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A Molecular Orbital Study of Nickel Dimethylglyoxime

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A molecular orbital treatment of nickel dimethylglyoxime has been performed using an extended Wolfsberg-Helmholtz method. No evidence was found for bonding between adjacent nickel ions in the ground state. Assignments are made for the 21 100 cm^{-1}, 23 700 cm^{-1} and 38 500 cm^{-1} bands in chloroform solution. The broad 18 000 to 29 000 cm^{-1} band, found in the crystal spectrum, is interpreted as an excitation to a crystal band formed by a b_{1u} orbital.

The use of dimethylglyoxime as an insoluble reagent for nickel ion is well known. The insolubility of nickel dimethylglyoxime has been attributed to nickel-nickel bonding in the crystal.[1] The crystal spectra [2,3] are also quite different than the solution spectra and this has been used as further evidence for nickel-nickel bonding [2] although there have been several other interpretations of the crystal spectra not requiring nickel-nickel bonding in the crystal.[3–5] In addition, there has been disagreement as to whether the solubility data for nickel dimethylglyoxime are indicative of nickel-nickel bonding.[5–8] In order to understand more fully the possibility of nickel-nickel bonding and the crystal spectra of nickel dimethylglyoxime a molecular orbital calculation of nickel dimethylglyoxime was undertaken and is described in this paper.

METHODS

The general method of calculation is described by Ballhausen and Gray.[9] In the secular equation the diagonal elements H_{ii} are set equal to $(VSIE)_i$ where $(VSIE)_i$ is the valence state ionization potential for the orbital i. For the off-diagonal elements K_{ij}, we take

$$H_{ij} = -2G_{ij}[(VSIE)_i \times (VSIE)_j]^{1/2}$$

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G_{ij} being the overlap integral between the atomic orbitals i and j. The charge on each atom was calculated by the Mulliken method and the VSIE were recorrected for the new charge. This was continued until the VSIE's were self-consistent. Twenty-five orbitals were considered, a sigma orbital on each nitrogen, and a p_z orbital on each nitrogen, oxygen and carbon atom. On the nickel atom the five $3d$ orbitals, one $4s$ and three $4p$ were used. The sigma orbitals on nitrogen were assumed to be sp^2 hybrids because the bond angles [10] about the nitrogen are approximately 120°.

The secular determinant was factored by means of D_{2h} symmetry and all orbitals are described by the irreducible representations of D_{2h} symmetry. The two N—Ni—N bond angles were taken as 80° and 100°, the smaller between the two nitrogens on the same dimethylglyoxime. The bond distances used are approximate averages of the experimental values [10] and are shown in Table 1. To compute the overlap integrals, SCF functions in terms of series

Table 1. Bond distances used for overlap integrals.

Ni—N	1.90 Å
C —C	1.53
C —N	1.25
N —O	1.38
Ni—Ni	3.24

of Slater orbitals were used for the $2s$ and $2p$ orbitals of nitrogen [11] in ^4S state and the $2p$ orbitals of carbon [11] and oxygen [11] each in the ^3P state.

Self-consistent-field functions [12–14] were also used for the $3d$, $4s$ and $4p$ functions of Ni^{+1}. The overlap integrals resulting from these orbitals are shown in Table 2. The valence state ionization potentials (VSIE) are shown

Table 2. Overlap integrals.

$\langle 2s(N)$	$\mid 3d\sigma(Ni)\rangle$	=	0.10205
$\langle 2s(N)$	$\mid 4s(Ni)\ \rangle$	=	0.32614
$\langle 2s(N)$	$\mid 4p\sigma(Ni)\rangle$	=	0.48581
$\langle 2p\sigma(N)$	$\mid 3d\sigma(Ni)\rangle$	=	0.09825
$\langle 2p\sigma(N)$	$\mid 4s(Ni)\ \rangle$	=	0.23053
$\langle 2p\sigma(N)$	$\mid 4p\sigma(Ni)\rangle$	=	0.18844
$\langle 2p\pi(N)$	$\mid 2pw(C)\ \rangle$	=	0.32361
$\langle 2p\pi(N)$	$\mid 2p\pi(O)\ \rangle$	=	0.19350
$\langle 2p\pi(N)$	$\mid 3d\pi(Ni)\rangle$	=	0.07432
$\langle 2p\pi(N)$	$\mid 4p\pi(Ni)\rangle$	=	0.22517
$\langle 2p\pi(C)$	$\mid 2p\pi(C)\ \rangle$	=	0.27121
$\langle 3d\sigma(Ni)$	$\mid 3d\sigma(Ni)\rangle$	=	0.01001
$\langle 3d\sigma(Ni)$	$\mid 4p\sigma(Ni)\rangle$	=	0.04947
$\langle 4p\sigma(Ni)$	$\mid 4p\sigma(Ni)\rangle$	=	0.39925

in Table 3 together with the appropriate dependence on charge, q. The charge dependence of the VSIE's for the sp^2 and p orbitals on nitrogen was assumed to be the same as for a nitrogen [15] hybridized to 107°. Fortunately, these corrections were small because nitrogen had a small charge. The corresponding

