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Henry Taube

Department of Chemistry  
Stanford University  
Stanford, California 94305

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The studies conducted under AT(04-3)-326 embrace the following subject areas:

- A. Ion Solvation
- B. Mechanistic Studies on Substitution Reactions in Metal Complexes
- C. Oxidation of Coordinated Ligands
- D. Mechanistic Studies on Electron Transfer Reactions
- E. Preparation and Characterization of New Species in the Aquo and Ammino Systems

The summary of results will conform to these categories, and will include a sixth section describing auxiliary studies which can most conveniently be accommodated under the heading F. "Miscellaneous."

Some introductory remarks on the evolution of the research may be in order. It began with an emphasis on the use of stable isotopes in characterizing species in solution and in studying their reactions, using both fractionation and tracer effects. Two influences, one negative and the other positive in character, brought about a change in emphasis. The negative influence can be stated simply: the isotope studies depended on mass spectrometric measurements of high quality, and I found that to keep the mass spectrometer operating at the necessary level of discrimination proved to be a financial burden which it was impossible to support on a continuing basis. In particular, there was no way of anticipating when a major failure, requiring for its correction a major investment in time and cost, would occur, and too often such costs had to be met out of general operating funds.

The second factor was more positive in nature. Whereas the work at the beginning was devoted to the characterization of known species, and to the examination of known kinds of reactions, involving usually species derived from first-row transition elements, it gradually became apparent, largely through lessons learned in a study of the chemistry of ruthenium complexes, that the chemistry of the second and third row elements could

not be predicted from that of their first-row congeners. Coupled to this was the realization that very little chemistry of the kind which had been emphasized in our work, had been done for second and third row transition elements. In fact for the later periods, species analogous to those which formed the subject of study for the first transition period had in many cases not been prepared. This led to the initiation of a program devoted to discovering new species for second and third row elements, with  $H_2O$  and  $NH_3$  as ligands, a program which had become the major thrust of our work under AEC auspices when support was terminated.

It is important to justify the emphasis in our work on  $NH_3$  and  $H_2O$  as ligands. The rationale of this choice is as follows. Much of the new chemistry of metal complexes in the past two decades has emphasized unsaturated ligands, or ligands such as those with P or As as donor atoms which to all intents and purposes, act as unsaturated ligands. This emphasis is fully justified by the results, many unexpected combinations having been discovered in the course of this work. But from the standpoint of a fundamental understanding of chemical behavior such work is bound to be incomplete. It is characteristic of such ligands that they tend to mask the individuality of the metal atoms - e.g.  $Fe(CO)_5$  and  $Ru(CO)_5$  are remarkably alike despite the obvious fact that the core elements belong to different periods. Saturated ligands, though they have in recent time received little attention, are nevertheless of basic interest, the individuality of the complexes with different metal centers being more pronounced with ligands such as  $H_2O$  or  $NH_3$  than it is with the unsaturated ones. Water is, of course, of special significance not only as ligand, but as comprising the most important reaction solvent.

A list of papers based on work sponsored by the AEC under Contract No. AT(04-3)-326 is appended to the summary of results which follows. They are classified according to subject category adopted in the introduction, and are referred to by a letter-number combination. Other references are given in the running text and are identified by numbers alone.

The work on ion solvation was an outgrowth of that done at the University of Chicago using the  $^{18}\text{O}$  isotope detection technique. With the discovery<sup>1/</sup> of an nmr resonance for  $^{17}\text{O}$ , the potential of the nmr technique for the study of ion solvation became apparent. I had a share in the earliest such applications,<sup>2/</sup> not in work supported by the AEC grant, but in collaboration with a group at Los Alamos where equipment and partially enriched  $\text{H}_2^{17}\text{O}$  was at hand. Only within the last few years, using equipment made available under an NSF Equipment Grant has the capability for doing this kind of work been at my disposal here. One study which was completed was the measurement of the rate of water exchange between  $\text{V}(\text{H}_2\text{O})_6^{2+}$  and solvent<sup>(A2)</sup>. These measurements were important for two reasons: (i)  $\text{V}^{2+}$  is isoelectronic with  $\text{Cr}^{3+}$  and with the completion of the research on  $\text{V}(\text{H}_2\text{O})_6^{2+}$ , a comparison of labilities for isoelectronic ions of differing charge was possible. (The effect on the rate is dramatic,  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  exchanging water at only  $10^{-8}$  of the rate for  $\text{V}(\text{H}_2\text{O})_6^{2+}$ .) (ii) A number of reactions of  $\text{V}(\text{H}_2\text{O})_6^{2+}$  as reducing agent appeared to be governed by the rate at which a polar group on the oxidizing agent can substitute on  $\text{V}(\text{H}_2\text{O})_6^{2+}$ , and the rate of water exchange for this species was of special interest in this context. The values of rates and of  $\Delta H^\ddagger$  for the water exchange proved to be in harmony with those recorded for oxidation reactions, the rates of which were presumed to be controlled by substitution.

The rate of water exchange for  $\text{V}(\text{H}_2\text{O})_6^{3+}$  has also been measured.<sup>(A4)</sup> At  $25^\circ$  the value of the specific rate is ca.  $10^3 \text{ sec}^{-1}$  compared with  $1.0 \times 10^2 \text{ sec}^{-1}$  for  $\text{V}(\text{H}_2\text{O})_6^{2+}$ , but the activation energy for the former process is considerably lower.

