

Clark R J H & Williams C S. The far-infrared spectra of metal-halide complexes of pyridine and related ligands. *Inorg. Chem.* 4:350-7, 1965.

[William Ramsay and Ralph Forster Laboratories, University College, London, England]

Metal-halide complexes involving pyridine and certain other nitrogen-donor ligands were extensively investigated by infrared spectroscopy in the 200-700 cm^{-1} region, leading to assignments for metal-halogen $\nu(\text{MX})$ and metal-ligand $\nu(\text{ML})$ stretching vibrations. The relationship between the numbers of bands attributable to $\nu(\text{MX})$ and $\nu(\text{ML})$ and the stereochemistry of a complex was delineated, as were the relationships between the wave numbers of bands attributed to $\nu(\text{MX})$ and both coordination number and oxidation state of the metal ion. [The SCI® indicates that this paper has been cited in more than 830 publications.]

An Early Study of Metal-Halogen Vibrational Modes

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I had already become interested in the vibrational spectroscopy of inorganic compounds in 1962 when a South African, Charles S. Williams from Potchefstroom, arrived at University College London wishing to work with me for a PhD degree. At that time, few systematic studies of metal-halogen, $\nu(\text{MX})$, or metal-ligand, $\nu(\text{ML})$, vibrational modes had been undertaken, and I decided to ask Williams to make a thorough infrared study of metal-halide complexes of pyridine and other related nitrogen-donor ligands, many of which had, by then, been characterized structurally, as well as by electronic spectroscopy and (where possible) by magnetic studies.¹ Metal-pyridine complexes were, and are, one of the most extensive sets of related complexes known; moreover, they include examples of complexes with skeletal geometries. These are tetrahedral ($\text{MX}_2\cdot 2\text{py}$), octahedral ($\text{MX}_2\cdot 4\text{py}$, $\text{MX}_3\cdot 3\text{py}$, and $\text{MX}_4\cdot 2\text{py}$, for all of which both *cis*- and *trans*-isomers are known), polymeric octahedral and distorted octahedral ($\text{MX}_2\cdot 2\text{py}$, each of which contains halogen bridges), and *cis*- and *trans*-planar ($\text{MX}_2\cdot 2\text{py}$).

Complexes of all of the above geometries were studied, using a newly acquired Grubb-Parsons DM2 spectrometer, that operated in the range 455-

200 cm^{-1} . This instrument, regarded as both insensitive and of very low resolution nowadays, nevertheless yielded all the essential information about the factors on which metal-halogen stretching frequencies depend. Thus, $\nu(\text{MX})$ was shown to depend on (a) the oxidation number of the metal ion, (b) the coordination number of the metal ion, and (as shown elsewhere) (c) the electron configuration of the metal ion and, in particular, on whether or not the ligand field is such that the metal ion is spin-free or spin-paired. Moreover, the selection rules for infrared spectroscopy proved to be such that it is remarkably easy to distinguish between *cis*- and *trans*-complexes, and monomeric from polymeric complexes. Thus, it was established that $\nu(\text{MX})$ are, in general, diagnostic of stereochemistry, oxidation state, and electronic configuration in metal-halide complexes.

The wide applicability of the relationships established for metal-halogen stretching frequencies was subsequently generalized to all metal-ligand stretching frequencies.² Thus, coupled with electronic spectroscopy and magnetism, infrared spectroscopy in the $\nu(\text{MX})$ region became one of the first techniques to be used in the characterization of new inorganic complexes. Indeed, the technique is more generally useful in this regard than the other two mentioned, this being undoubtedly why the paper became a *Citation Classic*.

It is noteworthy that the paper predates the subsequent and widespread use of Raman spectroscopy as a technique for the understanding of the structure of, and bonding in, inorganic complexes.³ However, the relationships established in the *Citation Classic* apply equally well to $\nu(\text{MX})$ values as determined by Raman spectroscopy, as countless subsequent studies revealed.⁴

The direct structural value of the vibrational information referred to is not as great now as it was 25 years ago, with the much greater current use of, and developments in, resonance (NMR and ESR) and diffraction (X-ray and neutron) techniques for structural work. Moreover, other forms of spectroscopy, e.g. resonance Raman spectroscopy, now provide very precise structural information relating to the excited as well as the ground states of a wide range of metal complexes, in particular of mixed-valence, metal-metal bonded, and linear-chain complexes.⁵

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5. ----- . Synthesis, structure and spectroscopy of metal-metal dimers, linear chains, and dimer chains. *Chem. Soc. Rev.* 19(2):107-31, 1990.

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