Electron Structure of $[\{Ni(\eta^5-C_5H_5)(\mu-CO)\}_2]$† by He(I) and He(II) Photoelectron Spectroscopy

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The electronic structure of the title compound is discussed on the basis of the He(I) and He(II) excited photoelectron spectra and extended Hückel calculations. The compared He(I) and He(II) band intensities proved to be of crucial importance in order to assign the very complicated spectral pattern. The most interesting result of this study is the observation that four metal-based *d* electrons are strongly involved in two back-bonding interactions to bridging carbonyl π* molecular orbitals which are localized respectively in- and out-of-the-plane defined by the $Ni_2(CO)_2$ core.

Polynuclear organometallic compounds represent a very intriguing class since they provide molecular models for catalytic systems;[1] furthermore, they provide a stimulating challenge from the theoretical point of view because the nature of their metal–metal and metal–ligand interactions is not yet completely rationalized.[2]

A number of papers have been devoted to the study of the bonding scheme in dimeric species by both theoretical and experimental approaches;[3–5] in the case of ligand bridged systems the main purpose was to assess whether a direct metal–metal interaction or indirect bonding *via* the bridging ligands occurs according to the nature of the bridge.[6–8] Recently,[9–13] both theoretical and experimental data have shown that the hypothesis of a direct metal–metal bond appears inadequate in $[Co_2(CO)_8]$, $[Fe_2(CO)_9]$, and *trans*-$[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2]$, whereas a delocalized multi-centred bond representing a back-donation interaction to the bridging carbonyl π* molecular orbitals (m.o.s) has been suggested.

In order to verify whether this bonding scheme also holds for other related compounds, we have undertaken the present study of the electronic structure of $[\{Ni(\eta^5-C_5H_5)(CO)\}_2]$ (Figure 1) by means of gas-phase u.v. photoelectron (p.e.) spectroscopy and extended Hückel calculations. This molecule is isoelectronic with both $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$; it would be interesting, then, to extend this study to these two molecules but their extensive decomposition in the ionization chamber does not allow the recording of their p.e. spectra.

Experimental

The title compound was prepared according to the published procedure.[14] Further purification by sublimation *in vacuo* was carried out before running the spectra. He(I) (21.217 eV) and He(II) (40.814 eV) excited p.e. spectra were measured on a Perkin-Elmer PS-18 spectrometer modified for He(II) measurements by inclusion of a hollow cathode discharge lamp which gives a high photon flux at He(II) wavelengths (Helectros Developments). The ionization energy (i.e.) scale was calibrated by reference to peaks due to admixed inert gases and to He $1s^{-1}$ self-ionization. The pertinent i.e. values are reported in Figure 2. The qualitative orbital diagram of Figure 3 is mainly based on extended Hückel calculations performed with the parameters reported in ref. 15. The geometry used in the calculations was taken from the structural determination of Byers and Dahl.[16] The molecular symmetry in the crystal state refers to the C_{2v} point group [bent $Ni_2(CO)_2$ core]; however, we adopted the C_{2h} symmetry since the same authors proposed that a planar $Ni_2(CO)_2$ core is favoured in the gas phase.

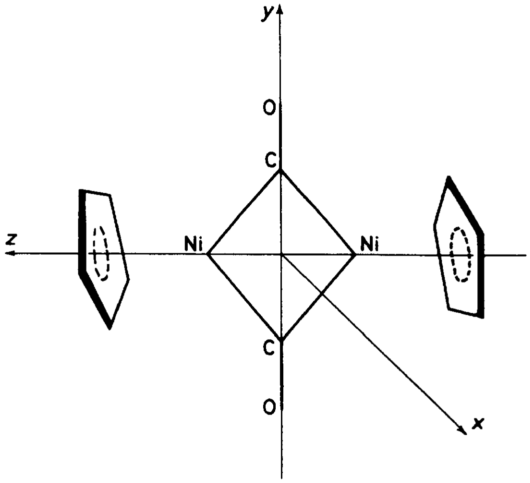

Figure 1. Schematic view of $[\{Ni(\eta^5-C_5H_5)(\mu-CO)\}_2]$ with the axis system adopted in the calculations

