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Polyimido Clusters of Neodymium and Uranium, Including a Cluster with an $M_6(\mu_3\text{-}N)_8$ Core

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NdI_3 reacted with 1 or 8/6 equiv. of [PhNMg(thf)], in thf or pyridine, to afford the imido clusters $[Nd_4(NPh)_4I_4(thf)_n]$ (n = 3, 4) or $[Nd_6(NPh)_8I_2(py)_6]$, which display a cubane or rhombododecahedron core structure, respectively. In contrast, the tetranuclear U^{IV} derivative $[U_4(NPh)_6I_4(py)_6]$ was obtained from the reaction of $UI_3(py)_4$ with [PhNMg(thf)]. The crystal structures of these clusters are presented.

Introduction

Imido complexes of the main-group and d-transition metals have gained a prominent position in coordination and organometallic chemistry, finding useful applications in the areas of catalysis and materials.[1] The flexible RN^{2-} anion can adopt either a terminal or a μ_2-, μ_3- or μ_4-bridging ligation mode, thus endowing the complexes with a rich diversity of structures, reactions and physico-chemical properties, which are strongly influenced by the nature of the R substituent. Interesting comparisons could be made between the imido complexes and analogues containing dianionic ligands like O^{2-}, S^{2-}, or R_2C^{2-} and RP^{2-}. In stark contrast, the imido chemistry of the f elements is much less developed.[2–4] It is particularly surprising, in view of the versatility of the imido linker for the construction of clusters, that such polynuclear assemblages are so scarce in f-element chemistry.[3] This situation was recently explained by the "lack of relevant synthetic routes".[2e]

We have recently isolated novel polyimido tetra- and heptanuclear uranium(IV) clusters, which exhibit unprecedented topologies.[4] It was then desirable to extend the scope of these studies to trivalent uranium and lanthanide derivatives, in particular for analyzing the respective role of the 4f and 5f electrons in the metal–imido bond and their influence on the reactivity and the structure of the complexes.[5] Our attempts led to the synthesis of a new tetranuclear uranium(IV) complex with a "deck chair"-like $U_4(\mu_2\text{-}N)_4(\mu_3\text{-}N)_2$ core and tetra- and hexanuclear lanthanide compounds with cubane $Nd_4(\mu_3\text{-}N)_4$ and rhombododecahedral $Nd_6(\mu_3\text{-}N)_8$ frameworks.

Results and Discussion

As for the previously reported uranium(IV) clusters, the complexes described here were obtained by introducing the PhN^{2-} group by means of the imide transfer Grignard reagent $\{[PhNMg(thf)]_6\}$.[6] Reaction of $UI_3(py)_4$ with the hexameric magnesium imide in the molar ratio of 6:(8/6) in pyridine at 100 °C afforded brown crystals of $[U_4(NPh)_6I_4(py)_6]\cdot5py$ (**1**·5py). Such $U^{III} \rightarrow U^{IV}$ oxidation in reactions of UI_3 is quite common,[7] particularly with hard ligands, and no imido complex of uranium(III) has been isolated up to now. The crystal structure of **1** (Figure 1) is very similar to that of the chloride counterpart, which was obtained un-

