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Bis(μ-acetato){μ-2,6-bis[(2-hydroxybenzyl)-(2-pyridylmethyl)aminomethyl]-4-methylphenolato}diindium(III) nitrate dihydrate

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Abstract

In the title compound, $[In_2(C_{35}H_{33}N_4O_3)(C_2H_3O_2)_2]$-$NO_3 \cdot 2H_2O$, a new binuclear In^{III} complex, the metal centers are linked by one phenolate and two acetate bridging groups. The In^{III} ions are in a distorted octahedral environment and they are related by imposed crystallographic C_2 symmetry.

Comment

^{111}In and ^{113}In are useful radionuclides for some diagnostic imaging procedures in nuclear medicine (Remy *et al.*, 1995; Jamar *et al.*, 1995). These isotopes are appropriate γ-emitters for imaging using techniques such as single-photon emission computed tomography.

Special conditions in the physiological environment (*e.g.* pH), and the high affinity between serum proteins in human blood (*e.g.* transferrin) and trivalent metal ions requires the development of indium complexes with high stability for radiopharmaceutical applications. They must be thermodynamically stable to avoid hydrolysis processes in the organism, as well as being kinetically inert to prevent demetalation by transferrin (Jurisson *et al.*, 1993).

A number of complexes with linear and tripodal polydentate amine–phenol ligands have been reported previously (Wong, Liu, Lügger *et al.*, 1995; Wong, Liu, Rettig & Orvig, 1995; Liu *et al.*, 1993). These ligands have been considered as effective chelating agents capable of producing highly stable mononuclear complexes with group 13 metal ions.

We report here for the first time the homodinuclear complex $[In_2(BBPMP)(OAc)_2]NO_3 \cdot 2H_2O$, (I), with an N_4O_3-donor dinucleating ligand which contains phenolate and pyridyl pendant arms {H_3BBPMP is 2,6-bis[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-methylphenol and OAc is acetate}. H_3BBPMP is a symmetric and non-linear amine–phenol ligand. It has a molecular structure suitable for the formation of binuclear phenolate-bridged complexes (Neves *et al.*, 1993, 1996; de Brito *et al.*, 1997). In this work, we have used the H_3BBPMP ligand to synthesize the first example of a binuclear indium complex with two bridging acetate groups.

(I)
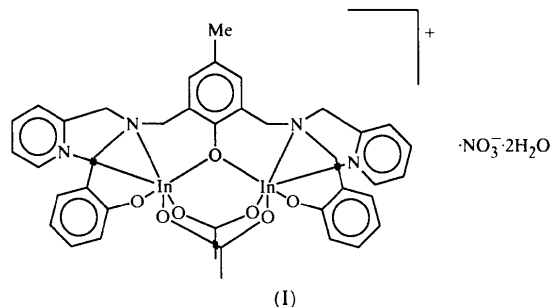
The $[In_2(BBPMP)(OAc)_2]^+$ cation has C_2 symmetry, with atoms O10, C11, C14 and C17 of the $BBPMP^{3-}$ ligand lying on the crystallographic twofold axis (Fig. 1). Each In^{III} ion is coordinated by one O (phenolate) and two N (amine and pyridyl) atoms of the main ligand in the external face, while three O atoms of one phenolate and two carboxylate bridging groups in the internal face complete the coordination sphere. The O atom of the terminal phenolate arm is coordinated in a *trans* position to the phenolate bridging group. A similar arrangement of the $BBPMP^{3-}$ ligand around a metal ion was also observed in the $[Fe_2(BBPMP)(OAc)_2]ClO_4 \cdot H_2O$ (Neves *et al.*, 1993), NH_4-$[Fe_2(BBPMP)(SO_4)_2]$ (de Brito *et al.*, 1997) and $[Fe_2(BBPMP)\{O_2P(OPh)_2\}_2]ClO_4 \cdot H_2O$ (Krebs *et al.*, 1994) complexes. As in the iron complexes, the greatest distortion in the coordination sphere of the metal is the acute N_{amine}—In—$N_{pyridyl}$ angle of 75.7 (1)°, imposed by formation of the five-membered chelate ring. The *M*—O—*M* angle varies according to the rigidity of the bridging groups. In the complexes $[In_2(BBPMP)(OAc)_2]NO_3 \cdot 2H_2O$ and $[Fe_2(BBPMP)(OAc)_2]ClO_4 \cdot H_2O$, which are

