

The final atomic parameters and selected inter-atomic distances are given in Tables 1 and 2 respectively.*

Discussion. The structure is related to that of perovskite in a simple way. A single slice of perovskite-type structure, one unit cell thick, has the composition $\text{Rb}_2[\text{MnBr}_4]$ and the tetrabromomanganate structure can be regarded as consisting of such slices stacked perpendicular to *c*, alternate slices being displaced $a/\sqrt{2}$ in the [110] direction. Mn and Br(2) ions lie in the middle of these slices, whilst Rb and Br(1) ions are situated on their surfaces and within the accuracy of the analysis lie on the same *z* planes.

The MnBr_6 octahedra within a perovskite-type slice share equatorial, Br(2), vertices to form a layer of com-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34093 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

position MnBr_4 . Because of the mutual repulsion of the Mn^{2+} ions in such a layer, Mn—Br(2) is significantly longer than Mn—Br(1). The mean Mn—Br and Br—Br distances are 2.65 and 3.75 Å, respectively, somewhat shorter than the corresponding values (2.68 and 3.79 Å) found in the MnBr_6 octahedron in $\text{Cs}[\text{MnBr}_3]$ (Goodyear & Kennedy, 1972). Each Br—Mn—Br angle is exactly 90°.

Each Rb ion is coordinated by four Br(2) and five Br(1) ions and the very short Rb—Br(1^{II}) bond can be explained by the unsymmetrical nature of this coordination group.

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The Structure of Triindenylcerium Pyridinate

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Abstract. $\text{Ce}(\text{C}_9\text{H}_7)_3 \cdot \text{C}_5\text{H}_5\text{N}$, $\text{C}_{32}\text{H}_{26}\text{CeN}$, orthorhombic, *Pbca*, $a = 13.106$ (3), $b = 26.364$ (7), $c = 13.832$ (2) Å, $Z = 8$; $D_x = 1.57$ Mg m^{-3} ; $\mu(\text{Mo } K\alpha) = 2.10$ mm^{-1} . Final $R = 0.028$. The π -bonded five-membered portions of the three indenyl groups and the σ -bonded N atom of the pyridine ring are arranged tetrahedrally around the metal Ce atom.

Introduction. The title compound was obtained by reaction of $\text{Ce}(\text{OPr}^i)_4 \cdot \text{Py}$ with AlEt_3 in indene at 323 K. Yellow, air-sensitive crystals were obtained by cooling the red-orange reaction solution to 273 K.

In view of the considerable interest now being shown in the organometallic chemistry and stereochemistry of lanthanides (Baker, Halstead & Raymond, 1976), the crystal structure determination of the title compound was undertaken. Preliminary Weissenberg photographs established the space group *Pbca* (systematic extinctions: $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$).

4673 independent intensities (maximum $\sin \theta/\lambda = 0.62$ Å⁻¹) were collected from a crystal of about $0.3 \times 0.3 \times 0.5$ mm, mounted with the *c* axis parallel to the spindle axis of an on-line Siemens AED diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), the θ – 2θ scan mode, and 'five-points' technique (Hoppe, 1969). 3222 intensities with $I > 3\sigma(I)$ were classed as observed and used in the structure determination. Absorption correction was ignored because of the irregular shape of the crystal used.

The structure was solved by conventional heavy-atom techniques and refined by a block-diagonal least-squares procedure. The function minimized was $\sum w(F_o - F_c)^2$, using Cruickshank's (1965) weighting scheme. Atomic scattering factors were those of Cromer & Mann (1968) for non-hydrogen atoms, and of Stewart, Davidson & Simpson (1965) for the H atoms. The anomalous-dispersion correction for Ce was taken into account in the structure factor calculations ($f' = -0.42$, $f'' = 3.04$) (Cromer, 1965). The computer

Table 1. Atomic fractional coordinates ($\times 10^4$) and isotropic thermal parameters for hydrogen atoms ($\times 10^2 \text{ \AA}^2$)

