Infrared Spectra of 1:10 Phenanthroline and its Addition Compounds with Antimony Trichloride and Antimony Pentachloride

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1:1 addition compounds of 1:10 phenanthroline with $SbCl_3$ and $SbCl_5$ have been prepared. Infrared spectra of the base and its adducts have been recorded and discussed.

Addition compounds of 1:10 phenanthroline are not reported earlier although it is known to posses electron donating properties. The present work reports the preparation and infrared spectra of the adducts of 1:10 phenanthroline with $SbCl_3$ and $SbCl_5$. The IR spectra were recorded in the medium infrared region (4000 to 650 cm^{-1}) with a view to understand the changes in the vibrational spectrum that the 1:10 phenanthroline molecule undergoes on co-ordination. The adducts were prepared by mixing accurately weighed amounts in 1:1 ratio of the base and antimony halide dissolved in dried distilled benzene. 1:10 phenanthroline was a GR grade E. Merck product. Antimony pentachloride was a Riedel product. Antimony trichloride was a LR grade BDH product. All the operations were carried out under vacuum and anhydrous conditions. Analytical data are listed in Table 1.

		Percentage		
Adduct		Theoretical	Found	Colour
1. $C_{12}H_8N_2 \cdot SbCl_3$	C	35.28	35.12	Yellow
	H	1.960	1.89	
	N	6.844	6.78	
	Sb	29.81	29.44	
	Cl	26.09	25.77	
2. $C_{12}H_8N_2 \cdot SbCl_5$	C	30.05	29.69	Yellow
	H	1.669	1.62	
	N	5.830	5.81	
	Sb	25.27	25.02	
	Cl	37.04	36.73	

Table 1. Analytical data.

IR spectra of the base and adducts were recorded in a KBr disc in the region $4000-650\ cm^{-1}$ using a model 221, double beam Perkin-Elmer Infrared Spectrophotometer, equipped with sodium chloride optics.

	Frequency in cm^{-1}		
	$C_{12}H_8N_2$	$C_{12}H_8N_2SbCl_3$	$C_{12}H_8N_2SbCl_5$
	3399 vs	3448 s	3571 s
	—	—	3333 vw
	—	—	3175 w
	3077 m	3077 s	3077 s
	— +	—	2857 w
	1639 w	—	1681 w, sh
	1613 w +	—	—
ν_{8a}	1578 s	1600 s +	1626 s +
ν_{8b}	1562 m	1575 vs	1575 m
ν_{19a}	1504 s	1512 s	1512 vw
ν_{19b}	1449 w	1449 w	1460 w
ν_{14}	1418 vs	1418 vs	1418 m
	—	—	1379 m
	1342 w	1342 w	1342 vvw
	1290 vw	1290 vw	1316 w
	1212 w	1212 vw	1250 w
			1227 w
	1136 m	1136 w	1156 w
	1087 w	1099 w	—
	1036 w	1042 w	1036 w
	990 m	990 w	1000 vvw
	885 vw	885 w	—
	870 vw	870 vw	—
	855 vs	855 vs	843 vs
	775 w	806 w	816 w
	763 vw	—	771 s
	735 vs	735 vs	—
		714 vs	
	704 w	699 m	694 m

+ = doublet; s = strong; vs = very strong; m = medium; w = weak; vw = very weak.

Table 2. Infrared spectra — vibrational frequencies of 1:10 phenanthroline and its adducts with $SbCl_3$ and $SbCl_5$.