Table 3. VSIE = $Aq^2 + Bq + C$ (in eV).

Orbital	A	B	C
p carbon	1.68	10.96	11.22
p oxygen	0.31	13.32	14.97
p nitrogen	1.43	12.30	14.51
sp^2 nitrogen	1.43	12.30	15.12

data for the nickel orbitals were taken from the summary by Ballhausen and Gray.[9] The hydrogens in the hydrogen bridge between the two oxygens were assumed to neutralize 1/2 negative charge on each oxygen so that a total of 6 electrons on four nitrogens was considered neutral. The final self consistency of the last calculation is shown in Table 4. The energy of the orbitals of interest are shown in Table 5. In some calculations [16] a constant VSIE for water has

Table 4. Self consistency of calculation.

	Input	Output
Ni Config.	$d^{8.634}\ s^{0.773}\ p^{0.377}$	$d^{8.635}\ s^{0.773}\ p^{0.376}$
Ni charge	+ 0.216	+ 0.216
N charge	+ 0.085	+ 0.094
O charge	− 0.172	− 0.167
C charge	+ 0.017	+ 0.014

Table 5.

Orbital	Energy (eV)	Description (approximate)
$3a_u$	0.5477	Ligand
$4b_{2g}$	− 7.0844	Ligand
$3b_{1u}$	− 9.6858	Ligand + $4p_z$
$2b_{1g}$	−10.6147	$\sigma N - d_{xy}$
$3b_{3g}$	−11.7725	Ligand
$2a_u$	−11.8576	Ligand
$3b_{2g}$	−13.2014	Ligand
$2b_{1u}$	−13.2386	Ligand
$2b_{3g}$	−14.4949	d_{yz}
$3a_g$	−14.5130	d_{z^2}
$2b_{2g}$	−14.6212	d_{xz}
$3a_g$	−14.7720	$d_{x^2-y^2}$
$1b_{2u}$	−16.4139	$\sigma N + 4p_y$

been used for oxygens adjacent to a positive center, but this raises the problem of how to treat the carbon and nitrogens in a corresponding manner. Fortunately, after correcting the oxygen VSIE for the charge on oxygen, the

final VSIE was −12.814 eV, a value very close to the value for water, −12.61 eV.

Ligand-ligand overlap between the nitrogens was not considered. This is quite negligible in the pi-system in which we are primarily interested and a correction, as described later, was made for the one sigma orbital of interest that was affected.

The energy of the upper and lower edge of the energy band formed by overlap of the nickel orbitals φ_r in molecular orbital, ψ_i was calculated from the equation.

$$E = [\mp 4(C_{ir})^2\langle\varphi_r \mid \varphi_r\rangle\text{VSIE})_r] \,/\, (1 + 2\langle\varphi_r \mid \varphi_r\rangle) + E_i$$

where $\langle\varphi_r \mid \varphi_r\rangle$ is the overlap between the nickel atomic orbitals on two adjacent nickel atoms and C_{ir} is the coefficient of the r-atomic orbital in the i-molecular orbital. This equation follows from the usual equation for a one dimensional band [17] with the approximation that the resonance integral, β is given by

$$\beta = 2\langle\varphi_r \mid \varphi_r\rangle(\text{VSIE})_r$$

EXPERIMENTAL

Nickel dimethylglyoxime was crystallized from hot solutions of nitrobenzene and washed with toluene. All spectra were taken on a Cary Recording spectrophotometer.

QUESTION OF NICKEL-NICKEL BONDING IN THE CRYSTAL

Various possible types of nickel-nickel bonds have been discussed [1,5] in which the empty orbitals in the monomer form bands in the crystal that become preferentially evacuated. Another suggestion [5] has been that the d_{z^2} and p_z orbitals hybridize to form alternate bonds along the nickel chain. The possibility of Ni—Ni bonding was investigated in four different methods. First a band was formed from the $3a_g$ (d_{z^2}) occupied orbitals. This gave a band with boundaries +0.509 eV and −0.492 eV from the unperturbed $3a_g$ orbital. The increase of 0.509 eV is not enough to raise this band above the other occupied orbitals so no bonding is possible.

