type ; displacement, as specified above, of the overlarge 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 La^{3+} can modify this configuration for the better is discussed in the accompanying communication.[6]) The nine-coordination group[7] of D_{3h} symmetry, the uniquely satisfactory choice[8] for La^{3+} in unconstrained circumstances, is quite unadapted to meet the stereochemical requirements of the chelating agent.

Of the four carboxylate oxygen atoms (O_u) which are not complexed by 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 $La-O_c$, $La-OH_2$, and $La-N$; 0.004–0.006 Å. for $C-O_c$ and $C-O_u$.) The averaged length, with mean deviation, for three of the four $La-O_c$ bonds is 2.537 (0.007) Å., and the corresponding data for the associated $C-O_c$ and $C-O_u$ bonds are, respectively, 1.261 (0.008) and 1.249 (0.004) Å.; this nearly trivial lengthening (0.012 Å.) of $C-O_c$ over $C-O_u$ bonds reflects the extremely weak complexing[9] to La^{3+}. The fourth $La-O_c$ bond length of 2.609 Å. is accompanied by $O_c-C = 1.210$ and $C-O_u = 1.288$ Å., and, additionally, by an apparent hydrogen bond, $O_uH\cdots$ 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 O_u atom rather than to the water molecule.[10] The averaged length of the $La-OH_2$ bonds, 2.592 (0.037) Å., is little, if any, shorter than the weakest $La-O_c$ bond (2.609 Å.) involving quasi-carbonyl oxygen, while the $La-N$ 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 $C-O_c$ and $C-O_u$ bond lengths in the most strongly complexed carboxylate groups suggests little electron withdrawal by La^{3+}. The $La-OH_2$ and $La-N$ 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[6] which appears to agree in detail with an electrostatic formulation.[6]

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.; $\beta = 91.75 \pm 0.10°$; the cell contains $4LaAH \cdot 7H_2O$ to give the calculated density, 1.953 g./cc. (that measured is 1.955 g./cc.). Intensity measurement utilized 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 $2\theta \pm 1.2°$. (Intensity data were collected for the potassium salt[6] concurrently.) Crystals of $LaAH \cdot 7H_2O$ displayed superior stability during measurement (at 85°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 $Nd(OH_2)_9^{3+}$ 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 $\cdot CH_2COOH$ 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 $(\sin \theta)/\lambda < 0.70$.

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On the Structure-Dependent Behavior of Ethylenediaminetetraacetato Complexes of the Rare Earth Ln^{3+} Ions[1]

Sir:

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

$$Ln(OH_2)_h{}^{3+} + A^{4-} = Ln(OH_2)_qA^- + (h - q)H_2O \qquad (1)$$

carries log K values which, as measured by Schwarzenbach, *et al.*,[2] range from 15.50 to 19.83 for $La^{3+}\ldots Lu^{3+}$; both the substantial magnitudes of the constants and the monotonic increase of log K with atomic number of Ln^{3+} are associated thermodynamically with controllingly large entropies of formation.[3] Cogent reasons for anticipating $q \geq 2$ in a bulky $Ln(OH_2)_qA^-$ ion of little or no symmetry are provided in the concurrent report[4] on the ten-coordinate $La(OH_2)_4AH$ molecule; the asymmetric nine-coordinate $La(OH_2)_3A^-$ ion (Figure 1), as it is shown, as outlined below, to exist in the potassium salt, $KLaA \cdot 8H_2O$, is described herein. Average hydration numbers (h) approaching nine for La^{3+} and eight for Lu^{3+} are probable on both theoretical[5] and experimental[6] grounds of long standing. Thus $h - q$ in reaction 1 can still be large $(\cong 6)$, as the dominating $\Delta S°$ 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, $MLnA \cdot 8H_2O$, shows that potassium salts with $Ln =$ La, Nd, or Gd, sodium salts with $Ln =$ Nd, Tb, or Er, and ammonium salts with $Ln =$ Nd or Gd all crystallize in the space group $Fdd2$ 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

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

(3) (a) L. A. K. Stavely 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 $Nd(OH_2)_9^{3+}$ in the crystalline bromate. Lu(III) must be effectively larger than the isoelectronic Hf(IV) which forms numerous complexes based upon MO_8 coordination.

anions which are at once so bulky and so retentive of a shape-determining chelation pattern (specifically, that found in $La(OH_2)_3A^-$ and illustrated in Figure 1) as to fix the basic character of the very general crystalline framework. Our observations further suggest that the f-electrons of Ln^{3+} have no voice in determining gross configuration or the pattern of primary bonding.[7]

The chelation pattern in $La(OH_2)_3A^-$ is basically the same as that described[4] for $La(OH_2)_4AH$, but loss of H^+ from the ten-coordinate molecule is accompanied by a significant tightening of all chelating linkages and rejection of one water molecule. Thus the displacement of La^{3+} from the mean plane of the trapezoidal array of four complexed O_c atoms (Figure 1) becomes 0.60 Å. in $La(OH_2)_3A^-$, a decrease of 0.17 Å., and the averaged La–N distance becomes 2.755 Å., a decrease of 0.110 Å. (Standard deviations are 0.005–0.006 Å. for individual La–N, La–O_c, and La–OH_2 bond lengths in $La(OH_2)_3A^-$, approximately twice those in $La(OH_2)_4$-AH.) The averaged length of four La–O_c bonds is 2.507 Å. in $La(OH_2)_3A^-$, significantly less than the 2.537- and the 2.555-Å. averages for, respectively, three and four La–O_c links in $La(OH_2)_4AH$. The average of three La–OH_2 distances, 2.580 Å., in the anion, by contrast, is only slightly less than the 2.592 Å. for four distances in the neutral molecule. We observe that the pattern of bond distances for the two EDTA chelates of La^{3+} correlates very well with a simple electrostatic model for the bonding interactions.

