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Semiempirical Molecular Orbital Considerations of the Electronic Structures of Transition Metal Complexes. I. Dioxygen Nickel Complexes

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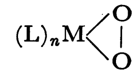
The electronic structure of $Ni(O_2)(HNC)_2$ as a model of "side-on" coordinated dioxygen nickel complexes has been investigated by the INDO method. Calculations show that the square-planar geometry is more stable than the pseudotetrahedral form in accord with the observed structure of $Ni(O_2)(t\text{-}BuNC)_2$. The central nickel atom possesses an approximately zerovalent configuration: $(3d)^{8.5}$ $(4s)^{0.5}$ $(4p)^{1.0}$. The dioxygen-nickel bonding is effected primarily through the donation and back-donation of electrons in which the O_2 π_u and $\pi_g{}^*$ orbitals parallel to the molecular plane participate. It is predicted that *both* the Ni–O and O–O bondings tend to have greater covalent bond strengths as the electron-attracting ability of the ligand isocyanide increases. Attempts are made to assign the electronic spectra.

A number of dioxygen complexes of transition metals have recently been isolated and characterized.[1-4] In connection with possible biochemical significance of these complexes, much of the current interest in this field is directed toward the understanding of the nature of the dioxygen–transition metal bondings.[5-8] The effect of such bondings upon the electronic structure of the dioxygen moiety is also receiving attention.[5]



Molecular orbital theory has given several useful suggestions to these problems. Thus, the dioxygen–metal bond in "side-on" complexes has been described in terms of the Dewar-Chatt-Duncanson model,[9,10] in which the donation and back-donation of electrons between metal d orbitals and dioxygen are considered to be essential.[11] Ohkubo and co-workers[12] investigated the interaction between onium compounds and molecular oxygen; the catalytic activity of onium compounds in oxidation reactions was ascribed to an effective interaction of oxygen with the partially occupied d orbitals of the central atom in onium compounds. Recently, Norman[13] has dealt with $Pt(O)_2(PH_3)_2$ by the SCF-X_α scattered wave method to show that a building-up of an extra electron density in the antibonding $1\pi_g$ orbitals of dioxygen is not necessarily due to the direct Pt $d\pi \rightarrow O_2$ $1\pi_g$ back-donation. Apparently, however, characteristics of molecular oxygen coordinated to transition metal are still debatable.

The purpose of the present study is to discuss the nature of the dioxygen–nickel bonding of a "side-on" coordination complex $Ni(O_2)(t\text{-}BuNC)_2$[14] in terms of an ASMO-SCF-MO method in the INDO approximation. Specifically, we examine the electronic structure of a model compound $Ni(O_2)(HNC)_2$ and the effects of its geometry and ligand structure on the dioxygen–nickel bonding as well as oxygen–oxygen bond. Assignment of the electronic spectra has also been attempted.

Method of Calculation

INDO Formalism. The approximation used in this work is basically that of the INDO method suggested by Pople *et al.*[15] Thus, all the two-electron integrals involving differential overlap are neglected, except for one-center exchange integrals of the type $(\mu\nu|\mu\nu)$.

However, our method differs somewhat from the original INDO method[15] in the evaluation of atomic integrals. First, both the one-center electron repulsion integrals $(\mu\mu|\nu\nu)$ and the one-center core attraction integrals $U_{\mu\mu}$ are obtained from the table by Oleari *et al.*[16-18] Second, the two-center repulsion integrals are approximated as:[19]

$$(\mu\mu|\nu\nu) = 14.3986/(R+a) \tag{1}$$

with

$$a = 28.7972/[(\mu\mu|\mu\mu)+(\nu\nu|\nu\nu)] \tag{2}$$

μ, on atom A; ν on atom B

where R is the distance (Å) between atoms A and B and $(\mu\mu|\mu\mu)$ *etc.* are represented in units of eV. The integrals $(\mu\mu|\nu\nu)$ for a given pair of atoms A and B may take on different values, depending on the type of the atomic orbitals, μ and ν. Third, the core resonance integrals $\beta_{\mu\nu}$ are evaluated by the Wolfsberg-Helmholtz expression:[20]

$$\beta_{\mu\nu} = -(\kappa/2)S_{\mu\nu}(I_\mu{}^A+I_\nu{}^B) \tag{3}$$

where $I_\mu{}^A$ and $I_\nu{}^B$ are the valence-state ionization potentials, $S_{\mu\nu}$ is the overlap integral between μ and ν, and the parameter κ is assumed to be 1.1.[21]