In the course of the work described<sup>(A2)</sup> the nuclear relaxation of  $^{17}\text{O}$  in  $\text{H}_2\text{O}$  as produced by  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  through outer-sphere interactions was also measured. These results inspired the work in progress by Anderson<sup>(A3)</sup> to

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<sup>1/</sup> H. E. Weaver, B. M. Tolbert and R. C. LaForce, J. Chem. Phys. 23, 1956 (1955).

<sup>2/</sup> J. A. Jackson, J. F. Lemons and H. Taube, J. Chem. Phys. 32, 553 (1960); J. Chem. Phys. 38, 836 (1963).

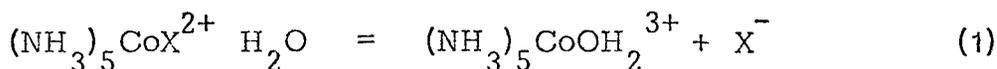
try to quantify "outer sphere" effects in the same way as has been found possible for inner sphere effects. This effort has not been productive of results here at Stanford during the past year because the major effort has been devoted to making the necessary improvements in the sensitivity and stability of the equipment. Some measurements were made by Anderson at Los Alamos during the past summer. These yielded the remarkable conclusion that there is no discrimination between  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  for "outer sphere" positions on  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ .

When water is a ligand, proton nmr for the molecule is of limited use because the O - H bond is often more readily cleaved than is the bond between oxygen and a metal ion. But for alcohols and related ligands, the protons can successfully be used as a tracer for the molecule. This potential was exploited, using proton nmr to determine the solvation number of  $\text{Mg}^{2+}$  in  $\text{CH}_3\text{OH}$ .<sup>(A1)</sup> At room temperature, the bands for coordinated methanol and solvent methanol coalesce, but they become resolved at low temperature making it possible to determine the coordination number of the magnesium ion. This work represents the first application of proton nmr to determining ion solvation numbers and the further application of the method has become a major research enterprise.

## B

The work on this heading was conducted solely using  $^{18}\text{O}$ . It was concerned with two themes (i) the mechanism of substitution at the metal ion centers, and (ii) studying exchange and tracer effects for complex ligands containing oxygen.

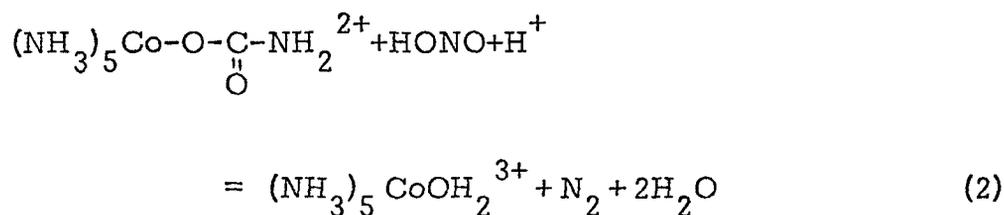
Under (i) we found<sup>(B1)</sup>, and to our disappointment, that  $^{18}\text{O}$  isotopic fractionations factors<sup>3/</sup> in a reaction of the type



<sup>3/</sup> F. A. Posey and H. Taube, J. Am. Chem. Soc. 79, 255 (1957).

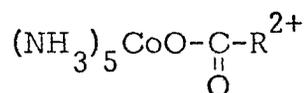
are not necessarily sensitive to the fine details of the mechanism of substitution. Other work<sup>4/</sup> had shown that although the mechanism of reaction I is largely dissociative, a genuine intermediate of lower coordination number is not produced with either  $X^-$  or  $H_2O$  as a leaving group but there is evidence that with a good leaving group a true intermediate is formed. Despite the difference in mechanism for the two classes, the fractionation factor  $d \ln^{16}O/d \ln^{18}O$ , as measured in the product water, proved to be the same within the capacity of our method to reveal differences (one part in  $10^3$ ). Product competition ratios were determined also for a number of different leaving groups, supporting the position that for a large class of such groups the distribution among products is affected by the leaving ligand.

As was mentioned, when good leaving groups are in question, the reactions apparently proceed through an intermediate of lower coordination number. The observations on the system implied by equation 2 are significant in this context:



Tracer studies showed that reaction takes place predominantly by Co - O bond cleavage. Nitrosation of the amide function produces  $CO_2$  in the coordination sphere of  $Co(III)$  and this is such a poor nucleophile that it is lost apparently without requiring assistance from the entering group.

For the work done under (ii) we were mainly concerned with the question of the position of bond breaking in the aquation or hydrolysis of complexes such as:

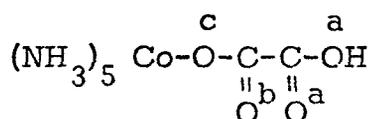



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<sup>4/</sup> Results of R. G. Pearson and J. W. Moore [Inorg. Chem. 3, 1334 (1964)] compared to those of A. Haim and H. Taube [*ibid.* 2, 1199 (1963)].

and with observing oxygen exchange between the ligand and solvent when the ligand is coordinated. Work was done with oxalate as a ligand, both in the chelate<sup>(B3), (B4)</sup> and monodentate forms<sup>(B4)</sup>, with acetate, formate and with trifluoroacetate.

