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Molecular Orbital Studies of Some Transition Metal Complexes

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A set of molecular orbital calculations based on a particular semi-empirical method, has been undertaken on a homologue series of bis(π-2-methylallyl)transition metal (Ni, Co, Fe, Cr) complexes (abbreviated as ML_2). Arguments are found for predicting the stability of the NiL_2 system, which is the only one that could be synthetized.

Eine Reihe von semiempirischen MO-Rechnungen wurde für die homologe Reihe von bis(π-2-methylallyl) Metallkomplexen (Ni, Co, Fe, Cr) durchgeführt. Gründe für die Stabilität der Ni-Verbindung, die als einzige synthetisiert wurde, werden angeführt.

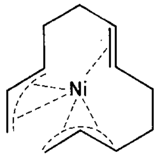
Un ensemble de calculs par une méthode semi-empirique particulière d'orbitales moléculaires a été effectué sur une série homologue de complexes bis (π-2-méthylallyl)-métal de transition (Ni, Co, Fe, Cr): ML_2.

Certains arguments sont trouvés en faveur de la stabilité du système NiL_2, le seul à avoir été synthétisé.

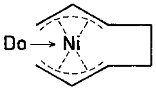
1. Introduction

It is well known that the oligomerisation of butadiene [9, 21, 35, 39] is catalysed by transition metal complexes (Ni, Fe, Co, Cr) in which the transition metal should be in a low oxidation state.

Wilke *et al.* [36, 37] and Bönnemann *et al.* [7] in the study of the cyclotrimerisation of butadiene leading to 1,5,9-cyclododecatriene, succeeded in isolating below 0° C the intermediate:



They put forward the hypothesis that the ends of the C_{12} chain are bonded to nickel through the π bonds of the allyl groups. A similar intermediate was also isolated by the cyclodimerisation of butadiene, the following complex being obtained (Do = donor):



Further support for the above-mentioned hypothesis was also given by the synthesis of bis(π-allyl) nickel, according to the overall reaction scheme:

$$NiBr_2 + 2\,CH_2{=}CH{-}CH_2MgBr \rightarrow Ni(CH_2{\overset{...}{=}}CH{\overset{...}{=}}CH_2)_2 + 2\,MgBr_2\,.$$

Curiously enough no other transition metal of the first period can give rise to the metallic bis(π-allyl) complex.

Since an X-ray analysis has been performed [33] on the bis(π-2-methylallyl) nickel complex (further referred to here as NiL_2 and more generally as ML_2), it seemed interesting to study the electronic structure of a series of similar complexes, involving different transition metal atoms (i.e. Ni, Co, Fe, Cr) and to try to obtain some understanding of the stability of the nickel complex relative to the others.

A particular molecular orbital calculation derived from the SCF Roothaan procedure was employed, in which the σ as well as the π-electrons are considered.

In these calculations, the three virtual systems were presumed to possess the same spatial geometry as the nickel complex.

A detailed electronic population analysis has been carried out and comparison of the results of the four systems provides grounds for predicting the stability of the existing system relative to the virtual ones. The atomisation energies, calculated according to the proposition of Boer *et al.* [6] for closed shell systems, also point to the greater stability of the nickel complex.

2. Method of Calculation

For a molecular orbital theory to be capable of furnishing useful information about the electronic structure of complex molecules, and related physical properties (see Ref. [16]), the formalism used must meet the following minimal requirements:

1. It must allow the π electrons as well as the σ electrons to be included in the chosen system.
2. It must take into account the electronic repartition per orbital inside the molecule. In this way the long-range electrostatic forces are systematically introduced into the theory.
3. It must be applicable to fairly large systems; however, the smallest number of molecular semi-empirical parameters should be used.

It is considered that the method employed [3] here complies, at least partially with these conditions. The method is based on the effective hamiltonian proposed by Longuet-Higgins and Pople [14]:

$$H_{\text{eff}} = h + \sum_j \frac{n_j}{2}(2J_j - K_j)\,. \tag{1}$$

The first term, h, represents the kinetic energy operator and the interaction operator with the core of the molecule (nuclei and inner electrons). The second term embraces the electronic interaction operators – coulomb and exchange – relative to the occupied molecular orbitals of the system. This type of hamiltonian does not differentiate between singly and doubly occupied molecular orbitals, except through their occupation numbers n_j. The summation extends over all occupied molecular orbitals.

By rigorous and consistent use of the Mulliken Ruedenberg approximations [28], the diagonal elements of the effective hamiltonian can be written [3] as:

$$H_{pp} = W_{pp} + \sum_{r(\mathrm{P})} q_r^{\mathrm{P}} (J_{pr} - \tfrac{1}{2} K_{pr}) + \sum_{\mathrm{L} \neq \mathrm{P}} \left[(V_{\mathrm{L},pp}^0) - \sum_{l(\mathrm{L})} (n_l^{\mathrm{L}} - q_l^{\mathrm{L}}) (J_{pl} - \tfrac{1}{2} K_{pl}) \right]. \tag{2}$$

The first term contains the kinetic energy and the interaction energy of one electron occupying the atomic orbital χ_p of atom P, with the core of this atom (nucleus and inner electrons; χ_p not included in the core of atom P).

In the second term, q_r^{P}, is the gross atomic population, as defined by Mulliken [18], i.e.

$$q_r = \sum_{j,s} n_j C_{rj} C_{sj} S_{rs} \tag{3}$$

the summation being extended over all occupied molecular orbitals. The second factor in the second term of Eq. (2) refers to the monocentric coulomb and exchange interactions among the atomic orbital basis set.

In the third term, $(V_{\mathrm{L},pp}^0)$ are the penetration integrals, V_{L}^0 referring to the potential interaction created by the neutral atom L. The third term embodies the contribution of the interatomic transfer of charges through the last summation of Eq. (2).

