

In summary, we believe the original rationalization of the structure of $\text{CpCoFeMe}_4\text{C}_4\text{B}_8\text{H}_8$ to contain several inconsistencies. At this stage, a rationalization of the peculiar skeletal geometry exhibited by $\text{CpCoFeMe}_4\text{C}_4\text{B}_8\text{H}_8$ requires two alternative bonding models, since it is impossible, from crystallographic data alone, to unambiguously distinguish between true covalent bonding interactions involving B(8) and B-(2')/B(6') and an apparent or pseudo double face capping caused by geometric and steric constraints.

Registry No. $\text{CpCoFeMe}_4\text{C}_4\text{B}_8\text{H}_8$, 58814-74-7.

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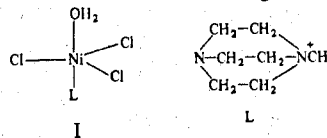
Interpretation of Volumes of Activation and the Effect of Bond Length Changes of the Nonexchanging Ligands

Sir:

In a recent letter to this journal,¹ it has been suggested that the use of volumes of activation to determine reaction mechanisms may be considerably complicated by important changes in the metal-ligand bond lengths of the nonexchanging ligands on going from reactant to transition state. The author tries to make two major points.

(a) For a dissociative reaction, as one ligand is lost, there is compression of the remaining bonds with reduction of the volume of the primary coordination sphere and collapse of the solvent onto this primary solvation sphere. In terms of a potential energy function $U(r)$, the equilibrium bond length is simply the distance at which the energy is minimum, i.e., when $\partial U/\partial r = 0$. If one adopts a classical function where both attractive and repulsive forces are simply proportional to the number of ligands, then the bond length must be independent of the number of ligands.² The contributions to the potential which give rise to changes in the equilibrium radius as the number of ligands is changed are clearly those that depend on the geometry of the complex. The most important of these are ligand-ligand repulsive (and attractive) forces.³ The crystal field effect also comes into this category, but for the purposes of this qualitative discussion, we shall restrict interest to d^0 , d^3 , and d^{10} ions where this effect is absent. Quantum mechanical calculations on ion-water clusters of the form $\text{M}(\text{H}_2\text{O})_n^{\pm}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{F}, \text{Cl}; n = 1, 10$) also predict such contractions. With Na^+ (effective ionic radius 1.02 \AA) as an example, the metal-oxygen bond length contracts from 2.35 to 2.32 \AA on going from $n = 6$ to 5.⁵ This would give rise to a volume contraction of about $3 \text{ cm}^3 \text{ mol}^{-1}$. We have no

quantum mechanical calculations for a 2+ ion of similar size, e.g., Ca^{2+} (1.00 \AA), but from considerations of a classical potential function, we might expect ligand-ligand interactions to be a smaller contribution to the overall energy, and hence the volume reduction would be less than $3 \text{ cm}^3 \text{ mol}^{-1}$. Since the transition state for a dissociative D reaction occurs before the reactive intermediate, this "negative contribution" to the volume of activation due to bond contraction would be less than that given above. Finally, it is accepted that water-exchange reactions generally proceed via interchange mechanisms.⁶ For an I_d mechanism, the transition state consists of five strong metal-water bonds and two weak ones,⁷ and thus we would expect the "negative contribution" to be less than that for a D mechanism. It would thus seem this contribution cannot be much larger than the accuracy to which ΔV^* can be measured ($\pm 1 \text{ cm}^3 \text{ mol}^{-1}$). It was suggested¹ that evidence for this contraction could be obtained by comparing the Ni(II)-water bond length in complex I of 2.10 \AA with the "normal radius sum of 2.16 \AA ". Pauling⁸ is cited for this sum.



The correct value for the Ni(II)-water bond length in $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ is in fact 2.05 \AA .⁹ It seems superfluous to add how inadvisable it is to try to compare small differences in bond lengths in complexes whose overall charges differ by two and where the attached ligands are so different. We conclude that bond contraction does occur going from six- to five-coordinate but, at least for an ion like Ca^{2+} , the effect on ΔV^* must be very small indeed.

(b) It is stated that across the first transition series, earlier members with few t_{2g} electrons should be more susceptible to contraction.¹ We do not dispute this.¹⁰ However, from this

(1) Langford, C. H. *Inorg. Chem.* 1979, 18, 3288.

(2) In general, the potential function can be written in the form $U(r) = -nU_{\text{att}}(r) + nU_{\text{rep}}(r)$, where n is the number of ligands and $U_{\text{att}}(r)$ and $U_{\text{rep}}(r)$ are the attractive and repulsive contributions. The equilibrium bond length occurs when $U'_{\text{att}}(r) = U'_{\text{rep}}(r)$, where the prime denotes the first differential with respect to r . If $U_{\text{att}}(r)$ and $U_{\text{rep}}(r)$ do not depend on n (i.e., there are no interactions that depend on the geometrical arrangement of ligands), then the equilibrium bond length will not depend on n .

