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Sodium Triaqua(ethylenediaminetetra-acetato)lanthanate(III) Pentahydrate and the Isomorphous Neodymium(III) and Europium(III) Salts

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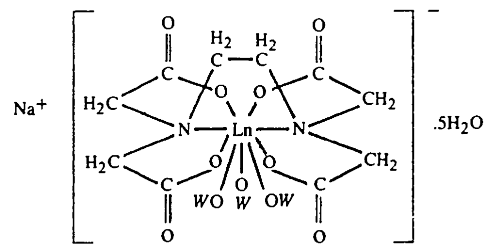
Abstract

Sodium triaqua[(1,2-ethanediyldinitrilo-κ^2N,N')tetraacetato-κ^4O^1,O^2,O^3,O^4]lanthanate(III) pentahydrate, $Na[La(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$, sodium triaqua[(1,2-ethanediyldinitrilo-κ^2N,N')tetraacetato-κ^4O^1,O^2,O^3,O^4]neodymate(III) pentahydrate, $Na[Nd(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$, and sodium triaqua[(1,2-ethanediyldinitrilo-κ^2N,N')tetraacetato-κ^4O^1,O^2,O^3,O^4]europate(III) pentahydrate, $Na[Eu(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$, are isomorphous and isostructural; all contain nine-coordinate lanthanoid ions, each of which bonds to two N atoms, four acetate O atoms and three water molecules.

Comment

The change in coordination number of lanthanoid(III) complexes in solution, arising from the lanthanoid contraction, has attracted much attention recently in connection with the anomalous behaviour (a double series or S-shaped) in their thermodynamic and physico-chemical properties (Yamaguchi, Nomura, Wakita & Ohtaki, 1988). For aqualanthanoid(III) complexes, it has been found from extended X-ray absorption fine structure (EXAFS) studies (Yamaguchi *et al.*, 1988) that in aqueous solution the hydration number of the lanthanoid(III) ions changes from nine for the light ions to eight for the heavy ions through an equilibrium between nine and eight for the intermediate ions. In the solid state, however, the nonaaqualanthanoid(III) ions are formed throughout the series (Kurisaki, Yamaguchi & Wakita, 1993). Thus, it is important to compare the coordination structures of lanthanoid(III) complexes both in solution and in crystals. A similar EXAFS study has been carried out on ethylenediaminetetraacetate (edta) complexes of a series of the lanthanoid(III) ions in solution (Nakamura, Yamaguchi, Wakita, Nomura & Choppin, 1993). The corresponding crystal structures are needed for comparison as structural standards in the EXAFS data analysis. The crystal structures of the lanthanoid(III)–edta complexes have previously been determined for orthorhombic $Na[Ln(edta)(H_2O)_3].5H_2O$ (Ln = Pr, Sm and Gd) (Templeton, Templeton, Zalkin & Ruben, 1982), monoclinic $Na[Ho(edta)(H_2O)_3].5H_2O$ (Templeton, Templeton & Zalkin, 1985), orthorhombic $Na[Dy(edta)(H_2O)_3].5H_2O$ and monoclinic $Cs[Yb(edta)(H_2O)_2].3H_2O$ (Nassimbeni, Wright, van Niekerk & McCallum, 1979). Only preliminary data are available for the potassium salt of the La(III)–edta complex (Hoard, Lee & Lind, 1965). In this study, we have determined the crystal structures of the hydrated sodium salts of the edta complexes of La^{III}, (1), Nd^{III}, (2), and Eu^{III}, (3).



(1) Ln = La
(2) Ln = Nd
(3) Ln = Eu
(I)

The three compounds crystallize in the orthorhombic space group *Fdd*2, as do the sodium salts of the analogous edta complexes of Pr^{III}, Sm^{III} and Gd^{III} (Templeton *et al.*, 1982), and Dy^{III} (Nassimbeni *et al.*, 1979), with which they are isomorphous and isostructural. The fractional atomic coordinates and the equivalent isotropic displacement parameters are listed in Tables 1, 2 and 3. *ORTEP*II (Johnson, 1976) plots of the coordination moieties for the complexes are given in Figs. 1, 2 and 3. The atomic positions in $Na[La(edta)(H_2O)_3].5H_2O$ are similar to those in $K[La(edta)(H_2O)_3].5H_2O$ (Hoard *et al.*, 1965).

