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Metal Alkoxycarboxylate Complexes. II. Poly[diaquabis(3-hydroxypropionato)-yttrium(III)] Bromide and *catena*-Poly[pentaaqua(3-hydroxypropionato)-yttrium(III)] Bromide Chloride

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Abstract

Poly[diaquayytrium(III)bis(μ-3-hydroxypropionato-O^3,-O^1:$O^{1'}$) bromide], $\{[Y(O_2CCH_2CH_2OH)_2(H_2O)_2]Br\}_n$, forms a layer structure consisting of sheets of cations in which the 3-hydroxypropionate ligands chelate to one metal *via* the hydroxyl and one carboxyl O atom, and bridge to adjacent metals *via* the second carboxyl O atom. The same chelating/bridging coordination of the carboxylate ligand occurs in *catena*-poly[[pentaaquayttrium(III)]-μ-(3-hydroxypropionato-O^3,O^1:$O^{1'}$) bromide chloride], $\{[Y(O_2CCH_2CH_2OH)(H_2O)_5](Br)Cl]\}_n$, to give cation chains which are arranged in layers. In both structures, the anions lie between the cation units and hold the latter together *via* hydrogen bonding.

Comment

Metal carboxylates decomposing at low temperatures to the corresponding oxide and volatile organic fragments are promising candidates for ceramic preparation by metallo-organic deposition (Apblett & Georgieva, 1994; Apblett *et al.*, 1992, 1997). This is particularly true if they melt below the decomposition point as this permits processing into thin films without the need for solvent. Such species could also be precursors for ceramic foams if the pyrolysis produces copious quantities of gas. In this context, metal 3-hydroxy-propionates are of considerable interest since they tend to have low melting points (the sodium and calcium salts melt in the range 413–418 K) and decompose to ethylene, carbon dioxide and the metal oxide. In addition, 3-hydroxypropionic acid and its salts are important in biological and environmental systems. For example, a novel autotrophic carbon dioxide fixation pathway involving 3-hydroxypropionate was identified in the phototrophic bacterium *Chloroflexus aurantiacus* (Straus & Fuchs, 1993), while 3-hydroxypropionate is a metabolite of the herbicide Magnacide (Smith *et al.*, 1995). Despite this interest, no structures of 3-hydroxypropionates appear to have been reported. We chose to prepare yttrium 3-hydroxypropionates for our entry into this area since we have used yttrium salts as the benchmark for comparison of decomposition temperatures and mechanisms in the investigations of low-temperature precursors for ceramics (Georgieva, 1995).

(1) (2)
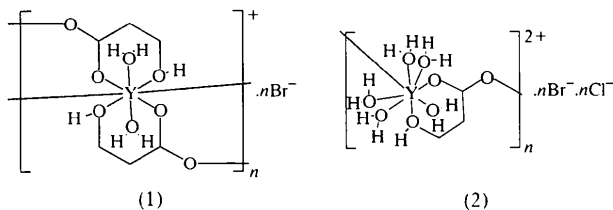
In poly[diaquabis(3-hydroxypropionato)yttrium(III)] bromide, (1), the two carboxylate ligands in the cation chelate to the metal *via* the hydroxyl and one of the carboxyl O atoms. Pairwise association of these units *via* coordination of the second carboxyl O atom of one of these ligands to the other metal forms dinuclear units which further associate *via* coordination of the second carboxyl O atom to adjacent metals to form sheets running parallel to (101) (Fig. 1). A similar chelating/bridging coordination mode has been found for methoxyacetate in $[Nd(O_2CCH_2OCH_3)_2(NO_3)(H_2O)]$ (Mague *et al.*, 1998). The sheets are held together by hydrogen bonding to the bromide ion. These involve the two ligand hydroxyl groups and one H atom on each of the two water molecules. In addition, the dinuclear units are reinforced by hydrogen bonds between the other H atom of each water ligand and the carboxyl O atom attached to the other metal (Fig. 1).