Secondly, a band was formed from the $3b_{1u}$ ($4p_z$) empty orbitals. This gave a band with boundaries +0.958 eV and −0.817 eV from the unperturbed $3b_{1u}$ level. The decrease of 0.817 eV is again not enough energy to lower the band into the occupied orbitals so again no bonding is possible.

In a third method the p_z and d_{z^2} orbitals were hybridized to form a dp hybrid. The bonded hybrid orbitals have an energy of −12.211 eV compared to −14.513 eV for the unhybridized and non-bonded $3a_g$ orbital. The excitation energy for an electron into an empty $3b_{1u}$ (p_z) orbital more than counteracts the small gain in forming bonds at this distance.

The fourth method was to make a linear combination of $3a_g$ and $3b_{1u}$ between two adjacent nickel atoms. The result was a bond containing only a very small amount of $3b_{1u}$ and stabilized by only 16 cal per monomer. This value is only approximate and may constitute a small interaction between

the nickel atoms in the ground state but is certainly far below the 10 kcal that some authors [8] have estimated from their interpretation of the solubility data.

SPECTRAL ASSIGNMENT

The experimental spectrum of nickel dimethylglyoxime in chloroform solution and in the crystal are shown in Table 6 and the calculated transitions that are orbitally allowed are shown in Table 7. These transitions were not

Table 6. Chloroform spectrum of $Ni(DMG)_2$

Max (cm^{-1})	Extinction coefficient	Ref.
38 200	24 500	21
38 200	24 500	21
30 600	4 580	21
26 700	3 430	21
23 700	525	19
21 100	120	19

Table 7. Allowed transitions in $Ni(DMG)_2$.

Excited state	Orbitals	Polarization	Frequency (10^3 cm^{-1})	Type of transition
$1B_{2u}$	$(3b_{3g}, 3b_{1u})$	Y	17.0	$L \rightarrow L$
$2B_{2u}$	$(2a_u, 4b_{2g})$	Y	38.5	$L \rightarrow L$
$3B_{2u}$	$(2b_{2g}, 3b_{1u})$	Y	39.3	$M \rightarrow L$
$1B_{3u}$	$(3b_{2g}, 3b_{1u})$	X	28.4	$L \rightarrow L$
$2B_{3u}$	$(2b_{2g}, 3b_{1u})$	X	40.4	$M \rightarrow L$
$1B_{1u}$	$(2a_u, 2b_{1g})$	Z	10.0	$L \rightarrow M$
$2B_{1u}$	$(2a_g, 3b_{1g})$	Z	41.5	$M \rightarrow L$
$3B_{1u}$	$(3a_g, 3b_{1u})$	Z	38.9	$M \rightarrow L$

corrected for electron repulsion because repulsion corrections must of necessity be rather arbitrary and are probably not warranted if configuration interaction is not included.

The band at 38 000 cm^{-1} occurs at approximately the same frequency in all dimethylglyoxime complexes including the uncomplexed chelator and has been assigned [18] to a ligand-ligand transition. A simple Hückel treatment of dimethylmethylglyoxime using the Wolfsberg-Helmholtz approximation for the off diagonal elements gives a transition from orbital i to orbital j at 38 700 cm^{-1} where orbitals i and j are described by the following expressions where π_a, π_a' *etc.* are normalized linear combinations of p-orbitals on the a-atoms:

$$\varphi_j = 0.340\pi_O + 0.804\pi_C - 0.764\pi_N$$
$$\varphi_i = 0.786\pi_O' - 0.541\pi_C' - 0.269\pi_N'$$

These orbitals are quite similar to the $2a_u$ and $4b_{2g}$ orbitals in a nickel dimethylglyoxime which are described by the following expressions:

$$\varphi(4b_{2g}) = 0.587\pi_0'' + 0.680\pi_C'' - 0.820\pi_N'' - 0.283d_{xz}$$
$$\varphi(2a_u) = 0.918\pi_0''' - 0.333\pi_C''' - 0.276\pi_N'''$$

It thus seems quite logical to assign the transition found at 38 200 cm^{-1} to $2a_u \rightarrow 4b_{2g}$ ($1A_g \rightarrow 2B_{2u}$) transition.

