METAL-ORGANIC COMPOUNDS

Yttrium sodium oxalate tetrahydrate, [Y(H₂O)]Na(C₂O₄)₂·3H₂O

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Abstract

Yttrium sodium oxalate tetrahydrate, [Y(H₂O)]Na-(C₂O₄)₂·3H₂O, was obtained from hydrothermal synthesis and its structure determined from single-crystal X-ray diffraction data. The structure consists of corrugated layers of ninefold-coordinated Y atoms linked together by oxalate groups. Na atoms and water molecules are intercalated between the layers through a complex hydrogen-bonding scheme.

Comment

The present structure determination is part of a systematic study of mixed oxalates, LnM(C₂O₄)₂·nH₂O, combining rare earths or yttrium elements (Ln) and monovalent cations (M). Among these compounds, only a few crystal structures have been reported, *e.g.* Ln(NH₄)(C₂O₄)₂·H₂O (Ln = Y, Sm–Tm; McDonald & Spink, 1967), [LnM(H₂O)$_n$](C₂O₄)₂·H₂O (M = Li, Ln = La–Gd, n = 1; M = Na, Ln = Ce–Nd, n = 2; Roméro *et al.*, 1995), YK(C₂O₄)₂·4H₂O (Bataille, Auffrédic & Louër, 1999) and [La(H₂O)₂]M(C₂O₄)₂·H₂O (M = K, NH₄; Bataille, Louër *et al.*, 1999).

[Y(H₂O)]Na(C₂O₄)₂·3H₂O was identified from X-ray powder diffraction data and the pattern was indexed with the dichotomy method program *DICVOL*91 (Boultif & Louër, 1991). This new compound is not isostructural with either the related yttrium ammonium and yttrium potassium phases or [LnNa(H₂O)₂](C₂O₄)₂·H₂O (Ln = Ce–Nd; Roméro *et al.*, 1995). Single-crystal diffraction data were used for the structure determination of the yttrium sodium compound.

The structure of the title compound (Fig. 1) consists of corrugated [Y(C₂O₄)₂⁻]∞ layers, parallel to (001), and intercalated Na atoms and water molecules. The layers are built from four-membered [Y(C₂O₄)]₄ rings (Fig. 2). A similar layered-type structure has also been observed recently in [La(H₂O)₂]M(C₂O₄)₂·H₂O (M = K, NH₄; Bataille, Louër *et al.*, 1999). The

Y atoms are ninefold coordinated by eight oxalate O atoms in the form of an Archimedean antiprism monocapped by a water molecule. Such a coordination is frequently encountered in mixed yttrium oxalate compounds, *e.g.* in YH(C₂O₄)₂·3H₂O (Picard, 1993) and Y(NH₄)(C₂O₄)₂·H₂O (McDonald & Spink, 1967). The mean Y—O distance [2.402 (4) Å; see Table 1] is in agreement with the values reported in the literature, *e.g.* 2.39 (1) Å in the ammonium compound (McDonald & Spink, 1967) and the theoretical value (2.426 Å) calculated by the bond-valence method (Brown, 1996) for yttrium bonded to nine O atoms. It is worth noting the elongated bond between the Y atom and the water molecule in each polyhedron, *i.e.* 2.470 (6) Å for Y1—OW2 and 2.481 (6) Å for Y2—OW1. The Na atoms are bonded to two oxalate O atoms and four water molecules in somewhat distorted octahedra. This Na coordination polyhedron is also observed in [LnNa(H₂O)₂](C₂O₄)₂·H₂O (Ln = Ce–Nd; Roméro *et al.*, 1995). The mean Na—O distance [2.488 (6) Å] compares well with the value (2.465 Å) calculated by the bond-valence method. The four oxalate groups chelate the Y atoms. The bond distances and angles within each oxalate ligand [mean C—C distance 1.539 (7) Å and mean C—O distance 1.252 (5) Å] agree with the values reported for oxalate compounds (see, for instance, Bataille, Auffrédic & Louër, 1999). The oxalate groups are planar, as shown by the mean atomic deviation from the least-squares plane of each oxalate, *i.e.* in the range 0.0090–0.0736 Å. The distances between the donor and acceptor atoms of the hydrogen bonds vary in the range 2.824 (9)–2.979 (7) Å (Table 2). Thus, it can be assumed that all hydrogen bonds are weak, since a strong interaction corresponds to a donor–acceptor distance of less than 2.7 Å (Brown, 1976).
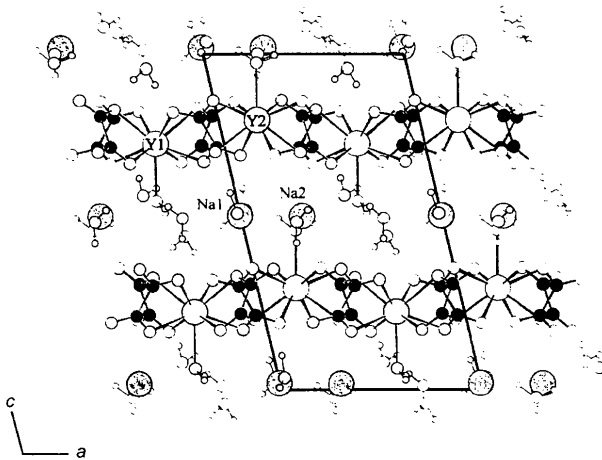

