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Metal–Halogen and Metal–Nitrogen Stretching Modes in the Far-infrared Spectra of Octahedral Halogen-bridged Complexes MX_2(pyridine)$_2$ and Related Systems. A Clarification of Confused Literature

MICHAEL GOLDSTEIN

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, U.K.

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Octahedral halogen-bridged complexes of first transition series metals of type $MX_2(Rpy)_2$, where (Rpy) is pyridine or a substituted derivative, have been extensively studied but continue to be the subject of further vibrational spectroscopic [1–9] or crystallographic [7, 9–11] investigations (the references cited are to a selection of papers published over the last five years). One reason for this is that such complexes provide very useful models for a vast range of coordination compounds, reports of which regularly fill page upon page of this and other journals [12]. In view of such wide-spread usage, it is of considerable importance that the properties of the compounds which purport to be the "model data" are reliable and accurately represented. Unfortunately, as far as the metal–ligand vibrational spectra are concerned, a situation of confusion and misconception has been created in the literature, because key publications have been overlooked and elementary theoretical principles have been ignored.

The purpose of this paper is to present in a clear manner the basis for the foregoing assertion, in the hope that it will assist future investigators, by clarifying several points and bringing a measure of order to the literature.

Basis for Deducing Number of Metal–Ligand Modes

The treatment [4, 7] of the vibrations of a halogen-bridged chain polymer of type $[MX_2L_2]_n$ as arising from a monomeric "MX_4L_2" unit is quite wrong. Because of the relationships between translations and rotations of the 'monomer' and genuine modes of vibration of the polymer chain, the symmetry and number of modes of each type will be erroneously deduced using the 'monomer' model. For example, rotation of a "MX_4L_2 monomer" about the LML axis is, in the polymer, an in-plane deformation of the $[MX_2]_n$ chains. As has previously been explained [13, 14], a suitable approach to prediction of the vibrational spectrum of a halogen-bridged chain is via the line group, commonly employed for organic polymers [15]. For the 'model compound' of known crystal structure, α-$CoCl_2$(pyridine)$_2$, the line group symmetry is D_{2h} if the pyridine groups are taken as point masses, or C_2 if orientation of these ligands is taken into account; the chain site symmetry in the crystal is also C_2 [14, 16]. It is, in a way, both fortunate and unfortunate that the same results for the number of infrared-active skeletal stretching vibrations, one ν(MN) and two ν(MX) modes, are predicted for the $[MX_2N_2]_n$ polymer using the D_{2h} line group approach [14, 16] as assuming C_i [4, 17] or C_{2h} [7] point groups.

Crystal Field Effects

Having correctly determined the number and symmetry of the modes of vibration for an isolated polymeric chain, due attention must be given to the effects of the crystal structure. A number of far-infrared bands observed for $[MX_2(\text{pyridine})_2]_n$ type species quite clearly show splitting due to correlation field effects [14, 16]. This is particularly noticeable for ν(MN) modes; unit-cell (factor) group analysis for the C_{2h}^4 (*P*2/*b*) space group structure of α-$CoCl_2$(pyridine)$_2$ gives (taking each pyridine as a point mass and noting that there are four chains per unit cell):

$$\Gamma_{MN}^{cryst} = 2a_g\,(Ra) + 2b_g\,(Ra) + 2a_u\,(ir) + 2b_u\,(ir).$$

Thus *four* ν(MN) bands are predicted to occur in the ir spectrum (and four different ones in the Raman spectrum). Explanation of the spectra in these terms has already been given [14, 16].

Use of Ligand Isotopic Shifts

While isotopic substitution of C_5D_5N for C_5H_5N may be very informative in the identification of ν(MN) modes in pyridine complexes (and has been used for this purpose for several years [14, 16, 18, 19]), it is most important to take careful note of the nature of the motions involved. Taking a simple model in illustration*, the antisymmetric ν(MN) mode of a linear (pyridine)–M–(pyridine) unit has an isotopic shift ratio $\nu_a(M\text{–}NC_5H_5)/\nu_a(M\text{–}NC_5D_5)$ calculated [20] to be less than 1.01 for M = Mn, Fe, Co, Ni or Cu and with the ligand taken as a point mass. In principle then, such a mode will show an isotopic shift of less than 2 cm^{-1}. Excepting in certain cases, where particular care is taken, such

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*Shifts expected for a real case are determined by the Teller–Redlich Product Rule, but this requires frequencies of the isotopomers for all the other vibrations belonging to the same symmetry class.

shifts will be difficult to detect reliably (despite confidence of authors) because

(a) at room temperature especially the bands in question are relatively broad (due in part to 'hot' band effects);

(b) most measurements are made at spectral resolutions and with reproducibilities significantly greater than 1 cm^{-1} (such data are rarely given in papers as determined, anyway);

(c) the bands in question physically overlap with ν(MX) and/or ligand mode bands, making the location of true band maxima difficult.

