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Tris(acetylacetonato)(1,10-phenanthroline)cerium(III) and Tris(acetylacetonato)(1,10-phenanthroline)praseodymium(III)

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Abstract

The crystal structures of the title compounds, [Ce(C$_5$H$_7$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)], (1), and [Pr(C$_5$H$_7$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)], (2), have been determined. There are two independent molecules in the asymmetric unit of (1), but only one molecule in the asymmetric unit of (2). In both compounds, the metal atom is eightfold coordinated by six O and two N atoms in a slightly distorted square-antiprismatic

arrangement. The ligands span the opposite edges of the two square faces of the coordination antiprism. Important bond-distance ranges are: Ce—O 2.434 (7)–2.499 (7), Ce—N 2.70 (1)–2.767 (9), Pr—O 2.392 (5)–2.437 (6) and Pr—N 2.659 (5)–2.690 (6) Å.

Comment

Rare earth metal complexes are of growing importance because of their chemical (Cotton, 1991), industrial (Niinisto, 1987), and biochemical and medicinal applications (Evans, 1990). As part of our study on rare earth metal complexes with N-donor and O-donor ligands, we report here the preparation and crystal structures of the title compounds, tris(acetylacetonato)(1,10-phenanthroline)cerium(III), (1), and tris(acetylacetonato)(1,10-phenanthroline)praseodymium(III), (2).

(1) M = Ce
(2) M = Pr
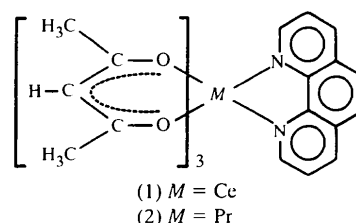
There are two crystallographically independent molecules in the asymmetric unit of compound (1) (Fig. 1), but only one molecule in the asymmetric unit of compound (2) (Fig. 2). In both compounds, the metal atom is eightfold coordinated by six O and two N atoms in a slightly distorted square-antiprismatic arrangement. The acetylacetonato and 1,10-phenanthroline (phen) ligands behave as bidentate chelates. One of the two square faces of the coordination antiprism, denoted as the *O*-face, is formed exclusively by O atoms [O1, O2, O3 and O4 for the first molecule of compound (1) and the molecule of compound (2), and O7, O8, O9 and O10 for the second molecule of compound (1)]. The other square face, denoted the *NO*-face, is formed by two N and two O atoms [N1, N2, O5 and O6 for the first molecule of compound (1) and the molecule of compound (2), and N3, N4, O11 and O12 for the second molecule of compound (1)]. These square faces are almost parallel, the angles between them being 2.1 (2), 2.9 (2) and 3.4 (2)° for the two molecules of compound (1) and the molecule of compound (2), respectively.

