characteristic of their respective anions. The following assignments are made by comparison with those reported by Schrauzer for his macrocycle[5] (990, 1010 cm^{-1}, B–F stretch; 1105, 1250 cm^{-1}, N–O stretch; 815, 1205 cm^{-1}, B–O stretch; 1375, 1430 cm^{-1}, $-CH_3$ deformations; 1623 cm^{-1}, C=N stretch).

The pmr spectrum of $[CoL]BF_4$ in acetonitrile consists of a singlet (0.5-cps half-width) at 34.3 cps downfield from the methyl resonance of the solvent. The equivalency predicted for the methyl groups (see Figure 1) is thereby demonstrated subject to the limit of resolution of the nmr spectrometer. The fluorine (^{19}F) magnetic resonance spectra also tend to confirm the structure in that (1) the splitting attributed to the boron of the terminal B–F units is observed,[20] and (2) corroborative evidence of the proposed formulation is obtained from relative intensity data. The spectrum for each salt in acetonitrile consists of a quartet (J_{B-F} = 17.3 ± 0.5 cps) upfield 957 and 5418 cps, respectively, from the characteristic fluorine resonances of BF_4^- and PF_6^-. Integration by use of a time-averaging computer gives a 1:2.1 ratio for the areas of the BF and BF_4^- resonances of $[CoL]BF_4$ (calcd, 1:2).

Further support for the proposed structure is found in the results from molecular weight determinations and from conductivity measurements. In acetonitrile the apparent molecular weights of the BF_4^- and PF_6^- salts are 278 ± 15 and 303 ± 15 (calcd: $[CoL]BF_4/2$, 273.6; $[CoL]PF_6/2$, 302.7). Conductivity measurements were made at 25° for acetonitrile and acetone solutions, and the equivalent conductances were calculated from these data using the molecular weight values which had been authenticated by the determinations mentioned above (found in acetonitrile: $[CoL]BF_4$ at 2.49×10^{-3} *M*, Λ_e = 140.6 ohm^{-1} $equiv^{-1}$ cm^2; $[CoL]PF_6$ at 9.30×10^{-4} *M*, Λ_e = 146.6 ohm^{-1} $equiv^{-1}$ cm^2). For 10^{-3} *M* solutions typical values of Λ_e range from 130 to 160 ohm^{-1} $equiv^{-1}$ cm^2.[21] In acetone, a plot of conductivity as a function of dilution (Λ *vs.* $\sqrt{C}$) resulted in a straight line typical of the classical Onsager limiting law for strong electrolytes. The slope of the line is 982 which is to be compared with 1000 observed for the uniunivalent electrolyte KI.[22] The equivalent conductance at infinite dilution (Λ_o) is 173 ohm^{-1} $equiv^{-1}$ cm^2, well within the range expected for such an electrolyte (157–190 ohm^{-1} $equiv^{-1}$ cm^2).[23]

The visible region of the electronic spectrum of $[CoL]BF_4$ in acetonitrile is dominated by the low-energy portion of an intense absorption whose maximum is in the ultraviolet. There is also a small shoulder (~21,370 cm^{-1} (ϵ ~500)) on this portion of the ultraviolet peak. Clearly no simple ligand field arguments can be applied to these data in order to extract bonding or symmetry information about the complex.

Acknowledgments. The authors are grateful to Mr. B. J. Nist for his invaluable aid in obtaining and interpreting the nmr spectra. The support of the National Science Foundation (GP-8524) is gratefully acknowledged.

(20) E. Fluck, "Anorganische und Allgemeine Chemie in Einzeldarstellungen," Band V, Springer-Verlag OHG, Berlin, 1963, p 163.

(21) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(22) S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p 93.

(23) M. J. McDowell and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 3293 (1951).

(24) Person to whom correspondence should be directed.

