represent the ground state of the molecule more accurately than do the experimental band positions in the photoelectron spectra. Nonetheless, it must be emphasized that for an oxidation, the experimental ionization potentials constitute a more accurate measure of relative energetics. Thus, the simple model for oxidation of such compounds, involving removal of an electron from a single orbital identified with the metal–metal bond, is clearly oversimplified and may well be inaccurate. It seems, rather, that the situation approaches that for organometallic clusters in which the highest occupied orbitals are thought to be metal in character and essentially nonbonding with respect to the cluster skeleton.[20] To a boron chemist, who would view both $Fe_2(CO)_6B_2H_6$ and $Fe_2(CO)_6S_2$ as four-atom clusters[21] rather than bridged, metal–metal bonded dinuclear complexes, this is not too surprising. A complete discussion of the photoelectron spectra of these compounds will be given elsewhere.

Registry No. $Fe_2(CO)_6B_2H_6$, 70130-42-6; $Fe_2(CO)_6S_2$, 58500-79-1.

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Comparative Photochemistry of *trans*-[Cr(en)₂NH₃F]²⁺, [Cr(NH₃)₅F]²⁺, and [Cr(en)ₓ(NH₃)₆₋₂ₓ]³⁺. Harmony and Discord with Recent Theory

Sir:

In two recently published papers,[1,2] Vanquickenborne and Ceulemans (VC) have presented a new theory of chromium(III) photochemistry, including both the prediction of the reaction modes of complexes and their stereochemistry. An earlier paper of ours[3] on the photochemistry of *trans*-[Cr(en)₂NH₃F]²⁺ and [Cr(NH₃)₅F]²⁺ reported that the results were in disagreement with the then-existing theories. Since they agree well with the new theory, at least as far as the prediction of the reaction modes is concerned, one purpose of this correspondence is to reinterpret those results in this light. Our other reasons for this correspondence relate to a study[4] of the photochemistry of [Cr(en)ₓ(NH₃)₆₋₂ₓ]³⁺ which confirms and strengthens the interpretation of the results[3] relating to the stereochemistry of axial and equatorial ammonia aquation in [Cr(NH₃)₅F]²⁺. These results have very important implications for the VC theory of the stereochemistry[2] of such processes.

The first of our objectives requires spectroscopic parameters for the ligands of interest. Following the VC theory, we adopt for ethylenediamine and ammonia ϵ_σ 7183 and ϵ_π 0 cm⁻¹ and for fluoride ϵ_σ 7633 and ϵ_π 1700 cm⁻¹. (These values ignore the small difference, 1.5%, in σ-donor strength of the first two ligands.) Hence, one calculates the $^4B_2/^4E$ spacing to be 1360 cm⁻¹, with ^4E being the lower of the two excited states, possessing 73.0% d_{z^2} character. Then, following eq 5 of ref 1, one finds for the ^4E state

$$I^*(Cr-NH_3) = (2 - 0.730)\epsilon_\sigma(NH_3) = 9125 \text{ cm}^{-1}$$

$$I^*(Cr-en) = [(2 \times 0.730 + 5)/4]\epsilon_\sigma(en) = 11\,600 \text{ cm}^{-1}$$

$$I^*(Cr-F) = (2 - 0.730)\epsilon_\sigma(F^-) + 3\epsilon_\pi(F^-) = 14\,800 \text{ cm}^{-1}$$

and for the $^4B_2$ state

$$I^*(Cr-NH_3) = 2\epsilon_\sigma(NH_3) = 14\,400 \text{ cm}^{-1}$$

$$I^*(Cr-en) = {}^5\!/_4\epsilon_\sigma(en) = 9000 \text{ cm}^{-1}$$

$$I^*(Cr-F) = 2\epsilon_\sigma(F^-) + 2\epsilon_\pi(F^-) = 18\,700 \text{ cm}^{-1}$$

On the basis of these calculated strengths for the various bonds, one expects that the ^4E state would lose predominantly ammonia and the $^4B_2$ predominantly ethylenediamine. (If the calculated bond-strength differences could be equated to activation-energy differences, then at room temperature ^4E would favor ammonia loss by a factor of 10⁵, and $^4B_2$ would favor ethylenediamine loss by a factor of 10¹¹.) The qualitative predictions of the theory are in complete agreement with the proposals made in our earlier paper where we concluded that the observations required participation by two excited states, most probably ^4E and $^4B_2$, leading to preferential ammonia loss and ethylenediamine loss, respectively, and remove many of the difficulties of interpretation discussed there.[3]

