for absorption effects based on ψ scans using the empirical method of North, Phillips & Mathews (1968); $T_{min} = 0.6332$, $T_{max} = 0.9988$. 3269 unique observed data $[F_o^2 > 3\sigma(F_o^2)]$ were obtained. Scattering factors, including anomalous-dispersion factors, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were carried out using the *MolEN* (Fair, 1990) package of programs on a VAX computer. From the systematic absences of $h0l$: $l \neq 2n$, $0k0$: $k \neq 2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$. The structure was solved by the heavy-atom method based on the assumption that an Re atom must be located at the origin. The rest of the structure was revealed in successive cycles of least-squares refinement and difference Fourier maps. Three peaks located near an inversion point clearly defined a hexane molecule. All of the non-H atoms, except those belonging to the C_6H_{14} molecule, were refined with anisotropic thermal parameters. The isotropic thermal parameters for two C atoms on the hexane molecule (C2 and C3) were constrained to be the same as the third (C1) which was refined without constraint. H atoms were not included in the refinement. $wR = \{[\sum w(|F_o| - |F_c|)^2]/[\sum w(F_o)^2]\}^{1/2}$ was minimized, where $w = \sigma^2(|F_o|^2)^{-1}$ and σ is the e.s.d. in a single measurement; final $R = 0.034$, $wR = 0.051$, $S = 1.88$ for 278 variables. The largest shift/e.s.d. in the final least-squares cycle was 0.02; the maximum and minimum residual electron density in the ΔF map were 0.92 (located near Re) and -0.23 e Å^{-3}, respectively. An *ORTEP* (Johnson, 1965) representation of the molecule (without the hexane entity) and the atomic labeling scheme is depicted in Fig. 1. Final positional and equivalent isotropic thermal parameters are listed in Table 1,* with important bond distances and angles in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a stereoscopic view of the unit-cell packing have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71073 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1045]

Related literature. The synthesis, by a different route, and the crystal structure of $[ReCl_2(Ph_2PCHCHPPh_2)_2]$ (without the hexane molecule of solvation) has been reported (Bakir, Fanwick & Walton, 1987).

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References

Bakir, M., Fanwick, P. E. & Walton, R. A. (1987). *Polyhedron*, **6**, 907–913.

Fair, C. K. (1990). *MolEN*. An interactive structure solution procedure. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Acta Cryst. (1993). C**49**, 1426–1428

Structure of Tetraphenylphosphonium μ-{[η^4-2,4-Bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane]cobalt(III)}tetranitratocerium(III) Dichloromethane

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Abstract. Bis(tetraphenylphosphonium) μ-{N,N'-(2,4-dimethyl-3-oxo-2,4-pentanediyl)bis[(2-hydroxy-1:2κ^2O)-2-methylpropanamido-2κN]}-tetranitrato-1κ^4O,1κ^4O'-cerate(III)cobaltate(III) dichloromethane, $[P(C_6H_5)_4]_2[Co(C_{15}H_{24}N_2O_5)\{Ce(NO_3)_4\}].CH_2Cl_2$, $M_r = 1523.2$, monoclinic, $P2_1/c$ (C_{2h}^5), $a = 22.168$ (5), $b = 13.266$ (2), $c = 24.330$ (6) Å, $\beta = 105.17$ (2)°, $V = 6905$ (3) Å^3, $Z = 4$, $D_x = 1.465$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.09$ mm^{-1}, $T = 293$ K, $F(000) = 3108$, $R = 0.036$, $wR = 0.045$ for 8166 independent reflections having 2θ(Mo $K\alpha$) < 50.7° and $I > 3\sigma(I)$. The title compound is a dinuclear complex in which a planar cobalt(III) complex is linked *via* secondary coordination to a cerium(III) center. The Ce^{III} atom has four bidentate nitrato ligands and is further bridged to the

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bidentate planar cobalt(III) complex ligand which is coordinated through two alkoxide O atoms. The cobalt–cerium non-bonded distance is 3.449 (1) Å. The cobalt(III) complex ligand remains planar on coordination to the $\mathrm{Ce^{III}}$ atom.

