Kinetics and mechanism of base hydrolysis of (.alpha..beta.S)–(salicylato)(tetraethylenepentamine)cobalt(III) ion

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a function of entering ligand and of the nature of the axial phosphines.

In Figure 1, the room-temperature, UV–vis toluene-solution spectra of complexes **1a–c** are presented. The lowest energy absorptions range from 489 nm for **1c** to 417 nm for **1b**, with the low energy band for **1a** at 428 nm. The position of the lowest energy transition in each of these complexes is relatively insensitive to solvent medium. This fact, as well as the moderate ϵ of this absorption, suggests that this band is predominently metal-centered d–d in origin. Several metal-centered d–d transitions are possible for the idealized C_{2v} structure which results from viewing the η^2-CS_2 group as a monodentate, spherical ligand. The increased quantum efficiency with increasing frequency of irradiating light may be the result of excitation of higher energy d–d states or may represent enhanced lability due to involvement of charge-transfer excited states. We have initiated detailed spectroscopic studies of **1** and related complexes in order to provide a more complete assignment of the lowest energy bands.

Registry No. 1a, 72557-49-4; **1b**, 64424-66-4; **1c**, 64424-68-6; **2a**, 78672-45-4; **2b**, 78672-46-5; **3a**, 78685-04-8; **3b**, 78685-05-9; Fe-(CO)$_2$(PEt$_3$)$_3$, 14837-55-9.

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Kinetics and Mechanism of Base Hydrolysis of (αβS)-(Salicylato)(tetraethylenepentamine)cobalt(III) Ion

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Previous studies[2-4] have dealt with the kinetics of acid and base hydrolysis of *cis*-(ammine)(substituted salicylato)bis-(ethylenediamine)cobalt(III) complexes. It was noted that the phenoxide form of such complexes, [N$_5$CoOCOC$_6$H$_3$O-(X)]$^+$ (X = H, 5-Br, 5-SO$_3^-$, 5-NO$_2$, 3-NO$_2$ for N$_5$ = *cis*-(en)$_2$(NH$_3$) and X = H for N$_5$ = (en)$_2$(im-H)),[5] aquates ~10^3 times faster than the corresponding phenol form under comparable conditions. Considering the overall charge of the leaving group, this appears to be an unusual reactivity contrast. Further, the observed linear correlation between log k_{aq} and pK_{OH} of the substituted salicylato complexes, *cis*-[Co(en)$_2$-(NH$_3$)(OCOC$_6$H$_3$O(X))]$^+$ (where k_{aq} is the aquation rate constant for the phenoxide form), with slope = 0.98 ± 0.03 indicates that the basicity of the unbound phenoxide group of the complex governs the rate of elimination of salicylate ligand from the cobalt(III) center.[3] The activation parameters for this path are consistent with a Co–O bond-breaking mechanism rather than the phenoxide-assisted hydration of the acyl carbon followed by ester type (i.e., C–O) cleavage. These lines of evidence suggest that the unbound phenoxide group generates the amine conjugate base, *cis*-[Co(en)$_2$-

(NH$_2$)OCOC$_6$H$_3$OH(X)]$^+$, in an intramolecular acid–base equilibrium step. Such a species would be expected to aquate much faster than its conjugate-acid analogue.

It is well-known that the rates of aquation of N$_5$CoCl^{2+} complexes (N$_5$ = (NH$_3$)$_5$, (en)$_2$(NH$_3$), (triethylenetetramine)(NH$_3$), and tetraethylenepentamine) decrease significantly with increasing chelation of the cobalt(III) center.[6] One would therefore anticipate that, in the absence of the internal conjugate-base mechanism referred to earlier, the phenoxide form of (salicylato)(tetraethylenepentamine)cobalt(III) species should undergo aquation at a rate slower than the corresponding (en)$_2$(NH$_3$) complex. To our surprise, the present study shows that the tetren phenoxide complex undergoes aquation within the stopped-flow time scale, very much faster than any of the (salicylato)(amine)cobalt(III) complexes studied so far. Base hydrolysis also occurs much more rapidly with the tetren species than with the salicylato analogues studied earlier but takes place considerably more slowly than with a number of halogen and pseudohalogen congeners containing the same amine–cobalt moiety.

