The Stabilities of Metal Ammine Complexes. I. The Absorption Spectra of a Series of Hexammine Ni(II) and Tetrammine Pt(II) Complexes

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Introduction

The formation constants of numerous metal complexes have been determined using the now familiar method established by J. Bjerrum[1]. From these results it was concluded that there existed a pretty good correlation[2,3,4] between the stability of the complex and the proton affinity of the ligand. This conclusion means, in case of ammine complexes, that the stronger basicity an amine has, the more stable

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution". P. Haase and Son, Copenhagen (1941).

[2] M. Calvin and Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

[3] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[4] W. S. Fyfe, *J. Chem. Soc.*, 2018 (1952).

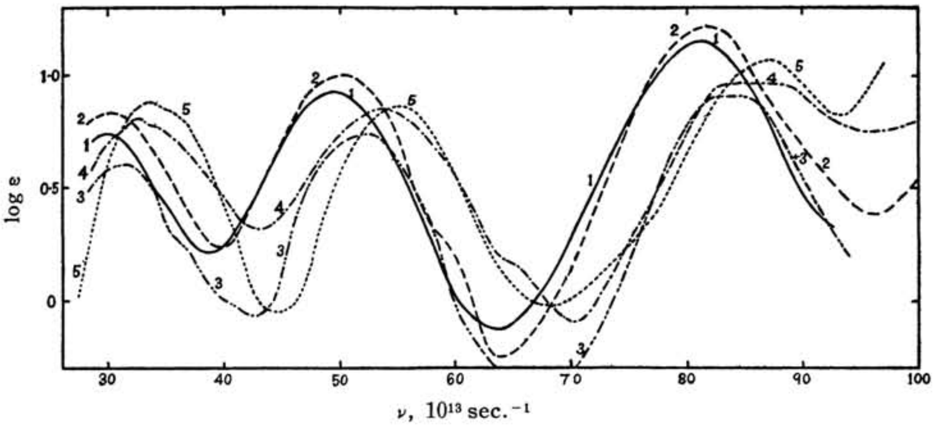

Fig. 1. The absorption spectra of hexammine Ni(II) complexes.

1 ——— $Ni(CH_3CH_2NH_2)_6^{2+}$
2 - - - - - $Ni(OHCH_2CH_2NH_2)_6^{2+}$
3 —··—·· $Ni(NH_3)_6^{2+}$
4 —·—·— $Ni(NH_2OH)_6^{2+}$
5 ············ $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

complex it produces. However, we must notice that the determination of the formation constant can be made only when the complex is fairly labile and when it forms a reversible equilibrium system with its components in a solution. Accordingly, it should be carefully reexamined from another kind of data, to discover whether or not the law which governs the stability of the complex of highly covalent character coincedes with the above mentioned conclusion. The absorption spectra of complexes can give such reexamining means. The ammine complex of a transition metal ion having an unsaturated d-shell shows, in general, a definite number of absorption bands characteristic of the metal ion concerned from the near infrared to the near ultraviolet regions. For examle, Cu(II) complexes have one, Co(III) and Cr(III) complexes have two, and Ni(II) complexes have three such absorption bands. Hitherto, such absorption bands have been considered to be originated from the energy transitions between the splitting d-levels of the central metal ion[5,6]. Accordingly, when we can get knowledge about the correlation between the field strength set up by the ligands and the degree of splitting of the d-levels, we can discuss the stability of the complex from the absorption data. In the present investigation the absorption spectra of a series of hexammine Ni(II) and tetramine Pt(II) complexes were measured, and from these results a very interesting experimental rule was found between the stability of a complex and the basic strength of the coordinating amine.

Experimental

The measured nickel ammine complexes were those of NH_2OH, NH_3, $OHCH_2CH_2NH_2$, CH_3NH_2, $CH_3CH_2NH_2$ and $NH_2CH_2CH_2NH_2$. As these complexes are all labile and hydrolyzed partly in a solution, the solution used in the measurement was prepared as follows: A solution containing an amine and its sulphate in the concentrations of 6 M and 2 M respectively was prepared. To such a solution, nickel sulphate was dissolved to 0.1 M. (Under these conditions, all nickel ions in a solution may be considered to exist as the form of hexammine complex ions.)