Experimental. The title compound, hereinafter referred to as $[(\mathrm{Co^{III}})\text{-}(\mathrm{Ce^{III}})]^{2-}$, was prepared by stirring one equivalent of an orange dichloromethane solution of the cobalt(III) complex (Brewer, Collins, Smith & Santarsiero, 1988) over one equivalent of solid $(NH_4)_2Ce(NO_3)_5$. One equivalent of tetraphenylphosphonium chloride was added in dichloromethane and the red $[(\mathrm{Co^{III}})\text{-}(\mathrm{Ce^{III}})]^{2-}$ compound was isolated in good yield (70%) following filtration and evaporation of the CH_2Cl_2. A single red–orange crystal of dimensions 0.52 × 0.58 × 0.63 mm was mounted on a glass fiber and coated with epoxy cement. Data collection was performed on a Nicolet four-circle $P\bar{1}$ autodiffractometer (Mo $K\alpha$ radiation, graphite monochromator). From the least-squares fit of the angular settings of 15 reflections ($12.6 < \theta < 17.7°$) final unit-cell parameters were obtained. The intensities were collected at 293 K using the ω-scan technique to generate a total of two shells: $3.0 < 2\theta \leq 43.0°$ ($6.0°\ \mathrm{min}^{-1}$) and $43.0 \leq 2\theta \leq 50.7°$ ($3.0°\ \mathrm{min}^{-1}$). The index ranges were $-26 \leq h \leq 25$, $0 \leq k \leq 15$, $0 \leq l \leq 29$. The six standard reflections measured every 300 reflections showed negligible intensity loss over the collection period. Of the 13 103 independent reflections collected with $2\theta(\mathrm{Mo}\ K\alpha) < 50.7°$, 8166 had $I > 3\sigma(I)$. The intensity data were corrected empirically for absorption effects using ψ scans for seven reflections having 2θ between 6.1 and 33.0° and were then reduced to relative squared amplitudes by means of standard Lorentz and polarization corrections. The range of relative transmission factors was 0.62–1.00. The structure was solved using heavy-atom Patterson techniques on a Data General Eclipse S-200 computer with the Nicolet *SHELXTL* (Sheldrick, 1990) software package as modified at Crystalytics Company. Function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + (0.03F_o)^2]^{-1}$. The structure was refined by counter-weighted cascade-block-diagonal least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for all H atoms. The eight methyl groups (C3*a*, C4*a*, C6*a*, C7*a*, C3*b*, C4*b*, C6*b*, C7*b* and their H atoms) were refined as rigid rotors with sp^3-hybridized geometry and a C—H bond lengths of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the H atoms. The final orientation of each methyl group was determined by three rotational parameters. The refined positions for the rigid-rotor methyl

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (× 10) *with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq} (Å^2)
Ce	3045 (1)	6047 (1)	1240 (1)	27 (1)
Co	2505 (1)	3607 (1)	1234 (1)	29 (1)
O1	4035 (2)	7104 (3)	1199 (2)	60 (1)
O2	4139 (2)	6160 (3)	1928 (2)	61 (1)
O3	4899 (2)	7132 (3)	1874 (2)	65 (1)
O4	3191 (2)	6188 (3)	225 (1)	47 (1)
O5	3719 (2)	4991 (2)	730 (1)	51 (1)
O6	3892 (3)	5394 (3)	− 76 (2)	81 (2)
O7	2132 (2)	7107 (3)	618 (2)	64 (1)
O8	2843 (2)	7990 (3)	1121 (2)	94 (2)
O9	2087 (3)	8712 (3)	510 (3)	98 (2)
O10	3041 (2)	6760 (4)	2230 (2)	81 (2)
O11	2173 (2)	6168 (3)	1783 (2)	63 (1)
O12	2286 (3)	6805 (4)	2626 (2)	96 (2)
N1	4370 (2)	6816 (3)	1673 (2)	44 (1)
N2	3608 (2)	5518 (3)	284 (2)	47 (1)
N3	2351 (2)	7957 (3)	744 (2)	56 (2)
N4	2498 (3)	6586 (4)	2224 (2)	57 (2)
O1*a*	1420 (3)	3111 (3)	− 264 (2)	109 (2)
O2*a*	2286 (1)	4729 (2)	786 (1)	34 (1)
O1*b*	3352 (2)	2334 (3)	2665 (1)	62 (1)
O2*b*	3121 (1)	4357 (2)	1693 (1)	30 (1)
O	1327 (2)	1141 (4)	1269 (2)	87 (2)
N1*a*	1966 (2)	2887 (3)	666 (2)	40 (1)
N1*b*	2693 (2)	2604 (2)	1771 (1)	33 (1)
C1*a*	1693 (3)	3440 (4)	204 (2)	52 (2)
C2*a*	1768 (2)	4571 (3)	305 (2)	39 (1)
C3*a*	1874 (3)	5089 (4)	− 208 (2)	52 (2)
C4*a*	1181 (2)	4972 (4)	442 (3)	59 (2)
C5*a*	1939 (3)	1768 (4)	671 (2)	54 (2)
C6*a*	2565 (4)	1354 (4)	615 (3)	75 (3)
C7*a*	1400 (5)	1311 (5)	202 (3)	117 (4)
C1*b*	3184 (2)	2831 (3)	2230 (2)	38 (1)
C2*b*	3523 (2)	3811 (3)	2157 (2)	32 (1)
C3*b*	4124 (2)	3544 (4)	2003 (2)	47 (1)
C4*b*	3634 (3)	4440 (4)	2703 (2)	48 (2)
C5*b*	2304 (2)	1711 (3)	1809 (2)	41 (1)
C6*b*	2684 (3)	730 (4)	1938 (3)	57 (2)
C7*b*	1970 (3)	1914 (5)	2273 (3)	72 (2)
C8	1816 (3)	1520 (3)	1249 (2)	49 (2)

