Chemistry

Academician A. A. Grinberg, Yu. S. Varshavskii

1964

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. A. Grinberg, Yu. S. Varshavskii

ACIDIC PROPERTIES OF AMMINES AND THE FREQUENCIES OF DEFORMATION VIBRATIONS OF COORDINATED AMMONIA MOLECULES

The changes undergone by ammonia molecules in the field of a metallic complex-forming ion are manifested, in particular, in an increase in the degree of their acid dissociation according to the equation $MNH_3 \to MNH_2^- + H^+$ (amido reaction). On the other hand, these changes can be characterized by the direction and magnitude of the shift of the vibrational frequencies of the NH_3 molecule upon formation of its coordination bond. It is natural to expect that between these manifestations of the effect of the central atom on the state of the coordinated NH_3 molecule there exists a certain (although perhaps very rough) correlation. The corresponding experimental data (values of the index of the acid dissociation constant pK_a and the frequencies (δ_s in cm^{-1}) of the symmetric deformation vibrations of the NH_3 molecule) are given in Table 1.

Table 1

Acidic properties of ammine complexes and frequencies of symmetric deformation vibrations of coordinated NH_3 molecules

Compound	pK_a	δ_s, cm^{-1}
$[Pt(NH_3)_6]Cl_4$	~ 7	1385
$[Pt(NH_3)_5Cl]Cl_3$	8.1	1360
$[Pt(NH_3)_5Br]Cl_3$	8.25	1350
$[Pt(NH_3)_5J]Cl_3$	8.6	1350
$[Pt(NH_3)_4Cl_2]Cl_2$ (trans)	11.2	1346
$[Pt(NH_3)_3Cl_3]Cl$	–	1324
$[Pt(NH_3)_2Cl_4]$ (trans)	–	1316
$K[Pt(NH_3)Cl_5]$	–	1312
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$	–	1320
$[Rh(NH_3)_6]Cl_3$	≥ 15	1320

In the spectra of the platinum ammine complexes studied, the band of the symmetric deformation vibrations of NH_3 is, in a number of cases, split into two components sharply differing from one another in intensity; Table 1 gives the value δ_s corresponding to the more intense component. In the spectrum of trans-diammine the splitting is absent. In the spectrum of hexammine the δ_s band consists of three components (1405, 1380, 1364 cm^{-1}) of nearly equal intensity; the average value 1385 cm^{-1} is given there. Preparations of iodo- and bromopentammines and of iodotetrammine Pt(IV) (in the form of nitrates) were kindly provided by Kh. I. Gildengershel' ; preparations of hexammine and monoammine by Yu. N. Kukushkin, to whom the authors express their deep gratitude. The remaining compounds were obtained specially for the purposes of the present work. The pK_a values for the platinum ammine complexes were taken from the works of A. A. Grinberg and co-workers (^{1,2}). An estimate of the lower limit of pK_a for $[Rh(NH_3)_6]Cl_3$ is contained in the work of H. K. Jørgensen (^{3}). The value δ_s for $[Rh(NH_3)_6]Cl_3$ is given according to the data of Poulet and Mathieu (^{4}).

The data of Table 1 show that a definite correspondence is indeed observed between the values of pK_a and δ_s: the higher the value of δ_s, the more strongly expressed are the acidic properties of the complex. Since the intrinsic value of pK_a of water is 15.75, the data presented make it possible to assume that ammonia complexes can be capable of splitting off protons in aqueous solutions to a noticeable extent only under the condition $\delta_s \gtrsim 1320$ cm^{-1}.

Indeed, ammine complexes, for example, of Pd^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} ($\delta_s =$ 1304, 1285, 1260, 1160 cm^{-1}, respectively (^{5}-^{7})), as well as the lower ammine complexes of tetravalent platinum and all the investigated ammine complexes of divalent platinum, do not exhibit an acid reaction. The value $\delta_s = 1324$ cm^{-1} in the spectrum of Pt(IV) triamine, lying close to the boundary determined by the condition $\delta_s \gtrsim 1320$ cm^{-1}, means that $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$ may possess only weakly expressed acidic properties.

