

Le cycle pyranique est du type 'bateau croisé'. En effet, C(2) et C(5) sont situés du même côté du plan moyen $P(B)$ défini par C(1), C(3), C(4) et O(6). Le premier en est éloigné de 0,40 (1) Å, le second de 0,62 (1) Å. En outre, les diagonales du quadrilatère C(1)C(3)C(4)O(6) se trouvent de part et d'autre de $P(B)$ et les distances à ce plan des atomes qu'elles joignent sont de 0,11 (1) ou de 0,120 (7) Å, c'est-à-dire pratiquement égales. Les valeurs de ΔC_s relatives à deux plans passant, l'un par C(2), l'autre par le milieu de C(3)—C(4), sont respectivement de 29,5 et de 29,7°. Elles traduisent l'écart entre la conformation observée et la conformation bateau idéale.

Dans le cycle C , les symétries dominantes sont la symétrie par rapport à un plan passant par C(14) ($\Delta C_s^{14} = 11,4^\circ$), ou par O(12) ($\Delta C_s^{12} = 16,2^\circ$), et la symétrie par rapport à un axe binaire issu de C(4) ($\Delta C_2^4 = 3,4^\circ$). C(3), C(4), O(12) et O(13) sont situés approximativement dans un même plan ($\chi^2 = 92$). La distance de C(14) au plan moyen $P(C)$ défini par ces quatre atomes est de 0,47 (1) Å. Ainsi, la forme de C peut être considérée comme intermédiaire entre la forme enveloppe et la forme demi-chaise.

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Structure of Tetraquaahexadecakis(2-pyridinecarboxylato)tetraneodymiumdibarium 11·6-Hydrate

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Abstract. [Ba₂Nd₄(C₆H₄NO₂)₁₆(H₂O)₄].11·6H₂O, $M_r = 3086.3$, monoclinic, $P2_1/n$, $a = 15.495$ (7), $b = 20.296$ (12), $c = 19.309$ (11) Å, $\beta = 110.75$ (3)°, $V = 5679$ (6) Å³, $Z = 2$, $D_m = 1.81$, $D_x = 1.805$ (2) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.61$ mm⁻¹, $F(000) = 3032$, $T = 300$ (1) K, final $R = 0.039$ for 6227 reflections. The title compound is a centrosymmetric aggregate, with four Nd and two Ba cations. There are two modes of Nd coordination. Each Nd ion is surrounded by four N atoms and either by five carboxylic O atoms or by one water and four carboxylic O atoms. The environment of the Ba cation consists of one water and eight carboxylic O atoms.

Introduction. This work is part of our study of the structures and properties of complexes with lanthanide–nitrogen bonds.

Experimental. The title compound was prepared by adding 2-pyridinecarboxylic (α -picolinic) acid to a warm aqueous suspension of Ba(OH)₂ and freshly precipitated neodymium carbonate. After two days parallelepiped pink-violet crystals were formed. A specimen 0.3 × 0.3 × 0.25 mm was cut from a larger crystal. D_m by flotation in C₂H₄Br₂/CHCl₃. Oscillation and Weissenberg photographs showed that the crystals belong to the monoclinic system, space group $P2_1/n$. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflections, $21 < 2\theta < 26^\circ$), variable $\omega/2\theta$ scan, $4 < 2\theta < 50^\circ$, two standards every 50 reflections, slight decay (10% every *ca* 180 h of exposure) was detected, mean relative e.s.d. of the control reflections (after correcting for the decay) 2.5%, 7045 intensities measured, of which 6227 were unique with $I \geq 3\sigma(I)$, $R_{\text{int}} = 0.016$, index range h 0→18, k 0→24, l -22→22, no

