METAL-ORGANIC COMPOUNDS

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Cerium(III) and Neodymium(III) Picrate Complexes with Tetramethylurea

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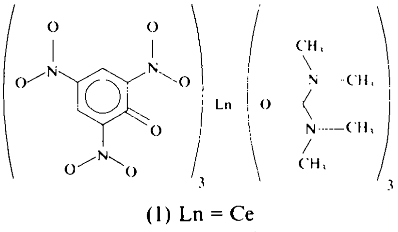
Abstract

In both title complexes, tris(1,1,2,2-tetramethylurea-κO)tris(2,4,6-trinitrophenolato-$\kappa O,O'$)cerium(III), $[Ce(C_6H_2N_3O_7)_3(C_5H_{12}N_2O)_3]$ (1), and tris(1,1,2,2-tetramethylurea-κO)tris(2,4,6-trinitrophenolato-$\kappa O,O'$)neodymium(III), $[Nd(C_6H_2N_3O_7)_3(C_5H_{12}N_2O)_3]$ (2), the lanthanide ion is coordinated to three bidentate picrate and three monodentate tetramethylurea (TMU) groups in a distorted tricapped-trigonal prismatic geometry.

Comment

The complexes (1) and (2) were prepared by treating the hydrated lanthanide picrates with TMU (molar ratio 1:3) followed by precipitation from solution by the addition of triethyl orthoformate (teof). Crystals were obtained by dissolving the compounds in a small amount of TMU and placing them in a dark teof atmosphere.



(1) Ln = Ce
(2) Ln = Nd

The neodymium ion is coordinated to nine O atoms: the phenolic O atom and one O atom of each *ortho*-nitro group of three different picrate groups and three O atoms of three TMU ligands, forming a tricapped-trigonal prism in which the O atoms of the *ortho*-nitro groups are sited at the apices.

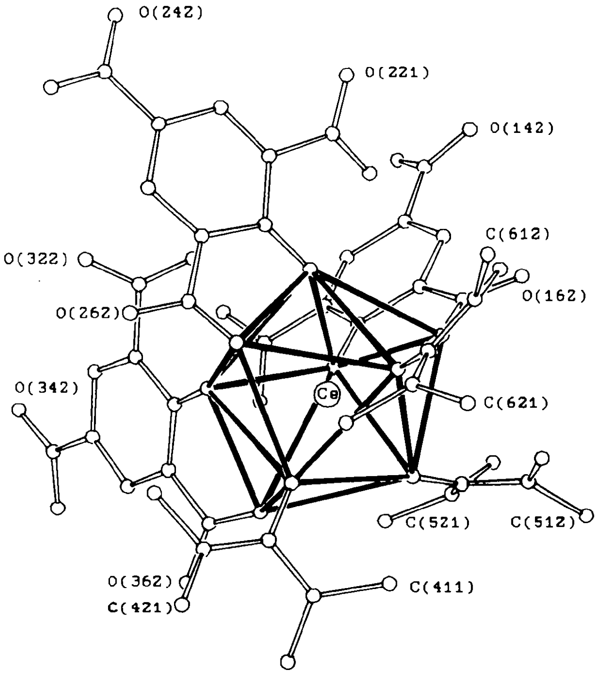


Fig. 1. View of $[Ce(C_6H_2N_3O_7)_3(C_5H_{12}N_2O)_3]$ showing the Ce^{3+} coordination and atom-labelling scheme.

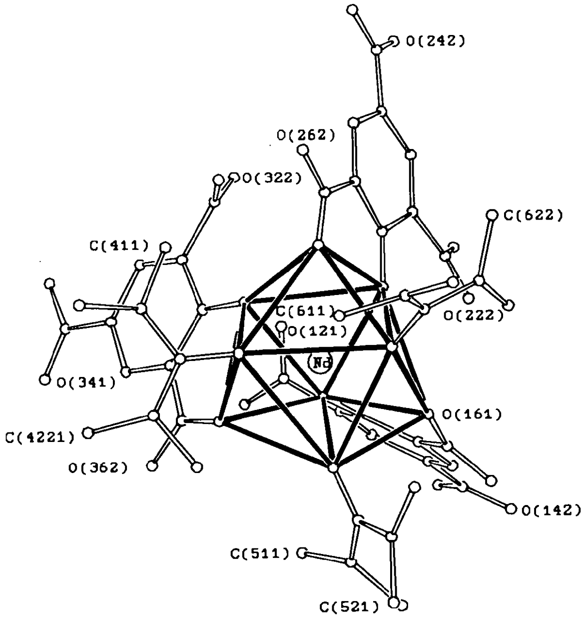


Fig. 2. View of $[Nd(C_6H_2N_3O_7)_3(C_5H_{12}N_2O)_3]$ showing the Nd^{3+} coordination and atom-labelling scheme.

