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Carbonylpentaammineruthenium(II) Chloride. Synthesis and Properties

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The synthesis and isolation of the carbonylpentaammineruthenium(II) complex, $Ru(NH_3)_5CO^{2+}$, as a chloride salt is described. The method of synthesis involved the ammination of the carbonyl halide anion, $Ru^{II}Cl_4(H_2O)CO^{2-}$, under mild conditions. A chemical and spectroscopic comparison of the carbon monoxide complex with the related molecular nitrogen complex is made, and the observed differences in the crystal structures and the infrared and electronic absorption spectra of the complexes are discussed.

Introduction

The isolation of the nitrogenpentaammineruthenium(II) complex, $Ru(NH_3)_5N_2^{2+}$, by Allen and Senoff[1] has prompted much interest in all aspects of the binding of simple molecular ligands to transition metals. We have synthesized the carbon monoxide analog of the molecular nitrogen complex of ruthenium in the hope that a comparison of the chemical and spectral properties of the complexes might provide a better understanding of certain features of the metal–ligand interaction. The CO complex described here, $Ru(NH_3)_5CO^{2+}$, has also been synthesized by others recently,[2] but by a different route.

Experimental Section

$(NH_4)_2[RuCl_5CO]$.—Ammonium pentachlorocarbonylruthenate(III), prepared by the method of Halpern,[3] was used as the starting material for the synthesis of the carbonylpentaammineruthenium(II) compound. Typically, 2.8 g of $RuCl_3 \cdot xH_2O$ (Matthey-Bishop, Malvern, Pa.; 36.58% Ru) was dissolved in 25 ml of 5 *M* HCl and carbon monoxide (Matheson, CP) gas was bubbled through the solution at 80° for 16 hr. To the resulting deep red solution, a stoichiometric amount of ammonium chloride was added, and the solution was allowed to evaporate at room temperature. The product which crystallized, $(NH_4)_2[RuCl_5CO]$, had the correct ir and uv spectrum but was slightly contaminated by ammonium chloride. *Anal.* Calcd for $(NH_4)_2[RuCl_5CO]$: C, 3.50; H, 2.36. Found: C, 3.17; H, 2.60.

$[Ru(NH_3)_5CO]Cl_2$.—A solution of 0.2 g of $(NH_4)_2[RuCl_5CO]$ in 15 ml of 5 *M* HCl was treated with a stream of hydrogen gas for 5 hr at 80°, in order to reduce the ruthenium(III) complex $RuCl_5CO^{2-}$ to the ruthenium(II) complex $RuCl_4(H_2O)CO^{2-}$. The resulting green solution containing the latter ion was cooled to below room temperature and 7 *M* NH_4OH was added until pH 9 was reached. This basic solution was then allowed to stand in a stoppered vessel for 48 hr at room temperature. The yellow-brown crystalline precipitate which had formed after this time was collected and redissolved in concentrated ammonium hydroxide with gentle boiling. The resulting clear, light yellow solution, upon cooling to 0°, yielded 0.060 g of the compound $[Ru(NH_3)_5CO]Cl_2$ as a white crystalline solid. *Anal.* Calcd for $[Ru(NH_3)_5CO]Cl_2$: C, 4.21; H, 5.31; N, 24.56. Found: C, 4.68; H, 5.45; N, 24.2.

Instrumentation.—Infrared spectra of the various salts in KBr disks were obtained using a Perkin-Elmer 621 grating spectrometer. Ultraviolet and visible spectra were obtained on a Cary 14 spectrophotometer. Proton magnetic resonance spectra were obtained on a Varian A60A nmr spectrometer. X-Ray diffraction patterns of powdered samples were recorded using a Siemens 114.6-mm diameter Debye–Scherrer camera and manganese-filtered iron (Fe) radiation ($\lambda(K\alpha)$ 1.9373 Å).

