Pentamethylcyclopentadienylnickelnitrosyl: synthesis and photoelectron spectrum [1]

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Abstract

The synthesis and photoelectron spectrum of $Ni(\eta\text{-}C_5Me_5)(NO)$ are reported. The vertical ionisation energies of the first three photoelectron bands are all lower than those of $Ni(\eta\text{-}C_5H_5)(NO)$. The magnitudes of the shifts indicate that the first band should be assigned to a $^2E_1$ ion state, the second to both a $^2A_1$ and a $^2E_2$ ion state and the third to a $^2E_1$ ion state. The first band shows a high energy shoulder, with a separation of $0.23 \pm 0.1\,eV$ ($1855 \pm 81\,cm^{-1}$) indicating excitation of an NO stretch, as was found for $Ni(\eta\text{-}C_5H_5)(NO)$.

Keywords: Nickel; Cyclopentadienyl; Photoelectron spectroscopy; Electronic structure; Nitrosyl

1. Introduction

In an earlier study, photoelectron (P.E.) spectra, with photon energies varying from 18–120 eV, were measured for $Ni(\eta^5\text{-}C_5H_5)(NO)$ [1]. Relative partial P.E. cross-sections and branching ratios were evaluated for the first three valence ionisation bands. The second band, though the lowest in intensity at low photon energies, becomes the most intense at photon energies above 38 eV, and at high photon energies it dominates the spectrum, achieving a branching ratio of 66%. This behaviour indicates a high degree of metal character for the orbitals from which this ionisation band originates. Density functional calculations were carried out to determine energies of ionisation to the lowest lying states of $[Ni(\eta^5\text{-}C_5H_5)(NO)]^+$, as well as the corresponding photoionisation cross-sections and the resulting branching ratios using LCGTO-DF and LDKL-DF methods respectively. The metal character found for the four orbital sets was 22% ($8e_1$) 91% ($15a_1$) 96% ($4e_2$) and 51% ($7e_1$). Both experimental and theoretical investigations lead to an ion state ordering $^2E_1 < {^2E_2} \sim {^2A_1} < {^2E_1}$, and an assignment of $^2E_1$ states to the first and third bands with the $^2A_1$ and $^2E_2$ states comprising the

second band. This differs from the original assignment in the literature, where the $^2A_1$ ionisation was assigned to a high energy shoulder on the first band [2,3]. The separation of this shoulder from the main band maximum of 0.23 eV ($1850 \pm 81\,cm^{-1}$) suggests that it may be caused by excitation of the NO stretching vibration in the ion. The neutral molecule has an NO stretch of $1832\,cm^{-1}$; the calculated wavenumbers for the neutral molecule and the cation are $1845\,cm^{-1}$ and $1911\,cm^{-1}$ respectively. Agreement between calculated and experimental ionisation energies (I.E.s) and good matching of the theoretical and measured branching ratios lent strong support to the new assignment of the P.E. spectrum.

Branching ratio data on the low I.E. P.E. bands $Ni(\eta^5\text{-}C_5H_5)(NO)$ have also been obtained by Li et al. [4]. The experimental findings are in good agreement with our own, but these authors favour the original assignment of ionisation of both the $8e_1$ and the $15a_1$ orbitals as giving rise to the first band. This is in part due to *their* I.E. and branching ratio calculations (using the continuum MS-Xα method) being in better agreement with the original assignment, and in part a result of a different deconvolution of the first band.

Extensive work on methylation and permethylation of metallocenes has established the magnitude of I.E. shifts found for metal and cyclopentadienyl P.E. bands on ring substitution, that of the cyclopentadienyl bands being greater than that of the metal d bands [5]. Inter-

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[1] This paper is dedicated to Malcolm Green on the occasion of his 60th birthday.

mediate shifts are found for bands arising from orbitals of mixed metal cyclopentadienyl character, such as the e_{1g} ionisations of metallocenes. Consideration of the I.E. shifts on monomethylation obtained from the He(I) spectra of $Ni(\eta^5-C_5H_5)(NO)$ and $Ni(\eta^5-C_5H_4Me)(NO)$ [1] showed them to be consistent with the relative amounts of cyclopentadienyl character deduced for the associated orbitals from the cross-section variation and from the density functional calculations. However, lack of five-fold symmetry in the monomethylated compound leads to a lifting of the degeneracy of the e_1 orbitals of the cyclopentadienyl ring, and consequently differing fine structure for the first band, with no well-resolved high energy shoulder, as is shown in the P.E. spectrum of the parent $Ni(\eta^5-C_5H_5)(NO)$. $Ni(\eta^5-C_5Me_5)(NO)$ should possess C_{5v} symmetry, and would be more likely to show a similar fine structure for the first band. Also, five methyl groups should result in more substantial shifts and help ascertain whether the first band consists of one primary ionisation process of mainly ligand character or two, one of ligand and one of metal character as proposed by Li et al. [4].

