

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction:
 semi-empirical ψ scans
 (North *et al.*, 1968)
 $T_{\min} = 0.529$, $T_{\max} = 0.584$
 3704 measured reflections
 3269 independent reflections
 2636 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R(F) = 0.025$
 $wR(F^2) = 0.059$
 $S = 1.057$
 3268 reflections
 225 parameters
 H-atom parameters
 constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$R_{\text{int}} = 0.012$
 $\theta_{\max} = 27^\circ$
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 13$
 $l = -24 \rightarrow 24$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.26%

$\Delta\rho_{\max} = 0.260 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.265 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0054 (2)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Zn—O3 ⁱ	1.9709 (13)	O1—C11	1.273 (2)
Zn—O1	2.0223 (13)	O2—C11	1.241 (2)
Zn—N2	2.1021 (15)	O3—C14	1.269 (2)
Zn—N1	2.120 (2)	O4—C14	1.239 (2)
Zn—O5	2.125 (2)		
O3 ⁱ —Zn—O1	108.85 (6)	N1—Zn—O5	170.06 (6)
O3 ⁱ —Zn—N2	134.92 (6)	C11—O1—Zn	127.98 (12)
O1—Zn—N2	115.35 (6)	C14—O3—Zn ⁱ	116.06 (12)
O3 ⁱ —Zn—N1	93.09 (6)	C5—N1—Zn	116.11 (12)
O1—Zn—N1	92.22 (5)	C1—N1—Zn	124.68 (13)
N2—Zn—N1	77.20 (6)	C10—N2—Zn	125.12 (13)
O3 ⁱ —Zn—O5	92.50 (7)	C6—N2—Zn	115.89 (12)
O1—Zn—O5	93.75 (6)	O2—C11—O1	126.2 (2)
N2—Zn—O5	93.05 (6)	O4—C14—O3	124.1 (2)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5A...O2	0.84	1.79	2.615 (2)	166
O5—H5B...O6 ⁱ	0.72	2.05	2.753 (3)	170
O6—H6A...O1	0.74	2.37	3.107 (3)	174
O6—H6B...O4 ⁱⁱ	0.84	1.94	2.774 (2)	173

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $-x, -y, 1 - z$.

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Data reduction: SHELXTL-Plus (Sheldrick, 1990a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990b). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1534). Services for accessing these data are described at the back of the journal.

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 Acta Cryst. (1999). **C55**, 1472–1475

A dihomonuclear complex: di- μ -methacrylate-*O*:*O'*-bis[(1,10-phenanthroline-*N,N'*)bis(methacrylate-*O,O'*)ytterbium(III)]

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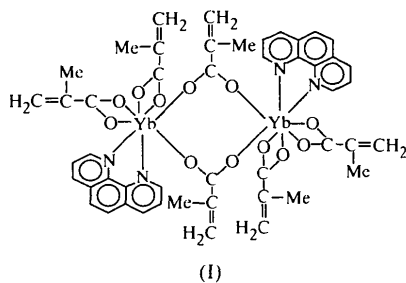
Abstract

In the structure of the title complex, [Yb₂(C₄H₅O₂)₆-(C₁₂H₈N₂)₂], each Yb³⁺ ion is coordinated by six O atoms from four methacrylate ligands and by two N atoms of a phenanthroline ligand, giving a coordination polyhedron which is a distorted square antiprism. Within each centrosymmetric dinuclear molecule, two Yb³⁺ ions are bridged by two bidentate bridging methacrylate ligands.

Comment

There is increasing interest in the stereochemistry of complexes of rare earth ions with unsaturated carboxylic acids because of the potential use of such complexes as extraction agents or as catalysts for hydrogenation, as well as the effect of the α -C=C double bond on

the coordination of carboxylate groups to rare earth ions. Several papers have been published describing the crystal structures of this kind of complex (Hansson, 1975; Xue *et al.*, 1992; Lu *et al.*, 1995). Furthermore, some lanthanide complexes of aromatic amines exhibit fluorescence, which is believed to be caused by the coupling of the *f*-electrons of the central ion with the π -electrons of the aromatic amine ligand. The present investigation of the title complex, (I), was undertaken in order to further the study both of the fluorescent properties of complexes and of the catalytic hydrogenation of lanthanide complexes, and also as part of our structural studies of rare earth complexes with unsaturated carboxylic acids.