Fig. 1. The structure of [Y(H₂O)]Na(C₂O₄)₂·3H₂O projected along the *b* axis showing the layers.
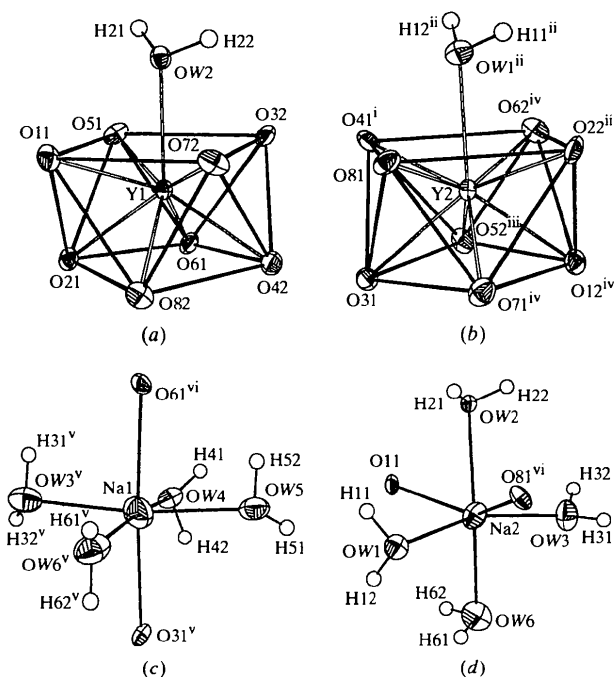
Fig. 2. Views of the environment of the (a) Y1, (b) Y2, (c) Na1 and (d) Na2 atoms. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry codes: (i) $x - 1$, y, z; (ii) x, $1 - y$, $\frac{1}{2} + z$; (iii) $x - 1$, $1 + y$, z; (iv) x, $1 + y$, z; (v) $1 + x$, y, z; (vi) x, $1 - y$, $z - \frac{1}{2}$.]

Experimental

Single crystals of [Y(H$_2$O)]Na(C$_2$O$_4$)$_2$·3H$_2$O were obtained from Y$_2$(C$_2$O$_4$)$_3$·9H$_2$O (0.5 mmol), Na$_2$C$_2$O$_4$ (1 mmol) and water (10 ml) acidified at pH 1–2 with HNO$_3$. These components were sealed in a 23 ml Teflon-lined acid digestion bomb (Parr) and heated to 423 K for 1 d, followed by cooling to ambient temperature over several hours.

Crystal data

[Y(H$_2$O)]Na(C$_2$O$_4$)$_2$·3H$_2$O
$M_r = 360.005$
Monoclinic
Pc
$a = 8.623\,(2)$ Å
$b = 8.6310\,(8)$ Å
$c = 14.896\,(3)$ Å
$\beta = 102.848\,(9)°$
$V = 1080.9\,(4)$ Å^3
$Z = 4$
$D_x = 2.212$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.069–11.484°$
$\mu = 5.498$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.200 \times 0.125 \times 0.075$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

3204 reflections with $I > 2\sigma(I)$

$\theta/2\theta$ scans
Absorption correction:
ψ scan (North et al., 1968)
$T_{min} = 0.555$, $T_{max} = 0.662$
4983 measured reflections
4733 independent reflections (plus 250 Friedel-related reflections)

$\theta_{max} = 34.93°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 23$
3 standard reflections every 250 reflections frequency: 60 min intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.096$
$S = 1.011$
4983 reflections
374 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.015$

$\Delta\rho_{max} = 1.27$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.0008 (5)
Scattering factors from International Tables for Crystallography (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.071 (7)

Table 1. Selected bond distances (Å)