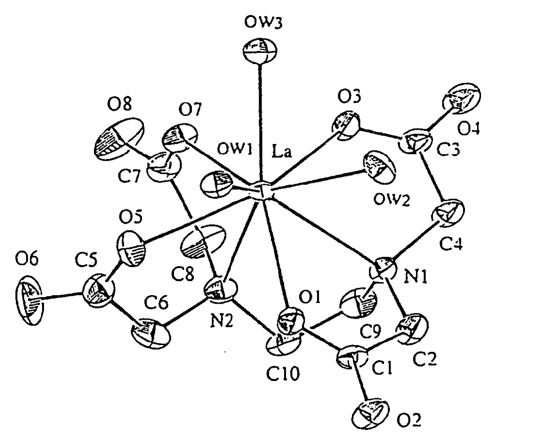


Fig. 1. *ORTEP*II (Johnson, 1976) plot for $Na[La(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

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The important interatomic distances and bond angles for these ions are listed in Tables 4, 5 and 6. The individual lanthanoid(III) ions have a typical ninefold coordination, consisting of two amino N atoms, four acetate O atoms, and three water molecules, as found for Pr^{III}, Sm^{III} and Gd^{III} (Templeton *et al.*, 1982), and Dy^{III} (Nassimbeni *et al.*, 1979). The Ln—O and Ln—N distances decrease with increasing atomic number, as expected from the lanthanoid contraction. The environment of the Na cation is best described in terms of its position at the center of a highly distorted octahedron. The Na—O distances vary from 2.378 (9) to 2.566 (6) Å. Probable hydrogen bonds are listed in Tables 4, 5 and 6; the O···O contacts lie between 2.60 (3) and 2.96 (2) Å.

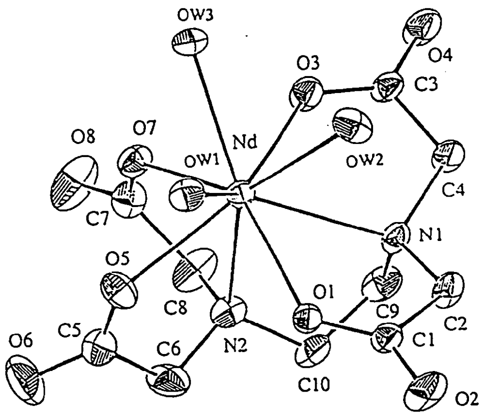

Fig. 2. *ORTEP*II (Johnson, 1976) plot for $Na[Nd(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

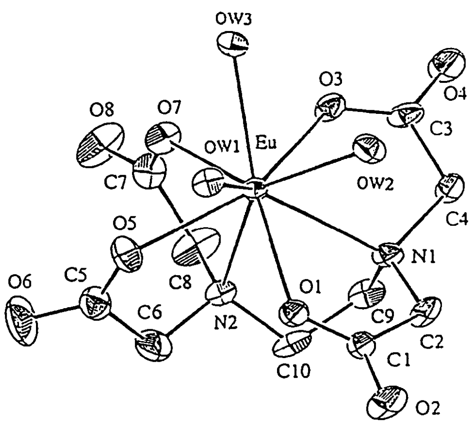

Fig. 3. *ORTEP*II (Johnson, 1976) plot for $Na[Eu(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals of the La– and Eu–edta complexes were prepared by refluxing 5 mmol of the relevant lanthanoid oxide with 10 mmol of H_4edta in 250 ml water and periodically adding small sodium hydroxide pellets until the oxide dissolved. The pH of the solutions was adjusted to 4.5 by adding aqueous NaOH. After slow evaporation of solvent at room temperature colorless prismatic crystals appeared in the mother solution. An aqueous solution of the Nd–edta complex was prepared by mixing commercially available $NdCl_3$ with the ligand in a 1:1 molar ratio in water. The pH of the solution was adjusted to 4.5 by adding aqueous NaOH. Violet prismatic crystals appeared on allowing the mother solution to stand at room temperature for a week.

Compound (1)

Crystal data

$Na[La(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$
$M_r = 594.23$
Orthorhombic
*Fdd*2
$a = 19.656$ (3) Å
$b = 35.939$ (2) Å
$c = 12.149$ (2) Å
$V = 8582$ (1) Å^3
$Z = 16$
$D_x = 1.839$ Mg m^{-3}
$D_m = 1.830$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CH_2BrCH_2Br$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20.56–22.93°$
$\mu = 2.081$ mm^{-1}
$T = 298$ K
Prismatic
0.4 × 0.3 × 0.3 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.79$, $T_{max} = 0.99$
2699 measured reflections
2440 independent reflections
2388 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 47$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 150 reflections intensity decay: 1.32%

Refinement

Refinement on *F*
$R = 0.027$
$wR = 0.034$
$S = 1.93$
2388 reflections
270 parameters
H atoms were not located
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$Na[Nd(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$
$M_r = 599.56$
Orthorhombic
*Fdd*2
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.79–13.13°$

