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Reaction of neodymium diiodide with methanol in acetonitrile. Structure of the cluster $[Nd_4(\mu_2\text{-}I)_{1.1}(\mu_3\text{-}I)(\mu_2\text{-}OMe)_{4.9}(\mu_4\text{-}O)(MeCN)_{12}]I_3$*

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The reaction of neodymium diiodide NdI_2 with excess methanol in acetonitrile produced the tetranuclear neodymium cluster $[Nd_4(\mu_2\text{-}I)_{1.1}(\mu_3\text{-}I)(\mu_2\text{-}OMe)_{4.9}(\mu_4\text{-}O)(MeCN)_{12}]I_3$ (**1**). In the latter, the isomorphic substitution of one methoxy group by an I^- anion with site occupancies (%) of 90 and 10, respectively, was observed. Due to the isomorphic substitution in the crystal, cluster **1** can be considered as a superposition of two complexes, $[Nd_4(\mu_2\text{-}I)(\mu_3\text{-}I)(\mu_2\text{-}OMe)_5(\mu_4\text{-}O)(MeCN)_{12}]I_3$ and $[Nd_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)(\mu_2\text{-}OMe)_4(\mu_4\text{-}O)(MeCN)_{12}]I_3$. The characteristic feature of cluster **1** is that the center of the Nd_4 cage is occupied by the μ_4-coordinated O^{2-} anion, which is indicative of the partial O—C bond cleavage in methanol. The reaction of NdI_2 with an equimolar amount of MeOH in an acetonitrile solution produced methoxide $NdI_2(OMe)(MeCN)_4$ in 49% yield.

Key words: neodymium, diiodide, cluster, methoxide, endohedral oxygen.

Studies of the reactivities of neodymium(II), dysprosium(II), and thulium(II) (LnI_2) iodides showed[1—3] that these compounds readily react with acetonitrile and benzonitrile to form acyclic and heterocyclic C—C- and C—N-coupling products. The analogous reactions in the presence of primary or secondary amines proceed in the presence of catalysts to give mono- and *N,N*-disubstituted amidines and lanthanide amidine complexes.[4] In the presence of NdI_2, *tert*-butanol was found[5] to undergo deprotonation in a THF solution under mild conditions to form the butoxide $Bu^tOLnI_2(THF)_4$. It was of interest to study the reaction of NdI_2 with acetonitrile in the presence of methanol, which would be expected to give imino ester and its complexes with neodymium. Such complexes containing O—Ln—N groups are generally stable in air and often exhibit high photo- and electroluminescence activity.[6—8] In the present study, we investigated the reaction of neodymium diiodide with an acetonitrile—methanol mixture and established the structure of the resulting tetranuclear neodymium cluster.

Results and Discussion

Neodymium diiodide actively reacts with excess methanol in acetonitrile at room temperature. The observed gas evolution is evidence for the attack of the reducing agent on the OH group of methanol, whereas the C≡N triple bond of acetonitrile remains unaffected. The absence of volatile compounds, other than MeOH and MeCN, indicates that the C≡N group does not undergo hydrogenation as well. The recrystallization of the solid residue obtained after removal of the volatile components afforded two products, *viz.*, $NdI_2(OMe)(MeCN)_3$ in 62% yield and colorless crystals with the composition $Nd_4I_{5.1}(OMe)_{4.9}(O)(MeCN)_{12}$ (**1**).

$$NdI_2 + MeOH \xrightarrow[-H_2]{MeCN}$$

$$\longrightarrow NdI_2(OMe)(MeCN)_3 + \underset{\mathbf{1}}{Nd_4I_{5.1}(OMe)_{4.9}(O)(MeCN)_{12}}$$

The former compound was identified based on the elemental analysis data and the IR spectrum. The X-ray diffraction study of the latter compound (**1**) showed that the reaction produced the tetranuclear neodymium cluster with the composition $[Nd_4(\mu_2\text{-}I)_{1.1}(\mu_3\text{-}I)(\mu_2\text{-}OMe)_{4.9}(\mu_4\text{-}O)(MeCN)_{12}]I_3$. In the crystal of compound **1**, the isomorphic substitution of one μ_2-bridging methoxy group by the iodide anion with site occupancies (%) of 90 : 10 was observed. Taking into account the isomorphic substitution in the crystal, cluster **1** can be considered as a superposition of two clusters, $[Nd_4(\mu_2\text{-}I)(\mu_3\text{-}I)(\mu_2\text{-}OMe)_5(\mu_4\text{-}O)(MeCN)_{12}]I_3$ and $[Nd_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)(\mu_2\text{-}OMe)_4(\mu_4\text{-}O)(MeCN)_{12}]I_3$, in a ratio of 9 : 1 (Fig. 1). Presumably, both complexes exist separately in solution.

