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Di-μ-acetato-κ^3O,O':O'-di-μ-trichloroacetato-κ^2O:O'-bis[aqua(trichloroacetato)(1,10-phenanthroline-κ^2N,N')praseodymium(III)] dimethylformamide disolvate

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The reaction of praseodymium(III) trichloroacetate with 1,10-phenanthroline (phen), acetic acid and 8-hydroxyquinoline gives the title centrosymmetric complex, $[Pr_2(C_2Cl_3O_2)_4(C_2H_3O_2)_2(C_{12}H_8N_2)_2(H_2O)_2]\cdot 2C_3H_7NO$. The geometry around the Pr^{III} ion corresponds to a monocapped square antiprism. Interestingly, the carboxylate groups coordinate in three different modes, *viz*. monodentate, bridging and bridging–chelating. In the crystal structure, there are weak intermolecular Cl···Cl and π–π-stacking interactions.

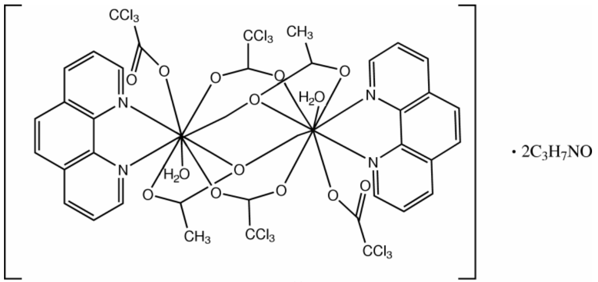
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.031
wR factor = 0.078
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Numerous quaternary complexes of lanthanides bearing heterocycle amines have been extensively reported since 1960 (Forsberg, 1973). In recent years, efforts have been actively made to synthesize novel quaternary mixed-anion complexes because of their interesting structures, coordination modes and functional properties (Dong *et al.*, 1993; Rogers & Rollins, 1995; Niu *et al.*, 1997; Li *et al.*, 2002; Zhu *et al.*, 1999; Zhu & Kitagawa, 2001). In general, the two anions in these complexes were based on nitrate and aliphatic or aromatic carboxylate ligands. However, systems containing two anions of aliphatic or aromatic carboxylates may show more interesting coordination modes. We report here an example of a quaternary complex, (I), with two anions of aliphatic carboxylates.



(I)

The complex is a dimer with a Pr···Pr separation of 4.125 (1) Å, and possesses a center of symmetry. Each Pr atom is nine-coordinate with a monocapped square antiprismatic geometry, involving six O atoms from three CCl_3COO^- and two CH_3COO^- groups, two N atoms from one phen, and one O atom from one water molecule. The four CCl_3COO^- anions in the dimeric complex show two coordination modes; one mode involves bonds to two Pr atoms through O2 and O3 and the other mode is monodentate coordination to the Pr atom. The acetate anions are chelated to one Pr atom through atoms O6 and O7; simultaneously O7 binds to another Pr atom with distances of 2.636 (3) and 2.399 (3) Å for O7—Pr1 and O7—Pr1^{i} [symmetry code: (i) $-x$, $1-y$, $-z$], respectively. The Pr—O(H_2O) bond length is similar to that of bridging Pr—

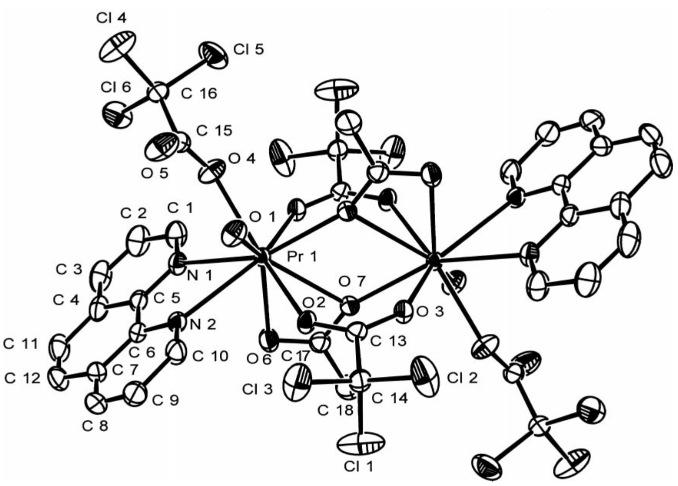


Figure 1
ORTEP-3 diagram (Farrugia, 1997) of the title complex, showing the atom-labeling scheme (DMF molecules and H atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 30% probability level. The labeled part of the molecule is related to the unlabeled part by the symmetry operator ($-x$, $1 - y$, $-z$).

