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The Vibrational Spectra of the Zn-Acrylonitrile Complex

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In a previous paper,[1] the present authors reported on the infrared spectra of zinc-halide complexes with acetonitrile; these complexes form σ-bonds between the Zn atom and the N atoms of the nitrile groups. In the present study the infrared spectrum of the zinc chloride-acrylonitrile complex has been investigated; it was also expected to be a σ-complex.

Experimental

The sample of $[ZnCl_2 \cdot CH_2CHCN]_n$ was prepared from $ZnCl_2$ and acrylonitrile by the method described in the previous paper.[1]

The infrared spectra, ranging from 4000 to 96 cm^{-1}, were measured by the mull method on a JASCO IR-G infrared spectrophotometer in the near-infrared region, and on a Hitachi FIS-21 infrared spectrophotometer in the far-infrared region.

Assignment and Normal Coordinate Analysis

A complete assignment for the in-plane vibrational modes of acrylonitrile has been made by Halverson *et al.*[2] and has been supported by Fritz and Schrauzer[3] and also by Devlin *et al.*[4] In the present study, the assignment of bands for the ligand was made by correlation with the spectra for the free acrylonitrile, while that for the skeleton about the Zn atom was made by referring to the spectra of analogous complexes.[1,5]

In order to see the strength of the coordination bond, normal coordinate analyses were carried out in two steps using the simple Urey-Bradley force fields. In the first step (Calculation 1), only the intra-ligand vibrations for the $CH_2 \cdot CH \cdot CN \cdot Zn$ system were treated by assuming them to be separable from the skeletal vibrations about the central Zn atom. The molecular geometry of gaseous acrylonitrile[6] was assumed to be maintained in the complexed ligand. All the force constants associated with the ligand vibrations except for the C≡N stretching, $\nu_{C\equiv N}$, were transferred from those which had been determined by the present authors by applying the overlay technique[4,7] to the observed frequencies for both acrylonitrile and fumaronitrile in the free states. In the second step (Calculation 2), the complex was assumed to be a Cl-bridged dimer of C_{2h} symmetry, in which the two-fold axis was the line connecting the two bridging chlorine atoms and in which the two linear R–C≡N–Zn (R: H_2C=CH) frames are located at *trans* positions on the horizontal plane. The bond distances and angles about the Zn atoms were assumed to be as follows: Zn–Cl=2.30 Å, Zn–N=2.00 Å, and all the valence angles were 109.5°. The force constants, K_{R-C}, $K_{C\equiv N}$, K_{Zn-N}, and $H_{Cl^bZnCl^b}$, were then determined so as to reproduce the observed frequencies by transferring the other force constants from those obtained for the acetonitrile complexes.[1] The observed and calculated frequencies and their assignments are shown in Table 1, while the force constants are shown in Table 2.

Results and Discussion

For comparison, the observed frequencies for the free ligand are reproduced in Table 1. Tables 1 and 2 indicate that the coordination has an appreciable effect only on the $\nu_{C\equiv N}$, and that the slight increase in the $K_{C\equiv N}$ value satisfactorily explains the observed frequencies for the acrylonitrile moiety. Such an effect of coordination has also been observed in the Zn-aceto-

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Table 1. The observed and calculated frequencies and their assignments for acrylonitrile and the $ZnCl_2$–acrylonitrile complex (in cm^{-1})

Acrylonitrile		$ZnCl_2$–Acrylonitrile			Assignment[d]
Obsd[a]	Calcd	Obsd	Calcd 1.[b]	Calcd 2.[c]	
3120	3120	3125	3118		$a\nu_{CH_2}$
3070	3065	3083	3067		ν_{CH}
3030	3031	3048	3031		$s\nu_{CH_2}$
2239	2237	2283	2282	2282	$\nu_{C\equiv N}$
1609	1603	1610	1605		$\nu_{C=C}$
1414	1419	1416	1428		δ_{CH_2}
1292	1277	1284	1281		ρ_{CH}
1098	1101	1095	1110		ρ_{CH_2}
875	881	895	894	890	ν_{C-C}
575	596	581	602		$\delta_{C=CC}$
236	247	348	274	310	$\delta_{C-CN}+\nu_{Zn-Cl^t}$
				305	$\nu_{Zn-Cl^t}+\delta_{C-C\equiv N}$
		328		339	ν_{Zn-Cl^b}
		280		263	$\nu_{Zn\cdot Cl^b}$
		153	151	155	ν_{Zn-N}
		110		97	ρ_{Zn-Cl^t}
				92	ν_{Zn-Cl^t}
				88	ρ_{Zn-L}
				76	γ_{Zn-Cl^t}
				29	$\delta_{Zn-NC}^{i.p.}$
				16	$\delta_{Zn-NC}^{o.p.}$