In acidic solution, only exchange studies are feasible, the products of the aquation reaction equilibrating with solvent too rapidly to permit tracer effects to be described with any degree of confidence. With oxalate in the chelated form, the external oxygens exchange rather readily, at a rate which is proportional to  $[H^+]$  while the oxygen atoms attached to the metal exchange at a much slower rate. When the ligand is in the monodentate form, three kinds of oxygen are distinguishable in strong acid

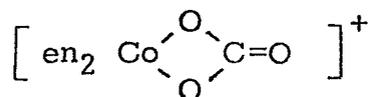


oxygen (b) exchanging most rapidly, then the two labelled (a) (the latter will be equivalent in exchange behavior, owing to the rapid shift of the proton from one oxygen to another). Perhaps the most interesting result is that oxygen (c) also exchanges. Studies on the rate of aquation of the oxalate complex and the affinity of  $\text{HC}_2\text{O}_4^-$  to Co(III) show<sup>(B7)</sup> that the exchange cannot arise from the aquation of the complex with subsequent reentry of the ligand. Apparently oxygens (b) and (c) interequilibrate by an intramolecular mechanism. At somewhat higher pH's, all the oxygens become equivalent in terms of exchange behavior. Thus there is also an intramolecular path for mixing oxygens (c) with (a) and (b). For  $\text{CF}_3\text{CO}_2^-$  and  $\text{HCO}_2^-$  as ligands, two oxygens can again be distinguished in terms of exchange behavior, but when  $\text{CH}_3\text{CO}_2^-$  is the ligand exchange is much less rapid than aquation.<sup>(B4)</sup>

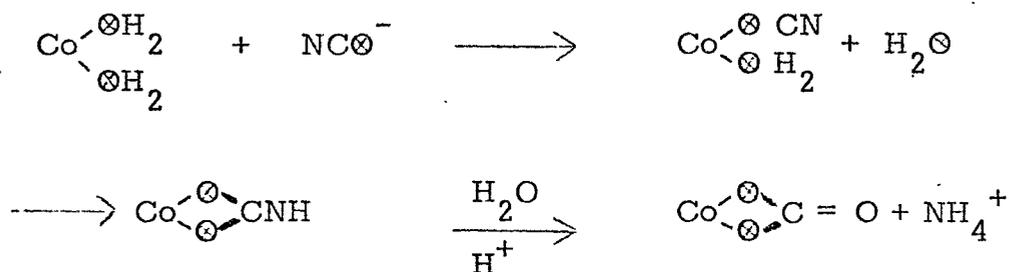
The alkaline hydrolysis of  $(\text{NH}_3)_5\text{CoO}_2\text{CCF}_3^{2+}$  proved to be especially interesting<sup>(B5), (B6)</sup>. The rate law shows that release of the ligand under the influence of  $\text{OH}^-$  takes place by two paths, one first order and the other

second order in  $[\text{OH}^-]$ . By the latter path, bond rupture is solely on the carbon center, and hydrolysis takes place without exchange; by the former path, bond rupture is solely at the metal atom, and extensive exchange accompanies reaction. This can be so large that the bridging oxygen as well as the carbonyl oxygen must be assumed to equilibrate with the solvent.

When  $\text{NCO}^-$  reacts with  $\text{Co en}_2 (\text{OH}_2)_2^{3+}$ ,  $\text{Co en}_2 \text{CO}_3^+$  is formed.



Oxygen tracer studies showed<sup>(B2)</sup> that one of the oxygen atoms in the chelate ring is derived from the original  $\text{NCO}^-$ , another from the aquo ion, and that the external oxygen is derived from the solvent. These results suggest the following course for the reaction



The reaction of  $\text{Hg}^{2+}$  or  $\text{Pb}^{2+}$  with  $\left[ (\text{NH}_3)_5 \text{CoOC}_\text{O} \right]^+$  in  $\text{H}_2^*\text{O}$  follows the isotopic course<sup>(B8)</sup> expressed by the products as  $(\text{NH}_3)_5 \text{CoOH}_2^{3+} \text{MC}^*\text{OO}_2$ . Carbondioxide from the complex is incorporated into  $\text{HgCO}_3$  or  $\text{PbCO}_3$ , without exchange.

The equilibrium and kinetic studies on the reaction of  $(\text{NH}_3)_5 \text{CoOH}_2^{3+}$  with  $\text{HC}_2\text{O}_4^-$  have already been referred to and their relevance to the subject of the mechanism of oxygen exchange between ligand and solvent noted. In the interests of providing a basic background for understanding carboxylate complexes of tripositive ions, a thorough study was made of  $\text{CrOAc}^{2+}$  in solution<sup>(B9)</sup>, including preparation, characterization and measuring the rate of aquation over a wide range of conditions.

It should be mentioned that apart from the intrinsic interest the oxygen isotopic studies might have as studies of mechanism, they are of importance in understanding the effects that metal ions exert on the reactivity of coordinated ligands. The significance of this subject is now much more widely appreciated than was the case when we began our studies, as is its relevance to the subject of metal ion catalysis including catalysis in biological systems.

