

Molecular Orbital Calculations on Transition Metal Complexes. Part XXIV. Bis-(π -pyridine)chromium and its Cation

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INDO SCF MO calculations have been carried out for the formally d^6 system bis-(π -pyridine)chromium, $\text{Cr}(\text{C}_5\text{H}_5\text{N})_2$, and the corresponding cation. For the neutral molecule the results indicate that the introduction of the nitrogen heteroatom should lead to an ionisation potential about 1.5 eV greater than for the parent bis-(π -benzene) chromium, but as for $\text{Cr}(\text{C}_6\text{H}_6)_2$ the d -electron ionisation energies follow the ordering $a_1(d_{z^2}) < e_2(d_{x^2-y^2}, d_{xy})$, and the dominant contributions to the bonding again arise from interactions between the metal $e_2(d_{x^2-y^2}, d_{xy})$ and $e_1(d_{xz}, d_{yz})$ levels and the π -orbitals of the ligand rings. Results for the cation, $[\text{Cr}(\text{C}_5\text{H}_5\text{N})_2]^+$, yield estimates for the one-electron d -orbital splitting parameters, ΔE_1 and ΔE_2 , which are quite similar to those found for $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$, and g_1 and A_H values comparable to those of the bis-benzene system are expected for the ${}^2A_1(e_2^4a_1)$ ground state, although the ${}^{14}\text{N}$ hyperfine interaction should be negligible. Calculations are also made of all the proton hyperfine coupling constants for the experimentally accessible bis-(π -2,6-dimethylpyridine)chromium cation. The calculated splittings of the mainly $3d$ e_1 and e_2 levels, due to the heteroatom, are in all cases small ($< 3,000 \text{ cm}^{-1}$), and in contrast to the bis-(π -borabenzene) metal, $M(\text{C}_5\text{H}_5\text{BR})_2$, species, the bis-(π -pyridine) derivatives behave in a very similar manner to the homocyclic bis-(π -benzene) systems.

Introduction

In the last twenty-five years a great deal of attention has been devoted to metal sandwich species containing carbocyclic ring systems. Recently, however, there has been renewed interest in the synthesis and characterisation of similar systems in which the ligand rings contain heteroatoms, and this has led to the preparation of various bis-(π -borabenzene)metal derivatives, $M(\text{C}_5\text{H}_5\text{BR})_2$ ($M = \text{Cr}, \text{Fe}, \text{Co}$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$), by Herberich and his collaborators [1–3], and to the isolation of the first symmetrical sandwich complex containing nitrogen atoms in the rings, bis-(π -2,6-dimethylpyridine)chromium, $\text{Cr}((\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_2$ [4, 5]. In these systems the borabenzene (BBz) ligand may be regarded as formally negatively

charged, $[\text{BBz}]^-$, in the same way as the cyclopentadienyl, $[\text{Cp}]^-$, ligand, whereas the pyridine group, $[\text{Py}]$, is formally neutral, thus resembling the analogous homocyclic ligand, benzene, $[\text{Bz}]$.

In earlier parts of this series [6–10] we have shown that the main bonding interactions in transition metal sandwich species are those involving the metal $3d$ orbitals of $e_1(d_{xz}, d_{yz})$ and $e_2(d_{x^2-y^2}, d_{xy})$ symmetry with the π -orbitals of the ligand rings, the former decreasing and the latter increasing in importance with increasing size of the ligand rings. Moreover, in investigating the effects of the introduction of heteroatoms into the ligand rings, we have established [11] that the borabenzene ligand, in its bonding behaviour, is much more closely akin to the cyclopentadienyl than to the benzene moiety, and it therefore appeared to be of interest to study the consequences of the insertion of the more electronegative nitrogen atom as contrasted with the results of introducing the more electropositive boron.

