

Enemark J H & Feltham R D. Principles of structure, bonding, and reactivity for metal nitrosyl complexes. *Coord. Chem. Rev.* 13:339-406, 1974.
[Department of Chemistry, University of Arizona, Tucson, AZ]

The structural isomers, linear and bent, found for metal nitrosyls (MNOs) are unique, and each isomer exhibits characteristic chemical reactions. This interpretive review interrelates the structure of the MNO complexes with their chemical reactions and spectroscopic properties by use of molecular orbital theory. The properties of all MNO complexes can be classified by n , the number of d -type electrons in the $\{MNO\}^n$ fragment. [The *SCI*® indicates that this paper has been cited in over 375 publications.]

John H. Enemark
and
Robert D. Feltham
Department of Chemistry
University of Arizona
Tucson, AZ 85721

May 30, 1988

Upon returning to Arizona from the Tenth International Conference on Coordination Chemistry in Japan in 1967, one of us (RDF) received a letter from the editor of *Coordination Chemistry Reviews*, Barry Lever. Over a cup of sake, RDF had agreed to write a review on transition metal nitrosyl complexes. Other events and commitments at Arizona precluded working on such a review for at least several months, so Lever's letter was filed away.

A few months later, JHE joined the Arizona faculty and we began a fruitful collaboration on transition metal nitrosyl complexes. In 1973 our joint research efforts resulted in another letter from Lever that stated, "Many moons

ago you indicated your interest in writing an article on nitrosyl chemistry...."

The time was now ripe for an interpretive overview of metal nitrosyl (MNO) chemistry. At the time one of the main questions being asked was: Why are some MNO groups linear, and why are some so strongly bent? We began to spend our regular afternoon coffee break in the student union, discussing MNO chemistry and planning an interpretive review. Often, we would return to our offices with several paper napkins filled with questions, bonding diagrams, and new ideas to explore. Many of these napkins became raw material for the first draft, and it was interesting to re-discover some of them while preparing this commentary.

The molecular structures of many MNO complexes had been determined and several theoretical and spectroscopic studies of MNOs had also been completed.¹⁻³ The challenge was to find some unifying principles that would explain existing data and help one plan and interpret new experiments. We chose to focus on the $\{MNO\}^n$ fragment and show how its geometry depended upon the other ligands coordinated to M and upon the number of d -type electrons (n) in the triatomic fragment. The frequent citing of this review probably is due in part to the formal development of the triatomic fragment approach for MNOs and to the breadth of coverage of synthesis, physical measurements, and theory in a single article. Recently, this $\{MNO\}^n$ formalism has been modified and used for describing redox processes in the chemistry of nitric oxide on surfaces.⁴

Finally, this review would not have been possible without the excellent work of many colleagues then involved in research on MNO complexes and with whom we shared uncounted hours discussing this fascinating subject. We take this opportunity to thank them again for their help and to thank Lever for his tenacity in soliciting the review.

1. Frenz B A & Ibers J A. Structural chemistry of transition metal complexes: (1) 5-coordination, (2) nitrosyl complexes. *MTP Int. Rev. Sci. Phys. Chem. Ser. One* 11:33-72, 1972. (Cited 80 times.)
2. Fenske R F & DeKock R L. Intramolecular effects on the bonding in transition metal-pentacyanonitrosyl complexes. *Inorg. Chem.* 11:437-44, 1972. (Cited 75 times.)
3. Johnson B F G & McCleverty J A. Nitric oxide compounds of transition metals. *Prog. Inorgan. Chem.* 7:277-356, 1966. (Cited 175 times.)
4. Rouston J L & Morrow B A. A notation for describing redox processes in the surface chemistry of nitrosyl complexes. *Inorg. Chem.* 27:1666-8, 1988.