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Far Infrared Spectra and Substitution Reaction Mechanism in Complexes of the Type $[M(N_3)_5OH_2]^{3+}$ (with M = Co, Rh, Ir)

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Received October 28, 1972

The far infrared spectra of the complexes $[M(NH_3)_5OH_2]^{3+}$ where M = Co, Rh, and Ir, have been measured in the range 600-350 cm^{-1}. The four bands observed are assigned to the expected metal-ligand stretching vibrations. The observed frequencies are sensitive to the nature of the metal and follow the sequence $Co<Rh<Ir$.

The Raman spectrum of the rhodium complex is also reported.

Bond dissociation energies are considered to follow the same $Co<Rh<Ir$ pattern.

The relationship between metal-ligand stretching frequencies and activation enthalpies of ligand substitution reactions is discussed and some conclusions are reached supporting previous mechanistic hypotheses.

Introduction

The mechanism of the substitution reactions of inert octahedral complexes is still a matter of lively discussion in spite of the great number of investigations carried out in this field.

Most of the work has been concerned with Co^{III} complexes and, among them, those belonging to the pentaammine class are the compounds which have been most thoroughly investigated.

There is now sufficient experimental evidence to state that in aqueous solution, complexes of the type $[Co(NH_3)_5X]^{n+}$ undergo substitution leading to the same aquo species through an activation process which is essentially dissociative.[1-4]

Recent data concerning the reactivity of the analogous complexes of the heavier d^6 transition metal ions Rh^{III} and Ir^{III} seem to indicate that bond formation makes a detectable contribution to the enthalpy and entropy of the activated state.[5-9]

One of the arguments on which these conclusions are based is that within the $[M(NH_3)_5X]^{n+}$ complex series an essentially dissociative mechanism should lead to ΔH^* values increasing in the order $Co<Rh<Ir$ since this should be the order of increasing metal-ligand bond strength.

However, *direct* information on even the relative M-X bond dissociation energies of $[M(NH_3)_5X]^{n+}$ complexes of the three metals is not available and only that fraction arising from the loss of crystal field stabilization energy can be estimated from electronic spectra.

This work was undertaken with the belief that the comparison of metal-ligand stretching frequencies could lead to a somewhat direct insight on this problem.

The aquopentaamminemetal(III) species have been chosen because the activation parameters of the water-for-water substitution reaction have been already determined,[4,5,9,10] including the activation volumes (M = Co, Rh) and are suitable for a more complete discussion.

Experimental Section

Chemicals. All reagents used in this work were pure grade chemicals.

Complexes. The aquopentaamminecobalt(III), -rhodium(III) and -iridium(III) perchlorates were prepared and purified by known methods.[9,11,12] Their purity was checked by comparing the electronic spectra with those reported in the literature.[13-15]

Spectra. The infrared spectra were measured using a Beckman IR9 spectrophotometer (600-400 cm^{-1}) and a Perkin-Elmer 521 spectrophotometer (600-350 cm^{-1}). The spectra were taken both as nujol mulls (CsI windows) and as KBr discs. The frequences of the absorption bands are listed in Table I. Figure 1a shows the spectrum of a $[Rh(NH_3)_5OH_2](ClO_4)_3$ sample which may be considered as typical. Since the bands were relatively flat and broad, the corresponding frequencies were determined on the basis of several independent spectra obtained with samples of different concentration. The reproducibi-

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(1) F. Basolo and R.G. Pearson, «Mechanism of Inorganic Reactions», John Wiley, New York, 2nd ed., 1967, p. 158 and foll.
(2) C.H. Langford and H.B. Gray, «Ligand Substitution Processes», W.A. Benjamin, New York, 1965, p. 90 and foll.
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(13) N. Linhard and M. Weigel, *Z. Anorg. Allg. Chemie*, *266*, 49 (1951).
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Table I. Metal-ligand stretching frequencies of aquopentaamminemetal(III) complexes.

