cation-exchange resins. Furthermore, mutarotation of the Λ-*S* diastereoisomer to equilibrium in 0.05 *M* NaOH resulted in a similar distribution of the Λ-*S* and Λ-*R* products. Thus in basic solution the free energy difference between the diastereoisomers is close to zero.

Clearly there is no substantial preference either kinetically or thermodynamically for the formation of one isomer relative to the other.

For a summary of results, see Scheme I.

**Registry No.** $[Co(en)_2CO_3]ClO_4$, 15155-12-1; Λ(+)-$[Co(en)_2(S\text{-glu})]ClO_4 \cdot H_2O$, 30617-15-3; Δ-$[Co(en)_2(S\text{-glu})]Cl_2$, 33293-37-7; ΛΔ-$[Co(en)_2(S\text{-glu})]^{2+}$, 38673-76-6; Δ-(−)D-$[Co(en)_2CO_3]ClO_4 \cdot {}^1/_2H_2O$, 38673-77-7; Δ-(−)D-$[Co(en)_2(OH)(H_2O)]^{2+}$, 38673-78-8; *S*-(+)-glutamic acid, 6899-05-4.

# Correspondence

## A General Bonding Model for Linear and Bent Transition Metal-Nitrosyl Complexes

*Sir*:

A recent paper which discussed a qualitative molecular orbital scheme for linear and bent transition metal-nitrosyl complexes[1] prompts me to report some Wolfsberg-Helmholtz calculations for the complex cation $[Co(NO)(NH_3)_5]^{2+}$ [2] (Co-N-O) = 180-90°). These calculations show that the angular distortion of the metal-diatomic ligand moiety from linearity influences the stabilities of only two metal-ligand molecular orbitals substantially. Such a simple result may be readily adapted to other metal-ligand systems and serves as a basis for a very general bonding model.

The calculations were performed using Slater atomic orbitals with exponents suggested by Gouterman.[3] These exponents emulate the overlap integrals of SCF functions for the bond distances of interest. The metal 3d, 4s, and 4p valence-state orbital ionization energies were expressed in a quadratic form to take into account their charge dependence. The necessary parameters were taken from Basch, Viste, and Gray.[4] For the ammine ligands $sp^3$ hybridization was assumed, and the nitrogen atoms' orbital ionization energies were set equal to the ionization potential of ammonia and the charge dependence suggested by Cotton and Haas[5] was used. Valence-orbital ionization energies suggested by Ballhausen and Gray were used for the nitrosyl nitrogen and oxygen atoms.[6] The off-diagonal elements for the 22 × 22 secular determinant were estimated from $H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2.00$ ($k = 2.25$) and the eigenvalues were calculated to self-consistent charge as judged by a Mulliken population analysis.[7]

Figure 1 shows the energies of the predominantly metal d orbitals and ligand $\pi^*$ orbitals for the nitrosyl complex with Co-N-O bond angles between 180 and 90° (other orbitals have been omitted from the figure for reasons of clarity). The following points emerge from the calculations.

(a) The $a_1(d_{z^2})$ antibonding metal-ligand $\sigma$ orbital and the $e_x(\pi^*(NO), d_{xz})$ metal-ligand antibonding orbital have the same symmetry and similar energies in the distorted molecule and consequently mix strongly to give rise to a more bonding, $a'(\pi^*(NO), d_{z^2})$, and less bonding, $a'(d_{z^2}, \pi^*(NO))$, pair of orbitals (for the molecule with Co-N-O ≠ 180° the point group is $C_s$ and all orbitals are either symmetric, a$'$, or antisymmetric, a$''$, with respect to the plane of symmetry). The energy separation between these orbitals is approximately proportional to the distortion angle (see Figure 1) and electron occupation of the more stable $a'(\pi^*(NO), d_{z^2})$ orbital will lead to an energetically favorable distortion. This behavior is analogous to the stabilization of the $2\pi_x{}^*$ antibonding orbital because of positive overlap with the hydrogen 1s orbital in HNO, when H-N-O ≠ 180°.[8]