The existence of a dependence between the quantities pK_a and δ_s makes it possible to put forward certain considerations concerning the reasons for the comparatively high acidity of solutions of iodochlorotetrammine $[\text{Pt}(\text{NH}_3)_4\text{ClJ}]^{2+}$ (^{8}) in comparison with $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$. Discussing the question of the "acidifying action of iodine," I. I. Chernyaev and V. S. Orlova (^{8}) put forward two assumptions on the basis of which this difference may be understood: (a) an increased degree of substitution of chlorine atoms by water molecules, associated with the high trans-influence of iodine, and (b) strengthening of the acid function of the ammine molecules. Since in the spectrum of $[\text{Pt}(\text{NH}_3)_4\text{ClJ}]\text{Cl}_2$ measured by us the value $\delta_s = 1350$ cm^{-1} is close to the values characteristic of bromopentammine, iodopentammine, and Gros' salt, it should apparently be assumed that the state of the NH_3 molecules in iodochlorotetrammine does not differ greatly from their state in the compounds indicated. Such a conclusion is also supported by the general similarity of the IR spectra of dichloro- and iodochlorotetrammines (the position and shape of the bands of the NH stretching vibrations, the degenerate deformation vibrations, and the rocking vibrations of NH_3). Thus, the spectroscopic data testify in favor of the first of the two assumptions advanced

Figure 1

Figure 1: Figure 1

by the authors (^{8}).

Fig. 1. Dependence between the degree of bond polarity of the unshared electron pair of the nitrogen atom and the ionization energy of the complex-forming metal.

The observed correspondence between the acidity of ammine complexes and the values of the frequency δ_s also makes it possible to use spectroscopic data for an approximate estimate of the magnitudes of compounds with low acidity that is difficult to measure. Such estimates may be made with the aid of the empirical equation

$$pK_a = 7 + 2 \cdot 10^{-3}(1385 - \delta_s)^2,$$

which describes the data of Table 1 with an accuracy of $±$1.2 pK_a units. Application of this equation to the hexammine of trivalent cobalt, in whose spectrum $\delta_s = 1325$ cm^{-1} (^{7}), gives $pK_a = 14.2$, which corresponds to a range of possible pK_a values from 13.0 to 15.4. This spectroscopic estimate agrees with the conclusions ($pK_a \gtrsim 12$) drawn earlier on the basis of potentiometric data (^{2}) and investigations of deuterium exchange (^{9}). For $[Pt(NH_3)_3Cl_3]Cl$ the equation gives $pK_a = 14.4 \pm 1.2$.

A more thorough analysis of the relationships connecting the acidic properties of complexes with the vibrational frequencies of coordinated ammonia requires taking into account a number of additional factors (statistical and electrostatic factors, the direct interaction of NH_3 molecules situated in cis positions relative to one another, the effect of the crystal field, etc.), which are capable of substantially affecting the acidic properties of the compounds. The vibrational frequencies of coordinated ammonia change noticeably depending on the nature of the outer-sphere anions with which they form hydrogen bonds of different strength. One may hope that comparison of the spectra of salts with identical anions will make it possible, to some extent, to weaken the influence of this effect.

Choosing, as a spectroscopic characteristic of coordinated NH_3 molecules, the value of the frequency of the symmetric deformation vibrations

vibrations, the authors were guided by the following considerations. As all the data available in the literature show (for bibliography see ^{10,11}), there is a sharp difference in the behavior of the absorption bands corresponding to the symmetric (δ_s) and pronounced antisymmetric (δ_a) vibrations of NH_3. Whereas the frequency δ_s increases strongly and regularly with increasing electron-acceptor properties of the central atom, the frequency δ_a changes only slightly and irregularly. In ^{5} this difference is explained by the fact that the expression for δ_s

