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REACTIVITY OF NEODYMIUM(III) ISOPROPOXIDE DERIVATIVES: SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF $[Nd_4(\mu_3\text{-}OH)_2(\mu_2,\mu_1\text{-}acac)_6(acac)_4]$

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Abstract—Reaction between neodymium chips and isopropanol led to the isolation of $[Nd(O^iPr)_3]_4 \cdot 4^iPrOH$. Its desolvation results in a soluble polynuclear neodymium(III) oxoisopropoxide, whose reactivity has been investigated. Reaction with acetylacetone produced a compound analysing as $Nd_2(OH)(acac)_5$, which has been characterized by IR and ESR spectroscopy, as well as by X-ray diffraction. It crystallizes in the monoclinic $P2_1/n$ system with unit cell dimensions $a = 14.52(5)$, $b = 14.20(4)$, $c = 15.25(5)$ Å, $\beta = 101.4°$ and $Z = 4$. Least-squares refinement converged to a final $R_w = 0.050$. The molecule is a centrosymmetric, tetranuclear neodymium(III) hydroxo acetylacetonate cluster, $[Nd_4(\mu_3\text{-}OH)_2(\mu_2,\mu_1\text{-}acac)_6(acac)_4]$. Two dinuclear $Nd_2(OH)(acac)_5$ units are linked by two triply bridging pyramidal μ-hydroxo ligands and by two bridging-chelating β-diketonate ligands. The metal atoms are eight-coordinated with a distorted square antiprism geometry.

High purity neodymium derivatives are of interest for optical fibers,[1] various non-linear optic materials[2] and high temperature superconductors.[3] Moreover, neodymium alkoxide, β-diketonates and related derivatives often display the highest activity among rare earth catalysts for polymerization reactions.[4] The commonest neodymium alkoxide, the trisisopropoxide, was reported to be obtained by oxidation of the metal by isopropanol,[5] as well as by a metathesis reaction between neodymium chloride and sodium isopropoxide.[6] However, this latter reaction appears complex, as it also forms $[Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_9(OR)_6]$ ($R = {}^iPr$), which has been structurally characterized.[7] Contamination of alkoxides by chloride residues might preclude their use as molecular precursors for high-tech oxide-based materials[8] via sol-gel or chemical vapour decomposition techniques.

Thus, the simple and direct synthetic approach, starting from the metal and isopropanol, appeared more attractive for obtaining pure neodymium(III) isopropoxide. This led to the isolation in high yields of a soluble, non-volatile polynuclear oxoisopropoxide. Investigation of its reactivity led to the isolation of a neodymium(III) hydroxoacetylacetonate, which was characterized by X-ray diffraction. It corresponds to a tetranuclear cluster, $[Nd_4(\mu_3\text{-}OH)_2(\mu_2,\mu_1\text{-}acac)_6(acac)_4]$ (acacH $= C_5H_8O_2$, acetylacetone).

EXPERIMENTAL

All reactions were routinely performed under dry, oxygen-free argon, using Schlenk tubes and vacuum-line techniques. Solvents were purified by standard methods. ESR and IR spectra were registered on Bruker ER-200D and IR S45 spectrometers, respectively. Microanalytical data were obtained from the Centre de Microanalyse du CNRS.

$Nd_4(O^iPr)_{12} \cdot 4^iPrOH$ (1)

Neodymium chips (23.4 g, 0.164 mol) were allowed to react with isopropanol in toluene (300 cm^3, 1 : 1 in volume). The catalyst ($HgCl_2 + Hg(OAc)_2$ 1 : 1, 15 mg) was added after heating at 80°C for 1 h and refluxing was maintained for

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a further 48 h. The hot reaction medium was filtered and light blue–pink crystals were obtained by cooling (46.9 g, 75.6%). Found: C, 37.4; H, 6.9. Calc. for $C_{48}H_{116}O_{16}Nd_4$: C, 37.7; H, 7.7%.

X-ray quality crystals were obtained directly from the reaction medium. Their structure could only be partially solved so far as a result of disorder problems due to the presence of coordinated isopropanol. Cell parameters: $a = 20.604(8)$, $b = 20.724(10)$, $c = 14.660(5)$ Å, orthorhombic.

