Actinide Structural Studies. Part 8.[1] Some New Oxygen-donor Complexes of Trichloro(cyclopentadienyl)neptunium(IV); The Crystal Structure of Trichloro(η^5-cyclopentadienyl)bis(methyldiphenylphosphine oxide)-neptunium(IV) †

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The complexes Np(cp)Cl_3·2L [cp = η^5-C_5H_5; L = dimethylformamide (dmf), MeCONPr$^i_2$, PMe_3O, EtCONPr$^i_2$, PMe_2PhO, or $PMePh_2O$] have been prepared. The crystal and molecular structure of [Np(cp)Cl_3($PMePh_2O$)$_2$] has been determined from three-dimensional *X*-ray diffraction data and refined by least squares to R = 0.061 for 4 248 observed [$I/\sigma(I) \geqslant 3.0$] reflections. The complex crystallises in space group $P1\,2_1/c$, with a = 10.199(4), b = 33.208(13), c = 20.661(7) Å, β = 113.04(2)°, and Z = 8. The neptunium atom is octahedrally co-ordinated, with the two $PMePh_2O$ ligands in *cis* positions, so that the cyclopentadienyl group is *trans* to one $PMePh_2O$ ligand. I.r. and near-i.r.–visible absorption spectra (dichloromethane solution) are reported.

Complexes of trichloro(cyclopentadienyl)actinides(IV) of composition M(cp)Cl_3·xL (cp = η^5-cyclopentadienyl) have been reported for M = Th with x = 2 [L = PPh_3O[2] or tetrahydrofuran (thf)[3]], x = 2.5 (ref. 2) [L = thf, $MeCONMe_2$ (dma), or $Me_3CCONMe_2$ (dmpva)], and x = 3 (L = MeCN[3]), whereas for M = U or Np only complexes with x = 2 are known [M = U, L = thf,[4] dma,[5] dmpva,[5] PMe_3O,[3] PMe_2PhO,[3] $PMePh_2O$,[3] PPh_3O,[5] or $P(NMe_2)_3O$;[6] M = Np,[7] L = thf, dma, dmpva, PPh_3O, or $P(NMe_2)_3O$]. As the radius of the M^{IV} centre decreases across the actinide series from M = Th to M = Np, there is an increasing tendency for the complexes M(cp)Cl_3·2L to disproportionate in solution to a mixture[7] of M(cp)$_3$Cl and MCl_4·2L, particularly when the ligand L is bulky. It was therefore of interest to investigate the behaviour of neptunium(IV) complexes of this type with ligands of intermediate bulk and to obtain structural information. Our aim was to ascertain whether the *cis* pseudo-octahedral geometry found[6] for the complexes [U(cp)Cl_3{$P(NMe_2)_3O$}$_2$] and [U(cp)Cl_3(PPh_3O)$_2$]·thf is adopted by analogous neptunium(IV) complexes.

Results and Discussion

The Complexes.—All of the complexes Np(cp)Cl_3·2L were rust-red except where L = PMe_3O (dark brown). They were prepared by treating the appropriate neptunium tetrachloride complex, $NpCl_4$·xL, with the stoicheiometric quantity of Tl(cp) in dry methyl cyanide, followed by vacuum evaporation of the supernatant to dryness. After dissolution of the residue in dichloromethane, the complex precipitated on addition of 2-methylbutane.

The near-i.r.–visible spectra of the complexes Np(cp)Cl_3·2L were almost identical (Table 1) and were very similar to those reported for other neptunium(IV) complexes of this composition.[7] The absence of a very strong absorption near 1 050 nm indicated that disproportionation to Np(cp)$_3$Cl had not occurred.