The chelating/bridging mode of coordination of the 3-hydroxypropionate ligand is also seen in *catena*-poly[pentaaqua(3-hydroxypropionato)yttrium(III)] bromide chloride, (2), but with only one ligand per
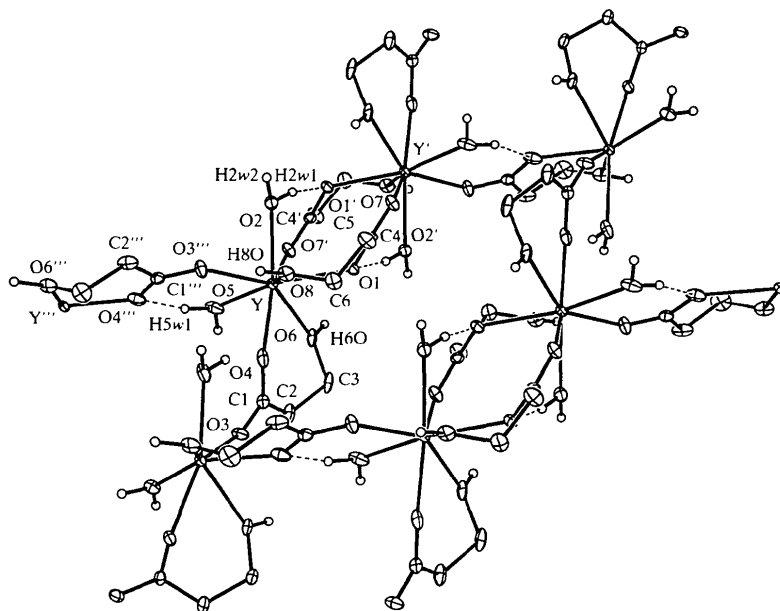
Fig. 1. Perspective view of a portion of the cation layer in (1). Ellipsoids are drawn at the 30% probability level with H atoms represented by spheres of arbitrary radii. H atoms attached to carbon are omitted. Primed atoms are related to non-primed atoms by $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$, while atoms in the unit based on Y‴ are related to the non-primed atoms by $-x$, $-1 - y$, $1 - z$.
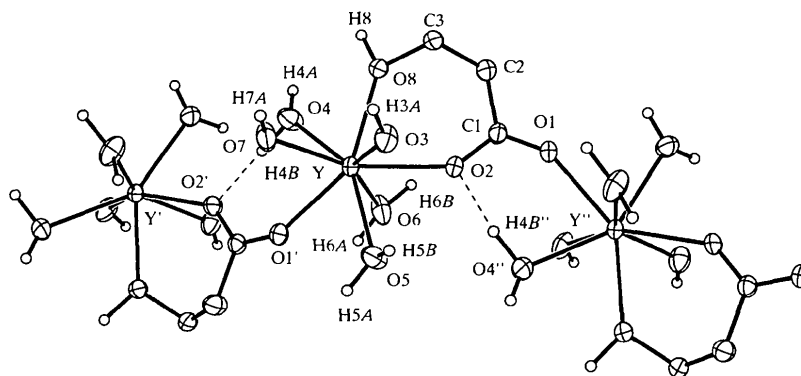

Fig. 2. Perspective view of a portion of the cation chain in (2). Ellipsoids are drawn at the 30% probability level with H atoms represented by spheres of arbitrary radii. H atoms attached to carbon are omitted. Primed atoms are related to non-primed atoms by $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$, while doubly primed atoms are related to the non-primed atoms by $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

metal, the $[Y(O_2CCH_2CH_2OH)(H_2O)_5]^{2+}$ cations forming chains running parallel to the *b* axis (Fig. 2). This association is reinforced by a hydrogen bond between the carboxylate O2 atom and the water molecule containing O4 at $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$ (O4″ in Fig. 2). The halide counter-ions are arranged in an apparently ordered fashion between the chains and serve to tie the chains together *via* hydrogen bonding to the ligand hydroxyl group (O8—H8) and four of the five water molecules. Although only one H atom each on O3 and O7 could be located, it is likely that each of these water molecules forms two hydrogen bonds to anions. Thus, O3 makes a contact of 3.348 (6) Å with the bromide at $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$, which is comparable with the bromine–oxygen

separations listed in Table 4 and, similarly, O7 makes a contact of 3.072 (6) Å with the chloride at $x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$. As a result, the chloride is involved in five hydrogen bonds while the bromide participates in four plus the weak interaction with H4A. In both complexes, the metal is eight-coordinate and the coordination spheres are similar.