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ce—O1	2.629 (4)	Ce—O7	2.600 (4)
Ce—O2	2.567 (3)	Ce—O8	2.620 (6)
Ce—O4	2.582 (3)	Ce—O10	2.589 (4)
Ce—O5	2.591 (4)	Ce—O11	2.615 (5)
Ce—O2*a*	2.476 (3)	Ce—O2*b*	2.483 (3)
Co—O2*a*	1.833 (3)	Co—O2*b*	1.817 (3)
Co—N1*a*	1.840 (3)	Co—N1*b*	1.835 (3)
O1*a*—C1*a*	1.221 (6)	O1*b*—C1*b*	1.218 (5)
O2*a*—C2*a*	1.425 (5)	O2*b*—C2*b*	1.438 (4)
N1*a*—C1*a*	1.348 (6)	N1*b*—C1*b*	1.374 (5)
N1*a*—C5*a*	1.485 (6)	N1*b*—C5*b*	1.483 (6)
C1*a*—C2*a*	1.522 (6)	C1*b*—C2*b*	1.536 (6)
C2*a*—C3*a*	1.496 (7)	C2*b*—C3*b*	1.516 (7)
C2*a*—C4*a*	1.521 (8)	C2*b*—C4*b*	1.534 (6)
C5*a*—C6*a*	1.532 (10)	C5*b*—C6*b*	1.537 (7)
C5*a*—C7*a*	1.544 (9)	C5*b*—C7*b*	1.528 (10)
C5*a*—C8	1.535 (8)	C5*b*—C8	1.523 (6)
O—C8	1.210 (8)		
O1—N1	1.256 (5)	O7—N3	1.234 (5)
O2—N1	1.254 (6)	O8—N3	1.230 (6)
O3—N1	1.222 (5)	O9—N3	1.223 (6)
O4—N2	1.263 (6)	O10—N4	1.224 (7)
O5—N2	1.260 (5)	O11—N4	1.254 (6)
O6—N2	1.213 (7)	O12—N4	1.225 (8)
O1—Ce—O2	48.5 (1)	O4—Ce—O10	153.5 (1)
O4—Ce—O5	49.3 (1)	O4—Ce—O11	140.7 (1)
O7—Ce—O8	47.1 (1)	O4—Ce—O2*a*	82.3 (1)
O10—Ce—O11	47.6 (1)	O4—Ce—O2*b*	118.6 (1)
O2*a*—Ce—O2*b*	61.3 (1)	O5—Ce—O7	118.2 (1)
O1—Ce—O4	67.0 (1)	O5—Ce—O8	125.6 (2)
O1—Ce—O5	71.2 (1)	O5—Ce—O10	141.8 (1)
O1—Ce—O7	102.7 (1)	O5—Ce—O11	150.6 (1)
O1—Ce—O8	65.8 (1)	O5—Ce—O2*a*	79.3 (1)

