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Spectroscopic, Structural and Photochemical Properties of Cu(I) Halide Adducts with *cis*- and *trans*-Crotonitrile.

Part I. Syntheses and Vibrational Spectra

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CtN·CuX complexes of cis- *and* trans-*crotonitrile (CtN) with copper(I) halides (X = Cl, Br, and I with* trans-*CtN) have been prepared. Their IR and Raman spectra were recorded between 4000 and 40 (IR) or ≃15 (Raman) cm^{-1}, then analyzed. Comparison of their spectra with those of the free ligands led to some modifications in the assignments generally admitted for the latter. The data relative to Cu(I) complexes show that the metal is bound to the nitrile through the nitrogen atom, that this coordination is accompanied by a strengthening of the C≡N bond and a slight weakening of the C=C bond, and that a significant π back-bonding from copper to nitrogen may exist. Moreover evidence is given for a* cis–trans *crotonitrile isomerization in the presence of Cu(I) halides.*

Introduction

Metallic salt complexes with nitriles play a prominent part in chemistry, due particularly to the fact that they often appear as intermediate compounds in reactions involving nitriles [1–3]. In order to understand the behaviour of metallic salts in such reactions, it is necessary to know the ordering of the ligands around the metal atom as well as the nature of the bonds which are formed, and to dispose of information about the electron transfer induced by coordination in the organic molecule.

With this object, we have undertaken an investigation of copper(I) halide adducts with various nitriles by radiocrystallography [4–7] and vibrational spectroscopy. The complexes which were examined were of the type: nitrile·n CuX, with n = 1 or 2. To our knowledge, only one brief report was previously devoted to such compounds, concerning the benzonitrile derivatives $C_6H_5CN·CuCl$ and $C_6H_5CN·CuBr$ [8].

Part I of the present work deals with the syntheses and the infrared and Raman study of *cis*- and *trans*-CtN·CuX complexes (CtN = crotonitrile $H(CH_3)C=CHCN$; X = Cl, Br, and I with *trans*-CtN). The results which were obtained show that crotonitrile undergoes a *cis–trans* isomerization in the presence of CuX. This feature was corroborated by an X-ray structural investigation and has been the starting point of a photochemical study of the complexes, which are both reported in Part II.

Experimental

Syntheses

The complexes were prepared by dissolving fresh-purified copper(I) halides in recently distilled crotonitrile, under an inert atmosphere, and then evaporating excess nitrile with an argon stream.

CuCl (Merck) and CuBr (Riedel de Häen) were purified according to a procedure very close to the one described in [9]: under an argon atmosphere, a mull of CuX in 1 N H_2SO_4 was stirred with a saturated sulfur dioxide aqueous solution and the powder thus obtained was washed several times with glacial acetic acid, then dried with anhydrous ethanol and ether. CuI (Riedel de Häen) has been used without any previous treatment.

The crotonitrile (Fluka) isomers were separated by fractional distillation through a Cadiot spinning-band column. The pure *cis*-isomer was obtained at

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[*] With the technical assistance of F. Voyron and H. Le Pesant.

115 °C. To isolate the pure *trans*-isomer (B_p = 122 °C), successive distillations were performed till the IR band at 727 cm^{-1} due to the *cis*-form had entirely disappeared from the distilled fraction spectrum.

The complexes are very sensitive to oxygen and water vapour and lost their nitrile very easily. They were collected as colourless crystals before the nitrile solution was completely evaporated, and were subsequently kept and handled under dry argon saturated with the nitrile vapour.

It should be noted that the *trans*-CtN•CuX complexes could be prepared with a good yield in spite of the very poor solubility of Cu(I) halides in *trans*-CtN. This result has been obtained after we have noticed that crystals which were isolated from CtN solutions containing both isomers in the same proportion as in the commercial nitrile (solutions in which Cu(I) halides dissolves easily) were pure *trans*-CtN•CuX complexes.

The following compounds have been prepared: *cis*-CtN•CuCl, *cis*-CtN•CuBr, *trans*-CtN•CuCl, *trans*-CtN•CuBr and *trans*-CtN•CuI. Their chemical analysis have been carried out. As an example, for *trans*-CtN•CuBr: calculated %C = 22.81, N = 6.66, H = 2.38, Br = 37.98, Cu = 30.17; found %C = 22.5, N = 6.5, H = 2.1, Br = 38.4, Cu = 30.5. For all the compounds, the thermograms indicate a 1:1 ligand to CuX ratio.

