[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Infrared Spectra of Metallic Complexes. II. The Absorption Bands of Coördinated Water in Aquo Complexes

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The characteristic bands of coördinated water molecules in Ni^{2+}, Cu^{2+}, Cr^{3+} aquo complexes have been found in the NaCl region. The presence and the absence of the bands in various compounds are discussed, based on the effects of coördination and hydrogen bonding.

Introduction

It is well known[1] that water vapor exhibits three fundamental bands, *e.g.*, asymmetric and symmetric stretching and bending vibrations at 3756, 3652 and 1595 cm.$^{-1}$, respectively. The absorption of water in aquo complexes will not differ greatly from the spectrum of the vapor state if the metal–oxygen bond is purely ionic. However, if the bond is covalent, we may expect new modes of vibrations such as wagging, twisting and rocking modes characteristic of coördinated water molecules. Therefore, an investigation of these bands in typical aquo complexes is of considerable interest because it provides much information on the nature of the metal–oxygen bond.

However, so far no attempt has been made to study the characteristic absorptions of coördinated water. This is partly due to their relative weakness and overlapping of other bands on these absorptions In the present paper, the infrared spectra of a number of aquo complexes have been examined, and the characteristic bands of coördinated water molecules found in the NaCl region.

Experimental

Preparation.—The compounds used in this study were prepared by the usual methods. $CuSO_4 \cdot 5D_2O$ was prepared by recrystallization of $CuSO_4$ from 99.98% D_2O.

Absorption Measurements.—The infrared spectra were obtained by a Perkin–Elmer Model 21 double beam infrared spectrophotometer using a NaCl prism. The Nujol mull technique was employed.

Results and Discussion

(1) **Ni Aquo Complexes.**—The infrared spectra of $Ni(glycine)_2 \cdot 2H_2O$ and $Ni(glycine)_2$ are shown in Fig. 1. Since a strong band at 795 cm.$^{-1}$ disappears upon dehydration, it is undoubtedly the absorption characteristic of the coördinated water molecules. A similar band was found at 730 cm.$^{-1}$ in $Ni(alanine)_2 \cdot 4H_2O$, but not in $Cu(glycine)_2 \cdot H_2O$.

The X-ray analysis of $Ni(glycine)_2 \cdot 2H_2O$[2] definitely indicates that the two water molecules are coordinated to the Ni atom (the Ni–OH_2 distance, 2.12 Å.) and, moreover, that they form hydrogen bonds to oxygen atoms of neighboring complexes (the OH–O distance, 2.72 Å.). Although the structure of $Cu(glycine)_2 \cdot H_2O$ is not known, the absence of the band seems to suggest that, in accord with the prediction of the crystal field theory of metallic complexes,[3] the water molecule of the Cu complex is not so strongly bound to the metal as in the Ni complexes. In other words, the metal–oxygen bond is rather ionic in the former whereas it is fairly covalent in the latter. The spectra of $Ni(glycine)_2 \cdot 2H_2O$ and $Cu(glycine)_2 \cdot H_2O$ have already been obtained by Sen, *et al.*,[4] but no argument has been given for this band.

The weak band at 2270 cm.$^{-1}$ in $Ni(glycine)_2 \cdot 2H_2O$ disappears by dehydration and, therefore, is reasonably assigned to the O–H stretching band. If we plot this frequency, together with the hydrogen bond distance on the "O–H stretching frequency *versus* bond distance diagram" obtained by Nakamoto, *et al.*,[5] it is found that this compound gives a large deviation from the straight line toward lower frequencies. It is apparent that this deviation is due to a superposition of the effects of coördination and hydrogen bonding, as suggested by the result of X-ray analysis. Using the above mentioned diagram, the contribution of coördination effect to the shift of the O–H stretching frequency is estimated to be $\Delta\nu = 3030\text{-}2270 = 760$ cm.$^{-1}$. It is interesting to note that the relation found by Nakamoto, *et al.*, is not valid if the effect of hydrogen bonding coöperates with the effect of coördination.

Similar bands have been found near 810 cm.$^{-1}$ in $NiCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$ and $[Ni\ en\ (H_2O)_4]SO_4$, but not in $Ni(ClO_4)_2 \cdot 6H_2O$ and $[Ni\ en_2(H_2O)_2](ClO_4)_2$. As stated in the previous paper,[6] formation of hydrogen bonds between the ligand and the outer-ion causes shifts of all the bending modes to higher frequency. Therefore the absence of absorption in the latter two compounds may imply that the lack of hydrogen bonding in the perchlorate salts retains the band in the lower frequency region.

