The Electronic Structure of Hydrotris(1-pyrazolyl)borate Ligand by He-I and He-II Photoelectron Spectroscopy

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The He-I and He-II excited photoelectron spectra of the sodium and thallium(I) derivatives of the hydrotris(1-pyrazolyl)borate ligand are reported.

Experimental criteria as well as quantum-mechanical calculations were used to assign photoelectron bands in the low ionization energy region. The spectra indicate a minor perturbation of metal ions on ligand based molecular orbitals. The results provide an adequate description of the electronic structure of the anion ligand itself.

Fig. 1. Perspective drawing of the $(HB(pz)_3)^-$ anion ligand.

Introduction

The hydrotris(1-pyrazolyl)borate $(HB(pz)_3)^-$ anion is a rare example of a uninegative tridentate ligand of C_{3v} symmetry (Fig. 1), which forms trigonally distorted octahedral complexes $M(HB(pz)_3)_2$ with divalent transition metal ions [1, 2]. These thermally stable complexes are volatile. They provide, therefore, the rare opportunity to study divalent metal ions in an octahedral environment by vapour-phase UV photoelectron (pe) spectroscopy. In this paper we report the results of a pe investigation on the volatile derivatives $M(HB(pz)_3)$ of sodium and thallium(I), the study being preliminar to a forthcoming paper on the mentioned octahedral complexes [3]. The sodium derivative is particularly interesting because the metal–ligand bonding is expected to be mainly ionic and, therefore, ligand based molecular orbitals (MOs) can only suffer an energy shift due to the electrostatic perturbation of the sodium ion. As a consequence, the electronic structure emerging from the present pe data must be in strict relation to that of the anion ligand itself.

In addition information on perturbation due to 'covalent' metal–ligand bonding may arise from the pe data of the thallium derivative, in which the
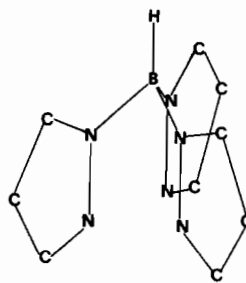
thallium $6s^2$ electron pair may be capable of covalent interaction with suitable ligand MOs.

Experimental

Sodium hydrotris(1-pyrazolyl)borate, $Na(HB(pz)_3)$, was prepared according to the literature [4]. It was purified first by crystallization from toluene and then by sublimation *in vacuo*.

The thallium(I) hydrotris(1-pyrazolyl)borate, Tl-$(HB(pz)_3)$, was prepared by mixing a suspension of thallium(I) chloride (2.39 g) with an aqueous solution (100 ml) containing potassium hydrotris(1-pyrazolyl)borate (2.52 g). The mixture was stirred for one hour. The white solid was filtered on a sintered-glass frit and washed several times with water. Finally it was crystallized from toluene (50 ml) and purified by vacuum sublimation onto a water-cooled probe.

M.p. 156 °C; mass spectrum (m/e, assignment): 418, $[Tl(HB(pz)_3)]^+$; 351, $[418 - pz]^+$; 272, $[Tlpz]^+$; 213, $[HB(pz)_3]^+$; IR (Nujol): ν_{BH} 2460 (m), 2474 (w) cm^{-1}; ^1H NMR (CDCl$_3$): δ 6.23 (t, 1H); 7.61 (d, 1H); 7.80 (d, 1H). Mass infrared and ^1H NMR spectra were obtained on a LKB 9000 S, Perkin-Elmer 257, and Bruker WP-80, respectively.

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TABLE I Experimental and Calculated IEs for Na(HB(pz)$_3$) and Tl(HB(pz)$_3$) *

Na(HB(pz)$_3$)			Tl(HB(pz)$_3$)	
calc IEs (eV)[a]	exp IEs (eV)	assignments	exp IEs (eV)	assignments
8 43 (a$_2$)	(8 43)		(8 40)	
8 44 (e)	8 77	pyrazole π MOs	9 00	pyrazole π MOs
8 80 (a$_2$)	(9 2)	(a$_2$, e, a$_2$, e)	(9 4)	(a$_2$, e, a$_2$, e) +
8 85 (e)				a$_1$ (6s Tl)
10 22 (a$_1$)	10 40	e(σ_N)	10 41	e(σ_N)
10 43 (e)	11 03	a$_1$ (σ_{BH}) + a$_1$(σ_N)	11 29	a$_1$ (σ_{BH})
11 29 (a$_1$)				
	13 28		13 0	
	15 1	inner π and σ MOs	13 7	a$_1$ (σ_N) +
	16 5		15 1	inner π and σ MOs
	17 8		16 7	
			18 0[b]	
			19 32[b]	Tl 5d ^{2}D$_{5/2}$
			21 46[b]	Tl 5d ^{2}D$_{3/2}$