The atomic fractional coordinates for Ce are multiplied by 10^5 ; standard deviations in parentheses, in this and in the following tables, refer to the last digit quoted.

	x	y	z	B
Ce	23521 (2)	13880 (1)	3223 (2)	
N	3544 (3)	572 (1)	588 (3)	
C(11)	2882 (4)	2433 (2)	371 (4)	
C(12)	2982 (4)	2248 (2)	1324 (3)	
C(13)	3816 (4)	1910 (2)	1361 (3)	
C(14)	5188 (3)	1669 (2)	65 (4)	
C(15)	5479 (4)	1778 (2)	-870 (5)	
C(16)	4938 (4)	2122 (2)	-1443 (4)	
C(17)	4068 (4)	2345 (2)	-1122 (4)	
C(18)	3727 (3)	2246 (2)	-152 (3)	
C(19)	4294 (3)	1914 (2)	443 (3)	
C(21)	1063 (4)	708 (2)	1262 (3)	
C(22)	478 (3)	1132 (2)	1068 (4)	
C(23)	772 (4)	1535 (2)	1659 (4)	
C(24)	2038 (4)	1556 (2)	3112 (4)	
C(25)	2715 (4)	1271 (2)	3648 (4)	
C(26)	2904 (4)	766 (2)	3381 (4)	
C(27)	2420 (4)	547 (2)	2621 (4)	
C(28)	1703 (3)	826 (2)	2071 (3)	
C(29)	1525 (3)	1341 (2)	2327 (3)	
C(31)	2188 (4)	897 (2)	-1524 (4)	
C(32)	2593 (4)	1380 (2)	1658 (4)	
C(33)	1835 (4)	1745 (2)	-1493 (3)	
C(34)	-120 (4)	1651 (2)	-1167 (3)	
C(35)	-874 (4)	1300 (2)	-1121 (4)	
C(36)	-660 (4)	781 (2)	-1138 (4)	
C(37)	305 (4)	601 (2)	-1229 (4)	
C(38)	1126 (4)	953 (2)	-1320 (3)	
C(39)	907 (4)	1487 (2)	-1295 (3)	
C(41)	3199 (4)	115 (2)	283 (4)	
C(42)	3622 (4)	-341 (2)	558 (4)	
C(43)	4431 (4)	-334 (2)	1183 (4)	
C(44)	4801 (4)	123 (2)	1520 (4)	
C(45)	4329 (4)	563 (2)	1203 (4)	
H(11)	2376 (32)	2636 (17)	132 (35)	258 (99)
H(13)	3986 (39)	1766 (19)	1918 (37)	411 (122)
H(15)	6082 (44)	1567 (22)	-1108 (44)	635 (145)
H(17)	3671 (36)	2581 (18)	-1423 (37)	407 (114)
H(22)	-39 (39)	1160 (19)	652 (39)	408 (124)
H(24)	1827 (45)	1881 (21)	3344 (43)	661 (149)
H(26)	3452 (48)	586 (23)	3645 (47)	749 (163)
H(31)	2503 (38)	571 (21)	-1674 (43)	484 (128)
H(33)	1853 (32)	2114 (16)	-1458 (31)	241 (94)
H(35)	-1546 (40)	1379 (18)	-1050 (39)	381 (118)
H(37)	487 (41)	241 (20)	-1362 (40)	469 (129)
H(42)	3281 (46)	-662 (22)	394 (41)	588 (139)
H(44)	5369 (39)	170 (19)	1929 (38)	469 (122)
H(12)	2454 (42)	2355 (23)	1736 (46)	695 (156)
H(14)	5606 (47)	1386 (21)	506 (42)	660 (146)
H(16)	5157 (42)	2194 (22)	-2168 (43)	590 (144)
H(21)	1068 (40)	380 (20)	832 (40)	507 (127)
H(23)	612 (40)	1886 (20)	1789 (39)	534 (134)
H(25)	3097 (46)	1425 (20)	4208 (44)	535 (142)
H(27)	2513 (36)	267 (21)	2314 (42)	496 (122)
H(32)	3346 (51)	1391 (22)	-1977 (48)	942 (172)
H(34)	-131 (36)	2015 (18)	-1164 (36)	341 (110)
H(36)	-1230 (43)	563 (21)	-1022 (43)	577 (147)
H(41)	2608 (41)	104 (23)	-138 (44)	492 (144)
H(43)	4699 (38)	-651 (19)	1455 (38)	410 (120)
H(45)	4591 (35)	861 (17)	1387 (34)	314 (102)