Experimental Section

Materials. Tetraethylenepentamine (tetren) was used as obtained from Matheson Coleman and Bell. All other chemicals were of reagent grade, and the distilled water was further deionized before use in a mixed-bed ion-exchange column. Sodium perchlorate was used for ionic strength adjustment.

Preparation and Characterization of Compounds. (αβ)-Chloro-(tetraethylenepentamine)cobalt(III) perchlorate was prepared as described by House and Garner.[7-9] (αβS)-[Co(tetren)-(OCOC$_6$H$_4$OH)](ClO$_4$)$_2$[10] was prepared from this chloro complex following the method described earlier for the preparation of *cis*-ammine(salicylato)bis(ethylenediamine)cobalt(III) perchlorate.[11] Anal. Calcd for [Co(C$_8$N$_5$H$_{23}$)(CO$_2$C$_6$H$_4$OH)](ClO$_4$)$_2$: C, 30.81; H, 4.83; N, 11.98; Co, 10.08. Found:[12] C, 30.74; H, 4.86; N, 11.88; Co, 10.06. The spectral parameters for the complex measured by means of a Cary 118 spectrophotometer are as follows [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 491 (170) and 298 (4318) in 0.1 M HClO$_4$ medium. These may be compared to the corresponding data for (salicylato)-pentaamminecobalt(III) ion [λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 510 (82.4), 298 (4417);[13] 503 (76.0), 298 (4400)[14]] and for *cis*-(ammine(salicylato)bis(ethylenediamine)cobalt(III) ion [500 (113), 298 (4474)[11]].

Rate Measurements. The kinetics of the hydrolysis of the salicylato complex was investigated at 20 °C ≤ t ≤ 35 °C over the range of 0.01 M ≤ [OH] ≤ 0.9 M (I = 1.0 M). The rate measurements were made at 380 nm on a computerized Durrum Model 110 stopped-flow assembly. One of the syringes of the apparatus contained the appropriate concentration of NaOH adjusted to I = 2 M, whereas the other syringe contained a complex solution in 0.001 M HClO$_4$ medium. Runs were made under pseudo-first-order conditions in the usual way with [complex]$_T$ = (3.6–5.0) × 10^{-4} M. The observed pseudo-first-order rate constants were calculated by use of a least-squares program and are reported as the mean of at least five kinetic runs.

Results and Discussion

In acidic solution (pH ~4) there was no evidence of hydrolysis of the complex during a period of up to 10 h at 25

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(1) On leave from the Department of Chemistry, Utkal University, Bhubaneswar 751004, India.

(2) Dash, A. C.; Mohanty, B. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1179.

(3) Dash, A. C.; Mohanty, B. *J. Inorg. Nucl. Chem.* **1978**, *40*, 309.

(4) Dash, A. C.; Mohanty, B. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 183.

(5) im-H = imidazole anion C$_3$H$_3$N$_2^-$.

(6) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 159.

(7) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 2097.

(8) House, D. A.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 272.

(9) For characterization also see: (a) Snow, M. R.; Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *J. Chem. Soc. D* **1969**, 891. (b) Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1627. (The α-Co(tetren)-OH^{2+} and α-Co(tetren)OH$_2^{3+}$ complexes described by House and Garner[8] are actually the αβS isomers.)

(10) The method of preparation involved heating a mixture of the chloro complex and salicylic acid at 70 °C after adjusting the pH of the solution to ~5. Under these conditions the αβS isomer is expected.[9]

(11) Dash, M. S.; Dash, A. C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 571.

(12) Galbraith Laboratories, Knoxville, TN 37921.

(13) Dash, A. C.; Nanda, R. K. *Inorg. Chem.* **1973**, *12*, 2024.

(14) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

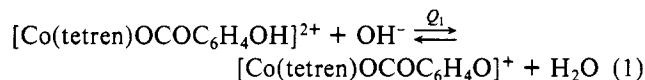**Table I.** Rate Data for Base Hydrolysis Reaction of $(\alpha\beta S)$-[Co(tetren)OCOC$_6$H$_4$O]$^+$ [a]