Experimental

3-Hydroxypropionic acid was generated *in situ* by the hydrolysis of 3-bromopropionic acid in the presence of basic anions (Read, 1932). Thus, a mixture of yttrium(III) carbonate (4.11 g, 10 mmol) and 3-bromopropionic acid (9.18 g, 60 mmol) in

100 ml of water was refluxed until the yttrium carbonate had dissolved. Removal of the solvent *in vacuo* followed by washing with acetone left a viscous yellow liquid which, over a period of six months, afforded colourless crystals of (1). Analysis calculated for $C_6H_{14}BrO_8Y$: C 18.82, H 3.68, Y 23.21%; found: C 18.89, H 3.73, Y 23.16%; ^1H NMR (d_6-DMSO): δ (p.p.m.) 2.28 (t, 2H, CH_2COO), 3.59 (t, 2H, CH_2OH), 4.58 (br, OH); ^{13}C {^1H} NMR (D_2O): δ (p.p.m.) 39.2 (s, CH_2COO), 58.5 (s, CH_2OH), 182.9 (s, COO); IR (cm^{-1}) (KBr): 3400 (s), 2970 (w), 2904 (w), 1618 (w, sh), 1558 (s), 1442 (s), 1377 (m, sh), 1329 (m), 1195 (w), 1035 (s), 879 (m), 684 (m, sh), 623 (m, sh). In a similar fashion, a mixture of YOCl (0.7 g, 5 mmol) and 3-bromopropionic acid (1.14 g, 7.5 mmol) in 20 ml of water was refluxed until clear. Solvent removal *in vacuo* and recrystallization of the residue from acetone/methanol afforded colourless crystals of (2). Analysis calculated for $C_3H_{15}BrClO_8Y$: C 9.40, H 3.94, Y 23.18, Cl 9.25%; found: C 9.53, H 3.95, Y 21.23, Cl 9.19%; ^1H NMR (D_2O): δ (p.p.m.) 2.40 (t, 2H, CH_2COO), 3.74 (t, 2H, CH_2OH); ^{13}C {^1H} NMR (D_2O): δ (p.p.m.) 38.9 (s, CH_2COO), 58.4 (s, CH_2OH), 183.3 (s, COO).

Compound (1)

Crystal data

[Y(C₃H₅O₃)₂(H₂O)₂]Br
M_r = 382.99
Monoclinic
$P2_1/n$
a = 10.258 (2) Å
b = 6.9198 (9) Å
c = 17.660 (4) Å
β = 90.65 (2)°
V = 1253.6 (4) Å³
Z = 4
D_x = 2.029 Mg m^{-3}
D_m = 2.1 Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–18°
μ = 7.862 mm^{-1}
T = 293 (2) K
Plate
0.40 × 0.30 × 0.16 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.095, T_{max} = 0.284
2840 measured reflections
2466 independent reflections

1891 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.95°
h = 0 → 12
k = 0 → 8
l = −21 → 21
2 standard reflections frequency: 120 min intensity decay: −2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.136
S = 1.086
2466 reflections
145 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0954P)^2 + 6.3305P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å) for (1)*

Y—O3^i	2.309 (5)	Y—O5	2.344 (5)
Y—O4	2.313 (5)	Y—O7^{ii}	2.359 (5)
Y—O1	2.342 (4)	Y—O6	2.395 (5)
Y—O2	2.343 (5)	Y—O8	2.412 (5)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $1 - x, -y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2w1···O1^i	0.91	1.80	2.693 (8)	164
O2—H2w2···Br^{ii}	1.01	2.28	3.223 (8)	155
O5—H5w1···O4^{iii}	0.95	1.82	2.729 (8)	160
O5—H5w2···Br^{iii}	0.99	2.36	3.291 (8)	157
O6—H6O···Br^{iv}	0.95	2.50	3.296 (8)	141
O8—H8O···Br	0.94	2.47	3.320 (8)	150

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (2)

