Table I. Stability Constants for Boric Acid Complexation with Four Ligands

ligand	K_{a_1}, K_{a_2}	K_1	K_2	K_1'/K_2[e]
α-hydroxyisobutyric acid[f]	1.4×10^{-4}	3.3×10^{-3}	7.0×10^{2}	4.7×10^{3}
catechol	5.4×10^{-10} 3.2×10^{-12}[a]	9.8×10^{-6}[b]	1.9[b]	4.9×10^{3}
glycerol[g]		1.7×10^{-8}	2.6	6.2
mannitol	3.2×10^{-14}[c]	6.5×10^{-7}[d]	1.5×10^{2}[d]	4.1

[a] Reference 12. [b] Reference 6. [c] Thamsen, J. *Acta Chem. Scand.* 1952, *6*, 270. [d] Reference 4. [e] $K_1' = K_1/K_a(B(OH)_3)$. [f] Reference 8. [g] Reference 2.

[1:2] as the pH was lowered from 11 to 6. This is consistent with Figure 2. All of the studies cited are correct in their conclusions. In the cases where bis complexes were not observed within experimental error, the reaction conditions were either too acidic[12] or too basic[23] or the reactant concentrations were too low[13] or were in the wrong proportion for bis complex formation to be seen.[14] Our isolation of a salt of a bis complex simply reflects a low solubility product constant. The salt precipitates under conditions where the concentration of anion is too low to detect by pH titration methods within experimental error.

A final point to consider is the ratio of the stability constants. As written, K_1 and K_2 cannot be directly compared. However, if eq 1 is rewritten to involve reaction of tetrahedral borate, a direct comparison can be made. Written this way, $K_1' = K_1/K_a(B(OH)_3)$. The appropriate ratio, K_1'/K_2, is included in Table I. From a purely statistical point of view $K_1'/K_2 = 12$. Obviously, the experimental ratio is close to the statistical ratio only for polyols, although it should be noted that even for polyols the ratio varies considerably.[3-5] The very high values for α-hydroxyisobutyric acid and catechol suggest that, in these cases at least, a bound ligand has a profound effect on the second complexation step.

Experimental ratios considerably *less* than those predicted from statistics have been observed in oxyanion systems with catechol, and a very interesting mechanistic explanation has been offered to account for the result.[24] This is of particular interest to us since we have previously pointed out[12] mechanistic similarities in the formation of 1:1 complexes with catechol of boron acids and oxyanions. The mechanistic reason for the very great difference in the formation of bis complexes is an open question under active investigation in our laboratory.

Acknowledgment. This work was supported by a PSC/BHE grant from the Faculty Research Award Program of the City University of New York.

Registry No. $K[(CH_3C_6H_3O_2)_2B]$, 83292-17-5.

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Cis and Trans Ammonia Labilization in the Thermal Aquation of $[Cr(NH_3)_5F]^{2+}$

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Received February 19, 1982

The complex $[Cr(NH_3)_5F]^{2+}$ has been the subject of several kinetic and photochemical studies,[1-4] and it is now well established that, except in strong acid, the molecule predominantly aquates ammonia, both thermally and photochemically. Whereas the photochemical reaction has been investigated with regard to the isomeric nature of the $[Cr(NH_3)_4H_2OF]^{2+}$ product, showing that it is 85% cis and 15% trans, no such study appears to have been carried out for the thermal reaction. Data on this point would be of interest as, if stereoretentitivy of aquation is assumed, they indicate the extent of cis vs. trans labilization of the ammonia ligands by the fluoride ligand.

Table I

$[H^+]$, M	$10^6 k_{F^-}$, s^{-1}[c]	$10^6 k_{F^-}$, s^{-1}[a]	$10^6 k_{NH_3}$, s^{-1}[c]	% trans[b]
0.01 ($HClO_4$)	0.55 (2)	2.13	6.1 (3)[d]	23
0.10 ($HClO_4$)	1.1 (1)	2.39	6.9 (2)[d]	23
1.0 ($HClO_4$)	8.5 (2)	5.00	7.8 (2)[d]	
0.10 (HCl)	0.76 (1)		3.8 (1)	27
1.0 (HCl)	8.3 (1)		3.0 (1)	27

[a] Calculated from the results of ref 2. [b] % trans refers to the $[Cr(NH_3)_4H_2OF]^{2+}$ product; analysis was by ion-exchange chromatography with estimated uncertainty ±5%. [c] Number of determinations in parentheses. [d] The calculated k_{NH_3} is $7.7 \times 10^{-6}\ s^{-1}$.

