

| $\frac{2 \pi\left(x z, y z, \pi^{*}(N O)\right)}{}$ | $\frac{2 e\left(x z, y z, \pi^{*}(N O)\right)}{}$ |
| :--- | :--- |
| linear $n \leqslant 4$ | linear $n \leqslant 6$ |
| bent $n>4$ | bent $n>6$ |

Figure 3. An orbital correlation diagram showing the splitting of the molecular orbitals of the $\left\{\mathrm{MNO}^{n}\right.$ group from Figure 1 c in a field of $C_{4 v}$ symmetry. The dependence of the $\mathrm{M}-\mathrm{N}-\mathrm{O}$ 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 $C_{4 v}$ 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 $\mathrm{O}_{2}$ and $\mathrm{N}_{2}$ ) and to metal cluster compounds. ${ }^{14,15}$

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John H. Enemark, Robert D. Feltham*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721
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Stereochemical Control of Valence. III. The $\{\mathrm{CoNO}\}^{8}$ Group in Ligand Fields of $C_{4 v}, C_{2 v}$, 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

[^0]the chemical reactivity of strongly bound compounds with no low-lying excited states. ${ }^{\text {a }, \text { d }}$ However, molecular orbital symmetry by itself may be insufficient for understanding the reactions of transition metal complexes. ${ }^{10}$ In the preceding communication ${ }^{2}$ 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 $\{\mathrm{MNO}\}^{n}$ group $^{3}$ in ligand fields. In this communication, the concept is applied to the specific problem of understanding the properties of the $\{\mathrm{CoNO}\}^{8}$ group in ligand fields of various symmetries.

Five-coordinate complexes containing the $\{\mathrm{CoNO}\}^{8}$ group exhibit $\mathrm{Co}-\mathrm{N}-\mathrm{O}$ angles ranging from 120 to $180^{\circ}$. Moreover, to date all linear $\{\mathrm{CoNO}\}^{8}$ groups occur in trigonal bipyramidal (TBP) geometry and strongly bent $\{\mathrm{CoNO}\}^{8}$ 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 $\mathrm{CoNOL}_{4}$ is $C_{4 v}$, and two possible molecular orbital orderings for it are shown in Figures 1 b and 1c. If the molecular ordering is that depicted in Figure 1c, then the electron configuration will be $(2 \mathrm{e})^{4}\left(1 \mathrm{~b}_{2}\right)^{2}(3 \mathrm{e})^{2}$. With the totally antibonding 3 e orbital doubly occupied, the $\{\mathrm{CoNO}\}^{8}$ group will bend ${ }^{2}$ producing $\mathrm{CoNOL}_{4}$ with $C_{s}$ symmetry (Figure 1 d ). If the $4 \mathrm{a}_{1}$ orbital is lowest (Figure lb) then the electron configuration is (2e) ${ }^{4}-$ $\left(1 b_{2}\right)^{2}\left(4 a_{1}\right)^{2}$. With two electrons in $4 a_{1}$, the $\{\mathrm{CoNO}\}^{8}$ group will not bend, but the $\mathrm{CoNOL}_{4}$ complex will distort to TBP geometry with $C_{2 v}$ symmetry. This distortion to TBP geometry makes $4 \mathrm{a}_{1}\left(\mathrm{~d}_{2^{2}}\right)$ less antibonding thereby lowering the energy of the complex. A TBP distortion also allows the $y z$ component of the e orbitals to interact with the $\sigma$ orbitals of the other two ligands in the equatorial plane of the TBP complex, thereby facilitating delocalization of electron density from the $\sigma$ orbitals of the equatorial ligands into the $\pi^{*}$ orbitals of the NO group. Thus, for five-coordinate complexes of the $\{\mathrm{CoNO}\}^{*}$ group, the choice between a $T B P$ structure of $C_{2 v}$ symmetry (Figure la) and a $T P$ structure with $C_{s}$ symmetry (Figure 1d) is dictated by the relative energies of the $4 a_{1}$ and $3 e$ orbitals of the hypothetical $C_{4}$ species. ${ }^{5}$

The presence of two electrons in the $4 \mathrm{a}_{1}$ and 3 e molecular orbitals gives rise to several electronic states. ${ }^{9}$ Figure 2 shows the relative energies of the manifold of singlet states arising from the $\left(4 a_{1}, 3 e\right)^{2}$ electronic configurations in $C_{40}$ symmetry and the behavior of these states in $C_{2 v}$ and $C_{s}$ symmetry. The far left-hand

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Figure 1. Molecular orbital correlation diagram for five-coordinate complexes of the $\{\mathrm{CoNO}\}^{8}$ group in ligand fields of $\mathrm{C}_{2 v}, C_{4 v}$, and $C_{s}$ symmetry. The orbitals are occupied by a total of eight electrons.
side of Figure 2 corresponds to $4 a_{1} \ll 3 \mathrm{e}$ and the molecule will have $C_{2 v}$ symmetry, a linear MNO group, and a nondegenerate singlet ground state ( ${ }^{1} \mathrm{~A}_{1}$ ). Likewise, the far right-hand side corresponds to $3 \mathrm{e} \ll 4 \mathrm{a}_{1}$ and a molecule with $C_{s}$ symmetry, a strongly bent MNO group, and a nondegenerate singlet ground state ( ${ }^{1} \mathrm{~A}^{\prime}$ ). 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 $1 d$ and show that the conversion of a linear $\{\mathrm{MNO}\}^{8}$ group into a bent $\{\mathrm{MNO}\}^{8}$ group requires the crossing of the $4 \mathrm{a}_{1}$ and 3 e orbitals.