Drying of **1** under vacuum at room temperature led to a progressive loss of alcohol and isopropylether with the formation of a compound analysing as $[Nd_6O_5(O^iPr)_8]$ (**2**) (30.9 g, 80%) after 48 h. Complex **2** is soluble in common organic solvents, including pentane (although dissolution is slow in this case). Found: C, 19.8; H, 4.0. Calc. for $C_{24}H_{56}O_{13}Nd_6$: C, 20.3; H, 4.0%.

By contrast with yttrium, no attack of the neodymium chips was observed in the absence of a mercury catalyst. No reaction occurs between neodymium and methanol or *t*-butanol in conditions similar to that of the synthesis of the isopropoxide derivative.

$Nd_2(OH)(acac)_5$ (3)

A solution of acetylacetone (6.3 cm^3, 60.3 mmol) in 15 cm^3 of toluene was added over 1 h to a solution of **2** (2.07 g, 1.46 mmol). After 24 h, the light blue solution was evaporated to dryness, and after recrystallization in acetone 1.9 g (88%) of $Nd_2(OH)(acac)_5$, only slightly air-sensitive, soluble in the common organic solvents (toluene, THF, $CHCl_3$ . . .) was obtained. Found: C, 37.6; H, 4.6. Calc. for $C_{25}H_{96}O_{11}Nd_2$: C, 37.5; H, 4.5%. IR (Nujol, cm^{-1}): 1607 [$\nu(C{=}O)$], 1520 [$\nu(C{=}C)$], 1258 [$\pi_{as}(C{-}O)$], 1016, 916, 650; 523, 449 [$\nu(Nd{-}O)$]. MS (m/e^+, %): Nd(acac)$_3$ (40%), Nd(acac)$_2$ (23%), Nd(OH)(acac) (5%), NdO (5%), acacH (25%), C_3H_7O (100%).

X-ray crystallography of $Nd_2(OH)(acac)_5$ (3)

A light blue–pink parallelepiped crystal, grown from acetone solution at room temperature, was introduced into a Lindemann capillary and mounted onto an Enraf–Nonius CAD-4 automatic diffractometer. The Laue symmetry and systematic absences, $h0l$ for $h+1 = 2n+1$ and $0k0$ for $k = 2n+1$, indicate monoclinic symmetry and space group $P2_1/n$. The lattice parameters were determined from 25 computer-centred reflections. The unit cell parameters and basic information about data collection and structure refinement are given in Table 1. Corrections for Lorentz and polarization effects were applied, but not for absorption. The atomic scattering factors were taken from Cromer and Waber.[9]

The structure was solved on a PDP 11/44 computer using the Enraf–Nonius SPP program.[10] The atomic positions were obtained by direct methods and subsequent Fourier differences series. Complex **3** is a dimer with a centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$. Refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of the 38 independent non-hydrogen atoms led to final values of 0.043 for R and 0.050 for R_w. The function minimized was $w = (|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Hydrogen parameters were not introduced in the refinement.

Positional parameters and equivalent isotropic thermal parameters are given as supplementary material.*

RESULTS AND DISCUSSION

Reactions between isopropanol and neodymium have been reported to lead to the isolation of $Nd(O^iPr)_3$.[5] Indeed, crystals, solvated by isopropanol (ν(OH): 3348 cm^{-1} in the IR) and analysing as $[Nd(O^iPr)_3]\cdot{}^iPrOH$ (**1**) were obtained from the reaction medium in high yields ($\simeq$ 75%). Their structure could only partially be solved so far, as a result of disorder problems and loss of the alcohol molecules, but appears to correspond to a tetranuclear species, $Nd_4(\mu_3\text{-}O^iPr)_2(\mu\text{-}O^iPr)_4(O^iPr)_6({}^iPrOH)_4$.[11] The analytical data of these light blue–pink crystals showed, after removal of the alcohol (drying *in vacuo* at room temperature for 48 h), a too-low carbon and hydrogen content with respect to a $Nd(O^iPr)_3$ composition, but were found to be in agreement with an oxoalkoxide of empirical formula $Nd_6O_5(O^iPr)_8$ (**2**). Complex **2** is highly soluble in common solvents including hydrocarbons, but its paramagnetic character precluded the obtaining of structural information by NMR techniques.

We have previously shown with yttrium, that although $Y(O^iPr)_3$ species solvated by alcohol are predominant in solutions, their isolation is achieved as a complex structural unit: $Y_5O(O^iPr)_{13}$.[12] Stabilization of other f element isopropoxides $Ln(O^iPr)_3$ as similar polymetallic oxoisopropoxides has also been observed for ytterbium[13] or lan-

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* Supplementary material. Tables of final fractional coordinates, anisotropic thermal parameters, complete bond lengths and angles (4 pp.), tables of calculated and observed structure factors (18 pp.) have been deposited with the Cambridge Structural Data File.

