

Figure 3. An orbital correlation diagram showing the splitting of the molecular orbitals of the $\{MNO\}^n$ group from Figure 1c in a field of C_{4v} symmetry. The dependence of the M–N–O angle upon *n* is shown for each symmetry.

sents the transition state for the conversion of the MNO group from linear geometry to bent geometry. Several electronic states arise from such a degenerate crossing point, and a simple electrostatic calculation has been carried out for a representative example in C_{4v} symmetry.¹² The results of the calculation and relationship of the state symmetry diagram to the reactions of mononitrosyl complexes are discussed in the succeeding paper.13

Finally, we suggest that the concept of inorganic functional groups has general utility for understanding covalently bound transition metal complexes. The concept should be especially applicable to metal complexes of other small molecules (such as O_2 and N_2) and to metal cluster compounds.^{14,15}

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Stereochemical Control of Valence. III. The {CoNO}⁸ Group in Ligand Fields of C_{4v} , C_{2v} , and C_s Symmetry

Sir:

The role of symmetry in chemical reactions has received much attention.¹ Consideration of molecular orbital symmetry alone provides significant insight into the chemical reactivity of strongly bound compounds with no low-lying excited states.^{1a,d} However, molecular orbital symmetry by itself may be insufficient for understanding the reactions of transition metal complexes.^{1c} In the preceding communication² we introduced the concept of an inorganic functional group and showed that the properties of mononitrosyl complexes could be understood by examining the behavior of the $\{MNO\}^n$ group³ in ligand fields. In this communication, the concept is applied to the specific problem of understanding the properties of the {CoNO}⁸ group in ligand fields of various symmetries.

Five-coordinate complexes containing the {CoNO}⁸ group exhibit Co-N-O angles ranging from 120 to 180°. Moreover, to date all linear {CoNO}⁸ groups occur in trigonal bipyramidal (TBP) geometry and strongly bent {CoNO}⁸ groups occur in tetragonal pyramidal (TP) geometry.⁴ The molecular orbital correlation diagram appropriate for these complexes is shown in Figure 1. The maximum symmetry possible for CoNOL₄ is C_{4v} , and two possible molecular orbital orderings for it are shown in Figures 1b and 1c. If the molecular ordering is that depicted in Figure 1c, then the electron configuration will be $(2e)^4(1b_2)^2(3e)^2$. With the totally antibonding 3e orbital doubly occupied, the $\{CoNO\}^{8}$ group will bend² producing $CoNOL_{4}$ with C_s symmetry (Figure 1d). If the 4a₁ orbital is lowest (Figure 1b) then the electron configuration is $(2e)^4$ - $(1b_2)^2(4a_1)^2$. With two electrons in $4a_1$, the $\{CoNO\}^8$ group will not bend, but the CoNOL₄ complex will distort to TBP geometry with C_{2v} symmetry. This distortion to TBP geometry makes $4a_1(d_{z^2})$ less antibonding thereby lowering the energy of the complex. A TBP distortion also allows the yz component of the e orbitals to interact with the σ orbitals of the other two ligands in the equatorial plane of the TBP complex, thereby facilitating delocalization of electron density from the σ orbitals of the equatorial ligands into the π^* orbitals of the NO group. Thus, for five-coordinate complexes of the $\{CoNO\}^{*}$ group, the choice between a TBP structure of C_{2v} symmetry (Figure 1a) and a TP structure with C_s symmetry (Figure 1d) is dictated by the relative energies of the $4a_1$ and 3e orbitals of the hypothetical C_{4v} species.⁵

The presence of two electrons in the $4a_1$ and 3emolecular orbitals gives rise to several electronic states.9 Figure 2 shows the relative energies of the manifold of singlet states arising from the $(4a_1, 3e)^2$ electronic configurations in C_{4v} symmetry and the behavior of these states in C_{2v} and C_s symmetry. The far left-hand

(2) J. H. Enemark and R. D. Feltham, J. Amer. Chem. Soc., 96, 5002 (1974).

(3) n is the number of electrons associated with the metal d orbitals and the $\pi * (NO)$ orbitals of the MNO group; *n* corresponds to the familiar number of d electrons on the metal when the nitrosyl ligand is formally considered to be NO. $^+$

(4) (a) B. A. Frenz and J. A. Ibers, MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Phys. Chem., Ser. One, 11, 33 (1972); (b) J. H. Enemark and R. D. Feltham, Coord. Chem. Rev., 13, 339 (1974).

(5) Molecular orbital correlation diagrams to account for the bending of MNO in M(NO)L₁ complexes have been proposed previously.⁶ However, those diagrams consider only ordering 1b of the C_{4v} case and correlate that ordering to both structures 1a and 1d. Such a scheme has no predictive power and is not consistent with Walsh's results8 for small molecules upon which the correlations are purportedly based.

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⁽¹⁾ See especially (a) R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 87, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abra-hamson, *ibid.*, 87, 2045 (1965); (c) T. H. Whitesides, *ibid.*, 91, 2395 (1969); (d) R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry," Verlag Chemie Gmbh, Academic Press, Weinheim, 1970; (e) R. G. Pearson, Accounts Chem. Res., 4, 152 (1971).