Crystal data

[Y(C₃H₅O₃)(H₂O)₅](Br)Cl
M_r = 383.42
Orthorhombic
$P2_12_12_1$
a = 7.564 (2) Å
b = 11.619 (2) Å
c = 14.361 (3) Å
V = 1262.1 (4) Å³
Z = 4
D_x = 2.018 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 23 reflections
θ = 13–17°
μ = 8.013 mm^{-1}
T = 293 (2) K
Plate
0.50 × 0.37 × 0.23 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.052, T_{max} = 0.154
1305 measured reflections
1305 independent reflections

1120 reflections with $I > 2\sigma(I)$
θ_{max} = 25.06°
h = 0 → 9
k = 0 → 13
l = 0 → 17
2 standard reflections frequency: 120 min intensity decay: −2.47%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.090
S = 1.118
1299 reflections
127 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 1.1250P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.687 e Å^{-3}
$\Delta\rho_{min}$ = −0.404 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (2)

Table 3. *Selected bond lengths (Å) for (2)*

Y—O1^i	2.318 (5)	Y—O2	2.332 (5)
Y—O6	2.318 (7)	Y—O5	2.353 (6)
Y—O7	2.330 (6)	Y—O4	2.407 (6)
Y—O8	2.332 (6)	Y—O3	2.408 (6)

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

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···Cl	1.02	2.27	3.127 (6)	140
O4—H4A···Br	0.85	2.70	3.451 (6)	148
O4—H4B···O2^i	1.04	1.74	2.754 (6)	164
O5—H5A···Cl^{ii}	0.92	2.24	3.142 (6)	152
O5—H5B···Br^{iii}	1.05	2.41	3.367 (6)	163
O6—H6A···Br^{ii}	1.07	2.32	3.321 (7)	163
O6—H6B···Cl^{ii}	1.11	2.01	3.057 (6)	157
O7—H7A···Cl	1.05	2.17	3.093 (7)	146
O8—H8···Br	1.11	2.11	3.219 (6)	173

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

For both structures, H atoms attached to carbon were placed in calculated positions (*SHELXL HFIX* 23 instruction; C—H = 0.97 Å) and allowed to ride with isotropic displacement parameters 20% larger than those of the attached C atom. Locations of H atoms bound to oxygen were obtained from difference maps. For (1), reasonable locations for all H atoms could be found but, for (2), one H atom each on O3 and O7 could not be located with confidence. Attempts to refine H atoms attached to oxygen were unsuccessful so they were positioned in the locations indicated by the difference maps and allowed to ride with isotropic displacement parameters 20% larger than those of the attached O atoms.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990) for (1); *XCAD4* (Harms & Wocadlo, 1987) for (2). Program(s) used to solve structures: *SIR*88 (Burla *et al.*, 1989) for (1); *SHELXS*86 (Sheldrick, 1990) for (2). Program(s) used to refine structures: *LSFM* in *MolEN* for (1); *SHELXL*93 (Sheldrick, 1993) for (2). For both compounds, molecular graphics: *SHELXTL-Plus* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL-Plus*.

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Bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]copper(II)}cadmium(II) Dioxane Solvate†

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Abstract

The title compound, [Cd{Cu(CH$_3$CO$_2$)(C$_{17}$H$_{16}$N$_2$O$_2$)}$_2$].-C$_4$H$_8$O$_2$, is a linear hetero-trinuclear complex with a central Cd^{II} ion and lies on an inversion centre. This central Cd^{II} ion has an irregular octahedral coordination. The coordination around the Cd^{II} ion involves four O atoms from two *N,N'*-bis(salicylidene)-1,3-propanediaminato (SALPD^{2-}) and two acetate ligands. The terminal Cu^{II} ions have an irregular square-pyramidal coordination. The coordination of the terminal Cu^{II} atom is provided by the two O and two N atoms from an SALPD^{2-} ligand and one O atom from an acetate ligand. The Cd···Cu bridging distance is 3.244 (3) Å.

Comment

Syntheses and structures of oxygen-bridged trimeric linear homometal and heterometal complexes based on Schiff base ligands, such as [Cd{Ni(SALPD)(CH$_3$CO$_2$)-

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† Alternative name: bis(μ-acetato)-1:2κ^{2}O:O';1:3κ^{2}O:O'-bis{μ-2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-1κ^{2}O,O':2κ^{4}N,-N',O,O';1κ^{2}O,O':3κ^{4}N,N',O,O'-cadmium(II)dicopper(II) dioxane solvate.