$a = 19.543$ (5) Å
$b = 35.683$ (8) Å
$c = 12.142$ (5) Å
$V = 8467$ (3) Å^3
$Z = 16$
$D_x = 1.881$ Mg m^{-3}
$D_m = 1.865$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CH_2BrCH_2Br$

$\mu = 2.551$ mm^{-1}
$T = 298$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Violet

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.86$, $T_{max} = 1.00$
4082 measured reflections
3550 independent reflections
2246 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 46$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 150 reflections intensity decay: 4.15%

Refinement

Refinement on *F*
$R = 0.025$
$wR = 0.031$
$S = 1.56$
2246 reflections
270 parameters
H atoms were not located
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (3)

Crystal data

$Na[Eu(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$
$M_r = 607.28$
Orthorhombic
*Fdd*2
$a = 19.460$ (3) Å
$b = 35.583$ (3) Å
$c = 12.127$ (3) Å
$V = 8397$ (2) Å^3
$Z = 16$
$D_x = 1.921$ Mg m^{-3}
$D_m = 1.920$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CH_2BrCH_2Br$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.04$–$19.90°$
$\mu = 3.081$ mm^{-1}
$T = 298$ K
Prismatic
$0.4 \times 0.3 \times 0.2$ mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.91$, $T_{max} = 1.00$
2646 measured reflections
2339 independent reflections

2275 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 46$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 150 reflections intensity decay: 3.12%

Refinement

Refinement on *F*
$R = 0.028$
$wR = 0.032$
$S = 1.97$
2275 reflections
270 parameters
H atoms were not located
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
La	0.58397 (2)	0.346292 (9)	0.5	1.44 (1)
Na	0.6375 (2)	0.3686 (1)	0.1886 (3)	3.7 (2)
O(1)	0.5197 (2)	0.3345 (1)	0.6758 (4)	2.1 (2)
O(2)	0.5143 (3)	0.3274 (2)	0.8590 (4)	3.1 (2)
O(3)	0.7088 (2)	0.3306 (1)	0.4756 (4)	2.3 (2)
O(4)	0.8132 (3)	0.3245 (2)	0.5411 (5)	3.9 (3)
O(5)	0.4697 (2)	0.3294 (1)	0.4328 (4)	2.4 (2)
O(6)	0.4052 (3)	0.2860 (2)	0.3517 (6)	5.2 (4)
O(7)	0.5983 (3)	0.3168 (1)	0.3192 (4)	2.3 (2)
O(8)	0.6063 (4)	0.2676 (2)	0.2090 (5)	4.3 (3)
O(*W*1)	0.5008 (2)	0.4039 (1)	0.5175 (4)	2.2 (2)
O(*W*2)	0.6382 (3)	0.3929 (2)	0.6346 (5)	2.8 (2)
O(*W*3)	0.6371 (3)	0.3969 (1)	0.3810 (4)	2.2 (2)
O(*W*4)	0.5164 (5)	0.3868 (3)	0.196 (1)	10.6 (7)
O(*W*5)	0.6164 (6)	0.3219 (2)	0.0542 (7)	8.3 (5)
O(*W*6)	0.8947 (5)	0.3485 (2)	0.720 (1)	8.4 (6)
O(*W*7)	0.6864 (3)	0.2102 (2)	0.1492 (5)	3.6 (3)
O(*W*8)	0.7295 (7)	0.2150 (3)	−0.064 (1)	12.4 (9)
N(1)	0.6506 (3)	0.3068 (2)	0.6659 (5)	1.8 (2)
N(2)	0.5588 (3)	0.2712 (1)	0.4962 (6)	2.3 (2)
C(1)	0.5445 (3)	0.3258 (2)	0.7689 (6)	2.1 (3)
C(2)	0.6195 (3)	0.3133 (2)	0.7749 (6)	2.6 (3)
C(3)	0.7509 (3)	0.3252 (2)	0.5541 (6)	2.2 (3)
C(4)	0.7232 (3)	0.3193 (2)	0.6680 (6)	2.6 (3)
C(5)	0.4510 (4)	0.2956 (2)	0.4153 (6)	2.9 (3)
C(6)	0.4841 (4)	0.2652 (2)	0.4802 (7)	3.2 (4)
C(7)	0.6004 (4)	0.2822 (2)	0.3013 (6)	2.4 (3)
C(8)	0.5973 (5)	0.2557 (2)	0.4013 (7)	3.2 (4)
C(9)	0.6497 (4)	0.2661 (2)	0.6360 (7)	2.8 (3)
C(10)	0.5807 (4)	0.2531 (3)	0.6002 (7)	2.5 (3)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Nd	0.58343 (2)	0.345481 (9)	0.5	1.48 (1)
Na	0.6375 (2)	0.3681 (1)	0.1860 (3)	3.8 (2)
O(1)	0.5182 (3)	0.3350 (2)	0.6678 (4)	2.0 (2)
O(2)	0.5118 (3)	0.3277 (2)	0.8514 (5)	3.1 (3)
O(3)	0.7062 (3)	0.3307 (2)	0.4702 (4)	2.4 (2)
O(4)	0.8121 (3)	0.3236 (2)	0.5318 (5)	3.6 (3)
O(5)	0.4706 (3)	0.3306 (1)	0.4277 (5)	2.4 (2)
O(6)	0.4027 (4)	0.2885 (2)	0.3475 (7)	5.1 (4)
O(7)	0.5974 (3)	0.3173 (1)	0.3168 (4)	2.3 (2)
O(8)	0.6060 (4)	0.2683 (2)	0.2061 (5)	4.3 (3)
O(*W*1)	0.5016 (3)	0.4028 (1)	0.5143 (5)	2.3 (2)
O(*W*2)	0.6368 (3)	0.3916 (2)	0.6274 (5)	2.5 (3)
O(*W*3)	0.6345 (3)	0.3953 (1)	0.3788 (5)	2.1 (2)
O(*W*4)	0.5189 (5)	0.3878 (3)	0.176 (1)	11.0 (8)
O(*W*5)	0.6180 (6)	0.3211 (3)	0.0474 (7)	8.0 (5)
O(*W*6)	0.8969 (5)	0.3490 (2)	0.703 (1)	8.3 (6)
O(*W*7)	0.6866 (3)	0.2104 (2)	0.1458 (6)	3.6 (3)
O(*W*8)	0.7376 (8)	0.2142 (5)	−0.061 (1)	17 (1)
N(1)	0.6495 (3)	0.3067 (2)	0.6601 (5)	1.9 (3)
N(2)	0.5574 (3)	0.2716 (2)	0.4921 (7)	2.2 (2)
C(1)	0.5429 (3)	0.3263 (2)	0.7625 (7)	1.9 (3)