Table 1. X-ray crystal data and data collection of $[Nd_4(OH)_2(acac)_{10}]$ at room temperature

Compound	$C_{25}H_{40}O_{11}Nd_2$
Colour	Light blue–pink
Molecular weight	805.07
Crystal system	Monoclinic
a (Å)	14.52(5)
b (Å)	14.20(4)
c (Å)	15.25(5)
α (°)	90
β (°)	101.4(1)
γ (°)	90
V (Å^3)	3085(3)
Z	4
Density (calc.) (g cm^{-3})	1.733
Crystal dimension (mm)	$0.5 \times 0.15 \times 10.15$
Space group	$P2_1/n$
$F(000)$ (e$^-$)	1592
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo-K_α ($\lambda = 0.71069$ Å)
Linear absorption coefficient (cm^{-1})	33.92
Scan type	θ–2θ
Scan range (°)	20–40
hkl limits	$-13 \leqslant h \leqslant +13$, $-13 \leqslant k \leqslant +13$, $l \leqslant 14$
Data collected	6032
Unique data used ($F_o^2 > 3\sigma(F_o^2)$)	5124
Number of parameters refined	342
$R = \Sigma(\lvert F_o \rvert - \lvert F_c \rvert)/\Sigma \lvert F_o \rvert$	0.043
$R_w = (\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/w\lvert F_o \rvert^2)^{1/2}$	0.050
Quality-of-fit indicator	2.1
Largest shift/ESD final cycle	0.7

thanum.[14] Although the origin of the oxo ligands may be multiple, we have established in the case of yttrium, that aggregation of metals into a closed polyhedral moiety represents an alternative for a trivalent metal to achieve high coordination numbers despite the loss of the labile isopropanol molecules. Thermal gravimetric analyses have shown that desolvation and condensation by elimination of diisopropyl ether occur simultaneously.[14]

Similar results are obtained in the case of neodymium. Although the structure of the polynuclear oxoalkoxide could not be established by X-ray diffraction so far, its formation in reproducible and high yields excludes accidental hydrolysis. Comparison of the reactions between the reaction medium and **2** with an excess of $Al(O^iPr)_3$ was made in a refluxing toluene–alcohol medium. No reaction was observed when starting from **2**, while that with the reaction medium offered, by fractional distillation, the heterometallic alkoxide[15] $Nd[Al(O^iPr)_4]_3$ in high yield (70%). These results are also supported by the behaviour of the yttrium isopropoxide derivatives: the reactivity of the species formed *in situ* and the isolated oxoalkoxide $Y_5O(O^iPr)_{13}$ are definitely different.[12]

In order to achieve the characterization of **2**, its reactivity was investigated, especially towards other potential oxygen mono- or bidentate ligands, which could also lead to molecular precursors of oxides.

No reaction occurred between **2** and *t*-butanol, in refluxing toluene; alkoxo exchange reactions and/or reactions involving the oxo ligands could however be achieved with acetic acid or acetylacetone, offering compounds analysing as $Nd_6O_3(OAc)_4(O^iPr)_8$ and $Nd_2(OH)(acac)_5$ (**3**), respectively. The solubility of **3** is attractive, by contrast with the poor solubility of the carboxylate derivative. Its IR spectra confirmed the obtaining of a species different from $Nd(acac)_3$, previously obtained by reaction between $[Nd(O^iPr)_3]_n$ and acetylacetone,[16,17] the main spectral differences being the presence of an additional absorption band at 725 cm^{-1} and a notable shift to higher frequencies (40 cm^{-1}) for the stretching $\nu_s(C{=}O)$ mode. By contrast with the isopropoxides derivatives **1** and **2**, which were ESR silent down to 100 K (probably due to very short relaxation times,