We, therefore, set out to synthesise $Ni(\eta^5-C_5Me_5)(NO)$ and to measure its P.E. spectrum. We also obtained a theoretical estimate of the I.E. shifts by carrying out density functional calculations on $Ni(\eta^5-C_5H_5)(NO)$ and $Ni(\eta^5-C_5Me_5)(NO)$.

2. Experimental

2.1. Ni(η⁵-C₅Me₅)(NO) [6]

A solution of $Ni(\eta^5-C_5Me_5)_2$ (2.5 g, 7.6 mmol) in pentane (100 cm³) was stirred vigorously at room temperature under an atmosphere of NO until there was no further uptake of NO gas. The reaction mixture changed from green to brown and a brown precipitate formed. The solution was removed by filtration, and the residue washed with pentane (3 × 300 cm³). The solvent was removed from the filtrate and washings, leaving a brown solid. $Ni(\eta^5-C_5Me_5)(NO)$ was sublimed from the solid at 110 °C as a bright orange microcrystalline solid. Yield 0.5 g (29%): NMR (C_6D_6) ^1H δ 2.00 (s): mass spectrum found m/z 223 (M^+), 193 $(M^+ - NO)$. IR $\nu(Nujol)/cm^{-1}$ 1787 (N–O).

The He(I) spectrum of $Ni(\eta^5-C_5Me_5)(NO)$ was obtained on a PES Laboratories 0078 spectrometer. The spectrum was calibrated using He, Xe and N_2.

Density functional calculations were carried out using the GAUSSIAN 94 code [7]. Full geometry optimisations were performed on both $Ni(\eta^5-C_5H_5)(NO)$ and $Ni(\eta^5-C_5Me_5)(NO)$ using local spin density approximation (Slater exchange [8] and Vosko, Wilk and Nusair correlation functionals [9]) and employing LanL2DZ basis sets [10–12].

3. Results and discussion

The He(I) P.E. spectrum is given in Fig. 1 and the vertical I.E. of key features are given in Table 1. It resembles that of $Ni(\eta^5-C_5H_5)(NO)$ in showing three main ionisation bands below 10 eV. These may be assigned in an analogous way: namely band A is assigned to the $^2E_1$ ground state of the molecular ion, band B to both the $^2E_2$ and $^2A_1$ excited states and band C to a $^2E_1$ excited state. Orbital $7e_1$ associated with band C is bonding between the cyclopentadienyl e_1 π orbitals, the Ni d_{xz} and d_{yz} and the NO 2π orbitals, whereas orbital $8e_1$ associated with band A is mainly localised on the two ligands and has very little metal character; the orbitals associated with band B are $15a_1$ which is largely Ni d_{z^2} and $4e_2$ which are Ni d_{xy} and $d_{x^2-y^2}$.

The I.E. shifts on permethylation are consistent with the new band assignment but are problematic with the old one. Typical shifts on permethylating metallocenes are 1.0 eV for metal bands and 1.2 eV for e_{1g} bands and 1.4 eV for e_{1u} bands, all to lower I.E. [5]. Band A shifts most by 1.03 eV, band B shifts least by 0.71 eV and band C shows intermediate behaviour shifting by 0.90 eV. This is consistent with the relative amounts of cyclopentadienyl character calculated for the associated orbitals.

Most crucially, within experimental error, the separation between the band maximum of band A and its high energy shoulder is unaltered on permethylation. The value obtained of $0.23(\pm0.01)$ eV corresponds to a

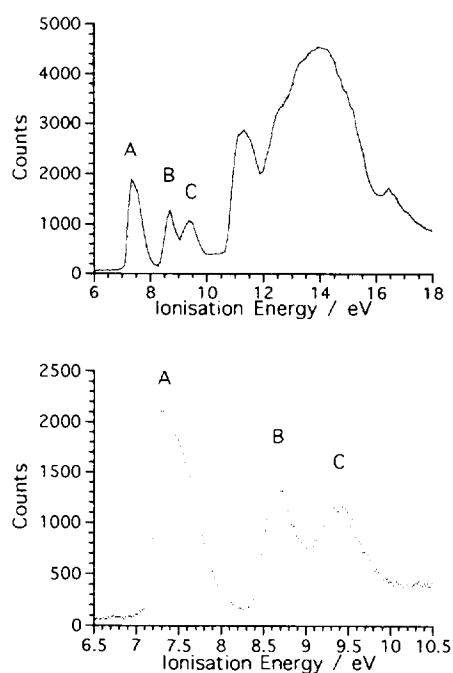Fig. 1. He I P.E. spectrum of $Ni(\eta^5-C_5Me_5)(NO)$.

