Absorption correction:
   empirical ψ scans
   (*XSCANS*; Siemens, 1994)
   $T_{min} = 0.378$, $T_{max} = 0.525$
4743 measured reflections
3843 independent reflections
3514 reflections with
   $I > 2\sigma(I)$

$h = -1 \rightarrow 9$
$k = -13 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections
   every 97 reflections
   intensity decay: $<3\%$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.085$
$S = 1.071$
3843 reflections
293 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1566P]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.280$ e Å^{-3}
$\Delta\rho_{min} = -0.471$ e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for Crystallography (Vol. C)

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

Cu—O1	1.9654 (14)	Cu—O4	2.690 (2)
Cu—O3	1.9669 (14)	O1—C11	1.267 (2)
Cu—N1	1.9742 (15)	O2—C11	1.239 (3)
Cu—N3	1.995 (2)	O3—C13	1.279 (2)
Cu—O2	2.4824 (15)	O4—C13	1.233 (2)
O1—Cu—O3	89.15 (6)	N1—Cu—O2	96.90 (6)
O1—Cu—N1	154.42 (6)	N3—Cu—O2	106.41 (6)
O3—Cu—N1	93.99 (6)	O1—Cu—O4	114.89 (6)
O1—Cu—N3	94.46 (6)	O3—Cu—O4	53.50 (5)
O3—Cu—N3	156.92 (6)	N1—Cu—O4	86.84 (6)
N1—Cu—N3	92.50 (6)	N3—Cu—O4	104.90 (5)
O1—Cu—O2	57.53 (5)	O2—Cu—O4	148.25 (6)
O3—Cu—O2	94.76 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1O5···O2	0.78 (3)	2.01 (3)	2.778 (3)	169 (3)
O5—H2O5···O3^i	0.76 (3)	2.11 (3)	2.845 (3)	164 (4)
O6—H1O6···O5^{ii}	0.76 (4)	2.04 (4)	2.798 (4)	174 (3)
O6—H2O6···O4	0.80 (3)	2.02 (3)	2.801 (3)	167 (3)
N2—H1N2···O6^{iii}	0.77 (2)	2.02 (2)	2.784 (3)	174 (2)

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x, y, z - 1$; (iii) $-x, -y, -z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1235). Services for accessing these data are described at the back of the journal.

References

Aduldecha, S. & Hathaway, B. J. (1991). *Acta Cryst.* C47, 84–86.
Hathaway, B. J. (1987). *Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties & Applications of Coordination Compounds* (Editor-in-Chief: G. Wilkinson; Executive Editors: R. D. Gillard & J. A. McCleverty), Vol. 5, Section 53, pp. 533–774. Oxford: Pergamon Press.
Lewis, D. L. & Hodgson, D. J. (1973). *Inorg. Chem.* 12, 2935–2938.
Munoz, M. C., Lazaro, J. M., Faus, J. & Julve, M. (1993). *Acta Cryst.* C49, 1756–1761.
Nardelli, M. (1995). *J. Appl. Cryst.* 28, 659.
Pavkovic, S. F. & Miller, D. (1977). *Acta Cryst.* B33, 2894–2896.
Procter, I. M., Hathaway, B. J. & Hodgson, P. G. (1972). *Inorg. Nucl. Chem.* 34, 3689–3697.
Ray, N., Tyagi, S. & Hathaway, B. J. (1982). *Acta Cryst.* B38, 1574–1577.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stephens, F. S. (1969). *J. Chem. Soc. A,* pp. 2081–2087.
Youngme, S., Pakawatchai, C. & Fun, H.-K. (1998). *Acta Cryst.* C54, 451–453.

Metal Alkoxycarboxylate Complexes. I. Poly[aquabis(methoxyacetato)(nitrato)-neodymium(III)]

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Abstract

The title compound, [Nd(O$_2$CCH$_2$OCH$_3$)$_2$(NO$_3$)(H$_2$O)]$_n$, contains nine-coordinate Nd atoms in which the carboxylate ligands chelate to one metal atom and each bridges to a second metal atom, resulting in the formation of pleated sheets. The Nd—O distances range from 2.375 (4) to 2.629 (4) Å.

