Chemistry

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1965

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Abstract

Full Text

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COORDINATION SENSITIVITY OF THE FREQUENCY OF THE WAGGING VIBRATIONS OF THE AMINO GROUP IN THE SPECTRA OF CYCLIC ETHYLENEDIAMINE COMPLEXES

In a previous paper ([1]) it was suggested that the high coordination sensitivity of the frequency of the symmetric deformation vibrations $\delta(A_1)$ of the ammonia molecule is explained by the participation in these vibrations of the unshared electron pair of the nitrogen atom. The fact of a periodic change in the state of the unshared pair in the course of vibrations of this type was noted in the literature ([2]) in connection with the question of the magnitude of the atomic dipole in the NH_3 molecule.

Fig. 1. Change in the state of the unshared electron pair of the nitrogen atom in the process of wagging vibrations of the amino group

During the vibrations $\delta(A_1)$, the pyramidal NH_3 molecule periodically flattens, approaching the state shown in Fig. 1a. In this limiting state the unshared pair must be completely displaced into the $2p$ orbital. As was noted in the preceding communication ([1]), formation of the metal–nitrogen coordination bond fixes the sp^3 state of the unshared pair and thereby leads to an increase in the force constant corresponding to the symmetric deformation vibrations of NH_3. In molecules of primary aliphatic amines, the wagging vibrations of the amino group (ω_{NH2}) must evidently possess analogous properties. The limiting state periodically approached by the amino group in the course of these vibrations is shown in Fig. 1b, borrowed from ([3]). In this case, formation of a coordination bond likewise fixes the tetrahedral hybridization of the electronic orbitals of the nitrogen atom, increasing the resistance of the CNH_2 group to periodic flattening. The increase in ω_{NH2} as a result of coordination can serve as a measure of the degree of bonding of the unshared pair of the nitrogen atom. In the spectra of ammine compounds, an analogous role is played ([1]) by the increase in the frequency $\delta(A_1)$. The data obtained by Powell and Sheppard ([4–6]) in a

systematic and detailed study of the infrared spectra of cyclic ethylenediamine complexes confirm the prediction, following from these considerations, of a high coordination sensitivity of the frequency of wagging vibrations of the amino group. A comparison of the spectra of the compounds $[MEn_2][PtCl_4]$, where M = Cu, Pd, Pt ([6]), shows that one of the frequencies assigned to ω_{NH2} changes along the series Cu–Pd–Pt most strongly and regularly (1166, 1189, and 1219 cm^{-1}, respectively).

It may be expected that, on passing to ethylenediamine compounds with stronger complex-forming agents (tetravalent platinum, trivalent gold), the frequencies ω_{NH2} will prove to be higher than in the spectra of compounds of other metals with an analogous arrangement of the ethylenediamine rings. The frequencies of scissoring and twisting deformation vibrations should change within narrower limits. Table 1 gives the frequencies measured by us for the wagging vibrations of the amino group in the spec-

of a number of complexes of square-planar and trans-octahedral structure. For comparison, Table 1 also includes data [6] for copper and palladium compounds. For Pt(II) complexes in Table 1 we used our data, which are in good agreement with the results of Powell and Sheppard. As follows from the data presented, the value of ω_{NH_2} in the spectra of palladium, platinum, and gold derivatives depends substantially on the nature of the outer-sphere anion. In most of the cases investigated, replacement of Cl^- ions by $[PtCl_4]^{2-}$ ions

Table 1

Wavenumbers of the maxima of absorption bands corresponding to wagging (ω) and twisting-deformation (τ) vibrations of amino groups

Cation	Coordination-sensitive band ω_{NH_2}	Coordination-sensitive band ω_{NH_2}	Other bands ω_{NH_2} and τ_{NH_2}	Other bands ω_{NH_2} and τ_{NH_2}	Other bands ω_{NH_2} and τ_{NH_2}
	Cl^-	$[PtCl_4]^{2-}$	$[PtCl_4]^{2-}$	$[PtCl_4]^{2-}$	$[PtCl_4]^{2-}$
$[CuEn_2]^{2+}$	–	1166	1321	1111	1017
$[PdEn_2]^{2+}$	1139	1189	1287	11271109	1006
trans-$[CoEn_2Cl_2]^+$	1211	1208	1312	1110	1008984
trans-$[RhEn_2Cl_2]^+$	–	1207	1310	1118	1005990
$[PtEn_2]^{2+}$	1164	1217	1292	1140	?
$[AuEn_2]^{3+}$	1185	1235	1294	11641150	990987
trans-$[PtEn_2Cl_2]^{2+}$	1190	1244	1299	11611127	991

leads to an increase in ω_{NH_2} by ~ 50 cm^{-1}. The cobalt and rhodium compounds behave differently in this respect. In the spectra of the nitrate, chloride, and

chloroplatinate of trans-$[CoEn_2Cl_2]^+$, the values of ω_{NH_2} are, respectively, 1211; 1211; and 1208 cm^{-1}. In the spectra of analogous rhodium compounds, the values of ω_{NH_2} are 1207 (chloroplatinate) and 1211 cm^{-1} (nitrate). A similar observation concerning $[CuEn_2]^{2+}$ and $[NiEn_3]^{2+}$ is contained in [6]. The influence of the nature of the anion apparently indicates the sensitivity of the frequency of the wagging vibrations of the amino group to the formation of hydrogen bonds N—H $\cdots$ anion. Therefore, in agreement with [6], for characterizing the dependence of ω_{NH_2} on factors acting within the complex cation, the data for chloroplatinates are preferable. The data of Table 1 show that in the spectra of chloroplatinates the frequency ω_{NH_2} changes in the sequence