As starting point for the evaluation of the required integrals of Eq. (2), a certain number of approximations currently applied to large systems have been made:

1. The penetration integrals have been neglected. This is often considered to be equivalent to a displacement of the zero point of the energy scale.

2. The exchange bicentric integrals, K_{pl}, are considered to be negligible.

In an early stage of the calculation we assumed that $n_l^{\mathrm{L}} \approx q_l^{\mathrm{L}}$. This is equivalent to assuming the intramolecular charge transfers to be small, thus excluding the application of the present method to systems with a pronounced ionic character. Eq. (2) then becomes:

$$H_{pp} = W_{pp} + \sum_{r(\mathrm{P})} q_r^{\mathrm{P}} (J_{pr} - \tfrac{1}{2} K_{pr}). \tag{2a}$$

In a second stage, we have approximated the bicentric coloumb integrals by the Nishimoto and Mataga relation [22]:

$$J_{pl} = \frac{27.2107}{\dfrac{R_{pl}}{0.529} + \dfrac{54.4214}{J_{pp} + J_{pl}}} \text{ (in eV)}. \tag{4}$$

In evaluating the non-diagonal elements of the effective hamiltonian, it is not easy to express them in a simple analytical form in the self-consistent field theory. We have used here the Wolfsberg-Helmholz approximation [38]:

$$H_{pq} = \tfrac{1}{2} K S_{pq} (H_{pp} + H_{qq}) \tag{5}$$

where K is a semi-empirical parameter to which values between 1.5 and 3 are usually given. From a theoretical point of view this formula has well known shortcomings [2] in that it is not invariant relative to linear transformations of the atomic basis, nor to shifts of the zero point of the energy scale. Moreover, it gives a wrong dependence of the kinetic integrals on the overlap integrals. However, the primitive approximation of the Wolfsberg-Helmholz model can be provisionally retained for semi-empirical studies, in so far as reasonable variations of K do not alter the qualitative picture of the molecule. The parameter K has here been taken to be equal to 3, a value which has previously given good results [8].

3. Molecular Orbital Determination in the Bis(π-Methylallyl) Transition Metal Complexes NiL_2, CoL_2, FeL_2 and CrL_2[1]

1. Symmetry of the Molecule

We have applied the method briefly described above to four organometallic complexes: NiL_2, CoL_2, FeL_2, and CrL_2, where

$$L = [CH_2 \quad C(CH_3) \quad CH_2],$$

the three latter systems being not synthetized. The molecular geometry (Fig. 1) has been obtained from an X-ray analysis [3] performed on bis(π-methylallyl)-nickel complex, and is here adopted for all four molecules.

The metallic atom has been placed at the origin of a trirectangular coordinate system, the y-axis of which is perpendicular to the plane formed by the allyl groups (C=C 1.414 Å). The hydrogens H(2) and H(3) are parallel to the (z, x) plane, whereas hydrogen H(1) lies in the (x, y) plane. The bond C(1)–C(2)

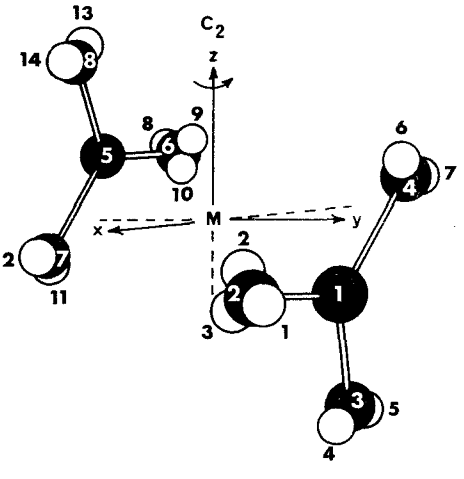


Fig. 1. Molecular geometry of the bis(π-methylallyl) transition metal complex (C_{2h} group of symmetry); ● = C, ○ = H

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[1] The calculations have been carried out partly at the IBM computer Centre, Rijswijk, on an IBM 7094 and partly at the Unilever Research Laboratory, Vlaardingen, on an IBM 1802.

(C—C 1.492 Å) lies in the (x, y) plane and is not coplanar with the allyl group, but is directed towards the "x"-axis at an angle of about 12°. All carbon hydrogen bonds have the same length (C—H 1.09 Å). The angles between the carbon-carbon bonds in the methylallyl groups and the valence angles of the methylene groups are both equal to 120°. The valence angles in the methyl groups are equal to 109.5°. Finally the two methylallyl groups are images of each other through the inversion centre and the C_2 axis of symmetry (along the z-axis of the reference frame) in such a way that this system belongs to the C_{2h} group of symmetry.

The atomic orbital basis contains 9 orbitals for the metal and 23 orbitals for each methylallyl group; these orbitals span a 55 × 55 reducible representation, whose irreducible components in the C_{2h} group are given by

$$\Gamma = 18\, a_g + 11\, b_g + 16\, b_u + 10\, a_u\,.$$

The symmetry orbitals have been obtained by use of the standard projection operator technique (see for example [15]).

2. *Calculation of the Overlap Integrals*

All the overlap integrals, including those between non-neighbouring atoms, appearing in Eq. (3) have been evaluated by the use of linear combinations of Slater functions [19, 25, 26]. For the hydrogen atom, the Slater function with an effective charge equal to 1.0, has been adopted. The numerical computations have been carried out with the aid of the analytical expressions given by Roothaan [27], Mulliken *et al.* [20] and Jaffé [12][2]. For convenience the x, y, z axis of the local frames are all oriented in the same way as the reference frame centred on the metallic atom.

