

Figure 1. Diagram showing that the coordination group of the bisnitrilotriacetatozirconate(IV) ion is of dodecahedral  $\text{Mo}(\text{CN})_8^{4-}$  type, but with the symmetry restricted (from  $D_{2d}$  to  $C_{2v}$ ). The chelation pattern of one nitrilotriacetate group is indicated; that of the other is generated by the twofold axis passing through the midpoints of two  $b$  edges (right front and left rear in the diagram).

ter, the *a priori* probability of cubic coordination in a discrete mononuclear complex is further diminished.

Orthorhombic, piezoelectrically active crystals, space group  $C_{2c}2$ , of the potassium salt were obtained from solutions prepared following Intorre and Martell.<sup>6</sup> A cell with  $a = 14.843 \pm 0.005$ ,  $b = 14.83 \pm 0.01$ , and  $c = 8.673 \pm 0.005$  Å., and containing, as proved by the structure analysis,  $4\text{K}_2\text{ZrA}_2 \cdot \text{H}_2\text{O}$  gives a calculated density of 1.984 g./cc. Intensity measurement utilized the stationary crystal-stationary counter technique with background evaluated for each reflection as the mean of the counts taken at  $2\theta \pm 1.2^\circ$ . Periodically checked reference reflections showed no significant changes of intensity with time. Approximately 2000 independent  $\{hkl\}$  reflections, some 87% of the geometrically possible total, were recorded with  $\text{Mo K}\alpha$  radiation for  $(\sin \theta)/\lambda < 0.81$ . The heavy atom method, with subsequent least-squares refinement of positional coordinates and anisotropic thermal parameters, gave the crystalline arrangement, for which  $R = 0.082$ .

(6) B. I. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 358 (1960).

(7) Author to whom correspondence should be addressed.

(8) Gulf Research and Development Co. Postgraduate Fellow, 1962–1963.

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### Structure and Bonding in a Ten-Coordinate Lanthanum(III) Chelate of Ethylenediaminetetraacetic Acid<sup>1</sup>

Sir:

Reaction of lanthanum carbonate with ethylenediaminetetraacetic acid (EDTA;  $\text{H}_4\text{A}$ ) yields a solution from which excellent monoclinic crystals of empirical composition  $\text{HLaA} \cdot 7\text{H}_2\text{O}$  are obtained by slow evaporation at room temperature. Accurate determination of the crystalline arrangement by X-ray analysis, as outlined below, leads to the structural formulation  $\text{La}(\text{OH}_2)_4\text{AH} \cdot 3\text{H}_2\text{O}$  for the solid and assigns the asymmetric ten-coordinate configuration shown in Figure 1

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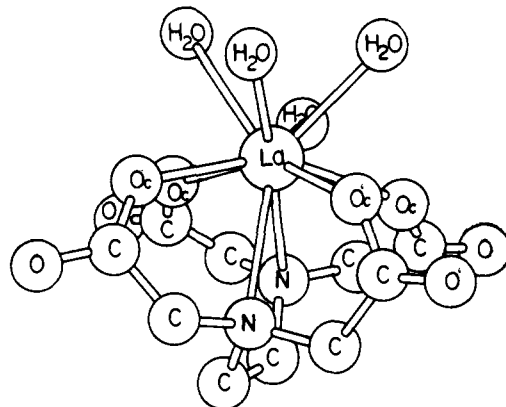


Figure 1. Scaled model in perspective of the  $\text{La}(\text{OH}_2)_4\text{AH}$  molecule. Two water molecules (front and rear), the lanthanum ion, and the two nitrogen atoms all lie in or near a plane which serves as a quasi-mirror for the coordination group. The positions,  $4\text{O}_c$ ,  $2\text{N}$ , and  $1\text{H}_2\text{O}$  (at rear), along with the mean position of the  $3\text{H}_2\text{O}$  at the top of the diagram, define the eight vertices of a dodecahedron of  $\text{Mo}(\text{CN})_8^{4-}$  type within which the  $\text{La}^{3+}$  ion is markedly off-center; the displacement (0.77 Å.) of  $\text{La}^{3+}$  from the plane of the  $4\text{O}_c$  trapezoid is responsible for the expansion into ten-coordination.  $\text{O}'$  is the oxygen atom carrying the acid hydrogen.