Results

We have been able to synthesize the carbonylpentaammineruthenium(II) cation by ammination of the recently discovered[3] carbonyl halide anion $Ru^{II}Cl_4(H_2O)CO^{2-}$, under mild conditions. The replacement of the chloride and water ligands by ammonia proceeds through a slightly soluble intermediate which we have not characterized completely; however, from infrared evidence[4] and insolubility we suggest this might be the neutral complex $Ru(NH_3)_3(CO)Cl_2$. Treatment of this inner complex with concentrated ammonia yields the desired salt $[Ru(NH_3)_5CO]Cl_2$. In addition to the chemical analysis, the formulation of the compound as containing the carbonylpentaammineruthenium(II) cation is consistent with the ir, uv, nmr, and X-ray evidence presented below.

The infrared spectrum of the compound in KBr is shown in Figure 1. The observed frequencies (in cm^{-1}) and their assignments[5] are: 3310, 3170 (N–H str); 1930, 1918 (C–O str); 1625 ($\delta_d(NH_3)$); 1282, 1231 ($\delta_s(NH_3)$); 808 ($\rho(NH_3)$); 588 (Ru–C str); 543 (Ru–C–O bend); and 449 (Ru–N str). The spectrum is very similar to that of the nitrogen complex[6] in terms of the number of bands and their approximate positions, except for the slight splitting of the C–O stretch and the larger splitting of the symmetric deformation of the ammonia ligands ($\delta_s(NH_3)$), both of which vibrations appear as single symmetrical bands in the spectrum of the nitrogen complex.[7] We feel that these splittings are related to the lower crystal symmetry of the chloride salt of the CO complex compared with that of the N_2 complex. The crystal structure of the nitro-

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[1] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[2] C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Swanwick, *J. Organometal. Chem.* (Amsterdam), **14**, 349 (1968).

[3] J. Halpern, B. R. James, and A. L. W. Kemp, *J. Am. Chem. Soc.*, **88**, 5142 (1966).

[4] The intermediate in the ammination showed a strong infrared band at 305 cm^{-1}, attributable to a metal–chloride stretch. Greater splitting of the C–O stretch (1932, 1908 cm^{-1}) and more extensive splitting in the regions of the ammonia ligand vibrations as compared to the carbonylpentaammine complex was also observed. No bands assignable to coordinated water were detected.

[5] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 143–146.

[6] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

[7] In the perchlorate salt of the CO complex, *i.e.*, $[Ru(NH_3)_5CO](ClO_4)_2$, both of the bands in question become single and symmetrical also, with ν(CO) 1948 cm^{-1} and $\nu(\delta_s NH_3)$ 1300 cm^{-1}.

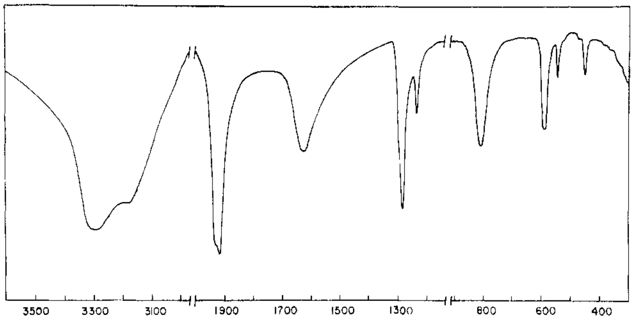

Figure 1.—Infrared spectrum of $[Ru(NH_3)_5CO]Cl_2$ in KBr.

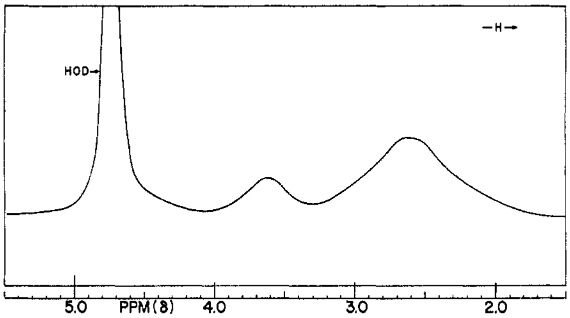

Figure 2.—Proton magnetic resonance spectrum of $[Ru(NH_3)_5CO]Cl_2$ in 0.1 M DCl in D_2O.