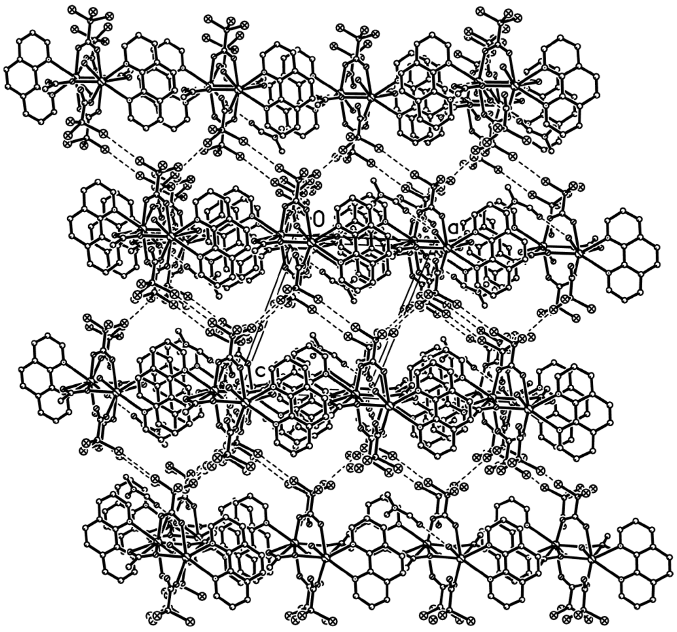


Figure 2
The packing of complex (I), showing weak Cl···Cl interactions (dashed lines), viewed along the *b* axis.

O(CCl_3COO^-) and the Pr—N distances are longer than the Pr—O distances (see Table 1). The phen ligands are situated in vacant sites and the complex therefore has little steric crowding. As expected, the Pr—N distances agree with those of the two ternary complexes bearing similar building blocks, the monomer complex [Pr(CCl_3COO)$_3$(2,2′-bipy)$_2$], (II) (Wang *et al.*, 1991), and the dimer complex [Pr(CCl_3COO)$_3$(phen)(C_2H_5OH)]$_2$, (III) (Dong *et al.*, 1990). In (II), all the trichloroacetate ligands are coordinated to the metal in chelating mode and the mean Pr—O bond length is 2.582 (4) Å, which is longer than that of (I) and (III). In complex (III), two coordination modes for the trichloroacetate groups were observed and the Pr—O distances for the chelating mode are similar to that in (I), while the Pr—O(CCl_3COO^-) distance for the monodentate mode is shorter than that in (I).

In recent years, weak interactions, such as the Cl···Cl interactions observed in (I), have been the focus of increased interest (Cui *et al.*, 2001). The Cl atom of the monodentate CCl_3COO^- group has a weak interaction with another Cl atom of a bridging CCl_3COO^- ligand from a neighboring molecule; the distance is 3.34 Å (see Fig. 2), which is shorter than the sum of the van der Waals radii of Cl···Cl (3.5 Å). Meanwhile, two phen rings from neighboring molecules are parallel to each other and result in significant π–π stacking, with an interplanar distance of 3.38 Å.

Experimental

Pr(CCl_3COO)$_3$.6H_2O (0.3 mmol) was dissolved in a mixture of ethanol (10 ml) and water (4 ml). A solution of 1,10-phenanthroline (0.84 mmol), 8-hydroxyquinoline (HQ, 1.0 mmol) and 6 mol l^{-1} CH_3COOH (3 ml) in a mixture of ethanol (10 ml) and *N*,*N*′-dimethylformamide (3 ml) was added to the above solution. After 3 d, crystals were obtained. Analysis calculated for $C_{21}H_{20}Cl_6N_3O_8Pr$: C 31.69, H 2.53, N 5.28, Pr 17.70%; found: C 31.48, H 2.47, N 4.62, Pr 17.43%. HQ is a key factor in the formation of quaternary complexes. In the absence of HQ in the synthesis, no product could be obtained because of the strong acidity. HQ can form H_2Q^+ with CH_3COOH. Moreover, it can decrease the acidity of the solution and keep a certain amount of CH_3COO^- to partly replace CCl_3COO^- anions of Pr(CCl_3COO)$_3$. Thus, the quaternary complex was formed.

