be possible to make further modifications on this semi-empirical scheme.

For completeness we have calculated the energy level diagram using (1) hybridized ligand orbitals and (2) just chlorine p orbitals. The agreement between the predicted transitions and the observed spectrum was poor in both cases. However, we must point out that the apparent agreement between the predicted and observed transitions may only be an artifact of the calculational procedures. It would be desirable to have polarization data from spectral investigations of single crystals in order to confirm by selection rules the indicated assignments. We have been unable to find a suitable crystal for this experiment.

Acknowledgments.—This work was supported by the Advanced Research Projects Agency. The authors wish to thank Dr. Paul Cade of the University of Chicago for the calculations of the atomic overlap integrals.

CONTRIBUTION FROM THE GEORGE HERBERT UONES LABORATORY,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

Isotopic Fractionation in Electron-Transfer Reactions. The Role of Nonbridging Ligands

BY M. GREEN, K. SCHUG, AND H. TAUBE[1]

Received March 31, 1965

The kinetic fractionation factors, d ln [N^{14}]/d ln [N^{15}], for the nitrogen atoms in the ammine ligands of $Co(NH_3)_5OH_2{}^{3+}$, $Co(NH_3)_5Cl^{2+}$, $Co(en)_2NH_3Cl^{2+}$, and $Co(en)_2NH_3OH_2{}^{3+}$ during reactions with $Cr^{+2}(aq)$ have been measured. It is significant that they are very small (1.002 and 1.001) for the first two ions and that they are identical for NH_3 *cis* or *trans* to the bridging group. Thus, in these particular reactions, there seems to be little rearrangement in the Co–NH_3 residue attendant on electron transfer.

Some work has been done on oxidation–reduction reactions between metal ions in which a bridging ligand is involved.[2] In the reaction between $(H_3N)_5CoOH^{2+}$ and chromous ion,[3] the complexes containing O^{16} react faster than those made up of O^{18}, the fractionation factor[4] having the high value of 1.035. The observation indicates that in the transition state of the reaction, the Co–O distance is considerably greater than in the starting compound. As the formal charge on the cobalt atom falls from +3 to +2 during the reaction, part of this increase might be attributed to the concomitant expansion of the coordination shell as a whole.

We have investigated here the extent to which the stretching of bonds between the cobalt center and any nonbridging ligands occurs during oxidation–reduction processes, by studying the fractionation of N^{14} compared with N^{15} in the NH_3 groups of various cobaltic complexes.

A further point was also investigated. If one accepts Orgel's suggestion[5] that the electron entering the cobalt complex goes into the d_{z^2} orbital, which assumes that the tetragonal (C_{4v}) symmetry of the N_5CoX system is retained in the transition state (X being the bridging ligand and z the axis on which it lies), then the greatest fractionation should occur in the nitrogen atoms *trans* to the bridging group. By using bis-(ethylenediamine) complexes containing ammine and bridging ligands differently arranged, we have attempted to assess the amount of fractionation in the *trans* position and have compared it with that in the *cis*.

Experimental

The salt $[Co(NH_3)_5Cl](ClO_4)_2$ was obtained from its chloride, which was prepared following the procedure of Hynes, Yanowski, and Shiller.[6] $[Co(NH_3)_5OH]_2(ClO_4)_3$ was made by the action of perchloric acid on $[Co(NH_3)_5CO_3]NO_3$, generated by the method of Basolo and Murmann.[7] *trans*-$[Co(en)_2Cl_2]Cl$ was prepared by Bailar's[8] method and used to obtain *cis*- and *trans*-$[Co(en)_2NH_3Cl]Cl$ and crude *trans*-$[Co(en)_2NH_3H_2O]Br_3$ following the procedure of Werner.[9] The crude aquoammine complex was recrystallized from aqueous ethanol several times. We were unable, however, to obtain in sufficient quantity (2 g.) *trans* complex containing less than 10% of the *cis* isomer, our criterion of purity being the spectra of Nyholm and Tobe.[10] *cis*-$[Co(en)_2NH_3H_2O]Br_3$ was prepared utilizing Tobe's[11] observation that the *trans* isomer is converted entirely to *cis* at equilib-

---

[1] Department of Chemistry, Stanford University, Stanford, Calif. 94305.

[2] For reviews, see H. Taube, *Can. J. Chem.*, **37**, 129 (1959); R. T. M. Fraser, *Rev. Pure Appl. Chem.*, **11**, 64 (1961).

[3] (a) R. K. Murmann, H. Taube, and F. A. Posey, *J. Am. Chem. Soc.*, **79**, 262 (1957); (b) H. R. Hunt and H. Taube, *J. Phys. Chem.*, **63**, 124 (1959).