In complex (I), each Yb^{3+} ion is coordinated by six O atoms from four methacrylate ligands and by two N atoms from a phenanthroline ligand to give a coordination polyhedron which is a distorted square antiprism. In each dinuclear unit of the com-

plex (Fig. 1), phenanthroline forms a five-membered chelate ring (N1/Yb/N2/C23/C24) with Yb^{3+} . Two methacrylate groups act as bidentate chelating ligands to Yb^{3+} through O1 and O2, and O3 and O4, while the third carboxylate group (O5/C9/O6) bridges Yb through O6, and Yb^i through O5 [symmetry code: (i) $1-x, 2-y, 1-z$]. The two four-atom mean planes through Yb/O1/C1/O2 and Yb/O3/C5/O4 make a dihedral angle of $86.8(3)^\circ$, and form dihedral angles with the eight-atom mean plane through Yb/O6/C9/O5/Ybⁱ/O6ⁱ/C9ⁱ/O5ⁱ of $115.6(2)^\circ$ and $86.3(1)^\circ$, respectively.

The carboxylate ligand has various possible modes of coordination to rare earth metal ions. Bidentate chelating carboxyl groups are the least common because of the strained nature of the four-membered chelate ring. Unlike the homodinuclear complex $[\text{Er}(\text{CCl}_3\text{-COO})_3(\text{phen})(\text{CH}_3\text{CH}_2\text{OH})_2]$ (phen = 1,10-phenanthroline), which contains four bidentate bridging trichloroacetate ligands on each central ion (Dong *et al.*, 1990), complex (I) is composed of centrosymmetric dinuclear units in which each Yb^{3+} ion is coordinated by two bidentate bridging methacrylate ligands and two bidentate chelating methacrylate ligands. This may be due to the effect of the $\alpha\text{-C}=\text{C}$ double bonds of the methacrylate ligands on the coordination of the carboxylate groups to rare earth ions, as well as to the sizes of the carboxylate and other ligands.

The structure of (I) has two distinct groups of $\text{Yb}\cdots\text{O}$ distances involving the methacrylate groups. For the four-membered rings, the range is $2.320(6)\text{-}2.406(6)\text{ \AA}$,

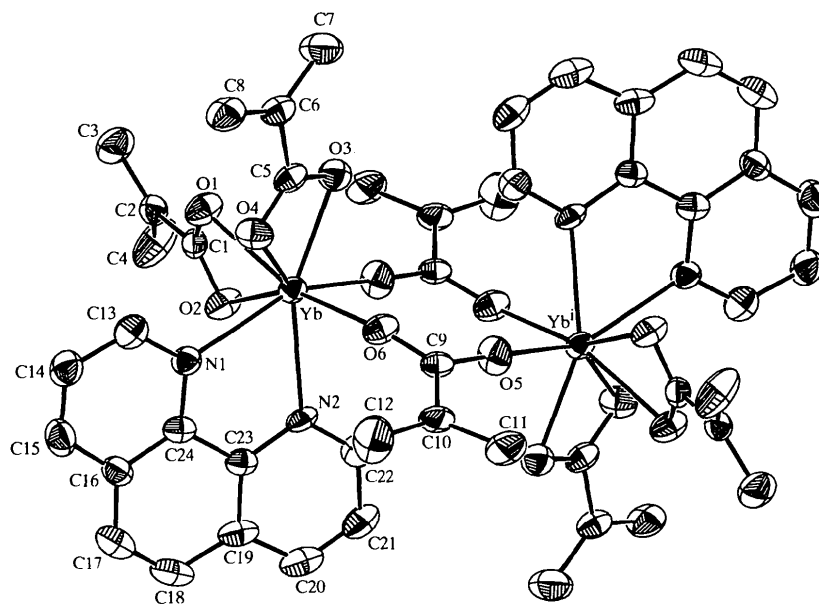


Fig. 1. The molecular structure and atom-numbering scheme for the title complex. Displacement ellipsoids are shown at the 40% probability level and H atoms have been omitted for clarity [symmetry code: (i) $1-x, 2-y, 1-z$].

while the values seen in the eight-membered ring are 2.203 (6) and 2.232 (6) Å. The former group of values is to be expected because the O1—Yb—O2 and O3—Yb—O4 angles of about 55° indicate ring strain. The Yb—N bond lengths are similar at 2.489 (7) and 2.494 (6) Å. The consistently shorter bond lengths to Yb³⁺ compared with the corresponding distances in the La³⁺ complex (Lu, Shao, Hu *et al.*, 1996) are characteristic of the lanthanide contraction.

