nate bond lengths exhibited with various types of donor atoms (e.g., Cu-N bonds = 1.95 Å in Cu(14-ane-N$_4$)(ClO$_4$)$_2$, while Cu-S bonds = 2.30 Å in Cu(14-ane-S$_4$)(ClO$_4$)$_2$).[14]

(iii) The similarity in k_f ratios exhibited by the corresponding open-chain and cyclic ligands for both the polyamines and polythiaethers implies that any ligand solvation effects contributing to the macrocyclic effect in the polyamine complexes must be manifested kinetically in the dissociation rate constants. Thus it is inferred that it is the difference in the solvation of complexed and partially bonded open-chain and cyclic ligands which gives rise to the reported solvation effects while the solvation of the uncomplexed and partially bonded species are not significantly different for the two ligand types.

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T. E. Jones, L. L. Zimmer
L. L. Diaddario, D. B. Rorabacher*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

L. A. Ochrymowycz
Department of Chemistry, University of Wisconsin-Eau Claire
Eau Claire, Wisconsin 54701

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Evidence for Metastable Five-Coordinate Cobalt(III) Intermediates

Sir:

The induced aquation of *trans*-MN$_3$Cl$^+$ (where M designates the Co^{III}(en)$_2$ group) with NO$^+$ gave (27 ± 3)% *cis*-MH$_2$OCl^{2+} and the rest trans product[1] and the induced aquation of *trans*-MCl$_2^+$ with Hg^{2+} gave (28 ± 5)% *cis*-MH$_2$OCl^{2+} and the rest trans product.[2] The induced aquation of *cis*-MN$_3$Cl$^+$ with NO$^+$ gave (79 ± 2)% *cis*-MH$_2$OCl^{2+} and the rest trans product[3] and the induced aquation of D-*cis*-MCl$_2^+$ with Hg^{2+} gave approximately 70% D-*cis*-MH$_2$OCl^{2+} and the rest trans product.[2] It is obvious that the induced aquations of the cis and trans reactants do not pass through a common nuclear configuration before the aquo-products are formed from the reactants. A trigonal bipyramidal intermediate with equatorial Cl$^-$ directing ligand has been postulated for the induced aquations of the cis reactants[2,3] and a square pyramidal intermediate for those of the trans reactants. Here the two different intermediates will be designated as *c*-MCl^{2+} and *t*-MCl^{2+} only for the purpose of indicating that they came from cis reactants and from trans reactants, respectively. Several different explanations are advanced below for the lack of a common nuclear configuration for the *c*-MCl^{2+} and *t*-MCl^{2+} moieties which depend on the lifetimes of these five-coordinate cobalt(III) moieties. Strong evidence will be reported here for the existence of the metastable intermediates described in the fourth explanation.

First, the five-coordinate MCl^{2+} moieties may exist only in activated complexes with the sixth ligand (H$_2$O) being attached as the point representative of the reacting system moves "downhill" from the activated complex region to the product region of phase space.

Second, the *c*-MCl^{2+} and *t*-MCl^{2+} intermediates may exist only long enough to survive a few collisions in escaping the solvent cages in which they were formed and, during this short lifetime, are changing toward a common intermediate but do not reach it before attaching the sixth ligand to form products.

Third, the two intermediates may have a lifetime shorter than the solvent cage lifetime ($<10^{-10}$ sec), so they cannot "hunt" for different nucleophiles in the bulk solution, nor do they relax toward a common configuration during this lifetime.

Fourth, the two intermediates may have sufficient stability to survive many collisions in diffusing through the solution and hence to rather selectively react with a choice of nucleophiles. We present evidence for this last explanation from an investigation of the competition reactions of the five-coordinate cobalt(III) moieties for H$_2$O and Cl$^-$ in aqueous chloride solutions. The facts are these.

(1) The ratio of *trans*-MCl$_2^+$/*cis*-MCl$_2^+$ products formed from the *trans*-MN$_3$Cl$^+$ + NO$^+$ reaction does not decrease with decreasing Cl$^-$ concentration in the range 2.0 $M \geq$ [Cl$^-$] $\geq$ 0.5 M and no measurable amounts of the cis isomer are formed; all entering Cl$^-$ ligands go in trans to the directing Cl$^-$ group.

(2) The ratio of *trans*-MH$_2$OCl^{2+}/*cis*-MH$_2$OCl^{2+} formed from the *trans*-MN$_3$OH$_2^{2+}$ + NO$^+$ reaction is approximately equal to 4 and does not decrease with decreasing Cl$^-$ concentration in the 0.5–2.0 M range.