Important bands of 1:10 phenanthroline and its adducts are listed in Table 2. No systematic discussion of the vibrational spectrum of 1:10 phenanthroline is available in the literature. There appears to be a general lack of assignments for 1:10 phenanthroline bands. Schilt and Taylor[1] have reported the IR spectrum of the base and have given assignments for a few bands. They based their argument on the suggestion of Bellamy[2] and Jones[3] that the generalisations based on the studies of benzene derivatives may be carried quite successfully to polycyclic molecules and that the introduction of a heteroatom into a ring usually results in only minor changes in the characteristic skeletal frequency of that hydrocarbon. It might be further possible to correlate 1:10 phenanthroline bands with those

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of pyridine for which complete and unambiguous assignments are available[4–10]. Both possibilities taken together lead to the following discussion. In the spectrum of 1:10 phenanthroline strong bands are observed in two frequency regions, namely from 700 to 900 cm^{-1} and from 1400 to 1650 cm^{-1}. The strong bands at 735 cm^{-1} and 855 cm^{-1} have been assigned by SCHILT and TAYLOR[1] (observed by them at 725 cm^{-1} and 850 cm^{-1}) to the out of the plane motion of the hydrogen atoms on the heterocyclic rings, and to the hydrogen on the centre ring respectively. The band at 735 cm^{-1} resembles the ν_{11} mode of the pyridine molecule (703 cm^{-1} out of plane C – H deformation). This band shows a splitting in the $SbCl_3$ adduct appearing as strong band at 735 and 714 cm^{-1}. The band appears at 714 cm^{-1} in the $SbCl_5$ adduct. There is a decrease in frequency on co-ordination. The 855 cm^{-1} band is not affected on coordination. This is quite expected as the primary effect of co-ordination is on the nitrogen atom, and the centre ring has no nitrogen atom to provide any donor site. Multiple weak bands observed in the region 735 to 870 cm^{-1} seem to arise from an out-of-plane hydrogen motion other than the one in which all atoms move in phase and also possibly from overtones of a low lying fundamental in resonance[1]. These bands don't exhibit any systematic variation in frequency in the adducts. A medium intensity 1:10 phenanthroline band at 990 cm^{-1}, which seems to correspond to the ν_1 vibration of the pyridine molecule (Class A_1, totally symmetric in plane ring breathing frequency) on co-ordination moves to 1000 cm^{-1} in the $SbCl_5$ adduct and is considerably reduced in intensity. The band is not affected in the $SbCl_3$ adduct. The bands in the region 1125 – 1250 cm^{-1} have been assigned by Schilt and Taylor to in-plane hydrogen deformation motions or possibly ring vibrations. All of these bands on co-ordination move to higher frequencies. Most intense and characteristic bands in the vibrational spectrum of 1:10 phenanthroline appear in the region 1400 to 1600 cm^{-1}. An almost parallel behaviour is noticed for the pyridine and 1:10 phenanthroline bands in this region of the spectrum. All of these bands involve C – C and C – N stretching vibrations. A very strong band at 1418 cm^{-1} resembles the ν_{14} mode of the pyridine molecule (Class B_1, in plane, antisymmetric ring deformation involving C – C and C – N stretching mode). Four other bands can be assigned to C – C and C – N vibrations, two of which give rise to symmetric and two anti-symmetric in plane ring deformation frequencies. The bands at 1449, 1504, 1562 and 1578 cm^{-1} closely resemble the ν_{19b} (in plane, antisymmetric, Class B_1), the ν_{19a} (totally symmetric ring stretching mode, class A_1), the ν_{8b} (in plane anti-symmetric ring vibration Class B_1) and the ν_{8a} (totally symmetric ring stretching mode, Class A_1) modes of pyridine molecules. All of these bands on co-ordination move to higher frequencies. The least sensitive of these vibrations appears to be one at 1418 cm^{-1}, which is not affected at all. Other vibrations increase in frequency by 8 to 54 cm^{-1}. Any discussion of the region beyond 1600 cm^{-1} is not profitable because of poor resolution. Some generalisations immediately follow from the above discussion. The in-plane vibrations are found to increase on co-ordination, whereas out of plane vibrations decrease. The largest shift in frequency is found with the vibrations involving C – C and C – N stretching modes. This is quite expected as the co-ordination takes place at nitrogen and the effect is transmitted throughout the region resulting into the readjustment of a electron density. If the magnitude of the frequency shift on co-ordination is any indication of acceptor strength, it can be concluded that $SbCl_5$ is a stronger acceptor than $SbCl_3$.