The attraction between an electron in atomic orbital μ of atom A and a core of atom B is assumed to be

$$(\mu|V_B|\mu) = -\sum_\nu^B N_\nu(\mu\mu|\nu\nu) \tag{4}$$

where N_ν refers to the number of valence electrons occupying ν. The elements of the Hartree-Fock matrix for a closed shell of electrons are then given by[22]

$$F_{\mu\mu}^{A,A} = U_{\mu\mu} + \sum_\nu^A P_{\nu\nu}\left[(\mu\mu|\nu\nu)-\frac{1}{2}(\mu\nu|\mu\nu)\right] + \sum_\nu^B (P_{\nu\nu}-N_\nu)(\mu\mu|\nu\nu) \tag{5}$$

$$F_{\mu\nu}^{A,A} = P_{\mu\nu}\left[\frac{3}{2}(\mu\nu|\mu\nu)-\frac{1}{2}(\mu\mu|\nu\nu)\right] \tag{6}$$

$$F_{\mu\nu}^{A,B} = \beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu) \tag{7}$$

where $P_{\mu\nu}$ *etc.* denote the bond orders.

The basis set of atomic orbitals used includes the following: 3d, 4s, and 4p of Ni; 2s and 2p of C, N,

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and O; and 1s of H. The initial electronic configurations of atoms assumed in the evaluation of the matrix elements (5)—(7) are $(3d)^{10}$ for Ni and $(2s)^2(2p)^m$ for C, N, and O, where m is 2, 3, and 4, respectively.

Evaluation of Integral Parameters. The one-center integrals appropriate to the present calculations are (i) core-electron attraction integrals U_{ss}, U_{pp}, and U_{dd}, (ii) Coulomb integrals $(\mu\mu|\nu\nu)$, and (iii) exchange integrals $(\mu\nu|\mu\nu)$. Oleari *et al.*[16,17] determined the one-center integrals by the least-squares fits of the total valence-state energies calculated therefrom for atoms as a function of their orbital occupation number. The calculations were based on the valence state energies taken from Moore's table.[23] The results are tabulated[18] for various valence-state quantities:[24]

$$U_{ss},\ U_{pp},\ U_{dd},\ g_{ss},\ g_{pp},\ g_{dd},\ g'_{sp},\ g'_{pp'},\ g'_{pd},\ \text{and}\ g'_{dd'}$$

where

$$g_{\mu\mu} = (\mu\mu|\mu\mu) = J_{\mu\mu} \tag{8}$$

and

$$g'_{\mu\nu} = (\mu\mu|\nu\nu) - \frac{1}{2}(\mu\nu|\mu\nu) = J_{\mu\nu} - \frac{1}{2}K_{\mu\nu}\ . \tag{9}$$

In evaluating the individual one-center two-electron integrals, one must resolve $g'_{\mu\nu}$ into the components. We have made the resolution using the theoretical relationships between the individual integrals and the Slater-Condon parameters. The expressions for the Coulomb and exchange integrals in terms of the Slater-Condon parameters have been given by Clack.[25] The resolutions of g'_{sp}, g'_{sd}, and g'_{pd} necessitate evaluations of the Slater-Condon parameters G^1(sp), G^2(sd), G^1(pd), and G^3(pd). These parameters were taken from the data compiled by Hinze and Jaffé[26] for ligand atoms and by Oleari *et al.*[17] for the metal atom. The various two-electron integral values finally adopted for C, N, O, and Ni are summarized in Table 1.

The valence-state ionization potentials necessary for the evaluation of $\beta_{\mu\nu}$ were obtained from Oleari's $U_{\mu\mu}$ data and relevant Slater-Condon parameters. They are listed also in Table 1. The overlap integrals were calculated using single Slater orbitals. The orbital exponents were chosen from the data by Zerner and Gouterman[27] for nickel and from those by Clementi and Raimond[28] for ligand atoms. They are given in Table 2.

