Theoretical CNDO Molecular-orbital Analysis of Metal–Ligand Bonding as a Function of Ligand Basicity in Some Purely σ-Bonding Systems

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A theoretical molecular-orbital (m.o.) analysis of the correlation of metal–ligand bond strength with the basicity of the ligands in a number of purely σ-bonding systems has been made at the CNDO level of approximation. An energy partitioning analysis consistent with the unrestricted Hartree–Fock (UHF) model at this level reveals the existence of linear correlations of the various energy contributions to metal–ligand interactions with ligand basicity. The diatomic ' shared electron density ' and exchange interaction energy ($E^2{}_{AB}$) are the most suitable parameters for assigning a covalency index to various metal–ligand bonds. An apparently irregular behaviour of the covalent interaction energy component ($E^1{}_{AB}$) computed at the CNDO level is critically examined.

THE factors that affect the strength or the stability of the co-ordinate bond formed between a donor (the ligand) and an acceptor (the metal ion) moieties are of considerable interest. Although a number of electrostatic models[1-4] exist for the theoretical treatment of co-ordination compounds, these are not suitable for application to strongly covalent complexes. In such cases, the best resort is to molecular-orbital (m.o.) theory.

This paper concerns a theoretical CNDO m.o. investigation on the variations in the energetics of metal–ligand bonds in a series of nickel(II)–amine complexes with changes in the basicity of the ligands. Its purpose is two-fold: (*i*) to provide a rationale for the observed variations of the strength of an M–L bond with increasing ligand basicity; (*ii*) to attempt to generate a m.o. parameter which can be used as a covalency index in the context of semiempirical orbital theories. However, the picture which has emerged out of an analysis made with the help of semiempirical orbital theories may not have a one to one correspondence with the actual molecular phenomena. Thus the results presented should be regarded as preliminary results to be refined later through more rigorous studies.

To isolate the effect of a single ligand variable a model system of ligands has been chosen in which (*a*) the co-ordination occurs through the same type of atom, (*b*) the state of hybridisation of the donor orbitals remains identical, (*c*) the chemical environment around the donor atom in the ligand moiety is constrained to remain the same, and (*d*) the only factor that changes from one donor to the other is the ionisation energy of the donor orbital. It is hoped that the trends observed in this somewhat idealised system will provide some insight into the behaviour of real systems.

The specific group of ligands chosen is NH_3, $NMeH_2$, NMe_2H, NMe_3, and NEt_3, in all of which the co-ordination is assumed to occur through the σ (sp^3 hybrid) lone pair of electrons on the nitrogen atom. The calculation proceeds in the following steps. (*i*) For each ligand, a perfect octahedral co-ordination is assumed and the optimum metal–ligand bond length is calculated by using LCAO-MO-SCF theory at the CNDO[5-7] level of approximation using UHF methodology. The parametrisation scheme adopted is the one recently developed by our group.[8-10] (*ii*) The total UHF energy of each system is partitioned into a number of components, *e.g.* coulombic interaction, exchange interaction, covalent interaction energies, *etc.* following which the variations of these quantities are analysed as functions of ligand basicity.

THEORETICAL

Partioning of the UHF-LCAO-MO-SCF *Energy in* CNDO *Approximation*.—Ehrensen and Seltzer[11] first invoked an energy-partitioning analysis in connection with CNDO-MO theory and applied it to develop a ' bond-strength index ' in closed-shell molecules. In the present case we are dealing with open-shell systems and hence the partitioning should refer to the unrestricted Hartree–Fock (HF) operator or to any other open-shell HF type of operator and wavefunction ($\psi^{\text{open shell}}$). Thus equation (1) is applicable, and with the