to the  $\text{La}(\text{OH}_2)_4\text{AH}$  molecule. This configuration, appearances to the contrary notwithstanding, exemplifies in full measure structural principles established in earlier studies of EDTA complexes. A summarizing principle, deduced from analysis of the octahedral  $\text{CoA}^-$  and  $\text{Ni}(\text{OH}_2)\text{AH}_2$  complexes,<sup>2</sup> and subsequently employed for successful *a priori* prediction<sup>3</sup> of the seven-coordinate nature of the  $\text{Mn}(\text{OH}_2)\text{A}^{2-}$  and  $\text{Fe}(\text{OH}_2)\text{A}^-$  ions,<sup>4</sup> tells us that the constraints attending multiple and multiply branched ring formation together with the effective size of the central atom take primary responsibility for the selection of coordination number and coordination polyhedron. A sexadentate EDTA complex in standard octahedral coordination (by which we mean only a six-coordinate recognizable approximation thereto) is feasible only for small central ions<sup>2</sup> and is quite impracticable—in any foreseen circumstances—for even the smallest ( $\text{Lu}^{3+}$ ) of the rare earth cations. The chelation framework, in this last case, may be able to reach as far as half-way around the central ion.

The four carboxylate oxygen atoms (designated as  $\text{O}_c$ ) which are complexed to  $\text{La}^{3+}$  (Figure 1) form a trapezoidal array that is planar within 0.01 Å., the lanthanum ion, however, lies 0.77 Å. out-of-plane on the side away from the nitrogen atoms, thus relegating the entire chelating agent to one hemisphere while leaving ample space for four water molecules in the other. Lanthanum and nitrogen positions define a plane which serves rather accurately as a quasi-mirror for the coordination group, but not so for the ethylene radical of the strongly puckered ethylenediamine ring. The two nitrogen and four  $\text{O}_c$  oxygen atoms along with one water molecule lie nearly at seven of the eight vertices required to define a (tetragonal  $D_{2d}$ ) dodecahedron of  $\text{Mo}(\text{CN})_8^{4-}$

(2) (a) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959); (b) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

(3) J. L. Hoard, G. S. Smith, and M. Lind in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, pp. 296–302.

(4) (a) S. N. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); (b) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964).

type; displacement, as specified above, of the over-large  $\text{La}^{3+}$  from a central position is responsible for the expansion into the previously unheard of ten-coordination group. (How the substitution of smaller rare ions for  $\text{La}^{3+}$  can modify this configuration for the better is discussed in the accompanying communication.<sup>6</sup>) The nine-coordination group<sup>7</sup> of  $D_{3h}$  symmetry, the uniquely satisfactory choice<sup>8</sup> for  $\text{La}^{3+}$  in unconstrained circumstances, is quite unadapted to meet the stereochemical requirements of the chelating agent.