Table 1. Atomic parameters[a)] (eV)

	Ni	C	N	O	H
I_s	7.19	19.39	25.00	32.37	13.60
I_p	3.10	10.83	13.84	16.39	
I_d	5.02				
J_{sp}	6.872	11.410	12.583	14.480	
$J_{pp'}$	5.768	9.841	11.588	12.335	
J_{sd}	10.088				
$J_{z,zx}$	8.583				
J_{x,z^2}	8.331				
$J_{z,xy}$	8.215				
J_{z,z^2}	8.699				
$J_{z^2,xy}$	15.015				
$J_{z^2,xz}$	15.644				
J_{xy,x^2-y^2}	15.854				
$J_{xz,yz}$	15.225				

a) The other parameters, $U_{\mu\mu}$ and $g_{\mu\mu}$, are tabulated in Ref. 18. The $K_{\mu\nu}$ values can be obtained from Eq. 9.

Table 2. Orbital exponents of the basis set used

	s	p	d
H	1.0000		
C	1.6083	1.5679	
N	1.9237	1.9170	
O	2.2458	2.2266	
Ni	1.4730	1.4730	2.960

Electronic Excitation. The energies and moments for singlet excitations were calculated by the conventional virtual orbital approximation without configuration interaction. The configurational energy corresponding to one-electron excitation from molecular orbital i to virtual orbital j is given by

$$\Delta^1E = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij} \tag{10}$$

where ε_j and ε_i respectively denote the energies of orbitals j and i, and J_{ij} and K_{ij} are the molecular Coulomb and exchange integrals, respectively. The dipole moment length is given by

$$M_{i\to j} = \sqrt{2} \sum_{A}^{\text{atoms}} \sum_{\mu}^{A} \sum_{\nu}^{A} C_{i\mu}C_{j\nu}(\mu|\boldsymbol{r}_A|\nu) \tag{11}$$

where $\boldsymbol{r}_A$ is the coordinate vector operator of atom A and $C_{i\mu}$ *etc.* are the LCAO coefficients. In evaluating $M_{i\to j}$, a contribution from atomic polarization was taken into account. This latter contribution is denoted by $M'_{i\to j}$.

Results and Discussion

Geometry of $Ni(O_2)(HNC)_2$. Detailed X-ray structual information is available for $Ni(O_2)(t\text{-}BuNC)_2$.[29] The two oxygen atoms lie on the plane containing the nickel and the two isocyanide groups.

To begin with, we have calculated the total energy of our model compound $Ni(O_2)(HNC)_2$ for two extreme geometries, in which the dihedral angle θ (Fig. 1) is 0 and 90°. The results are given in Table 3, together with the net charge on the oxygen atoms Q_O as well as the bond indices W[30] for the O–O and Ni–O bonds.

Table 3 indicates that the square-planar structure ($\theta=0°$) is more stable than the pseudotetrahedral

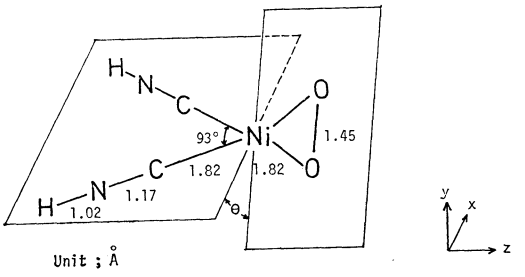

Fig. 1. Coordinate systems and structure for $Ni(O_2)(HNC)_2$.

TABLE 3. TOTAL ENERGY (E)[a], NET CHARGE ON OXYGEN (Q), AND BOND INDICES (W) FOR THE SQUARE-PLANAR AND PSEUDOTETRAHEDRAL CONFORMATIONS OF $Ni(O_2)(HNC)_2$