Infrared and Raman Measurements

The IR spectra were recorded with a Perkin-Elmer Model 325 spectrometer from 4000 to 200 cm^{-1} and with a Beckman RIIC FS 720 Fourier transform interferometer from 200 to 40 cm^{-1}. Samples were prepared in a glove-box, as nujol or fluorolube mulls.

The Raman spectra were obtained on a Jobin-Yvon Model Ramanor HG 2S spectrometer equipped with two holographic concave gratings. The excitation lines (514.5 and 488 nm) were provided by a Spectra-Physics Model 164 argon ion laser. Very weak powers (40 to 60 mW) were used for these lines to prevent the damage of complexes. Samples were examined in sealed glass-tubes, under an argon atmosphere saturated with the nitrile vapour.

Results and Discussion

Ligand Vibrational Modes

In the spectra of the studied Cu(I) species, the ligand internal normal modes were mainly identified on the basis of the attribution proposed by Durig *et al.* [10] for both crotonitrile isomers. However, some assignments reported by these authors had to be modified according: first, to our experimental results concerning the *cis*- and *trans*-crotonitrile (which slightly differ from the previous ones by the better resolution of a few bands and by the values obtained for some Raman polarization ratios); secondly to the new data provided by the spectra of *cis*-CtN•CuX and *trans*-CtN•CuX complexes; thirdly, to our attribution of the acrylonitrile and methacrylonitrile spectra [11].

Both isomers of crotonitrile belong to the C_s point group. Their 24 fundamentals (16 A′ and 8 A″, corresponding to planar and out-of-plane motions respectively) are both IR and Raman active. The A′ modes give rise to polarized Raman lines and the A″ modes to depolarized ones. Their numbering has been choosen so as to facilitate the comparison with the acrylonitrile and methacrylonitrile vibrations.

Trans-CtN and Trans-*CtN•CuX Complexes*

The spectra of *trans*-CtN and *trans*-CtN•CuBr in the frequency range 4000–160 cm^{-1} are shown in Fig. 1 (those of *trans*-CtN•CuCl and *trans*-CtN•CuI resemble the latter very closely). The corresponding data and the proposed attributions are reported in Table I.

For the first time, both components of the CH_3 asymmetrical deformation (ν_{20} and ν_{21}) were observed in the IR as well as in the Raman spectrum of the nitrile. They could be clearly separated in the case of the complexes.

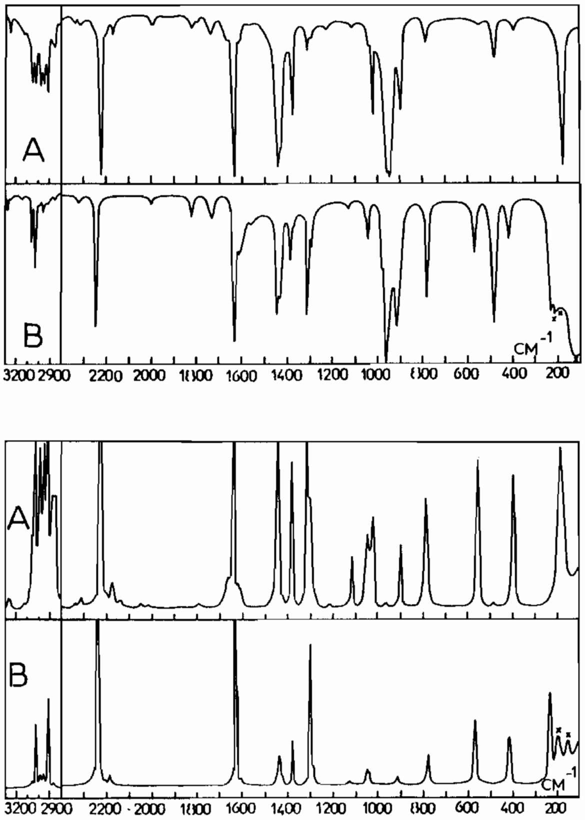

Fig. 1. Infrared spectra (upper part) and Raman spectra (lower part) of A: *trans*-crotonitrile and B: *trans*-crotonitrile•CuBr complex. 'x' marks indicate bands due to vibrations of the metal–ligand bonds.