$$E^{\text{Total}}_{\text{UHF}}(\text{CNDO}) = \text{Tr}P^{\alpha}h^{\text{core}}_{\text{CNDO}} + \text{Tr}P^{\beta}h^{\text{core}}_{\text{CNDO}} + \tfrac{1}{2}(\text{Tr}P^{\alpha}G^{\alpha}_{\text{CNDO}} + \text{Tr}P^{\beta}G^{\beta}_{\text{CNDO}}) + \sum_{A>B} E^{\text{core-core}}_{AB} \tag{1}$$

$$E^{(\text{CNDO})}_{\text{UHF}}(\text{CNDO}) = \sum_{i=1}^{3}\sum_{A=1}^{N} E^{i}_{A} + \sum_{A} E^{4}_{A} + \sum_{i=1}^{2}\sum_{A}\sum_{B\neq A} E^{i}_{AB} + \sum_{A>B} E^{\text{core-core}}_{AB} \tag{2}$$

usual definitions of G^{α}_{CNDO}, G^{β}_{CNDO}, and h^{core} we can write (2). The definitions[11] of other terms are given for one-centre interactions in equations (3)—(5) and for two-centre

$$E^{1}_{A} = \sum_{\mu\epsilon A} (P^{\alpha}_{\mu\mu} + P^{\beta}_{\mu\mu})U^{A}_{\mu\mu} \tag{3}$$

$$E^{2}_{A} = -\sum_{\mu\epsilon A}\sum_{\nu\epsilon A} [(P^{\alpha}_{\mu\nu})^2 + (P^{\beta}_{\mu\nu})^2]g^{0}_{AA} \tag{4}$$

$$E^{3}_{A} = [(P^{\alpha}_{AA})^2 + (P^{\beta}_{AA})^2]g^{0}_{AA} \tag{5}$$

where
$$P^{\alpha}_{\mu\nu} = \sum_{i}^{\text{occ}(\alpha)} C^{\alpha}_{\mu i}C^{\alpha}_{\nu i}$$

$$P^{\beta}_{\mu\nu} = \sum_{i}^{\text{occ}(\beta)} C^{\beta}_{\mu i}C^{\beta}_{\nu i}$$

$$E^{1}_{AB(A\neq B)} = \sum_{\mu\epsilon A}\sum_{\mu\epsilon B} 2\beta^{AB}_{\mu\nu}S_{\mu\nu}(P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}) \tag{6a}$$

$$E^{2}_{AB(A\neq B)} = -\sum_{\mu\epsilon A}\sum_{\nu\epsilon B} [(P^{\alpha}_{\mu\nu})^2 + (P^{\beta}_{\mu\nu})^2]g^{0}_{AB} \tag{6b}$$

interactions in equation (6). E^{1}_{AB} represents the so-called diatomic covalent interaction energy, a quantity arising entirely from the diatomic shared density. The occ(α) and occ(β) values correspond to the number of occupied orbitals having α and β spin respectively.

A simple explanation of the origin of the E^2_{AB} term is as follows. If the atoms A and B are bonded through the orbitals μ (on A) and ν (on B), the probability of simultaneously finding an electron in the orbital μ having, say, α spin and an electron on ν having similar spin is not simply $P^{AA}_{\mu\mu}(\alpha) \cdot P^{BB}_{\nu\nu}(\alpha)$. The Fermi correlation forces some of the electron density, *viz.* $(P^{\alpha}_{\mu\nu})$, into the bonding region, thereby reducing coulomb interaction between the electron pair by an amount equal to $(P^{\alpha}_{\mu\nu})^2 g^0_{AB}$. The probability is thus given by $P^{AA}_{\mu\mu}(\alpha) \cdot P^{BB}_{\nu\nu}(\alpha) - P^{AB}_{\mu\nu}(\alpha)$. E^2_{AB} is, therefore, directly associated with the occurrence of orbital overlap and chemical-bonding effects. Accordingly, it should be an important parameter for assessing the covalent character or strength of a given M–L bond. The analysis shows that this is indeed true. The residual two-centre interactions still present in $E^{\text{total}}_{\text{UHF}}$ (CNDO) are all of coulombic type. Thus, we can write expressions (7)—(9).