At all wavelengths both modes of photolysis are observed, but with different apparent activation energies for long-wavelength irradiation. At long wavelengths the ethylenediamine mode has an activation energy of about 50 kJ mol⁻¹. It is not clear whether this corresponds to the difference in activation energy for aquation of the ^4E state with ethylenediamine or ammonia loss, respectively, or if it corresponds to excitation of ^4E to $^4B_2$, with subsequent preferential loss of ethylenediamine from that state. It could also correspond to some other possibility such as, for example, activated absorption to $^4B_2$ from the ground state. From the above calculations the naive expectations for the activation energies for the first two mechanisms are 30 and 16 kJ mol⁻¹, respectively,

both lower than the observed value. In view of the uncertainties, including the unknown energy differences due to vibrational and solvent relaxation, this lack of agreement may have no significance, and a choice cannot be made. Obviously further data are required. A useful approach is the study of relative quenching of two reaction modes in such molecules,[5] and such studies are currently underway in our laboratory for *trans*-[Cr(en)$_2$NCSF]$^+$.

A second aspect of our work[3] concerned a comparison of the stereochemistry of photolysis of *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$ and [Cr(NH$_3$)$_5$F]$^{2+}$. When irradiated at 436 nm, where the ratio of the two photolysis modes has become wavelength independent, the former complex aquated 65% ammonia, yielding *cis*-[Cr(en)$_2$H$_2$OF]$^{2+}$ almost exclusively, while [Cr(NH$_3$)$_5$F]$^{2+}$ aquated to 15% *trans* and 85% *cis*-[Cr(NH$_3$)$_4$H$_2$OF]$^{2+}$, also wavelength independent. Comparing the behavior of the two complexes, we concluded that the latter result must arise by loss of 65% axial ammonia to give 65% *cis*-[Cr(NH$_3$)$_4$H$_2$OF]$^{2+}$ and loss of 35% equatorial ammonia yielding 15% trans and the remaining 20% cis. Hence, we concluded that the stereochemistry of equatorial ammonia loss was about 45% trans/55% cis.

This argument assumes (1) that axial ammonia loss in [Cr(NH$_3$)$_5$F]$^{2+}$ leads exclusively to *cis*-[Cr(NH$_3$)$_4$H$_2$OF]$^{2+}$, (2) that similar excited states, with similar labilizations, participate in photoreaction for the two complexes, and (3) that ethylenediamine and ammonia are the same as leaving groups.

The first assumption is fairly secure on the basis of considerable study of axial labilizations and in light of the clear result of *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$ ammonia labilization (see later). The second assumption is not quite so secure given our lack of knowledge of the photophysics of the systems but is supported by the similarity in overall quantum yields and their temperature and wavelength dependence for the two complexes and by the theoretical predictions for the labilizations.

Our study of [Cr(en)$_x$(NH$_3$)$_{6-2x}$]$^{3+}$ now provides data on the third assumption, which turns out to be incorrect in detail. For both *cis*- and *trans*-[Cr(en)$_2$(NH$_3$)$_2$]$^{3+}$ loss of ethylenediamine from the excited state had a rate constant 2.8 times that for ammonia, which we attribute to steric strain in the ethylenediamine chelate ring. This factor is likely to be similar in *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$, so, on the assumption that the same rate constant ratio applies for this complex, the observation of 35% ethylenediamine loss implies a 19% loss of equatorial ammonia in [Cr(NH$_3$)$_5$F]$^{2+}$ if the labilizations in the two complexes are the same. The products of the latter photolysis then arise as follows: 81% of the cis product from the 81% axial ammonia loss; the 15% trans, with 4% cis from the 19% equatorial ammonia loss, leading to a 20% cis/80% trans stereochemistry associated with equatorial labilization. The effect of correcting for the more facile ethylenediamine loss is clearly to increase significantly the percentage of trans product arising from equatorial labilization in [Cr(NH$_3$)$_5$F]$^{2+}$. Even if one argues that the rate-constant ratio does not carry over in the simple way assumed here, any more sophisticated analysis is not going to reverse the direction of the correction.

We conclude that at least 45%, more likely about 80%, but possibly even 100% of the product of equatorial labilization of ammonia is *trans*-[Cr(NH$_3$)$_4$H$_2$OF]$^{2+}$. The importance of this result is twofold. First, it demonstrates the stereomobility of equatorial labilization in this complex.