† *Supplementary data available* (No. SUP 56459, 5 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Principal features (nm) in the near-i.r.–visible spectra of the complexes in CH_2Cl_2 solution (ε/dm³ mol⁻¹ cm⁻¹ in parentheses) *

Np(cp)Cl_3·2dmf	636(63.0), 673(61.9), 709(67.4), 760(93.9), *781*(153.6), 885(70.7), 940(95.0), 968(82.9), 1 563(25.4)
Np(cp)Cl_3·2MeCONPr$^i_2$	637(41.2), 673(42.3), 709(49.5), 757(80.4), 762 (sh) (78.4), *781*(185.6), 886(70.1), 931 (sh) (66.0), 942 (95.9), 971(89.7), 1 557(48.4)
Np(cp)Cl_3·2EtCONPr$^i_2$	636(61.1), 672(60.0), 708(63.3), 757(91.7), 762 (sh) (97.5), *780* (196.5), 881(75.3), 931 (sh) (70.9), 940(97.1), 969(93.1), 1 552(39.3)
Np(cp)Cl_3·2PMe_3O	633(44.2), 670(51.3), 709(50.4), 757(79.6), 762(80.5), 779(175.2), 888(60.2), 932 (sh) (65.5), 942(95.6), 971(77.9), 1 565(37.2)
Np(cp)Cl_3·2PMe_2PhO	634(86.7), 671(85.0), 708(77.7), 762(113.9), 773(126.6), 779(175.4), 890(83.1), 932 (sh) (72.3), 943(94.0), 971(104.9), 1 658(39.8)
Np(cp)Cl_3·2$PMePh_2O$	634(50.2), 672(56.3), 708(58.2), 756(72.7), 762(77.8), *778*(166.0), 883(59.4), 931 (sh) (58.4), 942(94.2), 970(84.0), 1 567(38.9)

* sh = Shoulder. Wavelength values for the most intense peaks are italicised.

In the i.r. spectra of the complexes (Table 2) the shifts in ν(CO) or ν(PO) of the neutral ligands were of the same order as those observed in the spectra of the complexes $NpCl_4$·xL with these ligands, although these modes showed greater splitting than in the case of the latter complexes.

The Structure of [Np(cp)Cl_3($PMePh_2O$)$_2$].—The asymmetric unit of the crystal contains two independent molecules, which are virtually identical. Table 3 lists the individual bond lengths and angles, Figure 1 shows a view of molecule 1. The neptunium atom is octahedrally co-ordinated to the oxygen atoms of two $PMePh_2O$ ligands, which occupy *cis* positions, to three chlorine atoms, and to the cp ligand (considered as bonded to the centre of the ring) which is *trans* with respect to one $PMePh_2O$ ligand. The octahedral geometry is distorted due to the relative bulk of the ligands, particularly the cp ligand,

Table 2. Infrared spectra (cm^{-1}) of the complexes *

Compound	ν(X=O)	Δν(X=O)	ν(Np–cp)	ν(Np–Cl)
$Np(cp)Cl_3\cdot 2dmf$	1 639vs, vbr	16	251vs	230vs
$Np(cp)Cl_3\cdot 2MeCONPr^i_2$	1 567vs(sh), 1 552vs, br	66, 81	255s(sh)	234s
$Np(cp)Cl_3\cdot 2EtCONPr^i_2$	1 560vs(sh), 1 550vs, 1 531vs(sh)	74, 84, 101	258s	231s
$Np(cp)Cl_3\cdot 2PMe_3O$	1 099s, br, 1 061vs, br	62, 100	251m	233s
$Np(cp)Cl_3\cdot 2PMe_2PhO$	1 095s, 1 075vs, 1 061s	80, 100, 114	240m(sh)	228m
$Np(cp)Cl_3\cdot 2PMePh_2O$	1 081s(sh), 1 070vs(sh), 1 059vs	82, 93, 104	249m	231ms

* X = C or P; s = strong; m = medium; v = very; sh = shoulder, br = broad.