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In the cerium complex the arrangement is similar to that of the previous case if a picrate *ortho*-nitro O atom that is rather distant from the Ce [Ce···O(361) = 2.885 (7) Å] is included in the coordination polyhedron.

Experimental

Compound (1)

Crystal data

$[Ce(C_6H_2N_3O_7)_3$-
$(C_5H_{12}N_2O)_3]$
M_r = 1172.91
Triclinic
$P\overline{1}$
a = 11.495 (5) Å
b = 11.815 (5) Å
c = 18.40 (1) Å
α = 83.09 (5)°
β = 76.79 (5)°
γ = 77.00 (3)°
V = 2364 (2) Å^3

Z = 2
D_x = 1.65 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 19–45°
μ = 8.50 mm^{-1}
T = 291 K
Irregular
0.32 × 0.24 × 0.10 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.70, $T_{\max}$ = 1.76
7046 measured reflections
6795 independent reflections

6329 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.058
$\theta_{\max}$ = 60.0°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 20$
1 standard reflection
frequency: 30 min
intensity variation: ±1.1%

Refinement

Refinement on F
R = 0.0703
wR = 0.0745
S = 1.77
6329 reflections
658 parameters
$w = (\sigma^2|F_o| + 0.0033|F_o|^2)^{-1}$

$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.70 e Å^{-3}
$\Delta\rho_{\min}$ = −2.78 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$[Nd(C_6H_2N_3O_7)_3$-
$(C_5H_{12}N_2O)_3]$
M_r = 1177.03
Monoclinic
$P2_1/c$
a = 18.913 (5) Å
b = 12.386 (5) Å
c = 22.134 (5) Å
β = 112.20 (5)°
V = 4800 (2) Å^3
Z = 4

D_x = 1.63 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 15–50°
μ = 9.37 mm^{-1}
T = 291 K
Irregular
0.30 × 0.20 × 0.10 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.78, $T_{\max}$ = 1.41
9824 measured reflections
8270 independent reflections

6052 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.032
$\theta_{\max}$ = 60°
$h = -23 \rightarrow 19$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 15$
1 standard reflection
frequency: 30 min
intensity variation: ±1.0%

Refinement

Refinement on F
R = 0.060
wR = 0.0642
S = 1.44
6052 reflections
658 parameters
$w = (\sigma^2|F_o| + 0.0017|F_o|^2)^{-1}$