Comment

The discovery that lanthanide metal salts of 2-[2-(2-methoxyethoxy)ethoxy]acetate (MEEA) are room-temperature liquids (Apblett, Long *et al.*, 1994; Apblett *et al.*, 1995) has prompted an investigation of the structural chemistry of simpler alkoxycarboxylates so that the resulting structural and spectroscopic characterizations of these solid complexes can be used

towards a greater understanding of the behavior of the MEEA salts. In addition, methoxyacetate complexes have been shown to be useful ceramic precursors for materials such as barium titanate (Apblett, Georgieva & Raygoza-Maceda, 1994). In our initial attempts to prepare [Nd(O₂CCH₂OCH₃)₃] from sodium methoxyacetate and neodymium(III) nitrate, the mixed nitrate–carboxylate complex of empirical formula [Nd(O₂CH₂OCH₃)₂(NO₃)(H₂O)], (1), was the crystalline product isolated.

(1)
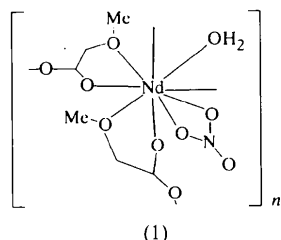
As shown in Fig. 1, the Nd atom is nine-coordinate, with the coordination sphere consisting of two methoxyacetate ligands chelating *via* one carboxylate oxygen and the ether oxygen, an asymmetrically chelating nitrate ion, a water molecule and the second carboxylate oxygen (O4 and O6″) of the methoxyacetate ligands on two adjacent metals. This leads to the formation of

pleated sheets running approximately parallel to **b**. Previous examples of methoxyacetate complexes whose structures are known involve both chelation as observed here and monodentate coordination *via* one carboxyl oxygen (Prout *et al.*, 1968; Prout, Allison & Rossotti, 1971; Prout, Barrow & Rossotti, 1971; Prout, Walker & Rossotti, 1971). The greater complexity of the present structure may, in part, be the result of the larger coordination number available to neodymium but is not limited to this particular example (Mague *et al.*, 1998). The various Nd—O distances compare favorably with those for their respective ligands obtained from the Cambridge Structural Database (Allen & Kennard, 1993), with the exception of those involving the ether O atoms (O2 and O3), which are significantly shorter than the average found (*ca* 2.68 Å). Hydrogen bonding occurs between the water molecule and a carboxylate oxygen on each of the two methoxyacetate ligands chelated to adjacent metals.

Experimental

The title compound was prepared by treating methoxyacetic acid (2.72 g, 30.2 mmol) with sodium carbonate (1.59 g, 15.0 mmol) in water (20 ml). Following cessation of carbon dioxide evolution, [Nd(NO₃)₃(H₂O)₆] (4.38 g, 10.0 mmol) was added and the solution stirred until all solids had dissolved. Addition of absolute ethanol to the cloud point and cooling
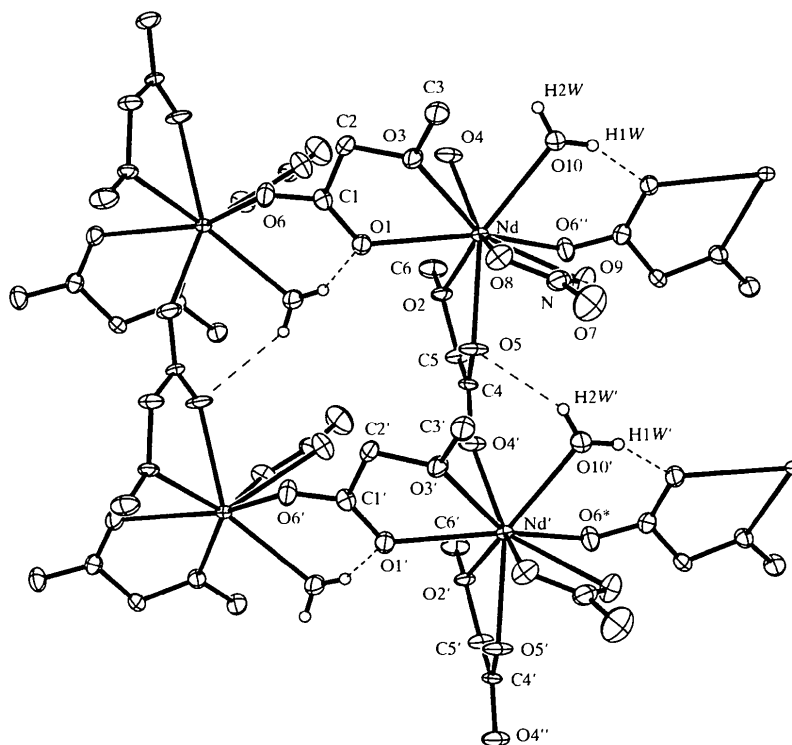

Fig. 1. View of a portion of the pleated-sheet structure adopted by (1). H atoms bonded to carbon have been omitted for clarity. The atoms at the extreme right of the drawing are additional Nd atoms with only part of their coordination spheres shown.

at 253 K for several months afforded a mass of purple cube-shaped crystals.