Second, the results allow a discriminating test of the new theory of chromium(III) photostereochemistry.

There are two aspects to be discussed. First, what should be the stereochemistry of the products arising from aquation from the lowest quartet excited state of [CrL$_5$F]$^{2+}$ complexes, and second, what would be the differences expected for the

stereochemistry of axial and equatorial L loss in such molecules?

For [CrL$_5$X]$^{2+}$, where X is a poorer σ donor than L, Vanquickenborne and Ceulemans[2] prove that, for a dissociative mechanism in which concerted reaction of a five-coordinate intermediate occurs, loss of axial L from the lowest quartet excited state (^{4}E) will lead to a trigonal-bipyramidal intermediate with equatorial X and that this will form *cis*-aquo-X product due to the symmetry restrictions on attack of the aquo ligand on the trigonal bipyramid. Hence, they predict that *cis*-aquoacido product will form in all such cases, except that they qualify the result where X = F$^-$ since ϵ_σ(F) > ϵ_σ(en). Here they predict the same intermediate but allow for some trans entry of water. In this way they account for the 8% trans product reported for photolysis of *trans*-[Cr(en)$_2$FCl]$^+$. Could this be the explanation of our finding of 15% trans product in aquation of [Cr(NH$_3$)$_5$F]$^{2+}$? We believe not. In the first place the experimental data on *trans*-[Cr(en)$_2$FCl]$^+$ was found to be difficult to rely upon by us.[3] But more positively, we have unequivocal results showing that *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$ loses ammonia to give virtually exclusively *cis*-[Cr(en)$_2$H$_2$OF]$^{2+}$. This constitutes an experimental confirmation that the intermediate [Cr(en)$_2$F]$^+$, F$^-$ equatorial, if it exists as postulated in the VC theory, behaves in the way predicted by the symmetry rules and in the same way as other CrL$_4$X intermediates would have to behave in order to accord with both theory and experiment. To summarize, axial ammonia loss from *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$ leads to *cis*-aquofluoro product; if the VC theory requires some trans product, then it has failed, if not, it remains consistent with experiment to this point.

The second aspect deals with the comparison of the stereochemistry of axial and equatorial labilization from [Cr(NH$_3$)$_5$F]$^{2+}$. The first problem met in considering this is whether or not the two reaction modes observed arise from the same or different excited states. It is quite likely that the latter occurs although the evidence also suggests that preferential and not exclusive reaction modes occur from particular excited states at room temperature. We therefore wish to consider all the reasonable possibilities from the standpoint of the VC theory.

Vanquickenborne and Ceulemans deal with the case of loss of the axial L ligand from the [CrL$_5$X]$^{2+}$ ^{4}E state and show this should lead to the trigonal bipyramid with X equatorial (A). This will lead to *cis*-aquo-X product, as observed for *trans*-[Cr(en)$_2$NH$_3$F]$^{2+}$ and presumed, by analogy, for axial ammonia loss from [Cr(NH$_3$)$_5$F]$^{2+}$. Loss of equatorial L from ^{4}E is not predicted to occur in the simple theory as the main labilization lies on the z axis. However, if it did occur as a minor process, it would leave a vacant site associated with the d$_{x^2-y^2}$ orbital which is partly destabilized in the excited state. The resulting tetragonal pyramid would be expected to rearrange, by movement of the X and L ligands out of plane, to the *same bipyramid A*, as before.[6] This mechanism, namely, both axial and equatorial L loss from the ^{4}E state of [CrL$_5$X]$^{2+}$, therefore leads to a prediction of pure *cis*-aquo-X product.

Unfortunately, VC did not consider, in their paper, reaction of the ^{4}B$_2$ state and therefore did not give calculated state-correlation diagrams. We therefore will argue on the basis of an orbital-energy model, which they showed was valid for the ^{4}E and ^{4}B$_1$ states. The ^{4}B$_2$ state arises from promotion of an electron from xy to $x^2 - y^2$ and is therefore $(xz)^1$, $(yz)^1$, $(x^2 - y^2)^1$, predicting equatorial labilization for this state. Loss of L from the x or y axis will yield a tetragonal pyramid in which the old z axis is not destabilized and in which the remaining three L ligands on the x and y axes are. Also xz and yz are occupied which will tend to reinforce the rigidity

