On the Crystal Structure of the Neodymium Iminodiacetate Compound $Nd_2(C_4H_5O_4N)_3 \cdot 2HCl \cdot 7H_2O$

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In a research programme at this Institute a series of crystal structure analyses deals with compounds formed between the trivalent rare earth ions and the related dicarboxylate ligands oxydiacetate,[1] iminodiacetate, and thiodiacetate. This communication is a preliminary report of the crystal and molecular structure of $Nd_2(OCOCH_2NHCH_2OCO)_3 \cdot 2HCl \cdot 7H_2O$. This compound was obtained in an attempt to prepare $Nd(OCOCH_2NHCH_2OCO)Cl \cdot nH_2O$ according to Prutkova *et al.*[2]

Equimolar water solutions of $NdCl_3$ and $Nd_2(OCOCH_2NHCH_2OCO)_3$ were mixed and the solution obtained was evaporated to a syrup on a steam bath. Addition of ethanol resulted in a microcrystalline precipitate which was treated hydrothermally at 80°C in a sealed glass tube for three weeks. Stacks containing five to ten small single crystal plates were formed. The compound, $Nd_2(OCOCH_2NHCH_2OCO)_3 \cdot 2HCl \cdot 7H_2O$, crystallizes in the monoclinic system with the unit cell dimensions $a = 8.73$ Å, $b = 18.33$ Å, $c = 9.31$ Å, and $\beta = 105.8°$. The only systematically absent reflections, $0k0$ with $k \neq 2n$, indicate the space groups $P2_1$ or $P2_1/m$. The elementary cell contains two formula units.

The intensity of 1009 independent reflections of the layers $0kl - 5kl$ were measured visually using non-integrated Weissenberg photographs, taken with Cu$K\alpha$ radiation. The crystal specimen had the approximate dimensions $0.2 \times 0.05 \times 0.2$ mm³ and consisted of a stack of *ca.* 5, almost parallel plates, grown together in the *ac* plane. Because of this some of the recorded spots were split, but it was impossible to find a more suitable single crystal even from repeated preparations.

Trial positions of the neodymium atoms were deduced from a three-dimensional Patterson synthesis, computed with the data reduction and Fourier calculation program DRF.[3] The Nd—Nd vectors are those expected for the space group $P2_1/m$ which was thus chosen. The preliminary atomic coordinates and the isotropic tem-

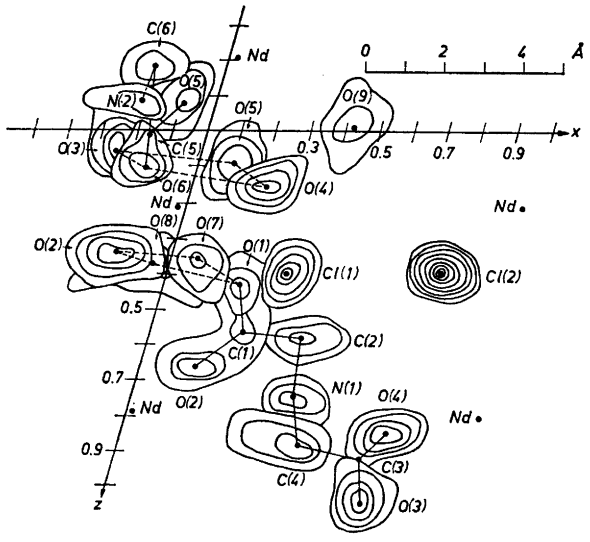

Fig. 1. Part of the electron density in a composite diagram on (010). The contours are drawn at an interval of 2 e/Å³, the zero contour being omitted.

Table 1. Approximate atomic parameters for the compound $Nd_2(OCOCH_2NHCH_2OCO)_3 \cdot 2HCl \cdot 7H_2O$. One water oxygen atom is not located. The space group is $P2_1/m$ (No. 11). B (Å^2) denotes the isotropic temperature factor.

Atom	Positions	Group	x	y	z	B
Nd	4(*f*)	—	−0.008	0.024	0.218	2.41
O(1)	4(*f*)	$-COO^-$	0.773	0.009	0.566	4.41
O(2)	4(*f*)	$-COO^-$	0.822	0.050	0.358	3.79
O(3)	4(*f*)	$-COO^-$	0.256	0.033	0.950	3.42
O(4)	4(*f*)	$-COO^-$	0.227	0.078	0.167	3.05
O(5)	4(*f*)	$-COO^-$	0.914	0.064	0.917	3.82
O(6)	4(*f*)	$-COO^-$	0.830	0.130	0.071	3.93
O(7)	4(*f*)	H_2O	0.066	0.138	0.373	3.94
O(8)	4(*f*)	H_2O	0.068	0.094	0.681	5.23
O(9)	2(*e*)	H_2O	0.446	0.250	−0.030	6.10
C(1)	4(*f*)	$-COO^-$	0.753	0.044	0.441	3.57
C(2)	4(*f*)	$-CH_2-$	0.573	0.081	0.409	3.21
C(3)	4(*f*)	$-COO^-$	0.297	0.062	0.081	2.73
C(4)	4(*f*)	$-CH_2-$	0.487	0.088	0.116	4.01
C(5)	4(*f*)	$-COO^-$	0.849	0.119	0.950	2.88
C(6)	4(*f*)	$-CH_2-$	0.781	0.181	0.823	4.79
N(1)	4(*f*)	$-NH_2^+-$	0.534	0.128	0.268	3.57
N(2)	2(*e*)	$-NH-$	0.782	0.250	0.913	4.33
Cl(1)	2(*e*)	—	0.360	0.250	0.410	6.37
Cl(2)	2(*e*)	—	0.811	0.250	0.400	5.01

perature factor for the neodymium atom were refined together with the inter-layer scale factors using the least-squares program LALS.[3] A three-dimensional ($F_o - F_c$) synthesis based upon the improved neodymium positions was then calculated. Fig. 1 gives part of the result in a composite diagram on (010).

