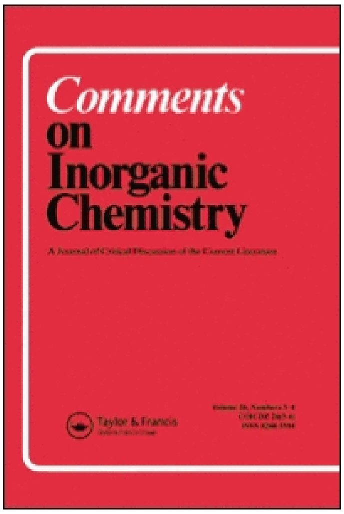

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Final Comments

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To cite this Article Solomon, Edward I.(1984) 'Final Comments', Comments on Inorganic Chemistry, 3: 5, 319 — 320
To link to this Article: DOI: 10.1080/02603598408080080
URL: http://dx.doi.org/10.1080/02603598408080080

IX. FINAL COMMENTS

In completing this overview of the basic principles and information content of different methods in inorganic spectroscopy, a few final comments seem appropriate. First, a fairly consistent experimental and theoretical picture of the ground state of $CuCl_4^{=}$ is developing. The molecular wavefunction can be viewed as having approximately 65% Cu $d_{x^2-y^2}$ character, with the rest being delocalized onto the 3 p_z orbitals of the chloride ligands. A small amount of Cl 3s also contributes (~3%), as does a few percent Cu 4s and Cu 4p in lower symmetry geometries. This description of covalency in $CuCl_4^{=}$ should permit relative estimates of covalency in other complexes as the ligands and/or metal ion are varied.

Several more specialized techniques provide high resolution information on electronic excited states. Even in the absence of excited state vibrational structure (discussed in Section VIII) resonance Raman spectroscopy can probe vibronic coupling and in particular excited state distortions in some detail. Further, magnetic circular dichroism (MCD) allows the Zeeman effect [which is determined for the ground state by EPR (see Section II)] to be studied in excited states having broad absorption bands. Together with polarized single crystal electronic absorption spectroscopy, these methods enable one to obtain a detailed picture of the electronic and geometric changes which occur upon excitation. Thus, excited states can be viewed as ideal systems for evaluating the effects of well-defined changes in electronic structure on the properties of an inorganic complex. One example, in which we have been involved, is the correlation of change in structure with inorganic photochemical reactions and excited state radiationless processes.[1] A second is an estimate of the magnitude of Jahn-Teller effects and their role in determining the geometric and electronic structure of a transition metal complex.[2]

Finally at the forefront of inorganic spectroscopy is the extension of the concepts which have been developed for high symmetry complexes to the unique spectral features associated with metal ion *active sites*[3] in metalloenzymes and heterogeneous catalysts. For these systems the contributions of a variety of inorganic spectroscopic methods, together with systematic chemical perturbations, can allow one to evaluate the role of unusual geometries and electronic structures in metal ion reactivity.

References

1. (a) R. B. Wilson and E. I. Solomon, Inorg. Chem. **17**, 1729 (1978).
   (b) R. B. Wilson and E. I. Solomon, J. Am. Chem. Soc. **102**, 4085 (1980).
   (c) V. M. Miskowski, H. B. Gray, R. B. Wilson, and E. I. Solomon, Inorg. Chem. **18**, 1410 (1979).
   (d) W. C. Trogler, S. R. Desjardins and E. I. Solomon, Inorg. Chem. **18**, 2131 (1979).
   (e) A. Lempicki, L. Andrews, S. J. Nettel, B. C. McCollum, and E. I. Solomon, Phys. Rev. Lett. **44**, 1284 (1980).
2. (a) M. Y. Chen, D. S. McClure, and E. I. Solomon, Phys. Rev. B **6**, 1690 (1972).
   (b) E. I. Solomon and D. S. McClure, Phys. Rev. B **6**, 1697 (1972).
   (c) E. I. Solomon and D. S. McClure, Phys. Rev. B **9**, 4690 (1974).
   (d) J. Ferré, R. H. Petit and E. I. Solomon, J. Physique **40**, 175 (1979).
3. E. I. Solomon, K. W. Penfield, and D. E. Wilcox, in *Structure and Bonding*, (Springer-Verlag, New York, 1983), Vol. 53.

Acknowledgments

I am grateful to Joseph Deaton, Mark Fletcher and Margaret Helton for all their help in the preparation of this manuscript. The scientific input into the research summarized in this article by my students, Susan Cohen, Andrew Gewirth, Joeseph Deaton, Lung-Shan Kau, Mark Allendorf, Dr. Kevin Penfield, Dr. Sylvia Desjardins and Dr. Randall Wilson and my collaborators, Dr. James Penner-Hahn, Professor Keith Hodgson and Professor Ronald Musselman is also greatly appreciated. We thank the National Science Foundation, grant CHE-82-04841, for funding this research.

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