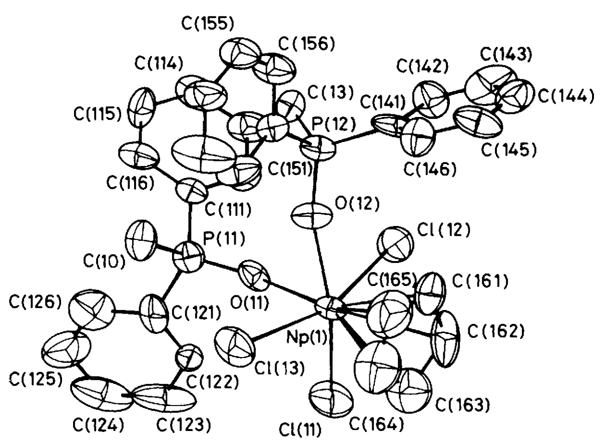

Figure 1. View of molecule 1 of $[Np(cp)Cl_3(PMePh_2O)_2]$ showing the atomic numbering; molecule 2 is virtually identical

causing deviation of the inter-ligand angles from 90°. The angles between the centroid of the cp ligand and the three chlorine atoms and between the centroid and O(2) of the $PMePh_2O$ ligand are all *ca.* 100°, indicating that the bulk of the cp ligand has forced these ligands below the plane of the central neptunium atom. This, in turn, reduces the angles between the chlorine atoms and the oxygen atoms whilst maintaining the angles between chlorine atoms close to 90°. This deviation from true octahedral geometry reflects the relative bulk of the ligands about the neptunium atom in the order: cyclopentadienyl > Cl^- > $PMePh_2O$.

The structure of the uranium(IV) analogue has not been determined, but the structure of $U(cp)Cl_3\cdot 2PPh_3O\cdot thf$ shows a general similarity to the present structure.[6] The neptunium to chlorine bond lengths average 2.65(2) Å and the neptunium to oxygen lengths average 2.27(5) Å. Both are very close to the corresponding values in the U^{IV} compound just mentioned, suggesting that these distances may be controlled by ligand–ligand contacts as well as by the metal atom size.

The view of the unit cell down *a* (Figure 2) shows the two orientations of the molecules within the cell and the small variation between the two independent molecules in each asymmetric unit.

Experimental

The complexes were prepared and handled under dry nitrogen (water ⩽ 20 p.p.m., oxygen ⩽ 10 p.p.m.) in glove boxes to protect samples against atmospheric oxidation and moisture,