### C

As an aspect of the influence which metal ions exert on the reactivity of ligands, I have had an interest<sup>5/</sup> in the oxidation of ligands attached to metal ions and in the question of participation by the central metal ions in oxidation by an external oxidant. The ligands referred to above are complex organic groups with the functions which are being oxidized located at a distance from the metal ions. Thusius<sup>(C1), (C2)</sup> showed that there is interest also in the case in which the function being oxidized is a simple molecule such as H<sub>2</sub>O or NH<sub>3</sub>, directly ligated to the central metal ion<sup>-</sup> which in most of our studies was Co(III). Only the strongest oxidizing agents are effective. Most of our work was done with the powerful 1e<sup>-</sup> oxidant, SO<sub>4</sub><sup>-</sup> or OH, which is generated by the decomposition reactions:



possibly followed by

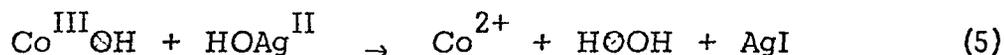


and some with the oxidizing species which is generated when Ag(I) is used as a catalyst for oxidation by S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

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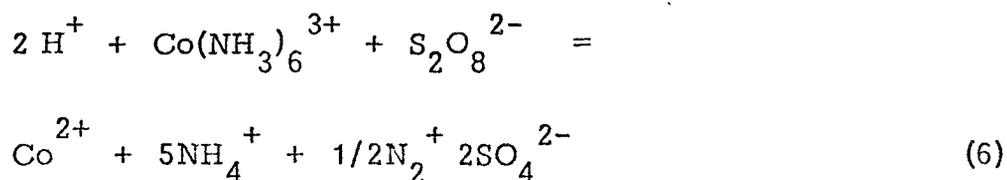
<sup>5/</sup> J. French and H. Taube, J. Am. Chem. Soc. 91, 6951 (1969);  
R. Robson and H. Taube, *ibid.* 89, 6487 (1967).

A particularly significant result was obtained by a tracer study on the oxidation of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  by the  $\text{Ag}^+ - \text{S}_2\text{O}_8^{2-}$  oxidizing system. <sup>(1)</sup> Oxygen is liberated and  $\text{Co}^{2+}$  is formed. Using  $\text{Co}(\text{NH}_3)_5^{18}\text{OH}_2^{3+}$ , it was found that as  $\text{Co}(\text{III})$  disappears, most of the bound oxygen appears in the gaseous  $\text{O}_2$  which is liberated. This is consistent with a reaction such as



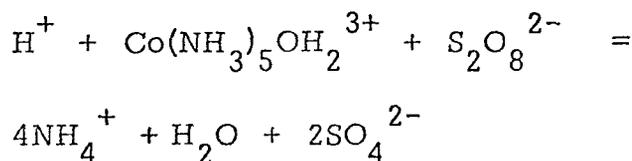
with the hydrogen peroxide being oxidized further to  $\text{O}_2$ . The reaction can be regarded as concerted withdrawal of electrons by  $\text{Co}(\text{III})$  and  $\text{Ag}(\text{II})$  from coordinated  $\text{OH}^-$  ions, O - O bond formation becoming possible as unpaired electrons are produced on each of the coordinated  $\text{OH}^-$  groups.

When a solution containing both  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{S}_2\text{O}_8^{2-}$  is heated, the reaction:



takes place. At rather low concentrations of  $\text{Co}(\text{NH}_3)_6^{3+}$ , the rate of consumption of this species becomes independent of its concentration, the rate of reaction then being governed solely by the rate of reaction (3). At the "saturation" rate, the  $\text{Co}(\text{III})$  complex is consumed at approximately half the rate at which  $\text{SO}_4^-$  is produced by reaction (3). Evidently in the saturation region, the oxidizing intermediate produced by reaction (3) is completely scavenged by  $\text{Co}(\text{NH}_3)_6^{3+}$ . The intermediate brings about the oxidation of coordinated  $\text{NH}_3$  with concomitant reduction of  $\text{Co}(\text{III})$ .

With  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ , the general behavior is similar, with the equation for the net change now being



When  $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$  is acted upon, the dominant reaction is still production of  $\text{N}_2$ , but approximately 5% of the gas is  $\text{N}_2\text{O}$ . For  $\text{Co}(\text{NH}_3)_2(\text{OH}_2)_4^{3+}$ ,  $\text{O}_2$  is the main gaseous product.

Tracer experiments show that the N - N bond in  $\text{N}_2$  is established by an intermolecular process, while the production of the N - O bond in  $\text{N}_2\text{O}$  is intramolecular. These results are best understood on the basis that Co(IV) is produced when a powerful 1e-oxidant attacks a cobaltamine. Cobalt (IV) in turn acts upon coordinated  $\text{NH}_3$  to produce  $\text{NH}$  which finally results in  $\text{N}_2$ , or on  $\text{NH}_3 + \text{H}_2\text{O}$  in the coordination sphere to produce  $\text{NH}_2\text{OH}$ , which finally results in  $\text{N}_2\text{O}$ .