(3) The ratio of *trans*-MH$_2$OCl^{2+}/*cis*-MH$_2$OCl^{2+} formed from the *cis*-MN$_3$OH$_2^{2+}$ + NO$^+$ reaction does not increase with decreasing Cl$^-$ concentration in the same range and no measurable amounts of trans isomer are formed; all entering Cl$^-$ ligands go in cis to the directing H$_2$O group.

(4) The ratio of *cis*-MH$_2$OCl^{2+}/*trans*-MH$_2$OCl^{2+} formed from the *cis*-M(DMSO(Cl^{2+} + MnO$_4^-$ reaction (DMSO = dimethyl sulfoxide) is the same as from the *cis*-MN$_3$Cl$^+$ + NO$^+$ and *cis*-MCl$_2^+$ + Hg^{2+} reactions.[2,3]

(5) The ratio of *trans*-MCl$_2^+$/*cis*-MCl$_2^+$ formed from the *cis*-M(DMSO)Cl^{2+} + MnO$_4^-$ reaction does not increase with decreasing Cl$^-$ concentration and no measurable amounts of the trans isomer are formed; all entering Cl$^-$ ligands go in cis to the directing Cl$^-$ group.

Fact 1 indicates that *t*-MCl^{2+} does not fit the second explanation because *t*-MCl^{2+} has to live longer at low Cl$^-$ concentrations than at high Cl$^-$ concentrations in order to react with Cl$^-$ yet the product ratio *trans*-MCl$_2^+$/*cis*-MCl$_2^+$ does not begin to approach that formed from *c*-MCl^{2+}.

Facts 2 and 3 also indicate that the *t*-MOH$_2^{3+}$ and *c*-

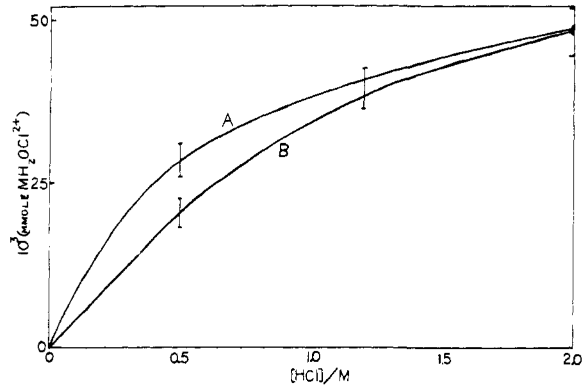

Figure 1. Millimoles of $Co(en)_2H_2OCl^{2+}$ formed as a function of HCl concentration: curve A, ionic strength equal to HCl concentration; curve B, $HClO_4$ added to maintain 2.00 *M* ionic strength.

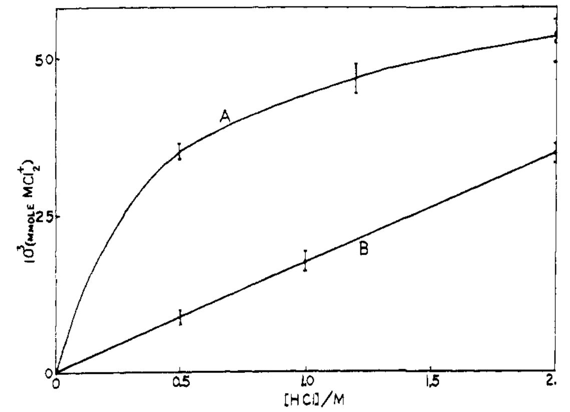

Figure 2. Millimoles of $Co(en)_2Cl_2^+$ formed as a function of HCl concentration: curve A, *trans*-$Co(en)_2Cl_2^+$ formation (variable ionic strength); curve B, *cis*-$Coen_2Cl_2^+$ formation (2.00 *M* ionic strength).

MOH_2^{3+} moieties do not significantly approach a common configuration as Cl^- concentration is decreased because the *trans*-MH_2OCl^{2+}/*cis*-MH_2OCl^{2+} product ratios do not begin to approach one another as Cl^- concentration is decreased.

Fact 4 indicates that the same *c*-MCl^{2+} moiety is formed in the *cis*-$M(DMSO)Cl^{2+}$ + MnO_4^- reaction as in the *cis*-MN_3Cl^+ + NO^+ and *cis*-MCl_2^+ + Hg^{2+} reactions.