Of the four carboxylate oxygen atoms ( $\text{O}_u$ ) which are not complexed by  $\text{La}^{3+}$ , the one carrying the acid hydrogen can be identified from the bonding data which follow. (Standard deviations for individual bond lengths are 0.0030–0.0035 Å. for  $\text{La}-\text{O}_c$ ,  $\text{La}-\text{OH}_2$ , and  $\text{La}-\text{N}$ ; 0.004–0.006 Å. for  $\text{C}-\text{O}_c$  and  $\text{C}-\text{O}_u$ .) The averaged length, with mean deviation, for three of the four  $\text{La}-\text{O}_c$  bonds is 2.537 (0.007) Å., and the corresponding data for the associated  $\text{C}-\text{O}_c$  and  $\text{C}-\text{O}_u$  bonds are, respectively, 1.261 (0.008) and 1.249 (0.004) Å.; this nearly trivial lengthening (0.012 Å.) of  $\text{C}-\text{O}_c$  over  $\text{C}-\text{O}_u$  bonds reflects the extremely weak complexing<sup>9</sup> to  $\text{La}^{3+}$ . The fourth  $\text{La}-\text{O}_c$  bond length of 2.609 Å. is accompanied by  $\text{O}_c-\text{C} = 1.210$  and  $\text{C}-\text{O}_u = 1.288$  Å., and, additionally, by an apparent hydrogen bond,  $\text{O}_u\text{H}\cdots\text{OH}_2$  (external) = 2.603 Å., which is too short unless, in gratifying agreement with all of the other data, the proton used belongs to the  $\text{O}_u$  atom rather than to the water molecule.<sup>10</sup> The averaged length of the  $\text{La}-\text{OH}_2$  bonds, 2.592 (0.037) Å., is little, if any, shorter than the weakest  $\text{La}-\text{O}_c$  bond (2.609 Å.) involving quasi-carbonyl oxygen, while the  $\text{La}-\text{N}$  distance of 2.865 (0.055) Å. bespeaks weak interaction.

Both the asymmetric configuration and the detailed pattern of bond distances strongly suggest that electrostatic interactions assume the primary role in the bonding. The near identity of the  $\text{C}-\text{O}_c$  and  $\text{C}-\text{O}_u$  bond lengths in the most strongly complexed carboxylate groups suggests little electron withdrawal by  $\text{La}^{3+}$ . The  $\text{La}-\text{OH}_2$  and  $\text{La}-\text{N}$  distances, involving uncharged but electrically unsymmetrical ligands, fall into line. Removal of the acid hydrogen to give the anion is accompanied by a general shrinkage<sup>6</sup> which appears to agree in detail with an electrostatic formulation.<sup>6</sup>

The monoclinic crystals, space group  $P2_1/a$ , have  $a = 11.85 \pm 0.01$ ,  $b = 18.08 \pm 0.02$ , and  $c = 8.80 \pm 0.01$  Å.;  $\beta = 91.75 \pm 0.10^\circ$ ; the cell contains  $4\text{LaAH} \cdot 7\text{H}_2\text{O}$  to give the calculated density, 1.953 g./cc. (that measured is 1.955 g./cc.). Intensity measurement utilized  $\text{Mo K}\alpha$  radiation in the stationary crystal-stationary counter technique with background evaluated for each reflection as the mean of the counts taken at  $2\theta \pm 1.2^\circ$ . (Intensity data were collected for the potassium salt<sup>6</sup> concurrently.) Crystals of  $\text{LaAH} \cdot 7\text{H}_2\text{O}$  displayed superior stability during measurement (at  $85^\circ\text{F}$ .); refer-

(5) (a) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963); (b) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **51**, 2853 (1939).

(6) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, **87**, 1612 (1965).

(7) As observed for  $\text{Nd}(\text{OH}_2)_9^{3+}$  by L. Helmholz, *ibid.*, **61**, 1544 (1939).

(8) Cf. L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, Chapter 13.

(9) That the rare earth-EDTA complexes owe their large stability constants to entropy effects is well known; see ref. 6 for references to original papers.

(10) We anticipate that the infrared absorption spectrum of the crystals (to be recorded) will show features which are commonly interpreted in terms of a free  $\cdot\text{CH}_2\text{COOH}$  arm in the molecule.

ence reflections showed no significant changes of intensity with time. The heavy atom method with least-squares refinement of positional coordinates and anisotropic thermal parameters gave the crystalline arrangement.  $R = 0.059$  for the 5028 independent  $\{hkl\}$  recorded for  $(\sin \theta)/\lambda < 0.70$ .

(11) Gulf Research and Development Co. Postgraduate Fellow, 1964–1965.