It should be mentioned that the studies described are the only ones of this kind to have been done. They are of interest as illuminating the interplay between oxidation of a central metal ion and coordinated ligands, and undoubtedly will play a role in the radiation chemistry of the substrates when work with the cobaltamines is extended in that direction.

#### D

One of my major research interests for almost two decades has been trying to understand electron transfer processes in systems of simple chemistry -- that is, in considering an elementary step involving a redox change, to attempt to describe and understand the factors that influence the rate of the charge transfer process.

Several studies have been carried out on the present grant which have been significant for the development and elaboration of the subject. It is known that in the reduction of  $(\text{NH}_3)_5\text{CoOH}^{2+}$  by  $\text{Cr}^{2+}$ , oxygen is transferred from the Co(III) complex to chromium, and there is a substantial isotopic fractionation effort attendant on this process ( $d \ln {}^{16}\text{O} / d \ln {}^{18}\text{O} = 1.03_5$ ).<sup>6/</sup> Clearly then, as part of the activation process for electron transfer there is a

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<sup>6/</sup> R. K. Murmann, H. Taube and F. A. Posey, J. Am. Chem. Soc., 79, 262 (1957); H. R. Hunt and H. Taube, J. Phys. Chem. 63, 124 (1959).

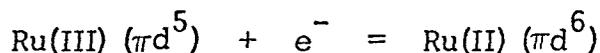
severe dislocation of the  $\text{Co}^{\text{III}}\text{-OH}$  bond, namely of the bond involving the bridging group. It is a matter of interest to learn whether dislocations of bonds involving non-bridging ligands are also called for in the activation process. To provide an answer, we have measured <sup>(D1)</sup> the fractionation factor ( $d \ln {}^{14}\text{N} / d \ln {}^{15}\text{N}$ ) for the ammonia ligands in  $(\text{NH}_3)_5\text{CoOH}^{2+}$ ,  $(\text{NH}_3)_5\text{CoCl}^{2+}$ , cis -  $\text{NH}_3\text{en}_2\text{CoOH}^{2+}$  and trans -  $\text{NH}_3\text{en}_2\text{CoOH}^{2+}$  when these species are reduced by  $\text{Cr}^{2+}$ . The fractionation factors are found to be very small, 1.001 to 1.002, and to be the same whether  $\text{NH}_3$  is cis or trans to the bridging group. We conclude that for the particular reactions under consideration, the only important bond dislocation in the electron transfer process involves the bridging group. This conclusion is not expected to apply to all such reactions -- in fact, DeChant and Hunt<sup>7/</sup> have observed a substantial oxygen isotopic fractionation factor in the reduction of trans- $\text{Cr}(\text{NH}_3)_4\text{OH}_2\text{Cl}^{2+}$  by  $\text{Cr}^{2+}$ , and somewhat less in the cis case. In both,  $\text{Cl}^-$  is the bridging ligand and  $\text{H}_2\text{O}$  is a non-bridging ligand. The important point is that it has been demonstrated that the measurement of isotopic fractionation effects on non-bridging ligands is a powerful tool in investigating the pattern of bond rupture in reduction of metal complexes.

Among the ligands which influence the rate of electron transfer from one metal complex to another, ammonia occupies a very special position. It is the most completely saturated ligand in the sense that unoccupied orbitals lie very high in energy, and probably play no important role in the electron transfer process. In contrast to water, which in other respects is closely related, coordinated ammonia has no unpaired electrons which can qualify it as a bridging ligand. Despite the special interest in ammonia complexes, little work has been done on their redox reactions and what has been done has involved  $\text{Co}(\text{III})$  or  $\text{Cr}(\text{III})$  complexes. These metal ions on being reduced, accept anti-bonding electrons into orbitals of  $\sigma$  symmetry. This calls for dramatic bond dislocations when the complexes are

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<sup>7/</sup> Sr. M. J. DeChant and J. B. Hunt, J. Am. Chem. Soc., 90, 3695 (1968).

reduced. Prior to our work on the reduction of Ru(III) amines and the oxidation of Ru(II) amines,<sup>8/</sup> nothing had been done for complexes in which the electron being transferred occupies an orbital of  $\pi$  symmetry.



Among the electron transfer processes those involving self-exchange are of particular interest.<sup>9/</sup> We succeeded in measuring the rate of self-exchange for the  $\text{Ru}(\text{NH}_3)_6^{3+,2+}$  system,<sup>(D2)</sup> and made an attempt at measurement for  $\text{Ru en}_3^{3+,2+}$ . (Our conclusions for the latter system, at least taken quantitatively, are probably incorrect.) We also studied the oxidation of  $\text{Ru}(\text{NH}_3)_6^{2+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  and  $\text{Ru en}_3^{2+}$  by  $\text{Fe}^{3+}$ , and found the behaviour of these systems to be generally in accord with that expected from the Marcus<sup>9/</sup> correlation.