includes the force constant of the deformation vibrations MNH, which changes substantially depending on the nature of the central atom M. It may also be said that the different sensitivity of the frequencies δ_s and δ_a to the nature of the central atom is explained by the different degree of participation of the unshared electron pair of the nitrogen atom in deformation vibrations of different classes. In the process of symmetric vibrations the valence angles HNH change in phase. The concomitant unidirectional changes in the character of hybridization of all three NH bonds are impossible without corresponding oppositely directed periodic changes in the character of the orbital occupied by the unshared pair. Formation of the metal—nitrogen coordination bond fixes the state of the unshared pair the more rigidly, the stronger this bond is. An increase in the force opposing periodic changes in the state of the unshared pair means an increase in the force constant corresponding to symmetric deformation vibrations and consequently leads to an increase in the frequency δ_s. Antisymmetric vibrations, in which changes in the hybridization character of individual NH bonds are to a considerable extent mutually compensated, proceed without substantial changes in the state of the unshared pair, and the frequency δ_a proves to be almost indifferent to the strength of the metal—nitrogen bond. The values of δ_a in the spectra of ammine complexes lie in the interval 1530-1640 cm^{-1} (for free ammonia 1628 cm^{-1}); the values of δ_s in the spectra of complexes vary from 1100 to 1400 cm^{-1} (for free ammonia 950 cm^{-1}).

Thus, the deviation of the frequency of the symmetric deformation vibrations from the value $\delta_s = 950$ cm^{-1}, characteristic of the free NH_3 molecule, may be regarded as a measure of the degree of binding of the unshared pair of the nitrogen atom. To characterize the degree of binding one may introduce the dimensionless parameter $\varepsilon = \dfrac{\delta_s - 950}{1385 - 950}$, where 1385 cm^{-1} is the value of δ_s for hexammine Pt (IV), the highest of the presently known values of δ_s. The empirical scale thus constructed covers values of ε from 0.36 ($[Na(NH_3)_4]J$; $\delta_s =$ 1105 cm^{-1} [12]) to 1.00 ($[Pt(NH_3)_6]Cl_4$). Figure 1 presents the dependence of the binding parameter ε on the total ($I_{1,2} = I_1 + I_2$) ionization energy for divalent metals. The parallelism between ε and $I_{1,2}$ confirms the reality of the parameter ε (or the frequency δ_s) as a characteristic of the metal—nitrogen bond. We also point out the linear dependence, noted in the literature [13], between δ_s^2 and the "electronegativity" of the central atom.

Received
1 VIII 1964

REFERENCES CITED

[1] A. A. Grinberg, Kh. I. Gildengershel, Izv. AN SSSR, OKhN, 1948, 479.
[2] A. A. Grinberg, L. V. Vrublevskaya et al., ZhNKh, 4, 1018 (1959).
[3] S. K. Jørgensen, Acta chem. scand., 10, 500 (1956).
[4] H. Poulet, J.-P. Mathieu, C. R., 255, 1514 (1962).
[5] G. F. Svatos, C. M. Sweeny et al., J. Am. Chem. Soc., 79, 3313 (1957).

[6] D. B. Powell, N. Sheppard, J. Chem. Soc., 1956, 3108.
[7] E. P. Bertin, I. Nakagawa et al., J. Am. Chem. Soc., 80, 525 (1958).
[8] I. I. Chernyaev, V. S. Orlova, ZhNKh, 6, 1272 (1961).
[9] J. S. Anderson, N. L. Spoor, H. V. A. Briscoi, Nature, 139, 508 (1937).
[10] F. Cotton, G. Wilkinson, *Modern Inorganic Chemistry*, Moscow, 1963, p. 334.
[11] A. V. Babaeva, O. N. Evstaf’ eva, ZhNKh, 6, 61 (1961).
[12] G. W. Leonard, F. R. Lippincott et al., J. Am. Chem. Soc., 77, 2029 (1955).
[13] J. K. Wilshurst, Canad. J. Chem., 38, 467 (1960).