Table 1

I.E., ion states and corresponding molecular orbitals for the P.E. spectra of Ni(η^5-C$_5$Me$_5$)(NO)(Cp*NiNO), and Ni(η^5-C$_5$H$_5$)(NO)(CpNiNO)

Band	Ionisation energy/eV		Ion states	MO [a]
	Cp*NiNO	(CpNiNO)		
A	7.30, 7.52	8.33, 8.56	$^2E_1$	$8e_1$
B	8.64	9.35	$^2A_1$, $^2E_2$	$15a_1$, $4e_2$
C	9.38	10.28	$^2E_1$	$7e_1$
	11.30	12.64		
	14.04	13.90		

[a] MO numbering is as given in Ref. [1].

wavenumber of 1855($\pm$81) cm^{-1}, consistent with excitation of an NO stretching mode. The neutral molecule shows a band in the IR at 1787 cm^{-1} assigned to such a mode. If the high energy shoulder originated from a metal a$_1$ ionisation, as proposed by Li et al. [4], the separation should increase by ca. 0.3 eV.

Density functional calculations were carried out on both Ni(η^5-C$_5$H$_5$)(NO) and Ni(η^5-C$_5$Me$_5$)(NO). The geometries were optimized subject to the constraint of C_{5v} symmetry. Optimized bond lengths are given in Table 2. As found previously [1], density functional calculations, even at the local level, give good geometry predictions for Ni(η^5-C$_5$H$_5$)(NO).

Density functional one-electron energies bear no formal relation to I.E.s: in ab initio SCF calculations, Koopmans' theorem provides an approximate link between orbital energies and I.E.s. However, paradoxically, the pattern of DFT energies often relates more closely to the I.E. bands of a P.E. spectrum than do SCF MO energies. Also, in a closely related series of compounds, the shifts in the I.E. bands are well modelled by the shifts in the DFT one-electron energies. For Ni(η^5-C$_5$H$_5$)(NO) the negative of the Kohn–Sham ground state eigenvalues were all smaller than the experimental I.E.s, as is commonly found, but gave a good estimate of the separation of the ionisation bands [1]. The Kohn–Sham ground state eigenvalues found for both Ni(η^5-C$_5$H$_5$)(NO) and Ni(η^5-C$_5$Me$_5$)(NO), and the shifts on permethylation are shown in Table 3. The changes found in the eigenvalues on permethylation are

Table 2

Optimised bond lengths (Å) for Ni(η^5-C$_5$Me$_5$)(NO)(Cp*NiNO), and Ni(η^5-C$_5$H$_5$)(NO) (CpNiNO) and experimental bond lengths (Å) for Ni(η^5-C$_5$H$_5$)(NO)

Bond	Cp*NiNO calc.	CpNiNO calc.	CpNiNO expt. [a]
Ni–C	2.109	2.120	2.11
Ni–N	1.609	1.611	1.626
N–O	1.214	1.205	1.165
C–C (ring)	1.443	1.437	1.43
C–CH$_3$	1.484		
C–H	1.105, 1.108	1.090	1.09

[a] Ref. [13].

Table 3

Calculated one-electron energies (eV) for Ni(η^5-C$_5$H$_5$)(NO), Ni(η^5-C$_5$Me$_5$)(NO) and their differences $\Delta\varepsilon$ compared with experimental differences in I.E.

CpNiNO	Cp*NiNO	$\Delta\epsilon$ theory	ΔI.E. expt.	Orbital
−6.44	−5.51	0.93	1.03	e_1
−7.01	−6.41	0.60	0.71	e_2
−7.09	−6.56	0.53	0.71	a_1
−8.51	−7.69	0.82	0.90	e_1

very close to the changes in I.E. found experimentally: the estimated shifts are all ca. 0.1 eV less than those found. Hence, further confirmation of the correctness of the new assignment is provided by these theoretical calculations.

4. Conclusion

Comparison of the P.E. spectrum of Ni(η^5-C$_5$Me$_5$)(NO) with that of Ni(η^5-C$_5$H$_5$)(NO) indicates that the first band has only one orbital origin. The magnitudes of I.E. shift on permethylation of the first three bands show the second band to have least cyclopentadienyl character, and the first band to have most cyclopentadienyl character. This is in agreement with earlier observations based on variable photon energy P.E. spectroscopy of Ni(η^5-C$_5$H$_5$)(NO) and density functional calculations. A high energy shoulder is observed on the first band of Ni(η^5-C$_5$Me$_5$)(NO) and shows an identical separation from the band maximum, as is found for the comparable feature of Ni(η^5-C$_5$H$_5$)(NO). The size of the separation of these shoulders suggests that they result from excitation of an NO stretch in the molecular ion.

The assignment of the P.E. spectra of both Ni(η^5-C$_5$H$_5$)(NO) and Ni(η^5-C$_5$Me$_5$)(NO) is that the first and third bands correspond to $^2E_1$ ion states and the second corresponds to both $^2A_1$ and $^2E_2$ ion states.

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