David R. Boston, Norman J. Rose[24]
Chemistry Department, University of Washington
Seattle, Washington 98105
Received September 20, 1968

Evidence for a "Proton Chelate" in Aqueous Salts of *dl*-Propylenediaminetetraacetic Acid

Sir:

There has been considerable discussion in regard to the conformations of salts of ethylenediaminetetraacetic acid (EDTA) and analogous polyaminocarboxylate compounds in aqueous solution at various pH values.[1–8] A knowledge of the conformations of these ligands is an important aid to understanding the thermodynamics and kinetics of their reactions. Various authors[1,3,7,8] have presented evidence in support of the suggestion that in monoprotonated salts of EDTA (HY^{3-}) and its homologs, the acidic proton is shared among several donor atoms in what might be termed a "proton chelate."

Recently we reported nmr studies of the conformations of aqueous salts of *dl*-propylenediaminetetraacetic acid (PDTA) which illustrate the power of this technique in detecting the presence of chelates—even the weakest of the alkali metal chelates.[9] Now we present conclusive evidence that monoprotonated PDTA (HL^{3-}) exists virtually completely in the *gauche* conformation with respect to the central carbon–carbon bond (as shown in I), and is thus a "proton chelate." Although complete information on the bonding and the conformations of carboxylate groups is lacking, the *gauche* conformation would not be favored in the absence of chelation involving both ends of the molecule.[9,9a] It is known that the acidic proton in HL^{3-} undergoes rapid exchange (mean lifetime is maximum ~10^{-3} sec), spending approximately 50% of its time on each of the nitrogen atoms.[10] In structure I the acidic proton is, therefore, bonded to one nitrogen atom and connected with dotted lines to the opposite nitrogen atom and its two

(1) G. Schwarzenbach and H. Ackerman, *Helv. Chim. Acta*, **30**, 1798 (1947).

(2) D. C. Olson and D. W. Margerum, *J. Amer. Chem. Soc.*, **82**, 5602 (1960).

(3) D. W. Rogers, D. A. Aikens, and C. N. Reilley, *J. Phys. Chem.*, **66**, 1582 (1962).

(4) D. T. Sawyer and J. E. Tackett, *J. Amer. Chem. Soc.*, **85**, 314 (1963).

(5) J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, **3**, 304 (1964).

(6) M. Eigen and W. Kruse, *Z. Naturforsch.*, 18, 857 (1963).

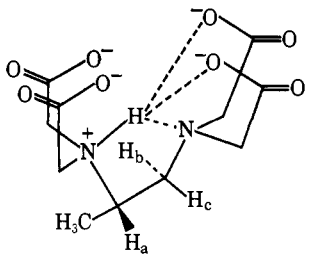
(7) D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, 3645 (1963).

(8) Y. Fujiwara and C. N. Reilley, *Anal. Chem.*, 40, 890 (1968).

(9) J. L. Sudmeier and A. J. Senzel, *ibid.*, **40**, 1693 (1968).

(9a) NOTE ADDED IN PROOF. As a result of the increased sum of J_{ab} and J_{ac} due to electronegativity effects in the present work, the values of J_{trans} (dihedral angle = 180°) and J_{gauche} (dihedral angle = 60°) employed in calculating formation constants (K_f) of chelates of monovalent cations have been reduced by an appropriate factor. This removes the undesirable result of having equal populations of rotamers IIa and IIIa in the absence of chelation as in the previous report.[9] Values of J_{trans} = 10.2 Hz and J_{gauche} = 3.0 Hz lead to ~0% rotamer IIa at probe temperature (35°) in Cs_4PDTA. The new values of K_f based on these assumptions are as follows: for KPDTA, 1.5 at 100° and 5.7 at 35°; for $[(CH_3)_4N]PDTA$, 0.10 at 100°; and for RbPDTA, 0.16 at 100°.

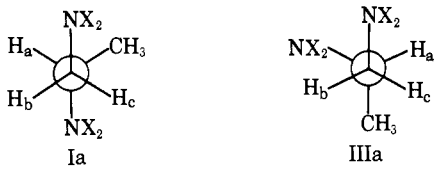
(10) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).



I

adjacent carboxylate groups. This structure is not intended to imply knowledge of a tetracoordinate proton or a tetrafurcated hydrogen bond, but merely to suggest that either the opposite nitrogen atom or carboxylate groups, or any combination of them in rapid alternation, are involved in some kind of chelate formation.