[4] An isotopic fractionation factor, f, is defined as X' dX/X dX' or d ln X/d ln X', where X and X' refer to the mole concentrations of two isotopes of a particular element. The fractionation factors used here are d ln [O^{16}]/d ln [O^{18}] and d ln [N^{14}]/d ln [N^{15}].

[5] L. E. Orgel, *Inst. Intern. Chim. Solvay, X^e Conseil Chim.*, 289 (1956).

[6] W. A. Hynes, L. K. Yanowski, and M. Shiller, *J. Am. Chem. Soc.*, **60**, 3053 (1938).

[7] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

[8] J. C. Bailar, *ibid.*, **2**, 222 (1946).

[9] A. Werner, *Ann.*, **386**, 1 (1912).

[10] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

[11] M. L. Tobe, *ibid.*, 3776 (1959).

rium; a mixture of isomers was dissolved in hot water and concentrated ammonia solution was added until a pH of 9 was reached. The solution was kept at 70° for 5 min., then cooled to 0°. Precipitation was effected (when necessary) by adding concentrated hydrobromic acid.

Solutions of chromous perchlorate (approximately 0.3 *M*) were prepared electrolytically by the reduction of chromic perchlorate in perchloric acid at a mercury cathode.

In each experiment the particular cobalt complex was dissolved in 0.30 *M* perchloric acid, free from oxygen, to make a solution approximately 0.05 *M* in metal ion. Sufficient chromous solution was added, drop by drop with stirring, to react with between 60 and 80% of the cobaltic salt. The chloro complexes appeared to react instantaneously, but in the cases of the aquo compounds a complete color change took several minutes.

The unreacted complex was separated by adding Dowex 50. This resin was separated by decantation and washed with 0.25 *M* perchloric acid, which removed free ammonium ion. The resin was then suspended in water through which gaseous hydrogen chloride was bubbled, whereupon the cobaltic complex containing the unreacted coordinated ammonia was liberated. The supernatant liquid was separated by decantation. The coordinated ammonia was liberated by the action of potassium hydroxide and separated from ethylenediamine (where necessary) by passage through a trap cooled in a carbon dioxide freezing mixture. Ammonia was converted to nitrogen using sodium hypobromite following the procedure of Sprinson and Rittenberg.[12] The isotopic assay of nitrogen was made by reading directly the ratio of intensities of the mass peaks 29 to 28 corresponding to $N^{14}N^{15}$ and $N^{14}N^{14}$.

Results and Discussion

In Table I are summarized the nitrogen isotopic fractionation factors observed in the ligand ammonia during the reduction of various cobalt(III) complexes by chromous ion.

TABLE I

NITROGEN FRACTIONATION IN THE REDUCTION OF PENTAAMMINE COBALT(III) COMPLEXES

~20°; [complex] ≃ 0.05 *M;* $[HClO_4]$ ≃ 0.30 *M;* added $[Cr(ClO_4)_2]$ ≃ 0.3 *M*

Complex	$f = d \ln [N^{14}]/d \ln [N^{15}]$ (see ref. 4)[b]
$Co(NH_3)_5Cl^{2+}$	1.001, 1.001
$Co(NH_3)_5OH^{2+}$ [a]	1.003, 1.002, 1.002
trans-$Co(en)_2NH_3Cl^{2+}$	1.001, 1.001, 1.002
cis-$Co(en)_2NH_3Cl^{2+}$	1.001, 1.001, 1.001
trans-$Co(en)_2NH_3OH^{2+}$ [a]	1.0045 ± 0.001, 1.0055 ± 0.001
cis-$Co(en)_2NH_3OH^{2+}$ [a]	1.004, 1.005

[a] At the acidity of the experiments, the reactant ion was probably the hydroxo rather than the starting aquo complex (*cf.* ref. 2). [b] Accuracy ±0.0005, except where stated otherwise (*cf.* ref. 13).

The isotopic fractionation factors[4] observed for the chloro complexes are all very small. These reactions are very fast (*e.g.*, the rate constant for the reaction between $Co(NH_3)_5Cl^{2+}$ and chromous ion[13] is about $3 \times 10^6 M^{-1}$ sec.$^{-1}$ at 25°), but not so fast that they are diffusion-controlled.[14]

The specific rate constant[15] for the reaction of Cr^{2+} with $Co(NH_3)_5OH^{2+}$ is approximately $2 \times 10^6 M^{-1}$ sec.$^{-1}$, which is also well below the value of about 10^{10} expected for a diffusion-controlled process. Hence our results for the aquo complexes can be discussed without considering this possibility. The values of the fractionation factors for the coordinated nitrogen in NH_3 are very much less than that of 1.035, mentioned in the introduction, which is observed for oxygen when OH^- acts as a bridging ligand. This comparison demonstrates the unique role which the bridging group plays here and also shows that there can be only very small disturbances in the $Co(NH_3)_5$ and $Co(en)_2NH_3$ units up to the time of reaching the transition state that determines the rate of the over-all oxidation–reduction process. During this interval, there can be little stretching of the Co–N bonds and none preferentially in a *cis* or *trans* sense. Failure to observe this latter effect cannot be attributed to changes in interbond angles, as these would also lead to isotopic fractionation. Therefore the tetragonal symmetry around the cobalt atom must be retained.