(2) **Cu Aquo Complexes.**—In Fig. 2, the infrared spectra of $[Cu(H_2O)_4]SO_4 \cdot H_2O$, $[Cu(D_2O)_4]SO_4 \cdot D_2O$ and $CuSO_4$ are given in the region between 925 and 800 cm.$^{-1}$. It is obvious that the strong band at 875 cm.$^{-1}$ is due to the coördinated water molecules, since it disappears upon deuteration and also dehydration. According to the X-ray analysis of $CuSO_4 \cdot 5H_2O$,[7] four water molecules which are linked to the central Cu by fairly covalent bonds (the Cu–OH_2 distance, 1.98 A.) also form strong hydrogen bonds of 2.75 A. with the oxygens of the sulfate ions.

However, similar bands were not observed in $CuSO_4 \cdot en \cdot 3H_2O$, $CuSO_4 \cdot en_2 \cdot 2H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu_2(CH_3COO)_4 \cdot 2H_2O$. The absence of the bands in these compounds may be attributed to the

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[1] For example, see G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

[2] A. J. Stosick, THIS JOURNAL, **67**, 365 (1945).

[3] J. Bjerrum, C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

[4] D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

[5] K. Nakamoto, M. Margoshes and R. E. Rundle, *ibid.*, **77**, 6480 (1955).

[6] J. Fujita, K. Nakamoto and M. Kobayashi, *ibid.*, **78**, 3295 (1956).

[7] C. A. Beevers and H. Lipson, *Proc Roy. Soc.* (*London*), **A146**, 570 (1934).

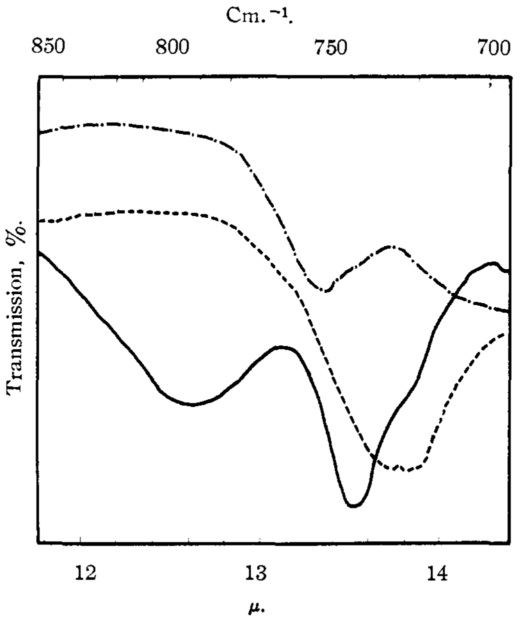

Fig. 1.—Infrared absorption spectra of: ——, Ni(glycine)$_2$·2H$_2$O; ------, Ni(glycine)$_2$; —·—·—, Cu(glycine)$_2$·H$_2$O.

lack of sufficient effects of hydrogen bonding and coördination.

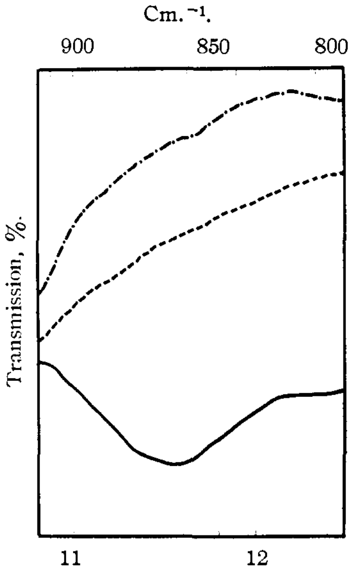

Fig. 2.—Infrared absorption spectra of: ——, [Cu(H$_2$O)$_4$]SO$_4$·H$_2$O; ------, [Cu(D$_2$O)$_4$]SO$_4$·D$_2$O; —·—·—, CuSO$_4$.