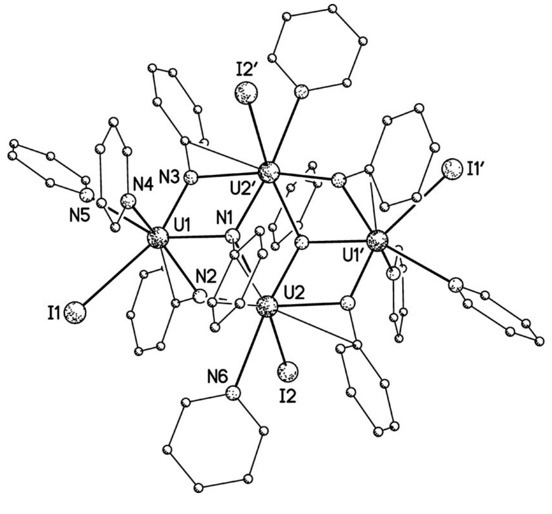

Figure 1. View of complex **1**. Symmetry code: ′ = 2 – x, –y, 1 – z. Selected bond lengths [Å] and angles [°]: U1–N1 2.340(6), U1–N2 2.285(7), U1–N3 2.139(6), U1–N4 2.599(7), U1–N5 2.627(7), U1–I1 3.1840(6), U2–N1 2.448(6), U2–N2 2.180(6), U2–N1′ 2.391(6), U2–N3′ 2.349(6), U2–N6 2.694(6), U2–I2 3.1229(8), U1···U2 3.6449(5), U1···U2′ 3.6504(5), U2···U2′ 3.8072(8); N1–U1–N2 75.6(2), N1–U1–N3 77.3(2), N1–U2–N1′ 76.2(2), N1–U2–N2 75.3(2), N1′–U2–N3′ 72.4(2), N2–U2–N3′ 166.2(2).

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der the same conditions when starting from UCl_4,[4] and will not be discussed in detail.

The only difference concerns the μ_3-N1Ph ligand which adopts an η^3- instead of an η^2-ligation mode, the U2 atom being involved in close contacts with the $C1_{ipso}$ and $C6_{ortho}$ atoms, at 2.919(8) and 3.033(8) Å, respectively. In addition, the U–C interactions with the *ipso*-carbon atoms of the peripheral μ_2-NPh ligands are ca. 0.1 Å larger than in the chloride analogue. The mean U–μ_3-N bond length is ca. 0.15 Å longer than the average U–N distance of the μ_2-NPh ligands; these distances are close to those previously reported.[4] The U–I distances are unexceptional with an average value of 3.15(3) Å, which is in the range of terminal U^{IV}–I bond lengths [2.933–3.233 Å].[8]

The tetra- and hexanuclear neodymium clusters $[Nd_4(NPh)_4I_4(thf)_n]$ (**2**) and $[Nd_6(NPh)_8I_2(py)_6]$ (**3**) were synthesized according to Equations (1) and (2), by reaction of NdI_3 with 1 or 8/6 equiv. of [PhNMg(thf)] in refluxing thf or pyridine, respectively. After filtration and concentration of the solution, complex **2** was isolated as a pale green powder in 60–72% yield, with the number of thf ligands (n = 3 or 4) depending on the time of drying.

$$4\ NdI_3 + 4\ [PhNMg(thf)] \xrightarrow[85\ ^\circ C]{thf} \underset{(2)\ n = 3 \text{ or } 4}{[Nd_4(NPh)_4I_4(thf)_n]} + 4\ MgI_2 \qquad (1)$$

$$6\ NdI_3 + 8\ [PhNMg(thf)] \xrightarrow[100\ ^\circ C]{pyridine} \underset{(3)}{[Nd_6(NPh)_8I_2(py)_6]} + 8\ MgI_2 \qquad (2)$$

The brown-green powder of **3** was isolated in 54% yield. The ^{1}H NMR spectrum of **2** in [D$_8$]thf exhibits three paramagnetic signals corresponding to the *ortho*-, *meta*- and *para*-hydrogen atoms of the equivalent NPh ligands; the spectrum is similar in [D$_5$]pyridine, indicating that the cluster **2** is not dissociated in this solvent. No ^{1}H NMR signal was detected for **3** in pyridine, a situation which was previously noticed with hexanuclear uranium complexes[4] and tentatively explained by the possible fluxionality of the complexes related to rapid ligand exchange reactions or disruption of the clusters in solution. IR spectroscopy is of poor interest in imido chemistry since no general trend has emerged in the assignment of the ν(MN) band of terminal and bridging imido groups.[1f,1h] Large crystals of $[Nd_4(NPh)_4I_4(py)_5(thf)_2]\cdot py$ (**4**·py), with cubic shape and light blue colour, were obtained by slow diffusion of diethyl ether into a solution of a 1:1 mixture of NdI_3 and [PhNMg(thf)] in pyridine/thf, whereas large brown crystals of the solvate $[Nd_6(NPh)_8I_2(py)_8]\cdot 5py$ (**5**·5py) were formed by slow diffusion of Et_2O into a solution of **3** in pyridine.