(3) See for example: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 62.

(4) In this work, we use the recent, extensive compilation of: Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* 1970, 26, 1076. This tabulation contains results for most metal ions in all common oxidation states, coordination numbers, and both high and low spin (where relevant).

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(9) We have found 11 accurate determinations of the Ni(II)-O bond length in $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, 6 in solution and 5 in the solid state. With one exception, ref 9g (2.15 \AA), all other values lie between 2.04 and 2.06 \AA (mean value 2.053; standard deviation 0.007 \AA). The solid-state values were the averaged bond lengths since the octahedron is frequently slightly distorted due to crystal-packing effects. (a) Grimes, N. W.; Kay, H. F.; Webb, M. W. *Acta Crystallogr.* 1963, 16, 823. (b) O'Connor, B. H.; Dale, D. H. *Ibid.* 1966, 21, 705. (c) Gallezot, P.; Weigel, D.; Pretre, M. *Ibid.* 1967, 22, 705. (d) Baggio, S.; Becka, L. N. *Acta Crystallogr., Sect. B* 1969, 25, 1150. (e) Bol, W.; Gerrits, G. J. A.; van Panthaleon Van Eck, C. L. *J. Appl. Crystallogr.* 1970, 3, 486. (f) Bigoli, F.; Braibanti, A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Acta Crystallogr., Sect. B* 1971, 27, 1427. (g) Shapovalov, I. M.; Radchenko, I.; Lesoristskaya, M. K. *Zh. Strukt. Khim.* 1972, 13, 140. (h) Ohtaki, H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* 1976, 49, 701. (i) Camini, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *Discuss. Faraday Soc.* 1977, 64, 62. (j) Sandrom, D. R.; Dodgen, H. W.; Lytle, F. W. *J. Chem. Phys.* 1977, 67, 473.

(10) We do, however, wish to make several points about Table II of ref 1. We presume the units should be pm not nm. The ionic radii used are those of Pauling⁸ and date "in part" from 1926. They do not show the well-established nonmonotonous variation along the first-row transition-metal series which is caused by crystal field effects. With the radii of Shannon and Prewitt,⁴ a trend similar to that reported in ref 1 is observed, but Ti and V do not continue the trend. The value for V is low and for Ti somewhat larger. This is readily explained when it is realized that d^3 and d^8 ions show most crystal field contraction which is why the values of V and Ni are low whereas the value for Cr is large since we are subtracting the radius of a d^3 ion. Much of the trend observed is thus simply due to crystal field effects. A better procedure would have been to compare 2+ and 3+ ions of similar d electron configuration. With regard to metal-ligand vibrations, the frequencies of the d^{10} ions are closely similar to those of the d^5 ions (see ref 8 of ref 1). It is again clear that much of the trend is simply a crystal field effect. Similar but less extensive data for 3+ ions and d^0 to d^5 ions also support this.

idea it is concluded that the negative contribution to the volume of activation (i.e., the contraction in bond length between six- and five-coordinate complexes) is larger as one moves to the left from Ni(II).¹ We dispute this strongly. From a consideration of potential functions we in fact conclude that the exact opposite behavior occurs. Again we restrict discussion to d^0 , d^5 , and d^{10} ions for simplicity. The discussion may be extended to crystal field stabilized ions,¹¹ but it is then necessary to consider how much the crystal field contributes to the overall potential, and this varies nonmonotonously from ion to ion due to different Dq values precluding qualitative discussion. The compressibility κ may be expressed in terms of the potential function $1/\kappa = V\partial^2 U/\partial V^2$ where V is the volume¹¹ and it is readily shown that κ is roughly proportional to a large power of the equilibrium metal–ligand bond length (r_0); e.g., for a predominantly ion–dipole attraction potential, κ is proportional to r_0^4/d , where d is the radius of the complex assumed to be spherical.¹² One would thus predict a decrease of about 1.7 in compressibility going from Ca^{2+} to Zn^{2+} in accord with the ideas expressed above. However, as discussed above, bond length contraction on going from six- to five-coordinate depends on the relative importance of ion–ligand and ligand–ligand interactions, and it is clear that the larger the ion, the less important become the ligand–ligand interactions. This is totally borne out by the quantum mechanical calculations which show that the bond length contractions are much more important for Li^+ than for Na^+ and more important for Na^+ than for K^+ . These gas-phase calculations thus totally confirm the idea that the larger the ion, the smaller will be the contraction and hence “negative contribution”. In the liquid state, the complex will be subjected to a large electrostrictive pressure, and we must also consider this effect. Several points must be made: (i) In accord with theory and experimentation, 2+ and 3+ ions are very incompressible.¹² (ii) The electrostrictive pressure on a 2+ ion is of the order of 2 GPa (20 000 atm).¹² (iii) According to theory, the compressibility of a five-coordinate complex should be smaller than that of a six-coordinate complex.¹² (iv) Larger ions are more compressible than smaller ions (see above). These ideas taken together readily show that the “negative contribution” for the large ions is even smaller than for the small ions in the liquid state than it is in the gas phase. *We thus conclude that, for a reaction with a dissociative activation mode, any “negative contribution” to the volume of activation is small and does NOT increase on going to earlier members of the transition-metal series.*¹³