Results

The low i.e. region (up to 10 eV) of the He(I) excited p.e. spectrum of the title compound is reported in Figure 2(*a*). At least six bands (labelled alphabetically) are well resolved. The region that follows (up to 18 eV) consists of two very broad composite structures centred at 13.4 and 16.7 eV respectively. There is no doubt in relating these two envelopes to ionizations deriving from the 5σ, 4σ, and 1π carbonyl m.o.s and from the σ C–C, C–H, and inner π ($a_g + b_u$ in C_{2h} symmetry) m.o.s of the cyclopentadienyl rings. The detailed analysis of this region is not relevant for our purposes and will not be further considered. The low i.e. region of the He(II) spectrum is reported in Figure 2(*b*). The relative intensity pattern is dramatically changed on switching from the He(I) to the He(II)

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† Bis[μ-carbonyl-(η⁵-cyclopentadienyl)nickel].

Non-S.I. unit employed: 1 eV ≈ 1.60×10^{-19} J.

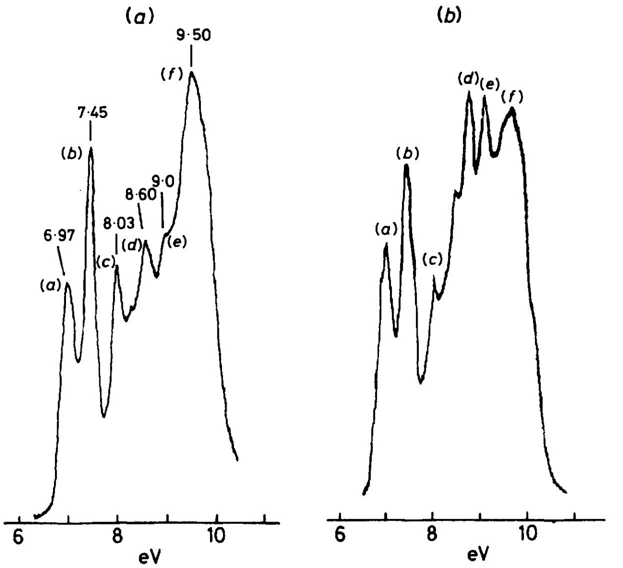


Figure 2. Low i.e. region of the (*a*) He(I) and (*b*) He(II) excited p.e. spectra of [{Ni(η^5-C_5H_5)(μ-CO)}$_2$]

excitation source; in particular, the major intensity change occurs for bands (*d*) and (*e*) whose He(II) intensities become comparable with that of band (*f*). Furthermore, band (*a*) is definitively stronger in the He(II) spectrum when compared to band (*b*).

Discussion

The title molecule is diamagnetic and the effective atomic number rule predicts an electron pairing between two Ni atoms in the formal (d^9) oxidation state +1 if the C_5H_5 rings are taken as anionic. Based on this observation, we can anticipate that 18 electrons, originating from m.o.s characterized by high contribution from Ni 3*d* atomic orbitals (a.o.s), will be present in the reported spectral region. Furthermore, it is reasonable to forecast that 12 of them occupy m.o.s which maintain 3*d* atom-like character (*i.e.* non-bonding set). The same spectral region will also contain eight electrons derived from the outermost occupied π m.o.s of the two cyclopentadienyl ligands (corresponding to the e_1'' m.o. of the free anion ligand in D_{5h} symmetry [17]). Reference to the reported p.e. data of other nickel–cyclopentadienyl derivatives [18] allows us to expect a significant mixing between these cyclopentadienyl m.o.s and suitable 3*d* a.o.s mainly because of favourable energy matching between them.

