THE ELECTRONIC STRUCTURES OF METAL NITROSYLS AND CARBONYLS[1]

Sir:

This note presents a molecular orbital (m.o.) energy level scheme for the large class of metal nitrosyls and carbonyls which contain one particularly strong M–NO or M–CO bond; this interaction therefore dominates the over-all ligand field.

For a distorted octahedral structure of the type (C_{4v}) shown in Fig. 1, the bonding is described as follows: a strong σ bond (a_1) between the N(or C) 2s orbital and the nd_{z^2} metal orbital; two strong π-bonds (e) involving the metal nd_{xz} and nd_{yz} orbitals and the NO(CO) π ($2p_x$, $2p_y$) antibonding orbitals; a σ bond (b_1) between the metal $nd_{x^2-y^2}$ orbital and the ($\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$) ligand orbital combination; the nd_{xy} metal orbital is non-bonding if metal–L π-bonding is ignored; finally, the metal ($n + 1$)s and ($n + 1$)p orbitals form four more σ bonds (a_1, a_1, e) with the ligand orbitals.[2a,2b]

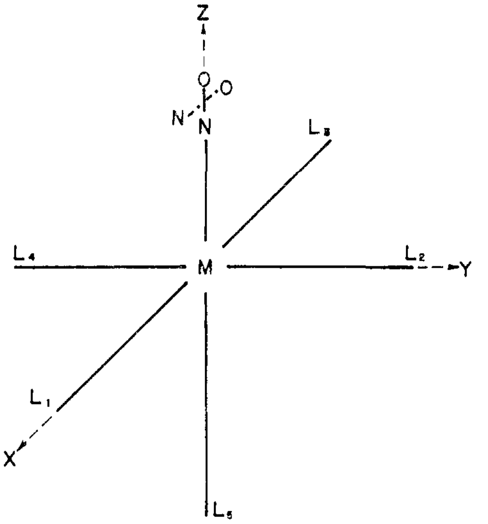

Fig. 1.—Distorted octahedral structure for $M(L)_5(NO)$ or $M(L)_5(CO)$ complexes.

The essential features of an m.o. energy level scheme for the bonding situation described above are given in Fig. 2. The ordering of the one electron m.o.'s is fixed for the model chosen, since $e(\pi^b)$ is more stable than b_2, and $a_1(\sigma^*)$ is more unstable than $b_1(\sigma^*)$. This is true whether or not the other axial ligand (L_5) is present.

The spectral and magnetic properties of $Fe(NO)[S_2CN(CH_3)_2]_2$ and $Mn(CO)_5X$ compounds will now be discussed in order to illustrate the usefulness of the derived m.o. scheme. The complex $Fe(NO)[S_2CN(CH_3)_2]_2$ probably has a rectangular-based pyramidal structure, analogous to the structure known[3] for $Co(NO)[S_2CN(CH_3)_2]_2$. In addition to the ligand σ electrons, which will always occupy the bonding σ levels, there are seven electrons (six from Fe, one from NO) to place in the m.o. level scheme shown in Fig. 2. This gives a ${}^2B_1$-$\{[e(\pi^b)]^4[b_2]^2[b_1(\sigma^*)]^1\}$ ground state. Thus the complex formally contains Fe^+ and NO^+; this formulation is consistent with the observation of an infrared band at 1735 cm.$^{-1}$ which is usually assigned[4] to coördinated NO^+.

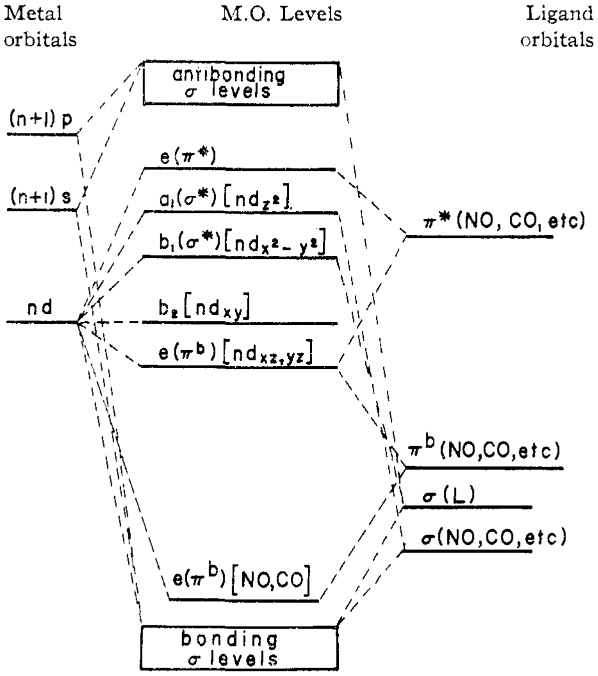

Fig. 2.—Molecular orbital energy level scheme for $M(L)_5(CO)$ or $M(L)_5(NO)$ complexes.