We may also apply such arguments to reactions with associative activation modes. As expected, there are larger bond length changes going from six- to seven- than from five- to six-coordinate, but for an associative interchange transition state, the “positive contribution” must be small. In accord with the ideas above, it would be larger for the smaller ions.

The above ideas, being based on model calculations, must always remain slightly speculative, but in the last part of this letter, we wish to show that the experimental ΔV^\ddagger values now becoming available are such as to tell a consistent story which is that, with certain readily explained exceptions, ΔV^\ddagger is a good mechanistic criterion. We have recently measured the volumes of activation for TPA exchange on Al^{3+} (+22.5), Ga^{3+} (+20.7), and In^{3+} (–22.8 $\text{cm}^3 \text{mol}^{-1}$) in the inert solvent nitromethane.¹⁴ It had previously been shown that the rate for

exchange on In^{3+} was proportional to the TPA concentration whereas for Al^{3+} and Ga^{3+} it was not.¹⁵ It seems unlikely that large changes in outer-sphere complexing ability occur between Ga^{3+} and In^{3+} , and we are thus confident of a change in mechanism which is dramatically borne out by the ΔV^\ddagger values. Similarly, values of ΔV^\ddagger for Me_2SO exchange on Ga^{3+} (+13.7),¹⁶ Fe^{3+} (–2.1),¹⁷ and Cr^{3+} (–11.3 $\text{cm}^3 \text{mol}^{-1}$)¹⁸ are available. We are confident Ga^{3+} is reacting dissociatively (the ΔV^\ddagger for Al^{3+} is similar (+15.3 $\text{cm}^3 \text{mol}^{-1}$) and the rate law in both cases is independent of Me_2SO concentration). It is well accepted that Cr^{3+} is reacting associatively. We may note that Cr^{3+} and Ga^{3+} have identical ionic radii. It seems only reasonable to suggest that the intermediate value for ΔV^\ddagger for Fe^{3+} is caused by an intermediate mechanism, and we are thus led to the conclusion of a mechanistic changeover going along the series. We have already reported a similar trend in ΔV^\ddagger for the 2+ ions from Mn^{2+} to Ni^{2+} in both methanol⁷ and water,¹⁹ and this gives added weight to our interpretation.

There are four systems demonstrated to go via a D mechanism where ΔV^\ddagger values are available: $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$,²⁰ $\text{Fe}^{\text{II}}(\text{CN})_5\text{L}$,²¹ NbX_5L , and TaX_5L ($\text{X} = \text{Cl}, \text{Br}$).²² The latter two are particularly interesting in that, depending on the nature of the ligand, the symmetrical exchange reaction goes via either a D or an I_a mechanism.²³ It was subsequently shown that the ΔV^\ddagger values were large and positive for the D mechanism and well negative for the I_a mechanism. The variation of ΔV^\ddagger with ligand for those reactions going by the D mechanism were well explained in terms of a hard-sphere model without the need for any bond contraction at the transition state. Large positive values of ΔV^\ddagger were also obtained for the substitution of $\text{Fe}^{\text{II}}(\text{CN})_5\text{L}$ where L were the pyridine-type ligands and the only D mechanism reaction giving anomalous values is $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$. However, the radius of low-spin Co^{3+} (0.53 Å) is so very much smaller than the other three ions, low-spin Fe^{2+} (0.61 Å), Nb^{5+} (0.64 Å), and Ta^{5+} (0.64 Å), it is likely that steric effects, i.e., strong ligand–ligand repulsive forces, may be responsible. In terms of a hard-sphere model, if the hole created in the center of the ligands of a six-coordinate complex is smaller than the metal ion, then, on going to the five-coordinate intermediate or transition state, contraction will occur.

The theoretical ideas discussed above when coupled with the experimental volumes of activation give us great confidence that, with the exception of the very small low-spin Co^{3+} , bond length changes of the nonexchanging ligands between reactant and transition state have only a very small effect on ΔV^\ddagger . We thus believe that volumes of activation may be reliably used for mechanistic assignment (and prediction).

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(13) Calculations using Basolo and Pearson's potential³ bear this out, but it is interesting to note that, over the range of metal–water bond lengths encountered for 2+ first-row ions, the calculated contractions going from six- to five-coordinate are all very similar.

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