Complex	frequencies (cm^{-1}			
$[Co(NH_3)_5OH_2](ClO_4)_3$	412	454	475	513
$[Rh(NH_3)_5OH_2](ClO_4)_3$	442	460	492	530
$[Ir(NH_3)_5OH_2](ClO_4)_3$	450	468	502	542

lity was usually better than ±5 cm^{-1}.

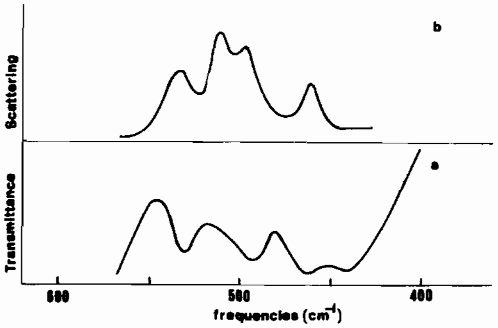

Figure 1. Far infrared (a) and Raman (b) spectrum of $[Rh(NH_3)_5OH_2](ClO_4)_3$.

The same frequencies were also observed for each complex at the liquid nitrogen temperature. The intensities were, however, generally higher.

Raman spectra of solid samples were recorded with a Jarrel Ash, Raman Spectrometer using an Argon ion laser Coherent, mod. 52. Unfortunately the cobalt (III) complex exploded in the laser beam. The rhodium and the iridium compounds were stable but only the first complex gave a clearly resolved spectrum which is reported in Figure 1b.

Results and Conclusions

If both the ammonia and water ligands are considered as point masses, the molecular symmetry of the species $[M(NH_3)_5X]^{n+}$ is C_{4v}. The 15 molecular normal modes are distributed among the symmetry classes of C_{4v} as $4A_1+2B_1+B_2+4E$. Only five modes $(3A_1+B_1+E)$ imply metal-ligand stretchings, four of whic are both ir and Raman active while one (B_1) is only Raman active.

According to published data,[16] the Co-N stretching frequencies of hexaammine- and acidopentaamminecobalt(III) salts are in the range 400-500 cm^{-1}. Data are also reported for the aquopentaamminerhodium (III) and iridium(III) bromides and again the metal-ligand stretching vibrations are found to occur within the range 450-530 cm^{-1}.[17] The outher anion has only a relatively small influence on the position of the peaks[18] and, in particular, perchlorate is apparently free from H-bonding complications.

Therefore, there is little doubt that the four ir bands observed for the aquopentaamminemetal(III) perchlorates correspond to the so called metal-ligand stretchings. Of course the observed frequencies are not due to *pure* metal-ligand stretching modes since they will interact to some extent with other vibrations of the same symmetry. No attempts were made to assign each observed ir band to a given mode.

Preliminary results of an X-ray investigation on the complex salts here discussed show that the geometry of the crystallographic unit is practically unchanged by changing the nature of the metal,(*) suggesting thus that also the metal-ligand bond length is not appreciably changed.[19] Because of such close structural analogy it is also reasonable to expect that the ir active modes will follow the same frequency sequence for all three complexes.

The Raman spectrum of the aquopentaamminerhodium(III) perchlorate shows four peaks. Two of them are coincident with the 497 cm^{-1} and 530 cm^{-1} bands observed in the infrared spectrum while the 510 cm^{-1} band should be assigned to the ir inactive B_1 mode. The 460 cm^{-1} band is due to the symmetric stretching mode of ClO_4^- ion.[20]

Table I shows that the vibration frequencies tend to *increase* as the atomc mass of the metal *increases.* Although the observed vibrations are not pure metal-ligand stretchings, the minor contribution due to other modes of the same symmetry should be virtually independent of the metal. Thus the trend shown by the observed stretching frequencies should reflect the trend of the pure metal-ligand stretchingv vibrations. Hence, the effect displayed by the metal atoms can be explained by assuming that the bond strength increases in the order Co < Rh < Ir. Were this not the case, a *decrease* of the frequencies would instead be expected because of the increased mass of the central atom.