TABLE I. Spectra of *trans*-Crotonitrile and *trans*-CtN·CuBr Nitrile Moiety.

trans-CtN		*trans*-CtN·CuBr		Attribution		*trans*-CtN		*trans*-CtN·CuBr		Attribution	
IR	Raman	IR	Raman			IR	Raman	IR	Raman		
3050 m	3053 ms, p	3053 m	3051 vw	ν_2	ν_aHC=CH	1290 w	1296 ms, p	1286 mw	1289 w	ν_6	δ_aHC=CH
3027 m	3033 vs, p	3026 ms	3025 m	ν_3	ν_sHC=CH	1112 w	1116 m, p	1122 w	1122 vw	ν_{22}	r′CH$_3$
2977 m	2983 s, p	2982 vw	2981 w	ν_{17}	ν'_aCH$_3$	1040 w	1044 m	1042 sh	1045 w	ν_{23}	r″CH$_3$
2950 m	2954 s, dp	2950 w	2949 w	ν_{18}	ν''_aCH$_3$	1023 s	1025 ms, p	1037 m	1040 w	ν_1	νC–CH$_3$
2918 ms	2922 vs, p	2916 vw	2915 ms	ν_{16}	ν_sCH$_3$	957 vs	962 vw, dp	951 vs		ν_9	$\gamma_{w(a)}$HC=CH
2223 vs	2227 vs, p	2238 s	2238 vs	ν_4	νC≡N	898 s	899 mw, p	907 s	911 w	ν_{11}	νC–CN
1637 vs	1638 vs, p	1624 vs	1628 vs	ν_5	νC=C	783 m	785 s, dp	774 s	777 mw	ν_{10}	$\gamma_{w(s)}$HC=CH
1443 vs	1444 s, p	1435 s	1437 mw	ν_{20}	δ'_aCH$_3$	555 vw	554 s, p	570 m	568 m	ν_{13}	δC=C–CN
1432 sh	1426 sh, dp	1426 m	1427 w	ν_{21}	δ''_aCH$_3$	482 m	483 vw, dp	488 s		ν_{12}	γ_tC=C
1378 s	1380 s, p	1379 m	1378 m	ν_{19}	δ_sCH$_3$	398 w	398 s, p	419 m	418 m	ν_7	δC=C–CH$_3$
1310 mw	1312 s, p	1300 s	1299 s	ν_8	δ_sHC=CH			284 vw		ν_{14}?	γC–C≡N
						184 vs	186 s, dp	230 s	232 ms	ν_{15}	δC–C≡N

Harmonic and combination frequencies (IR and Raman ( ) data):

trans-CtN-3080 sh (3082 w, p):$\nu_5 + \nu_{20}$; 2869 sh (2876 s, p):$2\nu_{20}$; (2864 ms, p):$\nu_{20} + \nu_{21}$; 2852 mw (2855 s, p): $2\nu_{21}$; 2814 vw (2818 vw, p):$\nu_{19} + \nu_{20}$; 2770 vw: $\nu_4 + \nu_{13}$; 2734 w (2738 m, p):$\nu_6 + \nu_{20}$; 2656 vw:$\nu_1 + \nu_5$; 2620 vw:$\nu_4 + \nu_7$ and $2\nu_8$; 2532 w (2533 w, p):$\nu_5 + \nu_{11}$; 2490 vw:$\nu_{19} + \nu_{22}$; 2402 w (2406 vw):$\nu_1 + \nu_{19}$; 2335 w (2338 vw):$\nu_{11} + \nu_{20}$; 2312 w (2310 w):$\nu_1 + \nu_6$:2200 sh (2200 sh):$\nu_8 + \nu_{11}$; 2170 w (2174 mw, p):$\nu_6 + \nu_{11}$; (2137 vw, p):$\nu_1 + \nu_{22}$; (2045 vw, p):$2\nu_1$; (2012 vw, p):$\nu_{11} + \nu_{22}$; 1998 w:$\nu_9 + \nu_{23}$; 1821 w:$\nu_{10} + \nu_{23}$; 1797 vw (1796 vw, p):$2\nu_{11}$; 1739 mw:$\nu_9 + \nu_{10}$; 1665 w (1665 mw, p):$\nu_{13} + \nu_{22}$; 1615 vw (1615 w, p):$\nu_{15} + \nu_{20}$; 1609 vw (1610 w):$\nu_{15} + \nu_{21}$; 1228 w:$\nu_5 - \nu_7$(?); (1213 vw, p):$\nu_1 + \nu_{15}$.