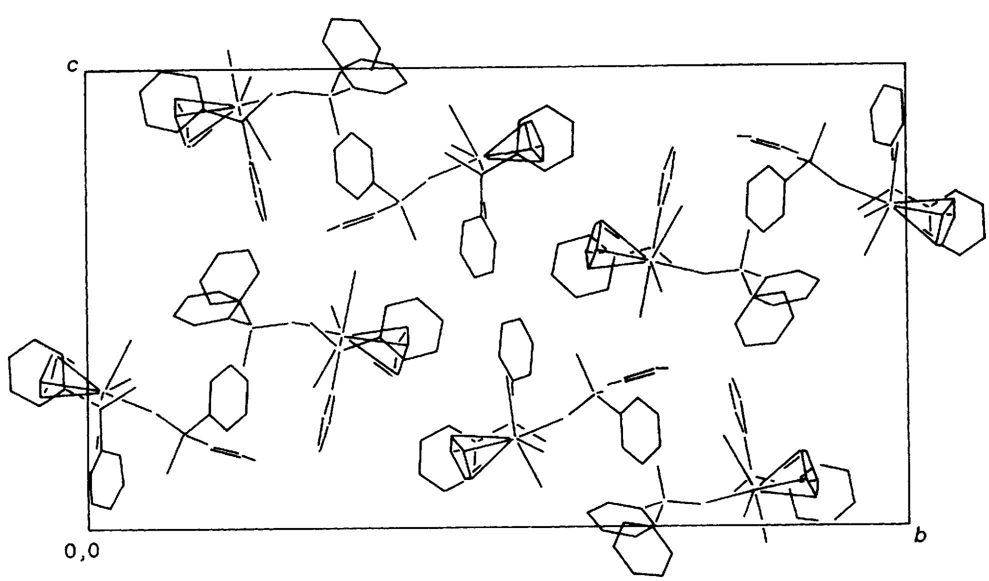

Figure 2. Unit cell of $[Np(cp)Cl_3(PMePh_2O)_2]$ viewed down *a*

Table 3. Bond lengths (Å) and angles (°) (with standard deviations in parentheses) for [Np(cp)Cl_3($PMePh_2O$)$_2$]. Each listed atom number is prefixed by 1 or 2 for molecule 1 or 2 respectively. Cnd is the centroid of the cyclopentadienyl group with co-ordinates 0.1271, 0.6181, 0.6191 for molecule 1 and 0.5661, −0.0466, 0.3473 for molecule 2

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
(*a*) Bond lengths			(*b*) Bond angles		
(*i*) Around Np					
Np–Cl(1)	2.634(5)	2.667(6)	Cl(1)–Np–Cl(2)	90.3(2)	159.0(2)
Np–Cl(2)	2.636(7)	2.656(6)	Cl(1)–Np–Cl(3)	94.4(2)	89.7(2)
Np–Cl(3)	2.652(6)	2.641(6)	Cl(1)–Np–O(1)	82.3(3)	81.0(3)
Np–O(1)	2.280(12)	2.265(12)	Cl(1)–Np–O(2)	161.5(4)	84.4(4)
Np–O(2)	2.283(12)	2.281(13)	Cl(2)–Np–Cl(3)	159.2(2)	91.7(2)
Np–C(61)	2.71(2)	2.67(2)	Cl(2)–Np–O(1)	81.1(4)	78.4(3)
Np–C(62)	2.70(2)	2.71(2)	Cl(2)–Np–O(2)	82.5(4)	87.4(4)
Np–C(63)	2.73(2)	2.67(2)	Cl(3)–Np–O(1)	79.5(4)	82.1(3)
Np–C(64)	2.75(3)	2.66(3)	Cl(3)–Np–O(2)	86.8(4)	160.6(4)
Np–C(65)	2.73(2)	2.69(2)	O(1)–Np–O(2)	79.8(4)	78.7(4)
Np–C(mean)	2.724(11)	2.682(11)	Cnd–Np–Cl(1)	100.0(1)	100.4(1)
			Cnd–Np–Cl(2)	101.0(1)	100.1(1)
			Cnd–Np–Cl(3)	98.1(1)	99.7(1)
			Cnd–Np–O(1)	176.8(3)	177.8(3)
			Cnd–Np–O(2)	98.1(3)	99.6(3)
(*ii*) Cyclopentadienyl group					
C(61)–C(62)	1.39(3)	1.34(3)	C(61)–C(62)–C(63)	108(3)	106(2)
C(62)–C(63)	1.44(4)	1.37(5)	C(62)–C(63)–C(64)	102(2)	114(3)
C(63)–C(64)	1.40(3)	1.34(4)	C(63)–C(64)–C(65)	113(3)	105(3)
C(64)–C(65)	1.23(4)	1.38(5)	C(64)–C(65)–C(61)	112(2)	108(2)
C(65)–C(61)	1.31(4)	1.43(4)	C(65)–C(61)–C(62)	108(3)	108(3)
(*iii*) Methyldiphenylphosphine oxide groups					
O(1)–P(1)	1.53(1)	1.53(1)	O(1)–P(1)–C(0)	113.0(8)	110.8(9)
P(1)–C(0)	1.81(2)	1.80(2)	O(1)–P(1)–C(11)	109.9(7)	110.1(7)
P(1)–C(11)	1.78(2)	1.78(2)	O(1)–P(1)–C(21)	110.2(7)	109.1(8)
P(1)–C(21)	1.79(2)	1.75(2)	C(0)–P(1)–C(11)	108.1(9)	108.2(9)
O(2)–P(2)	1.51(2)	1.48(2)	C(0)–P(1)–C(21)	109.5(9)	109.4(9)
P(2)–C(3)	1.79(2)	1.75(3)	C(11)–P(1)–C(21)	105.9(7)	109.3(7)
P(2)–C(41)	1.78(2)	1.81(2)	O(2)–P(2)–C(3)	112.2(9)	110.6(10)
P(2)–C(51)	1.80(1)	1.77(2)	O(2)–P(2)–C(41)	113.5(8)	110.4(7)
			O(2)–P(2)–C(51)	108.2(7)	108.8(10)
			C(3)–P(2)–C(41)	107.8(9)	107.9(11)
			C(3)–P(2)–C(51)	107.8(8)	111.0(9)
			C(41)–P(2)–C(51)	107.0(6)	108.1(8)