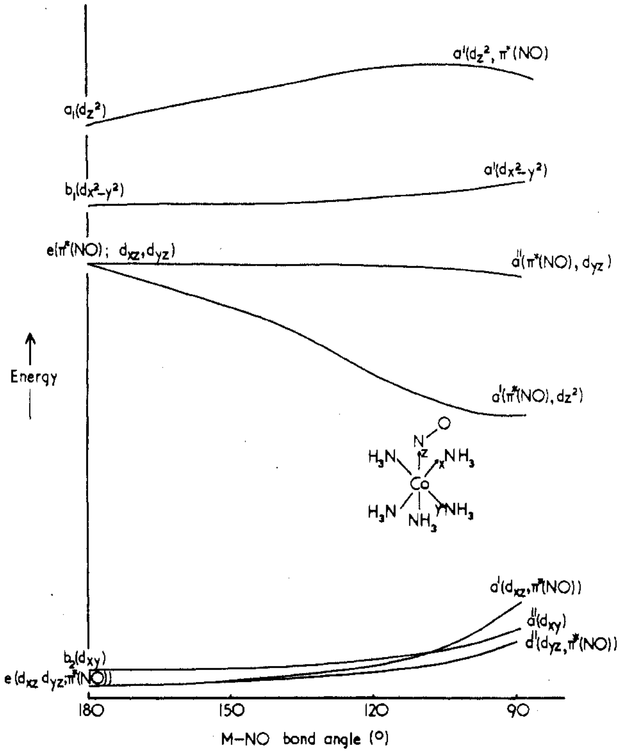

**Figure 1.** Variation of the molecular orbital energies with Co-N-O bond angle change for $[Co(NO)(NH_3)_5]^{2+}$.

(b) The $e_x(d_{xz}, \pi^*(NO))$ orbital is destabilized to a smaller extent by the distortion because of diminished "$\pi$-type" overlap with the ligand $\pi^*$ orbital.

(c) The energies of the other orbitals shown in the figure and the more stable molecular orbitals not shown in the fig-

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[1] C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, 93, 4905 (1971).

[2] B. A. Coyle, C. S. Pratt, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

[3] M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 4, 44 (1966); *Inorg. Chem.*, 5, 1699 (1966).

[4] H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, 44, 10 (1966).

[5] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 1004 (1964).

[6] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965.

[7] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

[8] (a) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953); (b) B. M. Gimarc, *J. Amer. Chem. Soc.*, 93, 815 (1971).

ure are only marginally affected by the Co-N-O bond angle change for Co-N-O = 180-90°.

(d) The stabilization of the $a'(\pi^*(NO), d_{z^2})$ orbital is governed by the stability of the $\pi^*$ orbital of the free ligand. Thus although $a'(\pi^*(NO), d_{z^2})$ is stabilized substantially on bending, the stabilization of $a'(\pi^*(XY), d_{z^2})$ ($XY = N_2$ or CO) in analogous carbonyl or dinitrogen complexes will be considerably smaller because the energies of metal $a_1(d_{z^2})$ and ligand $e(\pi^*(XY))$ orbitals are less well matched.

These calculations indicate that there will be an energy minimum at approximately Co-N-O = 120° for the $d^8$ nitrosyl complex which agrees reasonably well with the 120° bond angle commonly associated with tetragonal complexes of this type[1,2] (for electron-counting purposes coordinated nitric oxide is formulated as $NO^+$). It is evident from Figure 1 that for low-spin $d^n$ complexes ($n = 1, 6$) the linear metal-nitrosyl geometry is more stable.

As the energetics of distortion are largely determined by the energies of only two molecular orbitals, it becomes possible to generalize this model to other metal-ligand systems if reasonable estimates of the relative metal d orbital energies are made. Thus similar arguments apply to tetragonal five-coordinate complexes. Linear geometries are anticipated for $d^6$ complexes, and bent nitrosyl geometries with bond angles of approximately 120° for $d^8$ metal ions (see Figures 2a and b). $[Ir(CO)(NO)Cl(PPh_3)_2]^+$ (124 (1)°),[9] $Ir(NO)Cl_2(PPh_3)_2$ (123 (2)°),[10] and $[Ir(CO)(NO)I(PPh_3)_2]^+$ (125 (3)°)[11] are examples of such $d^8$ tetragonal complexes. An equatorially substituted trigonal-bipyramidal complex $MX_4(NO)$ ($C_{2v}$ symmetry) may be derived from the related square-pyramidal complex by bending back two of the ligands $X_1$ and $X_2$. Figures 2a and 2c suggest that the $a_1(d_{z^2})$ and $e_x(xz, \pi_x{}^*(NO))$ orbitals will be destabilized and $b_1(d_{x^2-y^2})$ stabilized by this motion and the other orbitals will be essentially unaffected. The resultant energy level scheme and electron occupation for the $d^8$ trigonal-bipyramidal complex (Figure 2c) will not favor a M-N-O bond angle change because the least stable occupied molecular orbital $(a_1(d_{x^2-y^2}))$ is essentially unaffected by bending.