programs used were those of Immirzi (1967*a,b*, 1973).

The H atoms were located by a ΔF map. The refinement with anisotropic thermal parameters and fixed contribution of the H atoms converged to $R = 0.030$. Two more cycles in which the H atoms were refined using isotropic thermal parameters led to a final R of 0.028. A final ΔF map showed no peaks greater than 0.5 e \AA^{-3} which were not within 1.0 \AA from the Ce atom.

Final atomic positional parameters are reported in Table 1.*

Discussion. A perspective view of the molecular structure of $\text{Ce}(\text{C}_9\text{H}_7)_3\cdot\text{Py}$ is shown in Fig. 1. Bond lengths and angles for the Ce inner coordination sphere are reported in Table 2(a). The σ -bonded N atom of the pyridine ring and the five-membered portions of the three π -bonded indenyl moieties are arranged almost tetrahedrally around the Ce atom. The distortions from the regular tetrahedral coordination are illustrated by the angles reported in Table 2(a), where the points 1, 2 and 3 stand for the points of intersection of the normals from the Ce atom to the least-squares planes of the C_5 portions of the indenyl groups (1), (2) and (3) respectively. The values of the N—Ce—(1), N—Ce—(2), N—Ce—(3) angles range from 95.6 to 104.3° , while those of the (1)—Ce—(2), (2)—Ce—(3), (1)—Ce—(3) angles range from 114.4 to 117.5° .

Analogous situations of distorted-tetrahedral coordination have been found in the structure of the related complexes $\text{U}(\text{C}_9\text{H}_7)_3\text{Cl}$ (Burns & Laubereau, 1971), $\text{U}(\text{C}_5\text{H}_5)_3(\text{C}_2\text{C}_6\text{H}_5)$ (Atwood, Hains, Tsutsui & Gebala, 1973), $\text{U}(\text{C}_5\text{H}_4\text{CH}_2\text{C}_6\text{H}_5)_3\text{Cl}$ (Leong, Hodgson & Raymond, 1973), $\text{U}(\text{C}_5\text{H}_5)_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2)$ and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33830 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

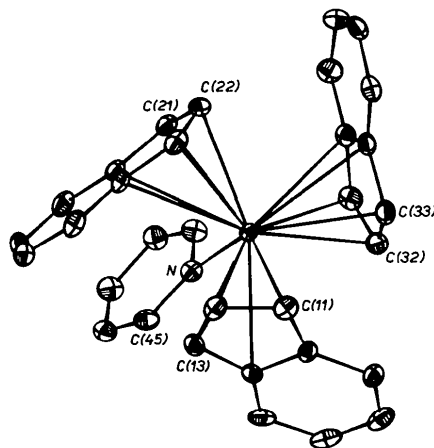


Fig. 1. A perspective view of the molecular structure of $\text{Ce}(\text{C}_9\text{H}_7)_3\cdot\text{C}_5\text{H}_5\text{N}$.