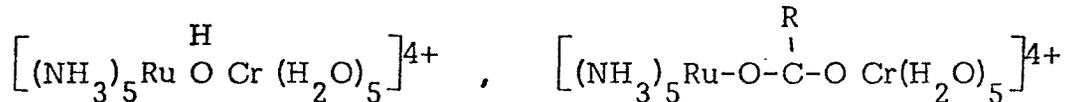
The work done by Meyer only represents a beginning in what will certainly be a very productive sub-field of electron transfer phenomena. Further work is being done in this area under other than AEC auspices, surrounding the Ru complexes with substituted amines bearing bulky groups. The opinion which many experts in the field have is that with small ligands such as  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , the probability of electron tunnelling does not affect the rate of electron transfer. By surrounding the Ru ions with bulky saturated organic matter, we hope to find systems in which the probability of tunnelling becomes at least partially rate determining.

Stritar<sup>(D3)</sup> extended the work with rutheniumammines of the type  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}$  to reactions in which the group L function as bridging ligands. His results afforded a very instructive comparison with results obtained in the reduction of Co(III) and Cr(III) complexes. A point of special interest is that a number of product complexes of appreciable kinetic stability such as

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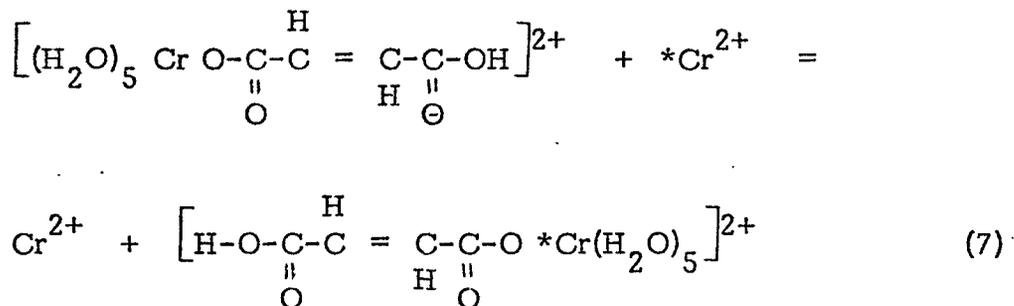
<sup>8/</sup> J. F. Endicott and H. Taube, J. Am. Chem. Soc. 84, 4987 (1962); *ibid.* 86, 1686 (1964); Inorg. Chem. 4, 437 (1965).

<sup>9/</sup> R. A. Marcus, Ann. Rev. Phys. Chem. 15, 155 (1964).



were encountered.

The role which a ligand such as fumarate, which has a conjugated bond system extending from one polar functional group to another, plays when it acts in a bridging capacity in electron transfer has long been a subject of speculation. We felt that an investigation of the self-exchange process



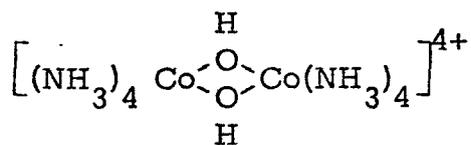
might provide some significant information in the general topic. The coefficients for the rate terms of the form  $[\text{Cr}^{2+}] [\text{Oxidant}]$  for the oxidant as fumaratopentaaquochromium(III), as fumaratoaquotetraamminecobalt(III) and as fumaratoaquobisethylenediamminecobalt(III) were found to be 3, 61 and  $91 \text{ M}^{-1} \text{ sec}^{-1}$  respectively. <sup>(D4)</sup> The insensitivity of rates to the nature of the acceptor center suggests a stepwise mechanism for electron transfer, involving the  $1e^-$  reduction of the bridging ligand as an intermediate step. The Cr(III) complex also features a rate term of the form

$$\frac{[\text{Cr}^{2+}] [\text{Oxidant}]}{[\text{H}^+]}$$

We infer that the reaction by this path involves an activated complex in which  $\text{Cr}^{2+}$  is associated with an oxygen of the adjacent carboxyl group and with an  $\text{OH}^-$  group in a cis position. It is remarkable that the rate with the fumarate complex by this path is some 5000 times faster than that with the

acetate complex reacting by a similar path.<sup>(B9)</sup> The comparison provides a striking illustration of the pendent group effect, namely that groups which are not in the direct line of electron transfer can profoundly affect the efficiency with which a particular function, here  $-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$ , operates in mediating in electron transfer.

The other studies done on electron transfer reactions are mainly of interest in adding to the descriptive matter of the subject area. They include a study of the reduction of  $(\text{NH}_3)_5\text{CoF}^{2+}$ ,  $(\text{NH}_3)_5\text{CoCl}^{2+}$  and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  by  $\text{Fe}^{2+}$  and by  $\text{V}^{2+}$ , with some attention to the effect of free halide ions on the rate,<sup>(D5)</sup> a study of the reduction<sup>(D6)</sup> of

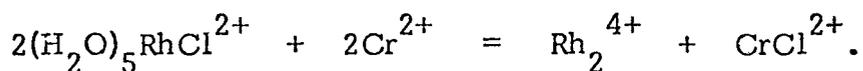


by  $\text{Cr}^{2+}$  and  $\text{Br}^{2+}$  -- a point of interest is that an intermediate is generated by the action of acid on the complex which is scavenged efficiently by the reducing agents -- of  $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$  by  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Br}^{2+}$  (D7) -- each of these produces  $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{4+}$ , which was characterized by its absorption spectrum -- of the reduction of a selected series of carboxylatepentaamminecobalt(III) complexes<sup>(D8)</sup> -- many of these involved putting insecure literature values on a firm basis.