Since it seems that the presence of the two methyl groups ortho to the nitrogen atom is only necessary to prevent the pyridine ligand acting as a σ - rather than a π -donor, we have based most of our calculations on the unsubstituted system, bis-(π -pyridine)chromium, CrPy_2 . It has however been brought to our notice [12] that the cation of the 2,6-dimethyl derivative can be obtained in the laboratory, and we have accordingly made some studies of this ion as well as of $[\text{CrPy}_2]^+$. We therefore now report our analysis of the bonding in neutral CrPy_2 , together with predictions relating to such quantities as ionisation energies, g_1 value, hyperfine coupling constants, and one-electron d -orbital splitting parameters, obtained from results for the cationic species.

Method

The calculations were carried out by the all valence electron INDO SCF MO method described earlier [13], and used in previous parts of this series [6–11]; the basis set included the metal $3d, 4s$, and $4p$, the carbon and nitrogen $2s$ and $2p$, and the hydrogen $1s$ orbitals. All energies of electronic states of the neutral or the cationic species quoted in the

TABLE I. Compositions of the Highest Lying Occupied Molecular Orbitals of the 1A_1 Ground State of $Cr(C_5H_5N)_2$.

ϵ^{SCF} (a.u.)	$d_{x^2-y^2}$	d_{xy}	d_z^2	d_{xz}	d_{yz}	4s	2p _z		2p _{x,y}		2s		1s
							N	C	N	C	N	C	H(C)
-0.195	44.58	—	0.18	0.24	—	0.02	19.13	34.21	0.01	1.48	—	0.03	0.10
-0.216	—	60.98	—	—	0.02	—	0	36.72	0.90	1.32	0	—	0.05
-0.249	0.50	—	92.03	0.27	—	1.34	0.13	0.24	1.11	0.31	0.24	0.30	3.54
-0.415	—	—	—	—	—	—	—	0.19	47.77	28.03	8.36	1.11	14.57
-0.425	0.97	—	0.46	0.13	—	0.03	0.13	0.45	46.79	26.46	8.66	1.09	14.81
-0.503	—	—	—	—	6.85	—	0	90.00	0.07	1.66	0	0.16	1.24
-0.510	0.01	—	—	6.17	—	—	36.47	52.97	0.23	2.41	0.02	0.10	1.62
-0.516	—	—	—	—	—	—	0	0.03	12.60	48.88	0	0.02	38.48
-0.527	—	1.34	—	—	0.02	—	0	0.08	11.94	48.19	0	0.02	38.40

text are given relative to that of the appropriate ground state.

The molecular geometry adopted was taken from the results of Riley and Davis [5], and the ligand rings were assumed to be *trans* to each other with respect to the nitrogen atoms (the X-ray data indicated that this arrangement was probably the more stable of the two conformers isolated).

Results and Discussion

By virtue of the nitrogen heteroatoms the overall symmetry of the *trans* conformer of bis-(π -pyridine)-chromium cannot be higher than C_{2h} , which in principle should permit intra-d-orbital mixing, especially between $d_{x^2-y^2}$ and d_z^2 . However it is clearly reasonable to expect that the system should show only small deviations from effective pseudo-axial symmetry. Consequently a one-electron d-orbital splitting sequence of $e_2(d_{x^2-y^2}, d_{xy}) < a_1(d_z^2) < e_1(d_{xz}, d_{yz})$ might be anticipated, by analogy with the cognate $CrBz_2$ complex, together with a diamagnetic $^1A_1(e_2^4 a_1^2)$ ground state. Moreover, we have shown [11] that in the borabenzene $M(BBz)_2$, series, despite earlier suggestions to the contrary [14], the 3d levels do indeed follow this ordering, with only relatively small (*ca.* 2,000 cm^{-1}) splittings of the mainly metal 3d e_1 and e_2 levels, even though there are small but appreciable differences in the metal mixing coefficients of these erstwhile degenerate levels for the analogous 3d⁶ system, $Fe(BBz)_2$.