and to afford protection against the α radiation emitted by ^{237}Np. Solvents were dried as described previously.[8]

The complexes $NpCl_4$·*x*L used as starting materials,[9] Cs_2NpCl_6,[10] Tl(cp),[11] PMe_3O,[12] PMe_2PhO,[3] $PMePh_2O$,[13] $MeCONPr^i_2$,[14] and $EtCONPr^i_2$[15] were prepared by the published methods; dimethylformamide (dmf) (B.D.H. Ltd.) was used as supplied.

Vibrational spectra were obtained using a Perkin-Elmer PE 180 (4 000—200 cm^{-1}) spectrometer with Nujol mulls. Electronic spectra in the near-i.r.–visible regions were recorded for solutions in dichloromethane using a Cary 14 spectrometer.

Preparations.—All of the complexes were prepared by adding the stoicheiometric quantity of Tl(cp) to the appropriate neptunium tetrachloride complex, $NpCl_4$·*x*L, in dry MeCN (5 cm^3), then stirring for 48 h. The supernatant was evaporated to dryness *in vacuo* and the residue was dissolved in the minimum quantity of dichloromethane, from which the complex precipitated on addition of 2-methylbutane. The products were washed with 2-methylbutane (3 × 2 cm^3), then dried *in vacuo* for 4 h. [Np(cp)Cl_3($PMePh_2O$)$_2$] was not completely precipitated from dichloromethane solution, but crystals separated on standing.

Table 4. Analytical data *(%)

	Np	Cl	Yield(%)
Np(cp)Cl_3·2dmf	41.8 (42.7)	18.7 (19.2)	28
Np(cp)Cl_3·2$MeCONPr^i_2$	34.7 (34.1)	15.3 (15.3)	62
Np(cp)Cl_3·2$EtCONPr^i_2$	32.4 (32.8)	14.7 (14.7)	64
Np(cp)Cl_3·2PMe_3O	39.8 (40.0)	17.9 (18.0)	84
Np(cp)Cl_3·2PMe_2PhO	32.7 (33.1)	14.7 (14.9)	56
Np(cp)Cl_3·2$PMePh_2O$	28.0 (28.2)	12.6 (12.7)	63

* Calculated values are given in parentheses.

Analyses.—Neptunium-237 was determined by α-counting aliquots of an acid solution of the complex and chloride was determined as described previously.[15] The analytical results and yields are summarised in Table 4.

Structure Determination.—*Crystal data*. $C_{31}H_{31}NpO_2P_2$, *M* = 840.9, monoclinic, space group $P2_1/c$, *a* = 10.199(4), *b* = 33.208(13), *c* = 20.661(7) Å, β = 113.04(2)°, *U* = 6 439.6(4) Å^3, *Z* = 8, D_c = 1.74 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 24.69 cm^{-1}, *F*(000) = 2 848.

The crystal was mounted on a quartz fibre, encapsulated in a Lindemann glass capillary. Data were collected with a Syntex