$$E^3_{AB} = -Z_B g^0_{AB}(P^{\alpha}_{AA} + P^{\beta}_{AA}) + Z_A g^0_{AB}(P^{\alpha}_{BB} + P^{\beta}_{BB}) \qquad (7)$$

$$E^4_{AB} = (P^{\alpha}_{AA}P^{\alpha}_{BB} + P^{\beta}_{BB}P^{\beta}_{AA} + P^{\alpha}_{AA}P^{\beta}_{BB} + P^{\beta}_{AA}P^{\alpha}_{BB})g^0_{AB} \qquad (8)$$

$$E^{\text{core-core}}_{AB} = Z_A Z_B g^0_{AB} \qquad (9)$$

RESULTS AND DISCUSSION

In Figure 1 total binding energies of the complex ions have been plotted against ionisation energies of the ligand,[12] the index of ligand basicity in the model. The plot clearly demonstrates the linear increase in M–L bond energies with increasing basicity of the ligand. The usual notion of a stronger metal–ligand bond with ligands of higher basicity is thus theoretically substantiated. Obviously, it would be of interest to isolate the specific two-centre interactions controlling this trend.

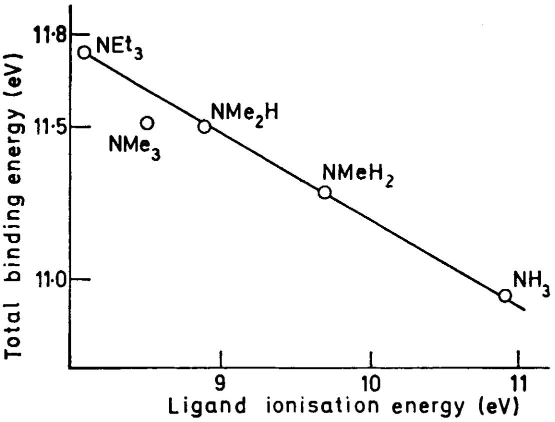

FIGURE 1 Net binding energy of a series of nickel(II)–amine complex ions shown as a function of ligand ionisation energy

Figure 2(*d*) presents a plot of unpaired electron density on a $3d$ orbital of Ni^{II} against ligand basicity. The plot clearly demonstrates that unpaired electron density in the metal $3d\sigma$ orbitals decreases linearly with increasing ligand basicity implying that a higher degree of L→M transfer of electron density occurs through the M–L charge-transfer interactions with ligands of higher basicity.

An examination of Table 1 reveals that the total ' diatomic overlap population ' $P_{AB}(= \sum_{\mu}^{A}\sum_{\nu}^{B} P^{AB}_{\mu\nu})$ between the metal and a ligand atom, conventionally called total bond order, increases with increasing ligand basicity. Thus, increased basicity of the ligand triggers a higher degree of charge localisation in the bonding region. It is interesting to note that while the $3d_{\sigma}L_{\sigma}$ and $4p_{\sigma}L_{\sigma}$ ' shared densities ' increase with increasing ligand basicity, the $4s_{\sigma}L_{\sigma}$ terms shows an opposite trend. However, the 4*s* orbital on the metal seems to play a relatively unimportant role in determining the general trends.

