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Preliminary communication

The Electronic Structure of Bis-(π-cyclobutadiene)nickel

Denis W. Clack and Keith D. Warren

Department of Chemistry, University College, Cardiff, Wales, United Kingdom.

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Summary

INDO SCF MO calculations have been carried out for the title complex, and comparisons with similar results for π-cyclopentadienyl-π-cyclobutadiene-cobalt, and π-cyclopentadienyl-π-cyclopropenyl-nickel, are used to shed light on the mode of bonding of the cyclobutadiene ligand to the metal.

Although the asymmetrical complex, π-cyclopentadienyl-π-cyclobutadiene-cobalt, CpCoCb, has been known for some time [1], there recently appeared [2] a report of the synthesis and characterisation of bis-(π-tetraphenylcyclobutadiene)nickel, which represents the first symmetrical sandwich system involving the cyclobutadiene ligand. It therefore seemed appropriate to compare the results of our SCF MO calculations [3] on CpCoCb [4] with a similar treatment of the symmetrical parent system, bis-(π-cyclobutadiene)nickel, $NiCb_2$, and also to make comparisons with previous calculations [5] on the iso-electronic π-cyclopentadienyl-π-cyclopropenyl-nickel, CpNiCpr, for which the triphenyl-cyclopropenyl derivative is known [6].

The method and parameterisation were as described earlier [3], D_{4h} symmetry being assumed, and with a ring C–C distance of 1.40 Å the total energy was a minimum at a metal to ring-plane distance of 1.58 Å. The dominant interaction was as usual that between the metal 3d orbitals and the ligand π-combinations,

Table I. Molecular Orbital Compositions for $NiCb_2$.

	MO	3d	π-Ligand	σ-Ligand	H	4s	$4p_{x,y}$	$4p_z$
d_{xy}	b_{2g}	92.00	8.00	-	-	-	-	-
d_{z^2}	a_{1g}	90.90	0.28	3.24	4.62	0.96	-	-
$d_{x^2-y^2}$	b_{1g}	93.72	4.35	0.52	1.41	-	-	-
	e_g	32.31	41.87	20.09	5.71	-	-	-
	e_u	-	71.87	18.54	0.12	-	9.46	-
	a_{2u}	-	94.83	2.23	0.20	-	-	2.7
	a_{1g}	3.24	68.59	14.87	11.83	1.45	-	-

Table II. Orbital Occupations for CpCoCb, $NiCb_2$, and CpNiCpr

	CpCoCb	$NiCb_2$	CpNiCpr
d_{z^2}	1.97	1.90	1.96
$d_{xz} + d_{yz}$	1.32	2.20	2.50
$d_{x^2-y^2}$	1.92	1.98	1.94
d_{xy}	1.96	2.00	1.94
d^x	7.17	8.08	8.34
4s	0.56	0.49	0.60
4p	1.84	2.01	1.89
C_σ (Cp)	2.86 (x5)	-	2.85 (x5)
C_π (Cp)	1.03 (x5)	-	1.02 (x5)
H (Cp)	1.00 (x5)	-	1.01 (x5)
C_σ (Cb)	2.81 (x4)	2.81 (x4)	-
C_π (Cb)	1.15 (x4)	1.10 (x4)	-
H (Cb)	1.01 (x4)	1.00 (x4)	-
C_σ (Cpr)	-	-	2.84 (x3)
C_π (Cpr)	-	-	1.10 (x3)
H (Cpr)	-	-	0.97 (x3)

although there was some appreciable participation by the ligand σ-framework. For simplicity only the Ni 3d - ligand-π interactions are shown in the H^{core} diagram of the Figure.