20.3 °C		24.2 °C		30.1 °C		35.4 °C	
[OH$^-$], M	k_{obsd}, s^{-1}	[OH$^-$], M	k_{obsd}, s^{-1}	[OH$^-$], M	k_{obsd}, s^{-1}	[OH$^-$], M	k_{obsd}, s^{-1}
0.029	0.115 ± 0.004	0.026	0.167 ± 0.018	0.010	0.285 ± 0.009	0.010	0.500 ± 0.013
0.049	0.160 ± 0.005	0.034	0.227 ± 0.008	0.020	0.390 ± 0.01	0.020	0.730 ± 0.033
0.079	0.256 ± 0.008	0.052	0.295 ± 0.014	0.030	0.482 ± 0.018	0.030	0.883 ± 0.025
0.098	0.280 ± 0.018	0.069	0.292 ± 0.009	0.040	0.555 ± 0.021	0.040	0.999 ± 0.030
0.199	0.443 ± 0.024	0.086	0.337 ± 0.014	0.050	0.598 ± 0.007	0.050	1.12 ± 0.02
0.299	0.625 ± 0.024	0.099	0.391 ± 0.007	0.080	0.759 ± 0.020	0.080	1.40 ± 0.04
0.400	0.895 ± 0.024	0.199	0.632 ± 0.023	0.099	0.846 ± 0.017	0.099	1.58 ± 0.04
0.499	1.04 ± 0.04	0.299	0.953 ± 0.016	0.200	1.40 ± 0.05	0.200	2.53 ± 0.07
0.599	1.28 ± 0.11	0.399	1.20 ± 0.02	0.300	1.91 ± 0.05	0.300	3.48 ± 0.15
0.799	1.70 ± 0.09	0.599	1.83 ± 0.07	0.400	2.59 ± 0.07	0.400	4.08 ± 0.30
0.899	1.90 ± 0.05	0.797	2.52 ± 0.12	0.500	3.05 ± 0.04	0.500	5.38 ± 0.14
		0.862	2.71 ± 0.10	0.600	3.53 ± 0.12	0.600	6.02 ± 0.29
				0.800	4.83 ± 0.14	0.800	8.15 ± 0.48
				0.900	5.27 ± 0.23	0.900	9.46 ± 0.60
k_1, s^{-1} 0.056 ± 0.015		0.083 ± 0.019		0.308 ± 0.023		0.585 ± 0.074	
k_2, s^{-1} 2.03 ± 0.03 M^{-1}		3.00 ± 0.05		5.53 ± 0.05		9.52 ± 0.17	

[a] $I = 1.0$ M.

Table II. Comparison of the Rate and Activation Parameter Data for the Aquation and Base Hydrolysis of Some Co(tetren)X^{n+} and Related Species at 25 °C, $I = 1.0$ M

complex	k_1, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	k_2, s^{-1} M^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	ref
(1) *cis*-[Co(en)$_2$(NH$_3$)OCOC$_6$H$_4$O]$^+$	5.3 × 10^{-5}	33.7 ± 1.2	+35 ± 4	4.6 × 10^{-4}	30.6 ± 1.9	+29 ± 6	3
(2) α-*cis*-[Co(trien)(NH$_3$)OCOC$_6$H$_4$O]$^+$	4.6 × 10^{-5}	39.6 ± 1.7	+55 ± 5	1.8 × 10^{-4}	24.1 ± 1.4	+10 ± 5	22
(3) *cis*-[Co(en)$_2$(im-H)OCOC$_6$H$_4$O]	2.3 × 10^{-5}	32.5 ± 0.9	+30 ± 3	1.6 × 10^{-4}	30.3 ± 3.3	+26 ± 11	4
(4) $(\alpha\beta S)$-[Co(tetren)OCOC$_6$H$_4$O]$^+$	0.116	29.0 ± 2.9	+35 ± 10	3.32	17.9 ± 0.2	+3.7 ± 0.8	this work
(5) [Co(NH$_3$)$_5$OCOCF$_3$]$^{2+}$	1.5 × 10^{-7}	26	-2	2.1 × 10^{-2}	22.7	+10	17
(6) [Co(NH$_3$)$_5$Cl]$^{2+}$	1.8 × 10^{-6}	22.9	-8.1	0.8	28.7	+37	17
(7) *cis*-[Co(en)$_2$(NH$_3$)Cl]$^{2+}$	3.7 × 10^{-7}	24.9	-4.3	8.1			17
(8) *cis*-[Co(trien)(NH$_3$)Cl]$^{2+}$	1.7 × 10^{-7}	24.9	-5.8				17
(9) $(\alpha\beta R)$-[Co(tetren)Cl]$^{2+}$	4.6 × 10^{-8}	26.4	-5	3.5 × 10^4	24 ± 2	+41 ± 8	18
(10) $(\alpha\beta S)$-[Co(tetren)Cl]$^{2+}$	1.3 × 10^{-5} [a]			1.7 × 10^6 [a]			18
(11) $(\alpha\beta R)$-[Co(tetren)N$_3$]$^{2+}$	1.1 × 10^{-10}	34.0 ± 0.6	+10 ± 2	3.2 × 10^2	26 ± 2	+41 ± 6	19
(12) $(\alpha\beta R)$-[Co(tetren)NCS]$^{2+}$				88	9.6 ± 1.9	-17 ± 6	20
(13) $(\alpha\beta S)$-[Co(tetren)NCS]$^{2+}$				108	10.1 ± 2.5	-15 ± 7	20
(14) $(\alpha\beta S)$-[Co(tetren)SO$_3$]$^+$ [b]				0.8 × 10^{-4}	27.6 ± 0.7	+15 ± 2	21