The Yb¹··Yb¹ separation in the dimer is 5.437 (2) Å. Compared with [La(C₄H₅O₂)₃(phen)(C₄H₆O₂)₂] (Lu, Shao, Hu *et al.*, 1996) or [Er(C₆H₅CHCHCOO)₃] (Lu *et al.*, 1997), in which the La³⁺ and Er³⁺ ions are bridged by two bidentate and two tridentate carboxylate groups, the Yb¹··Yb¹ distance in (I) is much longer than those of La¹··La¹ (4.046 Å) or Er¹··Er¹ (4.097 Å). This indicates that the distance between rare earth ions is shorter in these homodinuclear complexes if the ions are bridged by tridentate μ₂-O carboxylate groups. The same phenomenon is found in the case of [La(C₄H₅O₂)₃(H₂O)₂]₂ (Lu *et al.*, 1995). We note that the linear polymeric structures found for rare earth carboxylates become dinuclear when a phenanthroline ligand takes part in coordination to the central ion. This phenomenon has also been observed in the corresponding La^{III} complex and in lanthanide complexes with other bidentate aromatic amines, suggesting that *N,N'*-bidentate heterocyclic amines may coordinate more strongly to rare earth ions than do water molecules or even the O atoms of carboxylate groups.

Carboxyl groups give rise to very strong IR absorptions, which have been used to distinguish the different coordination modes of the ligands (*i.e.* ionic, monodentate or bidentate) by comparison of the band separation with that of the corresponding sodium salt (Deacon & Phillips, 1980). Separations between ν_{asym}(COO) and ν_{sym}(COO) which are substantially greater than the value of 146 cm⁻¹ for the sodium salt are indicative of monodentate coordination. However, the value for the title complex, where all the carboxylate ligands are bidentate, is 192 cm⁻¹, indicating that this spectroscopic technique could not correctly identify the coordination mode.

Experimental

Freshly prepared crystals of ytterbium α-methacrylate (0.642 g, 1.5 mmol; Lu, Shao, Chen *et al.*, 1996) were dissolved in ethanol/water (4:1 *v/v*) and the solution mixed with phenanthroline hydrate (0.297 g, 1.5 mmol) dissolved in the same solvent. The resulting solution was set aside at room temperature and single crystals suitable for X-ray work were obtained after a few days. Analysis calculated for C₄₈H₄₆N₄O₁₂Yb₂: C 47.37, H 3.81, N 4.60, Yb 28.44%; found: C 47.47, H 3.92, N 4.55, Yb 28.40%. IR spectra: ν_{asym}(COO) 1628, ν_{sym}(COO) 1436, ν(C=C) 1665, ν(C—C, phen ring) 1530, ν(C—H, out of phen ring) 731 and 850 cm⁻¹.

Crystal data

[Yb₂(C₄H₅O₂)₆(C₁₂H₈N₂)₂]
M_r = 1217.0
Monoclinic
P2₁/c
a = 10.182 (4) Å
b = 9.707 (5) Å
c = 23.455 (8) Å
β = 101.48 (3)°
V = 2271 (1) Å³
Z = 2
D_x = 1.779 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-7R diffractometer
ω/2θ scans
Absorption correction:
empirical via ψ scan
(North *et al.*, 1968)
T_{min} = 0.369, T_{max} = 0.435
3918 measured reflections
3664 independent reflections
2706 reflections with
I > 2σ(I)

Refinement

Refinement on F
R = 0.034
wR = 0.043
S = 1.54
2706 reflections
299 parameters
H atoms: see below
w = 1/σ²(F_o) + 4F_o²/σ²(F_o)²
(Δ/σ)_{max} = 0.01

Mo Kα radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 6.85–12.77°
μ = 4.159 mm⁻¹
T = 293 K
Needle
0.3 × 0.2 × 0.2 mm
Colourless

R_{int} = 0.041
θ_{max} = 25.01°
h = 0 → 10
k = 0 → 11
l = -27 → 27
3 standard reflections
every 200 reflections
intensity variation: ±1.4%