3. *Calculation of the Matrix Element, H_{pp}, Relative to a Metal Orbital*

It is customary to express the H_{pp} integral (see Eq. 2a) as a difference of spectroscopic terms. This procedure is formally identical to that used by Pariser and Parr [23] for π electrons of conjugated molecules. We replace the integrals J and K appearing in H_{pp} by a combination of Slater-Condon parameters [30] F^k, G^k. As the terms in $F^{(0)}(k=0)$ usually contribute most significantly to the final results, spectroscopic terms [17] have been used for the evaluation of these integrals. The integrals F^k, G^k for $k>0$ have been evaluated theoretically, using Richardson *et al.* [25, 26] data.

Tables 1–3 give the values of the Slater-Condon integrals calculated in this work, the metallic monocentric integrals, as well as the values of core parameters (the latter being easily calculated once the matrix element H_{pp} has been evaluated).

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[2] We are very grateful to Professor G. Berthier research group (Ecole Normale Supérieure, Paris) for having supplied us with the program with which this calculation has been performed.

Table 1. *Slater-Condon parameters (eV)*

	Ni^I	Co^I	Fe^I	Cr^I
Spectroscopic values				
$F^0(3d, 3d)$	21.87468	19.89918	17.99988	14.13324
$F^0(3d, 4s)$	15.47472	14.59854	13.74957	12.62849
$F^0(3d, 4p)$	11.03121	10.56591	10.07612	8.99858
$F^0(4s, 4s)$	13.63528	12.89243	12.48427	11.59176
$F^0(4s, 4p)$	10.42169	9.98088	9.58361	8.73463
$F^0(4p, 4p)$	8.99313	8.64484	8.28022	7.50743
Theoretical values				
$F^2(3d, 3d)$	9.87405	9.16140	8.41423	6.90259
$F^2(3d, 4p)$	0.64840	0.18637	0.67693	0.81739
$F^2(4p, 4p)$	2.63654	2.54465	2.45289	2.37707
$F^4(3d, 3d)$	6.03675	5.58009	5.10633	4.17437
$G^1(3d, 4p)$	0.21538	0.23059	0.25098	0.36962
$G^1(4s, 4p)$	2.38044	2.29075	2.20164	2.29279
$G^2(3d, 4s)$	1.26907	1.31709	1.38466	1.55859
$G^3(3d, 4p)$	0.14276	0.15265	0.16581	0.24339

Table 2. *Atomic parameters relative to* Ni^I, Co^I, Fe^I *and* Cr^I

Type of monocentric integral	Value of the integral (eV)			
$L_{pr} = J_{pr} - \frac{1}{2}K_{pr}$	Ni^I	Co^I	Fe^I	Cr^I
ss	6.81764	6.44621	6.24213	5.79588
sp	10.02495	9.59909	9.21667	8.35250
sd	15.34781	14.46683	13.61110	12.47263
pp	4.71058	4.52599	4.33634	3.56355
$p_xp_y = p_yp_z = p_zp_x$	8.62402	8.28859	7.93681	7.17464
$p_xd_{xy} = p_yd_{yz} = p_zd_{xz} =$ $p_xd_{xz} = p_yd_{xy} = p_zd_{yz} =$ $p_xd_{x^2-y^2} = p_yd_{x^2-y^2}$	11.03973	10.54602	10.08158	8.99640
$p_xd_{z^2} = p_yd_{z^2}$	10.98174	10.54198	10.02299	8.93061
$p_xd_{yz} = p_yd_{xz} = p_zd_{xy} = p_zd_{z^2}$	11.06873	10.54805	10.11088	9.02030
$p_zd_{x^2-y^2}$	10.95274	10.53995	9.99369	8.89772
dd	11.58675	10.55118	9.55179	7.51867
$d_{z^2}d_{x^2-y^2} = d_{z^2}d_{xy}$	20.64509	18.75849	16.95221	13.27389
$d_{z^2}d_{xz} = d_{z^2}d_{yz}$	21.64308	19.68617	17.80588	13.97539
$d_{x^2-y^2}d_{xy}$	21.97575	19.99537	18.09043	14.20921
$d_{x^2-y^2}d_{xz} = d_{x^2-y^2}d_{yz} =$ $d_{xy}d_{yz} = d_{xz}d_{yz} = d_{xy}d_{xz}$	20.97775	19.06773	17.23676	13.50773

Table 3. *Core atomic parameters (eV)*

Atom	W_{ss}	W_{pp}	W_{dd}
Ni^I	−145.56	−100.64	−196.36
Co^I	−115.23	− 86.73	−159.65
Fe^I	−102.13	− 74.57	−127.29
Cr^I	− 68.66	− 50.97	− 73.82
C^I	− 52.35	− 40.53	—
H	− 13.60	—	—

4. Calculation of the Matrix Element, H_{pp}, Relative to Carbon or Hydrogen Orbitals

These integrals are evaluated more simply by the use of valence state configuration energies given by Pilcher and Skinner [24], the latter being again calculated by means of atomic spectroscopic data. Combining, as usual, the valence state energies of the neutral atom and of its ions [23], the values summarized in Table 4 are found for the integrals J_{pr} and K_{pr}. Table 3 gives the core parameters for these atoms.