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Table 1. Final atomic coordinates and equivalent isotropic thermal U factors
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq} (\AA^2)
Nd1	0.46976 (4)	0.24155 (3)	0.93164 (3)	0.0288 (2)
Nd2	0.61001 (4)	0.47644 (3)	0.77314 (4)	0.0286 (2)
Ba	0.61275 (4)	0.43402 (3)	0.98287 (3)	0.0268 (2)
O11	0.6167 (5)	0.2982 (3)	0.9946 (3)	0.037 (3)
O21	0.7502 (6)	0.3196 (4)	0.9813 (5)	0.063 (4)
O12	0.4429 (5)	0.3559 (3)	0.9584 (3)	0.036 (3)
O22	0.3605 (6)	0.4358 (4)	0.9810 (4)	0.059 (4)
O13	0.7212 (5)	0.4781 (3)	0.9002 (3)	0.037 (3)
O23	0.8634 (5)	0.4861 (5)	0.9848 (4)	0.065 (4)
O14	0.4317 (5)	0.1399 (3)	0.9811 (4)	0.047 (3)
O24	0.4061 (8)	0.0771 (4)	1.0649 (5)	0.087 (5)
O15	0.5822 (5)	0.5259 (3)	0.6522 (3)	0.036 (3)
O25	0.5183 (6)	0.6106 (4)	0.5763 (4)	0.053 (3)
O16	0.5346 (5)	0.5106 (3)	0.8576 (3)	0.039 (3)
O26	0.4213 (5)	0.5500 (4)	0.8906 (4)	0.056 (3)
O17	0.4150 (5)	0.1632 (3)	0.8314 (4)	0.050 (3)
O27	0.3663 (6)	0.1364 (4)	0.7120 (4)	0.059 (4)
O18	0.5709 (5)	0.3802 (3)	0.8340 (3)	0.038 (3)
O28	0.5415 (5)	0.2734 (3)	0.8387 (3)	0.043 (3)
O/W1	0.7880 (5)	0.4448 (4)	1.0888 (4)	0.055 (3)
O/W2	0.7260 (6)	0.3944 (5)	0.7583 (5)	0.067 (4)
O/W3	0.1193 (7)	0.0339 (5)	0.0270 (5)	0.086 (5)
O/W4	0.2646 (10)	0.1077 (8)	0.1292 (7)	0.130 (8)
O/W5	0.1134 (13)	0.4402 (6)	0.8244 (7)	0.181 (10)
O/W6	0.4461 (9)	0.0106 (6)	0.8063 (7)	0.133 (8)
O/W7	0.3573 (11)	0.1612 (7)	0.3896 (8)	0.075 (5)**†
O/W8	0.0109 (17)	0.4113 (12)	0.9088 (13)	0.118 (9)**†
O/W9	0.5572 (23)	0.0042 (16)	1.0587 (18)	0.086 (10)**†
O/W10	0.9260 (24)	0.3821 (16)	0.8336 (18)	0.039 (9)**†
O/W11	0.9170 (24)	0.3457 (17)	0.9668 (18)	0.040 (9)**†
N1	0.6212 (6)	0.1722 (4)	0.9583 (4)	0.033 (3)
N2	0.3135 (6)	0.2666 (4)	0.9516 (4)	0.037 (3)
N3	0.7754 (6)	0.5308 (5)	0.7957 (5)	0.045 (4)
N4	0.5085 (7)	0.2349 (4)	1.0795 (5)	0.044 (4)
N5	0.6062 (6)	0.6060 (4)	0.7698 (4)	0.039 (3)
N6	0.4301 (6)	0.5072 (4)	0.7151 (4)	0.035 (3)
N7	0.3449 (6)	0.2864 (5)	0.8014 (4)	0.046 (4)
N8	0.5333 (6)	0.3733 (4)	0.6869 (4)	0.037 (3)
C11	0.6247 (9)	0.1078 (6)	0.9483 (6)	0.051 (5)
C21	0.7062 (10)	0.0755 (6)	0.9513 (6)	0.054 (5)
C31	0.7828 (10)	0.1120 (6)	0.9600 (7)	0.057 (6)
C41	0.7773 (8)	0.1797 (6)	0.9677 (6)	0.049 (5)
C51	0.6952 (8)	0.2074 (5)	0.9670 (5)	0.036 (4)
C61	0.6895 (8)	0.2806 (5)	0.9830 (5)	0.038 (4)
C12	0.2464 (9)	0.2196 (7)	0.9460 (7)	0.058 (5)
C22	0.1641 (9)	0.2356 (7)	0.9501 (8)	0.059 (6)
C32	0.1459 (10)	0.3003 (9)	0.9642 (8)	0.073 (7)
C42	0.2148 (9)	0.3491 (7)	0.9712 (7)	0.058 (5)
C52	0.2974 (7)	0.3288 (5)	0.9645 (5)	0.037 (4)
C62	0.3722 (8)	0.3780 (5)	0.9686 (5)	0.033 (4)
C13	0.8035 (9)	0.5584 (7)	0.7430 (7)	0.062 (6)
C23	0.8918 (10)	0.5823 (7)	0.7583 (8)	0.062 (6)
C33	0.9536 (9)	0.5777 (8)	0.8293 (8)	0.072 (6)
C43	0.9263 (9)	0.5498 (6)	0.8840 (7)	0.058 (5)
C53	0.8391 (8)	0.5286 (5)	0.8650 (5)	0.040 (4)
C63	0.8041 (8)	0.4930 (5)	0.9222 (6)	0.040 (4)
C14	0.5525 (9)	0.2793 (6)	1.1293 (6)	0.049 (5)
C24	0.5792 (10)	0.2691 (7)	1.2063 (6)	0.061 (6)
C34	0.5629 (11)	0.2118 (8)	1.2315 (6)	0.073 (6)
C44	0.5144 (10)	0.1622 (6)	1.1796 (6)	0.064 (6)
C54	0.4899 (8)	0.1772 (5)	1.1057 (6)	0.046 (5)
C64	0.4369 (9)	0.1271 (5)	1.0451 (6)	0.054 (5)
C15	0.6370 (9)	0.6440 (6)	0.8312 (6)	0.052 (5)
C25	0.6603 (10)	0.7081 (6)	0.8281 (7)	0.062 (6)
C35	0.6468 (12)	0.7370 (6)	0.7598 (9)	0.081 (7)
C45	0.6093 (10)	0.7000 (6)	0.6954 (6)	0.056 (5)
C55	0.5924 (8)	0.6341 (5)	0.7035 (5)	0.041 (4)
C65	0.5614 (7)	0.5875 (5)	0.6385 (5)	0.037 (4)
C16	0.3761 (8)	0.5100 (6)	0.6431 (5)	0.043 (4)
C26	0.2878 (8)	0.5343 (6)	0.6170 (6)	0.048 (5)
C36	0.2507 (8)	0.5597 (6)	0.6661 (6)	0.052 (5)
C46	0.3037 (8)	0.5583 (5)	0.7411 (6)	0.042 (4)
C56	0.3909 (7)	0.5339 (5)	0.7628 (5)	0.032 (4)
C66	0.4534 (7)	0.5317 (5)	0.8441 (5)	0.032 (4)
C17	0.3097 (9)	0.3469 (6)	0.7854 (6)	0.056 (5)
C27	0.2647 (9)	0.3697 (7)	0.7148 (7)	0.062 (5)
C37	0.2539 (10)	0.3278 (7)	0.6576 (6)	0.069 (6)
C47	0.2881 (9)	0.2651 (7)	0.6705 (6)	0.057 (5)
C57	0.3360 (8)	0.2447 (5)	0.7449 (5)	0.041 (4)
C67	0.3740 (8)	0.1769 (6)	0.7625 (6)	0.047 (5)
C18	0.5193 (8)	0.3676 (6)	0.6149 (6)	0.046 (5)
C28	0.5148 (9)	0.3111 (6)	0.5791 (6)	0.054 (5)