At the other end of the spectrum a weak absorption has been reported [3] in the crystal at 10 300 cm^{-1}. One is tempted to assign this to the $1A_g \rightarrow 1B_{1u}$ absorption which was calculated to occur at 10 000 cm^{-1}. In this work, no absorption was found in this region using both crystals and KBr discs containing 5 mg nickel dimethylglyoxime per 300 mg KBr. This casts serious doubts on whether such an absorption occurs. If there is no absorption at 10 000 cm^{-1} then the $1A_g \rightarrow 1B_{1u}$ transition is probably observed at 21 100 cm^{-1}. This is a large difference between the calculated 10 000 cm^{-1} and the observed frequency of 21 100 cm^{-1}, but the transition is from a ligand orbital to a metal sigma orbital ($2b_{1g}$) and is therefore opposed by a large electron repulsion. Inclusion of ligand-ligand overlap also helps somewhat. Allowing the $1b_{1g}$ orbital to interact through sigma overlap between the nitrogen changes the calculated $1A_g \rightarrow 1B_{1u}$ transition to 12 700 cm^{-1}. The crystal spectrum [3] shows a broad absorption predominately polarized parallel to the molecular plane which stretches between about 18 000 and 29 000 cm^{-1} and showed essentially no change on cooling to 83°K. This absorption has all the characteristics of a crystal band with a center at about 23 500 cm^{-1} and must correspond to the 23 700 cm^{-1} absorption in the chloroform spectrum. The most logical assignment for this transition is a $1B_{2u}$ excited state (calc. 17 000 cm^{-1}). The $1B_{2u}$ excited state includes a $3b_{1u}$ orbital which forms a band with a calculated width of 14 300 cm^{-1} in fair agreement with the experimentally observed width of 11 000 cm^{-1}. The assignment of the crystal band is essentially in agreement with the assignment of Zahner and Drickamer.[1]

The relative intensities calculated for these transitions are shown in Table 8. Essentially, the Z polarized bands are very weak and the X and Y polarized bands are very strong. The assignment of the 23 700 cm^{-1} to a $1A_g \rightarrow 1B_{2u}$ transition is not in agreement with the strong intensity calculated for the transition. About 90 to 95 % of this intensity is from the oxygen orbitals and only an extremely small intensity is from the $d \rightarrow p_z$ transition on the metal. Thus the transition is primarily ligand-ligand and is highly sensitive on the orbital coefficients on oxygen which in turn are highly sensitive to the VSIE used and configuration interaction with other $1B_{2u}$ states.

Table 8. Relative calculated oscillator strengths. From $1A_g$ ground state to excited state listed.

	f
$1B_{1u}$	0.00001
$2B_{1u}$	0.003
$3B_{1u}$	0.00006
$1B_{2u}$	1.00
$2B_{2u}$	1.2
$3B_{2u}$	0.075
$1B_{3u}$	0.20
$2B_{3u}$	0.25

Maki [19] assigned the 21 100 cm^{-1} and 23 700 cm^{-1} absorptions to $d-d$ transitions on the basis of crystal field theory. However, in the present work the $p-d$ transitions were found to occur at about 32 000 cm^{-1} and are probably hidden by intense charge transfer absorptions in this area. The $d-d$ bands have been assigned [20] at 22 500 cm^{-1} and 30 500 cm^{-1} in the $Ni(CN)_4^{2-}$ complex and probably occur at higher frequencies in nickel dimethylglyoxime.

Thus logical assignments can be made for the 21 100 cm^{-1} ($1A_1 \rightarrow {}^1B_{1u}$, 23 700 cm^{-1} ($1A_g \rightarrow 1B_{2u}$), and 38 200 cm^{-1} ($1A_g \rightarrow 2B_{2u}$) transitions in chloroform and the broad crystal band ($1A_g \rightarrow 1B_{2u}$) without the requirement of Ni—Ni bonding in the ground state. Perhaps some of the other experimental transitions in chloroform solution could be assigned also but assignments of these would be very uncertain at our present stage of investigation.

The present calculation points out two items that should be investigated further. The lowest unfilled orbital $2b_{1g}$, is only about 1 eV above the highest filled $3b_{3g}$ orbital. This is in the range of singlet triplet splittings and suggests that a triplet state may be thermally available in solution. The solubility in chloroform was too low to allow any measurement of paramagnetism on the Gouy balance.

Another item of interest is the possibility that a conduction band is formed by the excited $3b_{1u}$. If the present interpretation of the spectra is correct, then the crystal should exhibit photoconductivity.

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