The antiprismatic arrangement is common among eight-coordinate rare earth metal complexes. In some compounds, as in (1) and (2), and in the analogous Eu^{III} complex (Watson *et al.*, 1972), the ligands span the opposite edges of the two square faces of the coordination antiprism (*s* edges). In other complexes, as in tris(thenoyltrifluoroacetylacetonato)europium(III) dihydrate, the ligands span the edges of the triangular faces of the antiprism (*l* edges) (Lippard, 1967).
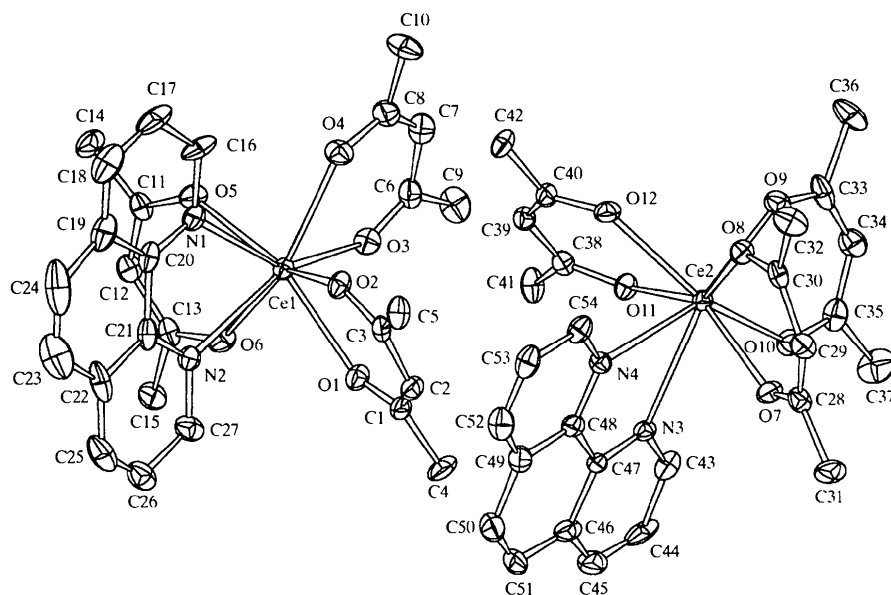
Fig. 1. The molecular structure of compound (1) with H atoms omitted for clarity. Displacement ellipsoids are plotted at the 30% probability level
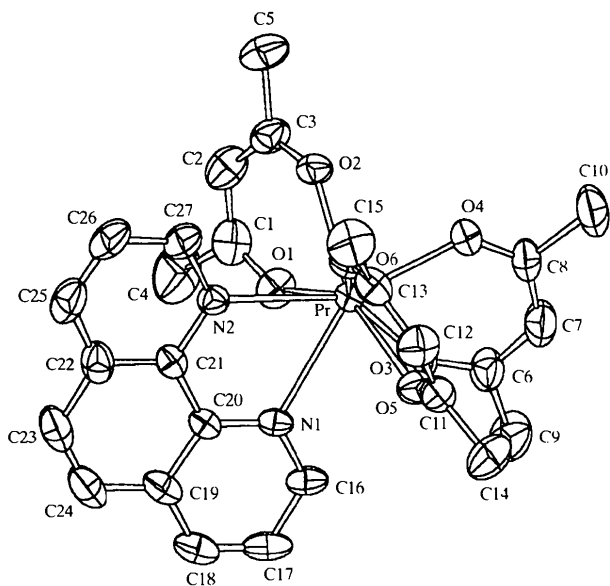

Fig. 2. The molecular structure of compound (2) with H atoms omitted for clarity. Displacement ellipsoids are plotted at the 30% probability level.

The Ce—O and the Ce—N bond-distance ranges are 2.434 (7)–2.499 (7) and 2.70 (1)–2.767 (9) Å, with mean values of 2.464 (2) and 2.741 (5) Å, respectively. These values are comparable with the bond distances observed in the [Ce₂(CH₃CO₂)₆(phen)₂] dimer (Panagiotopoulos et al., 1995), where the mean Ce—O distance, excluding the capping O1 atom, is 2.497 (1) Å, and the mean Ce—N distance is 2.679 (3) Å. Similarly, the Pr—O and the

Pr—N bond-distance ranges are 2.392 (5)–2.437 (6) and 2.659 (5)–2.690 (6) Å, with mean values of 2.414 (2) and 2.674 (4) Å, respectively.

The distances of the metal atoms from the O-face and the NO-face of the antiprisms are different: 1.291 (1)– 1.554 (1) and 1.262 (1)–1.586 (1) Å for the two molecules of compound (1), and 1.250 (1)–1.492 (1) Å for the molecule of compound (2). Moreover, due to the unequal bond distances between the metal atom and the atoms of the NO-face, the latter is translated parallel to the corresponding O-face. The geometrical features of the acetylacetonato and 1,10-phenanthroline ligands are as expected.

The molecular-packing motifs of the two compounds are quite different. While in the Ce complex the 1,10-phenanthroline moieties are arranged roughly parallel to the (100) plane, in the Pr complex they are arranged almost parallel alternatively to planes (011) and (01̄1). As a consequence, the structure of the latter compound appears more open than that of the former one, which is reflected in their calculated densities (1.385 Mg m⁻³ for the Pr complex compared with 1.493 Mg m⁻³ for the Ce complex).

Experimental

Compounds (1) and (2) were prepared from solutions of Ln(C₅H₇O₂)₃.3H₂O (Ln = Ce, Pr) (1 mmol) in acetone (30 ml), to which 1,10-phenanthroline (1 mmol) was added. Each mixture was stirred for 10 min, then filtered; the filtrate was kept in a fridge. After 24 h, each solution afforded crystals suitable for X-ray diffraction analysis. Ln(C₅H₇O₂)₃.3H₂O samples were prepared according to Pope et al. (1961).