	Square-Planar	Pseudotetrahedral
E(eV)	−2201.2126	−2200.6274
Q_O	−0.4367	−0.4781
W_{O-O}	1.0495	1.0193
W_{Ni-O}	0.8346	0.7391

a) In calculating the total energy, the total core-core repulsion energy was approximated as

$$\sum_{A}\sum_{B}\sum_{\nu}^{A}\sum_{\mu}^{B} N_\mu N_\nu (\mu\mu|\nu\nu).$$

one ($\theta=90°$), a result compatible with the X-ray structure of $Ni(O_2)(t\text{-}BuNC)_2$. Both the bond indices W_{O-O} and W_{Ni-O} are greater in the former geometry. Because the bond index can be regarded as a measure of the covalency of the bond in question,[30] the greater stability of the square-planar form can be ascribed to the greater covalent character of *both* the Ni–O and O–O bonds involved. The net charge Q_O, on the other hand, is smaller for the square-planar structure, implying a lesser extent of back-donation of electrons from Ni to O_2 as compared with the pseudotetrahedral structure. These two indications together suggest that the back-donation tends to reduce the covalency of the Ni–O as well as the O–O bond in the complex.

Electronic Structure. We have examined the electronic structure of $Ni(O_2)(HNC)_2$ of the square-planar form in detail. The magnetic susceptibility measurements of $Ni(O_2)(t\text{-}BuNC)_2$ revealed a feeble magnetic moment of 0.13 BM.[14b] The PMR spectrum of the complex was also measured; the chemical shift falls in the range for diamagnetic isocyanide complexes. On the basis of these observations, we may assume that this complex is in a closed electronic structure.

The upper portion of the occupied molecular orbitals is diagrammatically shown in Fig. 2, together with low-lying vacant orbitals. Appended to the orbital levels are their numberings and symmetry representations for the C_{2v} point group instead of the higher symmetry D_{2h}. The omitted lower portion of the diagram consists merely of the essentially unperturbed O_2 $2\sigma_g$ and $2\sigma_u$ and isocyanide σ_g, σ_u, and π_u orbitals in the range from −45.4 to −16.5 eV.

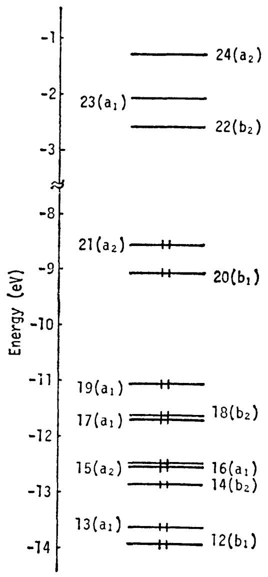

Fig. 2. Upper portion of the molecular orbital level diagram for $Ni(O_2)(HNC)_2$. The highest occupied level is $21(a_2)$.

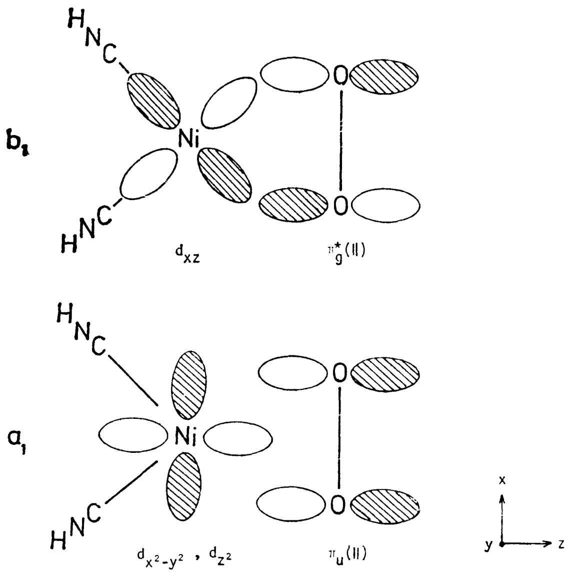

Fig. 3. Orbitals participating in the Ni–O_2 bonding of $Ni(O_2)(HNC)_2$.
b_1, the back-donation type; a_1, the donation type from O_2 to Ni.