a) Frequencies observed by the present authors; see also Ref. 2.
b) Calculated for the ligand; see text.
c) Calculated for the normal modes of A_u and B_u species of the skeleton; see text.
d) Cl^t, terminal Cl; Cl^b, bridging Cl; i.p., in plane; o.p., out of plane.

Table 2. Urey-Bradley force constants for the $ZnCl_2$–acrylonitrile complex (in mdyn/Å)[a]

Ligand (Calc. 1)					
$K_{C=C}$	(7.02)	$H_{C=CH_2}$	(0.22)	$F_{C=CH_2}$	(0.60)
$K_{C\equiv N}$[b]	17.58	$H_{C=CH}$	(0.15)	$F_{C=CH}$	(0.77)
K_{C-C}	(4.99)	H_{H-CH}	(0.31)	F_{H-CH}	(0.041)
K_{CH_2}	(4.78)	H_{C-CH}	(0.14)	F_{C-CH}	(0.37)
K_{CH}	(4.46)	$H_{C=CC}$	(0.31)	$F_{C=CC}$	(0.91)
K_{ZnN}	0.40	H_{C-CN}	(0.17)	F_{C-CN}	(0.0)
		H_{C-NZn}	(0.025)	F_{C-NZn}	(0.0)
Skeleton (Calc. 2)					
$K_{C\equiv N}$	17.32	H_{NZnCl^t}	(0.013)	$F_{N.Cl^t}$	(0.016)
K_{R-C}	6.84[c]	$H_{Cl^bZnCl^b}$	0.035	$F_{Cl^bCl^b}$	(0.075)
K_{Zn-N}	0.40	$H_{Cl^bZnCl^t}$	(0.075)	$F_{Cl^bCl^t}$	(0.075)
K_{Zn-Cl}	(1.10)	H_{ZnClZn}	((0.025))	$F_{Zn.Zn}$	((0.025))
		H_{CNZn}	(0.025)	$F_{C.Zn}$	(0.0)
		H_{RCN}	(0.12)	$F_{R.N}$	(0.0)

a) Values in parentheses were transferred; see text. Values in double parentheses were assumed.
b) The $K_{C\equiv N}$ for the free ligand, 16.70 mdyn/Å.
c) An effective value obtained by treating the olefinic group as a single mass point.

nitrile complexes; it may be considered to be characteristic of σ-coordination. In Calculation 2, the olefinic group was treated as a single mass point. This treatment produces only an insignificant change in the $K_{C\equiv N}$ value and no change in the K_{Zn-N} value, as compared with the results of Calculation 1. The K_{Zn-N} value was thus determined to be 0.40 mdyn/Å in both calculations, 1 and 2. This value is of the same order of magnitude as that in the Zn-acetonitrile complex, 0.65 mdyn/Å. This suggests that the Zn atom coordinates to the N atom of the nitrile group with a similar bond strength to that of the coordination bonds in the Zn-acetonitrile complexes.[1)]

As the geometry of the present complex has not yet been known, we assumed a bridged structure so as to account for the results of the chemical analysis. Then, the three bands observed at 348, 328, and 280 cm^{-1} were assigned to the three Zn–Cl stretching vibrations; the highest frequency band at 348 cm^{-1} may be due to the Zn-terminal Cl stretching, ν_{Zn-Cl^t}, while the broad band observed at 328 cm^{-1} is probably composed of two bands, one of which originates from the $\nu_{\mathrm{Zn-Cl}^t}$ and the CCN deformation. Since a Zn atom forms usually a tetrahedral coordination, and since the observed spectra could be interpreted on the basis of a Cl-bridged structure, the assumed structure for this complex seems most probable. In the present normal coordinate calculation, no particular attention was paid to the Zn–Cl stretching vibrations, all the Zn–Cl bonds being assumed to have the same force constant. If different Zn–Cl force constants are used for the terminal- and bridging-Cl atoms, the agreement between the observed and calculated frequencies will be improved. However, no further refinement was made.