Views of the tetranuclear cluster **4** and of its Nd_4N_4 cubane core structure with μ_3-imido bridges are shown in Figures 2 and 3, respectively, together with selected bond lengths and angles. To the best of our knowledge, the only other f-element complex to exhibit a cubane-like M_4N_4 core is the organometallic compound $[\{Cp'Ln(\mu_3\text{-}NCH_2Ph)\}_4]$ (Ln = Y, Lu; Cp′ = $C_5Me_4SiMe_3$), which was isolated from the reaction of the polyhydride $[\{Cp'Ln(\mu\text{-}H)_2\}_4(thf)]$ with benzonitrile.[3b] More generally, lanthanide and actinide complexes with an M_4E_4 cubane core (E = O,[9a,9b] S,[9c] Se[9d,9e]) are very scarce, by comparison with the large quantity of such compounds of the other metals, in particular those with E = N which are found with a variety of nitrogen ligands (imido, nitrido or cyanamido).[10] The *ipso*-carbon atoms (C1 and C7) of the N1Ph and N2Ph groups are in close contacts with Nd1 and Nd4, respectively, while both the *ipso*- and one of the *ortho*-carbon atoms of the N3Ph and N4Ph ligands interact with Nd3. The number of η^2-

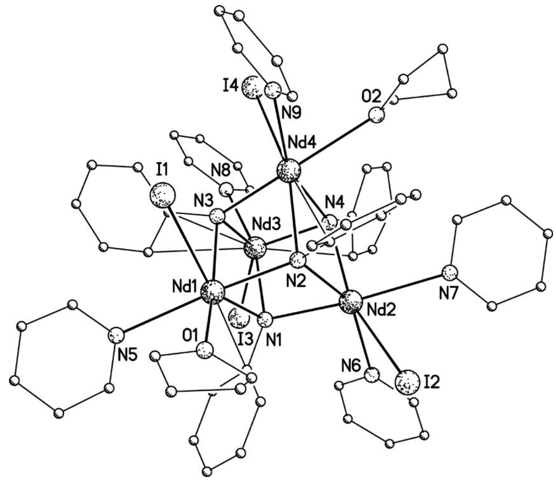

Figure 2. View of complex **4**. The hydrogen atoms are omitted, and only one position of the disordered parts is represented. Selected bond lengths [Å] and angles [°]: Nd1–N1 2.438(7), Nd1–N2 2.335(6), Nd1–N3 2.392(7), Nd1–N5 2.646(7), Nd1–O1 2.599(6), Nd1–I1 3.2369(7), Nd2–N1 2.420(6), Nd2–N2 2.378(6), Nd2–N4 2.412(7), Nd2–N6 2.681(7), Nd2–N7 2.695(7), Nd2–I2 3.1892(7), Nd3–N1 2.415(7), Nd3–N3 2.351(7), Nd3–N4 2.414(7), Nd3–N8 2.654(7), Nd3–I3 3.2012(7), Nd4–N2 2.478(7), Nd4–N3 2.366(7), Nd4–N4 2.417(7), Nd4–N9 2.682(7), Nd4–O2 2.641(6), Nd4–I4 3.1909(8), <Nd–*N*–Nd>$_{core}$ 100(2).