gen salt $[Ru(NH_3)_5N_2]Cl_2$ has been determined recently.[8] The salt crystallizes in the cubic system and the structure is disordered with the nitrogen molecules randomly occupying one of the six octahedral positions around the ruthenium ion. In contrast, examination of the colorless octahedrally shaped crystals of the carbonylpentaammineruthenium(II) chloride salt under a polarizing microscope indicates, from the extinction and interference patterns which they exhibit, that they belong to a biaxial crystal class. In addition, the X-ray powder diffraction pattern of the ruthenium carbonyl salt, Table I, shows a marked similarity to that of an analogous compound, cyanopentaamminecobalt(III) chloride. We have completed an X-ray structure determination on the latter salt recently[9] and have found its crystals to be orthorhombic, with space group Cmcm. The over-all structure of the cobalt salt is an ordered, orthorhombically distorted version of the cubic, disordered structure found for the nitrogen salt $[Ru(NH_3)_5N_2]Cl_2$. It is interesting to note that an identical splitting of the ammonia symmetric deformation mode has been reported for the cyanopentaamminecobalt(III) chloride salt.[10]

TABLE I

COMPARISON OF X-RAY POWDER DIFFRACTION PATTERNS[a] OF $[Co(NH_3)_5CN]Cl_2$ AND $[Ru(NH_3)_5CO]Cl_2$

	Co		Ru	
hkl[b]	*d*, Å	*I*	*d*, Å	*I*
111	5.55	10	5.63	10
002, 200	5.09	1	5.11	1
112, 021	4.05	1	4.10	1
202	3.61	8	3.61	7
220, 022	3.33	9	3.39	8
310	3.14	1	...	...
113, 311	3.03	1	3.07, 3.03	3
...	...	...	2.91	1
130, 222	2.78	6	2.82, 2.80	4
131, 312	2.68	2	...	...
004	2.57	6	2.58	6
400	2.53	4	2.54	6
...	...	...	2.27	2
040	2.17	1	2.22	3
422, 224	2.02	1	2.05	3

[a] Data were obtained by the Debye–Scherrer technique using manganese-filtered iron radiation (λ 1.9373 Å) and a 114.6-mm diameter camera. "*d* spacings" are uncorrected for any film shrinkage. Intensities are on a relative scale of 1 to 10. [b] The indices assigned to the reflections refer, strictly, only to the cobalt pattern since the assignments were made by comparison of observed to calculated "*d* spacings" using the cell dimensions—a = 10.15, b = 8.70, and c = 10.30 Å—found for the cobalt salt from the single-crystal study.[9] The assignment of the lines in the ruthenium pattern as implied by their arrangement in the table, opposite assigned cobalt lines, is based only on their similarity in "*d* spacing" and intensity to corresponding ones in the cobalt pattern. Where there was not a one to one correspondence no entry was made. In general the ruthenium pattern was much sharper than that of the cobalt.

The carbonyl complex is diamagnetic as evidenced by its normal proton magnetic resonance spectrum, Figure 2. Only two signals, with relative areas of 1:4 and a separation of 1.0 ppm, are observed. The more intense peak, at higher field, may be assigned to the 12 protons of the *cis* ammonia ligands, and the less intense, lower field peak, to the three protons of the *trans* ammonia ligand.

On the chemical side, it is apparent that the CO ligand considerably stabilizes the Ru(II) oxidation state since neither Ag^+ nor Hg^{2+} ions oxidize the $Ru(NH_3)_5CO^{2+}$ complex in aqueous solution at room temperature. Chatt[11] has observed a similar stability for the N_2 complex toward these reagents, if it has previously been purified from any hydrazine–ruthenium complex contaminants which occur in its synthesis *via* hydrazine. However, as is the case with the N_2 complex,[12] excess of the stronger oxidizing agent cerium(IV) causes rapid evolution of CO from the carbonyl complex upon the oxidation of the Ru(II) to a higher oxidation state. Boiling of a solution of the carbonyl complex in 6 M HCl produces the chloropentaammineruthenium(III) complex as determined by its electronic absorption spectrum.

The electronic absorption spectrum of the carbonyl complex in deoxygenated water, Figure 3, shows two bands, a weak one at ν_{max} 27,800 cm^{-1} (λ 360 mμ, ϵ 17.0) and a more intense one at ν_{max} 36,100 cm^{-1} (λ 277 mμ, ϵ 258). This spectrum is unchanged for periods up to 24 hr. However, decomposition, ascertained as an increasing absorbance at each of the above wavelengths and an accompanied yellowing of the solution color, occurs after longer periods of standing in solution.

