

Hathaway B J & Underhill A E. The infrared spectra of some transition-metal perchlorates. *J. Chem. Soc.* 1961:3091-6.
 [University of Hull, Hull, England]

The infrared spectra of some hydrated transition metal perchlorates, some transition metal perchlorate-methyl cyanide complexes, and anhydrous copper(II) perchlorate are reported. The spectra are interpreted in terms of ionic perchlorates, T_d symmetry; monodentate perchlorato groups, C_{3v} symmetry; and bidentate perchlorato groups, C_{2v} symmetry. [The *SCI*[®] indicates that this paper has been cited in over 465 publications since 1961.]

B.J. Hathaway
 Department of Chemistry
 University College
 Cork
 Ireland

August 4, 1982

"In the early-1950s, polyatomic anions such as the nitrate and perchlorate anions were generally considered to display a negligible ability to act as ligands to transition metal ions, especially in aqueous solution. By the mid-1950s, the pioneering work of C.C. Addison¹ (University of Nottingham) and his students, using liquid dinitrogen tetroxide as a solvent, had clearly demonstrated the coordinating ability of the nitrate ion to transition metal ions such as iron, cobalt, nickel, copper, zinc, and uranium to form not only the anhydrous nitrate, i.e., $Cu(NO_3)_2$, but nitrate complexes, i.e., $NO^+[Cu(NO_3)_3]$. Even in these clear coordination complexes the nitrate ion was still considered to be a weak ligand and coordination of the nitrate ion to a metal ion was readily broken by dissolution of these hygroscopic nitrate complexes in water. Nevertheless, the final confirmation of the covalency of the nitrate-metal bonding was the demonstration² of the volatility of anhydrous copper(II) nitrate, which could be sublimed under vacuum at ca. 200° to yield blue-green crystals on a 10 g scale.

"In the late-1950s, even against this background of the covalency of the nitrate

metal bond, the perchlorate ion was still considered to be the classic non-coordinating anion *par excellence*, and was traditionally used to maintain the ionic strength of aqueous solutions used in equilibrium studies of coordination complexes. But the demonstration³ of the volatility of anhydrous copper(II) perchlorate under vacuum likewise established the covalent character of the perchlorato-copper(II) bond. One effect of the coordination of a perchlorate group to a metal was that the point group symmetry of the free anion, T_d , would be lowered to C_{3v} in the monodentate perchlorato group and to C_{2v} in a bidentate perchlorato group. These symmetry changes in coordination of the perchlorate group are then reflected in both the number of infrared active vibrations, and also the energy at which the vibrations occur. In our infrared paper, those group theoretical predictions were set out and illustrated using the infrared spectra of a number of transition metal perchlorate complexes involving ionic, monodentate, and bidentate perchlorate groups, of which the latter was presumed to occur in anhydrous copper(II) perchlorate. Consequently, this paper established the use of a readily available physical technique, infrared spectroscopy, as a valid tool for the determination of the bonding role for the perchlorate ion in transition metal complexes. In addition, these infrared criteria of bonding have been used to establish that the perchlorato group, in elongated tetragonal octahedral complexes of the copper(II) ion, i.e., $[Cu(en)_2(OClO_3)_2]$, with long Cu-O distances of 2.6 Å, is still involved⁴ in weak or semi-coordination, and it is probably in this respect that this paper has become a *Citation Classic*.

"Our infrared paper was recently quoted by us in a crystallographic paper⁵ on the structure of *catena*-acetato(di-2-pyridylamine)- μ -perchlorato copper(II) monohydrate which reported the crystal structure and infrared evidence for a novel bridging perchlorato group involved in semi-coordination⁴ to the copper(II) ion."

1. Addison C C & Hathaway B J. Addition compounds of dinitrogen tetroxide and their application in preparative inorganic chemistry. *Recent aspects of the inorganic chemistry of nitrogen: report of a symposium held by the Chemical Society at Cambridge on April 10th-12th, 1957*. London: Chemical Society, 1957. p. 33-43.
2. The vapour pressure of anhydrous copper nitrate, and its molecular weight in the vapour state. *J. Chem. Soc.* 1958:3099-106.
3. Hathaway B J. Volatile copper perchlorate. *Proc. Chem. Soc.* 1958:344-5.
4. Procter I M, Hathaway B J & Nicholls P. The electronic properties and stereochemistry of the copper(II) ion. Part I. Bis(ethylenediamine)copper(II) complexes. *J. Chem. Soc. A* 1968:1678-84.
5. Ray N, Tyagi S & Hathaway B. *Catena*-acetato(di-2-pyridylamine)- μ -perchlorato copper(II) monohydrate. *Acta Crystallogr. Sect. B* 38:1574-7, 1982.