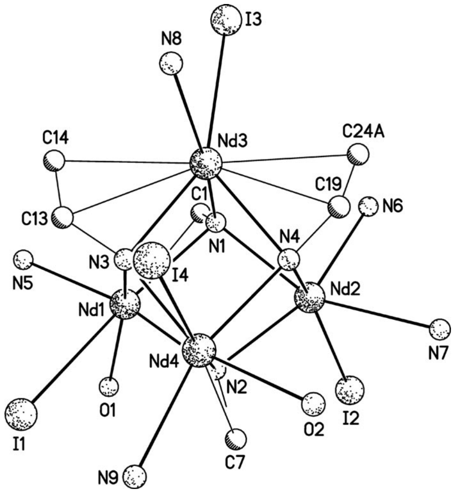

Figure 3. View of the Nd_4N_4 core in **4** and its environment of coordinating atoms at the periphery. Only one position of the disordered atom C24 is represented. Selected bond lengths [Å]: Nd1–C1 2.805(8), Nd3–C13 2.862(8), Nd3–C14 2.941(9), Nd3–C19 2.766(9), Nd3–C24A 2.842(16), Nd4–C7 2.939(8).

and η^3-coordinated NPh ligands increases with the decreasing electron richness of the metal centres, which possess, in addition to one iodide ligand, a single pyridine (Nd3), one pyridine and one thf (Nd1 and Nd4), and two pyridine (Nd2) ligands. The structures of **1** and **4** thus provide new examples of the η^3 coordination of an arylimide ligand, which was recently revealed in the anionic heptanuclear cluster $[U_7(NPh)_{12}Cl_5(thf)_6]^-$.[4] The Nd–($\mu_3$-N) distances vary from 2.335(6) to 2.478(7) Å, with an average value of 2.40(4) Å which is 0.13 Å larger than the average Lu–N distance in the aforementioned lutetium compound, in agreement with the variation in the radii of the Nd^{3+} and Lu^{3+} ions.[11] The variation of 0.14 Å in the extreme values of the Nd–(μ_3-N) distances reflects severe distortions due to steric constraints and asymmetric Nd–N–Nd bridges related to the presence of Nd···C interactions. The lowest Nd–(μ_3-N) distances can be compared to some Nd–N bond lengths of amido ligands.[12] The mean Nd–I, Nd–N(py) and Nd–O bond lengths of 3.20(2), 2.67(2) and 2.62(2) Å, respectively, are unexceptional. The average Nd···Nd distance is 3.69(4) Å; the N–Nd–N angles involving the NPh ligands are in the range 76.8(2)–80.6(2)°, and they average 79(1)°.

A view of the centrosymmetric hexanuclear complex **5** is shown in Figure 4, and the Nd_6N_8 core is represented in Figure 5. The structure exhibits an octahedron-like skeleton of Nd atoms, which are held together with μ_3-NPh ligands located above each face of the octahedron. One pyridine and one iodide or two pyridine ligands are coordinated to Nd1 and Nd2, respectively, and only one pyridine molecule is bound to Nd3. The Nd1 and Nd2 atoms are at the centre of almost orthogonal, slightly distorted trigonal prisms defined by the two trigonal faces N1–N2–I and N3–N4–N5, and N1–N2–N6 and N3′–N4′–N7, respectively, whereas the Nd3 environment is a pyramid whose square base is defined by the N1, N2′, N3, N4′ atoms. The Nd3 atom completes its coordination sphere with close contacts of 2.926(5)–2.970(4) Å with the three *ipso*-carbon atoms C1, C13 and C19′ of the μ_3-NPh ligands containing N1, N3 and N4′, respectively, whereas a single U···C interaction of 2.973(4) Å is found between Nd2 and the *ipso*-carbon atom C7 of the μ_2-N2Ph ligand. The mean Nd–μ_3-N bond length of 2.43(3) Å is quite identical to that measured in **4**; the average Nd–N(py) distance of 2.69(5) Å and the Nd–I distance are unexceptional. The average distances between proximal and opposite neodymium centres are 3.78(4) and 5.34(10) Å.