The use of the He(II) source provides a valuable aid in order to rationalize this very complex spectral pattern; in fact, the expected decrease of the photoionization cross-section ratio [19,20] $\sigma(C_{2p})/\sigma(3d)$ on going from He(I) to He(II) radiation is a powerful tool in evaluating the relative contribution from metal 3*d* or ligand 2*p* a.o.s in a particular m.o., when the Gelius [21] model for the photoionization cross-sections is adopted. By adopting this experimental criterion an unambiguous assignment of bands (*d*) and (*e*) to non-bonding 3*d* a.o.s is forwarded; on the other hand, band (*c*) and part of band (*f*) seem to be related to cyclopentadienyl π m.o.s. Further on this basis, bands (*a*) and (*b*) are likely to be related to ionizations involving the remaining six electrons which are engaged in the $Ni_2(CO)_2$ core bonding.

More detailed considerations about the experimental findings and the nature of the bonding interactions within the $Ni_2(CO)_2$ core can be forwarded by the qualitative orbital interaction diagram presented in Figure 3. This diagram has been built up by interacting the valence basis sets of the $Ni_2(C_5H_5)_2$ and $(CO)_2$ fragments.

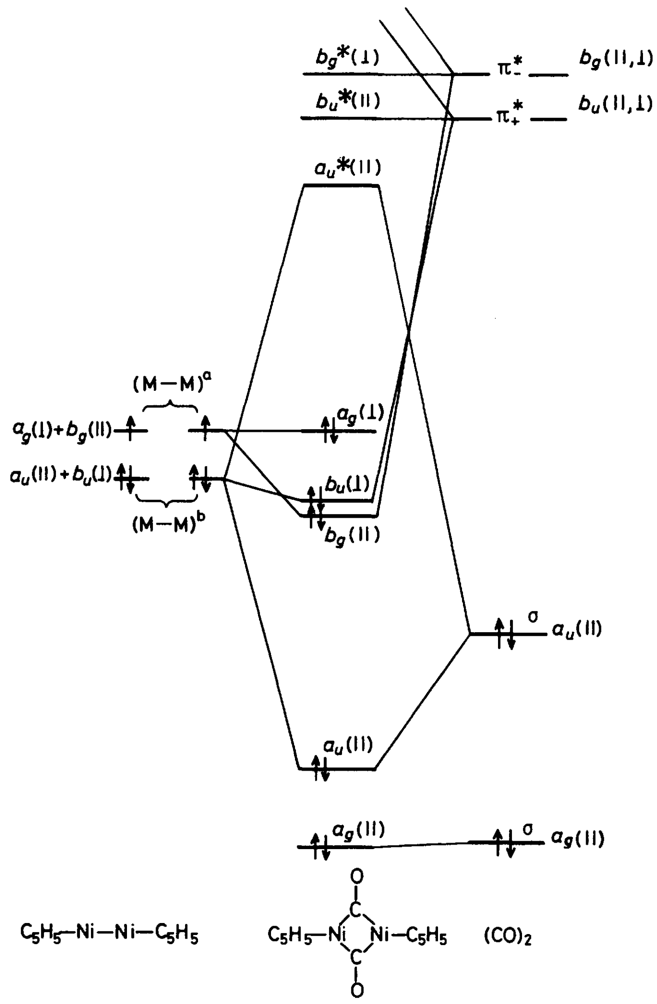
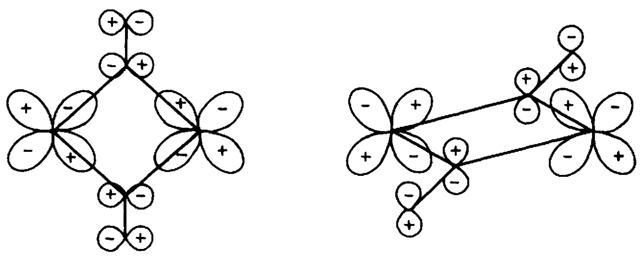


Figure 3. Orbital interaction diagram of [{Ni(η^5-C_5H_5)(μ-CO)}$_2$] from its constituent $Ni_2(C_5H_5)_2$ and $(CO)_2$ fragments

The symbolism $\perp$ and $\|$ shown in Figure 3 is adopted to indicate orthogonal and parallel directions respectively, based on the $Ni_2(CO)_2$ plane, while +/− subscripts refer to in- and out-of-phase combinations. For convenience, the m.o.s of the interacting fragments are labelled according to the irreducible representations of the C_{2h} point group pertaining to the whole molecule.