The highest occupied level, $\phi_{21}(a_2)$, consists of 100% O_2 $\pi_g^*(\perp)$ orbital,[31] virtually no mixing between the Ni $3d_{xy}$ and O_2 $\pi_g^*(\perp)$ orbitals being involved. Thus, the back-donation to the O_2 $\pi_g^*(\perp)$ orbitals can be ignored. A similar conclusion was reached by the SCF-X_α scattered-wave calculation for $Pt(PH_3)_2(O_2)$.[13] The overlap integral between Ni $3d_{xy}$ and O p_y is considerably small (0.016). The lowest unoccupied level, ϕ_{22} (b_2), consists of Ni $4p_y$ and isocyanide $\pi^*(\perp)$ with an appreciable $O_2\pi_u(\perp)$ character. The Ni–O_2 bonding is accomplished mainly through extensive mixings of the O_2 $\pi_u(\parallel)$ and σ_g orbitals with the Ni $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals, and of the O_2 $\pi_g^*(\parallel)$ with Ni $3d_{xz}$ orbital. The levels $\phi_{19}(a_1)$, $\phi_{17}(a_1)$, $\phi_{16}(a_1)$, and $\phi_{13}(a_1)$ involve the mixing of the former type while the level $\phi_{20}(b_1)$ is due to that of the latter. The two types of mixings, schematically shown in Fig. 3, are analogous to the donation and back-donation scheme in the Dewar-Chatt-Duncanson model.

The calculated valence-electron distributions over the atomic orbitals as well as the atoms present in the complex are summarized in Table 4. We see that the final electronic configuration of nickel is $(3d)^{8.49}$ $(4s)^{0.54}$ $(4p)^{0.98}$. Most of the d-orbital population resides in the d_{xy}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2} orbitals. The 4p orbital is appreciably occupied. The net charge on nickel is nearly zero, even though its d-orbital occupation number is between 8 and 9. The isocyanide

Table 4. Calculated electron distributions for $Ni(O_2)(HNC)_2$

Atom	Atomic orbital	Charge density	
		on orbital	on atom
Ni	s	0.537	10.001
	p	0.975	
	d_{xz}	0.580	
	d_{yz}	1.978	
	d_{xy}	1.988	
	$d_{x^2-y^2}$	1.982	
	d_{z^2}	1.959	
O	s	1.744	6.437
	p	4.693	
C	s	1.313	3.860
	p	2.547	
N	s	1.244	4.923
	p	3.679	
H	s	0.780	0.780

ligands assume overall positive charges, as would be expected from the nature of isocyanide as a donating ligand. The net charge on each oxygen atom is *ca.* −0.44. The charge transfer from $Ni(HNC)_2$ to O_2 thus amounts to about one electron equivalent.

In order to gain a deeper insight into the O–O bonding nature, we calculated individual π orbital populations in the O_2 moiety as follows:

$$q(\pi_u(\perp)) = 4\sum_{i(a_2)}^{occ} C^2_{iO(p_y)} \tag{12}$$

$$q(\pi_u(\parallel)) = 4\sum_{i(a_1)}^{occ} C^2_{iO(p_z)} \tag{13}$$

$$q(\pi_g{}^*(\perp)) = 4\sum_{i(b_2)}^{occ} C^2_{iO(p_y)} \tag{14}$$

$$q(\pi_g{}^*(\parallel)) = 4\sum_{i(b_1)}^{occ} C^2_{iO(p_z)} \tag{15}$$

where $C_{iO(p_y)}$ *etc.* denote the LCAO coefficients of the i-th MO for the oxygen p orbitals specified, the summations extending over the MO's of a given symmetry a_1, a_2, b_1, or b_2. The various π orbital populations calculated for the $Ni(O_2)(HNC)_2$ complex are summarized in Table 5, together with the O–O bond length and the O–O stretching force constant.[32] For the sake of comparison, the corresponding values for molecular $O_2(^3\Sigma_g{}^-, {}^3\Sigma_u{}^\pm)$, superoxide $O_2{}^-$, and peroxide $O_2{}^{2-}$ are also listed in Table 5.

The O–O bondings in dioxygen complexes have often been discussed on the basis of their analogy in bond length with those in $O_2{}^{n-}$ anions ($n=1$ and 2) and excited-state O_2.[5,7,32,33] The electronic configuration of O_2 in the complex here calculated certainly reflects the effects of both the charge transfer to O_2 and the local excitation of O_2. Thus, the sum of the π^* orbital populations exceeds 3, indicative of a partial $O_2{}^{2-}$ character while that of the π orbitals is less than 4, a result which would be expected if the coordinated dioxygen is assumed to partake of the character of excited $O_2(^3\Sigma_u{}^+$ or $^3\Sigma_u{}^-)$. The results can best be understood in terms of the intermolecular configuration interaction[34]; the ground state of the complex is represented by a superposition of the ground, charge-transfer, and locally-excited configurations made up of the molecular orbitals of the component molecules, $Ni(HNC)_2$ and $O_2(^3\Sigma_g{}^-)$.