As was found for CpCoCb [4], in which the cyclobutadiene ligand was the more strongly bound ring, the Cb rings in $NiCb_2$ are linked to the metal mostly via the mixing of the π-ligand $e_{(g)}$ level and the Ni $3d_{xz}$ and $3d_{yz}$ orbitals. Thus, in Table I we list the SCF orbital compositions of those MOs which are either mainly ligand-π or mainly metal 3d in character, and represent occupied levels, from which it is seen that the highest lying formally ligand level in fact contains more than 32 % of metal 3d contributions. Of the dominantly metal levels those of a_{1g}, b_{1g}, and b_{2g} symmetry (mostly d_{z^2}, $d_{x^2-y^2}$, and d_{xy} respect--ively) prove to be occupied, so that the system formally corresponds to a $3d^6$ configuration, i.e. Ni^{IV} $2Cb^{2-}$. Each of these levels is moreover virtually non-bonding, with the metal contributions all exceeding 90 %.

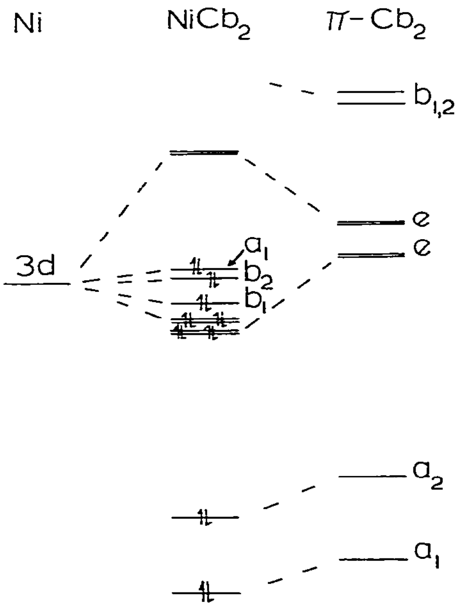

Figure. H^{core} Diagram for 3d - Ligand Interaction in $NiCb_2$.
(Note : Only levels arising dominantly from the metal 3d - ligand-π interactions are shown, and levels of mainly σ-character, even with appreciable 3d contributions, are omitted.)

The H^{core} stage of the calculations gives the energetic ordering of the mainly 3d levels as $d_{x^2-y^2} < d_{xy} < d_{z^2}$, but at the SCF stage this becomes $d_{x^2-y^2} < d_{z^2} < d_{xy}$. However, Koopmans' theorem is unreliable for metal sandwic systems, and by calculation of the total energies for the neutral molecule and for the appropriate cations the definitive sequence was found to be $d_{z^2} \sim d_{x^2-y^2} < d_{xy}$: the ionisation energy estimated for electron loss from the d_{xy} orbital was 9.14 eV., with loss from d_{z^2} or $d_{x^2-y^2}$ requiring an extra 0.50 eV.

In Table II we compare the charge distributions calculated for $NiCb_2$, CpNiCpr, and CpCoCb, from which it is evident that $NiCb_2$ closely resembles the iso-electronic CpNiCpr. Most notably, the latter system, formally $3d^{10}$ - Cp^-Ni^0 attains a d-orbital occupation of only 8.34 by virtue of the strong delocalisat of the d_{xz} and d_{yz} orbitals, whereas $NiCb_2$ - $3d^6$, Ni^{IV} $2Cb^{2-}$, actually acquires d-orbital electron density, again by virtue of the d_{xz}, d_{yz} - ligand mixing, th achieving a closely comparable occupation of 8.08. Moreover, in $NiCb_2$, the Cb ligand clearly behaves in a very similar manner to that found in CpCoCb [4], which we have shown formally constitutes a $3d^6$, $Cp^-Co^{III}Cb^{2-}$, species, although this is raised to $d^{7.17}$ by appreciable d_{xz}, d_{yz} - ligand mixing. Consequently, for metal sandwich systems containing the cyclobutadiene ring it is probably conceptually simpler to formulate the ligand as Cb^{2-} (rather than Cb^0), and thus to regard it as a strong π-donor. (For 2 Cb^{2-} rings at the same inter-nuclear separation as in $NiCb_2$, the calculated charges are C(σ) 2.80, C(π) 1.50, and H 1.20.)

References

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