trans-CtN·CuBr-(2862 vw):$2\nu_{20}$; 2845 vw:$2\nu_{21}$; 2802 w:$\nu_{19} + \nu_{20}$; 2730 w:$\nu_8 + \nu_{20}$; 2530 w:$\nu_5 + \nu_{11}$; 2410 vw:$\nu_1 + \nu_{19}$; 2315 w:$\nu_1 + \nu_6$;(2209 vw):$\nu_8 + \nu_{11}$; (2184 w):$\nu_6 + \nu_{11}$; 1994 w:$\nu_9 + \nu_{23}$; 1816 mw:$\nu_{10} + \nu_{23}$; 1723 mw:$\nu_9 + \nu_{10}$; 1602 w (1603 vw):$\nu_{12} + \nu_{22}$; 1598 w:$\nu_1 + \nu_{13}$; 1550 vw:$2\nu_{10}$; 1369 sh:$\nu_7 + \nu_9$;977 sh:$\nu_7 + \nu_{13}$; 284 vw:$\nu_{10} - \nu_{12}$(?).
s: strong; m: medium; w: weak; v: very; sh: shoulder; p: polarized; dp: depolarized.
ν, δ, γ: stretching mode, planar deformation mode and out-of-plane deformation mode, respectively.
w: wagging; t: twisting; r: rocking; ′: planar component; ″: out-of-plane component; a and s (for HC=CH motions): asymmetrical and symmetrical with regard to the C=C bond center, respectively.

TABLE II. Spectra of *cis*-Crotonitrile and of *cis*-CtN·CuCl Nitrile Moiety.

cis-CtN		*cis*-CtN·CuCl		Attribution	
IR	Raman	IR	Raman		
3075 m	3078 ms, p	3058 s	3062 w	ν_2	ν_aHC=CH
3052 sh	3053 vs, p	3039 ms	3044 m	ν_3	ν_sHC=CH
2976 m	2978 sh	2970 m	2974 w	ν_{17}	ν'_aCH$_3$
2952 mw	2953 ms, dp	2949 ms	2954 mw	ν_{18}	ν''_aCH$_3$
2920 mw	2922 vs, p	2907 w	2912 m	ν_{16}	ν_sCH$_3$
2219 vs	2221 vs, p	2229 s	2232 vs	ν_4	νC≡N
1627 s	1627 vs, p	1612 vs	1617 vs	ν_5	νC=C
1440 vs	1443 s, p	1431 vs	1436 m	ν_{20}	δ'_aCH$_3$
1432 sh		1422 vs		ν_{21}	δ''_aCH$_3$
1394 m	1395 m, dp	1389 s	1390 m	ν_6	δ_aHC=CH
1363 ms	1365 s, p	1362 ms	1363 m	ν_{19}	δ_sCH$_3$
1227 mw	1229 s, p	1222 vs	1225 ms	ν_8	δ_sHC=CH
1100 w	1102 m, p	1102 w	1105 w	ν_{22}	r'CH$_3$
1040 w	1043 m, dp	1034 mw	1038 mw	ν_{23}	r''CH$_3$
953 s		962 vs	966 vw	ν_1	νC–CH$_3$
	957 w, dp	944 vs	948 w	ν_9	$\gamma_{w(a)}$HC=CH
891 m	894 s, p	900 vs	905 mw	ν_{11}	νC–CN
727 vs	731 mw, dp	715 s	719 mw	ν_{10}	$\gamma_{w(s)}$HC=CH
658 w	660 m, p	669 s	672 ms	ν_{13}	δC=C–CN
519 m	520 m, dp	521 ms	522 m	ν_{12}	γ_tC=C
395 w	395 ms, p	399 m	402 w	ν_7	δC=C–CH$_3$
285 m	286 m, dp	297 ms	302 w	ν_{14}	γC–C≡N
169 ms	170 s, dp	201 s	204 mw	ν_{15}	δC–C≡N

Harmonic and combination frequencies (IR and Raman ( ) data):

cis-CtN-3065sh:$\nu_5 + \nu_{20}$; 3008 w:$\nu_5 + \nu_6$; 2970 sh (2971 m):$\nu_{15} + \nu_{19} + \nu_{20}$; 2876 vw (2876 mw, p):$2\nu_{20}$; 2851 w (2855 m, p):$2\nu_{21}$; 2835 sh:$\nu_6 + \nu_{20}$; (2803 vw, p):$\nu_{19} + \nu_{20}$; 2782 vw (2783 w, p):$2\nu_6$; (2747 vw, p):$\nu_6 + \nu_{19}$; (2721 w, p):$2\nu_{19}$; 2610 vw:$\nu_4 + \nu_7$; 2513 w (2515 vw, p):$\nu_5 + \nu_{11}$; 2460 vw:$2\nu_8$; 2345 w (2344 vw, p):$\nu_1 + \nu_6$; (2316 vw): $\nu_1 + \nu_{19}$; 2282 vw (2283 vw, p):$\nu_6 + \nu_{11}$ ou $\nu_5 + \nu_{13}$; 2252 w (2255 mw, p):$\nu_{11} + \nu_{19}$; 2195 sh (2197 sh); $2\nu_{22}$; 2168 w (2169 mw, p):$\nu_1 + \nu_8$; 1995 w:$\nu_9 + \nu_{23}$; 1906 w (1908 vw, p):$2\nu_9$; 1838 vw:$\nu_9 + \nu_{11}$ or $\nu_1 + \nu_{11}$; (1780 vw, p):$2\nu_{11}$; 1768 w:$\nu_{10} + \nu_{23}$; 1680 w:$\nu_1 + \nu_{10}$; 1680 w (1676 sh, p):$\nu_9 + \nu_{10}$; 1560 w:$\nu_6 + \nu_{15}$; 1325 w (1327 vw, p):$\nu_{14} + \nu_{23}$; 800 w:$\nu_{12} + \nu_{14}$; 790 sh:$2\nu_7$; 560 vw (566 vw, p):$2\nu_{14}$.