As reported earlier,[9] in the absence of chelation (*e.g.*, in the tetracesium salt at pH ~13), L^{4-} exists ~75% in the *anti* conformation (Ia) and ~25% in the *gauche* conformations (IIIa). In chelates, however, only IIIa is present to any appreciable extent, because Ia is geo-



Ia IIIa

$X = CH_2COO^-$

metrically unsuitable for chelation and IIa (not shown) has unfavorable steric interactions, with the methyl group being axial to the chelate ring.[11] Determination of the relative abundances of Ia, IIa, and IIIa is based upon a knowledge of spin coupling constants J_{ab} and J_{ac} in each of these forms, which was obtained with the aid of the Karplus equation[12] and spin coupling constants from a well-known stable chelate, CaL^{2-}. That is, assuming CaL^{2-} exists entirely as IIIa (which appears to be justified), and that the increased electronegativity of Ca^{2+} causes slightly larger vicinal coupling constants than those found in chelates of monovalent cations, spin coupling constants of 10.2 and 3.0 Hz for dihedral angles of 180 and 60°, respectively, are obtained.

In the present work, solutions of Cs_4L and K_4L (pH ~13) were gradually acidified until solutions of Cs_3HL and K_3HL (pH ~8) were obtained, and the nmr spectra at various stages were recorded on a Varian HA-100 spectrometer. The $NCH(CH_3)CH_2N$ portion of the ligand yields $ABCX_3$ patterns which were analyzed with the aid of the IBM 360-91 computer and the program LAOCOON III.[13] Because the x (methyl) protons exhibit negligible spin coupling to the b and c (methylene) protons, the analysis was carried out as a three-spin (ABC) case. This permitted the use of the optimization capabilities of the program (part II) in fitting the observed b and c resonances [the a (methine) proton was obscured by other lines]. By this method, values of J_{ab} and J_{ac} were obtained whose standard

(11) R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).

(12) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(13) An improved version of the program is described by S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 8363 (1964).

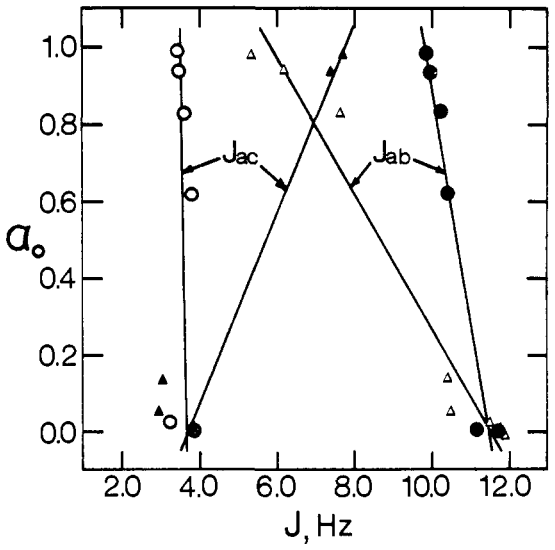


Figure 1. Vicinal spin coupling constants of cesium and potassium salts of *dl*-propylenediaminetetraacetic acid at various α_0 values: ▲ = J_{ac} in Cs_4L, Δ = J_{ab} in Cs_4L, ○ = J_{ac} in K_4L, ● = J_{ab} in K_4L.

deviations were far smaller than, and hence limited by, the accuracy of measuring line positions (~±0.5 Hz).

Figure 1 gives J_{ab} and J_{ac} at various values of α_0, the fraction of the ligand present as the tetraanion, L^{4-}. The chemical shift values of protons a, b, and c, respectively, in ppm *vs.* sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) are as follows: for Cs_4L, 3.20, 2.737, and 2.392; for Cs_3HL, 3.51, 2.894, and 3.007; for K_4L, 3.06, 2.591, and 2.085; for K_3HL, 3.45, 2.860, and 2.960 (note the crossover of b and c in both cases). The chemical shifts of protons b and c are accurate to ~±0.5 Hz, while the chemical shifts of proton a, which fortunately have negligible effect on the values of J_{ab} and J_{ac}, are accurate to only ~±5 Hz. The optimal value of the geminal spin coupling constant J_{bc} was ~ −13.5 Hz in L^{4-} and was ~ −14.5 Hz in HL^{3-}.