$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.07 e Å^{-3}
$\Delta\rho_{\min}$ = −1.48 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Ce	0.1998 (1)	0.2020 (1)	0.2281 (1)	2.24 (2)
O(1)	0.1032 (5)	0.3438 (5)	0.3213 (3)	3.4 (2)
C(11)	0.0413 (6)	0.4453 (6)	0.3267 (4)	3.0 (3)
C(12)	0.0506 (6)	0.5197 (6)	0.3806 (4)	3.2 (3)
N(12)	0.1288 (6)	0.4737 (6)	0.4334 (3)	3.6 (3)
O(121)	0.1378 (6)	0.3726 (5)	0.4567 (3)	4.4 (3)
O(122)	0.1769 (7)	0.5406 (6)	0.4543 (4)	6.0 (4)
C(13)	−0.0090 (7)	0.6323 (7)	0.3841 (4)	3.9 (4)
C(14)	−0.0858 (7)	0.6800 (7)	0.3354 (5)	4.2 (4)
N(14)	−0.1408 (8)	0.8025 (7)	0.3361 (6)	5.6 (5)
O(141)	−0.1356 (8)	0.8554 (7)	0.3852 (6)	7.4 (5)
O(142)	−0.1903 (7)	0.8446 (7)	0.2812 (6)	7.8 (5)
C(15)	−0.1070 (7)	0.6143 (7)	0.2849 (5)	4.0 (4)
C(16)	−0.0443 (7)	0.4990 (7)	0.2817 (4)	3.3 (3)
N(16)	−0.0714 (6)	0.4365 (7)	0.2281 (4)	4.3 (4)
O(161)	−0.0072 (5)	0.3422 (5)	0.2105 (3)	4.2 (3)
O(162)	−0.1606 (7)	0.4791 (8)	0.2005 (5)	8.0 (5)
O(2)	0.2464 (4)	0.3814 (4)	0.1582 (3)	3.0 (2)
C(21)	0.3331 (7)	0.4310 (6)	0.1315 (3)	2.7 (3)
C(22)	0.3204 (7)	0.5522 (7)	0.1101 (4)	3.4 (3)
N(22)	0.1989 (8)	0.6225 (6)	0.1139 (5)	4.9 (4)
O(221)	0.1854 (8)	0.7109 (7)	0.0753 (6)	9.0 (5)
O(222)	0.1142 (7)	0.5916 (8)	0.1521 (7)	13.9 (7)
C(23)	0.4109 (7)	0.6103 (6)	0.0849 (4)	3.2 (4)
C(24)	0.5295 (8)	0.5487 (7)	0.0871 (4)	3.7 (4)
N(24)	0.6312 (8)	0.6089 (8)	0.0492 (4)	4.7 (4)
O(241)	0.7355 (7)	0.5500 (7)	0.0399 (4)	6.6 (4)
O(242)	0.6040 (7)	0.7153 (6)	0.0369 (4)	6.0 (4)
C(25)	0.5561 (7)	0.4304 (7)	0.0935 (4)	3.4 (4)
C(26)	0.4590 (6)	0.3732 (6)	0.1173 (4)	2.6 (3)
N(26)	0.4948 (6)	0.2469 (6)	0.1265 (3)	3.7 (3)
O(261)	0.4188 (5)	0.1879 (4)	0.1326 (3)	3.4 (2)
O(262)	0.6008 (6)	0.2024 (6)	0.1242 (6)	7.7 (4)
O(3)	0.3635 (4)	0.2263 (4)	0.2846 (3)	3.1 (2)
C(31)	0.3750 (7)	0.2417 (7)	0.3496 (4)	3.2 (3)
C(32)	0.4194 (6)	0.3374 (5)	0.3636 (3)	2.3 (3)
N(32)	0.4401 (7)	0.4271 (6)	0.3011 (4)	4.1 (4)
O(321)	0.3551 (7)	0.4757 (6)	0.2772 (4)	5.9 (4)
O(322)	0.5430 (9)	0.4402 (8)	0.2797 (5)	8.4 (6)
C(33)	0.4456 (7)	0.3532 (7)	0.4294 (4)	3.6 (4)
C(34)	0.4243 (7)	0.2715 (8)	0.4884 (4)	3.9 (4)
N(34)	0.444 (9)	0.292 (1)	0.5608 (4)	6.5 (5)
O(341)	0.414 (1)	0.223 (1)	0.6126 (4)	10.2 (7)
O(342)	0.491 (1)	0.3708 (8)	0.5648 (4)	8.6 (6)