## E

The most promising of our work at the conclusion of the AEC support was that devoted to preparing new metal-containing species with saturated molecules such as  $\text{H}_2\text{O}$  and  $\text{NH}_3$  as ligands. The contributions made along the line of this general goal will be outlined first, even though this does not follow the chronological development of the subject.

A rather important discovery was the ion  $\text{Rh}_2^{4+}(\text{aq})$ , which Maspero<sup>(E1)</sup> found could be formed almost quantitatively by the reaction



The new dinuclear aquo ion at the time of its discovery, was the only one in addition to  $\text{Hg}_2^{2+}(\text{aq})$ , which has been known for a long time, which persists long enough for convenient study by ordinary methods. As far as we can tell,  $\text{Rh}_2^{4+}(\text{aq})$ , in the absence of certain ions such as  $\text{Cl}^-$  which promote disproportionation to  $\text{Rh}(\text{S})$  and  $\text{Rh}(\text{III})$ , and of  $\text{O}_2$ , which readily oxidizes it, will persist almost indefinitely.

Progress in studying the chemical and physical properties of the new species was hampered because until recently, we had no convenient way of providing the ion at high concentration in solution. Thanks to some recent work, <sup>(E2)</sup> such a method is now at hand.  $\text{Rh}_2(\text{OAc})_4$ <sup>10/</sup> can readily be prepared. This species reacts with  $\text{CO}_3^{2-}$  in solution and is converted to  $\text{Rh}_2(\text{CO}_3)_4^{4-}$ . Salts, such as  $\text{Na}_2\text{Rh}_2(\text{CO}_3)_4$ , containing this ion can readily be obtained, and can be handled in air with relative impunity. A solution of such a salt when treated with a strong acid containing an indifferent anion, produces  $\text{Rh}_2^{4+}$  at any desired concentration.

Earlier work <sup>(E1)</sup> using the Evans method<sup>11/</sup> for determining magnetic susceptibility had shown that a solution containing  $\text{Rh}_2^{4+}$  is slightly paramagnetic. This suggested to us the possibility that  $\text{Rh}^{2+}$  is in labile equilibrium with  $\text{Rh}_2^{4+}$ . We find that the species obeys Beer's Law over a wide range of concentration, showing that no significant conversion to  $\text{Rh}^{2+}$  takes place on dilution. Measurements of the magnetic susceptibility of the solution show the ion to have a magnetic moment corresponding approximately to 0.5 electrons per rhodium atom. That the ion might be paramagnetic though it has an even number of electrons poses no special mystery. For a molecule such as this with two metal atoms strongly interacting, accidental

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<sup>10/</sup> S. A. Johnson, H. R. Hunt and H. M. Neumann, *Inorg. Chem.* 2, 960 (1963).

<sup>11/</sup> D. F. Evans, *J. Chem. Soc.* 200, 3 (1959).

near-degeneracy of filled and unfilled orbitals can occur, and probably accounts for the magnetic properties.

The ion  $\text{Mo}_2^{4+}$  was first prepared by Bowen.<sup>(E3)</sup> We have not gone much further in characterizing the species than in the work described in our publication. Bowen has also prepared  $\text{Mo en}_4^{4+}$ , though not yet by a method that is completely to our satisfaction. The ion  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ , hitherto not prepared, was also characterized by Bowen. As expected for a  $d^3$  ion, or an ion isoelectronic with  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , substitution in  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$  is very slow, and the ion should lend itself to studies of the kind which have been done on  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and which depend on the substitution inertia of the complex.

Some progress has been made during the past year on the chemistry of technetium in low oxidation states with saturated ligand.<sup>(E4)</sup> Much of our time was devoted to a compound which is described in the literature<sup>12/</sup> as having the formula  $\text{Tc}(\text{NH}_3)_3 (\text{NH}_2\text{OH})_2 \text{H}_2\text{O Cl}_2$ . If this formula is correct, we already have in hand a compound with technetium in the oxidation state  $2^+$ , with only saturated ligands on the metal. The general properties of the substance made it seem unlikely that this formulation is correct. It seems to be much more stable to oxidation and to substitution to correspond to the composition and constitution claimed in the literature. On the basis of work now in progress, we are fairly certain that the substance is really a nitrosyl, e.g.,  $\text{Tc}(\text{NH}_3)_3 (\text{NH}_2\text{OH}) \text{NO H}_2\text{O Cl}_2$ . On this basis, we can consider it to be  $\text{TcI}$  (low spin  $d^6$ ) stabilized by the unsaturated ligand  $\text{NO}^+$ . The substance is however not so easily described in these terms. It does seem to be slightly paramagnetic. Possibly, our preparation was impure, and possibly electromeric forms of it exist.

Reduction of  $\text{Tc(IV)}$  complexes by  $\text{Eu}^{2+}$  in a non-complexing medium does produce cationic species. These have not yet been identified or characterized.

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<sup>12/</sup> J. D. Eakins, D. G. Humphries and C. E. Mellish, J. Chem Soc. 6012 (1963).

Work along the general lines described is continuing under other auspices, and we have hopes of further extending the chemistry of aquo complexes of transition metal ions.