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(8) F. Bottomley and S. C. Nyburg, *Acta Cryst.*, **B24**, 1289 (1968).

(9) J. A. Stanko and I. C. Paul, to be submitted for publication.

(10) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

(11) J. Chatt, R. L. Richards, J. E. Ferguson, and J. L. Love, *Chem. Commun.*, **23**, 1522 (1968).

(12) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

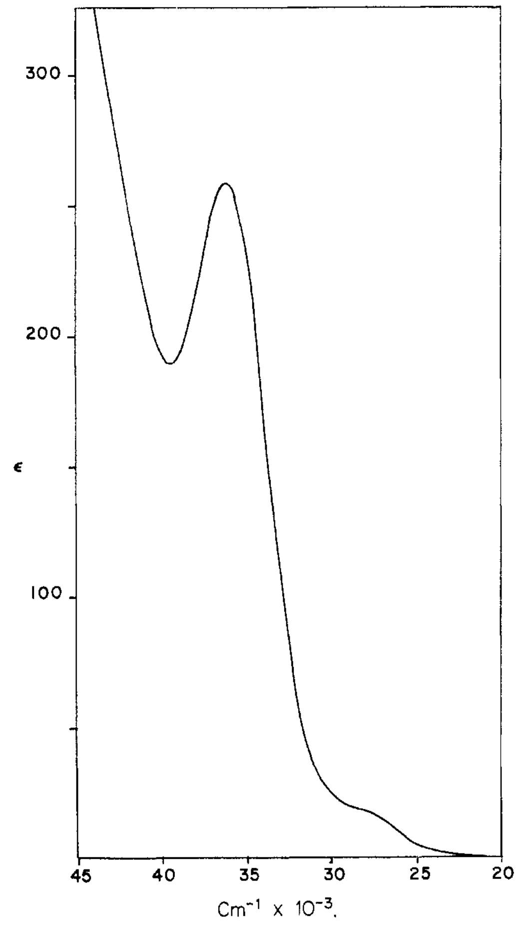

Figure 3.—Electronic absorption spectrum of $[Ru(NH_3)_5CO]Cl_2$ in H_2O.

Discussion

It is of interest to note what one can extract from a comparison of the spectroscopic data now available for the pentaammineruthenium(II) complexes of the isoelectronic ligands N≡N, C≡O, and $N≡O^+$, regarding their bonding to the metal. Table II gives selected infrared frequencies for these complexes as chloride salts in KBr disks. If the reduction of the diatomic ligand stretching frequency can be taken as a measure of the extent of metal–ligand $d\pi \rightarrow \pi^*$(ligand) type of π bonding, then judging from the observed magnitudes of these reductions this interaction is relatively large and nearly equal for the CO and N_2 ligands but much larger for the NO^+ ligand. In contrast, the magnitude of the metal–diatomic ligand stretching frequency would be expected to reflect contributions from both the $d\pi \rightarrow \pi^*$ type of metal–ligand π bonding and the normal, $d\sigma \leftarrow \sigma$(ligand) metal–ligand σ bonding. The smaller observed value for this frequency in the N_2 complex relative to the CO complex suggests a weaker σ-donor interaction for N_2 than for CO, if the π contribution can be presumed to be nearly the same for these ligands as judged above.[13] Again, the NO^+ ligand appears to have the strongest over-all bonding interaction with the metal as gauged by its metal–ligand stretching frequency being the largest of the three.

Table II

Infrared Data[a] for Ruthenium(II) Ammines

	ν(free ligand), cm^{-1}	ν(ligand), cm^{-1}	$\Delta\nu$, cm^{-1}	ν(Ru–ligand), cm^{-1}
$Cl_3(NH_3)_5Ru–NO$[b]	2220	1903	317	602
$Cl_2(NH_3)_5Ru–CO$[c,d]	2143	1918	225	585
$Cl_2(NH_3)_5Ru–NN$[d,e]	2331	2105	226	508

[a] KBr matrix. [b] Data taken from paper of E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, **5**, 1881 (1966). The value for $\nu(NO^+)$ of the free ligand is from a solution study of the nitrosonium ion in nitric acid as quoted in ref 5, p 71. The gas-phase value, as obtained from electronic spectra, is considerably higher (2377 cm^{-1}): E. Mescher, *Can. J. Phys.*, **33**, 355 (1955). [c] This work. [d] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 449. [e] Reference 6.