[a] At 70 °C. For the $\alpha\beta R$ isomer, $k_1 = 2.2 \times 10^{-5}$ s^{-1} and $k_2 = 5.7 \times 10^6$ s^{-1} M^{-1} at this temperature. [b] S-Bonded isomer.

°C. Addition of alkali to an aqueous solution of the complex (pH $\sim$12) caused an instantaneous color change from orange to yellow which rapidly decayed to pink. The spectrum of this pink product of base hydrolysis has an absorption maximum at 490 nm with $\epsilon = 135$ M^{-1} cm^{-1} which corresponds closely to that previously reported[8,9] for $(\alpha\beta S)$-[Co(tetren)OH]$^{2+}$. Acidification of this solution of reaction product to pH $\sim$1 causes a spectral shift to an absorption maximum at 470 nm ($\epsilon = 118$ M^{-1} cm^{-1}), which closely corresponds[8,9] to that of $(\alpha\beta S)$-[Co(tetren)OH$_2$]$^{3+}$. The instantaneous orange to yellow color change of the salicylato complex on addition of base is attributed to the formation of the phenoxide species:
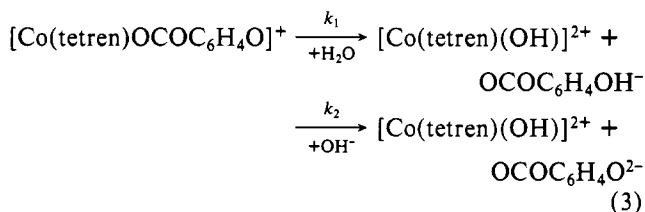
$$[\text{Co(tetren)OCOC}_6\text{H}_4\text{OH}]^{2+} + \text{OH}^- \underset{}{\overset{Q_1}{\rightleftarrows}}$$
$$[\text{Co(tetren)OCOC}_6\text{H}_4\text{O}]^+ + \text{H}_2\text{O} \quad (1)$$

A similar spectral change has been observed for (salicylato)pentaamminecobalt(III)[14] and *cis*-(salicylato)amminebis-(ethylenediamine)cobalt(III)[11] complexes. The spectral parameters of the phenoxide species, [Co(tetren)OCOC$_6$H$_4$O]$^+$ could not be determined with the fastest scan rate of the Cary 118 spectrophotometer due to its very rapid base hydrolysis. Table I presents the rate data for the hydrolysis reaction. In the range [OH$^-$] = 0.026–0.9 M, the pseudo-first-order rate constants fit the relationship

$$k_{obsd} = k_1 + k_2[\text{OH}^-] \quad (2)$$

The validity of eq 2 is in keeping with the fact that the sali-

cylato complex exists exclusively in the phenoxide form at [OH]$^- \geq 0.026$ M, and this form of the complex undergoes aquation (k_1 path) and base hydrolysis (k_2 path) as depicted in (3). Values of k_1 and k_2 calculated from the least-squares

$$[\text{Co(tetren)OCOC}_6\text{H}_4\text{O}]^+ \xrightarrow[+\text{H}_2\text{O}]{k_1} [\text{Co(tetren)(OH)}]^{2+} +$$
$$\text{OCOC}_6\text{H}_4\text{OH}^-$$
$$\xrightarrow[+\text{OH}^-]{k_2} [\text{Co(tetren)(OH)}]^{2+} +$$
$$\text{OCOC}_6\text{H}_4\text{O}^{2-}$$
$$(3)$$