$$[Cu(II)]^{2+} < [Pd(II)]^{2+} < [Co(III)]^{+} \simeq [Rh(III)]^{+} <$$

$$< [Pt(II)]^{2+} < [Au(III)]^{3+} < [Pt(IV)]^{2+}.$$

This sequence may be regarded as a series of increasing degree of bonding of the unshared pair of electrons of the nitrogen atom. Movement along this series from left to right corresponds to an enhancement of the electron-acceptor properties of the central atom in the given valence state and at the given magnitude of the total charge of the complex ion. The other three frequencies, assigned [6] to wagging and twisting vibrations of the NH_2 groups, change in the series considered much more weakly and not so regularly. Powell and Sheppard [6] point to the known uncertainty in the detailed

assignment of four frequencies, the values of which are given in the table. The material of the present work opens up the possibility of using the greatest coordination sensitivity as a feature making it possible to identify, in the range 950–1350 cm^{-1}, an absorption band which can with a considerable degree of confidence be assigned to the rocking vibrations of the amino group.

It is known ([7,8,1]) that accumulation of ammonia molecules in the inner coordination sphere of ammine complexes entails an increase in the frequency of the symmetric deformation vibrations of NH_3. This effect should evidently be associated with an enhancement of the electron-acceptor ability of the central atom as a result of an increase in the overall positive charge of the complex ion. An analogous increase in the frequency of the rocking vibrations of NH_2, as may be judged from the data of ([6]), occurs, for example, on going from $[PdEnCl_2]$ to $[PdEn_2][PtCl_4]$ and from $[PtEnCl_2]$ to $[PtEn_2] \cdot [PtCl_4]$. The data obtained by us make it possible to carry out a similar comparison also for the case of tetravalent platinum. In the spectra of $[PtEnCl_4]^0$ and trans-$[PtEn_2Cl_2][PtCl_4]$, ω_{NH2} = 1213 and 1244 cm^{-1}, respectively. The difference between the values of ω_{NH2} in the spectra of uncharged complexes and dicationic complexes is 31 cm^{-1} in the case of Pt(IV), and 27 and 24 cm^{-1} in the cases of Pt(II) and Pd(II).

Thus, with respect to sensitivity to the nature of the central atom, to its valence, and to the charge of the complex as a whole, the rocking vibrations of the amino group of ethylenediamine are similar to the symmetric deformation vibrations of the ammonia molecule. The values of ω_{NH2} can be used as a characteristic of the effects exerted on the amino group by the central atom. In work ([1]) a certain (rather rough) correspondence was established between the frequencies $\delta(A_1)NH_3$ and the acid properties of amminates. The insufficient amount of data on the acid properties of ethylenediamine complexes does not allow a similar comparison to be made for the frequency ω_{NH2}. The data of Table 1 nevertheless show that measurable acidity is possessed precisely by those complexes which are characterized by the largest values of ω_{NH2}, i.e., derivatives of Au(III) and Pt(IV). It is known ([9,10]) that $[AuEn_2]^{3+}$ has stronger acid properties than trans-$[PtEn_2Cl_2]^{2+}$, whereas on the basis of the values of ω_{NH2} the opposite relationship would seemingly be expected. In reality, however, it cannot be disregarded that the higher positive charge of the ion $[AuEn_2]^{3+}$ causes an enhancement of the acid dissociation of the coordinated amino groups not only by virtue of their greater polarization by the central atom (this effect, as indicated above, is "taken into account" by the value of ω_{NH2}), but also through the general increase in proton mobility. It may therefore be expected that the difference in the frequencies of the N-H stretching vibrations will prove more consistent with the direction of change in acid properties on going from $[PtEn_2Cl_2]^{2+}$ to $[AuEn_2]^{3+}$.

The data of the present work give grounds for supposing that bis(ethylenediamine) complexes with conditionally coplanar rings may exhibit a noticeable tendency toward proton elimination in aqueous solution only under the condition $\omega_{NH2} \gtrsim 1230$ cm^{-1} (in the spectra of platinates). A similar limiting condition for chlorides of ammine complexes ([1]) is: $\delta(A_1) \gtrsim 1320$ cm^{-1}.

In conclusion we note that the existence, discovered by Powell and Sheppard in 1959 ([4]), of two types (A and B) of spectra of coordinated ethylenediamine can evidently be explained by changes in the position of the ω_{NH2} band. In the spectra of compounds of relatively weak complex formers (Ni^{2+}, Cu^{2+}) this band lies in the region 1000-1170 cm^{-1} (spectra of chloroplatinates of type B). On going to Co^{3+}, Rh^{3+}, Au^{3+}, and Pt^{4+}, it is progressively shifted and reaches values close to 1250 cm^{-1} (spectra of chloroplatinates of type A). There is no sharp boundary between spectra of types A and B, as Powell and

Sheppard in one of his later papers ([5]). At the same time, the approximate correlation noted by these authors between the type of spectrum and the thermodynamic stability of ethylenediamine complexes becomes understandable.

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Received
18 II 1965

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Note: Figure translations are in progress. See original paper for figures.