Crystal data

[$Pr_2(C_4Cl_6O_4)_4(C_2H_3O_2)_2$-($C_{12}H_8N_2)_2(H_2O)_2$]·2$C_3H_7NO$
M_r = 1592.02
Triclinic, $P\overline{1}$
a = 10.351 (3) Å
b = 12.475 (3) Å
c = 13.424 (4) Å
α = 113.89 (3)°
β = 102.18 (2)°
γ = 102.786 (18)°
V = 1455.0 (7) Å^3
Z = 1
D_x = 1.817 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7133 reflections
θ = 1.8–23.3°
μ = 2.27 mm^{-1}
T = 293 (2) K
Prism, green
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.549, $T_{\max}$ = 0.659
7133 measured reflections
4163 independent reflections
3874 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.014
$\theta_{\max}$ = 23.3°
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.06
4163 reflections
360 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 3.6925P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 1.07 e Å^{-3}
$\Delta\rho_{\min}$ = −0.76 e Å^{-3}

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Table 1
Selected geometric parameters (Å).

Pr1—O7^{i}	2.399 (3)	Pr1—O6	2.538 (4)
Pr1—O4	2.458 (4)	Pr1—O7	2.636 (3)
Pr1—O1	2.500 (4)	Pr1—N2	2.646 (4)
Pr1—O2	2.502 (3)	Pr1—N1	2.665 (4)
Pr1—O3^{i}	2.507 (3)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O5	0.88 (2)	1.96 (4)	2.748 (6)	149 (6)
O1—H1$B\cdots$O8	0.89 (2)	1.84 (4)	2.690 (8)	159 (8)

All H atoms bonded to C atoms were included in calculated positions with C—H distances of 0.93 for most H atoms and 0.96 Å for methyl. They were then included in the refinement in riding-motion approximation with $U_{\rm iso}$ fixed at 0.08 Å^2. H atoms bonded to O atoms were refined freely with isotropic displacement parameters. The diffraction was measured to only $\theta = 23.3°$, and this, together with the lack of low-temperature facilities, limits the precision of the structural results. The maximum electron-density peak is 1.12 Å from Cl4.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*97 (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1997). *SMART* (Version 5.044), *SAINT* (Version 5.01) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cui, Y., Chen, J. T., Chen, G., Ren, J., Yu, W. C. & Qian, Y. T. (2001). *Acta Cryst.* C**57**, 349–351.

Dong, N., Wang, H., Barton, R. J. & Robertson, B. E. (1990). *J. Coord. Chem.* **22**, 191–204.

Dong, D., Zhu, L. G. & Xu, C. (1993). *Chin. J. Struct. Chem.* **12**, 133–136.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Forsberg, J. H. (1973). *Coord. Chem. Rev.* **10**, 195–226.

Li, X., Jin, L. P., Lu, S. Z. & Zhang, J. H. (2002). *J. Mol. Struct.* **604**, 65–71.

Niu, S. Y., Yang, Z. Z., Yang, Q. C, Yang,B., Yang, J. Q., Chao, G. D., Yang, E. & Zhong, S. (1997). *Polyhedron*, **16**, 1629–1635.

Rogers, R. D. & Rollins, A. N. (1995). *Inorg. Chim. Acta*, **230**, 177–183.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Wang, J. R., Dong, N., Wu, G. & Zheng, P. J. (1991). *Chem. J. Chin. Univ.* **12**, 1284–1288.

Zhu, L. G., Xie, X. P. & Yu, Q. S. (1999). *J. Rare Earths*, **17**, 12–16.

Zhu, L. G. & Kitagawa, S. (2001). *Chem. J. Chin. Univ.* **22**, 188–190.

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