Δρ_{max} = 1.04 e Å⁻³
Δρ_{min} = -1.41 e Å⁻³
Extinction correction:
secondary extinction
(Zachariasen, 1963)
Extinction coefficient:
4.22 × 10⁻⁷
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Yb—O1	2.356 (5)	O3—C5	1.25 (1)
Yb—O2	2.384 (6)	O4—C5	1.25 (1)
Yb—O3	2.406 (6)	O5—C9	1.246 (9)
Yb—O4	2.320 (6)	O6—C9	1.255 (9)
Yb—O5 ¹	2.203 (6)	C2—C3	1.41 (1)
Yb—O6	2.232 (6)	C2—C4	1.38 (1)
Yb—N1	2.489 (7)	C6—C7	1.43 (1)
Yb—N2	2.494 (6)	C6—C8	1.35 (1)
O1—C1	1.259 (9)	C10—C11	1.44 (1)
O2—C1	1.263 (9)	C10—C12	1.35 (1)
O1—Yb—O2	54.9 (2)	O4—Yb—N1	75.4 (2)
O1—Yb—O3	75.7 (2)	O4—Yb—N2	129.6 (2)
O1—Yb—O4	77.1 (2)	O5 ¹ —Yb—O6	86.1 (2)
O1—Yb—O5 ¹	101.5 (2)	O5 ¹ —Yb—N1	145.4 (2)
O1—Yb—O6	156.2 (2)	O5 ¹ —Yb—N2	84.2 (2)
O1—Yb—N1	84.9 (2)	O6—Yb—N1	101.7 (2)
O1—Yb—N2	127.3 (2)	O6—Yb—N2	75.5 (2)
O2—Yb—O3	122.0 (2)	N1—Yb—N2	65.9 (2)
O2—Yb—O4	126.4 (2)	Yb—O1—C1	92.8 (5)
O2—Yb—O5 ¹	78.6 (2)	Yb—O2—C1	91.3 (5)
O2—Yb—O6	148.7 (2)	Yb—O3—C5	88.9 (5)
O2—Yb—N1	77.7 (2)	Yb—O4—C5	92.7 (5)
O2—Yb—N2	75.8 (2)	Yb—O5 ¹ —C9 ¹	166.0 (6)

O3—Yb—O4	55.4 (2)	Yb—O6—C9	151.4 (5)
O3—Yb—O5 ¹	84.3 (2)	Yb—N1—C13	122.5 (6)
O3—Yb—O6	82.8 (2)	Yb—N1—C24	119.2 (5)
O3—Yb—N1	129.8 (2)	C13—N1—C24	117.4 (7)
O3—Yb—N2	156.1 (2)	Yb—N2—C22	125.5 (6)
O4—Yb—O5 ¹	139.1 (2)	Yb—N2—C23	118.6 (5)
O4—Yb—O6	82.4 (2)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

H atoms were located by ΔF methods but were not refined. C—H distances were in the range 0.74–1.11 Å.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1303). Services for accessing these data are described at the back of the journal.

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Tricarbonylchromium complexes of four methyl 4,6-*O*-[(η^6 -phenyl)alkylidene]- α -D-glucopyranosides

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Abstract

The crystal structures of the chiral non-racemic η^6 -tricarbonylchromium complexes of three methyl 4,6-*O*-benzylidene- α -D-glucopyranosides, (1)–(3), have been determined, as well as that of the 4,6-*O*-acetal, (4), derived from acetophenone. These compounds are tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(1*S*,3*R*)-(η^6 -3-trimethylsilylphenyl)methylene]- α -D-glucopyranoside}chromium(0), (1), [Cr(C₁₉H₃₀O₆Si)(CO)₃], tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(1*S*,2*R*)-(η^6 -2-trimethylsilylphenyl)methylene]- α -D-glucopyranoside}chromium(0), (2), [Cr(C₁₉H₃₀O₆Si)(CO)₃], tricarbonyl{(*R*)-methyl 2,3-*O*-(1-methylethylidene)-4,6-*O*-[(η^6 -phenyl)methylene]- α -D-glucopyranoside}chromium(0), (3), [Cr(C₁₇H₂₂O₆)(CO)₃], and tricarbonyl{(*S*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(η^6 -1-phenyl)ethylene]- α -D-glucopyranoside}chromium(0), (4), [Cr(C₁₇H₂₄O₆)(CO)₃].

Comment

In connection with a study into the utilization of (η^6 -arene)Cr(CO)₃ complexes in asymmetric synthesis (Woodgate *et al.*, 1998), we have reported in Rickard *et al.* (1998) the structure of tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(η^6 -phenyl)methylene]- α -D-glucopyranoside}chromium(0), (5), and three of its derivatives, (6)–(8), functionalized in the arene ring by a deprotonation (BuLi)/electrophile quenching sequence. In these derivatives, the newly introduced electrophile (SiMe₃, SME or PPh₂, respectively) occupies an *ortho* aromatic site and in each case the absolute stereochemistry of the η^6 -complexed ring was established as 1*R*,2*S* by single-crystal X-ray determinations.

As well as the *ortho*-SiMe₃ compound, (6) (40%), two other tricarbonylchromium complexes were present in the crude mixture obtained from reactions using Me₃SiCl to quench the intermediate (η^6 -phenyl)lithium anion generated in tetrahydrofuran (THF) (*cf.* Jin *et al.*, 1997). These two complexes have now been isolated and their crystal structures determined by X-ray analyses. Unexpectedly, the major product (48%) proved to be the