With the exception of the infrared spectra, the most characteristic spectroscopic feature so far identified with the complexing of molecular nitrogen to ruthenium has been the appearance of a sharp, intense electronic absorption maximum in the ultraviolet region. In the complex $Ru(NH_3)_5N_2^{2+}$ [12,14] this band occurs at 45,250 cm^{-1} (λ 221 mμ, ϵ 16,000) and in the complex $Ru(en)_2(H_2O)N_2^{2+}$ at 45,450 cm^{-1} (λ 220 mμ, ϵ 13,000).[15] Curiously, no such band maximum is observed in the spectrum of the CO complex, although there is a strong absorption up to the uv limit of our spectrometer (200 mμ). Of the bands that are observed for the $Ru(NH_3)_5CO^{2+}$ complex we tentatively assign the weaker one at 27,800 cm^{-1} to the lowest energy, spin-allowed "d–d" transition of the d^6 configuration ${}^1A_1 \rightarrow {}^1T_1$ and the more intense one, at 36,100 cm^{-1}, to a charge-transfer transition $d\pi \rightarrow \pi^*(CO)$. The basis of these assignments is principally an extrapolation of our spectroscopic work on the isoelectronic monocarbonyl halide anion of Rh(III), $RhCl_5CO^{2-}$, which we have synthesized recently and which has a very similar spectrum.[16]

The shift of the first "d–d" band of the CO complex to higher energy relative to the hexaammine complex[17] $Ru(NH_3)_6^{2+}$, where $\nu({}^1A_1 \rightarrow {}^1T_1)$ is 26,000 cm^{-1}, is consistent with the total ligand field strength of carbon monoxide being greater than that of ammonia.[18] Unfortunately, a representative spectrum of the nitrogen complex in these regions of the spectrum is not available for comparison. Only the intense ultraviolet transition, mentioned above, has been reported. The origin

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[13] Solid-state effects do not appear seriously to affect these conclusions since, where data are available for other halide salts of these pentaammine cations, a comparison shows similar trends in frequency shifts and magnitudes as observed from the chloride salts. For example, in the I^- salts of $Ru(NH_3)_5CO^{2+}$ and $Ru(NH_3)_5N_2^{2+}$ [2,6] $\Delta\nu$(C–O) = 188 cm^{-1} and $\Delta\nu$(N–N) = 202 cm^{-1}, respectively, and ν(Ru–CO) is 568 cm^{-1} while $\nu(Ru–N_2)$ is 489 cm^{-1}.

[14] D. E. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

[15] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. B. Pearson, *J. Am. Chem. Soc.*, **90**, 5295 (1968).

[16] J. A. Stanko and C. K. Thomas, to be sumitted for publication.

[17] H. H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, **49**, 2039 (1966).

[18] The observed chemical shifts of the ammonia protons in the CO complex, *i.e.*, *trans* to lower field than *cis*, also supports this conclusion by analogy with the nmr results on cobalt(III)–pentaammine complexes. See, for example, D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967). For the cobalt complexes $Co(NH_3)_5X^{2+}$ it has been observed that for X ligands lower in the spectrochemical series than ammonia, *cis*-ammonia protons occur at a lower field than *trans*, and the reverse, for ligands higher in the series than ammonia.

of this band in the N_2 complexes and its absence in the CO complex is puzzling. We would speculate that in the nitrogen complexes this band originates from a transition of the type $2p\pi_u \rightarrow 2p\pi_g^*$ on the N_2 molecule itself. Although these are strongly allowed transitions, they are observed at very high energy in the spectrum of the uncomplexed N_2 molecule.[19] However it seems conceivable that, owing to the expected bond lengthening upon coordination, correlated with the observed large reduction in the ligand stretching frequency, the π,π^* separation in the molecule could be reduced to near a value of 50,000 cm^{-1}, as observed for these bands in the N_2 complexes. The absence of a similar band in the CO complex in the accessible uv region would imply a larger excitation energy for this type of transition on the CO ligand than the N_2 ligand. Orgel, some time ago, in his consideration of the expected differences in the bonding of N_2 and CO to metals alluded to the fact of a larger π,π^* orbital separation in CO than N_2, based on the spectroscopy of the free molecules.[20]

Acknowledgments.—We wish to express appreciation to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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[19] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 449.

