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π-backbonding in the Metal–Nitrogen Bond in $Cr(CO)_5L$ Type Complexes

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Recently there has been some doubt concerning the π-backbonding capacity of pyridine in group VI **B** pentacarbonyl pyridine complexes. Contradictory conclusions could be drawn about this π-backbonding from different spectroscopic techniques. From optical spectroscopy it was invoked that π-backbonding is important in these complexes[*] [1, 2]. This same conclusion was reached in thermochemical studies [2, 3]. However, data from UV Photoelectron Spectroscopy (UPS) indicated that π-backbonding was not important [1, 4]. Daamen and Oskam [1] found no differences between the metal ionization energies of the two complexes. Also the nitrogen lone pair stabilization energies were found to be of the same order. Weiner *et al.* [4] studied a series of 4-substituted pyridine complexes and concluded, based on the correlation found between the σ_p ligand parameter and the metal d IE s, that π-backbonding is unimportant. This conclusion should be viewed with caution. Firstly the σ_p substituent constant is not a pure measure of the inductive effect, it is a measure of the total electronic effect of the substituent (resonance interactions included). Secondly, assuming the validity of Koopmans' theorem, shifts in metal IE s are probably more sensitive to changes in σ bonding than to changes in π-bonding. In a study on $Fe(CO)_4$ olefin complexes [5] we have shown that changes in metal to olefin π-backbonding are effectively compensated by changes in metal to carbonyl π-backbonding, leaving the metal essentially unaffected.

The vibrational spectra of a large series of $Cr(CO)_5$(subst)pyridine complexes have been studied by Graham [6]. In this study no variation was found of the CO force constants (which are generally held to be a sensitive probe of M–CO π-backbonding) with changes in π character of the substituents.

In order to get a more thorough understanding of the metal pyridine bond we have performed CNDO type MO calculations on $Cr(CO)_5$ piperidine and $Cr(CO)_5$ pyridine and on the ligands. We have used the extended CNDO program of Labarre *et al.* [7] which has proved quite successful in the study of mononuclear transition metal complexes. In a study on irontetracarbonyl olefin complexes [5] the following observations were made concerning this scheme: *a.* The metal d-IE s are reasonably well predicted while the ligand IE s show the well known CNDO/2 deviations, *b.* the (de) stabilization energies of the coordinating ligands are predicted surprisingly well and *c.* trends in π-backbonding and σ bonding are well reproduced and are in agreement with data from vibrational spectroscopy.

The calculations were carried out using the geometries determined by Loopstra [8]. In this crystal structure the pyridine ligand was found at a 45° angle with the equatorial plane.

The resulting eigen-values are listed in Table I together with experimental data from ref. 1.

TABLE I. A Comparison of Calculated CNDO/2 Eigen Values and Observed Ionization Energies (IE) for $Cr(CO)_5$ pyridine and $Cr(CO)_5$ piperidine[a].

$Cr(CO)_5$ pyridine

IE	CNDO eigen value	assignment
7.29	7.63	metal d ('e')
	7.66	
7.61	7.30	metal d ('a_1')
10.39 (9.79)	15.04(14.26)	a_2 ( ) pyridine
(10.51)	15.49(14.00)	b_1 ( ) pyridine
11.50 (9.67)	14.50(13.03)	(M–N) n_N pyridine

$Cr(CO)_5$ piperidine

IE	CNDO eigen value	assignment
7.39	7.34	
	7.36	metal d ('e')
7.69	7.29	metal d ('a_1')
10.50(8.67)	14.18(12.70)	n_N piperidine

[a] The values for the free ligands are in parentheses.

The calculated charge distributions are listed in Table II.

The metal d orbitals transform as b_2 and e (C_{4v} symmetry around the metal nuclear assumed). The relative ordering of these MO s has been inferred from intensity considerations and spin orbit effects (in the corresponding tungsten complexes [1, 9]. It is now

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[*] It is of course, strictly speaking, not possible to infer bonding information from the π^* position of the d–π^* MLCT transition. The interpretation of the optical spectra in terms of π backbonding [1, 11, 12] can be erroneous owing to the neglect of CI and relaxation effects.

TABLE II. Calculated Charge Distributions.

$Cr(CO)_5$pyridine		$Cr(CO)_5$piperidine
Cr	+0.42	+0.43
$\bar{C}$(carbonyl)	+0.02	+0.02
$\bar{O}$(carbonyl)	−0.13	−0.14
ligand	+0.17	+0.17

π and σ electron densities in complexed and free ( ) pyridine.

	σ	π
N	4.04 (4.08)	1.10 (1.07)
$C\alpha$	2.94 (2.94)	0.98 (0.97)
$C\beta$	3.00 (3.00)	1.01 (1.02)
$C\gamma$	3.02 (3.01)	0.94 (0.95)

generally accepted that the energies of the doublet states are in the order $^2E < {}^2B_2$. This is found for most d^6 metal complexes of C_{4v} symmetry. *Ab initio* calculations indicate the reverse ordering for instance $Cr(CO)_5NH_3$ [9]. This has been attributed to the large relaxation energies associated with the ionization of MO s of predominantly metal character.

The same ordering is suggested by the CNDO calculations. For both complexes the calculated metal d-energies are in very good agreement with experiment. As could be expected the ligand IE s are less well reproduced. However the stabilizations of the various ligand MO s are in qualitative agreement (Table I). Thus the CNDO scheme appears to give a fair description of the electronic structure of these complexes. Analysing the eigen-vectors of the pyridine complex it was evident that the only bonding interaction could come from n_N donation to the empty d_{z^2} orbital, and thus that π-backbonding is of minor importance.

The same Wiberg indices [10] were found for the Cr–N bonds in both complexes also indicating that piperidine and pyridine coordinate in the same way to chromium. This is shown most clearly by the calculated charge distributions. From Table II it is clear that the ligands coordinate identically to chromium. The metal charges are +0.43e and 0.44e respectively while the remaining charge on piperidine is +0.18e and on pyridine is +0.17e. The carbon monoxide ligands are as is well known very good π acceptors and they accommodate ~0.6e in both complexes.

From Table II it can also be seen that the observed upfield ^{13}C chemical shift of the carbon atom at the γ-position in the pyridine ring upon complexation [1] can probably not be interpreted in terms of an increase in π-electron density, as was also argued for other low spin d^6 pyridine complexes [11, 12]. The lowest unoccupied π^* orbital, capable of π backbonding has predominant γ carbon character and the γ carbon should therefore be an excellent probe of π backbonding interactions. However, the calculated (slight) *decrease* in π electron density upon complexation suggests that the observed chemical shift originates from other factors, such as polarization of C–C bonds owing to σ-bonding, changes in bondorders, magnetical anisotropic contributions *etc.*

It thus is clear that there is no π-backbonding present in the chromium–pyridine bond and that both imine(pyridine) and amine(piperidine) type ligands coordinate in the same way to chromium. The large difference in pK_α value between pyridine (5.17) and piperidine (11.2), which is suggested to be a measure of σ bonding capacity [2] is not reflected in the experimental and theoretical results. This can be caused by steric hindrance which can be a factor of importance in secondary and tertiary amines. Another factor of some importance could be the fact that the pK_a s have been determined in solution so that intermolecular association, which should be of great importance in pyridine, obstructs the transferability of these values to the gas phase. Proton affinities, determined in the gas phase show a less pronounced difference between the ligands [13].

It thus seems evident that the chromium–nitrogen bond in the pyridine and piperidine complexes is of the same nature. This can also be deduced from the thermochemical results of Meester *et al.* [2]. They found similar bond dissociation energies for both complexes.

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