Crystal data

[Nd(C₃H₅O₃)₂(NO₃)(H₂O)]	Mo $K\alpha$ radiation
$M_r = 402.41$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 23
$P2_1/c$	reflections
$a = 6.2457\,(11)$ Å	$\theta = 12.23–17.76°$
$b = 11.9757\,(9)$ Å	$\mu = 4.098$ mm⁻¹
$c = 17.1228\,(14)$ Å	$T = 293\,(2)$ K
$\beta = 90.081\,(2)°$	Block
$V = 1280.7\,(3)$ Å³	$0.33 \times 0.33 \times 0.23$ mm
$Z = 4$	Light purple
$D_x = 2.087$ Mg m⁻³	
$D_m = 2.1$ Mg m⁻³	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.021$
diffractometer	$\theta_{max} = 25°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 7$
Absorption correction:	$k = 0 \rightarrow 14$
by integration	$l = -20 \rightarrow 20$
$T_{min} = 0.412$, $T_{max} = 0.483$	2 standard reflections
2465 measured reflections	frequency: 120 min
2245 independent reflections	intensity decay: −5.3%
1823 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{max} = 1.781$ e Å⁻³
$wR(F^2) = 0.088$	$\Delta\rho_{min} = -0.738$ e Å⁻³
$S = 1.222$	Extinction correction: none
2245 reflections	Scattering factors from
165 parameters	*International Tables for*
H atoms: see below	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0540P)^2$	
$+ 1.1239P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O10—H1W⋯O1ⁱ	0.87	2.00	2.816 (7)	154
O10—H2W⋯O5ⁱⁱ	0.77	2.49	3.069 (7)	134

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

The water H atoms were placed in the locations obtained from the difference map, while those attached to carbon were placed in calculated positions. All were included as riding contributions with fixed isotropic displacement parameters 20% larger than those of the attached atoms. The largest features in the final difference map are 0.78–0.97 Å from the Nd atom, but there is no obvious source.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD4* (Harms & Wocadlo, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Siemens, 1994). Software used to prepare material for publication: *SHELXTL-Plus*.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Apblett, A. W., Cannon, S. M., Georgieva, G. D., Long, J. C., Raygoza-Maceda, M. I. & Reinhardt, L. E. (1995). *Mater. Res. Soc. Symp. Proc.* **346**, 679–683.
Apblett, A. W., Georgieva, G. D. & Raygoza-Maceda, M. I. (1994). *Ceram. Trans.* **43**, 73–77.
Apblett, A. W., Long, J. C., Walker, E. H., Schmidt, K. J. & Yarwood, L. N. (1994). *Phosphorus Sulfur Silicon*, **93–94**, 481–481.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1987). *XCAD4. Program to Extract Intensity Data from Enraf–Nonius CAD-4 Files*. University of Marburg, Germany.
Mague, J. T., Apblett, A. W. & Todorova, G. (1998). *Acta Cryst.* C54. In the press.
Prout, C. K., Allison, G. B. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3331–3335.
Prout, C. K., Armstrong, R. A., Carruthers, J. R., Forrest, J. G., Murray-Rust, P. & Rossotti, F. J. C. (1968). *J. Chem. Soc. A*, pp. 2791–2813.
Prout, C. K., Barrow, M. J. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3326–3331.
Prout, C. K., Walker, C. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 556–559.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *SHELXTL-Plus*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Dichloro(tetrahydrofuran-*O*)[tris(1-pyrazolyl-*N²*)borato]vanadium(III)

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Abstract

The title compound, [HB(pz)₃]VCl₂(thf) or [VCl₂-(C₉H₁₀BN₆)(C₄H₈O)] (pz = pyrazolyl, thf = tetrahydrofuran), is an analogue of the unknown η^5-CpVCl₂ (Cp =