Complex **5** is the first (polyimido)metal cluster with an $M_6(\mu_3\text{-NR})_8$ core. While complexes of the d-transition metals featuring an $M_6(\mu_3\text{-X})_8$ core are quite numerous for X = O, S, Se or halide,[13] they are very rare for X = N, NR; these are indeed limited to the (polyimido)(nitrido)titanium aggregate $[(LTi)_6(\mu_3\text{-NH})_6(\mu_3\text{-N})_2]$ [L = p-$MeC_6H_4C(NSiMe_3)_2$][14] and the (oxido)(polyimido)tantalum complex $[\{Ta(NAr)\}_6(\mu_3\text{-NPh})_8(\mu_6\text{-O})]$ (Ar = C_6H_5, m-ClC_6H_4), in which the interstitial μ_6-O^{2-} oxido group resulted from the presence of water during the synthesis.[15] Moreover, the $M_6(\mu_3\text{-X})_8$ core is not common in f-element complexes.[16,17] The $M_6(\mu_3\text{-O})_8$ core was only found in a few uranium(IV) and mixed-valence uranium(IV,V) clusters,[17] and the lack of a (polyoxo)lanthanide compound with this hexanuclear framework prevents any comparison with the polyimido complex **5**.

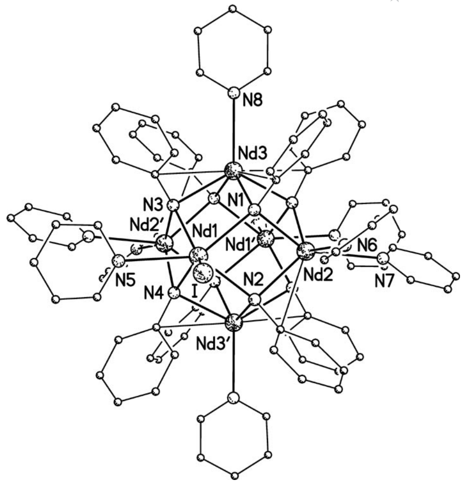

Figure 4. View of complex **5**. Symmetry code: ′ = –x, 1 – y, 1 – z. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd1–N1 2.397(4), Nd1–N2 2.415(4), Nd1–N3 2.478(4), Nd1–N4 2.459(3), Nd1–N5 2.748(4), Nd1–I 3.2714(4), Nd2–N1 2.446(4), Nd2–N2 2.446(4), Nd2–N3′ 2.423(4), Nd2–N4′ 2.380(4), Nd2–N6 2.722(4), Nd2–N7 2.654(4), Nd3–N1 2.408(4), Nd3–N2′ 2.424(4), Nd3–N3 2.418(4), Nd3–N4′ 2.435(4), Nd3–N8 2.627(4), <N–Nd–N>$_{core}$ 76.6(13), <Nd–N–Nd>$_{core}$ 102.2(14).

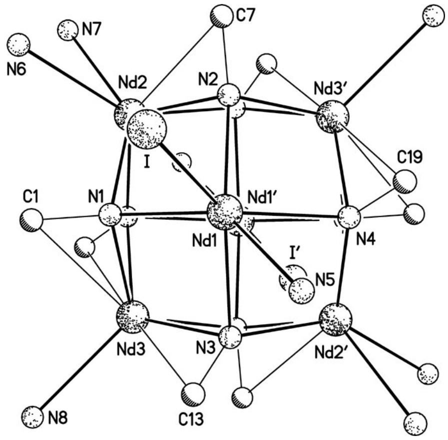

Figure 5. View of the Nd_6N_8 core of **5** and its environment of coordinating atoms at the periphery. Symmetry code: ′ = –x, 1 – y, 1 – z. Selected bond lengths [Å]: Nd2–C7 2.973(4), Nd3–C1 2.970(4), Nd3–C13 2.926(5), Nd3–C19′ 2.936(4).

Conclusions

The imide transfer Grignard reagent $[\{PhNMg(thf)\}_6]$ proved to be efficient in the synthesis of polyimido clusters of the f elements. The structural variety and novelty of the uranium and neodymium compounds are an incitement to further studies aimed at expanding the scope of these clusters, whose nuclearity and topology will vary with the metal and its oxidation state, the R substituent of the imido group and the ancillary ligands. Such large homo- or heterometallic imido assemblages could provide soluble materials with distinct reactivity and physicochemical properties, and diverse applications, for example in material engineering.