At the crossing point in $C_{4 v}$ symmetry (Figure 2), a fivefold degeneracy of the singlet states arising from ( $\left.4 \mathrm{a}_{1}, 3 \mathrm{e}\right)^{2}$ may exist. ${ }^{9}$ Vibronic coupling can mix these states and lead to a distorted ground state geometry for the $\mathrm{CoNOL}_{4}$ molecule. ${ }^{4 b, 9,9 a}$ Since there are several degenerate electronic states and several vibrational modes for the $\mathrm{CoNOL}_{4}$ complex, more than one form of the $\mathrm{CoNOL}_{4}$ complex may exist whenever $4 \mathrm{a}_{1}$ and 3 e are degenerate. Conversely, the existence of two forms of a $\mathrm{CoNOL}_{4}$ complex indicates that the complex is near the crossover and that the $4 a_{1}$ and 3 e orbitals are nearly degenerate. $\mathrm{Co}(\mathrm{NO}) \mathrm{Cl}_{2}\left[\mathrm{P}_{\left(\mathrm{CH}_{3}\right)}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2}\right]_{2}$ exhibits two distinct $\nu_{\mathrm{x}}$ o 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. ${ }^{10 a}$ However, the structure of one of the forms of this complex exhibits an intermediate $\mathrm{Co}-\mathrm{N}-\mathrm{O}$ bond angle ( $165^{\circ}$ ) and a very irregular coordination geometry. ${ }^{10 \mathrm{~b}}$ This distorted form of $\mathrm{Co}(\mathrm{NO})$ $\mathrm{Cl}_{2}\left[\mathrm{P}\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2}\right]_{2}$ 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 $\mathrm{Co}(\mathrm{NO})\left[\mathrm{P}\left[\mathrm{CH}_{3}\right]\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ with a

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Figure 2. Composite state correlation diagram for $C_{2 v}, C_{4 v}$, and $C_{s}$ symmetries showing the behavior of the singlet states arising from a $\left(4 \mathrm{a}_{1}, 3 \mathrm{e}\right)^{2}$ electron configuration in $C_{4 v}$ symmetry.
$\mathrm{Co}-\mathrm{N}-\mathrm{O}$ bond angle of $180^{\circ}$ and thus, the second form of this complex should differ primarily in the rotational orientation of the nonlinear CoNO group. ${ }^{\text {b }}$ An equivalent way of describing the two forms of $\mathrm{Co}(\mathrm{NO})$ $\mathrm{Cl}_{2}\left[\mathrm{P}\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2}\right]_{2}$ 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 $\{\mathrm{CoNO}\}^{8}$ group to a strongly bent $\{\mathrm{CoNO}\}^{8}$ group by a change in stereochemistry of the metal is the reaction ${ }^{12}$

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\mathrm{Co}(\mathrm{NO})(\mathrm{das})_{2}{ }^{2+}+\mathrm{NCS}^{-} \longrightarrow \mathrm{Co}(\mathrm{NO})(\mathrm{das})_{2} \mathrm{NCS}^{+}
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(11) This barrier is due to the necessity of rotating the bent CoNO group from the position in which the $x z$ component of 3 e is doubly oc. cupied to that in which the $y z$ component is doubly occupied. This interchange of $x z$ and $y z$ components can be brought about via the lowest lying " $\mathrm{A}^{\prime \prime}$ excited state and consequently, the energy separation between ' $A$ ' and ' $A$ '" represents the barrier to rotation of the bent CoNO group. For complexes with maximum $C_{2 v}$ symmetry the energies of the ${ }^{1} \mathbf{A}^{\prime}(x z)^{2}$ and ${ }^{\prime} \mathbf{A}^{\prime}(y z)^{2}$ states can differ and two distinct conformers are possible.
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John H. Enemark, Robert D. Feltham*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721
Received March 20, 1974

Oxathiiranes. Differential Orbital Correlation Effects in the Electrocyclic Formation of Sulfur-Containing Three-Membered Rings ${ }^{1}$

Sir:
A structurally simple sulfine, thiopropenal $S$-oxide (1), is generated enzymatically from $S$-(1-propenyl) cysteine sulfoxide ${ }^{2}$ in the plant species Allium cepa and has been identified as the lachrymatory factor of onions. The compound decomposes within hours at room tem-

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