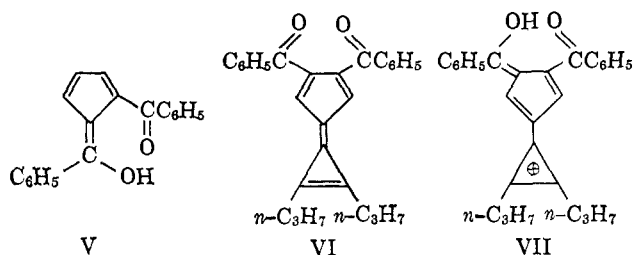


protons and the two equivalent propyl groups, a two-proton *singlet* at  $\tau$  3.25. The ultraviolet spectrum of the diketone VI in either cyclohexane or acetonitrile showed maxima at  $346\text{ m}\mu$  ( $\log \epsilon$  4.34) and  $255\text{ m}\mu$  ( $\log \epsilon$  4.25), but in hydrogen-bonding solvents (*e.g.*, methanol) there was observed a moderate bathochromic shift to  $361\text{ m}\mu$  ( $\log \epsilon$  4.35) and  $260\text{ m}\mu$  ( $\log \epsilon$  4.32). As a vinylogous cyclopropanone the diketone VI was reversibly converted by aqueous acid to a yellow cation [ $\lambda_{\text{max}}^{12\text{NHC1}}$   $430\text{ m}\mu$  ( $\log \epsilon$  4.36) and  $402\text{ m}\mu$  ( $\log \epsilon$  4.37)], provisionally represented as VII on the basis of its simple n.m.r. spectrum which showed a symmetrical molecule lacking new carbon-bound hydrogen. Spectrophotometric determination of the base strength of VI in aqueous hydrochloric acid (isosbestic point at  $385\text{ m}\mu$  ( $\log \epsilon$  4.32)) showed that half-protonation occurred at  $H_0 = -2.0 \pm 0.3$ , which makes this substance slightly more basic than diphenylcyclopropanone.<sup>9</sup>



Preliminary studies indicate that the present synthesis can be extended to utilize still simpler cyclopentadiene nucleophiles. Details of this work and further observations bearing on the "aromaticity" of the calicene system will be presented shortly.

(9) Half-protonation of diphenylcyclopropanone occurs at  $H_0 = -2.5 \pm 0.3$  (unpublished observations from this laboratory).

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### Stereochemistry of the Eight-Coordinate Bisnitrilotriacetatozirconate(IV) Ion<sup>1</sup>

Sir:

Stability of the bisnitrilotriacetatozirconate(IV) ion (to be written  $\text{ZrA}_2^{2-}$ ) clearly is dependent upon a mutual accommodation of the joint requirements of multidentate chelation and eight-coordination. Of the several constraints imposed upon branching glycinate ring formation which emerge from studies of ethylenediaminetetraacetato chelates,<sup>2</sup> we cite just two: the ring span, defined as the separation of the complexed nitrogen and oxygen atoms in the ring (or as the edge of the coordination polyhedron thereby spanned), should lie in the range  $2.66 \pm 0.06\text{ \AA}$ .; and the bond angles at nitrogen should be  $109.5 \pm 4^\circ$ . Experience further indicates that only the square ( $D_{4d}$ ) antiprism and the tetragonal ( $D_{2d}$ ) dodecahedron of  $\text{Mo}(\text{CN})_8^{4-}$

type are acceptable eight-coordination polyhedra.<sup>3</sup> For  $\text{ZrA}_2^{2-}$ , nonetheless, an apparently strong *a priori* case for quasi-cubic coordination can be put together from individually plausible considerations.

Maintenance of threefold symmetry in the disposition of the three glycinate rings branching from each nitrogen atom would lead quite naturally to the simplest possible configuration for a  $\text{ZrA}_2^{2-}$  complex—a configuration of  $C_{3i-3}$  symmetry<sup>4</sup> observing the required ring constraints while based upon a quasi-cubic coordination group. Chemical experience, in contrast with approximate bonding theory, would suggest very weak and, consequently, very long Zr–N bonds; a flattened octahedral  $\text{ZrO}_6$  group would become the heart of the configuration, and neither the practical availability nor the doubtful merits of f-orbitals for bonding<sup>5</sup> would be of real concern.