In the crystal structure of **1**, the Nd^{3+} cations occupy vertices of a distorted tetrahedron and are linked to each

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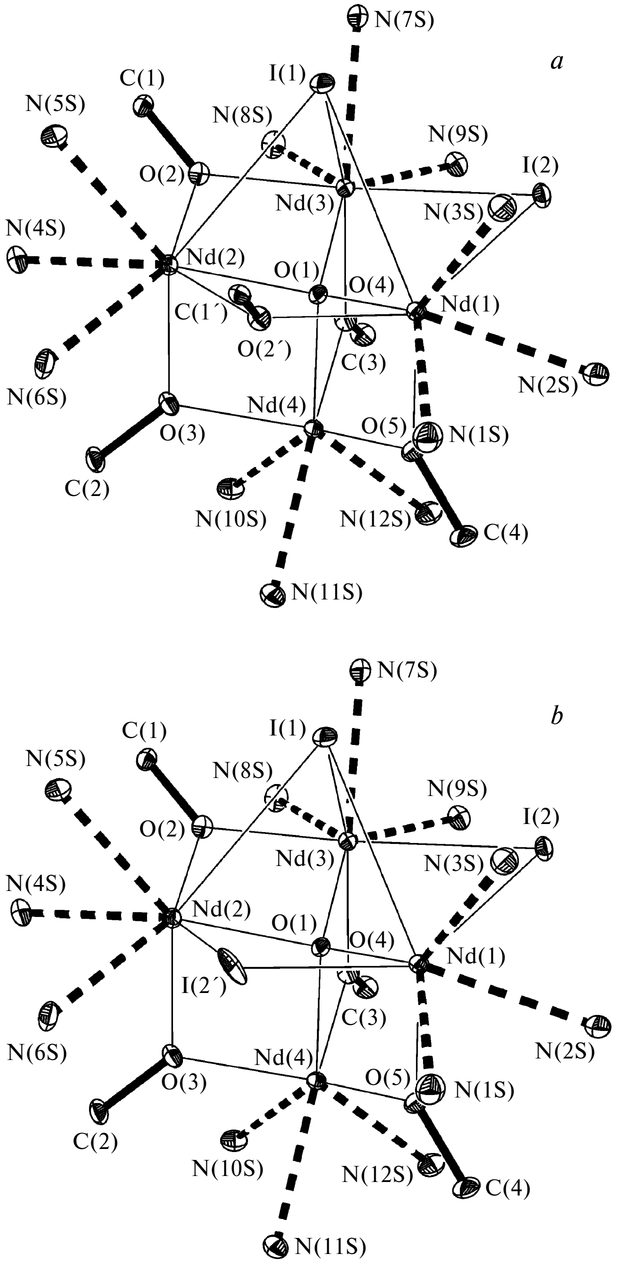

Fig. 1. Molecular structures of the $[Nd_4(\mu_2\text{-}I)(\mu_3\text{-}I)(\mu_2\text{-}OMe)_5(\mu_4\text{-}O)(MeCN)_{12}]I_3$ (*a*) and $[Nd_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)(\mu_2\text{-}OMe)_4(\mu_4\text{-}O)(MeCN)_{12}]I_3$ (*b*) clusters (displacement ellipsoids are drawn at the 30% probability level). The hydrogen atoms in the MeO groups, the MeC fragments of the acetonitrile ligands, and the I^- anions located outside the coordination sphere of Nd are omitted.

other by the bridging methoxy groups and I^- anions. The Nd—O(μ_2-OMe) distances are in the range of 2.296(2)—2.341(2) Å. According to the Cambridge Structural Database,[9] data on OMe-bridged neodymium fragments are lacking. As expected, the Nd—I(μ_2) distances (3.2369(3)—3.2518(3) Å) are much shorter than the Nd—I(μ_3) distances (3.4555(3)—3.6379(3) Å). The NdO(1)Nd angles are in the range of 106.97(10)—120.51(9)°. The Nd...Nd interatomic distances are in the range of 3.7301(3)—4.0094(3) Å. Each Nd cation is coordinated by three acetonitrile molecules. The Nd—N distances are in the range of 2.600(4)—2.681(3) Å.