These conclusions[16] suggest that while the reaction is reaching its rate-determining transition state, the Co–O distance increases, the oxygen atom departing along the *z* axis (*i.e.*, the N–Co–O axis of the initial complex), but that there is neither a large increase in electron density nor redistribution of charge around the cobalt atom. Now a transition state bears some resemblance to the reactants and the products im-

---

[12] D. B. Sprinson and D. Rittenberg, *J. Biol. Chem.*, **180**, 711 (1949).

[13] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

[14] In a diffusion-controlled process, the fractionation factor would be about 1.003. Although we are reasonably confident that our fractionation factors are accurate to ±0.0005, except where stated otherwise, we would not be so dogmatic as to rule out the possibility of unnoticed errors.

[15] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

[16] Dr. J. Halpern has suggested an alternative explanation for our observations, and although we believe, for reasons which we detail later, that the explanation is unlikely to prove to be correct, it merits consideration because it is reasonable and it cannot be disproven on the basis of present evidence. The suggestion which he has offered is that substitution on Cr^{2+}(aq) is rate-determining rather than, as we have chosen to infer, the dislocations at the Co(III) center.

Our arguments in refutation of the suggestion are the following. It should be noted first of all that the rate of the oxidation–reduction reactions we are concerned with is much less than the rate of replacement of water in $Cr(H_2O)_6^{2+}$ by solvent water. The rate of the former process when $(NH_3)_5CoCl^{2+}$ is 1×10^{-2} *M* would be $3 \times 10^4(Cr^{2+})$ *M* sec.$^{-1}$; for the latter, a lower limit on the rate is $8 \times 10^9(Cr^{2+})$ *M* sec.$^{-1}$ [C. W. Merideth and R. E. Connick, paper 106, Division of Inorganic Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965]. There is therefore a wide margin between the actual rate of the oxidation–reduction reactions and what may, but need not be, the maximum rate at which substitution on Cr^{2+}(aq) may take place (note that a maximum rate is set by the water exchange results only if the mechanism is SN1). The magnitudes of the oxygen and hydrogen isotopic fractionation effects seem to us to argue against Halpern's suggestion. The rate ratio for $(NH_3)_5CoOH^{2+}$ in H_2O against $(NH_3)_5CoOD^{2+}$ in D_2O reacting with Cr^{2+}(aq) is 2.7 (ref. 15), while for the substitution of Cl^- in $(NH_3)_5CoCl^{2+}$ by H_2O, $k_H/k_D = 1.5$ [A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261(1955)]. In bringing into evidence the latter comparison, we are drawing an analogy between $(NH_3)_5CoOH^{2+}$ replacing H_2O on $Cr(H_2O)_6^{2+}$ and HOH replacing Cl^- on $(NH_3)_5CoCl^{2+}$. The analogy is incomplete because a substantial isotope effect may reside in the replacement of water on a cation. This isotopic effect is small and for the reaction $Cl^- + (NH_3)_5CoOH_2^{3+}$ amounts to only 1.18 (this factor is obtained by combining the isotopic effect measured for the equilibrium [H. Taube, *J. Am. Chem. Soc.*, **82**, 524 (1960)] with the result obtained by Adamson and Basolo. The conclusion is that H isotope effects observed for substitution reactions are considerably less than for the oxidation–reduction reaction we have studied. We should note too that they are likely to be even less for substitution at $Cr(H_2O)_6^{2+}$ than for substitution at Co(III). The isotopic ratio $d \ln[O^{16}]/d \ln [O^{18}]$ for the aquation of $(NH_3)_5CoNO_3^{2+}$ is less than 1.01 (G. Dolbear, experiments in progress). Here we point to the analogy between H*O*H and $(NH_3)_5CoOH^{2+}$ replacing a group on a metal cation. This fractionation factor is much less than the value of $d \ln[O^{16}]/d \ln [O^{18}] = 1.035$ observed for the reaction of Cr^{2+} with $(NH_3)_5CoOH^{2+}$. We do not of course regard these arguments as conclusive and further experiments will be done with systems for which it is quite certain that substitution on the reducing agent is not rate-determining.