Experimental Section

General Considerations: All reactions were carried out under argon (<5 ppm oxygen or water) by using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Dried solvents were distilled immediately before use. The ^{1}H NMR spectra were recorded at 23 °C with a Bruker DPX 200 instrument and were referenced internally by using the residual protio solvent resonances relative to tetramethylsilane (δ = 0 ppm). IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded with a Perkin–Elmer FT-IR 1725X spectrometer. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Crystals of $[U_4(NPh)_6I_4(py)_6]$·5py (1·5py): An NMR tube was charged with $UI_3(py)_4$ (10 mg, 0.010 mmol) and [PhNMg(thf)] (2.7 mg, 0.014 mmol), and pyridine (0.5 mL) was condensed in. After 48 h at 110 °C, brown crystals of **1**·5py were deposited from the red solution.

Synthesis of $[Nd_4(NPh)_4I_4(thf)_n]$ (2): A flask was charged with NdI_3 (200 mg, 0.38 mmol) and [PhNMg(thf)] (72 mg, 0.38 mmol), and thf (15 mL) was condensed in. After 15 h in a sand bath at 85 °C, the pale-green solution was cooled to room temperature, inducing precipitation of a white salt. The solution was filtered and the solvent evaporated; the green residue was dried at 90 °C under vacuum for 2 h and extracted again with thf (10 mL). Filtration, evaporation of the solvent, and drying under vacuum (80 °C, 2 h) afforded a pure pale-green powder of $[Nd_4(NPh)_4I_4(thf)_4]$ (120 mg, 72%). $C_{40}H_{52}I_4N_4O_4Nd_4$ (1737.28): calcd. C 27.65, H 3.01, N 3.22; found C 27.41, H 3.01, N 3.36. ^{1}H NMR (200 MHz, [D$_8$]thf, 23 °C): δ = –5.58 (s, 2 H, *m*-H), –6.28 (s, 1 H, *p*-H), –65.18 (s, $w_{1/2} \approx 300$ Hz, 2 H, *o*-H) ppm. ^{1}H NMR (200 MHz, [D$_5$]pyridine, 23 °C): δ = 3.55 (s, 8 H, α-thf), 1.65 (s, 8 H, β-thf), –5.81 (s, 2 H, *m*-H), –6.21 (s, 1 H, *p*-H), –64.6 (s, $w_{1/2}$ = 300 Hz, 2 H, *o*-H) ppm. IR (in Nujol mulls between KBr round cell windows): $\tilde{\nu}$ = 1577 (s), 1545 (m), 1242 (vs), 1227 (vs), 1173 (s), 1073 (w), 1019 (s), 949 (m), 915 (w), 865 (s), 831 (vs), 758 (vs), 701 (s), 668 (w), 618 (w), 570 (m), 506 (s) cm^{-1}. In another experiment, the isolated pale-green sample obtained after drying at room temperature for 15 h analysed as $[Nd_4(NPh)_4I_4(thf)_3]$ (60% yield). $C_{36}H_{44}I_4N_4O_3Nd_4$ (1665.17): calcd. C 25.96, H 2.66, N 3.36; found C 25.83, H 2.63, N 3.02.

Synthesis of $[Nd_6(NPh)_8I_2(py)_6]$ (3): A flask was charged with NdI_3 (200 mg, 0.38 mmol) and [PhNMg(thf)] (96 mg, 0.50 mmol), and pyridine (15 mL) was condensed in. After 3 d at 100 °C, the red-brown solution was filtered at room temperature from the white deposit and the solvent evaporated off. The residue was then dried under vacuum (2 h at 25 °C) and extracted again with pyridine (10 mL). Addition of Et_2O (5 mL) onto the solution induced the deposition of a khaki powder, which was dried under vacuum at 85 °C for 2 h (80 mg, 54%). $C_{78}H_{70}I_2N_{14}Nd_6$ (2322.52): calcd. C 40.33, H 3.03, N 8.44; found C 39.54, H 3.41, N 8.84. IR (in Nujol mulls between KBr round cell windows): $\tilde{\nu}$ = 1593 (m), 1574 (s), 1540 (m), 1320 (w), 1251 (vs), 1169 (s), 1142 (m), 1065 (w), 1035 (w), 1002 (w), 979 (s), 868 (w), 818 (vs), 750 (vs), 695 (vs), 617 (m), 569 (s), 503 (s) cm^{-1}.