The coordination environment of the Nd(1)—Nd(3) atoms can be described as distorted bicapped trigonal prisms (coordination number is 8), whereas the coordination environment of the Nd(4) atom can be described as a distorted pentagonal bipyramid (coordination number is 7). Three iodide anions are outside the coordination spheres of the neodymium cations. Selected bond lengths and bond angles in the crystal of **1** are given in Table 1.

A specific feature of cluster **1** is the presence of the four-coordinated O^{2-} dianion within the framework formed by the Nd atoms, the bridging iodine atoms, and the oxygen atoms of the MeO groups. The Nd—(μ_4-O(1)) distances are in the range of 2.304(3)—2.344(2) Å and are comparable with the Nd—(μ_2-OMe) bond lengths. The Nd—(μ_4-O(1)) distances are noticeably shorter than the corresponding Nd—(μ_5-O) distances in the $Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5$ complex (2.440(8)—2.502(8) Å).[10]

Taking into account the most evident reaction pathway involving the displacement of the hydrogen atom of the OH group of methanol by diiodide NdI_2, the presence of the oxygen atom in the molecule of the reaction prod-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the crystal of $[Nd_4(\mu_2\text{-}I)_{1.1}(\mu_3\text{-}I)(\mu_2\text{-}OMe)_{4.9}(\mu_4\text{-}O)(MeCN)_{12}]I_3$*

Bond	*d*/Å	Angle	ω/deg
Nd(1)—O(1)	2.314(3)	Nd(1)—O(2′)—Nd(2)	106.73(7)
Nd(2)—O(1)	2.344(2)	Nd(1)—O(5)—Nd(4)	106.94(10)
Nd(3)—O(1)	2.304(3)	Nd(4)—O(1)—Nd(2)	107.12(9)
Nd(4)—O(1)	2.312(2)	Nd(3)—O(1)—Nd(2)	105.83(9)
Nd(1)—O(5)	2.311(3)	Nd(4)—O(1)—Nd(1)	107.48(10)
Nd(3)—O(2)	2.296(2)	Nd(3)—O(1)—Nd(1)	120.51(9)
Nd(3)—O(4)	2.305(3)	Nd(3)—O(1)—Nd(4)	108.26(10)
Nd(1)—O(2′)	2.314(2)	Nd(4)—O(3)—Nd(2)	106.72(9)
Nd(2)—O(2′)	2.3505(18)	Nd(3)—O(2)—Nd(2)	106.14(9)
Nd(2)—O(2)	2.343(2)	Nd(2)—I(2′)—Nd(1)	70.603(16)
Nd(2)—O(3)	2.341(2)	Nd(3)—I(2)—Nd(1)	76.327(7)
Nd(4)—O(4)	2.335(3)	Nd(2)—I(1)—Nd(3)	62.616(6)
Nd(4)—O(3)	2.327(2)	Nd(1)—I(1)—Nd(3)	68.898(7)
Nd(4)—O(5)	2.331(3)	Nd(1)—I(1)—Nd(2)	65.059(6)
Nd(1)—I(2)	3.2518(3)	N(1S)—Nd(1)—N(2S)	71.51(11)
Nd(1)—I(1)	3.4555(3)	N(1S)—Nd(1)—N(3S)	74.36(11)
Nd(1)—I(2′)	3.2389(8)	N(2S)—Nd(1)—N(3S)	73.71(10)
Nd(2)—I(2′)	3.2387(8)		
Nd(3)—I(1)	3.6279(3)		
Nd(3)—I(2)	3.2369(3)		
Nd(2)—I(1)	3.5052(3)		