fit of the rate data in the range [OH$^-$] = 0.026–0.9 M to eq 2 are collected in Table I. At [OH$^-$] < 0.026 M a slight negative deviation from the straight-line plot of k_{obsd} vs. [OH$^-$] is noted, which may be ascribed to incomplete conversion of the complex to the phenoxide form. Under this condition the pseudo-first-order rate constant takes the form

$$k_{obsd} = (k_1 + k_2[\text{OH}^-])Q_1[\text{OH}^-]/(1 + Q[\text{OH}^-]) \quad (4)$$

Values of Q_1 calculated from eq 4 utilizing the known values of k_1, k_2, and k_{obsd} at [OH$^-$] = 0.01 and 0.02 M turn out to be 523 ± 159 and 541 ± 263 M^{-1} at 30 and 35 °C, respectively. From these data and K_W (=2.5 × 10^{-14} and 3.6 × 10^{-14} M^2 at 30 and 35 °C, $I = 1$ M, respectively)[15] we obtain the

(15) Harned, H. S.; Hammer, W. J. *J. Am. Chem. Soc.* **1933**, *55*, 2194.

values of pK_{OH} of the phenol group of the complex ($K_{OH} = Q_1 K_W$) as 10.9 ± 0.1 and 10.7 ± 0.2 at 30 and 35 °C, $I = 1$ M, respectively. These are very similar to the values of pK_{OH} obtained for *cis*-[Co(en)$_2$(NH$_3$)O$_2$CC$_6$H$_4$OH]$^{2+}$ (11.22 at 29.5 °C, $I = 1$ M)[11] and *cis*-[Co(en)$_2$(imidazole-H)O$_2$CC$_6$OH]$^+$ (10.99 at 30 °C, $I = 0.3$ M).[4]

Typically, the aquation rate constants, k_1, of complexes of the type [N$_5$CoOCOC$_6$H$_4$O]$^+$ are of the order of magnitude 10^{-5} s^{-1}, while the base hydrolysis constants, k_2, are around 10^{-4} s^{-1} M^{-1} (see entries 1, 2, and 3 in Table II). In contrast, the tetren species is very much more reactive than the previously studied analogues, with both k_1 and k_2 values greater by a factor of $\sim 10^4$ (entry 4 in Table II). A molecular model of ($\alpha\beta S$)-[Co(tetren)OCOC$_6$H$_4$O]$^+$ ion reveals that the phenoxide oxygen must occupy a position in close proximity to one of the terminal NH$_2$ groups of the tetren ligand. This favors internal acid–base equilibration through hydrogen bonding of the type –NH$_2$---OC$_6$H$_4$OCO– $\rightleftharpoons$ –NH---HOC$_6$H$_4$OCO–, thus generating what amounts to the more reactive conjugate-base form of the complex ion. Thus the present work lends support to the mechanism previously suggested for the aquation of the (en)$_2$(NH$_3$), (trien)(NH$_3$), and (en)$_2$(im-H) analogues, except that the effect is much greater for the tetren species. Further corroboration of this concept is provided by the proposal by Poon and Tobe[16] that the facile cis → trans isomerization of [Co(cyclam)(OH)(OH$_2$)]$^{2+}$ is promoted by intramolecular proton transfer from an amine ligand to the hydroxo ligand. The pK_{OH} of the phenol group of the salicylato complex is at least 6 units greater than the first pK of the aqua ligand of *cis*-[Co(cyclam)-(OH$_2$)$_2$]$^{3+}$ ($pK = 4.9$ at 25 °C and $I = 0.5$ M, NaClO$_4$),[16] so the accelerating influence of the phenoxide group should be even more substantial. It should be noted that various types of N$_5$CoX^{2+} complexes aquate at very low rates (entries 5–11 in Table II), mainly as a result of low $\Delta S^{\ddagger}$ values. The highly positive activation entropies for the k_1 path of all four of the salicylato species may indeed result from the contribution of $\Delta S°$ from the internal conjugate-base equilibration, for which a large positive entropy change could well result from changes in the solvation pattern.