Compound (1)

Crystal data

[Ce(C$_5$H$_7$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)]
M_r = 617.65
Monoclinic
$P2_1/n$
a = 16.912 (1) Å
b = 18.188 (1) Å
c = 17.872 (1) Å
β = 91.009 (4)°
V = 5496.5 (5) Å^3
Z = 8
D_x = 1.493 Mg m^{-3}
D_m = 1.49 Mg m^{-3}
D_m measured by flotation in CCl$_4$/cyclohexane

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 31 reflections
θ = 12.54–15.44°
μ = 1.697 mm^{-1}
T = 293 K
Prism
0.54 × 0.20 × 0.16 mm
Orange

Data collection

Modernized Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (*EMPIR*; Stoe & Cie, 1988*b*)
  T_{min} = 0.581, T_{max} = 0.762
9702 measured reflections
9702 independent reflections

5607 reflections with $F > 4\sigma(F)$
θ_{max} = 25.02°
h = −20 → 20
k = 0 → 21
l = 0 → 21
3 standard reflections
  frequency: 120 min
  intensity decay: 4%

Refinement

Refinement on F
R = 0.053
wR = 0.043
S = 1.835
5607 reflections (see below)
649 parameters
H atoms not refined
w = 1/$\sigma^2(F_o)$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.7 e Å^{-3}
$\Delta\rho_{min}$ = −0.6 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (1)*

N1—Ce1	2.70 (1)	N3—Ce2	2.753 (8)
N2—Ce1	2.747 (9)	N4—Ce2	2.767 (9)
O1—Ce1	2.452 (8)	O7—Ce2	2.460 (8)
O2—Ce1	2.499 (7)	O8—Ce2	2.482 (7)
O3—Ce1	2.453 (9)	O9—Ce2	2.439 (8)
O4—Ce1	2.474 (9)	O10—Ce2	2.472 (9)
O5—Ce1	2.451 (8)	O11—Ce2	2.434 (7)
O6—Ce1	2.485 (8)	O12—Ce2	2.473 (8)
N1—Ce1—N2	59.9 (3)	N3—Ce2—N4	59.3 (3)
N1—Ce1—O5	72.6 (3)	N3—Ce2—O11	70.9 (3)
N2—Ce1—O6	73.0 (3)	N4—Ce2—O12	71.8 (3)
O1—Ce1—O2	69.1 (3)	O7—Ce2—O8	69.8 (2)
O1—Ce1—O3	80.4 (3)	O7—Ce2—O10	78.7 (3)
O2—Ce1—O4	77.3 (3)	O8—Ce2—O9	81.3 (3)
O3—Ce1—O4	69.8 (3)	O9—Ce2—O10	69.1 (3)
O5—Ce1—O6	69.7 (3)	O11—Ce2—O12	69.7 (3)

Compound (2)

Crystal data

[Pr(C$_5$H$_7$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)]
M_r = 618.45

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/n$
a = 9.515 (1) Å
b = 21.086 (9) Å
c = 14.978 (2) Å
β = 99.39 (1)°
V = 2965 (1) Å^3
Z = 4
D_x = 1.385 Mg m^{-3}
D_m = 1.38 Mg m^{-3}
D_m measured by flotation in CCl$_4$/cyclohexane

Cell parameters from 28 reflections
θ = 15.14–18.91°
μ = 1.681 mm^{-1}
T = 293 K
Prism
0.40 × 0.20 × 0.15 mm
Green

Data collection

Modernized Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (*EMPIR*; Stoe & Cie, 1988*b*)
  T_{min} = 0.632, T_{max} = 0.777
5233 measured reflections
5233 independent reflections

3742 reflections with $F > 4\sigma(F)$
θ_{max} = 25.03°
h = −11 → 11
k = 0 → 25
l = 0 → 17
3 standard reflections
  frequency: 120 min
  intensity decay: 4%

Refinement

Refinement on F
R = 0.043
wR = 0.045
S = 0.972
3742 reflections
325 parameters
H atoms not refined
w = 1/$\sigma^2(F_o)$

$(\Delta/\sigma)_{max}$ = 0.0084
$\Delta\rho_{max}$ = 0.766 e Å^{-3}
$\Delta\rho_{min}$ = −0.931 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (2)*