cis-CtN·CuCl-3052 sh:$\nu_5 + \nu_{20}$; 2990 vw:$\nu_5 + \nu_6$; 2855 w (2858 vw):$2\nu_{20}$; 2511 w:$\nu_5 + \nu_{11}$; 2259 m (2262 w):$\nu_{11} + \nu_{19}$; (2180 w):$\nu_1 + \nu_8$; 2066 vw:$2\nu_{23}$; 1980 w:$\nu_9 + \nu_{23}$; 1891 vw:$2\nu_9$; 1798 vw:$2\nu_{11}$; 1758 w:$\nu_7 + \nu_{19}$; 1667 mw:$\nu_1 + \nu_{10}$; 1630 w:$\nu_{15} + \nu_{20}$; 1583 w:$\nu_6 + \nu_{15}$; 1557 vw:$\nu_{15} + \nu_{19}$; 1467 w (1469 vw):$\nu_9 + \nu_{12}$; 819 w:$\nu_{12} + \nu_{14}$.

For all the notations, but a and s, see Table I. a and s (for HC=CH motions): asymmetrical and symmetrical with regard to the C=C bond median plane, respectively.

The out-of-plane deformation mode $\gamma C{-}C{\equiv}N$ (ν_{14}) was expected in the vicinity of 300 cm^{-1} (its wavenumber is 351 cm^{-1} for acrylonitrile, 282 cm^{-1} for methacrylonitrile and 285 cm^{-1} (see Table II) for *cis*-crotonitrile). It did not appear in the *trans*-CtN spectra. But the weak bands which were observed at $\simeq$280 cm^{-1} for the *trans*-CtN·CuX complexes may be due to this mode. Such an assignment must be compared to the localization of ν_{14} at $\simeq$ 246 cm^{-1} in the spectra of solid *trans*-CtN [10].

Our attribution of fundamentals is in complete agreement with that reported by Durig *et al.* [10]. On the contrary, our assignments concerning the harmonic and combination modes, which were carried out by taking the *trans*-CtN·CuX spectra into account, are mostly different from those proposed by the same authors.

Coordination is accompanied by an increase of 10 to 15 cm^{-1} in the C≡N stretching mode frequency. Such a behaviour is characteristic of a bond formation between Cu(I) and the ligand nitrogen atom. If the mechanical and electronic coupling between C–N and N–Cu bonds is assumed to be very small, the C≡N bond strengthening may be explained by the fact that the Cu–N–C angle is about 180° (see Part II). So, the metal atom and its halogen neighbours can repel the electronic cloud from the nitrogen atom towards the carbon atom and consequently the force constant of the nitrile group increases [12]. The low values observed for the $\Delta\nu C{\equiv}N$ variations may be due to the existence of a relatively strong π back-bonding from copper to nitrogen. This π-bonding, which is consistent with the d^{10} configuration of the metal ion, would weaken the C–N bond by placing electrons into the π^* C–N molecular orbital.

Moreover, it appears that the nitrile C=C stretching frequency slightly decreases upon coordination ($\Delta\nu C{=}C$ = $-$(10 to 13 cm^{-1})), indicating a weakening of the C=C bond.

Cis-*CtN and* cis-*CtN·CuX Complexes*

Figure 2 shows the IR and Raman spectra of *cis*-CtN and *cis*-CtN·CuCl obtained in the 4000–160 cm^{-1} range. Table II lists their frequencies and the proposed assignments. The spectra of *cis*-CtN·CuBr are not reproduced here, owing to their close similarity with those of *cis*-CtN·CuCl.