In Figure 2(*a*), (*b*), and (*c*) plots are shown of the $3d_{\sigma}L_{\sigma}$, $4s_{\sigma}L_{\sigma}$, and $4p_{\sigma}L_{\sigma}$ components of the metal–ligand covalent interaction energies (E^1_{AB}) against ligand basicity index. It is surprising that these energy quantities decrease with increasing basicity. The $3d_{\sigma}L_{\sigma}$ and the other exchange interactions contributing to E^2_{AB}, however, increase with increasing ligand basicity (Figure 3). One may recall that the diatomic exchange repulsion energy is directly proportional to the total ' shared density ' in the bond region; thus an increase in E^2_{AB} is expected if P_{AB} increases with increasing ligand basicity. The concomitant decrease in E^1_{AB} which also is a linear function of P_{AB}, however, needs explanation. It is a sum of the product of three terms, *viz.* $\sum_{\mu}^{A}\sum_{\nu}^{B} P^{AB}_{\mu\nu} \cdot \beta^{AB}_{\mu\nu} \cdot S^{AB}_{\mu\nu}$. An increase in the ligand basicity leads to an enhancement of the ' diatomic shared density ' $\sum_{\mu}^{A}\sum_{\nu}^{B} P^{AB}_{\mu\nu}$ but in turn $\beta^{AB}_{\mu\nu}$ decreases. This is not peculiar to the present CNDO model. Correlation of conventional CNDO bonding parameters (β^0_A) with atomic electronegativity [13] shows the generality of this behaviour. In the present case this decrease in β^{AB}_{ν} more than offsets the effect of an increase of electron density in the bonding region. Thus, the use of E^1_{AB} as an index of covalency in the CNDO model may give misleading conclusions for a series of closely related species. It is therefore emphasized that either $\sum_{\mu}^{A}\sum_{\nu}^{B} P^{AB}_{\mu\nu}$ or $\sum_{\mu}^{A}\sum_{\nu}^{B} P^{AB}_{\mu\nu} \cdot S^{AB}_{\mu\nu}$ or E^2_{AB} should be used to assess the degree of covalency in a given chemical bond, particularly when a CNDO type of model is employed in computing the one-electron density matrix.

TABLE 1

Variation of M–L overlap populations with ligand basicity in octahedral six-co-ordinate metal complexes of Ni^{II}

	Overlap population (o.p.)				
Ligand	$a =$ $3d_{\sigma}L_{\sigma}$	$b =$ $4s_{\sigma}L_{\sigma}$	$c =$ $4p_{\sigma}L_{\sigma}$	Total = $a + b + c$	o.p. per bond (P_{AB})
NH_3	0.623 6	0.999 8	2.607 0	4.230 7	0.705 1
$NMeH_2$	0.645 4	0.998 6	2.655 0	4.299 0	0.716 5
NMe_2H	0.667 4	0.996 2	2.682 0	4.345 6	0.724 2
NMe_3	0.668 4	0.994 2	2.700 6	4.359 6	0.726 6
NEt_3	0.674 0	0.991 6	2.721 6	4.386 6	0.731 1

Since E^1_{ML}, the so-called covalent (also called resonance) interaction-energy component of the ML bond, decreases in magnitude as the basicity of ' L ' increases, coulombic components must dominate the trends.

TABLE 2

Coulombic components (eV) of metal–ligand bond energy in a series of octahedral amine complexes of nickel(II)

	Interaction energies				
Ligand	Electron repulsion between M and L	Metal $3d$–ligand core	Metal $4s,4p$–ligand core	Ligand electron–metal core	Net electrostatic stabilisation of M–L bond
NH_3	83.994 0	−86.356 9	−23.640 7	−75.963 6	−1.650
$NMeH_2$	83.774 7	−86.556 0	−24.003 7	−77.399 4	−2.623
NMe_2H	83.540 6	−86.362 1	−24.790 6	−76.507 2	−2.298
NMe_3	83.414 5	−86.593 2	−25.283 1	−76.016 3	−2.511
NEt_3	83.207 8	−86.625 8	−25.912 8	−75.391 5	−2.755

1 eV $\approx 1.60 \times 10^{-19}$ J. The metal–ligand core–core repulsion energy is 101.967 2 eV in each case.