Only the frontier m.o.s of the $Ni_2(C_5H_5)_2$ fragment which are relevant for interacting with the $(CO)_2$ fragment are considered in Figure 3: the Ni 3*d* non-bonding m.o.s ($2a_g + b_g + a_u + 2b_u$) and the Ni–C_5H_5 bonding m.o.s ($a_g + b_g + a_u + b_u$) are not represented in the diagram. The $a_g(\perp)$, $b_g(\|)$, $a_u(\|)$, and $b_u(\perp)$ frontier m.o.s can be qualitatively described as antibonding Ni–C_5H_5 counterparts which are split in two sets by bonding (M–M)^b and antibonding (M–M)^a Ni–Ni π interactions. A net Ni–Ni σ bonding contribution is not present since both $3d_{z^2}$ bonding and antibonding combinations are occupied while the hybrid sp_z lies too high in energy.[22] The pertinent frontier m.o.s of the $(CO)_2$ fragment consist of the symmetry combinations of the 5σ $a_g(\|)$ and $a_u(\|)$ and π* $2b_g(\perp, \|)$ and $2b_u(\perp, \|)$ m.o.s (see Figure 3).

Now, severe symmetry selection rules together with



b_g(||) b_u(⊥)

Figure 4. Schematic picture of the b_g(||) and b_u(⊥) m.o.s which represent back-bonding interactions from d_{xz},d_{yz} to carbonyl π^* m.o.s

elementary overlap considerations allow us to discuss in a very simple way the reported orbital interaction scheme. The interaction with the σ a_u(||) m.o. of the $(CO)_2$ fragment strongly destabilizes the a_u(||) M–M^b m.o. of the $Ni_2(C_5H_5)_2$ moiety, mainly because of very favourable overlapping, giving rise to the l.u.m.o. a_u^*(||) (l.u.m.o. = lowest unoccupied molecular orbital). The h.o.m.o. a_g(⊥) (h.o.m.o. = highest occupied molecular orbital) is almost unchanged with respect to the $Ni_2(C_5H_5)_2$ fragment since no suitable partner is available. In fact, the a_g(||) of the $(CO)_2$ fragment, apart from the very limited energy matching, does not interact because of overlap reasons. As a consequence, the a_g(⊥) h.o.m.o. maintains its antibonding π Ni–Ni character as in the parent fragment. The subsequent b_g(||) and b_u(⊥) m.o.s (represented schematically in Figure 4) are stabilized with respect to the related fragment m.o.s by mixing with the $\pi_+{}^*b_u$(⊥) and $\pi_-{}^*b_g$(||) m.o.s of the $(CO)_2$ moiety; they represent, then, in- and out-of-plane back-donation interactions from $3d_{xz}$, $3d_{yz}$ Ni a.o.s to π^* carbonyl m.o.s. The former b_g(||), which is π Ni–Ni antibonding in nature, is more markedly stabilized than b_u(⊥) due to better overlapping with the metallic a.o.s.

The nature of this b_g(||) m.o. is very similar to that already proposed for the h.o.m.o. of *trans*-[{Fe(η^5-C_5H_5)$(CO)_2$}$_2$] on the basis of *ab initio* calculations,[10–12] apart from a stronger C_5H_5 contribution to this m.o. in the present molecule. On the other hand, the b_u(⊥) m.o. which is π Ni–Ni bonding in character, looks like (Figure 4) a π-bonding system delocalized over the whole planar $Ni_2(CO)_2$ core and represents a novel feature peculiar to this molecular system.* In the case of the isoelectronic $[Co_2(CO)_8]$ molecule, this π delocalized interaction is prevented by the non-planar $Co_2(CO)_2$ core.[13]