C(35)	0.3817 (7)	0.1760 (8)	0.4812 (4)	4.0 (4)
C(36)	0.3559 (7)	0.1629 (7)	0.4145 (4)	3.3 (3)
N(36)	0.3059 (7)	0.0619 (7)	0.4085 (4)	4.9 (4)
O(361)	0.2485 (6)	0.0617 (6)	0.3616 (4)	5.3 (4)
O(362)	0.3286 (9)	−0.0239 (7)	0.4538 (5)	8.3 (6)
O(4)	0.2991 (5)	0.0041 (4)	0.2179 (3)	3.4 (2)
C(41)	0.3408 (7)	−0.0996 (6)	0.2387 (4)	3.1 (3)
N(41)	0.2622 (7)	−0.1735 (7)	0.2619 (5)	5.2 (4)
C(411)	0.1401 (9)	−0.140 (1)	0.2451 (8)	7.1 (7)
C(412)	0.272 (1)	−0.2511 (9)	0.3314 (7)	7.1 (7)
N(42)	0.4583 (6)	−0.1399 (5)	0.2359 (3)	3.3 (3)
C(421)	0.5187 (9)	−0.2619 (8)	0.2278 (5)	4.5 (4)
C(422)	0.5363 (8)	−0.0550 (9)	0.228 (6)	5.4 (5)
O(5)	0.0241 (4)	0.1227 (4)	0.2923 (3)	3.2 (2)
C(51)	−0.0839 (7)	0.1494 (7)	0.3209 (5)	3.5 (4)
N(52)	−0.1209 (6)	0.1875 (7)	0.3905 (4)	4.6 (4)
C(521)	−0.033 (1)	0.153 (1)	0.4399 (5)	6.4 (6)
C(522)	−0.233 (1)	0.283 (1)	0.4107 (8)	7.2 (7)
N(51)	−0.1706 (6)	0.1431 (7)	0.2837 (4)	4.4 (4)
C(511)	−0.135 (1)	0.122 (1)	0.2044 (6)	5.9 (6)
C(512)	−0.2919 (8)	0.124 (1)	0.3198 (8)	6.5 (6)
O(6)	0.1661 (4)	0.1669 (5)	0.1089 (3)	3.3 (2)
C(61)	0.1622 (6)	0.1530 (7)	0.0439 (4)	3.0 (3)
N(61)	0.0992 (6)	0.2308 (6)	0.0030 (3)	3.7 (3)
C(611)	0.0152 (8)	0.3317 (8)	0.0380 (5)	4.7 (4)
C(612)	0.134 (1)	0.244 (1)	−0.0813 (4)	5.8 (5)
N(62)	0.2268 (6)	0.0527 (6)	0.0116 (4)	4.1 (3)
C(621)	0.178 (1)	−0.009 (1)	−0.0342 (6)	6.5 (6)
C(622)	0.3282 (9)	−0.0168 (8)	0.0426 (6)	5.0 (5)