Table 4. *Atomic parameters relative to* C^I *and* H

Atom	Type of monocentric integral	Value of the integral (eV)	
		J_{ij}	K_{ij}
C^I	*ss*	11.88	
	sp	11.82	2.59
	pp	10.44	
	pp'	9.17	0.64
H	*ss*	12.85	

4. Results

1. Preliminaries

It is convenient to choose a valence state configuration corresponding to the neutral atom to obtain at the outset an evaluation of the H_{pp} matrix. Thus

$$H^0_{pp} = W_{pp} + \sum_{r(\mathrm{P})} n^{\mathrm{P}}_r (J_{pr} - \tfrac{1}{2} K_{pr})$$

and

$$H_{pp} = H^0_{pp} + \sum_{r(\mathrm{P})} (q^{\mathrm{P}}_r - n^{\mathrm{P}}_r)(J_{pr} - \tfrac{1}{2} K_{pr}) .$$

In this way the occupation number for the orbital r of the hypothetically neutral atom is well defined, and its value determines the nature of spectroscopic terms to choose for the calculation of H_{pp}. Consequently it determines the way of evaluating W_{pp}.

2. Analysis of the Results of Molecular Orbital Calculations

A plausible charge distribution among the 55 atomic orbitals was selected for constructing the matrix elements of the hamiltonian: selfconsistency was considered to be achieved when the populations of the two successive interactions agreed within 0.002 electron. The results obtained for NiL_2, CoL_2, FeL_2, and CrL_2 have led us to the analysis of the following parameters:

1. Gross and partial atomic populations, the latter arising from the unpaired electron in CoL_2 (Tables 5 and 6).

2. Net charges upon different centres in the molecule (Table 7).
3. Total overlap population (Table 8).
4. Correlation diagram between a few eigenvalues (Fig. 2).
5. Atomisation energies calculated for closed shell systems (Table 9).
6. Orbital energies corresponding to diagonal elements of the effective hamiltonian (Fig. 3).

Before discussing these results (Section V):

a) The atomic orbital, r, will be called electro-repulsive when it corresponds to a negative value of the gross atomic population, q_r, and electro-attractive when $q_r > 0$.

b) The overlap population index follows the definition given by Mulliken [18]. In his notations:

$$n(k, l) = \sum_i \sum_r \sum_s 2N(i)\, C_{ir_k} C_{is_l} S_{r_k s_l}\,.$$

c) Following a proposition of Boer *et al.* [6], we have calculated for closed shell systems the atomisation energy, using the relation:

$$\Delta = \tfrac{1}{2}\left[\sum_i E_i^M - \sum_{j,\text{at}} (E'_j)_{\text{at}}\right] - A \tag{6}$$

Table 5. *Gross and partial atomic populations q_r and ϱ_r without explicit inclusion of bicentric Coulomb integrals*

		NiL_2	CoL_2		FeL_2	CrL_2
		q_r	q_r	ϱ_r	q_r	q_r
M	$4s$	0.666	−0.864	0.001	−1.053	−1.166
	$4p_x$	−0.412	−0.175	0.000	−0.084	0.086
	$4p_y$	−0.823	−0.401	0.000	−0.228	−0.013
	$4p_z$	−0.296	−0.062	0.000	−0.000	0.140
	$3d_{z^2}$	1.933	1.913	0.001	1.883	1.817
	$3d_{x^2-y^2}$	1.970	1.972	0.001	1.933	1.902
	$3d_{yz}$	1.739	1.634	0.000	1.460	0.543
	$3d_{xz}$	1.956	1.944	0.000	1.928	1.511
	$3d_{xy}$	1.917	1.803	0.109	1.223	0.436
C(1)	$2s$	1.090	1.087	0.004	1.102	1.083
	$2p_x$	0.960	0.931	0.065	0.894	0.969
	$2p_y$	0.932	0.947	0.000	0.996	0.971
	$2p_z$	1.034	1.028	0.000	1.013	0.996
C(2)	$2s$	0.915	0.905	0.003	0.916	0.893
	$2p_x$	1.094	1.066	0.054	1.046	1.109
	$2p_y$	1.111	1.112	0.000	1.110	1.102
	$2p_z$	1.146	1.149	0.000	1.149	1.136
C(4)	$2s$	0.972	0.981	0.001	1.016	1.019
	$2p_x$	1.079	0.967	0.071	0.924	0.885
	$2p_y$	1.208	1.270	0.043	1.273	1.256
	$2p_z$	1.038	1.059	0.012	1.031	1.042
H(1)	$1s$	0.934	0.917	0.003	0.915	0.920
H(2)	$1s$	0.952	0.936	0.000	0.931	0.930
H(6)	$1s$	0.969	1.024	0.026	1.001	1.000
H(7)	$1s$	1.009	0.998	0.004	0.985	0.961

Table 6. *Gross and partial atomic population q_r and ϱ_r with explicit inclusion of bicentric Coulomb integrals*

		NiL$_2$	CoL$_2$		FeL$_2$	CrL$_2$
		q_r	q_r	ϱ_r	q_r	q_r
M	$4s$	0.583	−0.867	0.001	−1.006	−1.217
	$4p_x$	−0.513	−0.329	0.000	−0.194	0.043
	$4p_y$	−0.938	−0.597	0.000	−0.345	−0.043
	$4p_z$	−0.413	−0.200	0.000	−0.090	0.080
	$3d_{z^2}$	1.930	1.910	0.001	1.881	1.787
	$3d_{x^2-y^2}$	1.968	1.971	0.001	1.932	0.010
	$3d_{yz}$	1.700	1.598	0.000	1.443	1.222
	$3d_{xz}$	1.951	1.940	0.000	1.927	1.905
	$3d_{xy}$	1.917	1.792	0.123	0.968	1.087
C(1)	$2s$	1.065	1.073	0.003	1.091	1.054
	$2p_x$	0.977	0.935	0.067	0.920	0.935
	$2p_y$	0.894	0.922	0.000	0.965	0.979
	$2p_z$	1.046	1.033	0.000	1.013	1.000
C(2)	$2s$	0.936	0.939	0.002	0.950	0.928
	$2p_x$	1.121	1.083	0.058	1.078	1.095
	$2p_y$	1.146	1.145	0.000	1.139	1.135
	$2p_z$	1.174	1.175	0.000	1.173	1.171
C(4)	$2s$	0.990	1.003	0.001	1.036	1.004
	$2p_x$	1.121	1.013	0.069	0.982	0.935
	$2p_y$	1.246	1.303	0.040	1.307	1.362
	$2p_z$	1.078	1.093	0.012	1.060	1.053
H(1)	$1s$	0.891	0.882	0.004	0.883	0.876
H(2)	$1s$	0.929	0.918	0.000	0.911	0.898
H(6)	$1s$	0.968	1.034	0.025	0.999	0.987
H(7)	$1s$	0.990	0.983	0.004	0.996	0.949