X-Ray studies have shown that the majority of five-coordinate $d^8$ metal-nitrosyl complexes are square pyramidal and have M-N-O bond angles of approximately 120° (see above) but some five-coordinate trigonal-bipyramidal complexes with 180° M-N-O bond angles have been isolated. $[Ru(NO)(diphos)_2]^+$ (diphos = $(P(C_6H_5)_2)_2C_2H_4$)[12] and $Mn(NO)(CO)_4$[13] have equatorially substituted trigonal-bipyramidal configurations (Figure 2c) and $RuH(NO)(PPh_3)_3$[12] and $IrH(NO)(PPh_3)_3{}^+$ [14] have axial nitrosyl ligands ($C_{3v}$ symmetry). For the latter compounds it may be shown that energy level order is closely related to that shown in Figure 2c[1] and therefore similar arguments may be made to rationalize the observed linear metal-nitrosyl geometries.

Generally five-coordinate $d^8$ nitrosyl complexes have M-N-O bond angles close to either 180 or 120° ($[Ru(NO)_2(PPh_3)_2Cl]^+$ is an exception with Ru-N-O = 136° [15]), and any worthwhile model must justify this extreme behavior. A possible explanation for this behavior may be gained from the orbital correlation diagram for the interconversion of structures in Figures 2b and 2c which shows that the ground state of Figure 2b correlates with an excited state of Figure 2c (*i.e.*, $a''(yz)^2 a'(xz)^2 a''(xy)^2 a'(\pi^*(NO), d_{z^2})^2$ correlates with $b_2(yz)^2 a_2(xy)^2 b_1(xz)^2 b_1(\pi^*(NO))^2$). This means that there will be an activation energy for the interconversion[16] and the simplicity of the correlation diagram suggests that the energy profile for the interconversion probably has energy minima only for the extreme geometries.

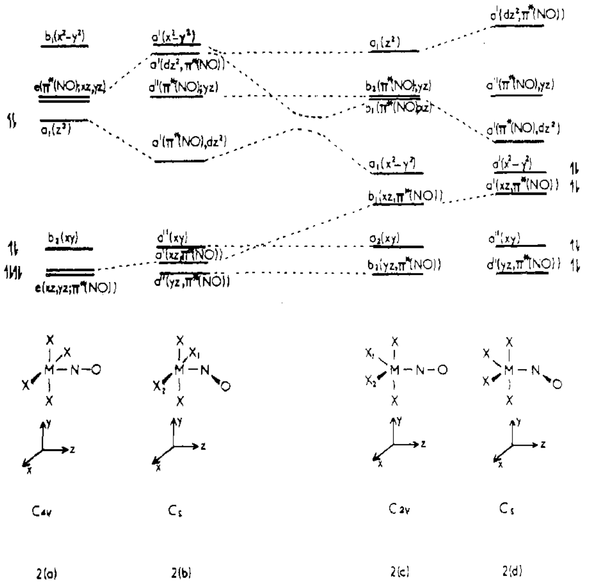

**Figure 2.** Suggested variation of molecular orbital energies for $M(NO)X_4$.

Consequently intermediate geometries are unlikely. The equilibrium concentrations of the two isomers will depend not only on the electronic factors indicated in the figure but also on the steric and electronic requirements of the ancillary ligands. For example, bulky and strong $\pi$-bonding ancillary ligands are likely to stabilize the trigonal-bipyramidal geometry.

