6)
C(29)	3703(22)	5293(14)	3935(18)	9(7)
C(30)	3873(24)	4767(15)	3448(19)	15(8)
N(13)	2076(21)	3444(14)	3363(17)	25(8)
C(31)	1953(23)	4035(14)	3062(18)	11(7)
C(32)	1721(21)	4512(13)	3546(17)	4(6)
C(33)	1587(22)	4396(13)	4382(18)	5(7)
C(34)	1664(24)	3791(5)	4698(20)	13(8)
C(35)	1915(27)	3319(16)	4173(22)	20(9)
N(14)	913(20)	5848(13)	6023(16)	16(7)
C(36)	1408(24)	5402(16)	6329(20)	17(8)
C(37)	1634(22)	4876(13)	5864(18)	5(7)
C(38)	1337(22)	4906(14)	4952(18)	5(7)
C(39)	841(23)	5391(14)	4592(19)	10(8)
C(40)	593(25)	5876(16)	5140(21)	21(8)

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

planes of the rings in each 4-bipy molecule on an inversion centre are necessarily parallel, but are offset by *ca.* 0.06 and 0.10 Å for the bridging and the uncoordinated molecule respectively. The 4-bipy N···N axes all lie parallel to the *ac* plane. They form stacks (Fig. 4) along the lines 0,y,0 (molecules parallel but offset) and ½,y,0 (two nearly perpendicular orientations); this feature also seems only to reflect the requirements of packing as the separations between 4-bipy molecules in the stacks (3.53 to 3.61 Å) are too large for specific π-interactions.

Experimental

The preparations of II, III and IV have been described previously [3].

Crystal Data

II, $C_{20}H_{22}HoN_7O_{12}$: monoclinic, $P2_1/c$, a = 15.830(10), b = 21.44(3), c = 15.70(3) Å, β = 100.4(2)°, Z = 8, d_{calc} = 1.818 g cm^{-3}; CuKα radiation (λ = 1.5418 Å), μ = 62.8 cm^{-1}.

III, $C_{60}H_{58}N_{20}Nd_2O_{28}$: monoclinic, $P2_1/c$, a = 18.723(10), b = 10.720(6), c = 18.027(10) Å, β = 94.43(5)°, Z = 2, d_{calc} = 1.651 g cm^{-3}; MoKα radiation (λ = 0.71069 Å), μ= 14.8 cm^{-1}.

IV, probably $C_{20}H_{22}N_7O_{12}Pr$: orthorhombic, $P2_1ma$, a = 16.119(12), b = 24.82(2), c = 7.142(3) Å, Z = 4, d_{calc} = 1.612 g cm^{-3}; Cu Kα radiation (λ = 1.5418 Å), μ = 139 cm^{-1}.

TABLE IV. Atomic Coordinates ($\times10^4$) and Thermal Parameters ($\times10^3$) for III, $(4\text{-bipyH})_2[(\mu\text{-}4\text{-bipy})Nd_2(NO_3)_8(H_2O)_4]\cdot3(4\text{-bipy})$ ($U_{eq} = 1/3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*a_i.a_j$).