Table 7. *Net charges upon different centres in the molecule* ML$_2$

Atom	Without bicentric Coulomb integrals				With bicentric Coulomb integrals			
	NiL$_2$	CoL$_2$	FeL$_2$	CrL$_2$	NiL$_2$	CoL$_2$	FeL$_2$	CrL$_2$
M	+1.35	+1.23	+0.94	+0.74	+1.82	+1.81	+1.48	+1.13
C(1)	−0.02	+0.01	−0.01	−0.02	+0.02	+0.04	+0.01	+0.03
C(2)	−0.26	−0.23	−0.22	−0.24	−0.38	−0.34	−0.34	−0.33
C(4)	−0.29	−0.27	−0.24	−0.20	−0.44	−0.41	−0.38	−0.35
H(1)	+0.06	+0.08	+0.08	+0.08	+0.10	+0.12	+0.12	+0.12
H(2)	+0.05	+0.06	+0.07	+0.07	+0.07	+0.08	+0.09	+0.10
H(6)	+0.03	−0.02	−0.00	+0.00	+0.03	−0.03	+0.00	+0.01
H(7)	−0.01	+0.00	+0.02	+0.04	+0.01	+0.02	+0.04	+0.05

where E_i^M is the ith molecular orbital energy, $(E_j')_{\mathrm{at}}$ the jth orbital energy corresponding to one particular atom in the molecule, and A the atomisation energy or binding energy (negative for stable systems), the summation over i and j being extended over occupied orbitals.

Table 8. *Total overlap population indices*

Atom	Without bicentric Coulomb integrals				With bicentric Coulomb integrals			
	NiL_2	CoL_2	FeL_2	CrL_2	NiL_2	CoL_2	FeL_2	CrL_2
M–C(1)	−0.364	−1.327	−0.735	−0.870	−0.541	−1.432	−0.733	−0.769
M–C(4)	−0.223	−1.247	−0.489	−0.537	−0.457	−1.386	−0.497	−0.616
M–C(2)	−0.264	−0.383	−0.268	−0.331	−0.374	−0.457	−0.298	−0.306

Table 9. *Atomisation energies of* ML_2 *(in eV) without* (ΔE^I) *and with* ΔE^{II}) *bicentric Coulomb integrals*

Type of atom	Metal						Carbon				H	ΔE^I	ΔE^{II}
	3*d*					4*s*	2*s*	2*p*			1*s*		
	z^2	x^2-y^2	yz	xz	xy			x	y	z			
Ni	↑↓	↑↓	↑	↑↓	↑↓	↑	↑	↑	↑	↑	↑	−154.22	−177.57
Fe	↑↓	↑↓	↑	↑↓	↑		↑	↑	↑	↑	↑	−152.07	−156.78
Cr	↑↓	↑↓	↑	↑			↑	↑	↑	↑	↑	−147.89	—
	↑↓		↑	↑↓	↑		↑	↑	↑	↑	↑	—	−159.75

These authors have shown by non-empirical calculations on simple systems that the quantity Δ is always a small term (0.1 or 0.3 a.u.) relative to the other variables appearing in Eq. (6). Consequently we consider the following might be a good approximation for atomisation energies:

$$A \approx \tfrac{1}{2}\left[\sum_i E_i^M - \sum_{j,\mathrm{at}} (E'_j)_{\mathrm{at}}\right]$$

5. Discussion

Let us recall that the purpose of these molecular orbital (MO) calculations was to find some arguments for explaining the existence of the NiL_2 system, as distinct from the virtual systems.

1. Gross and Partial Atomic Populations and Net Charges upon the Atoms

It can be seen from Table 8 that the net positive charges on the metallic atoms are higher when the bicentric Coulomb integrals (further abbreviated as J_{pl} contribution), are included. In a similar way Jørgensen *et al.* [13], discussing another series of first period transition metal complexes, also obtained, by including the so-called "Madelung energy", a higher net positive charge upon the metal than that given by a standard Wolfsberg-Helmholz calculation.

The results of the analysis of the gross atomic population parameters (see Tables 5 and 6) justify the following conclusions about the transition metal atoms.

a) Only in the case of the NiL_2 system is the $4s$ orbital electro-attractive, independent of the inclusion of J_{pl} contributions. For the CoL_2, FeL_2 and CrL_2 systems, the $4s$ electro-attractive character collapses. Moreover, it seems that the electro-repulsive character of the latter systems increases monotonously from the CoL_2 system.

b) Except for the CrL_2 system, the $3d$ orbitals are similarly populated.

c) The electro-repulsive character of the $4p$ orbitals diminishes from the NiL_2 towards the CrL_2 system, this character being generally higher with J_{pl} contributions.

From the foregoing it can be concluded that the negative net charges of the carbon atoms of the methylallyl group increase with the inclusion of J_{pl} contributions. What also emerges is the well known fact that the allylic hydrogens are more negative than those of the methyl group.