By geometrical considerations, preliminary positions of the ligand molecules were obtained from the electron density maps. Three water oxygen and two chlorine atoms were then placed in the remaining five independent peaks. The parameters of the atoms and the scale factors were refined in a series of least-squares calculations. After five cycles the discrepancy index R was 0.16. The atomic parameters are given in Table 1.

Each neodymium ion is coordinated by six carboxylic and two water oxygen atoms at the distances 2.3−2.6 Å (Fig. 1). The coordination polyhedron might be described as a distorted square antiprism. The hydrogen atoms of the "HCl's" in $Nd_2(OCOCH_2NHCH_2OCO)_3 \cdot 2HCl \cdot 7H_2O$ are most probably bonded to nitrogen atoms in the structure which thus should contain both $-NH_2^+-$ and $-NH-$ groups. The $-NH_2^+-$ groups are formed by the nitrogen atoms N(1) in fourfold positions while the nitrogen atoms N(2) in twofold positions form $-NH-$ groups. The iminodiacetate ions which contain N(1) are holding the structure together in the *ac* plane and the ions containing N(2) in the direction of the *b* axis. Neither N(1) nor N(2) are coordinated to neodymium. The dimensions of the iminodiacetate ions are those expected from known intermolecular distances between C, N, and O.

It has not been possible to detect the remaining water oxygen atoms. Thermogravimetric measurements indicate, however, that this water is very loosely bonded and it seems thus to be located in the interstices of the structure. More intensity data are now being recorded, this time along [010]. The continued work will also include the structures of other lanthanoid-iminodiacetate compounds.

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Effect of Solvent on Molecular Complex Formation. Correlation of Energy and Free Energy of Solution

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Recent reports from our laboratories have outlined a method for predicting the effect of solvation on molecular complex formation reactions.[1-3] The technique makes it possible to correlate the thermodynamic properties of the donor (D), acceptor (A) and complex (DA) involved in equilibria such as D+A=DA by using a single parameter, α, defined by

$$\alpha = \frac{\Delta E^\circ_{DA}}{\Delta E^\circ_{D} + \Delta E^\circ_{A}} = \frac{\Delta H^\circ_{DA}}{\Delta H^\circ_{D} + \Delta H^\circ_{A}} \quad (1)$$

(all terms ΔE° and ΔH° are $v \rightarrow s$)

in which the ΔE° and ΔH° terms represent the changes in internal energy and enthalpy, respectively, for transferring one mole of a species (DA, D or A) from the ideal vapour phase (v) to the infinitely dilute solution in solvent (s). For several association reactions it has been shown that α varies only slightly with changes of solvent and that the analogous equation

$$\alpha = \frac{\Delta G^\circ_{DA}}{\Delta G^\circ_{D} + \Delta G^\circ_{A}} \quad (2)$$

($v \rightarrow s$)

may be used to relate Gibbs free energy data; where standard states of 1 mole per liter, ideal dilute solution are used for each component in the vapour and in the condensed phase. Interaction energy parameters inferred from lattice treatments of non-electrolyte solutions [4] have been successfully employed to predict in advance values of the useful parameter α.[3]

Consideration of the extensive collection of gas solubility data given by Hildebrand and Scott [5] leads us to suggest that under fairly general conditions ΔE_i° and ΔG_i° ($v \rightarrow s$) may be linearly related for a variety of solutes (i) in a given non-polar or slightly polar solvent. Data for four typical non-polar solvents at 25°, taken from Appendix 3 of Ref. 5 and a recent report by Dymond,[6] are plotted in Fig. 1 in the form ΔG_i° *vs.* ΔE_i°. The values have been calculated for the required 1 mole/liter standard states by converting from pressure units and mole fractions to molarities and correcting for the thermal expansion of the solvent. Data for each solvent appear to be linearly related, with slopes of 0.63, 0.62, 0.64, and 0.51 for the solvents benzene, cyclohexane, CCl_4, and perfluoroheptane, respectively.

That the plots in Fig. 1 are linear is not remarkable in view of the linearity of numerous plots of $\bar{S}_2 - S_2^g$ *vs.* $-R \ln x_2$ published by Hildebrand and Scott and their co-workers. However, use of the unit molarity standard states simplifies the correlation of thermodynamic data for associating species and facilitates the formulation of a method for predicting the effect of solvation on complex formation equilibria. If the molarity convention is employed, the equilibrium constant for distribution of a solute A between vapour and solvent, K=[A(solvent)]/[A(vapour)], is dimensionless and approaches the value unity at the critical temperature of the solvent. Both at 0°K and at the critical temperature, $\Delta G^\circ_A = \Delta E^\circ_A$ ($v \rightarrow s$).

It might have been anticipated that each line should pass through the origin, corresponding to zero change in both energy and free energy. However, at $\Delta E_i^\circ = 0$ ($v \rightarrow s$) the free energy change ranges from 400 to 500 cal/mole in the four solvents. Thus, the entropy of solution of a solute which dissolves with zero internal energy change