both acetate-bridged, the M—O—M angles are similar, with values of 117.51 (14) and 118.3 (4)°, respectively, whereas in the sulfate- and diphenylphosphate-bridged complexes with H_3BBPMP, these angles are larger than 121°.
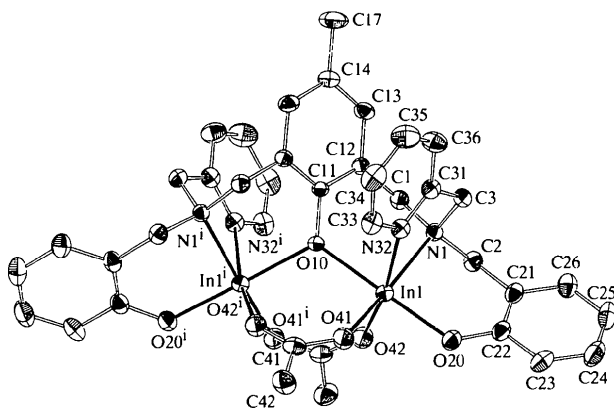

Fig. 1. A view of the title structure with displacement ellipsoids shown at the 40% probability level. Only a partial labeling scheme is presented. The nitrate anion and water solvate molecules have been omitted. [Symmetry code: (i) $-x$, y, $\frac{3}{2} - z$.]

The bond lengths In—O$_{phenolate}$ (average 2.119 Å), In—N$_{amine}$ [2.254 (4) Å] and In—N$_{pyridyl}$ [2.294 (4) Å] are comparable with those observed in [In(Clbbpen)]-ClO$_4$ [2.059, 2.313 (2) and 2.281 (2) Å, respectively; Clbbpen is the anion of N,N'-bis(5-chloro-2-hydroxy-benzyl)-N,N'-bis(2-pyridylmethyl)ethylenediamine; Wong, Liu, Rettig & Orvig, 1995], which is an amine-phenol ligand where both phenolate groups are *trans* to amine N atoms. In the title complex, the In—O$_{phenolate}$ distances (Table 1) are very similar with respect to each other and they are slightly longer than those observed in [In(Clbbpen)]ClO$_4$, so that there is not a pronounced *trans* effect from the phenolate moieties.

Hydrogen bonds from the water solvent molecules were observed in the three-dimensional packing arrangement of [In$_2$(BBPMP)(OAc)$_2$]NO$_3$·2H$_2$O. Each water molecule is linked *via* a hydrogen bond to an O atom (H···O20) of the terminal phenolate and to an O atom (H···O52) of the nitrate group. The geometric parameters of the hydrogen bonds are listed in Table 2.

Experimental

The H_3BBPMP ligand was prepared according to the literature procedure of Neves *et al.* (1993). The title complex was prepared from the reaction between the ligand (0.2 g, 0.35 mmol) and In(NO$_3$)$_3$·5H$_2$O (0.27 g, 0.7 mmol) in the presence of NaOAc (0.19 g, 1.4 mmol) in methanol. The solvent was removed. By addition of acetone (5 ml) to the residual oil, the binuclear indium complex was isolated as a white precipitate. Crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation from a CH$_3$OH/CH$_3$CO$_2$C$_2$H$_5$/

CH$_2$Cl$_2$ (1:1:1) solution of the title compound at room temperature.

Crystal data

[In$_2$(C$_{35}$H$_{33}$N$_4$O$_3$)-(C$_2$H$_3$O$_2$)$_2$]NO$_3$·2H$_2$O	Mo $K\alpha$ radiation
M_r = 1003.42	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25
$Pbcn$	reflections
a = 11.138 (2) Å	θ = 17.69–22.37°
b = 18.801 (4) Å	μ = 1.221 mm^{-1}
c = 19.121 (4) Å	T = 293 (2) K
V = 4004.0 (14) Å^3	Prismatic
Z = 4	0.33 × 0.26 × 0.13 mm
D_x = 1.665 Mg m^{-3}	Colorless
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	2555 reflections with $I > 2\sigma(I)$
ω–2θ scans	R_{int} = 0.048
Absorption correction:	θ_{max} = 25.18°
ψ scan (*PLATON*; Spek, 1990)	h = $-13 \rightarrow 0$
	k = $-22 \rightarrow 0$
T_{min} = 0.704, T_{max} = 0.853	l = $-22 \rightarrow 0$
4045 measured reflections	3 standard reflections
3601 independent reflections	frequency: 120 min
	intensity decay: 1.7%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$\Delta\rho_{max}$ = 1.45 e Å^{-3}
$wR(F^2)$ = 0.107	$\Delta\rho_{min}$ = -0.70 e Å^{-3}
S = 1.030	Extinction correction:
3601 reflections	*SHELXL97*
263 parameters	Extinction coefficient:
H-atom parameters constrained	0.00023 (16)
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 6.4081P]$	Scattering factors from *International Tables for Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