Crystallography: The data were collected at 100(2) K with a Nonius Kappa-CCD area-detector diffractometer[18] using Mo-K_α radiation and processed with HKL2000.[19] Only 87% data completeness was reached for **4**·py,[20] whereas complete data sets were collected for the other two compounds. The structures were solved by direct methods, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXTL.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Absorption effects were corrected empirically with DELABS (PLATON)[22] or SCALEPACK.[19] In **1**·5py and in **5**·5py, one solvent pyridine molecule is disordered around an inversion centre. In **4**·py, one NPh aromatic ring, one pyridine, and one tetrahydrofuran molecule were found to be disordered over two positions (sharing the heteroatom and/or one or two carbon atoms) which were refined with occupancy parameters constrained to sum to unity and some restraints on bond lengths and/or displacement parameters. The hydrogen atoms were introduced at calculated positions (except in the disordered parts) and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. CCDC-693468 (**1**·5py), -693469 (**4**·py) and -693470 (**5**·5py) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 1·5py: $C_{91}H_{85}I_4N_{17}U_4$, M = 2876.48, triclinic, space group $P\bar{1}$, a = 12.4423(15), b = 14.2001(19), c = 15.3128(13) Å, α = 101.079(7), β = 99.733(7), γ = 114.795(5)°, V = 2313.8(5) Å^3, Z = 1, D_c = 2.064 g cm^{-3}, μ = 8.365 mm^{-1}, $F(000)$ = 1330, 55186 measured reflections, 8721 independent (R_{int} = 0.058), 6387 with $I > 2\sigma(I)$, 523 parameters, R_1 = 0.041, wR_2 = 0.093, S = 0.968, $\Delta\rho_{min}$ = –1.85, $\Delta\rho_{max}$ = 1.18 e Å^{-3}.

Crystal Data for 4·py: $C_{62}H_{66}I_4N_{10}Nd_4O_2$, M = 2067.81, monoclinic, space group $C2/c$, a = 19.6981(7), b = 14.8285(6), c = 48.3783(14) Å, β = 98.790(2)°, V = 13965.0(9) Å^3, Z = 8, D_c = 1.967 g cm^{-3}, μ = 4.740 mm^{-1}, $F(000)$ = 7808, 37546 measured reflections, 11455 independent (R_{int} = 0.053), 8998 with $I > 2\sigma(I)$, 829 parameters, R_1 = 0.043, wR_2 = 0.101, S = 1.015, $\Delta\rho_{min}$ = –1.36, $\Delta\rho_{max}$ = 1.90 e Å^{-3}.

Crystal Data for 5·5py: $C_{113}H_{105}I_2N_{21}Nd_6$, M = 2876.42, triclinic, space group $P\bar{1}$, a = 13.4662(7), b = 14.7782(7), c = 14.9646(8) Å, α = 103.585(3), β = 103.290(3), γ = 103.756(3)°, V = 2679.9(3) Å^3, Z = 1, D_c = 1.782 g cm^{-3}, μ = 3.487 mm^{-1}, $F(000)$ = 1396, 47707 measured reflections, 10098 independent (R_{int} = 0.071), 8510 with $I > 2\sigma(I)$, 640 parameters, R_1 = 0.031, wR_2 = 0.067, S = 1.033, $\Delta\rho_{min}$ = –0.75, $\Delta\rho_{max}$ = 0.56 e Å^{-3}.

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