Table 2. Summary of geometrical data

(a) Ce inner coordination sphere

Distances (Å)

Ce—C(11)	2.842 (4)	Ce—C(21)	2.785 (5)
Ce—C(12)	2.783 (5)	Ce—C(22)	2.748 (5)
Ce—C(13)	2.764 (5)	Ce—C(23)	2.803 (5)
Ce—C(18)	2.966 (4)	Ce—C(28)	2.962 (4)
Ce—C(19)	2.903 (4)	Ce—C(29)	2.980 (4)
Ce—C(31)	2.871 (5)	Ce—N	2.684 (4)
Ce—C(32)	2.757 (5)		
Ce—C(33)	2.767 (5)		
Ce—C(38)	3.009 (5)		
Ce—C(39)	2.942 (5)		

Angles (°)

N—Ce—(1)	104.3	N—Ce—(2)	95.6
N—Ce—(3)	103.9	(1)—Ce—(2)	116.9
(1)—Ce—(3)	114.4	(2)—Ce—(3)	117.5

(b) Shortest non-bonded intramolecular contacts (Å)

C(12)—C(24)	3.313 (7)	C(17)—C(32)	3.280 (7)
C(45)—C(27)	3.179 (7)	N—C(27)	3.175 (7)

(c) Mean values (Å) of C—C bond distances in indenyl groups

Types of distance	Ce(C ₉ H ₇) ₃ , Py	Ru(C ₉ H ₇) ₂	<i>d</i> _{cal} *	Bond* number
(4)—(5), (6)—(7)	1.364 (11)	1.364 (15)	1.366	1.71
All the others	1.415 (17)	1.430 (12)	1.441–1.460	1.16–1.24

* Data taken from the structure of Ru(C₉H₇)₂ (Webb & Marsh, 1967).

U(C₅H₅)₃(*n*-C₄H₉) (Perego, Cesari, Farina & Lugli, 1976). In all the three indenyl groups the C₅ and C₆ portions are planar (maximum deviation of the atoms from their least-squares planes is 0.03 Å). However, the two parts in all cases are mutually bent, with the C₆ planes bent outwards with respect to the Ce atom. The angles of bending are 3.6, 2.5 and 6.7° for groups 1, 2 and 3 respectively. Almost rigorous planarity of the ligands has been reported in Ru(C₉H₇)₂ (Webb & Marsh, 1967), while no sure bending effects have been observed in U(C₉H₇)₃Cl previously cited and Sm(C₉H₇)₃ (Atwood, Burns & Laubereau, 1973). Bending effects were observed in U[C₈H₄(CH₃)₄]₂ which have been explained on the basis of the electronic structure of the molecule (Leong, Hodgson & Raymond, 1973). On the other hand, similar effects found for bipyridyl ligands in U(C₁₀H₈N₂)₄ were attributed to intermolecular interactions (Del Piero, Perego, Zazzetta & Brandi, 1975). In the present case the bending effects should arise from intramolecular C...C contacts between neighbouring five- and six-membered portions of the indenyl groups.

The Ce—C bond distances range from 2.75 to 3.01 Å (Table 2a), the shortest distances involving the non-bridging atoms of the C₅ portions of the indenyl

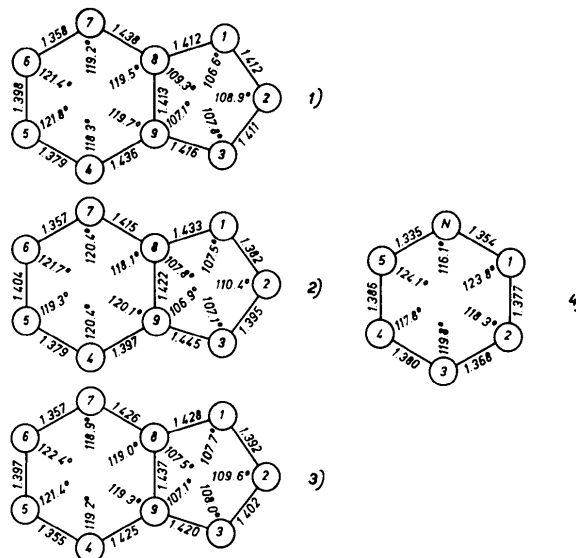


Fig. 2. Bond distances (Å) and angles (°) in the three indenyl groups and pyridine. The mean standard deviation for bond lengths is 0.007 Å, for angles 0.1°.

groups: this geometrical feature could indicate a 1,2,3 trihapto character of the ligand-to-metal coordination. The values of some intramolecular contacts (the shortest ones are given in Table 2b) indicate a steric situation quite similar to that observed for the complexes U(C₉H₇)₃Cl and Sm(C₉H₇)₃ cited above for which the authors are in favour of a 1,2,3,8,9-pentahapto coordination distorted by steric interference among the ligands.