Taking a step further, we will discuss the relative strengths of the O–O bondings of coordinated dioxygen, free oxygen anions, and various states of molecular oxygen. Since the π_u and $\pi_g{}^*$ orbitals are, respectively, bonding and antibonding in nature, the population in the former orbitals should tend to strengthen the bond while the latter to weaken it. The O–O bond strength may be related, to a first approximation, with the differential population between them, defined as

$$\Delta q = q(\pi_u(\perp)) + q(\pi_u(\parallel)) - q(\pi_g{}^*(\perp)) - q(\pi_g{}^*(\parallel))\ . \tag{16}$$

The values of Δq thus calculated for the various types of dioxygens are included in Table 5. They decrease in the order: $O_2(^3\Sigma_g{}^-) > O_2{}^- > Ni(O_2)(HNC)_2 > O_2{}^{2-} = O_2(^3\Sigma_u{}^\pm)$, in rough agreement with the decreasing order of the observed force constant f_{O-O} and the increasing order of bond length R_{O-O}. The f_{O-O} value used herewith for $O_2{}^{2-}$ appears to be somewhat too large. Perhaps, dioxygen in Na_2O_2 is not adequate as a model for a free $O_2{}^{2-}$.

Polar Effect of Isocyanide Substituent. The strengths of the M–O and O–O bonds in the dioxygen complexes vary depending on the identity of the metal and auxiliary

Table 5. Calculated orbital populations (q) and observed bond lengths (R) and force constants (f) for dioxygen in various states

	$Ni(O_2)(HNC)_2$	$O_2{}^-$	$O_2{}^{2-}$	$O_2(^3\Sigma_g{}^-)$	$O_2(^3\Sigma_u{}^+, {}^3\Sigma_u{}^-)$
$q(\pi_u(\perp))$	1.88	2.00	2.00	2.00	(3.00)[a]
$q(\pi_u(\parallel))$	1.89	2.00	2.00	2.00	
$q(\pi_g{}^*(\perp))$	2.00	(3.00)[a]	2.00	1.00	(3.00)[a]
$q(\pi_g{}^*(\parallel))$	1.46		2.00	1.00	
Δq	0.30	1.00	0.00	2.00	0.00
R_{O-O}(Å)	1.45[b]	1.28[d]	1.49[d]	1.20[f]	1.42[f], 1.60[f]
f_{O-O}(mdyne/Å)	3.5[c]	6.2[e]	5.5[e]	11.5[f]	3.2[f], 2.3[f]

a) The values given in parentheses are the sums of two q values. b) Taken from Ref. 29. c) Taken from Ref. 32. d) N. -G. Vannerberg, *Prog. Inorg. Chem.*, **4**, 125 (1962). e) Obtained for KO_2 and Na_2O_2; E. J. Blunt, P. J. Hendra, and J. R. Mackenzie, *Chem. Commun.*, **1969**, 278. f) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2, D. Van Nostrand Co. Inc., Princeton, N. J. (1950).

TABLE 6. NET CHARGE ON OXYGEN (Q), BOND INDICES (W), AND OXYGEN ORBITAL POPULATIONS (q) FOR VARIOUS I_s^H

I_s^H(eV)	15.6	13.6	11.6	9.6
Q_O	−0.4317	−0.4367	−0.4418	−0.4472
W_{O-O}	1.0514	1.0495	1.0476	1.0457
W_{Ni-O}	0.8384	0.8346	0.8305	0.8262
$q(\pi_u(\perp))$	1.8759	1.8764	1.8769	1.8774
$q(\pi_u(\parallel))$	1.8852	1.8857	1.8862	1.8867
$q(\pi_g^*(\perp))$	1.9999	1.9999	1.9999	1.9999
$q(\pi_g^*(\parallel))$	1.4535	1.4630	1.4728	1.4829
Δq	0.3077	0.2992	2.2904	0.2813

ligands. The O–O bond length ranges from 1.30 to 1.63 Å, while the M–O bond length from 1.82 to 2.09 Å. Also, the force constants of the O–O and M–O stretchings, determined by IR spectroscopy, range from 3.0 to 3.5 mdyn/Å and from 2.1 to 3.2 mdyn/Å, respectively.

