Anhydrous Neodymium(III) Acetate

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Abstract. Anhydrous neodymium(III) acetate, Nd(OAc)₃ was obtained as light purple single crystals by direct oxidation of neodymium metal with malonic acid in a glass ampoule at 180 °C. It crystallizes with the monoclinic space group $P2_1/a$ (no. 14) with a = 2201.7(2), b = 1850.0(1), c = 2419.0(3) pm, $\beta = 96.127(8)^\circ$, $V = 9796.8(1) \cdot 10^6 \cdot \text{pm}^3$, Z = 40 [Nd(OAc)₃], $R_1 = 0.0430$

 $[I_0 > 2\sigma(I_0)]$. Most of the Nd³⁺ cations are coordinated by nine (or eight) oxygen atoms of acetate ligands which bridge these polyhedra to slightly waved layers which are stacked in the [010] direction.

Keywords: Neodymium; Acetate; Crystal structure

Anhydrous rare-earth acetates may be obtained from acetic-acid solutions or from their hydrates by careful dehydration, usually as powders. Single crystals are obtained from acetic-acid solutions to which, for example, caesium acetate is added [1] or from an ammonium acetate melt in a closed system [2, 3]. An alternative only recently explored route to anhydrous rare-earth(III) acetates is the oxidation of the respective rare-earth metal with glacial acetic acid in a sealed ampoule at temperatures slightly above its boiling point. Thereby, the crystal structure of anhydrous europium(III) acetate was recently confirmed [4].

So far the crystal structures of the anhydrous acetates of lanthanum through praseodymium, samarium through lutetium, yttrium and scandium are known [1-4, 5], Table 1. Missing are those of neodymium and promethium. We herein report the synthesis [6] and the crystal structure [7] of anhydrous neodymium(III) acetate, Nd(OAc)₃, the last one not yet analyzed structurally which can be handled in a normal laboratory.

Results and Discussion

Instead of acetic acid (HOAc), malonic acid (H₂Mal) was used as the Liebig acid [8] for the oxidation of neodymium metal. Malonic acid is solid under ambient conditions and easier to handle under anhydrous conditions. It decarboxylates upon heating to 140-150 °C to acetic acid [9]. As our reaction was carried out at 180 °C, it must be assumed that acetic acid was actually the reactant.

In the crystal structures of the anhydrous rare-earth acetates, $M(OAc)_3$, coordination numbers range from 10 (M = La) to 6 (M = Sc) and M-O coordination polyhedra are connected via carboxylate groups to network (M = La-Pr [2, 3]) or to chain struc-

Table 1 Anhydrous rare-earth acetates, $M(OAc)_3$: Molar volumes V_m , coordination numbers CN, shortest (d1), longest (dn; n = CN)and mean (<d>) M-O distances

М	V _m /cm ³ mol ⁻¹	CN	d ₁ -d _n /pm	<d>/pm</d>	Ref.
La(C	DAc) ₃ type: network				
La	138.8*	10	247-279	261.5	[3]
Ce	136.0	10			[3]
Pr(C	OAc) ₃ type: network				
Pr	147.4	10	241-306	261.1	[2]
		9	244-263	253.5	
		9	239-287	255.6	
Nd(DAc) ₃ type: layer				
Nd	147.5	9	235-267	250.1	this work
		8	235-251	245.7	
Ho(OAc) ₃ type: chain				
Sm	146.2	8			[1]
Eu	145.9 / 145.1	8	229-257	242.5	[4, 1]
		8	231-256	242.2	
Gd	144.7	8			[1]
Tb	144.0	8			[1]
Dy	143.6	8			[1]
Y	143.4	8			[1]
Но	142.6 / 142.6	8	227-252	237.0	[1]
		8	224-256	238.1	
Er	141.0	8			[1]
Lu(C	OAc) ₃ type: chain				
Tm	144.9 / 144.1	7	222-244	228.5	[10]
Yb	144.0 / 143.7	7	219-243	228.6	[10]
Lu	143.2 / 141.7	7	220-242	227.5	[1]
Sc(C	OAc) ₃ type: chain				
Sc	144.7	6	208.4(1)	208.4	[5]

* Bold: from single crystal data; other values are from powder diffraction data.

tures (M = Sm-Lu, Y, Sc [1, 5]). In La(OAc)₃ and isotypic Ce(OAc)₃ the M³⁺ cations are ten-coordinate [2], in Pr(OAc)₃ coordination numbers are 10 and 9 (twice) [3]. The Ho(OAc)₃-type of structure represents the acetates with M = Sm-Er, Y with CN = 8. Lu(OAc)₃ with CN = 7 is isotypic with M(OAc)₃ (M = Tm-Lu) [1]. These two structure types are closely related to the crystal structure of Sc(OAc)₃ [5], CN = 6, a structure which is adopted from all acetates M(OAc)₃ with M = Sm-Lu, Y at elevated temperatures [1]. Table 1 gives an overview.