The principal features which differentiate our attribution of the free nitrile fundamentals from that by Durig *et al.* [10] are the following ones:

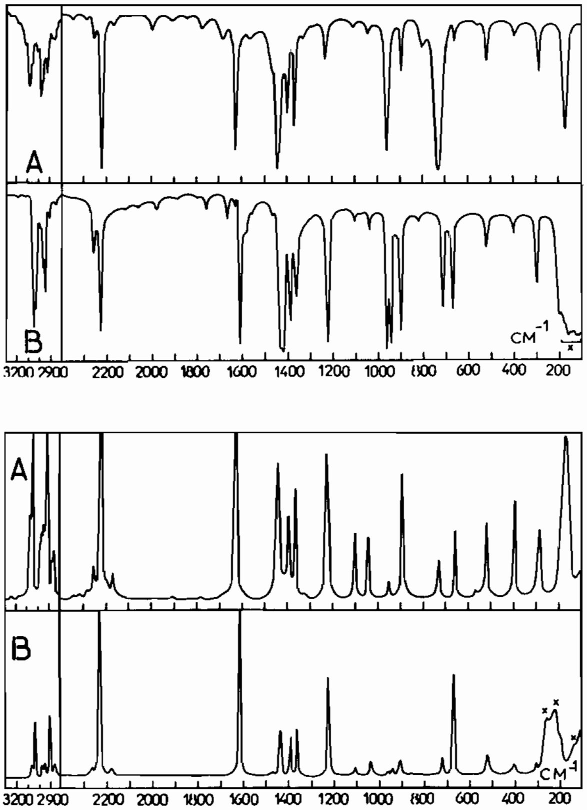

Fig. 2. Infrared spectra (upper part) and Raman spectra (lower part) of A: *cis*-crotonitrile and B: *cis*-crotonitrile·CuCl complex. For 'x' marks see legend to Fig. 1.

– on the basis of accurate wavenumber measurements, we did not establish any correspondence between the infrared and Raman bands of medium intensity both located between 2965 and 2980 cm^{-1}. Only the former (2976 cm^{-1}) was assigned to $\nu'_a CH_3$ (ν_{17}). The latter (2971 cm^{-1}) was explained by the combination mode ν_{15} + ν_{19} + ν_{20} (A'). Several reasons support this double attribution: a shoulder appears on both bands at ~2970 and ~2978 cm^{-1} respectively; the intensity of the Raman band associated to the combination mode is probably enhanced by a Fermi resonance between this mode and the A' fundamentals ν_{17} (2976 cm^{-1}), ν_3 (3053 cm^{-1}) and ν_{16} (2922 cm^{-1}); the binary combinations ν_{19} + ν_{20}, ν_{15} + ν_{20} and ν_{15} + ν_{19} are observed, the first one in the Raman spectrum of the *cis*-crotonitrile (at 2803 cm^{-1}), the two others in the IR spectrum of the *cis*-CtN·CuCl complex (at 1630 and 1557 cm^{-1});

– the in-plane ($\delta'_a CH_3$, ν_{20}) and out-of-plane ($\delta''_a CH_3$, ν_{21}) components of the CH$_3$ asymmetric deformation could be observed separately. ν_{20} was assigned to the polarized Raman line at 1440 cm^{-1} and its infrared counterpart at 1443 cm^{-1}; ν_{21} was associated to the shoulder observed at ~1432 cm^{-1} in the IR spectrum. Both modes give rise to well distinct bands near 1431 and 1422 cm^{-1} in the spectra of Cu(I) complexes;

– the planar symmetrical deformation $\delta_s HC{=}CH$ (ν_8) has been located at 1227 cm^{-1}, whereas Durig *et al.* [10] had identified it at ~1325 cm^{-1}. This new assignment was supported by several arguments: the corresponding Raman band is strong, as expected for a symmetrical mode (the one at 1327 cm^{-1} is very weak); the homologous vibration has been assigned at 1200 cm^{-1} and 1267 cm^{-1} in maleonitrile (*cis*-dicyanoethylene) [13] and *cis*-2-butene [14] respectively; finally, the bands at ~1327 cm^{-1}, which have no counterparts in the spectra of the complexes, can be satisfactorily associated to the combination mode $\nu_{14} + \nu_{23}$ (see Table II);

– the $C-CH_3$ stretching vibration (ν_1) was no more located at 1227 cm^{-1}. The strong IR absorption observed at 953 cm^{-1} was partly assigned to this mode (the out-of-plane unsymmetrical bending of HC=CH is also responsible of this absorption). Such an attribution is corroborated by several considerations: according to our previous results, ν_1 is expected in the frequency range 900–1000 cm^{-1} (it appears at 916 cm^{-1} for acetonitrile, 957 cm^{-1} for methacrylonitrile and 1023 cm^{-1} for *trans*-crotonitrile); in the *cis*-crotonitrile spectra, only the IR band at 953 cm^{-1} splits into two components (at ~950 and ~965 cm^{-1}) in all the Cu(I) complexes spectra, which seems to exclude the hypothesis of a splitting due to the correlation field in the crystals and thus shows the existence of two modes with close frequencies; furthermore, the polarized Raman bands observed at 3173, 2344 and 2169 cm^{-1} can only be assigned to combination modes involving a planar fundamental whose wavenumber is about 955 cm^{-1}.

