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The Action of Sodium on $NdCl_3$ and $PrCl_3$: Mixed Valence $NaNd_2Cl_6$ and Metallic $NaPr_2Cl_6$*

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In the course of our investigation of the action of sodium on lanthanide(III) chlorides, MCl_3, two cases have so far emerged. First, trichlorides with low (assessed) standard electrode potentials, $E^\circ(M^{3+}/M^{2+})$ [1], are reduced to dichlorides, MCl_2, with M = Eu, Yb, Sm, Tm, Dy [2]. Secondly, trichlorides with high E° values are reduced partly to the metal thereby producing NaCl. With surplus MCl_3 excellent media for crystal growth of Na_3MCl_6-type ternary chlorides (M = Gd [3], Er [4]) are provided.

The case of neodymium (next to dysprosium in the series of reduction potentials) remained puzzling. While the reduction of $NdCl_3$ with lithium and potassium to $NdCl_2$ and KNd_2Cl_5 is straightforward [5], the only well-crystallized 'product' of the sodium reduction of $NdCl_3$ was NdOCl [6], although in a negligible percentage. The main product, now analysed as $NaNd_2Cl_6$, would not crystallize nearly as perfectly and, more importantly, fooled us because it exhibits almost the same X-ray powder pattern as $NdCl_3$. Only a structure determination could reveal its true nature, that of a ternary mixed-valence Nd(II)–Nd(III) chloride.

With praseodymium (adjacent to neodymium in the lanthanide series and taking advantage of the above-mentioned knowledge) a close inspection of the sodium reduction of $PrCl_3$ seemed and proved worthwhile. Especially because the question still remains for praseodymium whether a divalent state in solid halides exists or not. In fact, it does neither in iodides (PrI_2 [7, 8] and Pr_2I_5 [9] are apparently metallic) nor in bromides, with Pr_2Br_5 having to be formulated as $(Pr^{3+})_2(e^-)(Br^-)_5$ [10]. Single crystals of $NaPr_2Cl_6$ could be isolated and, indeed, the structure determination reveals no evidence for divalent praseodymium.

Experimental

The ammonium chloride route ('wet' variant) [11, 12] was followed to convert Nd_2O_3 and 'Pr_6O_{11}' (Johnson–Matthey, 3 N) into the trichlorides $NdCl_3$ and $PrCl_3$. Equimolar amounts of sodium and the respective trichloride, e.g., 13.2 mg Na and 141.8 mg $PrCl_3$, were placed under anaerobic and anhydrous conditions into carefully cleaned tantalum tubes that were subsequently sealed by He-arc welding and jacketed in silica tubing under vacuum [13]. These were then kept for one week at around or above the melting points of the trichlorides (for Na/$PrCl_3$, 750 °C; for Na/$NdCl_3$, 850 °C) after which the power to the furnace was turned off.

$NaNd_2Cl_6$ (**1**) (green/black) and $NaPr_2Cl_6$ (**2**) (blue/black) are decomposed by moist air with the evolution of hydrogen. Water leads to immediate decomposition in the case of $NaNd_2Cl_6$, with the short intermediate appearance of an orange colour.

Single crystals of hexagonally columnar shape could be selected under sodium-dried petroleum. The crystals were sealed into thin-walled glass capillaries and their quality was checked by Weissenberg photographs. Details of the data collection and structure determination processes are summarized in Tables I and II.

Data Collection

A four-circle diffractometer, Philips PW 1100, was used for compound **1** and a Siemens AED for **2** with Mo Kα radiation and graphite monochromator: λ = 71.07 pm, ω-scan speed: 0.12 °/s (**1**), variable (**2**); scan width: 5.4° (**1**), 2.5–2.7° (**2**); $3^\circ \leqslant \theta \leqslant 30^\circ$; $F(000) = 233$ (**1**), 231 (**2**); $\mu = 126.95$ (**1**), 125.32 (**2**) cm^{-1}.