In the cesium case, J_{ab} shows a dramatic increase and J_{ac} shows a dramatic decrease in going from Cs_4L (α_0 = 1) to Cs_3HL (α_0 = 0), proving that the ligand undergoes a change in conformation from mainly *anti* (Ia) to virtually completely *gauche* (IIIa). There are three overlapping data points in Figure 1 for J_{ac} at α_0 = 0, all represented by contiguous black triangles. The values of J_{ab} and J_{ac} in the latter species (11.8 and 3.8 Hz) are larger than those found in CaL^{2-}, and are probably caused not by conformational changes, but merely by the increased electronegativity of protonated amino groups.[14]

In the potassium case, smaller changes in J_{ab} and J_{ac} were observed, as would be expected, in going from what is almost entirely a potassium chelate at α_0 = 1[9] to a "proton chelate" at α_0 = 0. The small increases in both J_{ab} and J_{ac} probably reflect electronegativity changes, and thus one can conclude only that the "proton chelate" is *at least* as stable as the potassium chelate (K_f = 5.7), although it could be many orders of magnitude more stable. The fact that J_{ab} and J_{ac} are identical for both Cs_3HL and K_3HL (at α_0 = 0) appears to discredit the existence of a 2:1 mixed chelate involving both K^+ and H^+ in the same PDTA molecule.

(14) J. L. Sudmeier, *J. Phys. Chem.*, **72**, 2344 (1968).

Acknowledgment. This work was supported by National Institutes of Health Grant No. AM-10889.

(15) National Defense Education Act Fellow, 1967–1970.

James L. Sudmeier, Alan J. Senzel[15]
Contribution No. 2289, Department of Chemistry
University of California, Los Angeles, California 90024
Received September 9, 1968

Structure of the New Boron Hydride $B_{16}H_{20}$

Sir:

The pyrolysis of $B_9H_{13}S(CH_3)_2$ has recently been shown[1] to yield a mixture of boranes, including a new compound characterized as $B_{16}H_{20}$. We report here preliminary results of an X-ray diffraction study of this compound, which we find to be the first structurally characterized neutral borane without molecular symmetry.

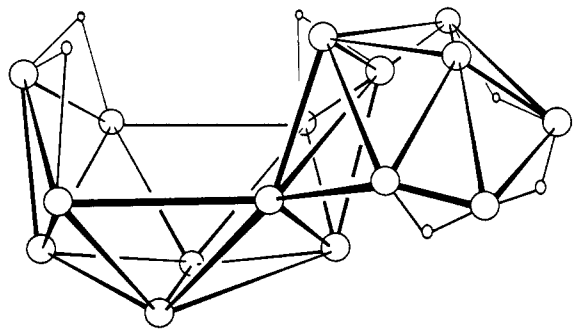


Figure 1. Structure of $B_{16}H_{20}$. Terminal hydrogen atoms are not included in the drawing.

