Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Introduction

Edward I. Solomon[a]
[a] Chemistry Department, Stanford University, Stanford, California

To cite this Article Solomon, Edward I.(1984) 'Introduction', Comments on Inorganic Chemistry, 3: 5, 227 — 229
To link to this Article: DOI: 10.1080/02603598408080072
URL: http://dx.doi.org/10.1080/02603598408080072

A summary of the basic principles and information content of the spectroscopic methods most often used to determine the electronic structure of transition metal complexes is presented. The methods covered are electron paramagnetic resonance (EPR), electronic absorption (associated with ligand-field and charge-transfer transitions), x-ray absorption, and photoelectron spectroscopies. The higher resolution information available through EPR (hyperfine coupling) and electronic absorption (vibronic coupling and bandshape analysis) spectroscopies is also considered. Attention throughout this Comment is focused on the relatively simple examples of the square planar and distorted tetrahedral $CuCl_4^=$ complexes.

I. INTRODUCTION

The purpose of this Comment is to present a condensed summary of the information content of the spectroscopic methods most often employed to elucidate the electronic structure of transition metal complexes. In Part 1, the basic principles of each method are briefly developed, the nature of the experiment is outlined, and the experimental results are compared with the results from ligand field and molecular bonding (in particular, SCF-Xα-SW) theories.[1] Two spectroscopic techniques can provide information which is of significantly higher resolution than is appropriate for an overview. These methods, EPR (electron paramagnetic resonance) and electronic absorption spectroscopy, are discussed in further detail in Part 2. Attention throughout this comment is focused on one of the simplest inorganic molecules, the $CuCl_4^=$ complex.

The free cupric ion has five degenerate d orbitals which are raised in energy and split into a t_{2g} and an e_g set upon placing the ion into an octahedral ligand field. The nine valence electrons of the cupric ion fill these d orbitals to produce a $(t_{2g})^6(e_g)^3$ ground many-electron configuration which contains one unpaired electron in a degenerate

Comments Inorg. Chem.
1984, Vol. 3, No. 5, pp.227–320
0260-3594/84/0305-227/$30.00/0

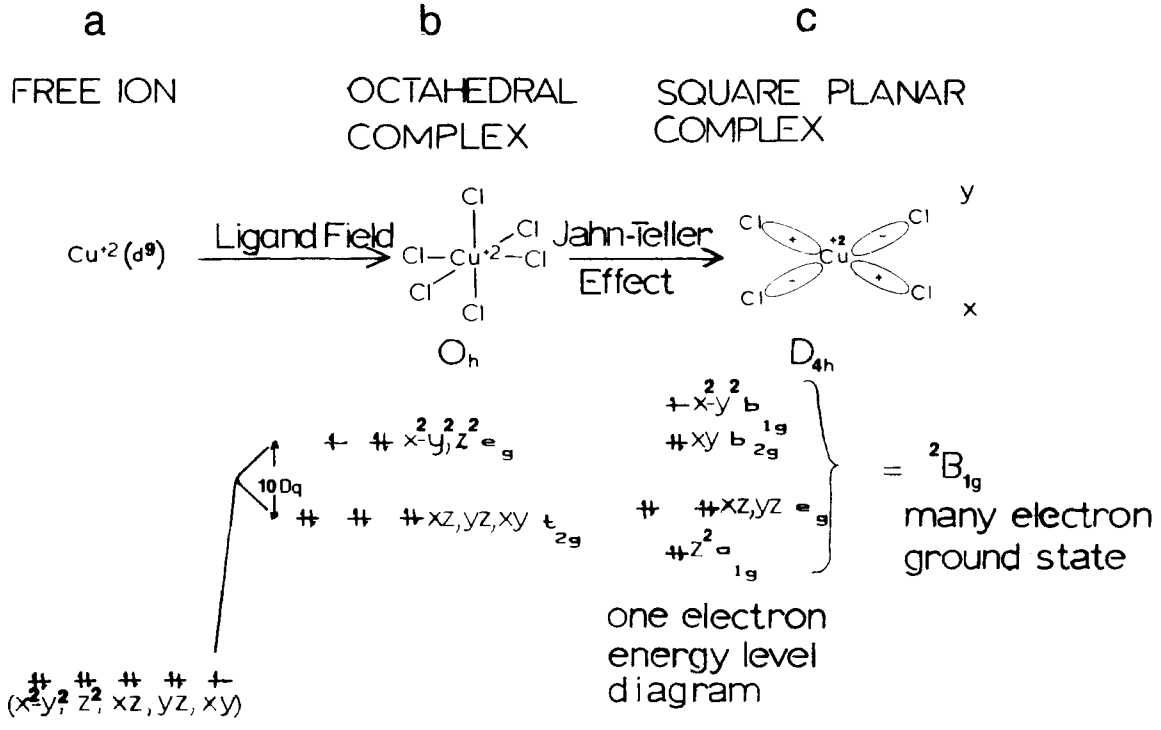

FIGURE I-1 Ligand field theory of $CuCl_4^{=}$: (a) $Cu^{+2}(d^9)$ free ion. (b) Effects of an octahedral ligand field. (c) Further effects of a large tetragonal distortion.

orbital set. Associated with this configuration is a "Jahn-Teller" force which causes the octahedral complex to undergo a tetragonal distortion.[2] For copper(II) this usually involves an axial elongation which leads to a square planar complex in the infinite distortion limit. The D_{4h} ligand field produced by the chloride ligands in this geometry results in the d orbital splitting shown to the right in Figure I-1 with the highest energy d orbital being $d_{x^2-y^2}(b_{1g})$ which is oriented along the four Cu–Cl bonds. The nine d electrons then generate a $(a_{1g})^2(e_g)^4(b_{2g})^2(b_{1g})^1$ many-electron configuration which corresponds to a $^2B_{1g}$ many-electron ground state. This ground state can be probed directly by EPR spectroscopy.

References

1. No attempt is made to present the basics of these inorganic bonding theories. However, useful references are given below:

Ligand-Field Theory

C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

D. S. McClure, *Electronic Spectra of Molecules and Ions in Crystals* (Academic Press, New York, 1959).

J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, London, 1964).

S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition Metal Ions in Crystals* (Academic Press, New York, 1970).

B. N. Figgis, *Introduction to Ligand Fields* (Interscience, New York, 1967).

Molecular-Orbital Theory

C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* (Benjamin Cummings, Reading, 1964).

C. J. Ballhausen and H. B. Gray, in *Coordination Chemistry*, Vol. 1, edited by A. E. Martell (Reinhold, New York, 1971), pp. 3–83.

C. J. Ballhausen, *Molecular Electronic Structures of Transition Metal Complexes* (McGraw-Hill, New York, 1979).

J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 1, *Electronic Structure of Molecules* (McGraw-Hill, New York, 1963).

SCF-Xα-SW

K. H. Johnson, Advan. Quantum Chem. 7, 143 (1973).

K. H. Johnson, J. G. Norman, Jr., J. W. D. Connolly, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, R. K. Nesbet (Plenum, New York, 1973).

J. W. D. Connolly, in *Semiempirical Methods of Electronic Structure Calculation, Part A: Techniques*, edited by G. A. Segal (Plenum, New York, 1977).

N. Rosch, in *Electrons in Finite and Infinite Structures*, edited by P. Phariseu, L. Scheire (Plenum, New York, 1977).

J. C. Slater, *The Calculation of Molecular Orbitals* (Wiley, New York, 1979).