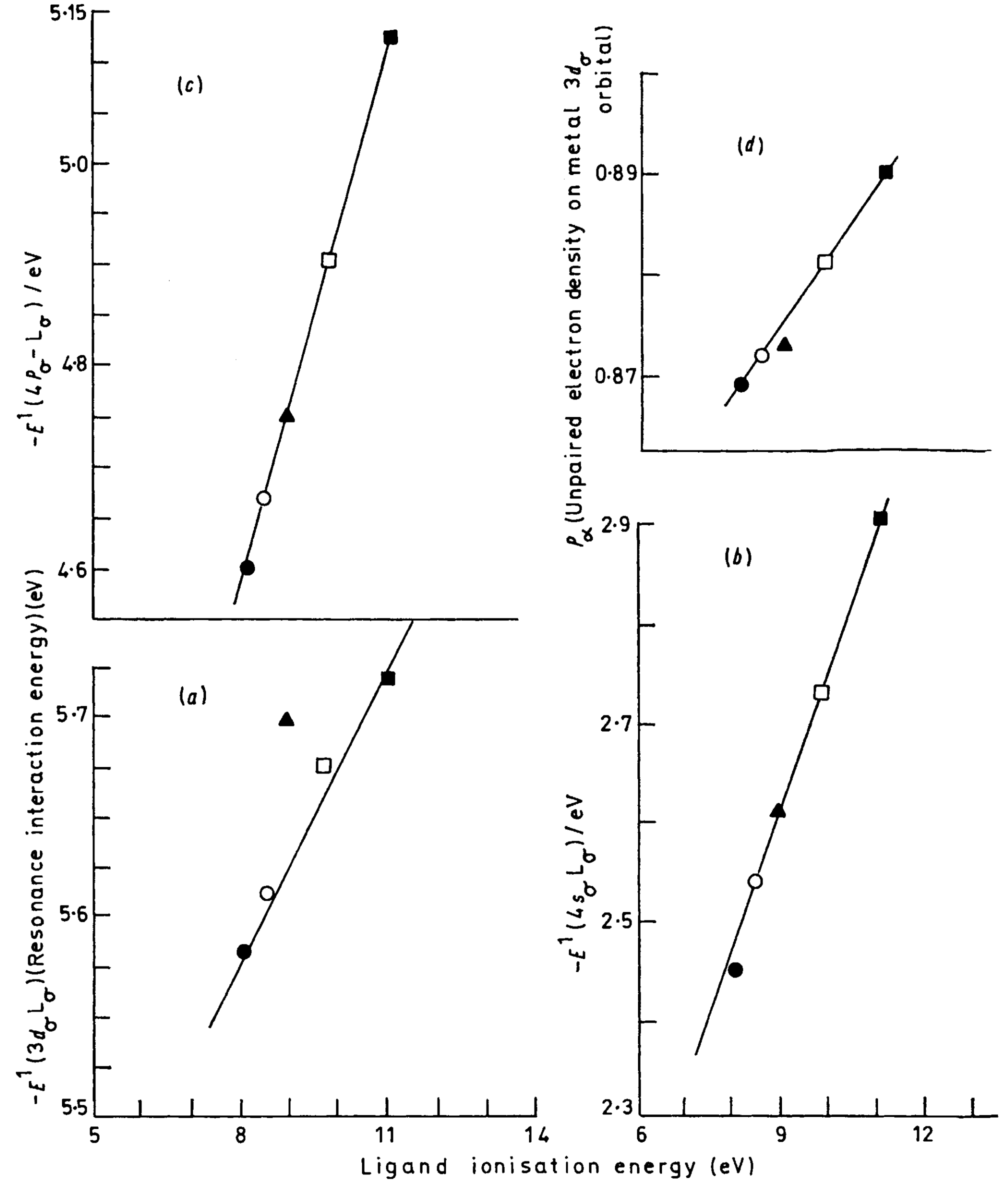

FIGURE 2 Different properties of a series of nickel(II) hexamine complex ions correlated with ligand basicity: (*a*) correlation of $3d_\sigma L_\sigma$ covalent interaction energy of metal–ligand bond; (*b*) $4s_\sigma L_\sigma$ covalent interaction energy of M–L bond; (*c*) $4p_\sigma L_\sigma$ component as in (*b*); (*d*) net unpaired electron density in a $3d_\sigma$ metal orbital, L_σ is a ligand orbital (σ type) with the same symmetry as that of the interacting metal orbital. Ligands: (○), NMe_3; (●), NEt_3; (□), $NMeH_2$; (▲), NMe_2H; (■), NH_3