C(2)	0.6182 (4)	0.3140 (2)	0.7694 (6)	2.4 (3)
C(3)	0.7495 (4)	0.3249 (2)	0.5467 (6)	1.9 (3)
C(4)	0.7228 (4)	0.3194 (3)	0.6619 (7)	2.7 (3)
C(5)	0.4503 (4)	0.2969 (3)	0.4119 (7)	3.0 (4)
C(6)	0.4821 (4)	0.2663 (2)	0.4766 (8)	3.0 (4)
C(7)	0.5990 (4)	0.2829 (2)	0.2986 (7)	2.4 (3)
C(8)	0.5949 (6)	0.2557 (3)	0.3972 (8)	3.1 (4)
C(9)	0.6483 (4)	0.2656 (2)	0.6319 (7)	2.6 (3)
C(10)	0.5786 (4)	0.2528 (3)	0.5961 (8)	2.6 (4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (3)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Eu	0.58319 (2)	0.345070 (9)	0.5	1.26 (1)
Na	0.6378 (2)	0.3677 (1)	0.1867 (4)	3.5 (2)
O(1)	0.5181 (3)	0.3354 (2)	0.6649 (5)	1.8 (2)
O(2)	0.5101 (3)	0.3283 (2)	0.8474 (5)	3.0 (3)
O(3)	0.7043 (3)	0.3314 (2)	0.4689 (4)	2.2 (2)
O(4)	0.8115 (3)	0.3234 (2)	0.5284 (5)	3.4 (3)
O(5)	0.4716 (3)	0.3314 (2)	0.4277 (5)	2.2 (2)
O(6)	0.4014 (4)	0.2902 (2)	0.3473 (7)	5.0 (4)
O(7)	0.5970 (3)	0.3179 (2)	0.3180 (5)	2.3 (2)
O(8)	0.6060 (4)	0.2688 (2)	0.2059 (5)	3.8 (3)
O(*W*1)	0.5026 (3)	0.4020 (1)	0.5142 (5)	2.2 (2)
O(*W*2)	0.6356 (3)	0.3900 (2)	0.6256 (5)	2.4 (3)
O(*W*3)	0.6329 (3)	0.3943 (2)	0.3786 (5)	1.8 (2)
O(*W*4)	0.5204 (6)	0.3871 (3)	0.169 (1)	9.7 (8)
O(*W*5)	0.6189 (7)	0.3211 (3)	0.0469 (8)	7.4 (6)
O(*W*6)	0.8956 (6)	0.3490 (2)	0.696 (1)	8.0 (7)
O(*W*7)	0.6873 (4)	0.2101 (2)	0.1465 (6)	3.4 (3)
O(*W*8)	0.7391 (9)	0.2126 (5)	−0.060 (1)	16 (1)
N(1)	0.6489 (3)	0.3064 (2)	0.6594 (6)	1.7 (3)
N(2)	0.5564 (3)	0.2720 (2)	0.4915 (7)	2.0 (2)
C(1)	0.5418 (3)	0.3268 (2)	0.7578 (8)	1.8 (3)
C(2)	0.6167 (4)	0.3140 (2)	0.7670 (7)	2.2 (3)
C(3)	0.7487 (4)	0.3247 (2)	0.5444 (6)	2.0 (3)
C(4)	0.7221 (4)	0.3189 (3)	0.6597 (7)	2.4 (4)
C(5)	0.4499 (5)	0.2981 (3)	0.4100 (7)	2.6 (4)
C(6)	0.4808 (5)	0.2669 (2)	0.4760 (8)	2.9 (4)
C(7)	0.5991 (4)	0.2830 (2)	0.2988 (7)	2.2 (3)
C(8)	0.5937 (6)	0.2561 (3)	0.396 (1)	3.2 (5)
C(9)	0.6477 (4)	0.2658 (2)	0.6329 (7)	2.3 (3)
C(10)	0.5774 (5)	0.2528 (3)	0.5958 (9)	2.5 (4)

