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LETTERS TO THE EDITOR

Sir:

A recent article in Coordination Chemistry Reviews, vol. 12, page 241 (1974) by Lars Johansson on "The Role of the Perchlorate Ion as Ligand in Solution" prompts me to follow your suggestion in the editorial of Volume 12 and to send you some comments concerning that article.

The author abstains explicitly from discussing the type of bonding in perchlorate complexes. In my opinion, the reasonable assumption that perchlorate association is in the first instance a matter of electrostatic attraction would have considerably clarified the problem. According to Coulomb's law, association energies should be proportional to the product of particle charges and inversely proportional to the particle distance. As the particle distance is the sum of cation and anion radii, for large complex cations the differences in anion radii are rather levelled off, so the association constant is to the first approximation a function of ion charges only. One may estimate ion-pair formation constants K_{IP} for an ionic strength $I = 0$ with the aid of the rule of thumb

$$K_{\text{IP}} = 2 \times 10^{-ab/2}$$

where a and b are the charges of the cation and the anion, respectively. Most association constants of outer-sphere systems, not only with perchlorate ion but with a large variety of anions, quoted by Beck in his excellent review in Coord. Chem. Rev. 3 (1968) 91 (ref. 6 in Johansson's paper), are in fair agreement with values estimated by this formula. It will, of course, give unreliable results if the type of bonding is not purely electrostatic or if the system involved has a high ionic strength.

On these premises we are able to understand perchlorate ion association and to compare perchlorate with other anions in complex formation reactions. We must, however, bear in mind that there is not only competition between anions but that water molecules on account of their dipole character and their large concentration in aqueous solution may be the dominating competitors.

(i) In complexes of the outer-sphere type perchlorate ion associates as strongly as any other univalent anion. Values of constants determined for the association of chloride, bromide, iodide and perchlorate with the hexaamminecobalt(III) complex in aqueous solution coincide within the limits of experimental error (ref. 51). In such a case there is no possibility of obtaining "true" constants from the apparent constants β_1 (in Johansson's notation) according to eqn. (39). If $\beta_{0,1} \approx \beta_{1,0}$, then the numerator in the fraction of eqn. (39) approaches zero. Different methods for the determination of equilibrium constants will obviously give different results if different concentrations of perchlorate are used to stabilize the ionic strength of the system studied.

(ii) For inner-sphere complexes the aforesaid is true as long as electrostatic bonding predominates. Here the influence of water dipoles is especially spectacular — perchlorate complexes have not been isolated from dilute aqueous solution. Competing anions, however, capable of bonding to other types may resist the water attack and form stable complexes. There are at present no data proving the association of perchlorate with labile aquated metal ions in solution, but the problem has long been disregarded and is still rather difficult to solve as appropriate experimental methods are lacking.

(iii) Higher charged anions will easily push away any electrostatically bound uninegative anion so in these systems disturbances by perchlorate ion are not very serious. This point of view is corroborated by the fact that for the association of sulphate ion with hexaamminecobalt(III) complex association constants given for $I = 0$ range only from 800 to 3000 (there are two misprints among these values in ref. 6) while for the association of chloride with the same complex constants range from 5 to 400 (ref. 51).

I would like to conclude with a bold translation of the latin motto, CAVE CANEM: Be aware of perchlorate association!

Universität des Saarlandes,
Fachbereich 13,
Anorganische Chemie,
66 Saarbrücken,
W. GERMANY.

Prof. Dr. Ludwig Heck

Sir:

I am grateful for this opportunity to give my comments on Ludwig Heck's letter.

My article was written from the point of view of the solution chemist who uses a perchlorate as supporting electrolyte. Thus, the consequences of perchlorate association were surveyed and the literature searched for evidence for or against perchlorate association. A discussion of the type of bonding in perchlorate complexes definitely would, in my opinion, have been outside the scope of the article. This does not mean to say that I do not find this matter very interesting in itself. Some aspects of the bonding in perchlorate (and nitrate) complexes are discussed in the excellent review by Rosenthal (J. Chem. Educ. 50 (1973) 331.)

A discussion based on the views of Ludwig Heck would, however, add more confusion than knowledge to this matter. He maintains that the bonding is electrostatic, and even provides a formula for the stability constant. A study of the relevant literature should convince anyone that a less dogmatic standpoint is necessary. Certainly, electrostatic forces are important, and the formula may be roughly applicable to many outer-sphere systems but, as usual, it is the exceptions that are interesting. From them we gain meaningful information and these exceptions are not few. Most perchlorate systems are indeed exceptional in this respect, even the hexaamminecobalt(III) perchlorate system, if it is borne in mind that Heck's value for this system (ref. 51) is too high (my article, p. 253). Since Heck does not reject the criticism in his letter, it must be inferred that he considers it justified.

Further, how does electrostatic attraction explain the fact that Tl^+, among all univalent ions, forms a detectable perchlorate complex? Why does Fe^{3+} form a much weaker perchlorate complex, if any, than $Co(NH_3)_6^{3+}$, $Coen_3^{3+}$, etc.? Why does $Coen_3^{3+}$ form a much stronger complex with *three* halide ions than does $Co(NH_3)_6^{3+}$? We are presently studying outer-sphere complexes of $Fephen_3^{2+}$. Iodide and perchlorate complexes are surprisingly strong, while those of fluoride and, probably, sulphate are much weaker (results to be published in Acta Chem. Scand.).

The examples cited should suffice to reinforce the concluding statement of my article, that "... the data on hand indicate no simple relation between the charge (or charge density) of an ion and its affinity to the perchlorate ion." There is thus no simple "rule of thumb".

Heck is wrong when he, in his paragraph (i), concludes that "true" constants cannot be obtained if $\beta_{0,1} \approx \beta_{1,0}$. It should be evident to anyone who reads eqn. (39) *and eqn. (40)* and the two sentences following these equations, that the "true" constants may readily be calculated even when they are equal. It should perhaps be pointed out again that Heck's assumption $\beta_{0,1} \approx \beta_{1,0}$ is based only on his own questionable values.

In conclusion, I would like to stress the importance, in scientific work, of having an open mind. "Rules of thumb" and dogmas may be valuable, but far too often they are equivalent to prejudices that delay progress.

As the Romans said,
CAVE CANEM: Beware of dogmas!

Lars Johansson

Chemical Center,
University of Lund,
Faculty of Science,
P.O. Box 740,
S-220 07, Lund 7,
SWEDEN.