Table 1 (cont.)

	x	y	z	U_{eq} (\AA^2)
C38	0.5213 (10)	0.2507 (7)	0.6171 (6)	0.066 (6)
C48	0.5314 (10)	0.2559 (6)	0.6925 (6)	0.057 (5)
C58	0.5388 (7)	0.3179 (5)	0.7250 (5)	0.033 (4)
C68	0.5530 (7)	0.3249 (5)	0.8062 (5)	0.033 (4)

* Site occupancy factors: O/W7 0.6; O/W8 0.5; O/W9 0.3; O/W10 0.2; O/W11 0.2.

† Refined isotropically, U_{iso} given.

correction for absorption or extinction. Structure was solved and refined with a locally modified version of *SHELX76* (Sheldrick, 1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), real and imaginary components for anomalous dispersion included for all non-H atoms. The Nd atoms were located from a Patterson map; the remaining non-H atoms from subsequent difference syntheses; some hydrate molecules appeared to be disordered, their occupancy factors were chosen on the basis of the peak heights in a difference synthesis; C-bonded hydrogens placed geometrically, water hydrogens from difference syntheses, not all found. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, disordered water oxygens isotropic, hydrogens isotropic with constrained positional parameters and common temperature factors, separately for C-bonded and water hydrogens, the constraints refined as additional parameters), $R = 0.0390$, $wR = 0.0378$, the maximum shift/e.s.d. ratio 0.35 , $\Delta\rho$ between -0.75 and 1.30 e \AA^{-3} , the highest peaks around Nd and Ba atoms, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1,* and the geometry of the coordination environment of the Nd and Ba ions is shown in Table 2, together with average bond lengths for the α -picolinate residues.