The attention of the reader is drawn to a very recent paper [34] in which an *ab-initio* computation of the ground state electronic wave function for bis(π-allyl)nickel is described. It emerges that a very satisfactory agreement with our results is obtained through the Mulliken population analysis carried out also in the latter paper. Specifically, a net charge of $+1.92$ upon the nickel atom is found by the *ab-initio* computation, whereas a charge of $+1.82$ is found in our case with explicit inclusion of J_{pl} contributions. Also the net charges upon the carbon as well as upon the hydrogen atoms in the allyl groups fit the *ab-initio* results more closely when J_{pl} contributions are involved. This fact emphasizes the role played by the bicentric Coulomb integrals in the effective hamiltonian used.

2. Back-Donation Effect

In transition metal olefinic complexes of π types, the back-donation effect is usually considered to be a lone pair transfer from a metallic orbital towards a ligand antibonding orbital (π^*). It must be stressed, however, that such effects are usually described [32] for a system possessing at least a ternary axis of symmetry. In other words, as is evident from the symmetry orbitals, the C_{2h} symmetry group is too low clearly to separate the σ and π electrons. The (x, metal, z) plane is *not* a symmetry plane for the *whole* system. Nevertheless, as suggested by the analytical forms of the symmetry orbitals, a pseudo-plane of symmetry can be envisaged (i.e. the plane formed by the allyl group alone) relative to which we could define a back-donation effect. The MO involved would belong to the a_g symmetry, which would imply that the highest filled MO effectively belongs to that symmetry. Then it might be imagined an electronic transfer through the lone pair $3d_{xy}$ towards $2p_y$ orbitals of the allyl groups. This point of view is roughly corroborated by the small components of the $4s$, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals relative to the $3d_{xy}$ component, obtained in the highest filled MO of the NiL_2 system.

Back donation might also be considered through the lone pair $3d_{yz}$ towards the non-bonding $2p_y$ orbitals of the allyl groups. This effect is confirmed by the electro-attractive characters of the $2p_y$ orbitals of the carbon atoms C_3, C_4, C_7, and C_8 (see Tables 5 and 6), the negative net charges upon the latter atoms and the relatively low electronic population of the metal orbital $3d_{yz}$.

3. *Koopmans Theorem and Ionisation Potential*

The diagonal matrix elements relative to $3d_{x^2-y^2}$, $3d_{xz}$, and $3d_{xy}$ orbitals of nickel, in a valence state as close as possible to the charge distribution obtained for the metal inside the complex, are very near the mean ionisation energy attributed by Slater [30] to the $3d$ nickel orbitals.

This means, at least for the NiL_2 system, that the molecule can be considered to be formed from atoms taken in their neutral valence state configurations. We find indeed: $H(x^2-y^2, x^2-y^2) = H(xz, xz) = H(xy, xy) = -9.67$ eV; I(Ni; $3d$) $= +9.93$ eV. In the frame of Koopmans theorem, the ionisation potential of NiL_2 is approximately equal, and of opposite sign, to the highest filled MO, i.e. -5.89 eV. As the latter is a a_g MO containing as main metal component the $3d_{xy}$ orbital for which we specifically obtain a good correlation with the value of the ionisation potential in the free atom, it is very likely that the decrease of about 3 eV, revealed by our calculation, represents a good estimation of the ionisation potential difference between the metal and the complex.

It should also be noted that the highest filled MO for the series of studied systems lie roughly between 5 and 6 eV. In this connection, it is also interesting to look at the sequence of first appearance potentials (I in eV) in the bis(cyclopentadienyl) series (Cp_2) of the following transition metals [5]:

$$\begin{aligned} NiCp_2 &\rightarrow Ni\overset{+}{C}p_2 + e^- && 7.06 \pm 0.1\,, \\ CoCp_2 &\rightarrow Co\overset{+}{C}p_2 + e^- && 6.2 \ \pm 0.3\,, \\ FeCp_2 &\rightarrow Fe\overset{+}{C}p_2 + e^- && 7.05 \pm 0.1\,, \\ CrCp_2 &\rightarrow Cr\overset{+}{C}p_2 + e^- && 6.91 \pm 0.2\,. \end{aligned}$$

The lack of correlation between the Slater $3d$ ionisation potentials corresponding to cobalt, iron and chromium atoms and the calculated orbital energies of the bis(π-methylallyl) complexes is probably due to the fact that the mean of the configurations used by Slater to define atomic $3d$ ionisation potentials, does not agree with the valence state configurations attributed by our calculation to the metal inside the complexes.

4. *Overlap Population Indices*

a) *Metal-Carbon Bond*

It seems quite clear (Table 8) that Ni–C bonds have the weakest antibonding character. The semi-polar character of these bonds should be correlated with the results obtained recently by Stevenson and Libscomb [31] on the systems ScH_3NH_3 and TiH_3F, where very slightly positive overlap population indices were obtained for Sc–N of Ti–H bonds. Similar results were obtained by Berthier and Millié [4] for organic molecules with semi-polar bonds.

b) *Carbon-Hydrogen and Carbon-Carbon Bonds*

It is well known that carbon hydrogen bonds of ethylenic compounds are more contracted than those corresponding to single bonds. This also applies to carbon carbon bonds occurring in unsaturated and saturated compounds. These features are reflected by the overlap population indices obtained for these bonds.

Specifically in the case of NiL_2 system, the overlap populations of the bonds C(1)–C(2) and C(1)–C(4) without and (with) explicit inclusion of bicentric Coulomb integrals are respectively 0.827(0.870) and 1.144(1.191).

Moreover, it seems on a general manner, whichever the system being considered, that inclusion of J_{pl} contributions raises substantially the values of the C–H of C–C overlap indices.