The calculated compositions of the nine highest lying occupied molecular orbitals of the 1A_1 ground state of $CrPy_2$ are now therefore shown in Table I, from which it may be seen that the dominant contributions to the bonding arise from interactions between the vacant π^* e_2 ligand level and the metal $3d_{x^2-y^2}$, $3d_{xy}$ orbitals, and from those between the occupied e_1 π -ligand level and the metal $3d_{xz}$ and $3d_{yz}$ orbitals. The populations of the various metal and ligand orbitals of $CrPy_2$, listed in Table II, are seen to be

TABLE II. Electronic Populations for the Free $(C_5H_5N)_2$ System and the Complex $Cr(C_5H_5N)_2$.

Orbitals	Free $(C_5H_5N)_2$	$Cr(C_5H_5N)_2$
$N_1, 2p_z(\pi)$	1.090	1.169
$C_2, 2p_z(\pi)$	0.959	1.027
$C_3, 2p_z(\pi)$	1.021	1.045
$C_4, 2p_z(\pi)$	0.951	1.062
$N_1, 2s, 2p_{x,y}(\sigma)$	4.112	4.008
$C_2, 2s, 2p_{x,y}(\sigma)$	2.902	2.794
$C_3, 2s, 2p_{x,y}(\sigma)$	2.994	2.893
$C_4, 2s, 2p_{x,y}(\sigma)$	2.977	2.853
$H_2, 1s$	1.029	1.038
$H_3, 1s$	1.016	1.027
$H_4, 1s$	1.025	1.035
$Cr, 3d_z^2$	—	1.917
$Cr, 3d_{xz}$	—	0.239
$Cr, 3d_{yz}$	—	0.244
$Cr, 3d_{x^2-y^2}$	—	0.944
$Cr, 3d_{xy}$	—	1.263
$Cr, 4s$	—	0.451
$Cr, 4p$	—	1.388

very similar to those previously calculated for $CrBz_2$ [6], apart from the asymmetry due to the nitrogens and the quite appreciable divergence between the occupancies of the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. The metal coefficient of presence in the occupied mainly $3d_z^2$ orbital, c_0 , given in Table III, is 0.9593, whilst for the two components of the mainly 3d e_2 level the corresponding average value of c_2 is 0.7265; in both cases the results closely resemble those for the related $CrBz_2 - c_0 = 0.9616$ and $c_2 = 0.7142$. Moreover, the calculated metal–ligand bond orders, shown in Table IV for $CrPy_2$ and certain cognate systems, also suggest that the Py ligand behaves very much like the parent Bz moiety on complexation, and certainly does not follow the BBz ligand in resembling Cp. Thus, the electronic population changes for the various ligands, given in Table V, show that for both Py and Bz the ring σ -orbitals lose electron density on

TABLE III. Metal Mixing Coefficients for CrPy₂ and [CrPy₂]⁺.

System and State	c ₀	c ₁		c ₂	
	d _{z²}	d _{xz}	d _{yz}	d _{x²-y²}	d _{xy}
CrPy ₂					
¹ A ₁	0.9593	—	—	0.6677	0.7809
[CrPy ₂] ⁺					
² A ₁	0.9503(α)	—	—	0.8165(α)	0.8682(α)
² E _{1(xz)} ¹	—	—	—	0.7741(β)	0.8417(β)
² E _{1(xz)} ¹	—	0.7342(α)	—	0.8022(α)	0.8705(α)
² E _{1(yz)} ¹	—	—	—	0.8089(β)	0.8537(β)
² E _{1(yz)} ¹	—	—	0.7740(α)	0.8180(α)	0.8688(α)
² E _{2(x² - y²)⁻¹}	—	—	—	0.7943(β)	0.8586(β)
² E _{2(x² - y²)⁻¹}	0.9057(α)	—	—	0.7245(α)	0.8441(α)
² E _{2(xy)} ⁻¹	0.9422(β)	—	—	—	0.8348(β)
² E _{2(xy)} ⁻¹	0.9592(α)	—	—	0.7885(α)	0.8632(α)
² E _{2(xy)} ⁻¹	0.9554(β)	—	—	0.7672(β)	—

TABLE IV. Comparison of Metal 3d–Ligand Bond Orders per Ring for Sandwich Species.