However, in favourable cases, substantial deuteriation effects should be detected, since for the linear triatomic (pyridine)–M–(pyridine) model used $\nu_s(M-NC_5H_5)/\nu_s(M-NC_5D_5)$ is calculated [20] to be about 1.03 (irrespective of M), implying shifts approaching 7.5 cm^{-1}. Thus a whole range of deuteration shifts of about 0–8 cm^{-1} may be observed for modes of genuine ν(MN) character.

On the other hand, it is essential to take cognizance of the nature of the modes being described, since these are considerably more complex than assumed in the afore-mentioned calculations and descriptions. In the first place there is the correlation field splitting effect described earlier, in which the coupled motion of eight M–N bonds is involved. Additionally, the point mass model adopted above, and the description "ν(MN)", imply that the C_5H_5N (and C_5D_5N) groups move *en bloc* during the motion giving rise to the bands in question, which may largely be true but not absolutely, so that the calculations above will represent the maximum shifts expected. Estimation of ^{15}N isotopic shifts (see [12] for examples of use) is particularly difficult for similar reasons. Of even greater importance is the influence of kinematic coupling between M–N bond stretching and other skeletal (or lattice) modes of the same symmetry type, notably metal–halogen stretching – particularly in view of the close proximity with these modes [see under *Consistency*, below].

The essential point to be emphasised here is that very low deuteriation shifts may result for ir bands which involve appreciable metal–nitrogen stretching character, so that if a particular band does not show a reliably measurable shift it is quite wrong to infer that it cannot be suitably described as "ν(MN)". Conversely, cases can arise where coupling induces measurable shifts in bands which have their origin in modes only partially "ν(MN)".

Metal Isotopic Shifts

Related considerations must also be applied to the use of metal isotopes (see [12, 21] for examples of use). A vivid illustration is again afforded by the linear (pyridine)–M–(pyridine) model, since the ν_s(NMN) mode will suffer *zero shift* on isotopic substitution of M because no motion of the metal atom is involved.

Sample Temperature and Spectral Range

The advantages of cooling samples subject to far-ir study (to 100 K or colder) must again be emphasised. Although there is the danger in overlooking the occurrence of phase changes, it is clear that much information and performance is lost at room temperature. This is especially important if one is attempting to correlate the number of bands with a particular structural type (contrast refs. [4] and [14]). Further, as full a spectral range as possible must be studied – the dangers in using instruments restricted to the region above 200 cm^{-1} for this kind of study have already been illustrated [14, 18].

Consistency

Despite the foregoing remarks, it is quite clear that the sensible use of isotopes can, in suitable cases, afford data useful for making vibrational assignments, providing *positive* evidence is used. However, the main conclusion which must be drawn when all the data are taken together is that there is significant coupling between stretching of metal–nitrogen and metal–halogen bonds, to the extent that the isotopic shift data are not as instructive as authors suppose. Further, it is essential that other criteria for making assignments are not ignored. For example, two bands at 210–230 cm^{-1} in the ir spectrum of $MnCl_2$(pyridine)$_2$ have been assigned [4] as ν(MnCl) rather than ν(MnN) because they showed deuteration shifts of only 1 cm^{-1}, but this study ignored the fact [14] that the two bands shift by only 5 cm^{-1} or less when chlorine is replaced by bromine!

Conclusions

This paper has emphasised some of the aspects of the vibrational spectra of halogen-bridged chain polymers $[MX_2L_2]_n$ which have been repeatedly overlooked in the literature. It must be stated that:

(a) there is no basis for revising the ν(MX) and ν(MN) assignments and spectral interpretation put forward for pyridine complexes some years ago [14, 16, 22] (save to note the approximate but acceptable nature of such descriptions)*;

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*For the tetragonally distorted complexes CuX_2(pyridine)$_2$, some re-appraisal of early assignments [23] now seems necessary and will be the subject of a future publication.

(b) an appropriate approach must be adopted in prediction of the number and symmetry of the vibrational modes possible;

(c) the careless use of one type of isotopic substitution without consideration of other proven criteria is to be deprecated.

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