Y1—O72	2.344 (4)	Y2—O71^{iv}	2.423 (5)
Y1—O11	2.358 (4)	Y2—O31	2.447 (4)
Y1—O51	2.374 (4)	Y2—OW1^{ii}	2.481 (6)
Y1—O21	2.383 (4)	Na1—OW3^{v}	2.452 (8)
Y1—O82	2.404 (5)	Na1—OW4	2.458 (7)
Y1—O32	2.411 (4)	Na1—OW6^{v}	2.460 (7)
Y1—O42	2.425 (4)	Na1—OW5	2.460 (7)
Y1—O61	2.470 (4)	Na1—O61^{vi}	2.623 (5)
Y1—OW2	2.470 (6)	Na1—O31^{v}	2.627 (5)
Y2—O41^{i}	2.341 (4)	Na2—OW6	2.436 (7)
Y2—O22^{ii}	2.365 (4)	Na2—O81^{vi}	2.438 (5)
Y2—O52^{iii}	2.366 (5)	Na2—OW3	2.446 (6)
Y2—O62^{iv}	2.373 (4)	Na2—O11	2.445 (5)
Y2—O81	2.393 (4)	Na2—OW1	2.499 (6)
		Na2—OW2	2.512 (7)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
OW1—H11···OW7^{i}	0.958 (12)	1.96 (3)	2.887 (9)	162 (7)
OW1—H12···OW4^{ii}	0.963 (12)	1.95 (4)	2.824 (9)	150 (7)
OW2—H21···OW8	0.953 (12)	1.938 (16)	2.887 (8)	173 (5)
OW2—H22···OW5	0.954 (12)	1.884 (15)	2.833 (7)	173 (5)
OW3—H31···O62^{iii}	0.963 (12)	2.09 (3)	2.897 (7)	141 (4)
OW3—H32···O72	0.961 (12)	2.37 (7)	2.960 (8)	119 (5)
OW4—H41···OW8^{iv}	0.958 (12)	2.06 (3)	2.963 (7)	157 (6)
OW4—H42···O52^{iv}	0.955 (12)	1.893 (19)	2.841 (7)	172 (8)
OW5—H51···OW7	0.963 (12)	2.03 (3)	2.951 (7)	160 (6)
OW5—H52···O21^{iii}	0.966 (12)	1.862 (13)	2.825 (6)	175 (2)
OW6—H61···O41^{v}	0.960 (12)	2.21 (4)	2.979 (7)	136 (5)
OW6—H62···O32^{vi}	0.957 (12)	2.44 (4)	2.901 (7)	109 (3)
OW7—H71···O71^{iv}	0.961 (12)	2.14 (6)	2.890 (7)	134 (7)
OW7—H72···O51^{iv}	0.959 (12)	1.97 (2)	2.908 (6)	165 (6)
OW8—H81···O42^{iii}	0.963 (12)	1.925 (15)	2.884 (6)	174 (6)
OW8—H82···O22	0.958 (12)	1.98 (2)	2.921 (7)	167 (7)

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

All 16 H atoms were found from a difference Fourier synthesis. They were refined with soft constraints applied on the distances to their water O atoms [0.960 (12) Å] and

to the nearest Na atoms. The largest residuals in the final difference Fourier map were $1.27 \, e\,\text{Å}^{-3}$ at 1.01 Å from O21 and $-0.97 \, e\,\text{Å}^{-3}$ at 1.21 Å from Y1. For comparison, the electron densities obtained during the structure determination were $6.64 \, e\,\text{Å}^{-3}$ for O*W*8 and $0.66 \, e\,\text{Å}^{-3}$ for H82. The isotropic displacement parameters of the H atoms were fixed equal to twice the U_{eq} value of their parent O atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*97.

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1,1'-Diacetylferrocene bis(thiosemi-carbazone) monohydrate

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Abstract

X-ray analysis reveals that both thiosemicarbazone groups of the title compound, [Fe(C₈H₁₀N₃S)₂]·H₂O, are in the keto tautomeric form and that the configuration of the azomethine C=N double bond is *E*. The two cyclopentadienyl rings are parallel and nearly eclipsed. The crystal structure is stabilized by extensive intra- and intermolecular hydrogen bonding involving the water molecule and the thiosemicarbazone moieties.

Comment

Ferrocene and its derivatives have aroused much interest recently as redox-active entities, with potential applications in areas such as materials for molecular electronics (Houlton *et al.*, 1992) and as biologically active compounds (Neuse *et al.*, 1988). In these contexts, considerable interest has been shown in the thio-Schiff base compounds containing a ferrocenyl group, which can coordinate readily with transition metals to give stable complexes (Garg & Kapur, 1990; Ismail, 1997) and which might exhibit large non-linear optical efficiency (Tian *et al.*, 1998). As part of our work on exploring functional coordination complexes for non-linear optical materials, we report here the crystal structure of 1,1'-diacetylferrocene bis(thiosemicarbazone) monohydrate, (I).

(I)
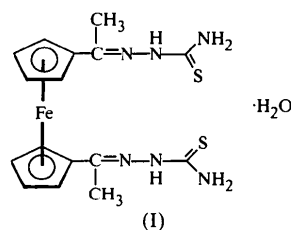
The bond lengths in the two thiosemicarbazone groups show slight differences and the C=N, N—N, N—Csp² and C=S bond distances are similar to