Replacement of La^{3+} in the $La(OH_2)_3A^-$ configuration by successively smaller Ln^{3+} ions should produce a general shrinkage of the anion with, in particular, a closer approach of Ln^{3+} to the mean plane of the $4O_c$ atoms. Consideration of relative ionic sizes then suggests that about half-way along in the sequence La^{3+}...Lu^{3+}, transition from nine-coordinate $Ln(OH_2)_3A^-$ to eight-coordinate $Ln(OH_2)_2A^-$ (of evidently dodecahedral type) should occur. Recalling that maintenance of the chelation framework in the anion permits the accommodation of $M^+ = Na^+$, K^+, or NH_4^+ within the general $MLnA \cdot 8H_2O$ crystalline arrangement, we surmise that it allows also the shifts in positions of water molecules required for the transition in coordination type. Change from a nine- to an eight-coordinate $Ln(OH_2)_qA^-$ in reaction 1 increases $h - q$ by unity, which we associate with a sharp increase in the standard entropy, and decreases q by unity to give a less favorable standard enthalpy. Examination of existing thermodynamic data[3] suggests that such effects occur—not all at once nor free of perturbations from (differential) crystal field interactions[7]— within the sequence Sm^{3+}...Tb^{3+}; we judge that the chelates of Eu^{3+} and Gd^{3+} are transitional in coordination type between a nine-coordinate $Sm(OH_2)_3A^-$ and an eight-coordinate $Tb(OH_2)_2A^-$. As a first test of this conclusion we are presently collecting three-dimensional X-ray intensity data from a single crystal of $NaTbA \cdot 8H_2O$ preliminary to determination of structure.

Orthorhombic piezoelectrically active crystals, space group Fdd2, of $KLa(OH_2)_3A \cdot 5H_2O$ have $a = 19.82 \pm 0.02$, $b = 36.18 \pm 0.03$, and $c = 12.24 \pm 0.01$ A.;

(7) Crystal field stabilization by f-electrons probably is substantial, but, for reaction 1, it is just the difference of such stabilizations in $Ln(OH_2)_qA^-$ and $Ln(OH_2)_h^{3+}$ which contributes to the enthalpy of formation.
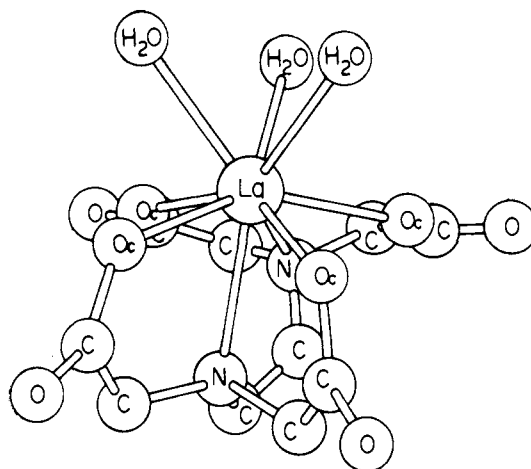

Figure 1. Scaled model of the $La(OH_2)_3A^-$ ion seen in perspective. The plane of the lanthanum and two nitrogen atoms serves as a quasi-mirror for the coordination group. H_2O (in the quasi-mirror), 2N, and $4O_c$ positions are at seven of the eight vertices of a dodecahedron of $Mo(CN)_8^{4-}$ type within which La^{3+} is off-center, i.e., out-of-plane from the $4O_c$ trapezoid, by 0.60 Å. The fourth water molecule present in $La(OH_2)_4AH$ has moved out of the primary coordination sphere of $La(OH_2)_3A^-$, but it remains nearby in the $KLa(OH_2)_3A \cdot 5H_2O$ crystalline arrangement.

the cell contains $16KLnA \cdot 8H_2O$ to give a calculated density of 1.847 g./cc. (that measured is 1.840 g./cc.). The technique of intensity measurement and the methods of structure analysis were as specified in the concurrent report[4] for $La(OH_2)_4AH \cdot 3H_2O$—excepting that only the 1977 independent $\{hkl\}$ recordable for $(\sin \theta)/\lambda < 0.60$ have thus far been used for structural refinement; $R = 0.065$.

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Tricyclic Norbornyl Analogs[1]

Sir:

We wish to draw attention to some of the novel geometric features in compound 1, which may be regarded as two superposed norbornyl frameworks and in which substituent Z is at the same time exo to one norbornyl unit and endo to the other. Interchange of the two groups (H and Z) at C-2 produces neither a diastereomer nor an enantiomer, but a molecule superposable on the original; i.e., 1a = 1b.

In norbornyl systems the rates of solvolysis of exo-substituted molecules exceed those of the corresponding endo analogs,[2] but disagreement persists whether these differences are attributable to abnormally high exo rates (due to anchimeric assistance)[3] or to abnormally

(2) For a perceptive review see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.
(3) S. Winstein and D. Trifan, J. Am. Chem. Soc., 74, 1147, 1154 (1952).