5. *Atomisation Energy*

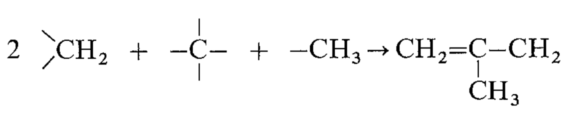
The atomisation energies or binding energies, given in Table 9, have been obtained defining a valence configuration, or the occupation numbers of particular valence orbital as close as possible to the SCF results (see Tables 5 and 6).

As already mentioned, Boer *et al.* [6] have proposed for closed shell systems a fairly simple relation for calculating the atomisation energy or binding energy, in simple organic molecules. This relation is not applicable for open shell systems and it can easily be shown that by defining the total energy as:

$$E' = \sum_i (I_i + e_i) + \tfrac{1}{2}(I_r + e_r)$$

this expression contains an additional term equal to $\tfrac{1}{4}J_{rr}$, resulting from the analytical form of the Longuet-Higgins and Pople hamiltonian (see Eq. 1).

It can be seen from Table 9 that, in any case, the atomisation energy is greater for NiL_2. From thermodynamic standard heats of formation of radicals in the gaseous phase [1] according to the following process



$$2\ \rangle CH_2 + -\overset{|}{\underset{|}{C}}- + -CH_3 \rightarrow CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2$$

and using the value $D(C{-}C) \simeq 3.3$ eV [10], it is readily found that $D(C{=}C) \simeq 8.3$ eV. Assuming a dissociation energy of 4.9 eV [11] for each hydrogen in the methyl group and of 4.2 eV [11] for each hydrogen of the methylene group, the energy content of the bis(methylallyl) groups is found to be $\simeq -93$ eV. The energy corresponding to the nickel atom in the valence configuration quoted is $\simeq -80.8$ eV.

Adopting the value -177 eV for the bonding energy in the complex NiL_2 (see Table 9) and supposing that the strengths of Ni–C bonds are roughly the same, it is found that the mean dissociation energy of one Ni–C bond, i.e. $\bar{D}$(Ni–C), is $\simeq 0.7$ eV. A value of about 3 eV for $\bar{D}$(Ni–C) in $NiCp_2$ [5] being currently proposed, our value qualitatively reflects a less stable compound than $NiCp_2$, the great stability of the latter being well-known.

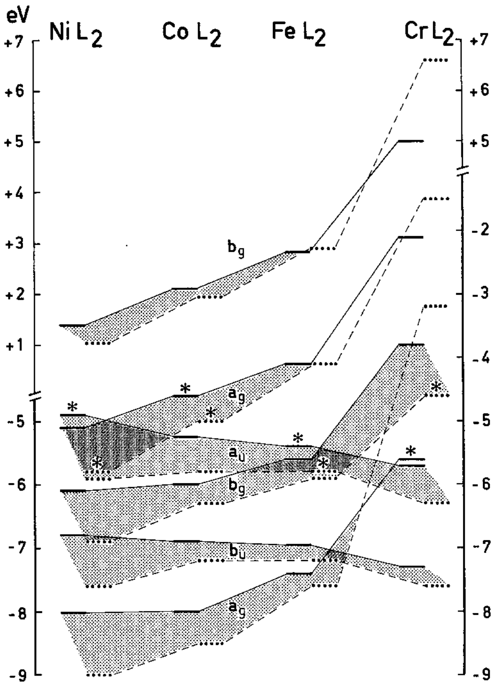


Fig. 2. Correlation diagram of some eigenvalues without (— —) and with (· · · · ·) J_{pl} contribution. The symbol * indicates the highest filled level for the particular ML_2 system

6. *Eigenvalue Spectra*

Two correlation diagrams (with and without J_{pl} contributions) between a few eigenvalues are shown in Fig. 2. Two aspects should be noted. First, as is to be expected, the height of the energy levels increases when the net charges upon the transition metals diminish. Secondly, the energy levels become more spaced out from NiL_2 to CrL_2 system. This is because the effect of overlap is more pronounced on energetically highly placed levels.

It is apparent that in the NiL_2 system, the a_u and a_g occupied levels are quite close to each other. It is not at all surprising that the sequence of these levels is inverted by incorporating the J_{pl} contributions into the hamiltonian, the symmetry a_g for the highest filled MO being more in accordance with the qualitative picture of the molecule.

No UV-spectroscopic studies of NiL_2 have been carried out. It should be interesting to see whether the assignment of electronic transitions corroborates the symmetry species of the MO's.

7. *Conclusion*

Fig. 3 shows an orbital energy diagram corresponding to the four systems studies (with J_{pl} contributions). It is striking in the NiL_2 system, and only in this system, that (*a*) the 4*s* orbital has a low energy and that (*b*) the

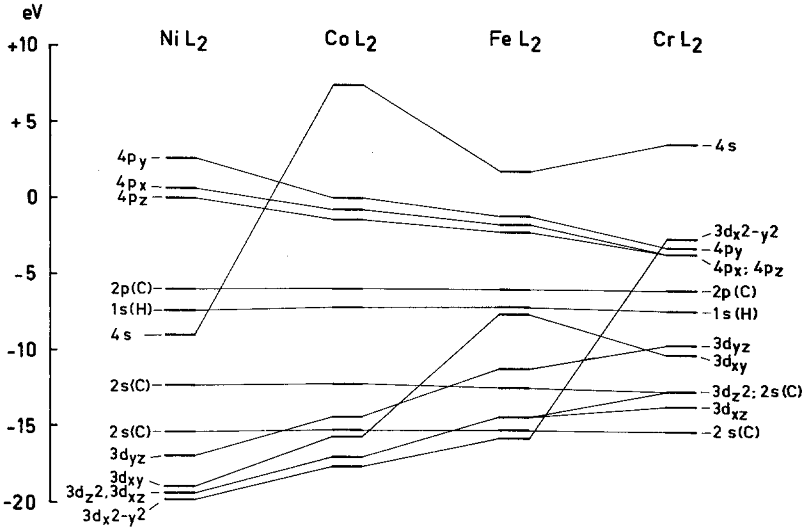


Fig. 3. Orbital energies corresponding to diagonal elements of the effective hamiltonian (with J_{pl} contribution)