The above discussed bonding scheme allows us to propose an assignment of the low i.e. spectral pattern; we suggest that band (*a*) is related to the a_g(⊥) h.o.m.o. and that the stronger band (*b*) represents the ionizations both from b_u(⊥) and b_g(||) m.o.s. This picture is also in tune with the already mentioned trend of the relative intensities in the He(II) spectrum since a larger 3*d* contribution can be forecast for the a_g(⊥) h.o.m.o. than for the b_u(⊥) and b_g(||) m.o.s. Moreover, the He(II) intensity changes combined with the reported bonding scheme give us the opportunity of a further speculation concerning the bonding/back-bonding synergism of the Ni-C_5H_5 interaction in this molecule. In contrast to the situation usually found where the d_{xz},d_{yz} metallic a.o.s assist the $C_5H_5 \longrightarrow M$ donation, we have found that in this molecule the same metallic a.o.s are strongly involved in the back-donation interaction toward the bridging carbonyl π^* m.o.s. It follows, then, that the remaining 3*d* metallic a.o.s show less tendency to back-donate to the C_5H_5 π^* m.o.s, so enhancing their non-bonding character. This feature is supported by the dramatic raising of the intensities of bands (*d*) and (*e*) in the He(II) spectrum which are associated with lone-pair *d* ionizations.

As a final remark we wish to point out that the most interesting result that emerges from this study is the absence of a net direct Ni–Ni bonding interaction, neither σ nor π in character. This implies that the main source for the stability of the dimer arises from the two in- and out-of-plane back-bonding interactions between the d_{xz},d_{yz} metallic a.o.s and the pertinent symmetry combinations of the bridging carbonyl π^* m.o.s. Furthermore, this bonding picture predicts that the Ni–C_5H_5 bond mainly involves one-way $C_5H_5 \longrightarrow Ni$ donation with large covalency character arising from strong mixing between the pertinent orbitals.

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References

1 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Bruker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.
2 H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 379.
3 W. C. Trogler, *J. Chem. Educ.*, 1980, **57**, 424.
4 J. L. Templeton, *Prog. Inorg. Chem.*, 1980, **26**, 211.
5 F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27.
6 R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, 1973, **50**, 53.
7 P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31.
8 P. S. Braterman, *Struct. Bonding (Berlin)*, 1971, **10**, 57.
9 A. Mitscher, B. Rees, and M. S. Lehmann, *J. Am. Chem. Soc.*, 1978, **100**, 3390.
10 M. Bénard, *J. Am. Chem. Soc.*, 1978, **100**, 7740.
11 M. Bénard, *Inorg. Chem.*, 1979, **18**, 2782.
12 G. Granozzi, E. Tondello, M. Bénard, and I. Fragalà, *J. Organomet. Chem.*, 1980, **194**, 83.
13 W. Heijser, E. J. Baerends, and P. Ros, *14th Faraday Symp.*, 1980, 211.
14 E. O. Fischer and C. Palm, *Chem. Ber.*, 1958, **91**, 1725.
15 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 7240.
16 C. R. Byers and C. F. Dahl, *Inorg. Chem.*, 1980, **19**, 680.
17 S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, 1972, 1847.
18 J. C. Green, *Struct. Bonding (Berlin)*, 1981, **43**, 37.
19 J. W. Rabalais, ‘ Principles of Ultraviolet Photoelectron Spectroscopy,’ Wiley, New York, 1977, p. 335.
20 C. Cauletti, J. C. Green, M. R. Kelly, P. Powell, J. van Tilborg, J. Robbins, and J. Smart, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **19**, 327.
21 U. Gelius, in ‘ Electron Spectroscopy,’ ed. D. A. Shirley, North Holland, Amsterdam, 1972, p. 311.
22 M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. D. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148.

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* A similar quasi-aromatic system has been previously proposed for a carbyne bridged Nb dimer.[15] However, the bonding pattern is rather different from that reported above since in the Nb dimer the carbyne lone pairs donate to two Nb^V d^0 atoms.