Table 2. *Bond distances* (Å) *and angles* (°) *around* Ce^{3+}

Ce—O(1)	2.442 (5)	Ce—O(361)	2.885 (7)
Ce—O(161)	2.638 (9)	Ce—O(4)	2.369 (7)
Ce—O(2)	2.444 (7)	Ce—O(5)	2.418 (6)
Ce—O(261)	2.704 (9)	Ce—O(6)	2.411 (7)
Ce—O(3)	2.432 (8)		
O(1)—Ce—O(161)	62.5 (2)	O(2)—Ce—O(3)	80.2 (2)
O(1)—Ce—O(2)	79.0 (2)	O(2)—Ce—O(361)	138.6 (2)
O(1)—Ce—O(261)	127.9 (2)	O(2)—Ce—O(4)	132.1 (2)
O(1)—Ce—O(3)	74.8 (2)	O(2)—Ce—O(5)	139.3 (2)
O(1)—Ce—O(361)	80.3 (2)	O(2)—Ce—O(6)	81.7 (2)
O(1)—Ce—O(4)	141.3 (2)	O(261)—Ce—O(3)	65.6 (3)
O(1)—Ce—O(5)	79.0 (2)	O(261)—Ce—O(4)	70.3 (2)
O(1)—Ce—O(6)	135.4 (2)	O(261)—Ce—O(5)	152.4 (2)
O(161)—Ce—O(2)	71.6 (2)	O(261)—Ce—O(6)	74.4 (3)
O(161)—Ce—O(3)	132.1 (2)	O(3)—Ce—O(361)	59.8 (2)
O(161)—Ce—O(4)	139.9 (2)	O(3)—Ce—O(4)	87.4 (2)
O(161)—Ce—O(5)	67.9 (2)	O(3)—Ce—O(5)	125.5 (2)
O(161)—Ce—O(6)	73.3 (3)	O(3)—Ce—O(6)	140.0 (3)
O(161)—Ce—O(261)	126.5 (3)	O(4)—Ce—O(5)	84.3 (2)
O(161)—Ce—O(361)	127.2 (2)	O(4)—Ce—O(6)	78.8 (2)
O(2)—Ce—O(261)	62.4 (2)	O(5)—Ce—O(6)	90.5 (2)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for* (2)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}
Nd	0.2245 (1)	0.1533 (1)	0.7634 (1)	3.39 (1)
O(1)	0.1521 (3)	0.0752 (4)	0.8201 (2)	4.2 (2)
C(11)	0.0973 (4)	0.0923 (6)	0.8392 (3)	3.8 (2)
C(12)	0.0896 (4)	0.0320 (6)	0.8911 (3)	4.3 (2)
N(12)	0.1532 (4)	−0.0386 (7)	0.9288 (4)	5.5 (3)
O(121)	0.2146 (4)	0.0018 (7)	0.9543 (3)	8.7 (3)
O(122)	0.1392 (5)	−0.1319 (7)	0.9326 (5)	10.1 (4)
C(13)	0.0297 (4)	0.0353 (7)	0.9105 (4)	4.6 (2)
C(14)	−0.0275 (4)	0.1097 (6)	0.8784 (3)	3.9 (2)
N(14)	−0.0928 (4)	0.1156 (6)	0.8979 (3)	4.9 (2)
O(141)	−0.0952 (4)	0.0532 (6)	0.9387 (3)	7.5 (3)
O(142)	−0.1412 (3)	0.1797 (6)	0.8717 (3)	6.9 (2)
C(15)	−0.0257 (3)	0.1741 (6)	0.8293 (3)	3.7 (2)
C(16)	0.0367 (4)	0.1664 (6)	0.8109 (3)	3.6 (2)
N(16)	0.0372 (3)	0.2393 (5)	0.7598 (3)	4.4 (2)
O(161)	0.0963 (3)	0.2556 (5)	0.7515 (3)	5.6 (2)
O(162)	−0.0221 (4)	0.2838 (6)	0.7274 (3)	7.6 (3)
O(2)	0.2488 (3)	0.2686 (4)	0.8529 (2)	4.6 (2)
C(21)	0.3022 (4)	0.2980 (6)	0.9040 (3)	4.0 (2)
C(22)	0.2873 (5)	0.3261 (6)	0.9624 (4)	4.4 (2)
N(22)	0.2091 (5)	0.3251 (8)	0.9577 (4)	7.4 (3)
O(221)	0.1591 (5)	0.342 (1)	0.9097 (5)	15.6 (6)
O(222)	0.1974 (6)	0.318 (2)	1.0017 (5)	24 (1)
C(23)	0.3418 (5)	0.3523 (7)	1.0217 (4)	5.2 (3)
C(24)	0.4155 (5)	0.3571 (7)	1.0252 (4)	5.4 (3)
N(24)	0.4762 (6)	0.3804 (9)	1.0865 (4)	8.6 (4)
O(241)	0.5413 (5)	0.389 (1)	1.0902 (4)	12.6 (4)
O(242)	0.4596 (5)	0.3854 (9)	1.1341 (4)	11.4 (4)
C(25)	0.4367 (5)	0.3376 (7)	0.9733 (4)	5.5 (3)
C(26)	0.3806 (5)	0.3099 (6)	0.9146 (4)	4.5 (2)
N(26)	0.4050 (4)	0.2889 (7)	0.8614 (4)	6.3 (3)
O(261)	0.3599 (3)	0.2543 (5)	0.8085 (3)	5.6 (2)
O(262)	0.4703 (5)	0.301 (1)	0.8712 (4)	13.8 (5)
O(3)	0.3114 (2)	0.0509 (4)	0.8512 (2)	3.9 (1)
C(31)	0.3154 (3)	−0.0384 (6)	0.8791 (3)	3.6 (2)
C(32)	0.3658 (4)	−0.0582 (6)	0.9453 (3)	3.8 (2)
N(32)	0.4113 (3)	0.0354 (6)	0.9803 (3)	5.1 (2)
O(321)	0.4473 (3)	0.0851 (5)	0.9549 (3)	6.1 (2)
O(322)	0.4111 (4)	0.0549 (7)	1.0343 (3)	8.0 (3)
C(33)	0.3712 (4)	−0.1507 (7)	0.9790 (4)	4.9 (2)
C(34)	0.3265 (4)	−0.2377 (7)	0.9462 (4)	4.9 (2)
N(34)	0.3309 (5)	−0.3388 (7)	0.9796 (4)	6.7 (3)
O(341)	0.2869 (4)	−0.4108 (6)	0.9513 (4)	9.4 (3)
O(342)	0.3791 (5)	−0.3490 (6)	1.0341 (4)	9.4 (3)
C(35)	0.2763 (4)	−0.2296 (7)	0.8833 (4)	4.5 (2)
C(36)	0.2720 (3)	−0.1321 (5)	0.8504 (3)	3.4 (2)
N(36)	0.2183 (3)	−0.1333 (5)	0.7839 (3)	4.0 (2)
O(361)	0.2100 (3)	−0.0536 (4)	0.7493 (2)	4.6 (2)
O(362)	0.1844 (4)	−0.2157 (5)	0.7623 (3)	7.4 (2)
O(4)	0.3055 (3)	0.0833 (4)	0.7117 (3)	4.5 (2)
C(41)	0.3362 (5)	−0.0010 (7)	0.7036 (4)	4.8 (3)
N(41)	0.4085 (4)	−0.0257 (7)	0.7415 (4)	6.3 (3)
C(411)	0.4513 (6)	0.042 (1)	0.7947 (5)	7.6 (4)
C(412)	0.4597 (7)	−0.088 (1)	0.7132 (7)	10.1 (6)
N(42)	0.2970 (5)	−0.0693 (7)	0.6542 (4)	6.2 (3)
C(421)	0.310 (1)	−0.188 (1)	0.6599 (9)	12.4 (7)
C(422)	0.2237 (7)	−0.035 (1)	0.6082 (5)	8.7 (4)
O(5)	0.1188 (3)	0.1184 (5)	0.6630 (3)	5.1 (2)
C(51)	0.0528 (5)	0.1219 (7)	0.6221 (4)	5.0 (3)
N(51)	−0.0030 (4)	0.0580 (7)	0.6266 (4)	7.2 (3)
C(511)	0.0182 (6)	−0.0331 (8)	0.6697 (5)	8.1 (4)
C(512)	−0.0824 (6)	0.095 (1)	0.6084 (7)	10.4 (5)
N(52)	0.0355 (4)	0.1886 (6)	0.5699 (3)	6.2 (2)
C(521)	−0.0230 (8)	0.163 (1)	0.5046 (6)	11.0 (6)
C(522)	0.0878 (6)	0.2773 (9)	0.5710 (5)	7.5 (4)
O(6)	0.2274 (3)	0.3139 (4)	0.7066 (2)	4.3 (2)
C(61)	0.2589 (4)	0.4028 (7)	0.7062 (4)	4.1 (2)
N(61)	0.3015 (4)	0.4153 (5)	0.6707 (3)	4.9 (2)
C(611)	0.3248 (6)	0.3181 (8)	0.6439 (5)	6.7 (4)
C(612)	0.3046 (6)	0.5181 (8)	0.6387 (6)	7.2 (4)
N(62)	0.2485 (4)	0.4895 (6)	0.7404 (3)	5.0 (2)
C(621)	0.1893 (6)	0.4878 (7)	0.7651 (5)	5.9 (3)
C(622)	0.3142 (6)	0.5618 (9)	0.7734 (6)	7.9 (4)