Table 4. *Selected geometric parameters* (Å, °) *for* (1)

La—O(1)	2.518 (5)	La—N(2)	2.743 (5)
La—O(3)	2.534 (4)	Na—O(5^{i})	2.472 (6)
La—O(5)	2.467 (5)	Na—O(7)	2.566 (6)
La—O(7)	2.455 (5)	Na—O(*W*1^{i})	2.555 (6)
La—O(*W*1)	2.646 (4)	Na—O(*W*3)	2.550 (6)
La—O(*W*2)	2.572 (5)	Na—O(*W*4)	2.47 (1)
La—O(*W*3)	2.548 (5)	Na—O(*W*5)	2.378 (9)
La—N(1)	2.792 (6)		
O(1)—La—O(3)	123.2 (2)	O(*W*1)—La—O(*W*2)	72.3 (2)
O(1)—La—O(5)	77.4 (2)	O(*W*1)—La—O(*W*3)	74.9 (2)
O(1)—La—O(7)	138.0 (2)	O(*W*1)—La—N(1)	129.0 (2)
O(1)—La—O(*W*1)	75.8 (2)	O(*W*1)—La—N(2)	131.3 (1)
O(1)—La—O(*W*2)	77.2 (2)	O(*W*2)—La—O(*W*3)	74.1 (2)
O(1)—La—O(*W*3)	143.9 (2)	O(*W*2)—La—N(1)	71.2 (2)
O(1)—La—N(1)	62.4 (2)	O(*W*2)—La—N(2)	136.5 (2)
O(1)—La—N(2)	76.0 (2)	O(*W*3)—La—N(1)	125.5 (2)
O(3)—La—O(5)	142.0 (2)	O(*W*3)—La—N(2)	140.1 (2)
O(3)—La—O(7)	71.9 (2)	N(1)—La—N(2)	66.2 (2)
O(3)—La—O(*W*1)	141.4 (2)	O(5^{i})—Na—O(7)	139.8 (2)
O(3)—La—O(*W*2)	79.5 (2)	O(5^{i})—Na—O(*W*1^{i})	71.4 (2)
O(3)—La—O(*W*3)	72.3 (2)	O(5^{i})—Na—O(*W*3)	74.1 (2)
O(3)—La—N(1)	61.1 (1)	O(5^{i})—Na—O(*W*4)	115.5 (3)
O(3)—La—N(2)	87.4 (2)	O(5^{i})—Na—O(*W*5)	129.0 (3)
O(5)—La—O(7)	72.6 (2)	O(7)—Na—O(*W*1^{i})	78.5 (2)
O(5)—La—O(*W*1)	69.9 (2)	O(7)—Na—O(*W*3)	73.8 (2)
O(5)—La—O(*W*2)	138.5 (2)	O(7)—Na—O(*W*4)	83.1 (3)
O(5)—La—O(*W*3)	111.2 (2)	O(7)—Na—O(*W*5)	81.9 (3)
O(5)—La—N(1)	122.7 (2)	O(*W*1^{i})—Na—O(*W*3)	77.6 (2)
O(5)—La—N(2)	65.7 (2)	O(*W*1^{i})—Na—O(*W*4)	155.6 (4)
O(7)—La—O(*W*1)	118.7 (2)	O(*W*1^{i})—Na—O(*W*5)	100.7 (3)
O(7)—La—O(*W*2)	143.4 (2)	O(*W*3)—Na—O(*W*4)	81.9 (4)
O(7)—La—O(*W*3)	75.8 (2)	O(*W*3)—Na—O(*W*5)	155.6 (3)
O(7)—La—N(1)	111.9 (2)	O(*W*4)—Na—O(*W*5)	92.5 (4)
O(7)—La—N(2)	65.2 (2)		
O(1)···O(*W*3^{ii})	2.745 (7)	O(8)···O(*W*7)	2.695 (9)
O(2)···O(*W*2^{ii})	2.717 (8)	O(*W*1)···O(*W*7^{v})	2.772 (7)
O(3)···O(*W*1^{i})	2.718 (7)	O(*W*3)···O(*W*7^{v})	2.703 (8)
O(4)···O(*W*2^{i})	2.676 (8)	O(*W*4)···O(*W*6^{iii})	2.78 (1)
O(4)···O(*W*6)	2.83 (1)	O(*W*4)···O(*W*8^{v})	2.81 (2)
O(6)···O(*W*6^{iii})	2.76 (1)	O(*W*7)···O(*W*8)	2.73 (1)
O(6)···O(*W*8^{iv})	2.84 (2)	O(*W*8)···O(*W*8^{vi})	2.64 (2)
O(8)···O(*W*5)	2.72 (1)		