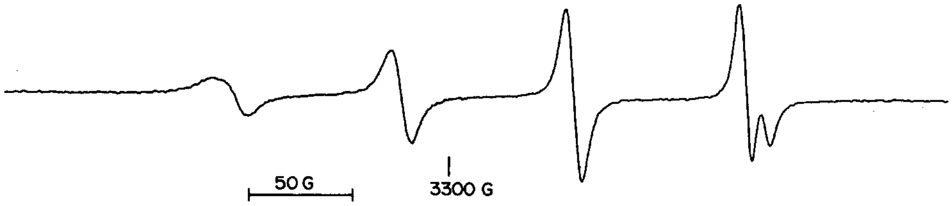

Fig. 1. ESR spectrum of $[Nd_4(\mu_3\text{-}OH)_2(\mu_2,\mu_1\text{-}acac)_6(acac)_4]$ in toluene solution at 298 K.

as often observed for lanthanide compounds), **3** displays a spectrum at room temperature (Fig. 1). However, since ESR spectra of f elements are mainly an illustration of spin–orbit effects,[18] an X-ray structure determination of **3** was undertaken.

The crystal structure of $[Nd_4(OH)_2(acac)_{10}]$ consists of a centrosymmetric tetranuclear cluster (Figs 2 and 3). Relevant interatomic distances and angles are collected in Table 2.

Two dinuclear $Nd_2(OH)(acac)_5$ units are linked by two triply bridging hydroxo and two bridging-chelating β-diketonate ligands. Although the hydrogen atoms were not crystallographically located, an unambiguous assignment as μ_3-hydroxo was made on the basis of several criteria. The sum of the Nd—O—Nd angles is 326.5 around O(1), close to the value (328.4) expected for pure sp^3 hybridized atoms.[19] Moreover, an oxo ligand would lead to mixed valency Nd^{III}–Nd^{IV} species. Although the stabilization of neodymium(IV) is possible with some ligands,[20] no molecular neodymium(IV) compounds have been reported so far. Finally, an O—H stretching mode is observed at 3450 cm^{-1} in the IR spectrum, confirming the presence of hydroxo ligands in the aggregate. Although both the metal atoms are eight-coordinated, with Nd—O bond lengths ranging from 2.370(7) to 2.654(6) Å, Nd(1) and Nd(2) have slightly different environments. The coordination polyhedra around the two metals are distorted square antiprisms (Fig. 4), but Nd(2) is surrounded by two hydroxo ligands, one chelating and three bridging-chelating acetylacetonato groups, while Nd(1) is linked to only one hydroxo group.

The Nd—O bond distances fall in the range of the values previously reported in the literature for neodymium oxide derivatives or Nd—O coordination bonds,[21,22] but are much longer than the values observed for terminal Nd—O^{i}Pr linkages.[7] The longest Nd—O bond distances correspond to β-diketonate oxygen atoms in bridging positions. The Nd—O bond lengths involving chelating acac ligands are significantly different (2.38, 2.44 Å), but close to the values determined in $Nd(acac)_3 \cdot 2H_2O$.

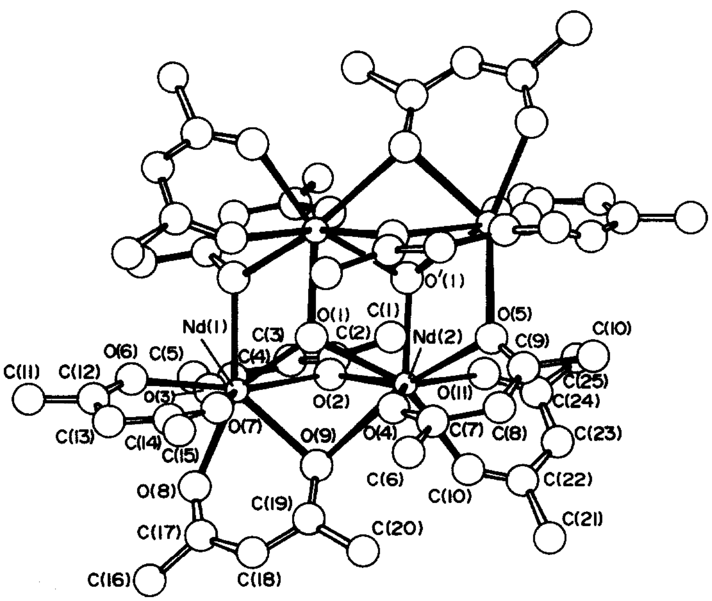

Fig. 2. ORTEP view of $[Nd_4(\mu_3\text{-}OH)_2(\mu_2,\mu_1\text{-}acac)_6(acac)_4]$, showing the atom numbering scheme.