of the old z axis and also confine rearrangement of ligands to the xy plane. We conclude that rearrangement will and can only occur to the trigonal bipyramid with X apical (B) and that attack by the entering water molecule will be limited by the electron distribution to the equatorial plane, with the same cis-attack symmetry rule as for bipyramid A. This intermediate can lead, therefore, only to *cis*-aquo-X product in the theory. The last possibility, loss of the axial L from the $^4B_2$ state, seems highly improbable as there is no labilization on this axis. If, however, it did occur, it would be expected to give a tetragonal pyramid of high reactivity, with a doubtful urge to rearrange to any trigonal bipyramid. It would therefore react with retention of configuration and would be expected to yield trans product exclusively. We consider it so improbable, however, that we do not entertain it as a real possibility.

We conclude that the VC theory predicts (1) that axial and equatorial ligand loss from the ^4E state lead to the same trigonal bipyramid and therefore give rise to the same product stereochemistry[6] and (2) that equatorial ligand loss from the $^4B_2$ state of $[CrL_5X]^{2+}$ leads eventually only to cis aquo product.

These predictions cannot account for the high proportion of trans product found as a result of equatorial ammonia loss in $[Cr(NH_3)_5F]^{2+}$, and we conclude that the VC theory of the stereochemistry cannot be correct. The author has argued before[7] that the unique features of the stereochemistry of Cr(III) photoreactions likely relate to the vacant t_{2g} orbital in the excited state, which enables bonding of an entering ligand, and that reaction by a concerted mechanism involving a seven-coordinate transition state is the most likely explanation of the stereomobility of the process. A theory along these lines would be most useful.

Registry No. *trans*-$[Cr(en)_2NH_3F]^{2+}$, 58410-71-2; $[Cr(NH_3)_5F]^{2+}$, 65982-64-1; *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$, 66008-06-8.

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Relationship of the *styx* Rules to Wade's Rules

Sir:

For simplicity, consider a neutral boron hydride B_pH_{p+q} in which there is one external terminal hydrogen on each boron. The *styx* rules[1,2] were formulated from the electrons of the inner polyhedral surface,[2] neglecting bonds to the outer surface of the external hydrogens, as

$$s + x = q$$
$$s + t = p$$
$$t + y + (q/2) = p$$

and hence are related to the total electron count of the inner surface. Addition of the first equation to the last yields

$$s + t + y + x = p + (q/2)$$

Either side of this equation is recognizable as the number of bonding pairs. Wade's rules[3] then follow upon identification of q values of 2, 4, 6, and 8 with the closo, nido, arachno, and hypho types of boron hydrides, corresponding to the earlier formulation initiated by Stock of B_pH_{p+2}, B_pH_{p+4}, B_pH_{p+6}, and B_pH_{p+8} series and to examples were addition of electrons open the polyhedra.[2]

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The Reaction Product of Uridine with Dimeric Copper Acetate: Not a Monomer

Sir:

Biological processes which distinguish between ribo- and deoxyribonucleosides frequently involve metal ions.[1] Berger et al.[1] have presented evidence that dimeric copper(II) acetate $(Cu_2(OAc)_4)$ in dimethyl sulfoxide (Me_2SO) reacts with ribonucleosides to form a unique type of dimeric complex in which the 2' and 3' furanose hydroxyl oxygens interact with each of the Cu atoms as in I. The distance between the O

I
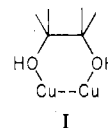
atoms is 2.7 Å and that between the Cu atoms in $Cu_2(O-Ac)_4\cdot2H_2O$ is 2.64 Å. Deoxynucleosides which lack analogous hydroxyl groups cannot form such a complex. The validity of this intriguing dimer model has been questioned.[2-4] The principal objection offered in the literature is that the available spectroscopic data can be accommodated by monomeric Cu(II) species.[2,3]

Some important observations reported earlier[1] for Me_2SO solutions of $Cu_2(OAc)_4$ include: a 50% hypochromic effect at ~715 nm upon addition of various ribonucleosides, no spectral change upon addition of pyrimidine deoxynucleosides, and a stoichiometry of one ribonucleoside to one $Cu_2(OAc)_4$ dimer.

Frozen Me_2SO solutions of $Cu_2(OAc)_4$ and ribonucleosides were investigated later by Brun et al.[2] using ESR. These frozen solutions had signals which were attributed to monomeric Cu(II) complexes. Without any experimental justification, it was concluded that monomers must also be formed at ~300 K. The visible spectral changes accompanying the