A positive conclusion on this point is of relevant interest when related to the mechanism of the substitution reactions of these aquopentaamminemetal(III) complexes and, particularly of the water exchange reactions.

In fact, since solvation effects are likely to be independent of the metal, the rate determining step of the limiting S_N1 process:

$$[(NH_3)_5M{-}OH_2]^{3+} \rightarrow [(NH_3)_5M]^{3+} + OH_2 \qquad (1)$$

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(16) K. Nakamoto, «Infrared Spectra of Inorganic and Coordination Compounds», John Wiley, New York, 2nd ed., 1970, p. 150.

(17) I.B. Baranovskii, Yu.Ya. Karitonov, and Ya.Mazo, *Zh. Neorg. Khim.*, *15*, 1715 (1970).

(18) N. Tanaka, M. Kamada, J. Fujita, and E. Kyuno, *Bull. Soc. Jap.*, *37*, 222 (1964).

(*) All three complexes are monometric. The rhodium and the iridium compounds belong to the space group F 43 m. The cell parameter is identical within the experimental error (a = 11.486 +0.001 Å). The space group requires that the metal-donor atom bonds and one of the three independent perchlorate ions lie along the *a*- axis. The The parameter *a* measured with crystals of the cobalt salt crystallized from water is nearly twice as large (*a* = 22.701+0.001 Å). Upon irradiation, the crystals convert to a form virtually identical to that of the heavier analogues.

(19) L. Scaramuzza *et al.*, work in progress. Chemistry Dept., University of Rome.

(20) S.D. Ross, *Spectrochimica Acta*, *18*, 225 (1962).

Table II. Activation parameters for the water exchange reaction of $[M(NH_3)_5OH_2]^{3+}$ ions.

M	ΔH^* (kcal/mole)	ΔS^* e.u.	ΔV^* (cm^3/mole)	Ref.
Co	26.7	+6.7	+1.2	5, 7, 10
Rh	24.1 [a]	—0.47 [a]	—4.1	4
Ir	28.2	+3.0	—	9

[a] Refined values calculated in ref. 7 from data of ref. 5.

would require an energy increasing in the order Co<Rh<Ir.*

Thus, when M is changed through the series Co, Rh, Ir, a substitution process taking place through the dissociation of the M-OH$_2$ bond should lead to activation enthalpies increasing in the order Co<Rh<Ir. Either an inversion or closely similar values are in contrast with a purely dissociative mechanism and both require that the exothermic contribution of a seventh bond to be taken into consideration. The water exchange reactions of the above aquopentaamminemetal(III) complexes have been studied kinetically over a wide range of conditions so that the activation enthalpies, entropies and volumes are known (see Table II). Only ΔV^* for the aquopentaammineiridium(III) cation has not yet been measured.

When the cobalt complex is compared with the rhodium analogue it appears that ΔH^* decreases with increasing the atomic mass of the metal. This indicates an exchange mechanism where the associative character increases from Co to Rh. It should be emphasized that it is impossible to evaluable the *individual* degree of bond formation but only to say that it *increases* in the given order. Both ΔS^* and ΔV^* are in agreement with such conclusion since a decrease of both the activation entropy and volume is expected if the associative character of the mechanism increases.[4,5,10]

Since the activation enthalpy for the water exchange of the iridium complex is the highest within the series, no information can be derived as to the mechanism which may or may not be associative in part.

(*) In addition to bond breaking and solvation, there are certainly other effects which should be taken into account when considering the overall energy balance of a limiting S_N1 process. Perhaps the most important of these (minor) effects is the relief of intramolecular repulsion due to the decreased coordination number, but again, the similarity of the coordination spheres should lead to nearly equal contributions for the three complexes under study.