*Shoulders are given in brackets   [a]Adopting Koopmans' theorem Values are rescaled to reproduce the first experimental IE
[b]Taken from He-II spectrum
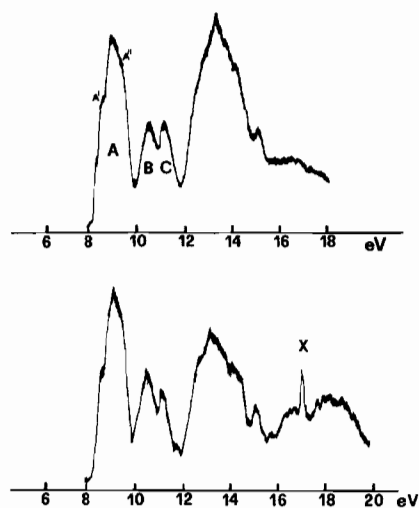
Fig 2 He-I (top) and He-II (bottom) pe spectra of Na(HB-(pz)$_3$) Band labelled X represents the He 1s^{-1} ionization produced by He-II (β) radiation

The photoelectron spectra were measured on a Perkin-Elmer PS 18 spectrometer, modified for He-II measurements by inclusion of a hollow-cathode discharge lamp (Helectros Developments)

The spectra were calibrated by reference to peaks caused by admixed noble gases and nitrogen Perti-

nent pe data are reported in Table I Quantum mechanical calculations were performed in the CNDO scheme [5] with the geometrical parameters of the anion ligand taken from an X-ray diffraction study [6]

Results and Discussion

The low ionization energy (IE) region of each spectrum consists of three well resolved bands labelled A, B, C in Figs 2 and 3 Band A generally shows two shoulders (labelled A' and A'') in the low and high IE sides respectively In the He-II spectra the bands A and B increase relative to band C In the case of thallium derivative the effect is more pronounced for band A The higher IE region consists of broad, slightly resolved, bands which represent mainly ionizations from σ and inner π MOs localized on the pyrazole ring These bands will not be considered further, because these orbitals are hardly involved in the metal ligand bonding Notably, the He-II spectrum of Tl(HB(pz)$_3$) contains two bands in form of an intense doublet in the 18–22 eV region (Fig 3)

Reference to pe spectra of pyrazole [7] and to those of several compounds containing the BH$_4^-$ group [8] suggests that the electrons detected in the low IE region of the present spectra should come
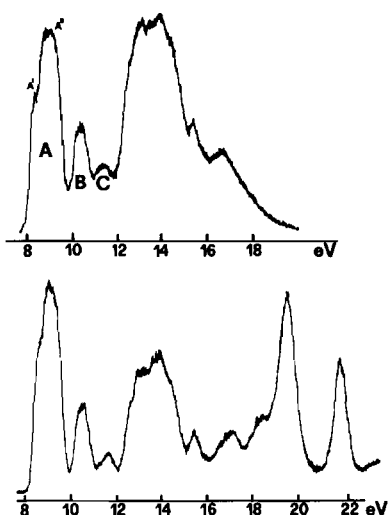
Fig. 3. He-I (top) and He-II (bottom) pe spectra of Tl(HB-(pz)$_3$).

$a_2(\pi)$

$e\,(\pi)$

$a_2(\pi)$

$e\,(\pi)$

$e(\sigma_N)$

$a_1(\sigma_N)$

$a_1(\sigma_{BH})$

Fig. 4. Qualitative diagram of outmost MOs levels of (HB-(pz)$_3$)$^-$ anion ligand.

from MOs which are in relation to the 2a″, 3a″ (π) and 15a′ (σ_N nitrogen lone pair) MOs of the simple pyrazole molecule (C_s symmetry). The bands must also include the ionization from the MO representing the σ_{BH} bond. A more detailed assignment can be deduced from a qualitative description of the electronic structure of the HB(pz)$_3^-$ anion ligand in terms of interactions among the above mentioned molecular MOs.