The authors do not consider in detail the C—C bond lengths in the indenyl groups, because of the relatively low accuracy achieved in the determination of the C positions. In the present case, as it clearly results from Fig. 2, the C(4)—C(5) and C(6)—C(7) bond distances are significantly shorter than all the others. This precise feature has been observed for the complex Ru(C₉H₇)₂ (Webb & Marsh, 1967) and agrees with a geometry calculated by Webb & Marsh (1967) on the basis of a simple valence-bond approach assuming full conjugation of the indenyl groups (see Table 2c). No intermolecular contacts have been observed shorter than 3.5 Å.

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Di- μ -glutarato-bis[(*N,N,N',N'*-tetraethylethylenediamine)copper(II)]

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Abstract. $[\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_2)(\text{C}_5\text{H}_6\text{O}_4)]_2$, $(\text{C}_{15}\text{H}_{30}\text{CuN}_2\text{O}_4)_2$, monoclinic, $P2_1/n$, $a = 9.365(4)$, $b = 15.211(15)$, $c = 12.738(11)$ Å, $\beta = 105.33(5)^\circ$, $Z = 2$, $D_m = 1.39$, $D_c = 1.39$ Mg m⁻³. The structure was refined to $R = 0.059$ for 1752 observed reflections. The structure is dimeric. Cu is coordinated to the N atoms of the diamine and to four O atoms of two different glutarate ions.

Introduction. Blue crystals of the title compound were prepared from CuCO_3 , glutaric acid and *N,N,N',N'*-tetraethylethylenediamine (Pajunen & Näsäkkälä, 1977) and recrystallized from ethanol. The space group was determined as $P2_1/n$ from systematic absences. The cell parameters and intensities of 3410 reflections up to $2\theta = 50^\circ$ were measured on a Syntex $P2_1$ four-circle diffractometer with monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Of these, 1752 were above the 2σ significance level. The structure was solved by direct methods with XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and refined by block-diagonal least squares. Anisotropic refinement of the nonhydrogen atoms converged at $R = 0.104$. The H atoms were located from a difference map and included in the refinement with a fixed $U = 0.06$ Å². Further refinement converged at $R = 0.059$. Scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for other atoms those of Cromer & Mann (1968). Real and imaginary anomalous-dispersion terms were included for Cu. The

final positional parameters are given in Table 1.* The molecular structure is shown in Fig. 1 and bond lengths and angles are listed in Table 2.

Discussion. The structure is dimeric (Fig. 1). The carboxylate groups of the glutarate ions are coordinated to different Cu atoms, so that the glutarate ions and Cu form 16-membered rings. The coordination of the ligands is similar to that in adipato(*N,N*-diethylethylenediamine)copper(II) (Pajunen & Näsäkkälä, 1977), but differs from that in glutarato(*N,N,N',N'*-tetramethylethylenediamine)copper(II) (Pajunen & Pa-

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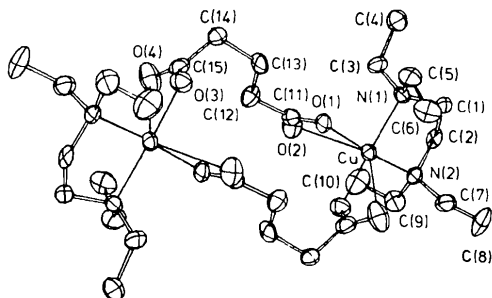


Fig. 1. Perspective view of the dimer.