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Lanthanide complexes of 2,2'-oxydiacetate: $\text{Na}_5[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3](\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M = \text{Nd}, \text{Sm}$ or Gd)

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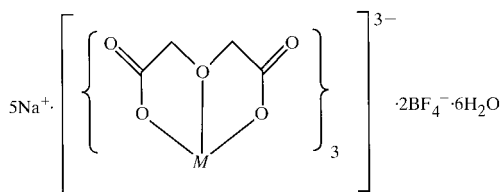
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The three title complexes, namely pentasodium tris(2,2'-oxydiacetato)neodymium(III) bis(tetrafluoroborate) hexahydrate and its samarium(III) and gadolinium(III) analogues, (I)–(III), respectively, are isomorphous and isostructural and have crystallographic D_3 symmetry. The lanthanide metal ions are nine-coordinate, binding to three O atoms of three oxodiacetate ligands. One Na^+ ion is octahedrally coordinated to six O atoms and the other Na^+ ion is octahedrally coordinated to four O atoms and two F atoms. The structure is effectively an infinite three-dimensional polymer, consistent with the exceptional crystal quality. The racemic solutions spontaneously resolve on crystallization. For the individual crystals selected for structural analysis, the Nd and Sm complexes have the Λ configuration, while the Gd complex has the Δ configuration. The lanthanide–oxygen distances show the expected contraction of *ca* 0.02 Å with increasing atomic number for the lanthanide metal.



(I) $M = \text{Nd}$
(II) $M = \text{Sm}$
(III) $M = \text{Gd}$

Experimental

The three title complexes were synthesized in an identical manner. The oxide $M_2\text{O}_3$ (0.5 mmol) ($M = \text{Nd}, \text{Sm}$ or Gd) was stirred in an aqueous solution of diglycolic acid (3.0 mmol in 30 ml water) and sodium bicarbonate (3.0 mmol). After an hour, NaBF_4 (2.0 mmol) was added, and the solution allowed to evaporate in air, yielding large

well formed crystals of the complexes. Small samples for the crystallographic analyses were cleaved from larger crystals.

Compound (I)

Crystal data

$\text{Na}_5[\text{Nd}(\text{C}_4\text{H}_4\text{O}_5)_3](\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$
 $M_r = 937.12$
Trigonal, $R32$
 $a = 9.7508$ (7) Å
 $c = 28.177$ (2) Å
 $V = 2320.1$ (3) Å³
 $Z = 3$
 $D_x = 2.012$ Mg m⁻³

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.425$, $T_{\max} = 0.834$
1134 measured reflections
1001 independent reflections
1001 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R(F) = 0.022$
 $wR(F^2) = 0.055$
 $S = 1.133$
1001 reflections
77 parameters
H-atom parameters constrained

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 18.5$ – 21.2°
 $\mu = 1.88$ mm⁻¹
 $T = 291$ (2) K
Cleaved from large crystal, violet
 $0.55 \times 0.45 \times 0.10$ mm

$R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 29.96^\circ$
 $h = -1 \rightarrow 13$
 $k = -11 \rightarrow 1$
 $l = -3 \rightarrow 39$
3 standard reflections
frequency: 120 min
intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.7263P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³
Absolute structure: Flack (1983),
121 Friedel pairs
Flack parameter = -0.010 (18)

Compound (II)

Crystal data

$\text{Na}_5[\text{Sm}(\text{C}_4\text{H}_4\text{O}_5)_3](\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$
 $M_r = 943.23$
Trigonal, $R32$
 $a = 9.7223$ (11) Å
 $c = 28.0728$ (14) Å
 $V = 2298.0$ (4) Å³
 $Z = 3$
 $D_x = 2.045$ Mg m⁻³
Mo $K\alpha$ radiation

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.352$, $T_{\max} = 0.427$
2301 measured reflections
1085 independent reflections
1085 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R(F) = 0.014$
 $wR(F^2) = 0.037$
 $S = 1.133$
1085 reflections
78 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0227P)^2 + 0.0430P]$
where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 25 reflections
 $\theta = 20.93$ – 22.27°
 $\mu = 2.12$ mm⁻¹
 $T = 291$ (2) K
Irregular block cleaved from larger crystal, colourless
 $0.6 \times 0.4 \times 0.4$ mm

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 29.98^\circ$
 $h = -12 \rightarrow 1$
 $k = -12 \rightarrow 1$
 $l = -39 \rightarrow 39$
3 standard reflections
frequency: 120 min
intensity decay: 2%

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0034 (2)
Absolute structure: Flack (1983),
209 Friedel pairs
Flack parameter = -0.014 (11)

Compound (III)

Crystal data

Na₅[Gd(C₄H₄O₅)₃](BF₄)₂·6H₂O
M_r = 950.13
 Trigonal, *R*32
a = 9.7041 (10) Å
c = 28.025 (6) Å
V = 2285.5 (6) Å³
Z = 3
D_x = 2.071 Mg m⁻³

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.336, *T_{max}* = 0.433
 2033 measured reflections
 1078 independent reflections
 1078 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R(*F*) = 0.012
wR(*F*²) = 0.032
S = 1.073
 1078 reflections
 78 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0226*P*)² + 0.5279*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 12.1–15.2°
 μ = 2.381 mm⁻¹
T = 291 (2) K
 Prism, colourless
 0.50 × 0.45 × 0.35 mm

R_{int} = 0.013
 θ_{max} = 29.98°
h = -13 → 1
k = -1 → 11
l = -39 → 39
 3 standard reflections
 frequency: 120 min
 intensity decay: 3%

(Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.38 e Å⁻³
 Δρ_{min} = -0.26 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00258 (15)
 Absolute structure: Flack (1983),
 206 Friedel pairs
 Flack parameter = -0.005 (10)

The methylene H atoms were placed in calculated positions (C–H = 0.96 Å) and refined with a riding model. The initial positions of the H atoms of the water molecules were determined from a difference Fourier map and the H atoms were then refined with a riding model and a common isotropic displacement parameter. All calculations were carried out using the *WinGX* package (Farrugia, 1999).

For all compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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