TABLE I. Lattice Constants (pm) and Molar Volumes (V_m) ($cm^3\ mol^{-1}$)

Compound	1	2
Formula	$NaNd_2Cl_6$	$NaPr_2Cl_6$
(I) Guinier–Simon [14, 15]		
a	762.60(5)	756.77(5)
c	438.66(4)	429.34(4)
V_m	133.05(2)	128.24(2)
(II) Four-circle diffractometer		
a	762.6	756.5
c	438.8	429.2
V_m	133.1	128.1
Crystal system	hexagonal	hexagonal
Space group	*P*6_3/*m* (no. 176)	*P*6_3/*m* (no. 176)
Z	1	1

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TABLE II. Atomic Coordinates and Temperature Factors[a]

	$NaNd_2Cl_6$ (1)	$NaPr_2Cl_6$ (2)
Na	(2a): 0, 0, $\frac{1}{4}$	(2b): 0, 0, 0
	k: 1.2(1)*	k: 0.99(6)*
Nd/Pr	(2c) $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$	
Cl	(6h) $x, y, \frac{1}{4}$	
	x: 0.3864(9)	x: 0.3881(2)
	y: 0.3043(9)	y: 0.3028(2)
Na	U_{11}: 177(88)	U_{11}: 193(49)
	U_{33}: 361(145)	U_{33}: 405(86)
	U_{12}: 89(44)	U_{12}: 97(24)
Nd/Pr	U_{11}: 208(7)	U_{11}: 144(2)
	U_{33}: 161(8)	U_{33}: 162(3)
	U_{12}: 104(3)	U_{12}: 72(1)
Cl	U_{11}: 678(53)	U_{11}: 139(5)
	U_{22}: 712(55)	U_{22}: 139(5)
	U_{33}: 343(33)	U_{33}: 206(6)
	U_{12}: 469(50)	U_{12}: 81(4)

[a] $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{13}hla^*c^*)]$, $U_{23} = U_{13} = 0$; for Na and Nd/Pr: $U_{22} = U_{11}$; U_{ij} in pm^2. Asterisk represents occupation factor.

Data corrections for background, polarization and Lorentz factors were made. Absorption: (2) ψ-scan for 10 reflections, transmission factors ranging between 0.225 and 0.412.

For compound **1**, 1395 data were collected, 246 unique reflections ($R_{int} = 0.071$), 202 reflections with $|F_o| \geqslant 2\sigma|F_o|$; for compound **2**, 2436 data were collected, 231 unique reflections ($R_{int} = 0.040$), 203 reflections with $|F_o| \geqslant 2\sigma|F_o|$.

Structure Determination

Program system SHEL-X 76 [16] was used with scattering factors from Cromer *et al.* [17, 18], Patterson (Nd/Pr) and difference Fourier syntheses (Cl, Na), full-matrix least-squares refinement, (1) $R = 0.068$, $R_w = 0.060$ [$w = 2.669\sigma^{-2}|F_o|$]; (2) $R = 0.019$, $R_w = 0.021$ [$w = 0.769\sigma^{-2}|F_o| + 9.37 \times 10^{-4}F_o^2$].

Results and Discussion

Both $NaPr_2Cl_6$ and $NaNd_2Cl_6$ ($Z = 1$) crystallize essentially with the UCl_3 structure type (Fig. 1) to which $PrCl_3$ and $NdCl_3$ belong [19, 20] with $Z = 2$, *i.e.*, with the unit cell content, for example, Nd_2Cl_6. Minute deviations of the lattice constants, a and c, and the molar volume, V_m, occur when sodium is taken up. For the couple $PrCl_3$ and $NaPr_2Cl_6$, only a expands considerably (742 to 756 pm) while c remains almost constant (427 *versus* 429 pm). In contrast, both lattice constants expand considerably from $NdCl_3$ to $NaNd_2Cl_6$ (740 to 763, and 424 to 439 pm, respectively). Accordingly, volume expansion is larger for the $2NdCl_3/NaNd_2Cl_6$ couple (121 to 133 cm^3 mol^{-1}) than for $2PrCl_3/NaPr_2Cl_6$ (123 to 128 cm^3 mol^{-1}). The latter volume expansion corresponds to the volume increment of one Na^+ per formula unit (6.5 cm^3 mol^{-1} from ref. 21), while for the neodymium chlorides the difference of 12 cm^3 mol^{-1} accounts not only for the volume increment of one Na^+ but, in addition, for the volume increase because of the reduction of half of Nd^{3+} to Nd^{2+}.

