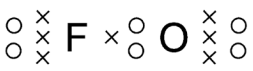
Letters

More on ClO and Related Radicals

I read with interest the recent article by Hirsch and Kobrak in which they present evidence for a new "novel" Lewis structure for the ClO radical and other related 13e isoelectronic species *(1)*. I would like to call attention to the fact that this structure is identical to that proposed by Linnett over 40 years ago for the same species on the basis of his well-known double-quartet approach to Lewis structures *(2),*



save that Linnett used naughts and crosses to indicate the different spin sets rather than black and white dots *(3)*. Though Linnett specifically illustrated his proposed structure using the OF radical, he indicated that it also applied to other 13e radicals such as ClO and the superoxide anion O_2^-.

Linnett also demonstrated in some detail how his modified Lewis structures correlated with the corresponding MO configurations *(4)* and, in the specific case of ClO, presented experimental evidence, in the form of force constant measurements, in support of his proposed structure as well as noting that it was consistent with the Cl atom bearing a formal charge of 0.5+ *(5)*. Since the bond polarity in OF is the opposite of that in ClO, it was further noted that the assignment of such a formal charge to the halogen atoms implied that the fluorine analog would most likely be far more unstable than the corresponding chlorine analog.

Though Linnett's double-quartet approach made some inroads into the textbook literature in the 1960s *(6),* it appears to have since dropped out of sight, even though it provides for a much more flexible approach to Lewis structures than does the conventional textbook version based solely on the use of 2c-2e bonds and resonance.

Literature Cited

1. Hirsh, W.; Kobrak, M. *J. Chem. Educ.* **2007**, *84*, 1360–1363.
2. Linnett, J. W. *The Electronic Structure of Molecules;* Wiley: New York, 1964; pp 50–52.
3. However, other writers on Linnett theory, such as Luder, used the identical black and white dot notation of Hirsch and Kobrak. See Luder, W. F. *The Electron Repulsion Theory of the Chemical Bond;* Reinhold: New York, 1967.
4. Linnett, J. W. *The Electronic Structure of Molecules;* Wiley: New York, 1964; Chapter 9.
5. Linnett, J. W. Molecular Forces Fields and Valency. In *Essays in Structural Chemistry;* Downs, A. J., Ed.; Plenum: New York, 1971; Chapter. 1.
6. See, for example, Pimentel, G. C.; Spratley, R. D. *Chemical Bonding Clarified Through Quantum Mechanics;* Holden-Day: San Francisco, 1969; pp 148–153. These authors suggest that Linnett's approach was proposed 20 years too late. Perhaps, with regard to the level of bonding theory used in introductory books, it was 40 years too soon.

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