The solution electronic spectrum of $Fe(NO)[S_2CN(CH_3)_2]_2$ below 30,000 cm.$^{-1}$ consists of three charge transfer band systems, with single maxima at 17,100 cm.$^{-1}$ (ϵ = 1200 in benzene) and 20,900 cm.$^{-1}$ (ϵ = 1900 in benzene) and a double peaked band with maxima at 27,500 cm.$^{-1}$ (ϵ = 5750 in acetone) and 28,900 cm.$^{-1}$ (ϵ = 5750 in acetone). These charge transfer bands are assigned to the three one electron transitions $b_1(\sigma^*) \rightarrow e(\pi^*)$, $b_2 \rightarrow e(\pi^*)$ and $e(\pi^b) \rightarrow e(\pi^*)$ in order of increasing energy. Note that all the transitions are from m.o.'s mainly located on the metal to $e(\pi^*)$, which is essentially localized on NO.[5] Thus the energy differences of the charge transfer band maxima, after suitably correcting for differences in interelectronic repulsion energies of the excited states,[7] yield the positions of the one electron m.o. levels $b_1(\sigma^*)$, b_2 and $e(\pi^b)$. This type of calculation gives $\Delta E[b_1(\sigma^*) - b_2]$ = 9,150 cm.$^{-1}$ and ΔE $[b_1(\sigma^*) - e(\pi^b)]$ = 13,650 cm.$^{-1}$ Thus a band is predicted

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[2] (a) In this model the most stable σ and π metal orbitals are made available to the NO(CO) ligand. (b) For C_{4v} symmetry, see C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[3] P. R. H. Alderman, P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

[4] J. Lewis, *Science Progress*, 506 (1959).

[5] (a) A simple calculation shows that the expected energy of the metal d to $e(\pi^*)$ charge transfer is consistent with the assignments given here. The ionization potential of NO is 74,400 cm.$^{-1}$. The valence ionization potential for a d orbital electron in Fe^+ is about 82,000 cm.$^{-1}$.[9] Thus a reasonable value of 22,000 cm.$^{-1}$ for the π-interaction (the π-interaction in VO^{2+} is about 25,000 cm.$^{-1}$)[2b] correctly places the charge transfer bands. (b) The intense $e(\pi^b)[nd_{xz,yz}] \rightarrow e(\pi^*)$ charge transfer has been identified in a number of other metal nitrosyl complexes: the "brown ring" complex, $Fe(H_2O)_5NO^{2+}$, at 32,200 cm.$^{-1}$,[12] $Co(NO)[S_2CN(CH_3)_2]_2$, at 31,200 cm.$^{-1}$,[6] and $Cr(CN)_5NO^{3-}$, at 43,850 cm.$^{-1}$.[12]

[6] R. L. Carlin, private communication.

[7] H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

in the near infrared corresponding to the $b_2 \rightarrow b_1$ (σ^*) "d–d" transition. Such a band is observed at 10,250 cm.$^{-1}$ (ϵ = 8.3 in acetone), in excellent quantitative agreement with theory. All other "d–d" bands are expected to be hidden under the intense charge transfer spectrum.

An acetone solution of $Fe(NO)[S_2CN(CH_3)_2]_2$ shows a sharp e.s.r. spectrum consisting of three bands spaced by 12.5 gauss with $\langle g \rangle$ = 2.04. The $\langle g \rangle$ factor is expected for the $^2B_1$ ground state; the hyperfine splitting is due to the nitrogen of the NO group. The calculated one electron m.o. energies may be used, along with an estimate of 50 cm.$^{-1}$ for the spin-orbit coupling constant for Fe^+ in $Fe(NO)^{2+}$ to predict the anisotropy of the $\langle g \rangle$ value[8]; this gives $g_{\parallel} = 2.04$, $g_{\perp} = 2.03$. By analyzing the e.s.r. spectrum of $Fe(NO)[S_2CN(CH_3)_2]_2$ in Styrofoam,[9] the experimental values $g_{\parallel} = 2.04$, $g_{\perp} = 2.02$ were obtained, in close agreement with theory.