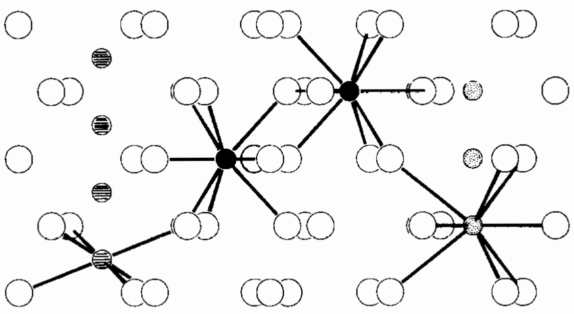

Fig. 1. A side-view of the chloride layers of the crystal structures of NaM_2Cl_6 (M = Pr, Nd) with two polyhedra around M (●) outlined. The (2a) (⊜, left) and (2b) (◍, right) sites that may be occupied statistically by Na^+ in $NaNd_2Cl_6$ and $NaPr_2Cl_6$, respectively, are indicated; most of the possible Na^+ positions are omitted for clarity.

This would then suggest that $NaNd_2Cl_6$ is a mixed valence chloride according to the formulation $(Na^+)(Nd^{2+,3+})_2(Cl^-)_6$ with di- and trivalent neodymium statistically distributed over the sites of Nd^{3+} in $NdCl_3$. This view is supported by a comparison of the mean distances Nd^{n+}–Cl^- in $NdCl_3$ (290 pm), $NaNd_2Cl_6$ (299 pm) and $NdCl_2$ (313 pm), for details see Table III. Because neodymium is nine-coordinate in all three chlorides, the average oxidation state n+ in $NaNd_2Cl_6$ may well be accepted as +2.5. Difficulties arise from the rather minor quality of the $NaNd_2Cl_6$ crystals when compared with $NaPr_2Cl_6$. Although the R values for $NaNd_2Cl_6$ are acceptable, standard deviations and temperature factors are quite large. The essential problem, however, is the occupation of the (2a) sites by, statistically, about one Na^+. This site is nine-coordinate with three short (269 pm) and six large (347 pm) distances of Na^+–Cl^-. The average of 321 pm, however, is quite acceptable when compared with eight-coordinate Na^+ in Na_3ErCl_6, $\bar{d}(Na^+\text{–}Cl^-) = 313$ pm [4]. Furthermore, a comparison of the electrostatic (Madelung) parts of the lattice energy, MAPLE [22], of $NaNd_2Cl_6$ with the binaries NaCl, $NdCl_2$ and $NdCl_3$ gives good correspondence (see Table IV). On the other hand, such a strange nine-coordination of Na^+ could well be an artefact arising through merohedral twinning of individuals when the (2b) sites are occupied statistically by Na^+.

TABLE III. Important Interatomic Distances (pm) in $NaPr_2Cl_6$ and $NaNd_2Cl_6$ and Related Chlorides

$d(Na^+–Cl^-)$	
$NaPr_2Cl_6$	288.1 (6×)
$NaNd_2Cl_6$	268.9 (3×), 347.0 (6×); $\bar{d}^a$: 320.9
NaCl	282.0
Na_3ErCl_6	Na1: 273.3 (2×), 277.9 (2×), 285.4 (2×); $\bar{d}$: 278.9 Na2: 281.9, 282.2, 284.6, 285.4, 319.4, 329.8, 348.1, 374.1; $\bar{d}$: 313.2
$d(Pr^{3+}–Cl^-)$	
$NaPr_2Cl_6$	293.6 (6×), 298.3 (3×); $\bar{d}$: 295.2
$PrCl_3$	290.9 (6×); 293.5 (3×); $\bar{d}$: 291.8
$d(Nd^{n+}–Cl^-)$	
$NaNd_2Cl_6$	298.6 (3×), 299.2 (6×); $\bar{d}$: 299.0
$NdCl_2$	295.0, 296.0 (2×), 302.7, 310.0, 313.8 (2×), 344.6 (2×); $\bar{d}$: 312.9
$NdCl_3$	288.7 (6×), 292.5 (3×); $\bar{d}$: 290.0