Al-Shatti and co-workers[2] have summarized the evidence that a number of chromium(III) pentaammines with ligands containing uncoordinated oxygen atoms exhibit significant cis labilization of ammonia. This phenomenon has been ascribed to one of (i) direct coordination of oxygen to the metal to form a seven-coordinate intermediate, (ii) H bonding to an adjacent coordinated ammonia, interpreted variously as causing weakening[5] or strengthening[6] of the Cr–N bond, or (iii) H bonding to an adjacent coordinated ammonia to give an intramolecular conjugate base effect, leading to the loss of a different ammonia ligand. They further note that the effective cis-labilizing ligands appear to be those capable of forming seven-coordinate intermediates and that labilization by hydroxide and fluoride presumably would occur via ligand to metal π donation. Consequently, the question of whether cis or trans labilization occurs with fluoride is of some interest and was convenient for us to investigate in light of our experience of such analyses.[3]

The compound $[Cr(NH_3)_5F](ClO_4)_2$ was prepared and recrystallized as in the literature.[2] The thermal aquation of 1.0×10^{-2} M $[Cr(NH_3)_5F]^{2+}$ solutions was investigated in the dark at 50 °C in aqueous 1 M lithium perchlorate media at various acid concentrations in the range 1×10^{-2} M and to conversions in the range 10–20%. For the highest acid concentrations the use of hydrochloric acid was mandated, to avoid solubility problems. Rate constants for ammonia and fluoride aquation were determined by direct analysis for ammonia by coulometric titration[7] and for fluoride with a solid-state fluoride electrode, after isolation of the respective free ions with ion-exchange columns. The nature of the aquo products of ammonia loss was investigated by cation-exchange chromatography on a 20 cm × 8 mm column of Hamilton HC8X resin.

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Rate constants for ammonia loss in good agreement with those reported by Al-Shatti et al.[2] were obtained, but overall rates for fluoride loss about one-third of those reported were observed (Table I). For the three acid concentrations accessible in ClO_4^- medium, linear regression leads to $k_{F^-} = (8.1 \times 10^{-6})[H^+] + 4.4 \times 10^{-7}$ s^{-1}. This rate constant for the acid-catalyzed path is over 3 times greater than, and the acid-independent rate constant about one-fifth of, the values reported earlier by Al-Shatti et al. Since our measurements were directly of fluoride released, while Al-Shatti et al. relied on the absorbance change at an isosbestic point of $[Cr(NH_3)_5H_2O]^{2+}$ and $[Cr(NH_3)_4H_2OF]^{2+}$, we believe our values for k_{F^-} to be more reliable. We noted also that the ammonia loss rate constants were a factor of 2 lower for aquation in hydrochloric acid media. The slight pH dependence of the ammonia rate constant was outside our experimental uncertainty.

The focus of this note, however, is the isomeric nature of the ammonia aquation product, shown in Table I to be 25% trans and 75% cis, independent (as might be expected) of H^+ concentration. Since it has been shown consistently that chromium(III) aquations are stereoretentive (although this is not necessarily true for solutions in ammonia[8] and aprotic[9] solvents), we take this product distribution to reliably reflect the relative rates of loss of the ammonias cis and trans to fluoride.

In interpreting these results, it is necessary to remember the statistical factor of 4 favoring loss of cis ammonia from $[Cr(NH_3)_5Y]^{2+}$, where both cis and trans ammonias have equal individual aquation labilities. With recognition of this, there is no cis-labilizing influence of fluoride in this complex. Indeed the slight imbalance is in favor of trans since the "single ligand" rate constants calculated from our data are $k_{trans} = 1.7 \times 10^{-6}$ s^{-1} and $k_{cis} = 1.3 \times 10^{-6}$ s^{-1}.