It is interesting to note that Ni(CH$_3$COO)$_2$·4H$_2$O shows bands at 963 and 910 cm.$^{-1}$, whereas Cu$_2$(CH$_3$COO)$_4$·2H$_2$O has no absorption in this region. The X-ray data for these two compounds are as follows

	M–OH$_2$ distance (A.)	O–H- - -O distance (A.)
Ni(CH$_3$COO)$_2$·4H$_2$O[8]	2.06, 2.11	2.59, 2.65
Cu$_2$(CH$_3$COO)$_4$·2H$_2$O[9]	2.20	2.82, 2.89

Thus these structural data seem to suggest the importance of both the effects of coördination and hydrogen bonding.

(3) **Cr Aquo Complexes.**—Figure 3 compares the spectra of *trans*-[Cr(ox)$_2$(H$_2$O)$_2$]K·3H$_2$O and [Cr(ox)$_3$]K$_3$·3H$_2$O. The former compound shows two bands at 1012 and 965 cm.$^{-1}$, but the latter does not. Therefore it is expected that these bands are due to the absorption characteristic of the coördinated water molecules in the former compound. It is noteworthy that infrared spectra in this region can discriminate between coördinated water and crystal water.

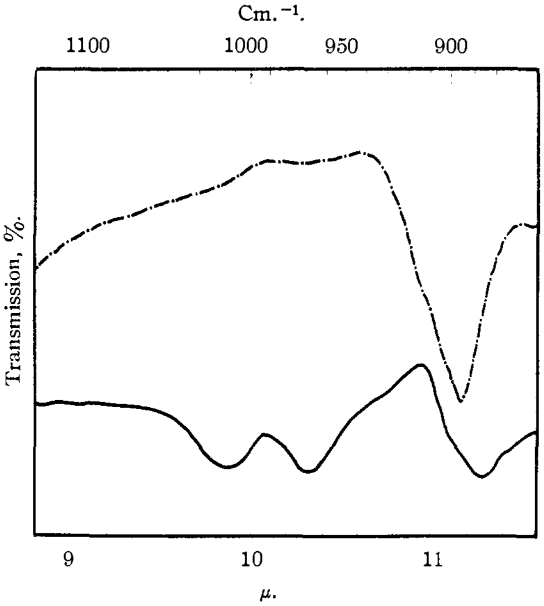

Fig. 3.—Infrared absorption spectra of: ——, *trans*-[Cr(ox)$_2$(H$_2$O)$_2$]K·3H$_2$O; —·—·—, [Cr(ox)$_3$]K$_3$·3H$_2$O.

According to the X-ray analysis of [Cr(ox)$_2$(H$_2$O)$_2$]K·3H$_2$O,[10] the Cr–O (coördinated water) distance is 2.02 A., and these two molecules of coördinated water form strong hydrogen bonds (2.66 and 2.72 A.) with the crystal water. Similar bands to the above exist at 910 cm.$^{-1}$ in KCr(SO$_4$)$_2$·12H$_2$O and KAl(SO$_4$)$_2$·12H$_2$O, but not in [Cr(NH$_3$)$_5$H$_2$O](ClO$_4$)$_3$. The absence of the absorption in the latter compound may be due to the lack of strong hydrogen bonding or the overlapping of NH$_3$ rocking band.

Summary

From the foregoing discussion, it is concluded that the characteristic bands of coördinated water in the NaCl region are observable only when the water molecules are linked to the metal by fairly covalent bonds, and also to the outer-ion or the ligand of the neighboring complex by strong hydrogen bonds. If either of these two conditions is absent, the absorption does not appear in the NaCl region.

Table I summarizes the results obtained above. It is seen that the band of coördinated water goes to higher frequency in the order of Ni^{2+}, Cu^{2+} and Cr^{3+} complexes. At the same time, the critical temperature of dehydration of these compounds

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(8) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 609 (1953).

(9) J. N. van Niekerk and F. R. L. Schoening, *ibid.*, **6**, 227 (1953).

(10) J. N. van Niekerk and F. R. L. Schoening, *ibid.*, **4**, 35 (1951).