Structure determination for the crystalline potassium salt by means of the three-dimensional X-ray analysis described briefly in the final paragraph provides an unequivocal answer to the question of coordination type. The configuration of  $\text{ZrA}_2^{2-}$ , as indicated by Figure 1, is firmly based upon the dodecahedral coordination group<sup>3</sup>; the symmetry of  $C_{2-2}$ , allowed by the pattern of ring connexities, is required in the crystal. In rather surprisingly close agreement with expectations<sup>3</sup> listed for the case of monodentate ligands, the Zr–O<sub>A</sub> bonds ( $2.251\text{ \AA}$ .) are significantly longer than the Zr–O<sub>B</sub> links ( $2.124, 2.136\text{ \AA}$ .), and the eight *g* edges (averaging  $2.785\text{ \AA}$ .) are significantly longer than the four *m* edges (averaging  $2.62\text{ \AA}$ .) and the two *a* edges ( $2.68\text{ \AA}$ .). By far the largest distortion of the coordination group from an effectively higher symmetry is that produced by the extraordinarily long Zr–N bonds ( $2.439\text{ \AA}$ .). (Standard deviations of  $0.007\text{--}0.008\text{ \AA}$ . for individual Zr–O and Zr–N bond lengths and  $0.010\text{--}0.013\text{ \AA}$ . for individual polyhedron edges, *i.e.*, ring spans, apply in the noncentrosymmetric crystalline arrangement.) Ring spans are  $2.62, 2.68,$  and  $2.75\text{ \AA}$ ., of which the last corresponds to a naturally long *g* edge of the coordination polyhedron. The observed configuration is unique among the possible stereoisomeric types in its maximal use of short ring spans. Averaged angles, with accompanying mean deviations, at nitrogen are  $108.1 \pm 0.4^\circ$  within rings and  $110.8 \pm 0.1^\circ$  between rings.

With the full panoply of 4d and 5sp<sup>3</sup> orbitals of Zr(IV) available for bonding, it is not at all apparent from present approximate theory why the interaction of Zr(IV) with amino nitrogen should be so weak. Although the hypothetical quasi-cubic configuration for  $\text{ZrA}_2^{2-}$  would seem to gain relatively by virtue of the weak Zr–N interactions, it remains definitely inferior to the dodecahedral configuration in respect to steric repulsions—a property nearly independent of the assumed bonding type. Using methods outlined earlier,<sup>3</sup> we estimate that it would cost the  $\text{ZrA}_2^{2-}$  ion an additional 9–10 kcal./mole in ligand repulsive energy to transform from dodecahedral to quasi-cubic coordination. With each definitive study of the mat-

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

(2) Cf. M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964), and earlier papers cited therein.

(3) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963), give complete descriptions and a critical comparison of the eight-coordination polyhedra.

(4) It is readily demonstrable that for so large a central atom the glycinate ring must be nonplanar, thus precluding the higher symmetry of  $D_{3d-3m}$ .

(5) Cf. G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

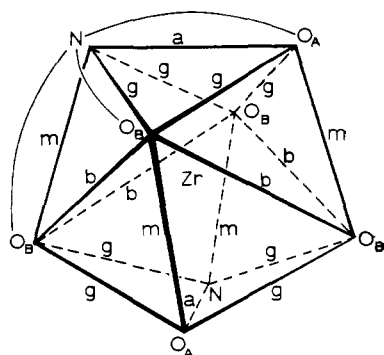


Figure 1. Diagram showing that the coordination group of the bisnitrilotriacetatozirconate(IV) ion is of dodecahedral  $\text{Mo}(\text{CN})_8^{4-}$  type, but with the symmetry restricted (from  $D_{2d}$  to  $C_{2v}$ ). The chelation pattern of one nitrilotriacetate group is indicated; that of the 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

(1) Support by 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.

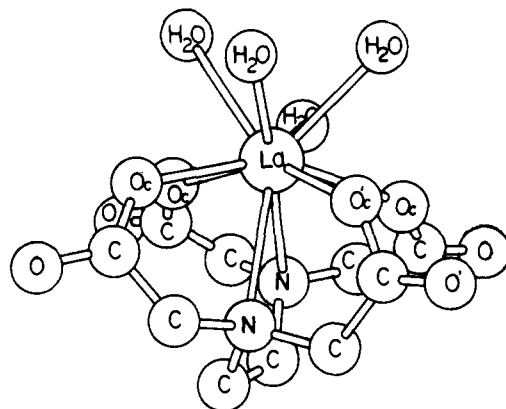


Figure 1. Scaled model in perspective of the  $\text{La}(\text{OH}_2)_4\text{AH}$  molecule. Two water molecules (front and rear), the lanthanum ion, and the two nitrogen atoms all lie in or near a plane which serves as a quasi-mirror for the coordination group. The positions,  $4\text{O}_c$ ,  $2\text{N}$ , 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).