The in-plane C–C≡N bending mode (ν_{15}) has been located at 170 cm^{-1} and ~205 cm^{-1} for the free and the complexed forms of *cis*-CtN respectively. This correspondence could be established according to the band shapes and also to the fact that the $\nu_6 + \nu_{15}$ combination mode, which appears at 1560 cm^{-1} in the nitrile IR spectrum, has its counterpart at 1583 cm^{-1} in the *cis*-CtN·CuCl IR spectrum.

As in the case of *trans*-crotonitrile, our assignments of harmonic and combination modes, which have been chiefly carried out on the basis of the data provided by the complexes spectra, are significantly different from those proposed by Durig *et al.*

Cis-crotonitrile bonding to Cu(I) induces a shift of the C≡N stretching mode towards higher frequencies: this led us to conclude that, here also, the metal atom was bound to the nitrogen of the nitrile group. The ΔνC≡N shifts (10–11 cm^{-1}) have the same order of magnitude than those observed upon *trans*-crotonitrile coordination. Their low values indicate that a significant π back-bonding from copper to nitrile may exist. Furthermore, the olefinic double bond appears to be looser in the Cu(I) complexes than in the free ligand, as shown by the shift of the C=C stretching mode towards lower frequencies on coordination (ΔνC=C = –(10 to 15 cm^{-1})).

Low Frequency Vibrational Modes

In the frequency range of metal–ligand vibrations, the spectra of *cis*-CtN·CuCl, *cis*-CtN·CuBr, *trans*-CtN·CuCl and *trans*-CtN·CuBr show large similarities with those of aN·CuCl, aN·CuBr (aN = acetonitrile), BN·CuCl and BN·CuBr (BN = benzonitrile) respectively [11]. Consequently the stereochemistry of the crotonitrile complexes could be thought to be of the same type as that of the acetonitrile and benzonitrile complexes, which had been previously described [4, 5] and were shown to exhibit a close analogy. Such an hypothesis was later on corroborated by an X-ray study of the *trans*-CtN·CuX (X = Cl, Br) compounds (see Part II).

So, each copper atom was supposed to admit a tetrahedral (C_{3v}) environment involving one nitrogen and three halogen atoms. The numbering of metal–ligand vibrations was carried out, in a first approximation, by only taking this nearest environment into account.

Under the C_{3v} symmetry, six fundamentals ($3A_1$ + 3E) are expected for the $CuNX_3$ tetrahedron, all of them being both IR and Raman active. These motions can be approximately described as a stretching mode: νCu–N(A_1), a symmetric and an antisymmetric stretching modes: ν_sCu–X (A_1) and ν_aCu–X (E), a symmetric and an antisymmetric deformation modes: δ_sX–Cu–X and δ_aX–Cu–X, a rocking mode of the '$CuCl_3$' group around the Cu–N bond: δ_rCu–X (E). Three additional vibrations have to be considered in the complexes: they correspond to the librations of the nitrile molecule with regard to its metal-bonded nitrogen atom. It is obvious that all these modes may be coupled, either between themselves or with the ligand low frequency vibrations. Moreover the E mode degeneracy may be lifted owing to the very low symmetry of the complexes.

The Raman low frequency spectra exhibit well resolved bands. The infrared ones only show a few peaks in a very broad feature.

Trans-*CtN·CuX Spectra (X = Cl, Br, I)*

These spectra are given in Fig. 3.

The bands of medium intensity which appear at 201 and 150 cm^{-1} in the *trans*-CtN·CuBr Raman spectrum are assigned without any ambiguity, the former to νCu–N, the latter to ν_sCu–Br. The asymmetrical ν_aCu–Br mode is postulated to give rise to the strong IR absorption located at 213 cm^{-1}. The shoulder shown by this band at 207 cm^{-1} may arise from the splitting of the previous mode, due to the correlation field in the crystals. The bending motions of the metal–ligand bonds are not identified in the Raman spectrum but may be partly responsible of the broad infrared feature whose maximum is at 114 cm^{-1}.