Table 4. *Bond distances* (Å) *and angles* (°) *around* Nd^{3+}

Nd—O(1)	2.384 (5)	Nd—O(361)	2.584 (5)
Nd—O(161)	2.659 (6)	Nd—O(4)	2.394 (6)
Nd—O(2)	2.342 (5)	Nd—O(5)	2.401 (6)
Nd—O(261)	2.681 (6)	Nd—O(6)	2.365 (5)
Nd—O(3)	2.382 (5)		
O(1)—Nd—O(161)	64.0 (2)	O(2)—Nd—O(4)	131.9 (2)
O(1)—Nd—O(2)	76.7 (2)	O(2)—Nd—O(5)	136.2 (2)
O(1)—Nd—O(261)	130.6 (2)	O(2)—Nd—O(6)	84.3 (2)
O(1)—Nd—O(3)	73.2 (2)	O(261)—Nd—O(3)	71.2 (2)
O(1)—Nd—O(361)	66.8 (2)	O(261)—Nd—O(361)	123.4 (2)
O(1)—Nd—O(4)	134.7 (2)	O(261)—Nd—O(4)	69.7 (2)
O(1)—Nd—O(5)	88.3 (2)	O(261)—Nd—O(5)	140.6 (2)
O(1)—Nd—O(6)	139.0 (2)	O(261)—Nd—O(6)	66.1 (2)
O(161)—Nd—O(2)	70.9 (2)	O(3)—Nd—O(361)	65.1 (2)
O(161)—Nd—O(261)	121.4 (2)	O(3)—Nd—O(4)	80.1 (2)
O(161)—Nd—O(3)	131.1 (2)	O(3)—Nd—O(5)	137.4 (2)
O(161)—Nd—O(361)	114.2 (2)	O(3)—Nd—O(6)	137.2 (2)
O(161)—Nd—O(4)	148.1 (2)	O(361)—Nd—O(4)	69.0 (2)
O(161)—Nd—O(5)	65.5 (2)	O(361)—Nd—O(5)	72.3 (2)