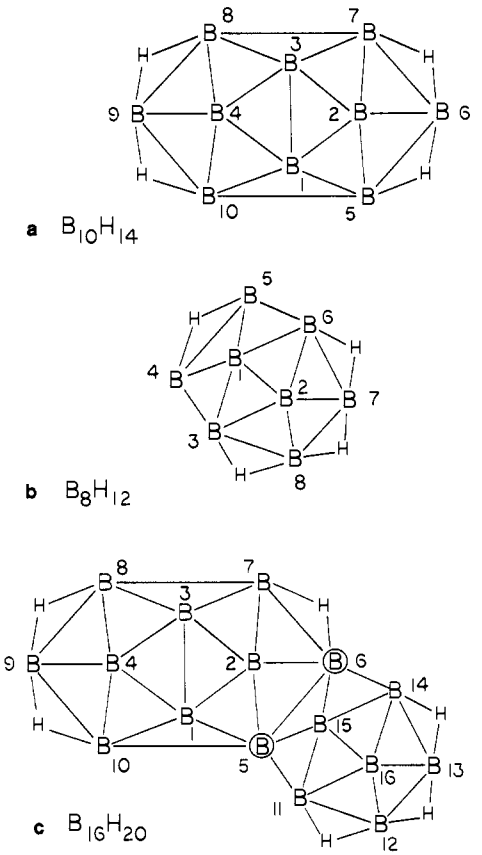


Figure 2. Projection drawings and numbering schemes for (a) $B_{10}H_{14}$, (b) B_8H_{12}, (c) $B_{16}H_{20}$. One terminal hydrogen atom has been omitted from each boron atom except for the encircled B-5 and B-6 of $C_{16}H_{20}$, which do not have terminal hydrogen atoms.

A small sample of $B_{16}H_{20}$ was supplied by Drs. Jaromír Plešek and Stanislav Heřmánek of the Institute of Inorganic Chemistry, Prague-Řež, Czechoslovakia. Single crystals were grown by sublimation and were found to belong to the monoclinic space group C_{2h}^5-$P2_1/c$. The assumption that the unit cell with dimensions $a = 5.85 \pm 0.01$, $b = 13.67 \pm 0.02$, $c = 16.75 \pm 0.03$ Å, $\beta = 100° 50' \pm 5'$ contains four molecules of $B_{16}H_{20}$ leads to a calculated crystal density of 0.98 g cm^{-3}. This value is in reasonable agreement with experimental measurements (flotation technique) which bracket the density between 0.94 and 1.00 g cm^{-3}. The high solubility of the compound and the limited amount of sample preclude a more accurate density determination.

Intensities of diffraction maxima were measured on a Picker automated X-ray diffractometer, and the boron positions were found by iterative application of Sayre's equation[2] using the multiple solution program of Long[3] which had been appropriately modified for the local computer. All hydrogen atoms were located unambiguously in a three-dimensional electron density map from which the contribution of the boron atoms had been subtracted. At the current stage of refinement, with isotropic thermal parameters, the conventional crystallographic discrepancy factor, R, is 0.08 for the 1059 observations.

The boron framework, illustrated in Figure 1, may be described as a B_{10} icosahedral fragment which shares an edge with a B_8 fragment in such a way that the two fragments open in opposite directions. It is convenient to regard the $B_{16}H_{20}$ molecule as a $B_{10}H_{14}$ unit[4] and a B_8H_{12} unit[5] with the shared edge consisting of B-5 and B-6 from $B_{10}H_{14}$ and B-4 and B-5 from B_8H_{12}. The symmetry observed for $B_{10}H_{14}$ and for B_8H_{12} is lost in the unsymmetrical fusion of the two units. There are six bridging hydrogen atoms in $B_{16}H_{20}$, three of which occupy positions corresponding to those found in $B_{10}H_{14}$, and the other three occupying positions corresponding to those in B_8H_{12}. Projection drawings of $B_{16}H_{20}$, $B_{10}H_{14}$, and B_8H_{12} are included in Figure 2.

The 14 terminal hydrogen atoms of $B_{16}H_{20}$ are distributed one per boron atom, with the two boron atoms (B-5 and B-6) connecting the two icosahedral fragments lacking terminal hydrogens. The B–B bond distances are in the range from 1.7 to 1.8 Å, except for the B-5–B-6 value of 1.68 Å, which compares well with the corresponding value of 1.67 Å in the B_8H_{12} molecule,[5] and the predictably[4,6] large values of 1.91 and 2.02 Å

(1) J. Plesek, S. Hermanek, B. Stíbr, and F. Hanousek, *Collection Czech. Chem. Commun.*, **32**, 1095 (1967); **33**, 699 (1968).
(2) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).
(3) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), UCLA, 1965.
(4) J. S. Kapser, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950).
(5) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964); *Inorg. Chem.* **3**, 1659 (1964).
(6) (a) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963); (b) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **39**, 2339 (1963).