Analogous arguments (see Figure 3) for four-coordinate $d^{10}$ tetrahedral and square-planar complexes $MX_3(NO)$ suggest that distortion of the metal-nitrosyl geometry is favorable for the square-planar complex (see Figures 3c and d) but not the tetrahedral complex (see Figures 3a and b). In the former, preferential occupation of $a'(\pi^*(NO), d_{z^2})$ will result in a more stable bent nitrosyl complex, but in the latter both $a'(\pi^*(NO), d_{z^2})$ and $a'(d_{z^2}, \pi^*(NO))$ are occupied leading effectively to cancelation of any stabilization energy for the bent configuration. Similar arguments have been proposed to explain the linear geometries of $I_3{}^-$ and $XeF_2$.[8] Consideration of the energy levels of Figure 3b (tetrahedral linear NO) and Figure 3c (square-planar bent NO) shows that the ground states for the molecules in these extreme geometries correlate (*i.e.*, $e(x^2-y^2,xy)^4\ a_1(z^2)^2\ e(\pi^*(NO);xz, yz)^4$ with $a''(yz, \pi^*(NO))^2\ a'(xz, \pi^*(NO))^2\ a''(xy)^2\ (a'(x^2-y^2)^2\ a'(\pi^*(NO), z^2)^2)$. This indicates a very low activation energy for the interconversion and the complexity of the correlation diagram suggests the possibility of potential energy minima for intermediate geometries. X-Ray structures of such four-coordinate complexes have established the tetrahedral linear nitrosyl geometry for $Ir(NO)(PPh_3)_3$[17] and intermediate

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[9] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

[10] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

[11] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969).

[12] C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3050 (1971).

[13] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

[14] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

[15] C. G. Pierpont, D. G. Van DerVeer, W. Burland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

[16] T. H. Whitesides, *J. Amer. Chem. Soc.*, **91**, 2395 (1969).

[17] V. G. Albano, P. L. Bellon, and M. Sansoni, personal communications (see ref 14 also).

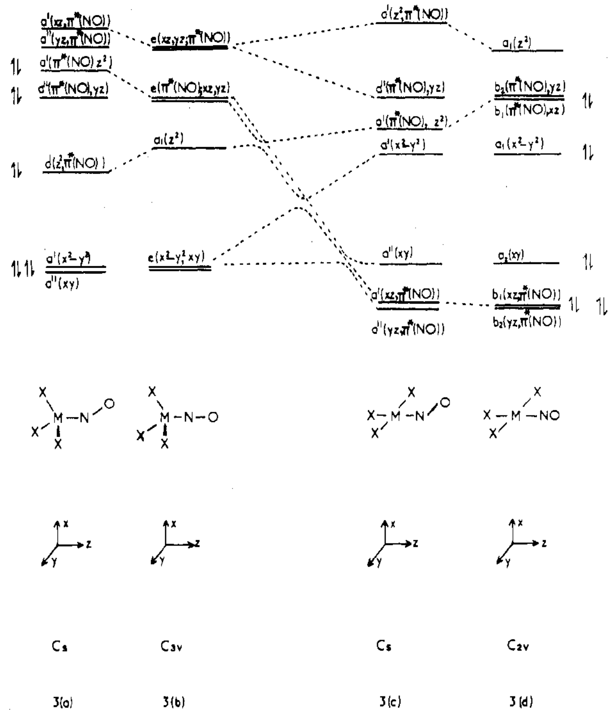

**Figure 3.** Suggested variation of molecular orbital energies for $M(NO)X_3$.

geometries for $Ni(N_3)(NO)(PPh_3)_2$,[18] $Ir(NO)_2(PPh_3)_2^+$,[19] and $[Co(NO)_2I]_n$[20] which have M-N-O bond angles between 166 and 153°. To date no complexes with the extreme square-planar bent nitrosyl geometry have been reported.