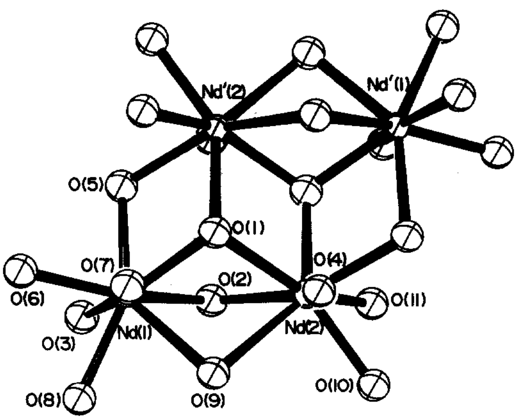

Fig. 3. Neodymium oxygen core of **3**.

The Nd(μ_3-OH) linkages are in agreement with the value observed for other triply bridged metal–hydroxo bonds.[19]

The rest of the bonding in the acac ligands appears normal, with C—O and C—C bond lengths ranging from 1.25(1) to 1.31(2) Å and from 1.38(1) to 1.52(2) Å, respectively. Close intermolecular contacts between most oxygen atoms are noted, as commonly observed for β-diketonate derivatives. The bridging-chelating ligands, especially those of the $Nd_2(OH)(acac)_5$ unit, display a larger bite and more deviation towards planarity of the cycle than the simple chelating ones. The shortest metal–metal distances correspond to those of the dinuclear $Nd_2(OH)(acac)_5$ unit with a value of 3.833 Å.

The synthesis of $[Nd_4(\mu_3\text{-}OH)_2(acac)_{10}]$ from the oxoalkoxide in nearly quantitative yield implies that the oxo ligands, or at least some of them, are reactive towards acetylacetone, as also previously observed for oxo species of various elements.[23] The hydroxo ligand can thus result from direct reactivity with the β-diketone or from further hydrolysis of an $Nd(acac)_3$ species, since water appears as a byproduct. Hydroxo species formulated as $Ln(acac)_2OH$ have been previously suggested to form by hydrolysis of $Ln(acac)_3$ or by thermal decomposition of their hydrates, but were not characterized.[23,24] Complex **3** belongs to the very few hydroxide lanthanide derivatives structurally characterized[25] and is the first one for neodymium.

Table 2. Selected bond lengths and angles for $[Nd_4(\mu_3\text{-}OH)_2(acac)_{10}]$