Table 5. Atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses for [Np(cp)Cl_3($PMePh_2O$)$_2$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Np(1)	1 348.8(8)	6 876.5(2)	5 787.4(4)	Cl(21)	4 787(7)	549(2)	4 176(3)
Np(2)	4 921.1(9)	207.5(3)	3 035.7(4)	Cl(22)	4 540(7)	111(2)	1 697(3)
Cl(11)	−1 399(5)	7 025(2)	5 156(3)	Cl(23)	7 442(6)	542(2)	3 338(4)
Cl(12)	1 497(6)	6 745(2)	4 560(3)	O(21)	4 157(12)	828(4)	2 590(6)
Cl(13)	1 628(7)	7 256(2)	6 964(3)	P(21)	3 380(6)	1 173(2)	2 106(3)
O(11)	1 516(12)	7 527(3)	5 474(6)	C(20)	2 035(22)	985(8)	1 304(9)
P(11)	1 902(6)	7 975(2)	5 578(3)	C(212)	4 302(11)	1 862(5)	1 655(8)
C(10)	3 160(21)	8 091(7)	6 458(8)	C(213)	5 292(11)	2 085(5)	1 492(8)
C(112)	2 433(12)	7 893(3)	4 383(8)	C(214)	6 581(11)	1 911(5)	1 558(6)
C(113)	2 945(12)	8 020(3)	3 882(8)	C(215)	6 881(11)	1 513(5)	1 786(6)
C(114)	3 683(12)	8 383(3)	3 974(8)	C(216)	5 892(11)	1 290(5)	1 948(6)
C(115)	3 909(12)	8 619(3)	4 567(8)	C(211)	4 602(11)	1 465(5)	1 883(6)
C(116)	3 397(12)	8 492(3)	5 068(8)	C(222)	3 238(12)	1 509(4)	3 268(9)
C(111)	2 659(12)	8 129(3)	4 978(8)	C(223)	2 639(12)	1 752(4)	3 631(9)
C(122)	−1 012(17)	8 108(4)	4 995(7)	C(224)	1 384(12)	1 963(4)	3 264(9)
C(123)	−2 218(17)	8 353(4)	4 771(7)	C(225)	728(12)	1 931(4)	2 533(9)
C(124)	−2 084(17)	8 763(4)	4 930(7)	C(226)	1 327(12)	1 689(4)	2 169(9)
C(125)	−745(17)	8 928(4)	5 313(7)	C(221)	2 582(12)	1 478(4)	2 537(9)
C(126)	461(17)	8 683(4)	5 536(7)	O(22)	2 515(13)	139(4)	2 684(7)
C(121)	327(17)	8 273(4)	5 377(7)	P(22)	1 070(6)	169(2)	2 692(3)
O(12)	3 762(12)	6 934(4)	6 150(6)	C(23)	937(25)	598(7)	3 156(13)
P(12)	5 202(5)	6 914(2)	6 102(3)	C(242)	1 299(13)	−290(5)	3 853(9)
C(13)	5 379(21)	7 280(6)	5 508(10)	C(243)	1 095(13)	−634(5)	4 191(9)
C(142)	5 468(14)	6 353(5)	5 157(7)	C(244)	292(13)	−954(5)	3 796(9)
C(143)	5 724(14)	5 966(5)	4 974(7)	C(245)	−306(13)	−931(5)	3 063(9)
C(144)	6 106(14)	5 660(5)	5 477(7)	C(246)	−101(13)	−588(5)	2 725(5)
C(145)	6 233(14)	5 741(5)	6 161(7)	C(241)	701(13)	−267(5)	3 120(9)
C(146)	5 977(14)	6 128(5)	6 344(7)	C(252)	−1 456(19)	396(5)	1 680(9)
C(141)	5 594(14)	6 435(5)	5 842(7)	C(253)	−2 453(19)	440(5)	992(9)
C(152)	6 152(11)	7 118(4)	7 514(8)	C(254)	−2 196(19)	268(5)	436(9)
C(153)	7 196(11)	7 190(4)	8 183(8)	C(255)	−942(19)	54(5)	569(9)
C(154)	8 633(11)	7 160(4)	8 297(8)	C(256)	56(19)	11(5)	1 258(9)
C(155)	9 027(11)	7 058(4)	7 743(8)	C(251)	−201(19)	182(5)	1 814(9)
C(156)	7 983(11)	6 986(4)	7 074(8)	C(261)	5 241(26)	−408(6)	3 917(10)
C(151)	6 546(11)	7 016(4)	6 960(8)	C(262)	4 459(27)	−571(6)	3 290(13)
C(161)	2 150(27)	6 093(6)	6 003(12)	C(263)	5 329(28)	−580(7)	2 927(13)
C(162)	696(27)	6 086(7)	5 594(13)	C(264)	6 634(31)	−430(7)	3 289(17)
C(163)	10(23)	6 224(6)	6 046(14)	C(265)	6 643(31)	−335(7)	3 940(16)
C(164)	1 174(25)	6 283(7)	6 681(12)				
C(165)	2 323(25)	6 219(7)	6 633(14)				