Symmetry codes: (i) $\frac{1}{4}+x, \frac{3}{4}-y, z-\frac{1}{4}$; (ii) $x-\frac{1}{4}, \frac{3}{4}-y, \frac{1}{4}+z$; (iii) $x-\frac{1}{2}, y, z-\frac{1}{2}$; (iv) $1-x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{5}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; (vi) $\frac{3}{2}-x, \frac{1}{2}-y, z$.

Table 5. *Selected geometric parameters* (Å, °) *for* (2)

Nd—O(1)	2.432 (5)	Nd—N(2)	2.685 (5)
Nd—O(3)	2.483 (5)	Na—O(5^{i})	2.448 (6)
Nd—O(5)	2.432 (5)	Na—O(7)	2.535 (6)
Nd—O(7)	2.456 (5)	Na—O(*W*1^{i})	2.535 (6)
Nd—O(*W*1)	2.602 (5)	Na—O(*W*3)	2.534 (7)
Nd—O(*W*2)	2.487 (6)	Na—O(*W*4)	2.42 (1)
Nd—O(*W*3)	2.513 (5)	Na—O(*W*5)	2.408 (9)
Nd—N(1)	2.712 (6)		
O(1)—Nd—O(3)	126.6 (2)	O(*W*1)—Nd—O(*W*2)	72.3 (2)
O(1)—Nd—O(5)	78.1 (2)	O(*W*1)—Nd—O(*W*3)	74.2 (2)
O(1)—Nd—O(7)	138.9 (2)	O(*W*1)—Nd—N(1)	130.2 (2)
O(1)—Nd—O(*W*1)	75.1 (2)	O(*W*1)—Nd—N(2)	131.1 (2)
O(1)—Nd—O(*W*2)	78.5 (2)	O(*W*2)—Nd—O(*W*3)	74.4 (2)
O(1)—Nd—O(*W*3)	143.8 (2)	O(*W*2)—Nd—N(1)	72.0 (2)
O(1)—Nd—N(1)	64.6 (2)	O(*W*2)—Nd—N(2)	138.6 (2)
O(1)—Nd—N(2)	77.3 (2)	O(*W*3)—Nd—N(1)	126.2 (2)
O(3)—Nd—O(5)	141.0 (2)	O(*W*3)—Nd—N(2)	138.4 (2)
O(3)—Nd—O(7)	70.9 (2)	N(1)—Nd—N(2)	67.4 (2)
O(3)—Nd—O(*W*1)	140.5 (2)	O(5^{i})—Na—O(7)	139.9 (2)
O(3)—Nd—O(*W*2)	80.0 (2)	O(5^{i})—Na—O(*W*1^{i})	69.6 (2)
O(3)—Nd—O(*W*3)	71.4 (2)	O(5^{i})—Na—O(*W*3)	76.6 (2)
O(3)—Nd—N(1)	62.3 (2)	O(5^{i})—Na—O(*W*4)	114.6 (3)
O(3)—Nd—N(2)	88.2 (2)	O(5^{i})—Na—O(*W*5)	126.7 (3)
O(5)—Nd—O(7)	71.6 (2)	O(7)—Na—O(*W*1^{i})	80.0 (2)
O(5)—Nd—O(*W*1)	68.8 (2)	O(7)—Na—O(*W*3)	71.8 (2)
O(5)—Nd—O(*W*2)	138.5 (2)	O(7)—Na—O(*W*4)	86.7 (3)
O(5)—Nd—O(*W*3)	107.6 (2)	O(7)—Na—O(*W*5)	83.7 (3)
O(5)—Nd—N(1)	125.4 (2)	O(*W*1^{i})—Na—O(*W*3)	77.7 (2)
O(5)—Nd—N(2)	66.5 (2)	O(*W*1^{i})—Na—O(*W*4)	160.7 (4)
O(7)—Nd—O(*W*1)	116.7 (2)	O(*W*1^{i})—Na—O(*W*5)	101.3 (3)
O(7)—Nd—O(*W*2)	141.9 (2)	O(*W*3)—Na—O(*W*4)	85.0 (4)
O(7)—Nd—O(*W*3)	73.4 (2)	O(*W*3)—Na—O(*W*5)	155.3 (3)
O(7)—Nd—N(1)	112.8 (2)	O(*W*4)—Na—O(*W*5)	90.9 (5)
O(7)—Nd—N(2)	65.6 (2)		
O(1)···O(*W*3^{ii})	2.747 (8)	O(8)···O(*W*7)	2.698 (9)
O(2)···O(*W*2^{ii})	2.696 (8)	O(*W*1)···O(*W*7^{v})	2.786 (8)
O(3)···O(*W*1^{i})	2.718 (8)	O(*W*3)···O(*W*7^{v})	2.716 (8)
O(4)···O(*W*2^{i})	2.682 (8)	O(*W*4)···O(*W*6^{iii})	2.78 (1)
O(4)···O(*W*6)	2.81 (1)	O(*W*4)···O(*W*8^{v})	2.736 (2)
O(6)···O(*W*6^{iii})	2.78 (1)	O(*W*7)···O(*W*8)	2.71 (1)
O(6)···O(*W*8^{iv})	2.96 (2)	O(*W*8)···O(*W*8^{vi})	2.60 (3)
O(8)···O(*W*5)	2.70 (1)		