		Bond lengths (Å)			
Nd(1)—O(1)	2.428(6)	Nd(1)—O(8)	2.374(6)	Nd(2)—O'(1)	2.418(6)
Nd(1)—O(2)	2.594(5)	Nd(1)—O(9)	2.542(6)	Nd(2)—O(9)	2.654(6)
Nd(1)—O(3)	2.370(7)	Nd(2)—O(1)	2.459(5)	Nd(2)—O(10)	2.371(6)
Nd(1)—O(5)	2.564(6)	Nd(2)—O(2)	2.625(6)	Nd(2)—O(11)	2.420(6)
Nd(1)—O(6)	2.384(6)	Nd(2)—O(4)	2.417(5)		
Nd(1)—O(7)	2.445(6)	Nd(2)—O(5)	2.485(6)		
		Angles (coordination polyhedron) (°)			
O(1)—Nd(1)—O(2)	70.4(2)	O(5)—Nd(1)—O(9)	135.0(2)	O(2)—Nd(2)—O(4)	133.4(2)
O(1)—Nd(1)—O(3)	134.9(3)	O(6)—Nd(1)—O(7)	70.9(2)	O(2)—Nd(2)—O'(1)	78.0(2)
O(1)—Nd(1)—O(5)	69.3(2)	O(6)—Nd(1)—O(8)	76.2(3)	O(2)—Nd(2)—O'(5)	147.5(2)
O(1)—Nd(1)—O(6)	120.0(2)	O(6)—Nd(1)—O(9)	136.5(2)	O(9)—Nd(2)—O(4)	77.5(2)
O(1)—Nd(1)—O(7)	68.6(2)	O(7)—Nd(1)—O(8)	85.2(2)	O(9)—Nd(2)—O'(1)	133.1(2)
O(1)—Nd(1)—O(8)	139.4(2)	O(7)—Nd(1)—O(9)	77.7(2)	O(9)—Nd(2)—O'(5)	145.5(2)
O(1)—Nd(1)—O(9)	72.6(2)	O(8)—Nd(1)—O(9)	71.9(3)	O(10)—Nd(2)—O(4)	82.6(2)
O(2)—Nd(1)—O(3)	71.9(3)	O(1)—Nd(2)—O(2)	69.4(2)	O(10)—Nd(2)—O'(1)	140.9(2)
O(2)—Nd(1)—O(5)	77.7(2)	O(1)—Nd(2)—O(9)	70.1(2)	O(10)—Nd(2)—O'(5)	82.1(2)
O(2)—Nd(1)—O(6)	154.3(3)	O(1)—Nd(2)—O(10)	147.2(2)	O(11)—Nd(2)—O(4)	137.9(2)
O(2)—Nd(1)—O(7)	132.3(3)	O(1)—Nd(2)—O(11)	142.6(2)	O(11)—Nd(2)—O'(1)	76.3(2)
O(2)—Nd(1)—O(8)	112.2(2)	O(2)—Nd(2)—O(9)	65.5(2)	O(11)—Nd(2)—O'(5)	75.6(2)
O(2)—Nd(1)—O(9)	67.6(2)	O(2)—Nd(2)—O(10)	119.2(2)	O(4)—Nd(2)—O'(5)	69.4(2)
O(3)—Nd(1)—O(6)	87.0(2)	O(2)—Nd(2)—O(11)	88.5(2)	O(4)—Nd(2)—O'(1)	111.9(2)
O(3)—Nd(1)—O(7)	155.1(2)	O(9)—Nd(2)—O(10)	84.6(2)	O(5')—Nd(2)—O'(5)	70.8(2)
O(3)—Nd(1)—O(8)	78.3(2)	O(9)—Nd(2)—O(11)	128.4(2)	Nd(1)—O(1)—Nd(2)	103.3(2)
O(3)—Nd(1)—O(9)	114.0(2)	O(10)—Nd(2)—O(11)	69.9(3)	Nd(1)—O(1)—Nd'(2)	113.2(2)
O(5)—Nd(1)—O(6)	84.4(2)	O(1)—Nd(2)—O(4)	72.0(2)	Nd(2)—O(1)—Nd'(2)	110.0(2)
O(5)—Nd(1)—O(7)	108.8(2)	O(1)—Nd(2)—O'(1)	70.0(2)	Nd(1)—O(2)—Nd(2)	94.5(2)
O(5)—Nd(1)—O(8)	150.9(2)	O(1)—Nd(2)—O'(5)	107.0(2)	Nd(1)—O(9)—Nd(2)	95.1(2)
				Nd(1)—O(5)—Nd'(2)	106.5(2)

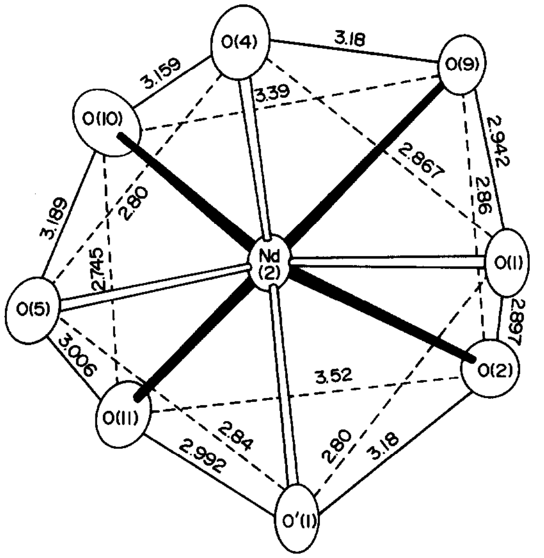

Fig. 4. Coordination polyhedron around Nd(2), showing the extent to which the faces are distorted from the ideal square.

Octacoordination appears to be favoured for the lanthanides in β-diketonate derivatives, as illustrated by the structural data of $Ln(acac)_3 \cdot nH_2O$ (Ln = Y, La, Nd, Eu; $n = 2$ or 3) and $[Ln(dpm)_3]_2$ (Ln = Pr, Er; dpmH = dipivaloylmethane).[20,23] Thus formation of a tetranuclear cluster for $[Nd_4(\mu_3\text{-}OH)_2(acac)_{10}]$, the first example of such a structural unit for neodymium, allows the metal to attain this coordination number.

These results, as well as those obtained on yttrium with the formation of $Y_5O(O^iPr)_{13}$,[12] suggest extensive and promising oxopolymetallic chemistry for lanthanides with anionic oxygen donor ligands.

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