TABLE I

CHARACTERISTIC BANDS OF COÖRDINATED WATER IN Ni^{2+}, Cu^{2+} AND Cr^{3+} AQUO COMPLEXES

Metal	Compound	νH_2O (cm.$^{-1}$)	$M-OH_2$ (A.)	OH–O (A.)	Temp. for dehydration, °C.
Ni^{2+}	$Ni(glycine)_2 \cdot 2H_2O$	795	2.12	2.72	135 ~ 140
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	875	1.98	2.75	220
Cr^{3+}	$[Cr(ox)_2(H_2O)_2]K \cdot 3H_2O$	965	2.02	2.66	High
		1012		2.72	

increases in the same order. As is shown by the $M-OH_2$ and O–H----O distances, the effects of coordination and hydrogen bonding are also increasing in the same order. Therefore we conclude that a coöperative effect of coördination and hydrogen bonding is responsible for the shift of the band and the rise of temperature of dehydration.

Although the vibrational mode of the band is not yet determined, it is attributable to either one of the modes among wagging, twisting and rocking vibrations. A detailed study of the nature of this band is now in progress and will be reported later together with the measurements in the KBr region.

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Platinum Olefin Coördination Compounds. I. The Structure of Dicyclopentadienedichloroplatinum(II)

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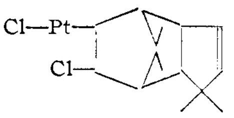
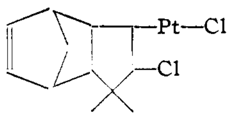
The previously proposed structure of dicyclopentadiene platinous chloride has been re-examined and shown to be inconsistent with newly determined data. A new structure is proposed in which the dicyclopentadiene acts as a bidentate ligand with both double bonds coördinated to the platinum in the *cis*-positions of the coördination sphere.

Introduction

Recent interest in the olefin coördination compounds of platinum has prompted a re-examination of the structure of the compound formed by the reaction of dicyclopentadiene and potassium chloroplatinite as reported by Hofmann and Narbutt.[2] They believed that platinous chloride added across one of the double bonds of dicyclopentadiene in a manner similar to the reaction of mercuric chloride and olefins. This type of addition would yield compounds having a structure similar to the possibilities shown in Ia or Ib.

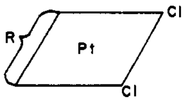


Ia



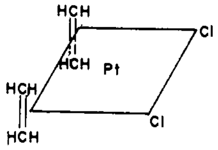
Ib

Jensen[3,4] has prepared a series of compounds in which cycloöctatetraene and 1,6-hexadiene act as bidentate ligands. The double bonds of the diolefin occupy adjacent positions in the coördination sphere of the platinum, giving a *cis*-configuration to the molecules as shown in II.



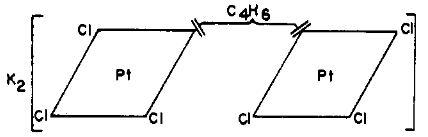
II

Chatt[5] has recently reported a rather unstable bisethylene platinous chloride, III, in which he proposes that the molecules of ethylene occupy *cis*-positions



III

Chatt and Duncanson have reported the preparation of a platinum–olefin compound containing 1,4-butadiene in which this diolefin acts as the bridging group as in IV.



IV

In determining the structure of dicyclopentadienedichloroplatinum(II) all of the various types discussed above have been considered and in addition the possibility of a bis-cyclopentadienyl derivative of platinum was examined.

Experimental

Dicyclopentadienedichloroplatinum(II).—Five grams of potassium chloroplatinite was dissolved in a mixture of 60 ml. of water and 15 ml. of *n*-propyl alcohol. Eight ml. of dicyclopentadiene dissolved in 25 ml. of ethyl ether was added to this clear red solution. The solutions were mixed in a 250-ml. flask and allowed to react at room temperature for three days. The dark brown precipitate which formed was removed by filtering and washed with two 10-ml. portions of ethyl ether. The crude product was redissolved in hot chloroform, clarified with decolorizing carbon and the solution evaporated to 25 ml. Ethyl alcohol was then added to the hot chloroform solution until the mixture began to cloud, and upon cooling to room temperature small needle shaped ivory colored crystals separated. The crystals

(1) Abstracted in part from the doctoral dissertation presented to the Graduate School of Tulane University, 1955.

(2) K. A. Hofmann and J. V. Narbutt, *Ber.*, **41**, 1625 (1908).

(3) K. A. Jensen, *Acta Chim. Scand.*, **7**, 866 (1953).

(4) K. A. Jensen, *ibid.*, **7**, 868 (1953).

(5) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).