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Relationes

Electrostatic Energies of the $\{CoNO\}^8$ Group in Ligand Fields

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

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The qualitative features of the electronic states of the $\{CoNO\}^8$ group are investigated by calculating the electrostatic energies of the $(d_{z^2}, d_{xz}, d_{yz})^2$, $(d_{xz}, d_{yz})^2$, and $(d_{z^2})^2$ electron configurations in D_4' symmetry. The geometries of the $\{CoNO\}^8$ group are correlated with the behavior of the singlet electronic states in the D_4' ligand field.

Key words: CoNO group in ligand fields

The geometry of most $\{MNO\}^n$ [1] groups is determined by the nature of the highest occupied molecular orbital [1]. However, some mononitrosyl complexes exhibit variable ground state geometries. For such complexes, a more detailed understanding of their properties can be obtained from an examination of their electronic states. The $\{CoNO\}^8$ group is of particular interest because bond angles ranging from 120° to 179° have been observed for it [1]. In five- and six-coordinate complexes of the *linear* $\{CoNO\}^8$ group, the highest occupied molecular orbital, either a_1 (d_{z^2} and σ ligand) or e (π^*_{NO} and d_{xz}, d_{yz}), is antibonding. When the a_1 orbital is lowest and doubly occupied the $\{CoNO\}^8$ group remains linear, but when the e orbital is lowest and doubly occupied the $\{CoNO\}^8$ group becomes strongly bent. A $\{CoNO\}^8$ complex with intermediate geometry also exists [2], and moreover, linear $\{CoNO\}^8$ and strongly bent $\{CoNO\}^8$ complexes can be interconverted chemically [3]. These results imply that in some complexes the a_1 and e orbitals may be nearly degenerate or become so during their reactions.

To understand the $\{CoNO\}^8$ group in more detail, the electrostatic energies of the various electronic states arising from the configurations of $(d_{z^2}, d_{xz}, d_{yz})^2$ have been calculated using the D_4' double group. Although these calculations neglect covalency, its inclusion would mainly serve to decrease the electrostatic repulsion energies. Consequently, the electrostatic energies here calculated represent the *upper limit* for the energy separation between the states of the $\{CoNO\}^8$ group. There are six electronic states which are derived from the $(d_{z^2}, d_{xz}, d_{yz})^2$ electron configurations: $^1A_1(d_{z^2})^2$; $^{1,3}E(d_{z^2})^1(d_{xz}, d_{yz})^1$; $^1A_1$, $^1B_1$, $^1B_2$, and ^3E (all from $(d_{xz}, d_{yz})^2$). The relative energies (in units of B) of these electronic states have been determined as a function of the energy separation between the d_{z^2} and d_{xz}, d_{yz} orbitals (also in units of B) using the methods of

[1] n corresponds to the total number of d electrons in the complex when nitric oxide is assumed to be coordinated as $(N \equiv O)^+$.

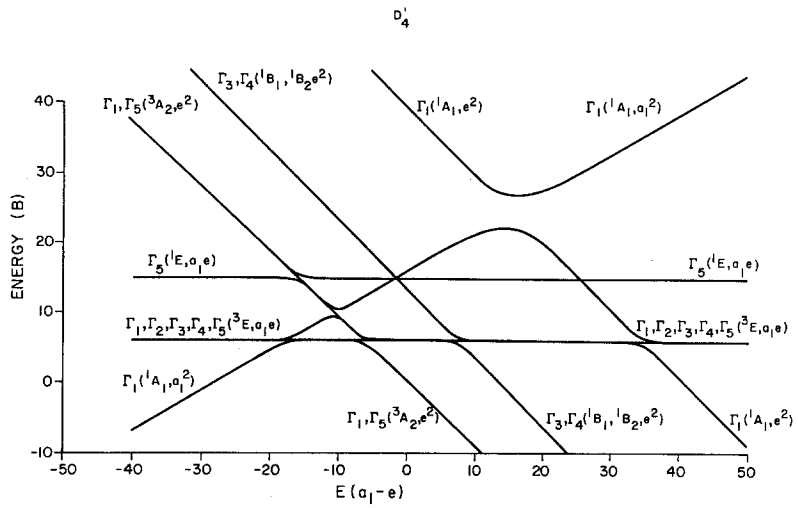

Fig. 1. The electrostatic energies of the states arising from $(a_1, e)^2$ configurations as a function of the energy separation between d_{xz}, d_{yz}, and d_{z^2} orbitals in the D_4' double group

Griffith [4]. Since these calculations are well understood, only the results are presented in Fig. 1.

Several conclusions can be drawn from Fig. 1. When $E(d_{z^2}) \ll E(d_{xz}, d_{yz})$, the ground state, Γ_1, is non-degenerate, and the system should be stable to all but an a_1 distortion. However, when $E(d_{xz}, d_{yz}) \ll E(d_{z^2})$, there is a symmetry imposed accidental degeneracy of the Γ_3 and Γ_4 states, and the system will be unstable. The degeneracy of the Γ_3 and Γ_4 states can be removed by bending the $\{CoNO\}^8$ group which destroys the four-fold axis, thereby lifting the degeneracy of the d_{xz} and d_{yz} orbitals from which Γ_3 and Γ_4 are derived. Finally, at the crossover point where the a_1 and e orbitals become degenerate, there is a five-fold degeneracy of the singlet electronic states ($\Gamma_1, \Gamma_3, \Gamma_4, \Gamma_5$). This system will also be unstable, but unlike the case of the degenerate Γ_3 and Γ_4 states, these singlet states are derived from both a_1 and e orbitals. *Vibronic coupling of the degenerate singlet states, Γ_1 through Γ_5, can cause simultaneous distortions of the coordination sphere and of the* Co–N–O *angle.*

In summary, there are three definable circumstances arising from the $(a_1 e)^2$ configurations: 1. $\Gamma_1(a_1)^2$ is lowest and the system is stable; 2. Γ_3, $\Gamma_4(e)^2$ are lowest, the system is unstable and the $\{CoNO\}^8$ group should bend; 3. Γ_1, Γ_3, Γ_4, and $\Gamma_5(a_1$ and $e)^2$ are lowest, the system is unstable and the $\{CoNO\}^8$ group and the coordination sphere about the cobalt should simultaneously distort. Finally, the manifold of triplet states has been ignored in the above discussion because no paramagnetic $\{CoNO\}^8$ complexes are yet known. The lack of ground state triplets may be a direct result of the decreased electrostatic repulsion due to the covalency of the MNO group.

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Prof. Dr. R. D. Feltham
Department of Chemistry
College of Liberal Arts
The University of Arizona
Tucson, Arizona 85721, USA