Turning now to the base hydrolysis reaction described by k_2, the tetren salicylato is, as mentioned above, much more reactive than any of the other comparable salicylato species or even than the other singly charged complex ion, the S-bonded tetren sulfito complex (entry 14). However, the tetren salicylato ion is not unusually reactive as compared to various other complexes of the [N$_5$CoX]$^{2+}$ family, which are seen to fall within a very wide range of reactivity ($10^{-2} \leq k_2 \leq 10^4$ at 25 °C — see entries 5–13 in Table II). The [N$_5$Co(sal)]$^+$ species are unusual in these comparisons in that k_2 differs from k_1 by only an order of magnitude, while for all the other species for which the appropriate data are tabulated the rate ratios are within the range $10^5 \leq k_2/k_1 \leq 10^{12}$. This observation further supports our concept of an "internal S$_N$1cB" mechanism for the k_1 path for the salicylato complexes, since further increase of [OH$^-$] would be expected to promote the second-order k_2 path, but not with a large increase, conjugate-base conditions having already been established. It is also worth noting that the large increase in base hydrolysis rate (k_2 path) on changing from *cis*-[Co(en)$_2$(NH$_3$)(OCOC$_6$H$_4$O)]$^+$ to the

tetren analogue is paralleled by a similar large increase in changing from *cis*-[Co(en)$_2$(NH$_3$)Cl]$^{2+}$ to its tetren analogue. Apparently these parallel rate contrasts are the result of the change in the nature of the N$_5$ grouping, not of anything inherently very different in the (OCOC$_6$H$_4$O)$^{2-}$ ligand as compared to the Cl$^-$ ligand, except for the change in overall charge of the complex ion. Other things being equal, it is apparent that the doubly charged species are more receptive to the S$_N$1cB mechanistic requirements than are those of single charge.

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Hydrogen Bonding. 11. Infrared Study of the Water–Chloride Ion Cluster in Tetraethylammonium Chloride Hydrate[1]

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In previous work we have demonstrated that tetramethylammonium fluoride hydrate[3,4] and tetraethylammonium fluoride hydrate[5] contain discrete H$_4$O$_2$F$_2$$^{2-}$ water–fluoride clusters and have proposed that these clusters can be described as a tetrahedron of electronegative atoms with bridging protons on the faces of the tetrahedron.[6] This structure is consonant with theoretical treatments of tetrahedral clusters by Kettle[7] or Hoffmann,[8] with the protons interacting with the A$_1$ + T$_2$ face-centered bonding orbitals. Such a cluster would be isoorbital with, for example, methyllithium tetramer;[7,9] however, the electronegative atoms in the fluoride monohydrate cluster would facilitate the presence of electrons in the remaining E + T$_1$ + T$_2$ orbitals much as the electronegative atoms in a three-centered hydrogen bond[10] facilitate the presence of nonbonding electrons, in contrast to the hydrogen bridge bond in boranes.[11]

Structural information on these unique and extraordinarily stable hydrates would be of considerable interest; however, both of the fluoride monohydrates studied are obtained by dehydration of higher solid hydrates and are thus fine, micro-

(16) Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1968**, *7*, 2398.
(17) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47 and references cited in the tabulations therein.
(18) Ni, T.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1071.
(19) El-Awady, A. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1264.
(20) El-Awady, A. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1463.
(21) Dash, A. C.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160.
(22) Dash, A. C.; Dash, M. S., unpublished result.

(1) Reported in part: K. M. Harmon, J. M. Gabriele, P. A. Mounts, and A. S. Nuttall, "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 26, 1980; American Chemical Society: Washington, DC, 1980; INOR 144.
(2) Petroleum Research Fund-American Chemical Society scholar, 1980.
(3) K. M. Harmon and I. Gennick, *Inorg. Chem.*, **14**, 1480 (1975).
(4) K. M. Harmon and I. Gennick, *J. Mol. Struct.*, **39**, 39 (1977).
(5) I. Gennick, K. M. Harmon, and J. Hartwig, *Inorg. Chem.*, **16**, 2241 (1977).
(6) References 3–5 discuss in detail the evidence on which this structural formulation is based.
(7) S. F. A. Kettle, *Theor. Chim. Acta*, **4**, 150 (1966).
(8) R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **100**, 6088 (1978).
(9) A. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, **2**, 197 (1964).
(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, 1960, p 236 ff.
(11) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963, p 30 ff.