From Table 2, one can see how the different two-centre coulombic energy components vary with ligand basicity. The balance of different coulombic interaction energies has been plotted against ligand basicity in Figure 4. A non-linear correlation emerges. It may be pointed out that in Mulliken's[14] valence-bond theory of charge-transfer (c.t.) complexes also, the stability of the c.t. complexes shows a similar non-linear correlation with the ionisation energy of the donor. In the present case, the quantity plotted in Figure 4 is essentially the c.t. stabilisation of the M–L bond defined in the context of m.o. theory. However, the result that the trends in the stability of the M–L bonds are not determined by what is usually defined as covalent interactions in the language of semiempirical m.o. theories needs further analysis. One may point out that the total two-centre coulombic energy component as defined in CNDO theory incorporates in it the effects arising from M–L transfers of electron density, a phenomenon definitely controlled by covalent interactions between the donor and acceptor orbitals. It is, thus, debatable whether E^1_{AB} alone can be regarded as the diatomic covalent interaction-energy component. *Ab initio* calculations and parallel analyses would provide a clearer physical picture.

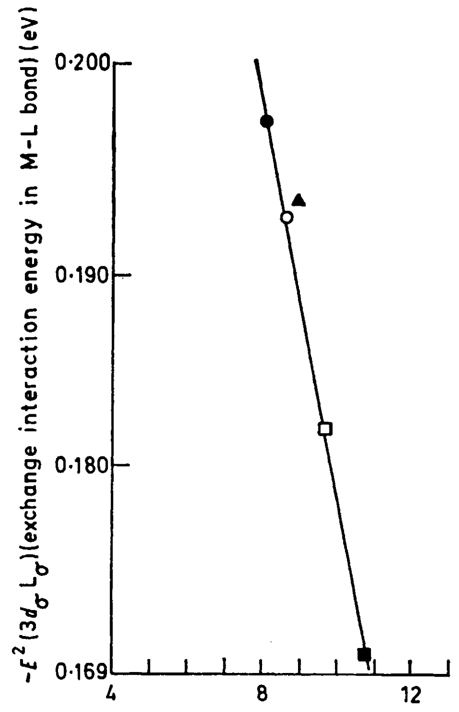

FIGURE 3 $3d\sigma L\sigma$ Exchange interaction energy of the metal-ligand bond shown as a function of ligand basicity. Ligands: (○), NMe$_3$; (●), NEt$_3$; (□), NMeH$_2$; (▲), NMe$_2$H; (■), NH$_3$

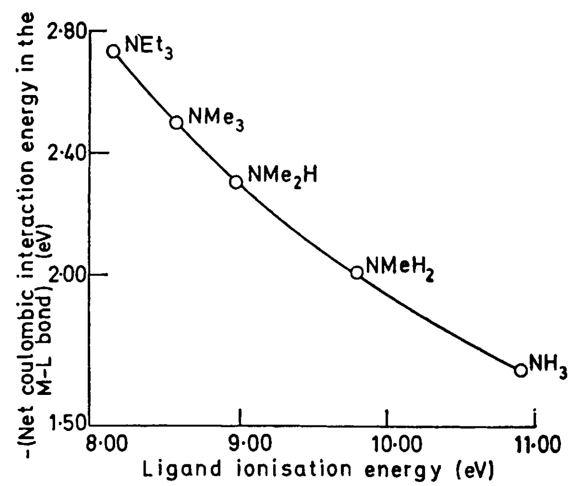

FIGURE 4 Net coulombic contribution to the stabilisation of the metal-ligand bond correlated with ligand basicity

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