[a] $\bar{d}$ = mean distance.

TABLE IV. A Comparison of the Madelung Parts of the Lattice Energies (MAPLE) of NaCl, $NdCl_2$ and $NdCl_3$ with $NaNd_2Cl_6$ and $NaPr_2Cl_6$ (in kcal/mol)

		$NaNd_2Cl_6$	$NaPr_2Cl_6$
Na^+	102.8	59.9	58.4
Nd^{2+}	365.9		
Nd^{3+}	745.5	521.0 (2×)	528.0 (2×)
Cl^a	102.8		
$Cl1^b$	96.9	116.7 (6×)	117.9 (6×)
$Cl2^b$	90.8		
Cl^c	104.7 (3×)		
Σ	1818.8	1802.1	1821.8

[a] From NaCl; [b] from $NdCl_2$; [c] from $NdCl_3$.

Such an occupation of octahedral sites (Na in (2b)) is indeed observed for the much better quality crystals of $NaPr_2Cl_6$ with the occupation factor refining very well to one Na^+ on the two-fold site. Still, the (overall) oxidation state of praseodymium could also be +2.5. However, as the above-mentioned volume comparison for $2PrCl_3$ with $NaPr_2Cl_6$ indicates, this can hardly be the case. Support for the view that there is only Pr^{3+} present in $NaPr_2Cl_6$ arises from comparison of the Pr^{n+} to Cl^- distances in $NaPr_2Cl_6$ and $PrCl_3$, where coordination numbers are equal (nine). Average distances are: 295 ($NaPr_2Cl_6$) and 292 pm ($PrCl_3$). Although slightly different, one should bear in mind that a $Pr^{2+}–Cl^-$ distance would be expected to be around 315 pm and with $Pr^{2.5+}$ one would expect $d = 305$ pm. Therefore, $NaPr_2Cl_6$ can safely be formulated as $(Na^+)(Pr^{3+})_2(e^-)(Cl^-)_6$ and, hence, should be metallic; a proposition that is supported by the metallic lustre of the ternary chloride.

With $NaPr_2Cl_6$ being metallic and praseodymium trivalent therein, there is presently no evidence left for a stable divalent state in a bulk praseodymium halide. As the true nature of $PrCl_{2.31}$ [23] is unknown, it could, again, be thought that this chloride could be mixed valent. However, with Pr_2Br_5 ($\equiv PrBr_{2.5}$), previously thought to be $PrBr_{2.38}$ [24] and being in fact $(Pr^{3+})_2(e^-)(Br^-)_5$ and given additionally the knowledge about $NaPr_2Cl_6$, one might rather suspect that $PrCl_{2.31}$ according to $(Pr^{3+})_{0.6}(Pr^{3+})_2(e^-)_{1.8}(Cl^-)_6$ would be analogous to $NaPr_2Cl_6$.

The apparent non-existence of divalent praseodymium can be brought into accord with the sequence of the (assessed) standard electrode potentials $E°$ for the couples M^{3+}/M^{2+}. These are for M = Tm, Dy, Nd, Ho, Pr: −2.27, −2.42, −2.62, −2.80, −3.03 V. With true divalent states in dichlorides known for the first three metals, holmium is obviously the last element in this series with a divalent state, although only in the mixed-valence chloride Ho_5Cl_{11} [25]. For praseodymium and beyond, a divalent state in the presence of halide ions is then apparently non-existent.

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