usual sequence of transition metal orbitals is found, the *d* orbitals being the deepest, followed by the 4*s* and finally, the 4*p* orbitals. When passing to hypothetical bis(π-methylallyl) complexes, one observes a gradual dispersion among the 3*d* orbitals, starting from the NiL$_2$ system, and a monotonous decrease of the 4*p* orbitals. It is very gratifying that this diagram is a mirror of the results of the population analysis given in Tables 5 and 6. For example, in the NiL$_2$ system, and only in the latter system, a low energetic value of $H(4s, 4s)$, i.e. $\simeq -9$ eV, corresponds to a positive charge index upon the 4*s* orbital or to its electro-attractive character.

All these facts strongly support the special ability of nickel for giving such complexes. However, contrary to the usual opinion [29], the results of MO calculations suggest a semi-polar character for the nickel-carbon bonds.

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References

1. Bernecker, R. R., Long, F. A.: J. physic. Chem. **65**, 1565 (1961).
2. Berthier, G., del Re, G., Veillard, A.: Nuovo Cimento **44** B (2), 315 (1966).
3. — Lemaire, H., Rassat, A., Veillard, A.: Theoret. chim. Acta (Berl.) **3**, 213 (1965).
4. — Millié, Ph.: Colloq. Intern. Centre Natl. Rech. Sci. Paris, in press.
5. Birmingham, J. N.: In: Advan. Organometal. Chem., Vol. 2, p. 365, ed. by F. G. A. Stone and R. West, New York/London: Academic Press 1964.
6. Boer, F. P., Newton, M. D., Libscomb, W. N.: Proc. nat. Acad. Sci. USA **52**, 890 (1964).
7. Bönnemann, H., Bogdanovic, B., Wilke, G.: Angew. Chem. Intern. Ed. Engl. **6**, 804 (1967).
8. de Brouckère, G.: Bull. Soc. chim. Belges **76**, 407 (1967).
9. Carbonaro, A., Greco, A., Dall'Asta, G.: Tetrahedron Letters 2037 (1967).

10. Cottrell, T. L.: The Strengths of Chemical Bonds, London: Butterworths 1968.
11. Herzberg, G.: Molecular Spectra and Molecular Structure, Vol. II, D. van Nostrand Co. 1960.
12. Jaffé, H. H.: J. chem. Physics **21**, 258 (1953).
13. Jørgensen, Chr. K., Horner, F. M., Hatfield, W. E., Tyree, F. Y., Jr.: Int. quant. Chemistry **1**, 191 (1967).
14. Longuet-Higgins, H. C., Pople, J. A.: Proc. physic. Soc. (London) A **68**, 591 (1955).
15. McWeeny, R.: An Introduction to Group Theory and its Applications, London/New York: Pergamon Press 1963.
16. — J. chem. Physics **42**, 1717 (1965).
17. Moore, Ch. E.: Atomic Energy Levels, Natl. Bur. Std. U.S., Circ. 467 (1949).
18. Mulliken, R. S.: J. Chem. Physics **23**, 1833 (1955).
19. — Rev. mod. Physics **32**, 232 (1960).
20. — Rieke, C. A., Orloff, D., Orloff, H.: J. chem. Physics **17**, 1248 (1949).
21. Natta, G., Giannini, U., Pino, P., Cassata, A.: Chim. e Ind. (Milano) **47**, 524 (1965).
22. Nishimoto, K., Mataga, N.: Z. Physik. Chem. (Frankfurt) **13**, 140 (1957).
23. Pariser, R., Parr, R. G.: J. chem. Physics **21**, 466, 767 (1953).
24. Pilcher, G., Skinner, H. A.: J. Inorg. Chem. **24**, 937 (1962).
25. Richardson, J. W., Nieuwpoort, W. C., Powell, R. R., Edgell, W. F.: J. chem. Physics **36**, 1057 (1962).
26. — Powell, R. R., Nieuwpoort, W. C.: J. chem. Physics **38**, 796 (1963).
27. Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
28. Ruedenberg, K.: J. chem. Physics **19**, 1433 (1951).
29. Schrauzer, G. N.: In: Advan. Organometal. Chem., Vol. 2, p. 38, ed. by F. G. A. Stone and R. West, New York/London: Academic Press 1964.
30. Slater J. C.: Quantum Theory of Atomic Structure, Vol. I and II, New York: McGraw-Hill 1960.
31. Stevenson, Ph. E., Libscomp, W. N.: J. chem. Physics **50**, 3306 (1969).
32. Ugo, R.: Coord. Chem. Rev. **3**, 319 (1968).
33. Uttech, R., Dietrich, H.: Z. Kristallogr. **122**, 60 (1965).
34. Veillard, A.: Chem. Comm. **1969**, 1427.
35. Wilke, G.: Angew. Chem. **75**, 10 (1963).
36. — Bogdanivić, G.: Angew. Chem. **73**, 756 (1961).
37. — Bogdanović, B., Hardt, P., Heimbach, P., Keim, W., Kröner, M., Oberkirch, W., Tanaka, K., Steinrücke, E., Walter, D., Zimmermann, H.: Angew. Chem. **78**, 157 (1966).
38. Wolfsberg, M., Helmholz, L.: J. chem. Physics **20**, 837 (1952).
39. Yamamoto, A., Morifuji, K., Ikeda, S., Saito, T., Uchida, Y., Misono, A.: J. Amer. chem. Soc. **90**, 1878 (1968).

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