Molecule	Metal 3d Levels	Bond Orders		
		2s	2p _x + 2p _y	2p _z
FeCp ₂ ^a	a ₁ d _{z²}	0.015	0.127	0.042
	e ₁ d _{xz} + d _{yz}	0.297	0.506	0.958
	e ₂ d _{x²-y²} + d _{xy}	0.134	0.066	0.696
CrBz ₂ ^a	a ₁ d _{z²}	0.010	0.167	0.053
	e ₁ d _{xz} + d _{yz}	0.282	0.463	0.684
	e ₂ d _{x²-y²} + d _{xy}	0.119	0.045	1.380
Fe(C ₅ H ₅ BH) ₂ ^b	a ₁ d _{z²}	0.031	0.091	0.072
	e ₁ d _{xz} + d _{yz}	0.339	0.725	0.916
	e ₂ d _{x²-y²} + d _{xy}	0.138	0.159	0.905
CrPy ₂	a ₁ d _{z²}	0.048	0.171	0.064
	e ₁ d _{xz} + d _{yz}	0.305	0.577	0.750
	e ₂ d _{x²-y²} + d _{xy}	0.131	0.156	1.371

^aD. W. Clack and K. D. Warren, *Inorg. Chim. Acta*, 30, 251 (1978).

^bReference 11.

complex formation to much the same extent, and appreciably more so than either BBz or Cp, whilst the ring π -orbitals of Py and Bz both show a comparable gain of electron density when the Cp and BBz ligands are losing charge from their π -systems. Thus for CrPy₂, as for CrBz₂ [6], the dominant bonding interaction is that between the metal 3d e₂ levels and the corresponding ligand- π orbitals, leading to a strongly bonding mainly metal 3d e₂ molecular orbital. The virtual anti-bonding, mainly 3d e₁, molecular orbital shows some ligand- σ as well as ligand- π admixture, but the occupied and bonding,

TABLE V. Electronic Population Changes for Sandwich Ligands on Complexation.

Molecule	Ring σ -Orbitals	Ring π -Orbitals	Hydrogen Atoms
FeCp ₂ ^a	-0.255	-0.630	-0.440
CrBz ₂ ^{a,b}	-0.618	+0.323	+0.055
Fe(C ₅ H ₅ BH) ₂ ^a	-0.410	-0.409	-0.415
CrPy ₂	-0.647	+0.375	+0.049

^aReference 11.

^bReference 6.

dominantly ligand- π e₁, level shows an appreciable (6.5%) 3d contribution.

The SCF orbital energies of the occupied dominantly 3d molecular orbitals of CrPy₂ are given in Table I; these follow the sequence a₁ < e₂, opposite to the H^{core} result, although in both instances the d_{xy} level lies below d_{x²-y²}, the separation amounting to 900 cm⁻¹ at H^{core} but reaching 4,600 cm⁻¹ at e^{SCF}. Nevertheless, since Koopmans' theorem cannot safely be invoked to estimate ionisation energies in metal sandwich species, we derived these quantities by calculating the differences in total energy between the ¹A₁ ground state of the neutral molecule and the various accessible states of the [CrPy₂]⁺ cation.

In our previous studies, calculations of total energies have proved reliable in predicting the ground electronic levels, and for [CrPy₂]⁺ a ²A₁(e₂⁴a₁) ground state is predicted, as for [CrBz₂]⁺ [6]. The calculated ionisation energy, from ¹A₁ CrPy₂ is 6.48 eV, 1.45 eV greater than that similarly obtained [6] for CrBz₂, where the theoretical value of 5.03 eV was in good agreement with the experimental result of 5.43 eV. The ²E₂(e₂³a₁²) level of [CrPy₂]⁺ is pre-

dicted to lie $8,600\text{ cm}^{-1}$ above the 2A_1 ground state, but the calculated splitting of this 2E_2 state amounts only to $2,200\text{ cm}^{-1}$, the $(z^2)^2(x^2 - y^2)^2(xy)^1$ component lying lower. Similarly, the ${}^2E_1(e_2^4e_1)$ level was calculated to lie some $20,600\text{ cm}^{-1}$ above the 2A_1 ground state, the splitting there amounting to $2,600\text{ cm}^{-1}$ with $(x^2 - y^2)^2(xy)^2(xz)^1$ lying lower.