Fact 5 (analogous to fact 1) indicates the *c*-MCl^{2+} is not changing rapidly toward an equilibrium configuration common to *c*-MCl^{2+} and *t*-MCl^{2+}.

Facts 1-5 fit the first explanation if Cl^- ions as well as H_2O molecules were in the solvation shell of the activated complex. The entering group could replace the leaving group during deactivation of the activated complex (facts 1, 3, and 5) or the entering group could go in cis and trans to the directing group (facts 2 and 4) as dictated by the energetics of the activated complex. These facts also fit the third explanation if Cl^- ions as well as water molecules occupy positions in the solvent cage of the very short-lived intermediates. Likewise these facts fit the fourth explanation with the five-coordinate intermediates having sufficient stability to establish ion-pair equilibria and to finally react in preferred orientations with different nucleophiles without significantly approaching a common equilibrium nuclear configuration. If the first or third explanation were correct, the entering Cl^- ions must be in the solvation shell of the five-coordinate cobalt(III) moieties so that the Cl^- ion can occupy the sixth coordination site as well as water; these Cl^- ions are there as a result of ion-pair formation with the reactant(s). These three explanations can be tentatively distinguished by further facts given below.

(6) For the *trans*-$MN_3OH_2^{2+}$ + NO^+ reaction, the number of millimoles of MH_2OCl^{2+} formed shows (see Figure 1) a saturation effect with increasing Cl^- concentration both for varying and constant ionic strength conditions while the value of the product ratio r_1 defined by eq 1 decreases from 0.48 ± 0.06 at 0.50 *M* HCl to 0.28 ± 0.04 at 2.00 *M* HCL.

$$r_1 = \frac{(\text{total mmol of } MH_2OCl^{2+})}{[Cl^-](\text{total mmol of } M(H_2O)_2^{3+})} \tag{1}$$

(7) For the *trans*-MN_3Cl^+ + NO^+ reaction, the number of millimoles of *trans*-MCl_2^+ formed shows (see Figure 2) a strong saturation effect at variable ionic strength while the value of the product ratio r_2 defined by eq 2 decreases from 0.95 ± 0.05 at 0.50 *M* HCl to 0.34 ± 0.04 at 2.00 *M* HCl. (Insolubility of [*trans*-$MN_3Cl]ClO_4$ prevented use of $HClO_4$ to maintain constant ionic strength.)

$$r_2 = \frac{(\text{total mmol of } Co(en)_2Cl_2^+)}{[Cl^-](\text{total mmol of } MH_2OCl^{2+})} \tag{2}$$

(8) For the *cis*-$M(DMSO)Cl^{2+}$ + MnO_4^- reaction, the number of millimoles of *cis*-MCl_2^+ formed does not show (see Figure 2) a saturation effect at constant ionic strength and the product ratio r_2 is constant at 0.14 ± 0.02.

Fact 6 is more consistent with production of the *t*-MOH_2^{3+} intermediate and saturation with respect to *t*-$MOH_2^{3+}\cdot Cl^-$ ion-pairs with increasing Cl^- concentration than with the first and third explanations because +3 cations are known to be better ion-pair formers than +2 cations. Fact 7 virtually excludes the first and third explanations because saturation with respect to *trans*-$MN_3Cl^+\cdot Cl^-$ ion pairs in the Cl^- concentration range used is not a very acceptable explanation. Facts 7 and 8 are consistent if *t*-MCl^{2+} forms more ion pairs with Cl^- corrected positioned for reaction trans to the Cl^- directing group than *c*-MCl^{2+} forms for reaction cis to the Cl^- directing group.

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W. L. Reynolds,* N. Morey, S. C. McFarlan
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

M. Collins, M. Rigney
Department of Chemistry, St. John's University
Collegeville, Minnesota 56321

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Electron Spin Resonance Spectrum of F_3NO^-. A Hypervalent Radical from First-Row Elements[1]

Sir:

We wish to report the ESR detection and identification of the trifluoramine oxide radical anion, F_3NO^-. This radical is of particular interest because it represents the first example of a 33 valence electron species derived solely from first-row elements, although the related phosphoranyl radicals PF_4[2] and Cl_3PO^-[3] are well established. Perhaps the discovery of this novel radical is not entirely unexpected in the light of previous work showing that the electronic structure of phosphoranyl radicals does not require extensive d-orbital participation.[3]