Atom	x	y	z	U_{eq}
Nd	2464(0.2)	1223(0.4)	2427(0.2)	28(1)
O(1)	2481(3)	113(7)	3683(3)	69(2)
O(2)	1494(3)	−108(6)	3028(3)	47(2)
O(3)	1494(3)	−1211(7)	4038(4)	69(2)
N(1)	1892(4)	−435(7)	3594(4)	45(2)
O(4)	3698(3)	466(6)	2906(3)	51(2)
O(5)	3713(3)	2059(6)	2177(4)	59(2)
O(6)	4700(3)	1046(8)	2490(4)	95(3)
N(2)	4047(4)	1187(8)	2524(4)	55(2)
O(7)	2564(3)	−1094(6)	2189(3)	45(2)
O(8)	3049(3)	31(6)	1380(3)	44(2)
O(9)	3105(4)	−1996(7)	1319(4)	71(3)
N(3)	2910(4)	−1053(8)	1629(4)	46(2)
O(10)	1379(3)	2547(6)	2634(3)	47(2)
O(11)	661(3)	4107(6)	2538(4)	62(2)
O(12)	1598(4)	4217(6)	3293(4)	62(2)
N(4)	1216(4)	3612(8)	2820(4)	38(2)
Aq(1)	2795(3)	2795(6)	3361(4)	74(2)
Aq(2)	2382(3)	2863(6)	1471(3)	45(2)
N(5)	1409(3)	569(6)	1393(3)	35(2)
C(1)	1538(4)	430(8)	676(4)	40(2)
C(2)	1000(5)	188(8)	108(5)	45(3)
C(3)	300(4)	102(7)	291(4)	31(2)
C(4)	160(4)	239(8)	1044(4)	40(2)
C(5)	730(4)	453(8)	1598(4)	39(3)
N(6)	3459(4)	4483(7)	992(4)	47(2)
C(6)	4126(4)	4521(9)	1341(5)	43(3)
C(7)	4730(5)	4714(8)	981(4)	44(3)
C(8)	4673(4)	4924(8)	211(4)	33(2)
C(9)	3978(5)	4920(9)	−150(5)	48(3)
C(10)	3401(5)	4690(9)	255(5)	52(3)
N(7)	2874(4)	6515(7)	3281(4)	55(3)
C(11)	2815(4)	6345(10)	4019(5)	62(3)
C(12)	3412(5)	6392(9)	4534(5)	54(3)
C(13)	4085(4)	6637(8)	4291(5)	44(3)
C(14)	4143(5)	6880(10)	3523(5)	60(3)
C(15)	3511(6)	6779(11)	3048(6)	69(4)
N(8)	5984(4)	6727(8)	5789(5)	64(3)
C(16)	6032(5)	6625(9)	5039(6)	53(3)
C(17)	5426(4)	6580(8)	4536(5)	46(3)
C(18)	4752(4)	6652(7)	4802(5)	38(2)
C(19)	4691(5)	6762(9)	5585(5)	56(3)
C(20)	5338(6)	6770(10)	6036(5)	67(4)
N(9)	1762(4)	6550(6)	2238(4)	41(2)
C(21)	1871(5)	6146(8)	1544(5)	47(3)
C(22)	1326(4)	6212(8)	976(5)	40(2)
C(23)	645(4)	6679(7)	1149(4)	36(2)
C(24)	561(5)	7101(8)	1872(4)	41(2)
C(25)	1129(5)	7012(9)	2409(5)	52(3)
N(10)	−1137(4)	6683(6)	−499(4)	45(2)
C(26)	−1240(4)	6669(8)	238(5)	43(3)
C(27)	−676(4)	6659(8)	780(5)	38(2)
C(28)	32(4)	6688(7)	566(4)	32(2)
C(29)	153(5)	6687(7)	−197(4)	37(2)
C(30)	−447(5)	6672(8)	−707(5)	42(3)

Intensity data for II and IV were obtained photographically; equi-inclination Weissenberg films were scanned by use of a microdensitometer (SERC Service, Daresbury Laboratory). The layers recorded were *h*0–1*l* and 0–9*kl* for II (2335 unique data) and 0–5*kl* and *hk*0–4 for IV (1271 unique data). Absorption corrections were applied in the case of IV. Data for III were obtained by use of a Stoe STADI-2 two-circle diffractometer from a crystal measuring *ca.* 0.3 × 0.4 × 0.3 mm mounted on *b* (layers 0–8; 6693 unique data, 4931 with $|F| \geqslant 3\sigma(F)$ used in refinement). The merging indices R_{int} were 0.060, 0.029, 0.068 for II, III, IV.

The heavy atoms were located from the Patterson function and the structures of II and III were completed by conventional methods. The strong vector peaks for IV could be interpreted for space-group $P2_1ma$, with two independent Pr atoms on crystal mirror planes, but not for the alternative space-groups $Pm2a$ and $Pmma$. The emerging structure of IV was clearly disordered. Each coordination group about a Pr atom appeared to have two orientations related by reflection in a plane normal to *c*, and each 4-bipy molecule was un-coordinated and had alternative, adjacent sites. The analysis was therefore abandoned in view of the inadequate ratio of data to necessary parameters. Least-squares refinement for the other structures converged at R 0.091, wR 0.116 for II ($wR = [\Sigma w\Delta^2/\Sigma wF^2]^{1/2}$; Ho anisotropic, unit weights, 331 parameters) and at R 0.066, wR 0.069 for III (all non-hydrogen atoms anisotropic, 496 parameters, $w = 2.349\ [\sigma^2(F) + 0.00065F^2]^{-1}$ in last cycle). Some 15 probable H atoms of 4-bipy were located in the final difference synthesis for III, but were not included in the calculations as the peaks were not significantly stronger than the stronger 'noise' peaks. The SHELX-76 program system [6] was used in all calculations. Atomic coordinates and values of U_{iso} or U_{eq} are listed in Tables III and IV.

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