Symmetry codes: (i) $\frac{1}{4}+x, \frac{3}{4}-y, z-\frac{1}{4}$; (ii) $x-\frac{1}{4}, \frac{3}{4}-y, \frac{1}{4}+z$; (iii) $x-\frac{1}{2}, y, z-\frac{1}{2}$; (iv) $1-x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{5}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; (vi) $\frac{3}{2}-x, \frac{1}{2}-y, z$.

Table 6. *Selected geometric parameters* (Å, °) *for* (3)

Eu—O(1)	2.391 (6)	Eu—N(2)	2.653 (6)
Eu—O(3)	2.436 (5)	Na—O(5^{i})	2.438 (7)
Eu—O(5)	2.392 (5)	Na—O(7)	2.514 (7)
Eu—O(7)	2.425 (6)	Na—O(*W*1^{i})	2.524 (7)
Eu—O(*W*1)	2.566 (5)	Na—O(*W*3)	2.515 (7)
Eu—O(*W*2)	2.432 (6)	Na—O(*W*4)	2.40 (1)

Eu—O(*W*3)	2.484 (5)	Na—O(*W*5)	2.40 (1)
Eu—N(1)	2.695 (7)		
O(1)—Eu—O(3)	127.8 (2)	O(*W*1)—Eu—O(*W*2)	72.3 (2)
O(1)—Eu—O(5)	78.3 (2)	O(*W*1)—Eu—O(*W*3)	73.8 (2)
O(1)—Eu—O(7)	139.7 (2)	O(*W*1)—Eu—N(1)	130.1 (2)
O(1)—Eu—O(*W*1)	74.6 (2)	O(*W*1)—Eu—N(2)	130.9 (2)
O(1)—Eu—O(*W*2)	78.0 (2)	O(*W*2)—Eu—O(*W*3)	75.2 (2)
O(1)—Eu—O(*W*3)	143.4 (2)	O(*W*2)—Eu—N(1)	71.8 (2)
O(1)—Eu—N(1)	65.0 (2)	O(*W*2)—Eu—N(2)	138.6 (2)
O(1)—Eu—N(2)	77.7 (2)	O(*W*3)—Eu—N(1)	126.9 (2)
O(3)—Eu—O(5)	141.3 (2)	O(*W*3)—Eu—N(2)	138.1 (2)
O(3)—Eu—O(7)	70.9 (2)	N(1)—Eu—N(2)	67.7 (2)
O(3)—Eu—O(*W*1)	139.4 (2)	O(5')—Na—O(7)	139.8 (3)
O(3)—Eu—O(*W*2)	79.8 (2)	O(5')—Na—O(*W*1')	68.3 (2)
O(3)—Eu—O(*W*3)	70.9 (2)	O(5')—Na—O(*W*3)	77.8 (2)
O(3)—Eu—N(1)	63.2 (2)	O(5')—Na—O(*W*5)	125.7 (3)
O(3)—Eu—N(2)	89.3 (2)	O(5')—Na—O(*W*4)	114.9 (3)
O(5)—Eu—O(7)	71.7 (2)	O(7)—Na—O(*W*1')	81.2 (2)
O(5)—Eu—O(*W*1)	68.3 (2)	O(7)—Na—O(*W*3)	70.5 (2)
O(5)—Eu—O(*W*2)	138.1 (2)	O(7)—Na—O(*W*4)	87.6 (4)
O(5)—Eu—O(*W*3)	106.2 (2)	O(7)—Na—O(*W*5)	84.9 (3)
O(5)—Eu—N(1)	126.2 (2)	O(*W*1')—Na—O(*W*3)	78.0 (2)
O(5)—Eu—N(2)	66.9 (2)	O(*W*1')—Na—O(*W*4)	163.3 (5)
O(7)—Eu—O(*W*1)	116.3 (2)	O(*W*1')—Na—O(*W*5)	102.0 (4)
O(7)—Eu—O(*W*2)	141.8 (2)	O(*W*3)—Na—O(*W*4)	86.6 (4)
O(7)—Eu—O(*W*3)	72.5 (2)	O(*W*3)—Na—O(*W*5)	155.2 (3)
O(7)—Eu—N(1)	113.4 (2)	O(*W*4)—Na—O(*W*5)	89.3 (5)
O(7)—Eu—N(2)	66.1 (2)		
O(1)···O(*W*3^{ii})	2.764 (8)	O(8)···O(*W*7)	2.72 (1)