In an attempt to elucidate the effect of the substituent of the isocyanide ligand on the O–O and M–O bond strengths, we have carried out model calculations by varying the ionization potential $I_s^H(=-U_{ss}^H)$ for the hydrogen atom of isocyanide, with the other parameters being fixed. When I_s^H is smaller than 13.6 eV, the hypothetical isocyanide ligand (CNH′) should be more electron-releasing than CNH, and *vice versa.*

The net charges on oxygen Q_O calculated with various I_s^H values are listed in the first line of Table 6. It can be seen that Q_O increases in magnitude as the isocyanide ligand becomes more electron-releasing. Thus, electropositive ligands tend to enhance the back-donation of electrons from nickel to dioxygen.

Also listed in Table 6 are the bond indices W_{O-O} and W_{Ni-O}, together with the values for q as well as Δq. The quantities Δq and W_{O-O}, both of which are the measures of the O–O covalent bond strength, decrease with decreasing I_s^H. The results indicate that the substitution of electron-releasing ligands leads to a decrease in the O–O bond strength. The trend can easily be accounted for in terms of the increasing back-donation from nickel to O_2 π_g^* orbital; $q(\pi_g^*(\parallel))$ increases considerably as I_s^H decreases. Similar situations are encountered in olefin and acetylene complexes.35)

As for the strength of the nickel-oxygen bond, the W_{Ni-O} also decreases with the increasing electron-releasing character of the isocyanide ligand. The result might appear strange. With olefin and acetylene complexes, the relative strengths of metal–olefin (or metal–acetylene) π-bonding interaction reflect the amount of back-donation; a weaker C–C bond is usually accompained by a stronger metal–olefin bond.35,36)

The most important difference between dioxygen and olefin (or acetylene) is that the former is much more electronegative than the latter, the half-occupied π_g^* orbital of the former being much lower in energy than the lowest vacant orbital of the latter. The nickel orbitals of the isocyanide complex may lie as high as or even higher than the π_g^* orbitals of dioxygen. In order to ascertain this possibility, the UHF-INDO calculations were performed for two isolated molecules, O_2 and $Ni(HNC)_2$. The latter molecule was assumed to be in the lowest triplet state, its geometry being assumed to be the same as in Fig. 1. The resulting HOMO (degenerate) of the α-spin orbital for O_2 is at −12.05 eV, while that for $Ni(HNC)_2$, at −6.21 eV. The former is significantly lower than the latter, indicative of the higher electronegativity of O_2. Indeed, the dioxygen–nickel bonding orbital $\phi_{20}(b_1)$ possesses a large dioxygen character, in harmony with the lower O_2 π_g^* orbital as compared with the HOMO of $Ni(HNC)_2$.

Under these circumstances, the covalency of the Ni–O bond and, hence, its bond strength should decrease as the nickel atom becomes more electron-releasing. The view is supported by the IR spectra, which show that the frequency of the rhodium–oxygen stretching ν_{Rh-O} for various dioxygen rhodium complexes32) tends to increase in the order of electron-attracting ability of the substituents. This is in contrast with the results for Vaska's dioxygen complexes, where the reversibility of oxygen coordination was realized in the presence of electron-attracting ligands.33) However, the reversibility may not necessarily be correlated with the dioxygen–metal bond strength.