$P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range −1.0 to +1.1 (2θ) around the $K_{\alpha1}$—$K_{\alpha2}$ angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed a slight reduction during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 4 248 Observed reflections [$I/\sigma(I) \geqslant 3.0$] (12 325 collected) were used in refinement, and corrected for Lorentz, polarisation and absorption effects, the last with ABSCOR;[16] maximum and minimum transmission factors were 0.66 and 0.46. The crystal dimensions were 0.17 × 0.58 × 0.40 mm. Systematic absences $h0l, l \neq 2n$; $0k0, k \neq 2n$ indicate space group $P2_1/c$.

Two neptunium atoms were located in the asymmetric unit by Patterson techniques and the remaining non-hydrogen atoms were found on successive Fourier syntheses. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.07—0.12 Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Phenyl rings were held as rigid hexagons (C–C, 1.395 Å). Final refinement was on F by cascaded least-squares methods. Largest positive and negative peaks on a final difference Fourier synthesis were of height ±1.2 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0005 was used and shown to be satisfactory by a weight analysis. Final R = 0.061. Maximum shift/error in final cycle was 0.6 (mean 0.1). Computing was with SHELXTL[17] on a Data General NOVA3, apart from absorption correction on a Burroughs B6800. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 18. Final atomic co-ordinates are given in Table 5.

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References

1 Part 7, N. W. Alcock, D. J. Flanders, and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1985, 1001.

2 K. W. Bagnall, A. Beheshti, and F. Heatley, *J. Less-Common Met.*, 1978, **61**, 63.
3 I. Ahmed and K. W. Bagnall, *J. Less-Common Met.*, 1984, **99**, 285.
4 K. W. Bagnall and J. Edwards, *J. Organomet. Chem.*, 1974, **80**, C14.
5 K. W. Bagnall, J. Edwards, and A. C. Tempest. *J. Chem. Soc., Dalton Trans.*, 1978, 295.
6 K. W. Bagnall, F. Benetollo, G, Bombieri, and G. de Paoli, *J. Chem. Soc., Dalton Trans.*, 1984, 67.
7 K. W. Bagnall, M. J. Plews, and D. Brown, *J. Less-Common Met.*, 1983, **90**, 29.
8 K. W. Bagnall, J. Edwards, J. G. H. du Preez, and R. F. Warren, *J. Chem. Soc., Dalton Trans.*, 1975, 140.
9 K. W. Bagnall, G. F. Payne, and D. Brown, *J. Less-Common Met.*, in the press.
10 K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1961, 1611.
11 E. O. Fisher, *Angew, Chem.*, 1957, **69**, 207.
12 A. B. Burge and W. E. McKee, *J. Am. Chem. Soc.*, 1951, **73**, 4590.
13 D. D. Cofman and C. S. Marvel, *J. Am. Chem. Soc.*, 1929, **51**, 3496.
14 K. W. Bagnall, J. G. H. Du Preez, J. Bajorek, L. Bonner, H. Cooper, and G. Segal, *J. Chem. Soc., Dalton Trans.*, 1973, 2682.
15 K. W. Bagnall, M. J. Plews, and D. Brown, *J. Organomet. Chem.*, 1982, **224**, 263.
16 N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgard, Copenhagen, 1970.
17 G. M. Sheldrick, SHELXTL User Manual, Nicolet Instrument Co., 1983.
18 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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