Table 2 (*cont.*)

O1—Ce—O10	92.6 (1)	O5—Ce—O2*b*	75.2 (1)
O1—Ce—O11	136.1 (1)	O7—Ce—O10	98.8 (1)
O1—Ce—O2*a*	146.7 (1)	O7—Ce—O11	72.3 (1)
O1—Ce—O2*b*	122.5 (1)	O7—Ce—O2*a*	77.8 (1)
O2—Ce—O4	106.6 (1)	O7—Ce—O2*b*	134.3 (1)
O2—Ce—O5	77.2 (1)	O8—Ce—O10	72.6 (2)
O2—Ce—O7	143.8 (1)	O8—Ce—O11	82.4 (2)
O2—Ce—O8	96.8 (1)	O8—Ce—O2*a*	124.7 (1)
O2—Ce—O10	66.7 (1)	O8—Ce—O2*b*	158.0 (2)
O2—Ce—O11	111.3 (1)	O10—Ce—O2*a*	120.4 (1)
O2—Ce—O2*a*	138.4 (1)	O10—Ce—O2*b*	86.2 (1)
O2—Ce—O2*b*	79.7 (1)	O11—Ce—O2*a*	76.3 (1)
O4—Ce—O7	71.2 (1)	O11—Ce—O2*b*	78.8 (1)
O4—Ce—O8	83.3 (2)		
O2*a*—Co—O2*b*	87.7 (1)	O2*b*—Co—N1*a*	169.0 (2)
O2*a*—Co—N1*a*	87.5 (1)	O2*b*—Co—N1*b*	88.0 (1)
O2*a*—Co—N1*b*	170.9 (1)	N1*a*—Co—N1*b*	98.0 (1)
Ce—O1—N1	95.8 (3)	Ce—O7—N3	98.9 (3)
Ce—O2—N1	98.9 (2)	Ce—O8—N3	98.0 (3)
Ce—O4—N2	96.5 (3)	Ce—O10—N4	99.4 (3)
Ce—O5—N2	96.1 (3)	Ce—O11—N4	97.2 (4)
Co—O2*a*—Ce	105.3 (1)	Co—O2*b*—Ce	105.6 (1)
Co—O2*a*—C2*a*	113.6 (2)	Co—O2*b*—C2*b*	114.7 (2)
Ce—O2*a*—C2*a*	141.0 (2)	Ce—O2*b*—C2*b*	139.4 (2)
O1—N1—O2	116.6 (4)	O7—N3—O8	115.6 (4)
O1—N1—O3	122.6 (4)	O7—N3—O9	121.7 (4)
O2—N1—O3	120.8 (4)	O8—N3—O9	122.7 (4)
O4—N2—O5	117.4 (4)	O10—N4—O11	115.8 (5)
O4—N2—O6	121.0 (4)	O10—N4—O12	121.9 (5)
O5—N2—O6	121.6 (4)	O11—N4—O12	122.3 (6)
Co—N1*a*—C1*a*	113.9 (3)	Co—N1*b*—C1*b*	113.9 (3)
Co—N1*a*—C5*a*	122.2 (3)	Co—N1*b*—C5*b*	126.6 (3)
C1*a*—N1*a*—C5*a*	122.7 (4)	C1*b*—N1*b*—C5*b*	118.3 (3)
O1*a*—C1*a*—N1*a*	126.1 (4)	O1*b*—C1*b*—N1*b*	125.8 (4)
O1*a*—C1*a*—C2*a*	120.6 (4)	O1*b*—C1*b*—C2*b*	120.8 (4)
N1*a*—C1*a*—C2*a*	113.3 (4)	N1*b*—C1*b*—C2*b*	113.4 (3)
O2*a*—C2*a*—C3*a*	110.5 (4)	O2*b*—C2*b*—C1*b*	107.2 (3)
O2*a*—C2*a*—C4*a*	108.6 (4)	O2*b*—C2*b*—C3*b*	109.2 (4)
C1*a*—C2*a*—C3*a*	110.6 (4)	O2*b*—C2*b*—C4*b*	109.4 (3)
C1*a*—C2*a*—C4*a*	108.4 (4)	C1*b*—C2*b*—C3*b*	108.6 (4)
C3*a*—C2*a*—C4*a*	110.7 (4)	C1*b*—C2*b*—C4*b*	109.3 (4)
N1*a*—C5*a*—C6*a*	108.6 (5)	C3*b*—C2*b*—C4*b*	112.9 (4)
N1*a*—C5*a*—C7*a*	114.3 (4)	N1*b*—C5*b*—C6*b*	113.2 (4)
N1*a*—C5*a*—C8	103.8 (4)	N1*b*—C5*b*—C7*b*	108.0 (4)
C6*a*—C5*a*—C7*a*	109.7 (5)	N1*b*—C5*b*—C8	111.4 (4)
C6*a*—C5*a*—C8	112.7 (4)	C6*b*—C5*b*—C7*b*	110.1 (5)
C7*a*—C5*a*—C8	107.7 (5)	C6*b*—C5*b*—C8	105.4 (4)
O—C8—C5*a*	120.2 (5)	C7*b*—C5*b*—C8	108.8 (5)
O—C8—C5*b*	117.9 (5)		
C5*a*—C8—C5*b*	122.0 (5)		