The plato ammine complexes measured were those of NH_2OH, NH_3, CH_3NH_2, $CH_3CH_2NH_2$, and $NH_2CH_2CH_2NH_2$. These complexes were prepared from K_2PtCl_4 and the corresponding amine through Magnus' salt. For the absorption measurement, 0.01 M solution of the complex was used in every case.

The absorption measurement was carried out by means of the Beckman DU spectrophotometer using tungsten and hydrogen lamps and 1 cm. quartz cells.

Results

The absorption spectra of Ni ammine complexes are shown in Fig. 1. As the curves of both methylamine and ethylamine complexes are quite similar to each other, only that of the ethylamine complex is shown in the figure. All these curves have three absorption bands which are called the first, second and third bands from the long wavelength. The maximum positions of these three absorption bands and the pK*

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[5] R. Tsuchida, This Bulletin, **13**, 388 (1938).

[6] M. Linhard and W. Weigel, *Z. anorg. u. allgm. Chem.*, **264**, 321 (1951).

[7] "Inorganic Systheses", Mc Graw-Hill, New York (1949), Vol. II, 250.

* Negative logarithm of the ionization constant.

values of the coordinating amines are tabulated in Table I.

TABLE I

MAXIMUM POSITIONS OF THE THREE ABSORPTION BANDS OF Ni(amine)$_6^{2+}$

(ν, 10^{13} sec.$^{-1}$)

Amine	pK	1st Band	2nd Band	3rd Band
$CH_3CH_2NH_2$	3.27	29.70	49.2	81.5
CH_3NH_2	3.37	30.0	50.0	81.5
$OHCH_2CH_2NH_2$	undetermined	30.0	50.0	81.5
NH_3	4.75	31.6	51.7	84.5
NH_2OH	7.97	32.4	53.6	86.0
$NH_2CH_2CH_2NH_2$	5.45*	33.5	55.0	87.0

From the table it is easily seen that these three absorption bands shift to the same direction in variation of ligands. At the same time it is seen that the maximum position of the bands of the complex shifts with the basic strength of the coordinating amine.

The results obtained about Pt(II) ammine complexes are shown in Fig. 2.

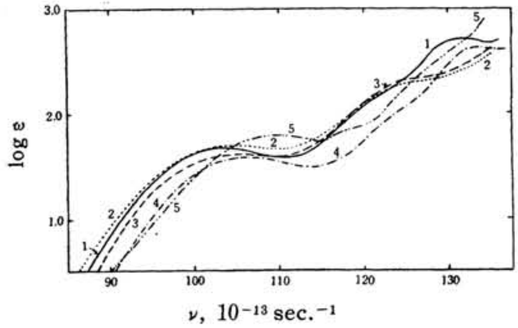

Fig. 2. The absorption spectra of tetrammine Pt(II) complexes

1 ——— Pt($CH_3CH_2NH_2$)$_4^{2+}$
2 ············ Pt(CH_3NH_2)$_4^{2+}$
3 - - - - - Pt(NH_3)$_4^{2+}$
4 —·—·— Pt($NH_2CH_2CH_2NH_2$)$_2^{2+}$
5 —··—·· Pt(NH_2OH)$_4^{2+}$

TABLE II

MAXIMUM POSITIONS OF THE FIRST ABSORPTION BAND OF Pt(amine)$_4^{2+}$

(ν, 10^{13} sec.$^{-1}$)

Amine	1st Band
$CH_3CH_2NH_2$	103.4
CH_3NH_2	105.0
NH_3	105.0
$NH_2CH_2CH_2NH_2$	107.0
NH_2OH	110.1

In this case, the general feature of the absorption spectra is considerably complicated. Except the one appearing in the long wavelength region, the absorption bands in the shorter wavelengths have large values of log ε, and the discrimination from the charge transfer bands is difficult. Consequently, only the maximum position of the the absorption band in the long wavelength region is listed in Table II.

Here it is also shown that the maximum position of the absorption band shifts with the basic strength of an amine.

Discussion

Before discussing the stability of the metal ammine complex from its absorption bands, we must consider the general relationship between the absorption bands and the electronic states of the complex radical.