For the $Mn(CO)_5X$ series, radiocarbon monoxide exchange experiments indicate that the axial CO is bound much more strongly than the other four CO groups,[10] and thus these compounds fit the description of the model. There are six electrons from Mn to place in the m.o.'s, giving a $^1A_1\{[e(\pi^b)]^4[b_2]^2\}$ ground state. The first charge transfer band for solutions of these compounds in chloroform is observed[11] at 26,670 cm.$^{-1}$ (ϵ = 1200, $X^- = NO_3^-$), 26,520 cm.$^{-1}$ (ϵ = 620, $X^- = Cl^-$), 25,870 cm.$^{-1}$ (ϵ = 420, $X^- = Br^-$) and 24,750 cm.$^{-1}$ (ϵ = 390, $X^- = I^-$). These bands are assigned to the $b_2 \rightarrow e(\pi^*)$ transition. The $n \rightarrow \pi^*$ assignment also is supported by the fact that the maximum of the band for $Mn(CO)_5Br$ is shifted to higher energies on increasing the polarity of the solvent employed (350 cm.$^{-1}$ shift from benzene to ethanol).

The m.o. energy level scheme also has been used successfully to account for the spectral and magnetic properties of $M(H_2O)_5NO^{n+}$ [12] and $M(CN)_5NO^{n-}$ [12,13] type complexes.

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[8] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **A205**, 135 (1951).

[9] I. Bernal and H. B. Gray, to be published.

[10] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

[11] C. C. Addison, M. Kilner and A. Wojcicki, *J. Chem. Soc.*, 4839 (1961).

[12] H. B. Gray and P. T. Manoharan, unpublished results.

[13] H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, **36**, 1151 (1962).

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ON THE SIGNS OF CH AND HH COUPLING CONSTANTS

Sir:

Although theoretical calculations have indicated that both geminal and vicinal HH coupling constants should be positive in sign,[1] it has been found recently that their signs are opposite in several typical molecules.[1] In order to determine which of the two theoretical calculations leads to the correct result, one must know the absolute signs of the HH coupling constants. Karplus[1] has suggested that these signs may be obtained by comparisons with directly-bonded CH coupling constants, whose signs are almost certainly positive. We have determined the relative signs of directly-bonded CH and vicinal HH coupling constants in several molecules by double resonance experiments similar to those proposed by Karplus,[1] with the results outlined below.

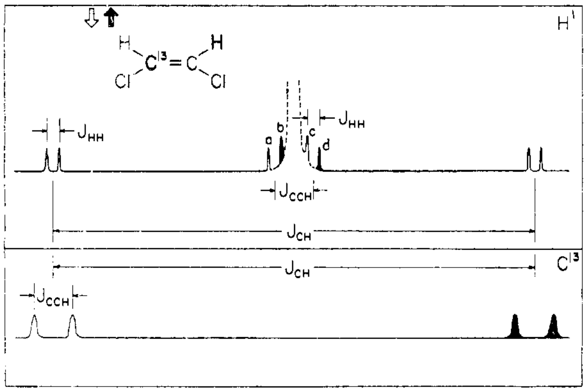
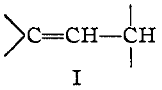


Fig. 1.—Diagrammatic spectra.

The first experiment, carried out on *cis*-1,2-dichloroethylene, containing C^{13} in natural abundance, will be described in some detail to illustrate the techniques and principles involved. Diagrammatic spectra are shown in Fig. 1. The black peaks in the H^1 and C^{13} spectra correspond to the "up" orientation of the proton directly bonded to C^{13}. Irradiation of the high field (low frequency) doublet in the C^{13} spectrum at a frequency of about 15.085 Mcps. and an rf. field of about 10 to 20 milligauss while observing the inner C^{13} satellites in the H^1 spectrum at 60 Mcps. caused peaks b and d to move inward. Irradiation of the low-field C^{13} doublet, at a frequency about 200 cps. (J_{CH}) higher, caused peaks a and c to draw together. It follows that the sign of the HH coupling constant is the same as that of the one-bond CH coupling constant. *trans* HH couplings in substituted ethylenes have been found to be of the same sign as *cis* couplings,[2] as have couplings between protons in the relationships I[3] and II.[4]



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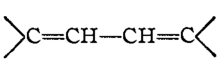

II

All, therefore, probably are positive.

To determine the signs of vicinal couplings in saturated compounds, a double resonance experiment similar to that described above was performed on 1,2-dichloroethane. The sum of the vicinal HH couplings was found to have the same sign as the CH coupling. Since large geminal couplings

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[1] See M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962), for a review and references.

[2] S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958); C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); S. Castellano and C. Caporiccio, *J. Chem. Phys.*, **36**, 566 (1962).

[3] F. S. Mortimer, *J. Mol. Spectroscopy*, **3**, 335 (1959); A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.*, **A252**, 488 (1959); B. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); R. Freeman, *Mol. Phys.*, **4**, 385 (1961).

[4] J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959).