groups gave C—C—H angles which ranged from 105 to 114°. The remaining H atoms were included in the structure-factor calculations at idealized positions (assuming sp^2- or sp^3-hybridization of the C atoms and a C—H bond length of 0.96 Å) 'riding' on their respective C atoms. The isotropic thermal parameter of each H atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the C atom to which it is covalently bonded. The refinement of 863 parameters converged with $R = 0.036$, $wR = 0.045$ and $S = 1.1$. The maximum shift for all parameters was $0.12\sigma_p$ and the average shift for all parameters was $0.03\sigma_p$. There were no peaks present in the final difference Fourier map above the background level. The maximum and minimum electron density in the final difference Fourier map were 0.55 and -0.49 e Å^{-3}, respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) as contained in *SHELXTL* (Sheldrick, 1990).

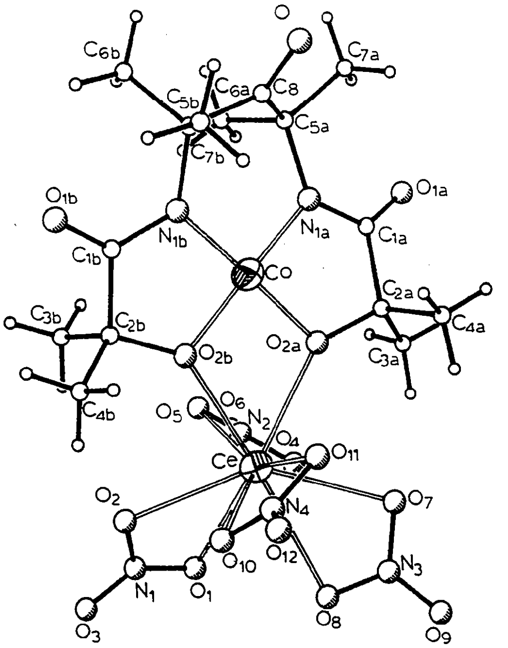

Fig. 1. Thermal ellipsoid drawing of the dinuclear complex shown to encompass 50% of the electron density with the atom-numbering scheme.

A thermal ellipsoid drawing of the dinuclear complex with the atom-numbering scheme is shown in Fig. 1. Atomic coordinates and final equivalent isotropic thermal parameters of all non-H atoms included in the refinement are given in Table 1.* Selected interatomic distances and angles are listed in Table 2.

Related literature. The title compound is the first known dinuclear coordination complex involving a planar cobalt(III) complex and a lanthanide metal ion. A related planar cobalt(III) complex coordinated to a sodium cation (Collins, Richmond, Santarsiero & Treco, 1986) has been structurally characterized.

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* Lists of structure factors, anisotropic thermal parameters, complete bond distances and angles, H-atom parameters and non-bonded distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55970 (70 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1036]

References

Brewer, J. C., Collins, T. J., Smith, M. R. & Santarsiero, B. D. (1988). *J. Am. Chem. Soc.* **110**, 423–428.

Collins, T. J., Richmond, T. G., Santarsiero, B. D. & Treco, B. G. R. T. (1986). *J. Am. Chem. Soc.* **108**, 2088–2090.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.