* The isomorphic substitution of the O(2′)Me group by the I(2′) anion.

uct seems unexpected and can be attributed to the following two factors: the occasional presence of water in the reaction mixture or the C—O bond cleavage in the MeO^- anions by the strong reducing agent NdI_2. The formation of complexes containing the O^{2-} dianion, for example, $[Cp_2Yb(2\text{-}NH\text{-}4\text{-}MeO\text{-}6\text{-}MeOpm)_2(\mu_3\text{-}O)(YbCp)]$ (pm is pyrimidine),[11] $(CpGd)_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$, and $[Na_2(Bu^tOGd)_4(\mu_3\text{-}OBu^t)_8(\mu_6\text{-}O)]$,[12] has been observed earlier in the reactions of $[Cp_2Yb\{2\text{-}NH\text{-}4,6\text{-}Me_2pm\}]_2$ with aminodimethylpyrimidine and of $GdCl_3$ with CpNa and MeONa, or Bu^tOK, respectively. The presence of the oxygen atom in these reaction products was attributed to the side reaction of the substrates with water that is occasionally present in the reaction mixture. However, the formation of the $Nd_4[Bu^tC(O){=}CHCMe{=}N(CH_2)_3N{=}CMeCH{=}C(O)Bu^t]_4(\mu_3\text{-}O)_2(THF)$ complex in the reaction of amide $Nd[N(SiMe_3)_2]_3$ with imino alcohol $Bu^tC(OH)CHCMeN(CH_2)_3NCMeCHC(OH)Bu^t$ in THF was accounted for by the cleavage of the solvent under the synthesis conditions.[13] The C—O bond cleavage was observed also in the synthesis of oxoalkoxides $Ce_4(\mu_4\text{-}O)(\mu\text{-}OPr^i)_{14}$ (see Ref. 14) and $Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu_2\text{-}OPr^i)_6(OPr^i)_5(Pr^iOH)_2$.[15] We believe that the presence of the μ_4-O atom in complexes **1a** and **1b** is also due to the partial C—O bond cleavage in the methanol molecule.

The reaction of NdI_2 with an equimolar amount of methanol in MeCN was accompanied by the appearance of the dark-blue color of the reaction mixture. This reaction also afforded the methoxy iodide $NdI_2OMe(MeCN)_4$ as a blue crystalline powder in 49% yield. Another half of the starting salt produced an unidentified substance, which was isolated from the reaction solution as a gray-blue amorphous material after removal of the volatile components. The neodymium and iodine contents in this product differ only slightly from those in $NdI_2OMe(MeCN)_4$, but its IR spectrum shows an additional band at 2193 cm^{-1}. The appearance of this band and the blue color of the compound untypical of Nd^{II} and Nd^{III} compounds are apparently indicative of the involvement of acetonitrile in the reaction. We failed to determine the structure of this product.

Thus, the reaction of NdI_2 with methanol in acetonitrile affords methoxide $NdI_2OMe(MeCN)_x$ ($x = 3$ or 4) as the major product regardless of the reagent ratio. However, the reaction with excess methanol is accompanied by the C—O bond cleavage and the formation of tetranuclear iodide oxomethoxide clusters with different numbers of the bridging OMe^- and I^- anions.

Experimental

The syntheses were carried out in evacuated systems using the standard Schlenk technique. Methanol was dried according to a standard procedure.[16] Acetonitrile was dried and distilled over P_2O_5. The IR spectra were recorded on a Specord M-75 spectrometer in the 4000—450 cm^{-1} region. Samples were prepared as Nujol mulls. Diiodide NdI_2 was synthesized according to a known procedure.[17]