Figure 1. Molecular orbital correlation diagram for five-coordinate complexes of the $\{CoNO\}^{s}$ group in ligand fields of C_{2v} , C_{4v} , and C_{s} symmetry. The orbitals are occupied by a total of eight electrons.

side of Figure 2 corresponds to $4a_1 \ll 3e$ and the molecule will have C_{2v} symmetry, a linear MNO group, and a nondegenerate singlet ground state $({}^{1}A_{1})$. Likewise, the far right-hand side corresponds to $3e \ll 4a_{1}$ and a molecule with C_s symmetry, a strongly bent MNO group, and a nondegenerate singlet ground state $({}^{1}A')$. The right- and left-hand extremes of the state diagram are consistent with the conclusions drawn from the molecular orbital diagrams of Figure 1a and 1d and show that the conversion of a linear $\{MNO\}^{s}$ group into a bent $\{MNO\}^{s}$ group requires the crossing of the $4a_{1}$ and 3e orbitals.

At the crossing point in C_{4v} symmetry (Figure 2), a fivefold degeneracy of the singlet states arising from $(4a_1, 3e)^2$ may exist.⁹ Vibronic coupling can mix these states and lead to a distorted ground state geometry for the CoNOL₄ molecule.^{4b, 9, 9a} Since there are several degenerate electronic states and several vibrational modes for the $CoNOL_4$ complex, more than one form of the CoNOL₄ complex may exist whenever $4a_1$ and 3e are degenerate. Conversely, the existence of two forms of a CoNOL₄ complex indicates that the complex is near the crossover and that the $4a_1$ and 3e orbitals are nearly degenerate. $Co(NO)Cl_2[P(CH_3)(C_6H_5)_2]_2$ exhibits two distinct ν_{NO} bands, and it has been proposed that a TBP complex with a linear CoNO group and a TP complex with a bent CoNO group are both present in equilibrium.^{10a} However, the structure of one of the forms of this complex exhibits an intermediate Co-N-O bond angle (165°) and a very irregular coordination geometry.^{10b} This distorted form of Co(NO)- $Cl_2[P(CH_3)(C_6H_5)_2]_2$ is inconsistent with the previous proposal for an interconversion between TBP and TP geometries but is consistent with the vibronic coupling model. The vibronic coupling model precludes the existence of a form of $C_0(NO)[P[CH_3](C_6H_5)]_2$ with a



Figure 2. Composite state correlation diagram for C_{2v} , C_{4v} , and C_s symmetries showing the behavior of the singlet states arising from a $(4a_1, 3e)^2$ electron configuration in C_{4v} symmetry.

Co–N–O bond angle of 180° and thus, the second form of this complex should differ primarily in the rotational orientation of the nonlinear CoNO group.^{4b} An equivalent way of describing the two forms of Co(NO)- $Cl_2[P(CH_3)(C_6H_5)_2]_2$ is to consider them as vibronomers of a somewhat bent CoNO group with a small barrier to rotation.¹¹ To our knowledge, the only well-documented example of the conversion of a linear {CoNO}⁸ group to a strongly bent {CoNO}⁸ group by a change in stereochemistry of the metal is the reaction¹²

 $Co(NO)(das)_2^{2+} + NCS^- \longrightarrow Co(NO)(das)_2NCS^+$

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(11) This barrier is due to the necessity of rotating the bent CoNO group from the position in which the xz component of 3e is doubly occupied to that in which the yz component is doubly occupied. This interchange of xz and yz components can be brought about via the lowest lying ${}^{1}A''$ excited state and consequently, the energy separation between ${}^{1}A'$ and ${}^{1}A''$ represents the barrier to rotation of the bent CoNO group. For complexes with maximum C_{2v} symmetry the energies of the ${}^{1}A'(xz)^{2}$ and ${}^{1}A''(yz)^{2}$ states can differ and two distinct conformers are possible.

(12) J. H. Enemark and R. D. Feltham, Proc. Nat. Acad. Sci. U. S., 69, 3534 (1972).

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Oxathiiranes. Differential Orbital Correlation Effects in the Electrocyclic Formation of Sulfur-Containing Three-Membered Rings¹

Sir:

A structurally simple sulfine, thiopropenal S-oxide (1), is generated enzymatically from S-(1-propenyl) cysteine sulfoxide² in the plant species Allium cepa and has been identified as the lachrymatory factor of onions. The compound decomposes within hours at room tem-

⁽⁹a) NOTE ADDED IN PROOF. On the basis of extended Hückel molecular orbital calculations, it has been similarly concluded (R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, submitted for publication) that the relative energies of $4a_1$ and 3e (Figure 1) are important in determining the ground state geometries of {MNO}[§]L₄ complexes. These calculations also predict intermediate coordination geometries and intermediate M-N-O angles may occur when $4a_1$ and 3e are nearly degenerate. The authors thank Professor Hoffmann for providing a preprint of his paper prior to publication.

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