N1—Pr	2.659 (5)	O3—Pr	2.407 (5)
N2—Pr	2.690 (6)	O4—Pr	2.437 (6)
O1—Pr	2.423 (6)	O5—Pr	2.408 (6)
O2—Pr	2.418 (5)	O6—Pr	2.392 (5)
N1—Pr—N2	61.2 (2)	O1—Pr—O3	76.9 (2)
N1—Pr—O5	74.5 (2)	O2—Pr—O4	79.2 (2)
N2—Pr—O6	71.0 (2)	O3—Pr—O4	71.3 (2)
O1—Pr—O2	70.6 (2)	O5—Pr—O6	70.9 (2)

For both compounds, all non-H atoms were refined with anisotropic displacement parameters. H atoms, except those of the terminal methyl groups, were placed at calculated positions (C—H 0.95 Å) with isotropic displacement parameters equal to the equivalent isotropic displacement parameters of the parent atoms and kept fixed. For compound (1), in order to enhance the reflection-to-parameter ratio, 1735 weak reflections with $F_c > F_o$, in addition to the 5607 observed ones, were used in the least-squares matrix. For the total of 7342 reflections used, convergence produced R = 0.076, wR = 0.044 and S = 1.628. The corresponding residual values, which refer to the observed reflections only, are given for comparison in the *Refinement* section above. In the same compound, the displacement parameters of atom C24 exhibited pronounced anisotropy, indicative of probable disorder. An attempt, however, to refine the structure using a split-atom model proved unsuccessful.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1988*a*); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe &

Cie, 1988c); program(s) used to solve structures: *Xtal3.2 SIMPEL* (Hall *et al.*, 1992); program(s) used to refine structures: *Xtal3.2 CRYLSQ*; molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

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by the O atom of the coordinated water molecule at a distance of 2.388 (3) Å. The monomeric units are associated through hydrogen bonds, forming infinite chains. There are two magnetically different copper(II) polyhedra.

Comment

The tetrameric structure of (4-ethylpyridine)(*N*-salicylideneglycinato)copper(II), which crystallizes with a tetragonal unit cell, has been reported recently (Warda, 1997). In this communication, the structure of the closely related title complex, aqua(2-ethylpyridine)(*N*-salicylideneglycinato)copper(II), (I), is reported.

(I)
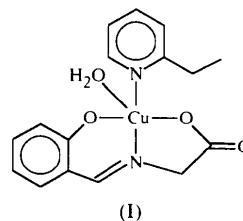
The Cu^{II} ion has square-pyramidal [4+1] coordination geometry, with the tridentate Schiff base *N*-salicylideneglycinato dianion and the monodentate 2-ethylpyridine ligand in the basal plane (Fig. 1). The apical position is occupied by a water O atom at a distance of 2.388 (3) Å. It is noteworthy that coordination of water to Cu^{II} is invariably at the apical site of a tetragonally elongated square pyramid. This seems to be a general result for five-coordinate Cu^{II} complexes (Warda, 1998, and references therein).

Aqua(2-ethylpyridine-*N*)(*N*-salicylideneglycinato-*O,N,O'*)copper(II)

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Abstract

In the title compound, [Cu(C₉H₇NO₃)(C₇H₉N)(H₂O)], the copper(II) centre has a square-pyramidal environment with a tridentate *N*-salicylideneglycinato Schiff base dianion and a 2-ethylpyridine ligand coordinated in the basal plane. The apex of the pyramid is occupied
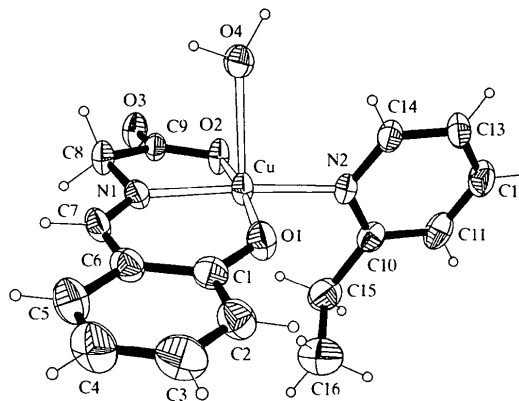
Fig. 1. The asymmetric unit of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

The pyridine ring is inclined with respect to the basal plane (through atoms O1, O2, N1 and N2) at an angle of 80.0 (1)° and the Cu atom lies 0.155 (1) Å out of this plane, displaced towards the O4 atom (*PLATON*;