Transition Energies and Dipole Moment Lengths. Ultraviolet and visible absorption spectra have been reported for $Ni(O_2)(t\text{-}BuNC)_2$ both in a $CHCl_3$ solution and in the solid state.14b) Assignment of the greatest wavelength absorption band was also given,14b) where the ground electronic state of the complex was assumed to be $^3A_2$. However, the assumption is probably not valid in view of the data of magnetic susceptibility and PMR spectrum, as has already been

TABLE 7. TRANSITION ENERGIES (Δ^1E) AND TRANSITION MOMENT LENGTHS (M) FOR $Ni(O_2)(HNC)_2$

Transition	Symmetry	Calcd			Obsd b)	
		Δ^1E(eV)	M(Å)	M'(Å) a)	Δ^1E(eV)	ε
$\phi_{15}\to\phi_{26}$	$^1B_2$	1.80	0.008	0.008	2.07	33
$\phi_{16}\to\phi_{26}$	$^1B_1$	2.80	0.244	0.033	3.26 c)	316
$\phi_{21}\to\phi_{26}$	$^1B_2$	2.81	0.023	0.023		
$\phi_{21}\to\phi_{22}$	$^1B_1$	2.94	0.170	0.004		
$\phi_{13}\to\phi_{26}$	$^1B_1$	3.18	0.007	0.004		
$\phi_{20}\to\phi_{23}$	$^1B_1$	3.49	0.124	0.009		

a) Contribution from atomic polarization. b) Observed in $CHCl_3$ solution. See Ref. 13. c) Observed as a superposition of many peaks.

mentioned. Thus, we here attempt reassignments of the electronic spectra, assuming that the replacement of *t*-BuNC by HNC does not affect the spectra significantly.

Table 7 gives the energies Δ^1E and dipole moment lengths M calculated for the singlet transitions in the low-energy region, together with the experimental data. Considering the observed extinction coefficients ε and the calculated M, we may ascribe the band observed at 2.07 eV to the $\phi_{15}\rightarrow\phi_{26}$ ($^1A_1\rightarrow{}^1B_2$) transition. The transition has an appreciable d-d band character with a slight charge-transfer from nickel d orbitals to ligand π_g^* orbitals. The band appearing at 3.26 eV can be ascribed primarily to the three $^1A_1\rightarrow{}^1B_1$ transitions, $\phi_{16}\rightarrow\phi_{26}$, $\phi_{21}\rightarrow\phi_{22}$, and $\phi_{20}\rightarrow\phi_{23}$. The $\phi_{16}\rightarrow\phi_{26}$ transition reveals a considerable mixing of the d-d excitation with charge-transfer from the oxygen $\pi_u(\parallel)$ orbital to the isocyanide $\pi^*(\parallel)$ orbital, the resulting M being large as compared with that for a d-d transition. On the other hand, the latter two transitions are almost completely of charge-transfer type. The $\phi_{21}\rightarrow\phi_{22}$ transition corresponds to the charge-transfer from the oxygen $\pi_g^*(\perp)$ orbital to the nickel p_z and the isocyanide $\pi^*(\perp)$ orbitals, while the $\phi_{20}\rightarrow\phi_{23}$ transition from the oxygen $\pi_g^*(\parallel)$ and the nickel d orbitals to the isocyanide $\pi^*(\parallel)$ orbitals.

It should be noted that the energies calculated for the $\phi_{15}\rightarrow\phi_{26}$ and $\phi_{16}\rightarrow\phi_{26}$ transitions are relatively small (1.80 and 2.80 eV, respectively) despite their large orbital energy gaps (12.01 and 11.89 eV, respectively). Apparently, this is a consequence of their interorbital Coulomb repulsions J_{ij} being relatively large (11.14 and 10.19 eV, respectively). That these particular transitions have large J_{ij} is not surprising, since both of them possess an appreciable d-d (and hence largely local) excitation character to which the contribution of one-center Coulombic repulsions should be dominant. It is also noteworthy that for these two transitions the contribution M' of atomic polarization to dipole moment length is not negligible.

Concluding Remarks

The results given above indicate that our modified INDO method can satisfactorily account for the structure of the nickel dioxygen complex studied. It can well serve as a tool in illuminating the nature of the chemical bondings involved.

One point that may be raised against the present treatment will be the accuracy of the INDO theory itself when extended to include d orbitals. However, recent success[37,38] of the theory in quantitative interpretation of the photoelectron spectra for several transition metal complexes does appear to warrant its reliability. Description of the ground-state properties of the nickel dioxygen complex studied herein is probably reliable enough at least qualitatively.

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