It is of interest to note that the feasibility of distorting the metal-nitrosyl geometry for the four-, five-, and six-coordinate complexes discussed above could have also been predicted on the basis of the second-order Jahn-Teller effect, which relates the symmetries of the ground and first excited states of the complex to the symmetry of the distorting vibrational mode.[21] The valence-bond formulation of bent nitrosyl complexes as Lewis acid adducts of $NO^+$ also bears a resemblance to the molecular orbital model because it emphasizes donation of a lone pair from a metal $d_{z^2}$ orbital to the empty ligand $\pi^*$ orbital.[22] The previous molecular orbital model[1] did not emphasize the strong interactions between $a_1(d_{z^2})$ and $e(\pi^*(NO), d_{xz})$ in the bent molecule and consequently cannot be generalized to all transition metal-nitrosyl complexes.[23] In particular it would be difficult to explain the observed linear nitrosyl geometries in certain $d^{10}$ complexes according to the Eisenberg-Pierpont model[1] which associates bending with occupation of a strongly antibonding $\sigma$ wave function. In a $d^{10}$ complex a $\sigma^*$ orbital must be occupied by two electrons, yet $d^{10}$ complexes with linear metal-nitrosyl geometries are well established, *e.g.*, $Ir(NO)(PPh_3)_3$. Also their localized assignment of orbitals according to $sp^2$(N) lone pair, $sp^2$(O) lone pair, etc., leads to an unduly complicated and formal correlation diagram. Such a scheme neglects the important point that nitric oxide, unlike carbon monoxide and dinitrogen, forms linear and bent complexes primarily because it has a low-lying $\pi^*$ orbital.

**Registry No.** $[Co(NO)(NH_3)_5]^{2+}$, 38402-80-1.

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[18] J. H. Enemark, *Inorg. Chem.*, 10, 1952 (1971).

[19] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970).

[20] L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 91, 1653 (1969).

[21] D. M. P. Mingos, *Nature Phys. Sci.*, 229, 193 (1971); 230, 154 (1971).

[22] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 90, 4486 (1968).

[23] It is interesting to note that calculations of overlap populations for $[Co(NO)(NH_3)_5]^{2+}$ show that the long Co-$NH_3$(trans) bond[2] also results from mixing of the $a_1(d_{z^2})$ and $e(\pi^*(NO), d_{xz})$ orbitals. The former molecular orbital, which is unoccupied when Co-N-O = 180°, is particularly antibonding between the metal and the nitrogen atom trans to the nitrosyl ligand and this antibonding character is imparted to the occupied $a'(\pi^*(NO), d_{z^2})$ orbital in the complex when Co-N-O ≠ 180°.

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## Spin Delocalization in $\sigma$ Systems. An Analysis of INDO Calculations

*Sir:*

In an appendage, inserted in proof to a recent article, DeSimone and Drago[1] (DeS and D) averred that in our INDO calculations[2] on a simulated pyridine $\sigma$ radical[3] we failed to "factor out"[4] the spin polarization (SP) of the $\pi$ system and that this negated our criticism of Cramer and Drago's[5] (C and D) extended Huckel molecular orbital (EHMO) analysis of spin delocalization in pyridine-type ligands coordinated to nickel(II). The purpose of this letter is to clarify the situation and to present additional insight into $\sigma$ spin delocalization in these systems by further analysis of the INDO results.

The controversy is to some extent a semantic one over what exactly is meant by the description $\sigma$ or $\pi$ radical or $\sigma$ or $\pi$ spin delocalization. By $\sigma$ radical we mean that the unpaired electron is contained in a one electron MO which has no out-of-plane ($p_z$) components. For the phenyl radical model employed in our calculations[3,6] this is the case, and the probability of finding the unpaired electron in the highest bonding $\sigma$ orbital is unity. This unpaired electron of course influences the spin *distribution* in the remaining filled MO's by SP. This applies to filled MO's of both $\pi$ and $\sigma$ symmetries. An analysis of our INDO results reveals the presence of three filled $\pi$ levels (these occur in pairs of $\alpha$ and $\beta$ spin[7] containing MO's in the open-shell INDO calculation) centered at 2.12, 2.32, and 11.65 eV below the $\alpha$-spin-containing $\sigma$ level. Taken as $\alpha,\beta$ pairs none of these $\pi$ levels contains any

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[1] R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, 11, 668 (1972).

[2] Intermediate neglect of differential overlap: J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968); P. A. Dobosh, CNINDO, Program 141, Quantum Chemistry Program Exchange, Indiana University, 1969.

[3] W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, 10, 1835 (1971).

[4] Just how this factorization was to be achieved in a rigorous manner was not specified.

[5] R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, 92, 66 (1970).

[6] A rationale and partial justification for our use of the hydrocarbon radicals as models for spin delocalization in coordinated pyridines is given at some length in the fourth paragraph and footnote 13 of ref 3. A further comment on this point is made in the final paragraph of the present article.

[7] $\alpha$ spin is here taken to indicate that the electron magnetic moment is parallel to the applied magnetic field, while $\beta$ spin indicates the opposite.