It follows that there is no support in this data for the suggestion that fluoride may exert a cis-labilizing influence by the proposed mechanism of π donation from ligand to metal, even though both "single ligand" constants are slightly larger than the "single ligand" rate constant[10] for $[Cr(NH_3)_6]^{3+}$ of 8.1×10^{-7} s^{-1}.

The observation of trans labilization rather than cis is consistent with an earlier study[11] of *cis*-$[Cr(NH_3)_4F_2]^+$, where it was found that the ammonia ligands located trans and cis to fluoride were more labile than those cis to two fluorides by a factor of about 4 (rather uncertain due to resin-catalyzed decomposition). The observed overall rate constant at 50 °C was 8.4×10^{-6} s^{-1}, giving "single ligand" rate constants of 3×10^{-6} and 8×10^{-7} s^{-1}, respectively.

These findings bring into focus the difficulties associated with establishing genuine cis labilization in an ML_5X system. One obtains 80% cis product in the situation of stereoretentive loss of equally labile cis and trans L ligands; very careful cis/trans product analysis is demanded to establish either that cis > 80% or that trans < 20%. In one study[12] it was shown that the relevant product was more than 93% cis, clearly establishing the case for cis labilization, but not all authors have so carefully specified the isomeric purity of their products, and none appear to have explicitly recognized the statistical factor of 4.

Acknowledgment. The authors thank the NSERC and the University of Victoria for financial support.

Registry No. $[Cr(NH_3)_5F]^{2+}$, 19443-25-5.

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Bond Energies in Solid Oxides

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Received May 3, 1982

It has been long established that bond energies in a large class of molecules can, to a good first approximation, be considered constant. The energy of atomization of a molecule can thus be considered as the sum of the energies required to break the component bonds. In this procedure one of course uses different bond energies for single, double, etc. bonds. In solids, however, the concept of bond order is more usefully replaced by that of *bond strength*. In a symmetrical environment the bond strength is simply the valence divided by the number of bonds. (Here, and throughout, "valence" is used in the sense of the absolute value of the formal oxidation state of an atom—for the main-group atoms in the compounds considered here, this is just the group number.) Thus, in MgO with octahedral coordination of the atoms the strength of the Mg–O bond is $^1/_3$; in Al_2O_3 with octahedral coordination of Al by O and tetrahedral coordination of O by Al the strength of the Al–O bond is $^1/_2$. For less symmetrical environments, bond strengths can be assigned on the basis of bond-strength–bond-length correlations.[1] A generalization of Pauling's electrostatic valence rule is that, for each atom in a solid, the sum of all the bond strengths is equal to the valence. In a metal oxide, in the absence of metal–metal bonding, the sum of all the bond strengths is just twice the number of oxygen atoms. The range of bond strengths encountered in solid oxides is from $^1/_{12}$ (i.e., for a 12-coordinated K atom) to $^7/_4$ (in perchlorates) with often a wide range, perhaps a factor of 3, for a given atom. It is not therefore practical to assign bond energies in solids in the same way as is done for molecules, many of which contain only bonds of integral order.

In this work we have investigated whether the energy of atomization of solid oxides can be divided into components, not according to the number of bonds but according to the contribution of each metal atom to the total bond strength. Thus, it was investigated whether Mg, for example, contributes the same amount per equivalent to the energy of atomization in $MgAl_2O_4$ (in which it is in tetrahedral coordination) as it does to that of Mg_2SiO_4 (in which it is in octahedral coordination). This was found indeed to be the case of high accuracy. The results should be of considerable interest to those interested in the theory of bonding in oxides and related solids.

Data Analysis

The starting point for the analysis was the heats of formation of solid oxides at 298 K. These were taken first from the compilation of Robie, Hemingway, and Fisher[2] and, for compounds not listed there, from Kubaschewski, Evans, and Alcock.[3] Enthalpies of atomization were then calculated by using enthalpies of atomization of the elements taken from Stull and Prophet.[4] Data for all compounds of 15 main-group elements (those listed in Table I) and Fe(II) were included. For reasons explained below, the data for binary compounds were considered separately. In all, there were data for 16 binary and 95 ternary, etc. oxides. The compounds ranged

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