Copper–Halogen Stretching Frequencies: Some Further Obervations

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IN a recent report[1] on the far-infrared spectra of some copper–halogen compounds, it was suggested that only the higher frequency *X*-sensitive band observed[2–4] in each of the spectra of $Cupy_2X_2$ (X = Cl, Br) arises from copper–halogen stretching, the other having a different (but obscure) origin.

However, the occurrence of two *X*-sensitive vibrations in the normal copper–halogen stretching regions of the spectra of CuL_2X_2 compounds (L = monodentate ligand or L_2 = bidentate ligand) is not limited to the bis(pyridine) complexes. An analogous situation has been found for $Cu(\gamma\text{-pic})_2X_2$[5] and $Cu(dith)Cl_2$[6] (γ-pic = γ-picoline; dith = 1,4-dithiane). We now report the observation of two such bands (Table) in the spectra of Cu $trzX_2$, Cu $scCl_2$ and Cu $tscX_2$ (trz, sc, tsc = the bidentate ligands 1,2,4-triazole, semicarbazide, and thiosemicarbazide, respectively). The sc and tsc compounds contain copper atoms in distorted octahedral environments (electronic spectra[7,8]) and their most likely structures are analogous to that of Cu $trzCl_2$ in which the bidentate trz bridges adjacent copper atoms along distorted $[CuCl_2]_n$ chains,[9] or alternatively one in which the ligands bridge copper atoms between such chains. In either case the symmetry of the copper–halogen framework will be close to that in the bis(pyridine) complexes, for which two copper–halogen stretching frequencies are predicted and observed. In agreement with this interpretation is the assignment[1] of two main bands (Table) in the spectra of $CsCuX_3$ (X = Cl, Br) to stretching vibrations of the copper–halogen chains; the chain structures of these compounds[10] have been compared[1] with that of Cu $trzCl_2$.

It has been argued, however, that the "long" Cu–Cl distance in $Cupy_2Cl_2$ (2Cl at 2·28 Å, 2Cl at 3·05 Å; ref. 11), being appreciably greater than the bridging chlorine distance in $CsCuCl_3$ (2·35 Å; ref. 10), should not give rise to ν(CuX) absorption in the normal region.[1] In fact such absorption is found for all the complexes mentioned above, with the lower frequency ν(CuX) band 20—50 cm.$^{-1}$ higher in $CsCuX_3$ than in the other compounds of corresponding halides (Table). Furthermore, the two ν(CuX) bands observed both arise from the $Cu-X\cdots Cu$ system, so that although the individual force constants may be quite different, each vibration involves both of these; the exact forms of the vibrations are of course unknown. This explains the overlapping of the ranges observed for bridging and terminal ν(CuX) modes.[1,2]

In the compounds $M_2[CuCl_4,2H_2O]$, (M = K, Rb, NH_4), which consist of *trans*-$[Cu(H_2O)_2Cl_2]$ units with two longer Cu–Cl distances (2·95 Å for M = K; ref. 11), only one ν(CuCl) mode is observed, indicating that the "long" bonds do not give rise to absorption in the normal region.[1] In agreement with this interpretation we report that Cu sc_2Cl_2 [planar bis(chelated) Cu sc_2 groups with two chlorine atoms completing octahedral co-ordination[12]] does not show any ν(CuCl) absorption above 200 cm.$^{-1}$ even though the Cu–Cl distance (2·84 Å) is shorter than the "long" bond in Cu py_2Cl_2. We find a similar situation in the analogous complexes Cu sc_2Br_2, Cu tsc_2X_2 and Cu $scac_2X_2$ (scac = acetone semicarbazone). However, in these examples all the halogens are non-bridging, so that the situation is not comparable with Cu py_2X_2.

$Cu(H_2O)_2Cl_2$ and $Cu(NH_3)_2X_2$ have structures[11] analogous to those of Cu py_2X_2, and in the light of the foregoing evidence are expected to show two ν(CuX) modes. In fact, only one such band has been identified in each case.[1] However, the bromide dihydrate, being unknown under ordinary conditions, was not available for comparison with $Cu(H_2O)_2Cl_2$, and if a second ν(CuCl) absorption were present in the spectrum of the latter it might well be masked by the band at 242 cm.$^{-1}$ [236 cm.$^{-1}$ in $Cu(D_2O)_2Cl_2$] assigned[1] to $\delta(Cu–OH_2)$ (*cf.* Table). The interpretation of the spectra of the ammines is the least satisfactory. Since the lower frequency ν(CuX) band is generally weaker than the higher frequency mode and often separated from it by *ca.* 50 cm.$^{-1}$, it might well be obscured in a spectrum with half-band widths of this order[1] (*cf.*, $\Delta\nu_{\frac{1}{2}} \sim 15$ cm.$^{-1}$ for Cu py_2X_2). Furthermore, if the spectra reported were of the β-forms of these complexes (no details were given) where all the Cu–X distances are very similar, then

TABLE

The two X-*sensitive vibrations* (*cm.*$^{-1}$) *of halogen-bridged* CuL_2X_2 *complexes in the* ν(*CuX*) *regions*

L =	py	py	γ-pic	γ-pic	½dith	½sc	½tsc	½tsc	½trz	½trz	½Cl[a]	½Br[a]
X =	Cl	Br	Cl	Br	Cl	Cl	Cl	Br	Cl	Br	Cl	Br
Ref.	2—4	2—4	5	5	6	b	b	b	b	b	1	1
	287s	256s	296vs	237s	329s	310vs	312vs	251s	275vs	$\left\{\begin{array}{c}243\text{s}\\226\text{w}\end{array}\right\}$[c]	$\left\{\begin{array}{c}293\text{s}\\287\text{s}\end{array}\right\}$	$\left\{\begin{array}{c}256\text{s}\\251\text{s}\end{array}\right\}$
	229ms	204s	209s	190s	*ca.*270br	226s	234s	184s	246ms	206s	263s	234s

[a] $CsCuX_3$.
[b] This work. Full details will be the subject of a forthcoming publication.
[c] This splitting probably arises from the non-planarity of the $[CuX_2]_n$ chains.

the two ν(CuX) modes would be expected to be even closer together (*cf.* Cu trzCl_2 and $CsCuCl_3$, Table).‡

We conclude that halogen-bridged CuL_2X_2 systems generally show the expected two ν(CuX) absorptions in the normal regions. When the groups L are bulky, however, halogen-bridging is inhibited and only one ν(CuX) mode is observed.[2,13]

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‡ Often the lower ν(CuCl) mode is very close in frequency to the higher ν(CuBr) mode in analogous pairs of compounds (Table). This does not invalidate our assignments since we have made comparison with the spectra of corresponding oxyacid salts and/or of the parent ligands, and eliminated internal ligand and ν(Cu–L) absorptions.

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