The splitting of d-levels due to the influence of various outer fields was first evaluated by H. Bethe[8], and this view was further developed by J. H. Van Vleck[9] to the more general theory to account for the magnetic properties of crystals. The idea of using this crystal field theory on the complex radical is due to H. Hartmann and F. E. Ilse[10], who applied it to explain the absorption spectra of the titanium(III) and vanadium(III) complexes. Recently, C. J. Ballhausen[11] and L. E. Orgel[12] extended this theory to the spectra of many other transition metal complexes. Although various mechanisms are able to remove the degeneracy of the d-orbitals as there are various intermediates between the purely ionic and highly covalent bonds, in the crystal field theory the splitting of the degeneracy of the d-orbitals is regarded as the consequence of the electrostatic field set up by the ligands. Here the covalent character of the bond is expressed by the polarization of the ligand. Now it is easily understood that the energy intervals between the splitting d-levels increase with the increase of the electrostatic field set up by the ligands. As the energy transitions between such splitting d-levels appear as the characteristic absorption bands of the complex, it can be said that the stronger the field by the ligands is, the more the absorption bands of the complex appear in the shorter wavelength.

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* As ethylenediamine is a diacidic base and coordinates to the metal ion as a bidentate ligand, the mean value of pk$_1$ (4.08) and pk^2 (6.81) was taken as the pk for comparison. This mean pk value can give a rough estimation of the relative coordinating ability in the monoamine series.

[8] H. Bethe, *Ann. Physik.* 5 Folge, **3**, 133 (1929).

[9] J. H. Van Vleck, "The Therory of Electric and Magnetic Susceptibilities", Oxford Press (1932).

[10] H. Hartmann and F. E. Ilse, *Z. physik. Chem.*, **197**, 239 (1951) ; *Z. Naturforschg.*, **6A**, 751 (1951).

[11] C. J. Ballhausen, *Dan. Mat. Fys. Med*, **29**, No.4 (1954) ; ibid., **29**, No. 8 (1955).

[12] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

As indicated by C. J. Ballhausen, the polarization of the ligand in case of Ni(II) complexes is pretty large and the resulting induced dipole moment of the ligand is much larger than its permanent dipole moment. Accordingly, in the ammine complex whose ligand is neutral, it is concluded that the amount of polarization chiefly determines the field strength. In other words, the blue shift of the absorption bands of the complex in variation of the ligand corresponds to the increase of the field strenth set up by the ligand, and the increase of the field strength corresponds to the increase of polarization.

The present experimental results about Ni(II) and Pt(II) ammine complexes indicate that the weaker the basic strength of an amine is, the more the absorption bands of the produced complex appear in the shorter wavelength. Therefore, when this fact is connected with the above mentioned conclusion about the relationship between the absorption bands and the field strength by the ligands, the following rule can be drawn: In the complex of a transition metal ion with an unsaturated d-shell, the weaker the basicity of an amine is, the larger its polarization by the metal ion is. The increase in the polarization indicates the increase in the interaction between the ligand and the metal ion, and the increase in the interaction can be regarded as the increase of the stability of the complex.

Here it should be noticed that this conclusion is quite reverse to that presumed by many investigators. After the view hitherto believed, the affinity of the amine toward the metal ion should be in principle parallel with that toward hydrogen ion. However, we must point out that the data which formed the basis of such a view were all those about the ammine complexes of pseudo-inert gas type ions, such as Ag^+, Hg^{2+} etc. As the d-shell of the pseudo-inert gas type ion is completely closed, the contribution of the d-electrons to the coordination bond may be considered to be negligibly small. Therefore, it is quite natural that such an ion behaves in the same manner with hydrogen ion. While, in the complex of transition metal ions with an unsaturated d-shell, the contribution of d-electrons to the coordination bond must be taken into account. Consequently, it is possible that such an ion with an unsaturated d-shell shows the quite different behaviour from the pseudo-inert gas type ion.

Summary

The absorption spectra were measured about a series of hexammine Ni(II) and tetrammine Pt(II) complexes having various amines as ligands. These amines were hydroxylamine, ammonia, ethanolamine, methylamine, ethylamine and ethylenediamine. The results of the measurement indicate that the weaker the basic strength of an amine is, the more the absorption bands of the produced complex appear in the shorter wavelength. This fact was connected with crystal field theory, and the following rule was drawn: In the complex of a transition metal ion having an unsaturated d-shell, the weaker the basic strength of an amine is, the more stable the produced complex is.

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