Reaction of NdI_2 with excess MeOH in acetonitrile. Acetonitrile (4.30 g, 105 mmol) and methanol (3.35 g, 105 mmol) were added to a NdI_2 powder (1.98 g, 4.97 mmol) at liquid nitrogen temperature. Upon heating of the reaction mixture to −70—−50 °C, the reaction started, as was evidenced by the evolving of gas bubbles. After storage of the reaction mixture at room temperature for 15 min, the gas evolution ceased, the precipitate of NdI_2 dissolved, and the solution turned red-orange. The mixture was centrifuged, the solution was decanted from the precipitate containing insoluble impurities, and volatile compounds were removed *in vacuo*. The GLC analysis of the condensate revealed nothing but MeOH and MeCN. The solid residue was dissolved in MeCN (12 mL), and the solution was concentrated to 4 mL and cooled to −20 °C. The finely crystalline pale-violet precipitate that formed was separated by decantation, washed with cold MeCN, and dried *in vacuo*. The yield of the substance was 2.49 g. The repeated recrystallization of the product from MeCN afforded colorless crystals of complex **1** in a yield of 0.41 g (17%), m.p. 52 °C. The crystals were used for the X-ray diffraction study. Upon storage of the mother liquor at −20 °C, pale-violet crystals of $NdI_2OMe(MeCN)_3$ precipitated. The yield was 1.690 g (62%), m.p. 54—56 °C. Found (%): Nd, 25.89, I, 48.55. $C_7H_{12}I_2N_3NdO$. Calculated (%): Nd, 26.12, I, 45.96. IR (Nujol), ν/cm^{-1}: 3343 s, 2300 s, 2269 s, 1604 m, 1673 s, 1088 w, 1011 s, 992 s, 930 s, 773 w.

Reaction of NdI_2 with MeOH (1 : 1) in acetonitrile. Acetonitrile (15 mL) and MeOH (0.198 g, 6.18 mmol) were added to NdI_2 (2.482 g, 6.24 mmol) under the conditions of the previous experiment. The thawing of the reaction mixture was accompanied by the gas evolution and the formation of a gray precipitate. After storage of the mixture at room temperature for 15 h, the solution turned dark-blue. The gray-blue precipitate was separated from the solution by centrifugation followed by decantation and then dried *in vacuo*. The yield of $NdI_2OMe(MeCN)_4$ was 1.748 g (47%). Found (%): Nd, 24.42, I, 42.84. $C_9H_{15}I_2N_4NdO$. Calculated (%): Nd, 24.31, I, 42.78. IR (Nujol), ν/cm^{-1}: 2300 s, 2268 s, 1605 m, 1018 s, 931 m. The blue mother liquor was concentrated to 5 mL and cooled to −20 °C, which additionally gave 0.079 g (2%) of $NdI_2OMe(MeCN)_4$. The total yield of the compound was 49%. After removal of volatile components and drying of the foaming residue *in vacuo* at 50 °C for 1 h, the solid noncrystalline blue compound was obtained in a yield of 1.63 g; the neodymium and iodine contents were 23.68% and 46.62%, respectively. IR (Nujol), ν/cm^{-1}: 2299 s, 2269 s, 2193 m, 1640 m, 1580 m, 999 s, 932 w.

X-ray diffraction study of 1. Experimental X-ray intensities were measured on a Bruker AXS SMART APEX diffractometer (φ-ω-scanning technique, Mo-Kα radiation, graphite monochromator) at 100 K. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXTL program package.[18] Absorption corrections were applied using the SADABS program.[19] The hydrogen atoms were positioned geometrically and refined isotropically using a riding model. In addition to the molecule of complex **1**, the asymmetric unit contains five acetonitrile solvent molecules in general positions. The crystallographic data and the X-ray diffraction data collection and refinement statistics are as follows: $C_{38.9}H_{65.74}I_{5.09}N_{17}Nd_4O_{5.91}$, M = 2088.93, orthorhombic system, space group $P2_12_12_1$, a = 11.6421(5) Å, b = 22.0774(9) Å, c = 27.0547(11) Å, V = 6953.8(5) $Å^3$, Z = 4, d_{calc}= 1.995 g cm^{-3}, μ = 5.243 mm^{-1}, $F(000)$ = 3901, $1.77 \le \theta° \le 26.0$, 42391 measured reflections, 13657 independent reflections (R_{int} = 0.0321), R_1 ($I \ge 2\sigma(I)$) = 0.0274, wR_2 (based on all X-ray data) = 0.0596, the absolute structure parameter is 0.400(8), the maximum and minimum residual electron densities are 1.686 and –0.594 e $Å^{-3}$, respectively.

The atomic coordinates and the complete tables of bond lengths and bond angles were deposited with the Cambridge Structural Database (CCDC 645245).

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