The complex molecule is an oligonuclear centrosymmetric aggregate built around four neodymium and two barium cations. The *ORTEP* view (Johnson, 1976) of the complex molecule is given in Fig. 1. All bond lengths are unexceptional (Sinha, 1976). The coordination figure of Nd1 may best be described as a tricapped trigonal prism with O12, N4, N2 and O28, N1, O17 forming the bases and O11, O14, N7 forming the caps. The Δ parameter is 0.067 \AA^2 ($\Delta = \sum d_i^2/9$, d_i is the distance between the real position of the i th atom, and the relevant vertex in the ideal, least-squares-fitted polyhedron; Drew, 1977). The

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53276 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cules (4), (5) and (7)]; however, the carboxyl oxygen involved in the chelate ring may also be bonded to the barium cation [molecule (3)]; both carboxyl oxygens may be bonded to the same barium [molecule (1)], to two different bariums [molecules (2) and (6)], or to the barium and the other neodymium ion [molecule (8)]. There is a pair of intramolecular hydrogen bonds in the complex molecule (represented by dashed lines in Fig. 1). The structure is held together by an elaborate network of intermolecular hydrogen bonds. The crystal packing is shown in Fig. 2 (the disordered waters OW8, OW9, OW10 and OW11 have been omitted for the sake of clarity).

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Carbonyl(η^5 -cyclopentadienyl)bis(trimethyl phosphite)ruthenium(II) Tetrafluoroborate

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Abstract. [Ru(CO){P(OCH₃)₃}₂(C₅H₅)] [BF₄], $M_r = 529.13$, monoclinic, $P2_1/c$, $a = 11.455$ (2), $b = 11.648$ (4), $c = 15.709$ (2) Å, $\beta = 99.40$ (1)°, $V = 2067.87$ Å³, $Z = 4$, $D_x = 1.700$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 9.577$ cm⁻¹, $F(000) = 1064$, $T = 296$ K, $R = 0.039$ for 2941 observed reflections. The crystal structure of the title compound consists of discrete [Ru(CO){P(OMe)₃}₂(Cp)]⁺ cations and [BF₄]⁻ anions. The cation displays a typical 'three-legged piano stool' geometry about ruthenium with significant distances Ru—P1 2.258 (1), Ru—P2 2.260 (1), Ru—C1 1.880 (6), C1—O1 1.115 (6) Å, and angles Ru—C1—O1 176.9 (5), C1—Ru—P1 90.3 (2), C1—Ru—P2 89.8 (2) and P1—Ru—P2 92.2 (1)°.

Introduction. The [Ru(L)(PR₃)₂(Cp)] system is extensively studied, particularly for $L = PPh_3$ because the starting material [RuCl(PPh₃)₂(Cp)] is easily synthesized and handled (Bruce, Hameister, Swincer, Wallis & Ittel, 1982) and both its chloride and phosphine ligands are substitutionally labile (Albers, Robinson & Singleton, 1987). We are interested in the chemistry of [Ru(L)(PR₃)₂(Cp)] complexes with smaller ancillary phosphines such as trimethyl phosphite (Ashby, Bruce, Tomkins & Wallis, 1979; Bruce, Cifuentes, Snow & Tiekink, 1989; Treichel, Komar & Vincenti, 1984). We recently obtained single crystals of [Ru(CO){P(OMe)₃}₂(Cp)] [BF₄]

(I) during attempted slow recrystallization of [Ru(C₂H₂){P(OMe)₃}₂(Cp)] [BF₄], evidently *via* the oxidation of the C₂H₂ ligand by traces of air (Bruce, Swincer & Wallis, 1979). Compound (I) has not previously been reported.

Experimental. [Ru(CO){P(OMe)₃}₂(Cp)] [BF₄] (I) was prepared and crystallized by passing a stream of nitrogen gas saturated with diethyl ether over [Ru(η^2 -HC≡CH){P(OMe)₃}₂(Cp)] [BF₄] (Frank & Selegue, 1990) dissolved in a minimum of dichloromethane. A 0.42 × 0.47 × 0.53 mm crystal suitable for X-ray diffraction was cut from one of the resulting large, pale yellow crystals. IR (CH₂Cl₂): $\nu(\text{CO})$ 2022 vs, $\nu(\text{BF})$ 1094 vs cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ_{H} 4.43 (*t*, ³ $J_{\text{PH}} = 1.0$ Hz, 5 H, Cp), 3.53 (virtual *t*, ³ $J_{\text{PH}} + ^5J_{\text{PH}} = 5.3$ Hz, 18 H, POCH₃). Data were measured with an Enraf-Nonius CAD-4 diffractometer controlled by a MicroVAX computer, graphite-monochromated Mo $K\alpha$ radiation; ω -2 θ scan technique. Cell parameters were determined by least-squares refinement of 25 reflections ($6 < \theta < 16^\circ$). A total of 3989 reflections ($2 < \theta < 25^\circ$) were measured in the range $-13 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq l \leq 18$. Minor variation (max. 13%) was noted in the net intensities of three reference reflections (135, 137, 133) measured every 5000 s. Of 3773 unique reflections, 2941 satisfied $I \geq 3\sigma(I)$. An empirical absorption correction was applied using