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# Short Communications

## $Na_3[Nd(OCOCH_2OCH_2OCO)_3]$ — a Case of 9-Coordination

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In a study of the thermodynamic properties of rare earth complexes, Grenthe [1,2] has determined the amounts and the compositions of the complexes formed in solution between various lanthanoids and diglycolate, $OCOCH_2OCH_2OCO^{2-}$, or dipicolinate, $OCOC_5H_3NOCO^{2-}$. Mononuclear complexes of high stability are formed and the maximum value of $\bar{n}$ is three, *i.e.* only the species $MA_1$, $MA_2$, and $MA_3$ are formed. Both ligands have three possible coordinating groups and presumably they act as tridentate ligands. The central lanthanoid ions must thus possess at least nine coordinating sites. In order to establish the coordination in these complexes, sodium salts of $[Nd(diglyc)_3]^{3-}$, $[Nd(dipic)_3]^{3-}$, and $[Er(diglyc)_3]^{3-}$ have been isolated from solutions with $\bar{n} = 3$ and examined using X-ray diffraction methods.

In a first setting, $Na_3[Nd(diglyc)_3]$ seemed to be monoclinic with space group $F2$, but as the structure determination proceeded it was found that a higher symmetry should be adopted, and a set of trigonal axes was ultimately found. The systematically absent reflexions were $hkl$ with $-h + k + l \neq 3n$ and the diffraction symmetry was $\bar{3}m$. The possible space groups are thus, $R32$ (No. 155), $R3m$ (No. 160), and $R\bar{3}m$ (No. 166). Space group $R32$ is most compatible with reasonable molecular structures and has been chosen.

The unit cell dimensions are $a = 9.78$ Å and $c = 28.56$ Å. Chemical analyses show that the compound has the formula $Na_3[Nd(diglyc)_3]\cdot 6H_2O$. There are three formula units in the elementary cell.

Placing the neodymium atoms in the positions 3*a* (000; 1/3 2/3 2/3; 2/3 1/3 1/3) a three-dimensional Fourier synthesis, $\varrho_{obs}$, was undertaken using a programme written for the Saab D21 computer.[3,4] From this synthesis, probable positions of all the atoms, except the water oxygen,

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*Table 1.* Approximate atomic parameters in $Na_3[Nd(OCOCH_2OCH_2OCO)_3]$, space group $R32$ (No. 155).

| Atom | Group | Positions | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|
| $Nd_1$ | | 3 *a* | 0 | 0 | 0 |
| $Na_1$ | | 9 *e* | 0.285 | 0.285 | 1/2 |
| $O_1$ | C–O–C | 9 *d* | 0.745 | 0 | 0 |
| $O_{10}$ | $-COO^-$ | 18 *f* | 0.976 | 0.174 | 0.054 |
| $O_{28}$ | $-COO^-$ | 18 *f* | 0.842 | 0.254 | 0.105 |
| $C_1$ | $-CH_2-$ | 18 *f* | 0.921 | 0.623 | 0.046 |
| $C_{19}$ | $-COO^-$ | 18 *f* | 0.827 | 0.151 | 0.057 |

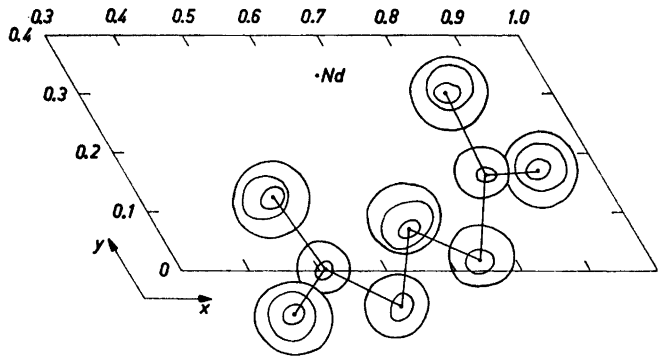


*Fig. 1.* Part of the electron density in a composite diagram on (001) showing one third of the coordination around the neodymium atom at 2/3 1/3 1/3. The contours are drawn at an interval of 2 e/Å$^3$, the zero contour being omitted.

were found. The values of the parameters were improved by difference syntheses, $\varrho_{obs}-\varrho_{calc}$, and partial least square treatments. The obtained positions are collected in Table 1. Good agreement is obtained between the calculated and observed structure factors, the $R$ factor being 0.23. A three-dimensional synthesis of $\varrho_{obs}$ was again undertaken using the improved parameters to calculate the phases. Fig. 1 shows part of $\varrho_{obs}$ in a composite diagram on (001). The species $[Nd(diglyc)_3]^{3-}$ contains a threefold axis and in a plane perpendicular to it a set of twofold axes, *i.e.* the molecular symmetry is $D_3$.

The coordination around the neodymium atom can be described in the following way. The three tridentate groups are located along three noncrossing edges of a distorted octahedron, the carboxyl oxygen atoms occupy positions in the corners of the octahedron, while the ethereal oxygen atoms are located in the middle of the octahedral edges. The preliminary determined value for the neodymium-carboxyl oxygen bond distance is 2.4 Å and for the neodymium-ethereal oxygen bond distance it is 2.5 Å. The molecular structure resembles that of $[Nd(H_2O)_9]^{3+}$, one of the few hitherto known 9-coordinated complexes.[5]

It has not yet proved possible to locate the water oxygen atoms even if it seems probable that they occupy positions around the sodium atoms. Another difficulty is that the unit cell lacks a centre of symmetry. Since we do not possess a least square programme which is suitable for hexagonal symmetries this causes a complete cycle of refinement to be very time-consuming.[6] However, transformation to rombohedral indices would seem to be promising since it diminishes the number of necessary parameters.

The crystal symmetry of $Na_3[Nd(dipic)_3]$ is triclinic but the coordination around the neodymium atom is the same as for the diglycolate compound. $Na_3[Er(diglyc)_3]$ has the same unit cell symmetry and dimensions as $Na_3[Nd(diglyc)_3]$ and the molecular structure is probably the same. The work on the compounds described in this paper will be continued, and investigations of related compounds are also planned.

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