In the C_{3v} point group, which describes properly the anion ligand, the symmetry combinations of these orbitals encompass the following irreducible representations:

$\pi_{(pyrazole)}$ . . . $2a_2 + 2e$

σ_N . . . . $a_1 + e$

σ_{BH} . . . . a_1

Simple group-overlap arguments as well as consideration of IE data related to various subunits [7, 8] provide the MO energy ordering reported in Fig. 4. In the case of the spectrum of Na(HB(pz)$_3$) (Fig. 2) this qualitative diagram leads to the assignments of band A and shoulders A′ and A″ to the πMOs on the pyrazole rings. The band B is assigned to the ionization from the $e(\sigma_N)$ MO while the band C must represent the $a_1(\sigma_N)$ and $a_1(\sigma_{BH})$MOs. This assignment implies an intensity ratio among bands A, B and C (under the assumption that the total pe cross-sections for the different MOs are of comparable magnitude) which fits quite well the intensity ratio found in the He-I spectrum. Moreover, the changes in relative intensities, when passing from the He-I to the He-II spectrum, agree with the proposed assignment. The reduced intensity of band C in the He-II
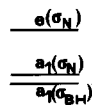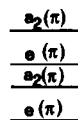
spectrum indicates, in fact, that the band should include the ionization from the $a_1(\sigma_{BH})$MO. The pe cross section of this MO is expected to be rather low under He-II excitation because of the reduced H_{1s} cross section at He-II wavelength [9].

Quantitative CNDO calculations, performed for Na(HB(pz)$_3$), are consistent with our assignment (Table I).

The pe spectrum of Tl(HB(pz)$_3$) is very similar to that of the sodium derivative. In the He-I spectrum, band A is more intense, whereas band C appears smaller than in the Na(HB(pz)$_3$) derivative. These differences can be understood when bonding interactions between the thallium $6s^2$ electron pair and ligand MOs of a_1 symmetry are considered. Such interactions have been invoked to interpret pe spectra of thallium(I) derivatives [10, 11]. Such interactions were found to lead to a stabilization of ligand MOs of a_1 symmetry suited for overlap with the thallium 6s atomic orbital. The $a_1(\sigma_N)$ MO fulfills these conditions and the decrease in intensity of band C found in Tl(HB(pz)$_3$) reflects, in our opinion, the shift to higher IE of the component corresponding to ionization from the $a_1(\sigma_N)$ MO. In contrast to Na(HB(pz)$_3$), band C in the spectrum of the Tl derivative represents only the $a_1(\sigma_{BH})$MO. The ionization from the antibonding counterpart of $a_1(\sigma_N)$ MO, which is expected to possess mainly Tl $6s^2$ character, may be hidden under the large envelope of the band A. In fact, this band increases in intensity under He-II irradiation because the one-electron cross-section of the Tl 6s AO increases at the He-II excitation energy.

Finally we turn to the intense doublet found in the 18–22 eV region of the Tl(HB(pz)$_3$) spectrum. These bands must be related to production of the $^2D_{5/2}$ and $^2D_{3/2}$ final states upon ionization of thallium in the $5d^{10}$ ground state configuration. Our spectra do not show evidence of ligand field splitting of the metal d structure. This result, analogous to that found for Tl(C$_5$H$_5$) is in contrast to the pe data found for thallium(I) halides [10], which produced spectra with very rich structures caused by

metal 5d ionizations. This behaviour has been already interpreted by considering that in Tl(I) compounds ·the ligand field perturbation on inner d subshells is purely electrostatic in origin while halide anions produce a more effective internal electrostatic field.

The average metal d IE (20.18 eV), calculated according to the multiplicities of the final states, is lower than the value reported for the neutral Tl atom (21.38 eV) but comparable to that for $Tl(C_5H_5)$ (20.30 eV) [11]. As discussed in the case of the cyclopentadienyl complex [11], the extra-atomic relaxation effect in the d^{-1} ionic states seems to be operating also in the present case. In particular an enhanced stabilization of the strongly localized d^9 hole state by polarization of the ligand electron density seems to be the more compelling explanation to account for the observed trend.

Acknowledgements

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