O(2)···O(*W*2^{ii})	2.696 (9)	O(*W*1)···O(*W*7^{v})	2.772 (8)
O(3)···O(*W*1^{i})	2.721 (8)	O(*W*3)···O(*W*7^{v})	2.719 (8)
O(4)···O(*W*2^{i})	2.684 (9)	O(*W*4)···O(*W*6^{iii})	2.80 (2)
O(4)···O(*W*6)	2.76 (1)	O(*W*4)···O(*W*8^{v})	2.71 (2)
O(6)···O(*W*6^{iii})	2.78 (1)	O(*W*7)···O(*W*8)	2.70 (2)
O(6)···O(*W*8^{iv})	2.96 (2)	O(*W*8)···O(*W*8^{vi})	2.69 (4)
O(8)···O(*W*5)	2.69 (1)		

Symmetry codes: (i) $\frac{1}{4}+x, \frac{3}{4}-y, z-\frac{1}{4}$; (ii) $x-\frac{1}{4}, \frac{3}{4}-y, \frac{1}{4}+z$; (iii) $x-\frac{1}{2}, y, z-\frac{1}{2}$; (iv) $1-x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{5}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; (vi) $\frac{3}{2}-x, \frac{1}{2}-y, z$.

The structures were solved by Patterson and Fourier techniques using *DIRDIF* (Beurskens *et al.*, 1992). All non-H atoms were refined anisotropically (*SAPI*91; Fan, 1991). H atoms were not located. Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Phenylpiperazinium Trichloromercurate

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Abstract

The structure of *N*-phenylpiperazinium trichloromercurate, $(C_{10}H_{15}N_2)[HgCl_3]$, consists of isolated bitetrahedral $[Hg_2Cl_6]^{2-}$ units, di-μ-chloro-bis(dichloromercury), sharing one edge, with two short bonds of 2.346 (7) and 2.365 (7) Å, and two long bonds of 2.852 (5) and 2.624 (7) Å. The organic cation, $(C_{10}H_{15}N_2)^+$, is located between the $[Hg_2Cl_6]^{2-}$ units. The phenylpiperazinium groups are connected to the Hg_2Cl_6 dimer by hydrogen bonds to the Cl atoms.

Comment

The reaction of substituted ammonium halogenides with metal halogenides leads to a series of compounds of the general formula RMX_3, with R being an alkyl or aryl substituent, M a divalent metal and X = Cl, Br, I.

These substances exhibit interesting structural and physical properties such as ferroelectricity {*e.g.* $[N(CH_3)_4][HgBr_3]$ (White, 1963) and (CH_3NH_3)-$[HgCl_3]$ (Ben Salah, Bats, Kalus, Fuess & Daoud, 1982)}.