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

In1—O20	2.065 (3)	In1—O10	2.173 (2)
In1—O41	2.096 (4)	In1—N1	2.254 (4)
In1—O42	2.164 (3)	In1—N32	2.294 (4)
O20—In1—O41	91.72 (14)	O42—In1—N1	95.96 (14)
O20—In1—O42	89.56 (14)	O10—In1—N1	87.48 (12)
O41—In1—O42	98.51 (15)	O20—In1—N32	101.60 (14)
O20—In1—O10	174.10 (10)	O41—In1—N32	90.03 (15)
O41—In1—O10	92.80 (12)	O42—In1—N32	165.78 (14)
O42—In1—O10	86.02 (11)	O10—In1—N32	82.21 (12)
O20—In1—N1	89.10 (14)	N1—In1—N32	75.65 (14)
O41—In1—N1	165.51 (15)	In1^i—O10—In1	117.39 (19)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O20	0.88	1.96	2.822 (6)	168
O1W—H1WB···O52^i	0.94	2.21	3.111 (8)	159

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

H atoms attached to C atoms were placed at idealized positions, with C—H distances and U_{eq} values taken from the

default settings of the refinement program. The water H atoms were found from difference Fourier maps and were treated as riding atoms. The H atoms bonded to C17 show rotational disorder about the twofold axis and their occupancies were fixed at 0.5. In the nitrate group, one O atom was found disordered about a twofold axis. The N50 atom lies on the axis, whereas the original peak for the O51 atom was found about 0.75 Å to the side of it. The disorder of NO_3 was modeled using the *SADI* and *DFIX* instructions in the *SHELXL97* program (Sheldrick, 1997a), where N—O and O···O distances were restrained. The O51 atom was constrained to a special position, lying on the crystallographic twofold axis, and was refined isotropically with 0.5 site occupancy. The highest peak (1.45 e Å^{-3}) and deepest hole (−0.70 e Å^{-3}) are located 0.95 and 0.75 Å, respectively, from O51.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *SET*4 in *CAD*-4 *EXPRESS*. Data reduction: *HELENA* (Spek, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997a). Molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996). Software used to prepare material for publication: *SHELXL*97. All calculations were performed on a PC/PentiumII computer running *LINUX*.

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The twinned structure of the μ-isopropoxido-diisopropoxido(*p*-tolylimido)-vanadium(V) dimer,† twin refinement against CCD area-detector data

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Abstract

The title compound, $[V_2(C_7H_7N)_2(C_3H_7O)_6]$, crystallizes as a non-merohedral twin in the triclinic space group $P\bar{1}$. The twin operation is a twofold rotation around the reciprocal [110] direction, leading to split reflections. The intensities of both twin domains were evaluated separately and the structure refinement resulted in a population ratio of 72.6 (1):27.4 (1). The molecular geometry of this dimeric compound is in line with similar vanadium compounds found in the literature. The vanadium is in a distorted trigonal-bipyramidal environment. The dimer is formed by the asymmetric bridging of two isopropoxido groups with bond lengths of 1.8560 (13) and 2.2151 (13) Å.

Comment

Catalytic polymerization of α-olefins by the use of homogeneous systems is of commercial interest for the production of tailored polymers (Ewen, 1997). Although group IV metal-based systems generally show enhanced activity, vanadium catalysts have several favourable properties, for example, in the production of polymers with a narrow molecular-weight distribution, in the preparation of copolymers or in the generation of syndiotactic polypropylene (Murphy & Turner, 1997). In the context of our investigations in this field, we succeeded in the crystallization of the title compound, (I). While the association in solution was established to be monomeric by cryoscopic molecular-weight determination in benzene, we were interested in the aggregation in the crystalline state. It is known from similar com-

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† Systematic name: di-μ-isopropoxido-bis[diisopropoxido(4-methylphenylimido)vanadium(V)].