mediately on either side of it, but, in general, more to whichever is closer in energy to it. Our results can be explained if the primary products of the oxidation–reduction processes are "intermediates" like $Co(NH_3)_5^{2+}$. This entity has to be in a low spin state and to be tetragonally pyramidal in shape, with the cobalt atom lying in the square face (which we will suppose contains the x and y axes). Lying in the z axis in place of a sixth ligand there must be a localized orbital containing a single electron. In order to achieve satisfactory localization a considerable admixing with the $3d_{z^2}$ orbital by the $4p_z$ is necessary. The $Co(NH_3)_5^{2+}$ "intermediate" will almost certainly have a high energy relative to the reactants, and therefore a similarity in geometry between it and the transition state would be expected. It would be interesting if the "intermediate" were a metastable entity corresponding to a minimum in the potential energy surface, although it need, from the point of view of our argument, to have no more physical significance than that associated with the region on the slope leading downward once the transition state saddle has been crossed.

The single electron associated with the hybrid orbital is one of those involved in the oxidation–reduction process. How it ultimately reaches the cobalt atom cannot be said, but it leaves the oxygen through a σ orbital.

The nitrogen fractionation in NH_3 is greater in the $Co(en)_2NH_3OH^{2+}$ complexes than in the pentaammine analog. This effect suggests that what slight changes do occur in the Co–N links tend to be restricted to those involving ammonia rather than ethylenediamine, which is reasonable as it is probably harder to distort a chelated structure than the bond to a monodentate ligand.

The fractionation factors for the hydroxo complexes are significantly greater than for the chloro. It is possible that there is a difference in the fundamental process of electron transfer in the two cases. Chlorine, but not oxygen, has vacant low-lying orbitals and these may well play an important role for they would facilitate a synergic process in which one electron was transferred to the crucial bridging atom at the same time as another left it.

Acknowledgments.—This research was supported by the Atomic Energy Commission (Contract No. AT-(11-1)-378) and by the National Science Foundation (Grant No. G-20954).

We wish to thank Dr. J. P. Hunt of Washington State University for making his mass spectrometer available to us. Michael Green expresses his gratitude for a Fulbright Travel Grant.

CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.,
MURRAY HILL, NEW JERSEY 07971

Hydrogen Bonding in Ferrocyanic, Ruthenocyanic, and Osmocyanic Acids

BY A. P. GINSBERG AND E. KOUBEK

Received March 11, 1965

The infrared spectra of the anhydrous metallocyanic acids $H_4M(CN)_6$ and $D_4M(CN)_6$ (M = Fe, Ru, and Os) were measured in the solid state from 10,000 to 300 cm.$^{-1}$ at room temperature and at 80°K. The results indicate that these compounds consist of $H_4M(CN)_6$ units, with the *trans* arrangement of the hydrogen atoms, which are linked together by asymmetrical N–H···N hydrogen bonds into a three-dimensional network. *All four* hydrogen atoms per $H_4M(CN)_6$ unit are involved in hydrogen bonding, but two of them are more strongly hydrogen-bonded than the other two. Assignments are given for most of the bands in the spectra.

Introduction

The protonation of transition metal cyanide complexes has been the subject of several recent papers.[1,2] This work demonstrated that strong acids reversibly diprotonate the complexes dicyanobis(1,10-phenanthroline)iron(II), dicyanobis(2,2′-bipyridine)iron(II), -ruthenium(II), and -osmium(II). It was at first suggested that the protons are directly bound to the metal atom as in various protonated transition metal carbonyl complexes and carbonyl hydrides. However, later work[2-4] indicated that this is incorrect and that the protons are linked to the nitrogen of the cyanide groups, *e.g.*, $[(phen)_2Fe(CNH)_2]^{2+}$. Surprisingly though, there appears to be no evidence of NH stretching or bending absorptions in the infrared spectra of the solid protonated complexes.[2]

The results outlined above prompted us to investigate the infrared spectra of the metallocyanic acids $H_4M(CN)_6$ and $D_4M(CN)_6$, M = Fe, Ru, and Os. Although $H_4Fe(CN)_6$ was first reported in 1820[5] there was until recently no direct evidence bearing on the arrangement or bonding of the protons. The spectra of these compounds are not simple, but they yield interesting information about the arrangement of the protons as well as their bonding. While this work was in

---

(1) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000, 5779 (1960).

(2) A. A. Schilt, *ibid.*, **85**, 904 (1963).

(3) N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

(4) G. Wilkinson in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p. 56.

(5) J. J. Berzelius, *Schweigger's J.*, **30**, 44 (1820).