In the Raman spectra of *trans*-CtN·CuCl, the strong diffusion intensity observed at 198 cm^{-1} is assigned both to νCu–N and to ν_sCu–Cl. The latter mode is located at 190 cm^{-1} in the IR spectrum. The Raman peak at 135 cm^{-1} is attributed to the last A_1

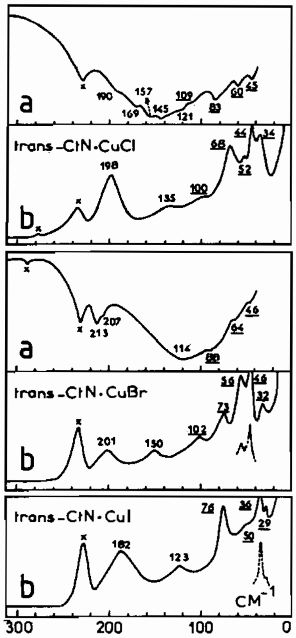

Fig. 3. Infrared (a) and Raman (b) low-frequency spectra of *trans*-crotonitrile·CuX complexes. Underlined frequencies are assigned to lattice vibrations.

mode which has not yet been identified, namely: δ_sCl–Cu–Cl. The broad IR absorption pointing at 150 cm^{-1} may be partly associated with the three E motions of the metal–ligand bonds.

The νCu–N and ν_sCu–I vibrations of *trans*-CtN·CuI are located without any difficulty at 182 and 123 cm^{-1} respectively in the Raman spectrum.

The bands which appear below ~100 cm^{-1} in all the spectra are assigned to lattice vibrations. Their similarity suggests that the three complexes may have very close structures. The X-ray structural investigation reported in Part II for *trans*-CtN·CuCl and *trans*-CtN·CuBr corroborates this assumption.

Cis-*CtN·CuX spectra (X = Cl, Br)*

These spectra are shown in Fig. 4.

The Raman bands located at 160 and 225 cm^{-1} in the spectra of *cis*-CtN·CuBr and *cis*-CtN·CuCl respectively are associated the former with νCu–Br, the latter with νCu–Cl. Coupling between νCu–X and νCu–N modes is expected to be more important for X = Cl than for X = Br, according to the closer proximity of the unperturbed frequencies in the first case. The fact that νCu–N appears at a higher wavenumber in the Raman spectrum of *cis*-CtN·CuCl (258 cm^{-1}) than in the one of *cis*-CtN·CuBr (243 cm^{-1}) is consistent with this assumption.

Between 200 and 100 cm^{-1} the infrared spectrum of *cis*-CtN·CuCl shows a very broad feature, including several components, which resembles the one observed for *trans*-CtN·CuCl. As this latter, it is essentially assigned to the three deformation modes of the '$CuNCl_3$' tetrahedron. In particular the peak at 122 cm^{-1} and its Raman counterpart at 127 cm^{-1} are associated to the A_1 symmetrical planar motion δ_sCl–Cu–Cl. *Cis*-CtN·CuBr infrared spectrum could not be obtained below 200 cm^{-1}.

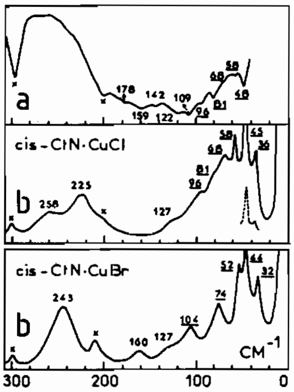

Fig. 4. Infrared (a) and Raman (b) low-frequency spectra of *cis*-crotonitrile·CuX complexes. Underlined frequencies are assigned to lattice vibrations.

For both complexes, lattice vibrations have been located below ~100 cm^{-1}. The close analogy shown by the Raman spectra in this low frequency range suggests that *cis*-CtN·CuCl and *cis*-CtN·CuBr crystalline structures may present large similarities.

Evidence for a cis-trans *Isomerization of Crotonitrile*

The IR and Raman spectra of *trans*-CtN·CuX and *cis*-CtN·CuX complexes which were prepared with pure *trans*-crotonitrile and pure *cis*-crotonitrile respectively have been well characterized.

However, we noticed that crystals which were obtained with crotonitrile containing both *cis*- and *trans*-isomers in a *cis*/*trans* ratio up to 80% had the same spectra as the homologous *trans*-CtN·CuX complexes. In those species, the crotonitrile moiety is under its *trans*-form. Spectra showed that there were no traces of the *cis*-form. Moreover it appeared that synthesis yields were greater than they would have been if only the *trans*-crotonitrile was completely coordinated. Therefore evidence was given for a *cis–trans* isomerization of crotonitrile in the presence of copper(I) halides.

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