

Clark R J H. Metal-halogen stretching frequencies in inorganic complexes.

Spectrochimica Acta 21:955-63, 1965.

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

Metal complexes containing metal-chlorine, metal-bromine, or metal-iodine bonds give rise to relatively intense infrared bands in the region below 650 cm^{-1} . The bands, assigned to metal-halogen stretches, have wave numbers which may be correlated with the oxidation state, mass, coordination number, and electron configuration of the metal atom, and with the stereochemistry of the complex. [The *SCI*[®] indicates that this paper has been cited over 290 times since 1965.]

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"In 1959, when working on the chemistry of the early transition metals, I became involved in trying to determine the nature of the red product formed on treating a solution of TiCl_3 in acetic acid with *o*-phenylenebisdimethylarsine (diars). The red product was not stable as such in any solvent, and so neither molecular weight nor conductivity data could be obtained. There was little information in the electronic spectrum of the complex to indicate its correct formulation, nor in the infrared spectrum which, being confined to the region above 500 cm^{-1} , implied only that the diars was coordinated in a bidentate manner. The structure of the complex could only be revealed by X-ray diffraction studies, these showing it to be $\text{TiCl}_2 \cdot 2$ diars, the first eight-coordinate complex known for a first-row transition metal.¹ With this challenge to accepted tenets of chemical belief, the whole subject of high coordination numbers received great impetus.

"What irked me (as a New Zealander) at the time was that it took some persuasion (and beer!) to talk crystallographers into attempting to solve the crystal structures of

somewhat air-unstable, but key, species. These were exciting times at University College London, with many new complexes being produced each week with the enthusiastic encouragement of Ron Nyholm. It was clear that there was a real need, in order to support this synthetic programme, for a rapid spectroscopic method for telling the likely oxidation state and coordination number of a metal atom in a complex. It seemed that metal-ligand stretching frequencies should hold the key, since these must be intimately connected with the strengths of metal-ligand bonds within complexes. These thoughts coincided with our purchase of a Grubb-Parsons DM2 spectrometer which operated in the range $455\text{-}200\text{ cm}^{-1}$. This, by present-day standards very poor, instrument nevertheless provided all the essential information with which to reveal the factors on which metal-ligand stretching frequencies depend.

"The research programme covered a wide range of transition-metal complexes, some studied with the Australian Tom Dunn and others with the South African Charles Williams (the paper describing the latter work is the most heavily cited [> 550 citations] of my publications.²) Many other studies of this nature³ eventually allowed me to draw the whole field together in the cited paper, which clearly delineated the ways in which metal-halogen stretching frequencies varied (for a given coordination number) with the oxidation state of the metal, and (for a given oxidation state) with the coordination number of the metal. Subsequently, the influence of the electronic configuration of the metal, for a given oxidation state and coordination number, was outlined, as were the effects of halogen bridging, etc., on metal-halogen stretching frequencies. The wide applicability of the relationships established for metal-halogen stretching frequencies, and subsequently generalized to all metal-ligand stretching frequencies, is undoubtedly the reason for the paper becoming a *Citation Classic*. The paper predates the subsequent exciting and widespread use of Raman and resonance Raman spectroscopy⁴ as tools for understanding the structure of, and bonding in, inorganic complexes."

1. Clark R J H, Lewis J & Nyholm R S. Diarsine complexes of quadrivalent-metal halides.

J. Chem. Soc. 1962:2460-5.

2. 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.

3. Clark R J H. *The chemistry of titanium and vanadium*. Amsterdam: Elsevier, 1968. 327 p.

4. ----- . Resonance Raman spectra of inorganic molecules and ions. (Clark R J H & Hester R E, eds.)

Advances in infrared and Raman spectroscopy. London: Heyden, 1975. Vol. 1. p. 143-72.