[20] L. E. Orgel, "An Introduction of Transition-Metal Chemistry," 1st ed, Methuen and Co., Ltd., London, 1960, pp 137–138.

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Kinetics of the Reaction of Some Monoacidopentaaquonickel(II) Complexes with 4-(2-Pyridylazo)resorcinol

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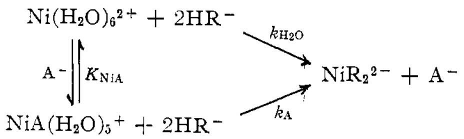
Kinetics and mechanism of the reaction of monoacetato-, monoazido-, monofluoro-, and monohydroxonickel(II) complexes with 4-(2-pyridylazo)resorcinol have been studied spectrophotometrically at $\mu = 0.10$ and at 25.0°. The reaction scheme can be described as



where A^- is a monodentate ligand such as hydroxide, azide, acetate, and fluoride and HR^- refers to monoionic species of 4-(2-pyridylazo)resorcinol. The stability constants, K_{NiA}, of the monoacidonickel(II) complexes and rate constants, k_{H_2O} and k_A, are kinetically determined: $K_{NiOH} = 10^{4.3\pm0.1}$, $K_{NiN_3} = 10^{0.66\pm0.10}$, $K_{NiO_2CCH_3} = 10^{0.74\pm0.15}$, $K_{NiF} = 10^{1.1\pm0.1}$, $k_{H_2O} = (1.7 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$, $k_{OH} = (1.0 \pm 0.15) \times 10^4\ M^{-1}\ sec^{-1}$, $k_{N_3} = (1.1 \pm 0.15) \times 10^4\ M^{-1}\ sec^{-1}$, $k_{CH_3CO_2} = (4.5 \pm 0.4) \times 10^3\ M^{-1}\ sec^{-1}$, $k_F = (1.1 \pm 0.2) \times 10^3\ M^{-1}\ sec^{-1}$. The difference of reactivity of these nickel(II) complexes is discussed in terms of electron donation of coordinated ligands on the basis of a model in which loss of the first water molecule coordinated to nickel(II) is the rate-determining step. The effect of electron donation of ligands on the rate of loss of water molecule is thus quantitatively accounted for.

Introduction

The kinetics of complex formation of nickel(II) with various ligands have been extensively studied.[1-3] These studies have shown that the rate of complex formation is primarily determined by the rate of loss of a water molecule coordinated to nickel(II). In studies on the kinetics of the ligand substitution reaction[4] of the cobalt(II)- and nickel(II)-(ethylene glycol)bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetate complexes with 4-(2-pyridylazo)resorcinol (PAR), we found that the rate of incorporation of the second PAR is much faster than the rate of addition of the first PAR to the metal ion. Similar results are noticed also in some other reactions.[5-8] Margerum and Rosen[9] have pointed that the electron-donor ability of coordinated groups is important in the rate of replacement of the remaining coordinated water molecules. Moorhead and Sutin[10] have shown that in the formation of the monooxalate complex of iron(III) the rate of reaction of $Fe(H_2O)_5OH^{2+}$ with oxalate ion is about 20 times faster than that of reaction of $Fe(H_2O)_6^{3+}$ with oxalate

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[1] M. Eigen and R. W. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

[2] N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

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[5] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962); *J. Phys. Chem.*, **67**, 528 (1963).

[6] C. B. Honaker and H. Freiser, *ibid.*, **66**, 127 (1962).

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[8] R. G. Pearson and P. Ellgen, *ibid.*, **6**, 1379 (1967).

[9] D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).

[10] E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).