The calculated ionisation energies are thus compatible with the orbital energy sequence $e_2 < a_1$, and this is consistent with the results obtained when the one-electron energies for the a_1 , e_1 and e_2 levels are estimated from the energies of the 2A_1 , 2E_1 , and 2E_2 states. Thus, using simple ligand field theory [15], and assuming the same value of the Racah parameter, B , as for $[\text{CrBz}_2]^+$ — 400 cm^{-1} [10], the one-electron 3d splittings, ΔE_1 and ΔE_2 are both found [9] to be $16,600\text{ cm}^{-1}$. Here ΔE_1 is the effective H^{core} energy difference between the e_1 and a_1 levels, and ΔE_2 that between a_1 and e_2 , and the results deduced compare closely with the $[\text{CrBz}_2]^+$ values, $\Delta E_1 = 20,100\text{ cm}^{-1}$ and $\Delta E_2 = 16,600\text{ cm}^{-1}$ [10].

For a ${}^2A_1(e_2^4a_1)$ system in pseudo-axial symmetry ligand field theory [15] predicts $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.0023 - 6c_0^2c_1^2\xi/\Delta E$, where $\Delta E = E({}^2E_1) - E({}^2A_1)$, c_0 and c_1 are the metal coefficients of presence in the a_1 and e_1 orbitals respectively, and ξ is the appropriate spin-orbit coupling constant. For $[\text{CrBz}_2]^+$ we find $c_0 = 0.9675$, $c_1 = 0.7744$, and $\Delta E = 24,100\text{ cm}^{-1}$, which with the experimental g_{\perp} value [16] of 1.9785 yields $\xi = 170\text{ cm}^{-1}$, in good agreement with the value of 190 cm^{-1} given by Garrett and Cole [17]. For $[\text{CrPy}_2]^+$, using the same value of ξ , together with $c_0 = 0.9503$, $c_1 = 0.7540$, and $\Delta E = 20,600\text{ cm}^{-1}$ one therefore predicts $g_{\perp} = 1.9768$, a value of very much the same magnitude as for $[\text{CrBz}_2]^+$.

Furthermore, from our calculations we may estimate the magnitudes of the proton hyperfine coupling constants for the ligands, and in this case also that for the nitrogen atom due to the ${}^{14}\text{N}$ nucleus. For this latter however the A value proves to be vanishingly small, whilst for the hydrogen atoms in the 2-, 3-, and 4-positions of the pyridine rings A_{H} is calculated to be 1.56, 2.01, and 3.04 G respectively. Although the bis- $(\pi$ -2,6-dimethylpyridine)chromium cation is now known [12], no esr data have been reported, but the predicted A_{H} values are an average

of -0.32 G for the methyl protons, and 2.12 and 2.88 G respectively for those at the 3- and 4-positions.

To summarise therefore the π -pyridine ligand is found to behave in a very similar manner to the π -Bz moiety on complexation, in contrast to the π -borabenzene ligand, but as for the borabenzene derivatives the splittings of the mainly 3d e_1 and e_2 levels brought about by the heteroatoms are relatively small. However, the σ -framework of the ring is found to lose electron density on complex formation to about the same extent from the carbon atoms and from the nitrogen atom, leading to the suspicion that the nitrogen will still be quite a good σ -donor even after complexation. However, examination of the π mobile bond orders within the pyridine ring shows that on average these are reduced on complex formation by 0.127 units, again resembling the CrBz_2 system in which the corresponding reduction is 0.124 units [18].

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