O(161)—Nd—O(6)	75.5 (2)	O(361)—Nd—O(6)	142.5 (2)
O(2)—Nd—O(261)	63.0 (2)	O(4)—Nd—O(5)	87.2 (2)
O(2)—Nd—O(3)	77.3 (2)	O(4)—Nd—O(6)	84.4 (2)
O(2)—Nd—O(361)	133.2 (2)	O(5)—Nd—O(6)	80.7 (2)

Data were corrected for Lp effects. H atoms were not included in either model. The refinement was by blocked-matrix least-squares methods. Programs used were *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71577 (108 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1055]

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An Iridium Complex of Tris(4-methoxyphenyl)phosphine

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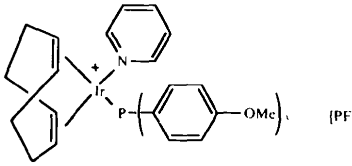
Abstract

The structure determination of (η^4-1,5-cyclooctadiene)(pyridine)[tris(4-methoxyphenyl)phosphine]-iridium(I) hexafluorophosphate, [$Ir(C_{21}H_{21}O_3P)(C_8H_{12})(C_5H_5N)$][$PF_6$], revealed approximately square-planar coordination at the Ir atom. The geometry is less distorted than in related complexes with more bulky phosphines.

Comment

We have been interested for some time in the structures and the conformation in solution of cationic Ir complexes of a range of monophosphines (Abbassioun, Hitchcock & Chaloner, 1989; Abbassioun, Chaloner & Hitchcock, 1990*a*,*b*; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991; Chaloner, Hitchcock & Reisinger, 1992). Many such complexes have been used as catalysts for homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). The title complex (I) was prepared by reaction of [{IrCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) with the phosphine in light petroleum/dichloromethane (1:3) to give [IrCl(cod){$P(C_6H_4$-4-OMe$)_3$}], which was used without further purification (Winkhaus & Singer, 1966). This was reacted with pyridine in methanol, and then with ammonium hexafluorophosphate to give the required salt in 74% yield. The structure of the complex is shown in Fig. 1. The geometry at Ir is approximately square planar, as expected. By comparison with [Ir(cod)(py)(PCy_3)][PF_6] (Abbassioun, Hitchcock & Chaloner, 1989) and [Ir(cod)(py){$P(C_6H_4$-2-



(I)

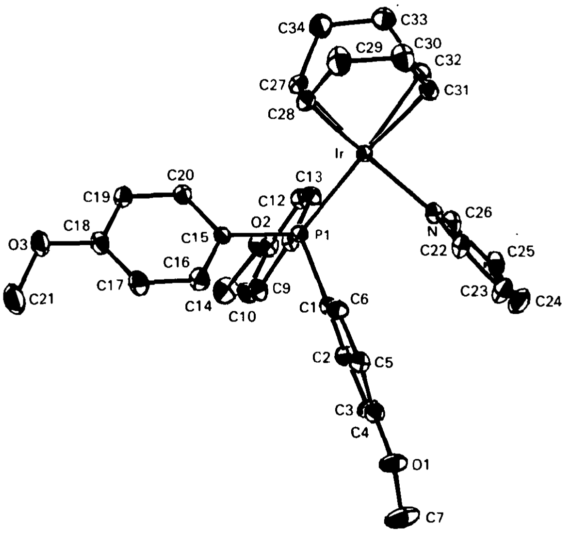


Fig. 1. Molecular structure and atom-numbering scheme of the title compound.