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Table 2 Internuclear Nd-O distance ranges d_1 - d_n /pm (n = CN) and averaged distances <d> for Nd(OAc)₃ (<<d>> is the average of the average distances)

	CN	d ₁ -d _n /pm	<d>/pm</d>
Nd1-O	9	244.6(9)-255.9(9)	252.1
Nd2-O	8	236.6(10)-251.0(9)	245.9
Nd3-O	9	237.2(8)-261.7(10)	250.6
Nd4-O	9	245.4(10)-260.6(10)	251.1
Nd5-O	9	240.9(10)-266.6(9)	248.8
Nd6-O	8	236.6(10)-251.3(10)	245.5
Nd7-O	9	237.3(9)-259.5(10)	249.2
Nd8-O	9	235.0(10)-255.2(9)	249.5
Nd9-O	9	240.6(9)-265.6(10)	249.4
Nd10-O	9	241.8(10)-254.8(10)	250.1
Nd-O		< <d>></d>	249.2



Fig. 1 The connection of ten-membered Nd-O rings in one layer of the crystal structure of Nd(OAc)₃ (above) and projection of Nd-O polyhedra of one such layer with methyl groups onto (010) (below).

The crystal structures of the anhydrous acetates $M(OAc)_3$ with M = Nd and Pm were elusive. Surprisingly, the now-determined crystal structure of anhydrous neodymium(III) acetate, Nd(OAc)_3, represents the missing link, a layer structure.



Fig. 2 Two layers stacked in the [010] direction in the crystal structure of Nd(OAc)₃ (above) and a superposition of these two layers (without methyl groups) exhibiting the offset of about 1/4a (below).

The large unit cell of Nd(OAc)₃ contains 40 such formula units with 10 symmetry-independent neodymium atoms. Eight of these are nine-coordinate, the remaining two eight-coordinate. Nd-O distances are summarized in Table 2. Distances range from 235 to 267 pm, averaged distances from 246 to 252 pm, and the average of the averaged distances is 249.2 pm. This mean Nd-O distance in Nd(OAc)₃ for a coordination number of almost CN = 9, lies in between the mean Pr-O distance in Pr(OAc)₃ (256.7 pm) and the mean Eu-O distance in Eu(OAc)₃ (242.4 pm), for which single-crystal structure analyses were carried out. For further details see Table 1.

The ten symmetry-independent Nd-O polyhedra are connected to layers roughly parallel (010), space group $P12_1/a1$, Figure 1. Although the connection modes are complicated in detail (bidentatebridging, tridentate-chelating and-bridging as well as tetradentatechelating), these layers consist of ten-membered rings attached to each other, Figure 1. The methyl rings of the acetate anions are oriented towards the open space within the rings (Fig. 1) and between the layers which are stacked in the [010] direction, see Figure 2. The layers are somewhat waved and shifted against each other by roughly one quarter in the [100] direction, thereby avoiding open space through the creation of channel structure, Figure 2.

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- [6] Nd(OAc)₃: 72.1 mg (0.5 mmol) neodymium metal (Chempur, 99.9 %) and 140.1 mg (1 mmol) of anhydrous malonic acid (Riedel-de Haen, 99.5 %) were filled under exclusion of air/humidity in a dry box (argon, MBraun, Garching) in a glass ampoule. The ampoule was sealed outside the dry box at a vacuum line with a methane/oxygen burner. The reaction was carried out at 180 °C for two weeks in an oven. Some crystals were selected under a microscope in a dry box and sealed in thin-walled glass capillaries. They were transferred to a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS) to collect a complete intensity data set at ambient temperature.
- [7] Nd(OAc)₃: $C_{60}H_{90}O_{60}Nd_{10}$ (3213.72 g mol⁻¹); diffractometer IPDS-II, Stoe, Darmstadt; Mo-K_{α} (graphite monochromator, $\lambda = 71.073$ pm); T = 293(2) K; $2\theta_{max} = 50.5^{\circ}$; 120 images, $0^{\circ} \le \omega \le 180^{\circ}$, $\varphi = 0^{\circ}$; $0^{\circ} \le \omega \le 60^{\circ}$, $\varphi = 90^{\circ}$; $\Delta \omega = 2^{\circ}$; indices:

 $-26 \le h \le 25, -21 \le k \le 21, -28 \le l \le 28; \rho_{calc} = 2.179 \text{ g}$ cm⁻³; 78369 reflection intensities measured of which 17257 were symmetrically independent, $R_{int} = 0.1834$, F(000) =6120, $\mu = 52.95 \text{ mm}^{-1}$. Monoclinic, P2₁/a (no. 14), a = 2201.7(2), b = 1850.0(1), c = 2419.0(3) pm, β = 96.127(8)°, $V = 9796.8(1) \ 10^6 \cdot \text{pm}^3$, $Z = 40 \ [Nd(OAc)_3]$. Structure solution and refinement were carried out using the programs SHELXS-97 and SHELXL-97 (G. M. Sheldrick, Programmsysteme, Göttingen, 1997). A numerical absorption correction was applied after optimisation of the crystal shape (X-RED and X-SHAPE (Stoe & Cie, Darmstadt 1999, 2001)). R values: R_1/wR_2 for 6972 reflections with $[I_0 > 2\sigma(I_0)]$: 0.0430/ 0.0522 and for all data: 0.1380/0.0671; $S_{all} = 0.652$. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 653325. Copies of the data can be obtained, free of charge, on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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