In the course of the work, a rather general method for preparing complexes of  $(\text{NH}_3)_5\text{Co(III)}$  with even poor nucleophiles was introduced, <sup>(E5)</sup> which has since been applied a great deal in our laboratory and in other laboratories as well. The reaction of  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  with  $\text{NO}^+$  in a medium such as sulfolane (or any of a number of other solvents comprised of molecules which are weak nucleophiles) produces  $(\text{NH}_3)_5\text{Co sulfolane}^{3+}$ . The sulfolane is so weakly bound to Co(III) that it is readily replaced by better nucleophiles. In this way, the first complex of an ester bound to Co(III) was produced. <sup>13/</sup>

The first complex of a metal ion containing  $\text{SH}^-$  as ligand was prepared in the course of the present work. <sup>(E6)</sup> The species in question is  $(\text{H}_2\text{O})_5\text{CrSH}^{2+}$ . There is currently enormous interest in the chemistry of complexes containing sulfur ligands. This is motivated by the important role played by such species in biochemical systems. Our own efforts in trying to develop the chemistry of sulfur ligands has taught us that the behavior of the species, and their preparation is not a trivial or simple extension of known chemistry. The subject will turn out to be important in its own right as teaching us new effects which donor ligands exert in influencing the properties of the complexes of which they are a part.

The ion  $(\text{NH}_3)_5\text{Co(OH}_2)_5^{3+}$  was first prepared by White <sup>(E7)</sup> in pursuing his interest in studying the oxidation of cobaltammines. This ion had been of special interest as being the only missing member of the series



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<sup>13/</sup> J. K. Hurst and H. Taube, J. Am. Chem. Soc. 90, 1174 (1968).

Our examination of its chemistry was only cursory, but it did indicate that the ion merits detailed study, particularly in respect to its properties as an oxidizing agent.

## F

The most significant of the "miscellaneous" studies was that devoted to measuring the tendency of  $\text{CF}_3\text{SO}_3^-$  to form complexes. Perchlorate ion has been widely used as an indifferent anion, but it has two serious shortcomings. It is reduced at a rapid rate at room temperature by some of the heavier transition metal ions in low oxidation states, for example by Ru(II), Mo(II), Mo(III). Secondly, many salts are potentially explosive, especially when organic ligands are present, and this poses an extremely serious hazard in work involving them. Trifluomethylsulfonic acid is known to be very strong, and the anion is reported to be quite resistant to hydrolysis.<sup>14/</sup> To qualify  $\text{CF}_3\text{SO}_3^-$  as a replacement for  $\text{ClO}_4^-$ , the complexing tendency of the ion needs to be measured. We chose Cr(III) as reactant because this is the only cation for which the perchlorate complex has been characterized in solution.<sup>15/</sup> Our work shows that  $\text{CF}_3\text{SO}_3^-$  lies between  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  in its affinity for Cr(III). Translated into more directly practical terms, for cation such as  $\text{Cr}^{3+}$ ,  $\text{CF}_3\text{SO}_3^-$  can be used at the 6M level without converting a significant fraction of the cation to a complex. This knowledge has been essential to the progress we have made in the chemistry of Mo(II) and Mo(III), and in our experience, there have been no complications attributable either to complex formation or to reduction of  $\text{CF}_3\text{SO}_3^-$ .

Some tracer experiments were done on the oxidation of  $\text{CH}_3\text{O}-\text{C}-\text{C}-\text{OH}$  by Ce(IV). The incentive for this work was the possibility

$$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$$

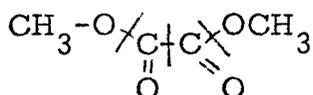
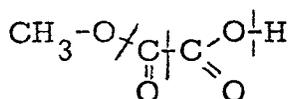
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<sup>14/</sup> R. Haszeldine and J. M. Kidd, J. Chem. Soc., 4228 (1954),  
T. Gramstad and R. Haszeldine, *ibid.* 4069 (1957).

<sup>15/</sup> K. M. Jones and N. Bjerrum, Acta Chem. Scand. 19, 974 (1965).

that the intermediate  $\text{CH}_3\text{-O-C(=O)-C(=O)O}^\cdot$  which is expected on  $1e^-$  oxidation

might fragment to  $\text{CH}_3 + 2\text{CO}_2$  and the reaction might thus provide a simple route to  $\text{CH}_3$  radicals in solution. On this basis, no incorporation of solvent oxygen into  $\text{CO}_2$  would be expected. The products of the oxidation are  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  for both the monomethyl and dimethyl esters. We observed for the former substrate, 0.5 atoms of solvent oxygen incorporated per mole of product  $\text{CO}_2$ , and for the later 1.00. Thus, the patterns of bond breaking are as follows



These conclusions should not be taken to imply that CO is an intermediate in either reaction. Carbon monoxide, if formed, would escape oxidation, and the stoichiometry observed shows that CO is not liberated.

For comparative purpose, in the course of work done on the exchange of oxygen between carboxylatepentaaminecobalt(III) species and water, exchange studies on monomethyl and dimethyl oxalate were run, and an effort was made to measure the oxygen isotope fractionation in the hydrolysis of the esters. This work, owing to difficulties in communicating with C. Andrade who returned to Chile after being awarded his Ph.D. here, is only now being prepared for publication.

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