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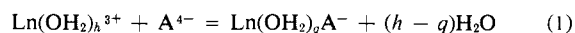
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## On the Structure-Dependent Behavior of Ethylenediaminetetraacetate Complexes of the Rare Earth $\text{Ln}^{3+}$ Ions<sup>1</sup>

Sir:

Complexing of rare earth  $\text{Ln}^{3+}$  ions by ethylenediaminetetraacetate ( $\text{A}^{4-}$ ) ion in aqueous solution (eq. 1)



carries  $\log K$  values which, as measured by Schwarzenbach, *et al.*,<sup>2</sup> range from 15.50 to 19.83 for  $\text{La}^{3+} \dots \text{Lu}^{3+}$ ; both the substantial magnitudes of the constants and the monotonic increase of  $\log K$  with atomic number of  $\text{Ln}^{3+}$  are associated thermodynamically with controllably large entropies of formation.<sup>3</sup> Cogent reasons for anticipating  $q \geq 2$  in a bulky  $\text{Ln}(\text{OH}_2)_q\text{A}^-$  ion of little or no symmetry are provided in the concurrent report<sup>4</sup> on the ten-coordinate  $\text{La}(\text{OH}_2)_4\text{AH}$  molecule; the asymmetric nine-coordinate  $\text{La}(\text{OH}_2)_3\text{A}^-$  ion (Figure 1), as it is shown, as outlined below, to exist in the potassium salt,  $\text{KLaA} \cdot 8\text{H}_2\text{O}$ , is described herein. Average hydration numbers ( $h$ ) approaching nine for  $\text{La}^{3+}$  and eight for  $\text{Lu}^{3+}$  are probable on both theoretical<sup>5</sup> and experimental<sup>6</sup> grounds of long standing. Thus  $h - q$  in reaction 1 can still be large ( $\approx 6$ ), as the dominating  $\Delta S^\circ$  of reaction would seem to demand.

We report first that exploratory X-ray study together with density measurement and piezoelectric testing of eight salts representative of the usual type formula,  $\text{MLnA} \cdot 8\text{H}_2\text{O}$ , shows that potassium salts with  $\text{Ln} = \text{La}$ ,  $\text{Nd}$ , or  $\text{Gd}$ , sodium salts with  $\text{Ln} = \text{Nd}$ ,  $\text{Tb}$ , or  $\text{Er}$ , and ammonium salts with  $\text{Ln} = \text{Nd}$  or  $\text{Gd}$  all crystallize in the space group  $\text{Fdd}2$  with sixteen-molecule units of comparable and similarly ordered dimensions. This apparent isomorphism, astonishing in its indifference to the choice of univalent cation, clearly is to be charged to the presence of asymmetric chelated

(1) Support of the National Science Foundation, the National Institutes of Health of the Public Health Service, and the Advanced Research Projects Agency is gratefully acknowledged. We thank also the Cornell Computing Center, John W. Rudan, Director.

(2) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

(3) (a) L. A. K. Staveland and T. Randall, *Discussions Faraday Soc.*, **26**, 157 (1958); (b) R. H. Betts and O. F. Dahlinger, *Can. J. Chem.*, **37**, 91 (1959); (c) J. L. Mackey, J. E. Powell, and F. H. Spedding, *J. Am. Chem. Soc.*, **84**, 2047 (1962).

(4) M. D. Lind, B. Lee, and J. L. Hoard, *ibid.*, **87**, 1611 (1965).

(5) Cf. L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, Chapter 13, and references cited therein.

(6) L. Helmholz, *J. Am. Chem. Soc.*, **61**, 1544 (1939), demonstrated the elegantly nine-coordinate nature of  $\text{Nd}(\text{OH}_2)_9^{3+}$  in the crystalline bromate.  $\text{Lu}(\text{III})$  must be effectively larger than the isoelectronic  $\text{Hf}(\text{IV})$  which forms numerous complexes based upon  $\text{MO}_6$  coordination.