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Evidence of Spin Crossover Phenomena Deduced from Gas-Phase Photoelectron Spectra of the Bis[tetrakis(pyrazol-1-yl)borato]iron(II) Complex

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The gas-phase He I and He II photoelectron spectra of the bis[tetrakis(pyrazol-1-yl)borato]iron(II) complex have been recorded. In striking contrast with the low-spin only $^1A_1$ state so far associated with its d^6 ground configuration, the spectral pattern of the d^{-1} final ion states is almost identical to that produced upon ionization from the $^5T_2$ ground state of the thermally activated high-spin bis[tris(pyrazol-1-yl)borato]iron(II) parent complex. The multiplet onset structure in the photoelectron spectrum suggests the occurrence of the $^5T_2$ ground state and, hence, of spin crossover phenomena. The energies associated with the onset multiplet structure have been used to fit the corresponding Racah equations for the electrostatic energies of the ion states produced upon ionization from the $^5T_2$ ground state. A 1.53-eV ligand field Δ value has been found. There is indication of a more pronounced trigonal distortion of the present complex with respect to the bis[tris(pyrazol-1-yl)borato]iron(II) parent complex.

Introduction

The poly(pyrazol-1-yl)borate complexes of main Group[1] and of transition[1a,2] metals constitute a large and active research area. Among these, the complexes of the Fe(II) ion form a very interesting class of their own due to their intriguing magnetic properties.[3]

It is well-known that the d^6 metal ion in octahedral fields may have either $^5T_2$ or $^1A_1$ ground states.[4] Therefore "spin crossover" phenomena must be expected close to critical values of the field strength so that simple variations of temperature can tip the scales in favor of one or the other of the ground states.[3b,d,5] In this context, bis[poly(pyrazol-1-yl)borato]iron(II) complexes, hereafter referred to as $Fe[H_xB(pz)_{4-x}]_2$ ($x = 0, 2$), possess magnetic moments typical of either low- or high-spin ground states.[3] They depend either on changes in the nature of substituents at the periphery of the molecules[3] or on temperature.[3,5] Thus, while $Fe[HB(3,5\text{-}Me_2pz)_3]_2$ and $Fe[HB(4\text{-}Mepz)_3]_2$ are paramagnetic and fully high-spin systems ($\mu \approx 5.2$ and $5.03\ \mu_B$, respectively), $Fe[HB(pz)_3]_2$ has an intermediate μ value ($2.7\ \mu_B$) which is very much dependent on the temperature due to the spin equilibrium.[3] Interestingly enough, the $Fe[B(pz)_4]_2$ complex remains low-spin in the entire temperature range studied to date.[3,5]

The spin state can, of course, be revealed through photoelectron (PE) spectra,[6] and in a previous paper,[7a] we have shown that the spectral pattern of final states upon ionization found in the PE spectra of the $Fe[HB(pz)_3]_2$ complex is completely in accordance with the $^5T_2$ molecular ground state. An obvious consequence is that PE gas-phase investigations can provide evidence of spin crossover phenomena in a temperature range which goes beyond that of typical magnetic moment measurements.

In this perspective, there is sufficient reason for studying the PE spectrum of $Fe[B(pz)_4]_2$, and in this paper, we present the first ever case of evidence of spin crossover in Fe(II) complexes deduced from gas-phase PE spectra.

Experimental Section

The $Fe[B(pz)_4]_2$ complex was synthesized according to the published procedure.[8] It was purified by sublimation in vacuo and gave satisfactory analytical results (IR, UV–vis).[3a,8] Electron impact mass spectra (EI MS) show prominent signals (related to the isotopes ^{11}B and ^{56}Fe) at *m/z* 614 (M^+), 547 [$(M-pz)^+$], 402 [$(M-B(pz)_3)^+$], and 335 [$(M-B(pz)_4)^+$]. The MS patterns accurately fit the expected statistical distribution of natural isotopes (^{11}B, ^{10}B; ^{56}Fe, ^{54}Fe) and do not depend upon the energy (10–70 eV) of the bombarding electrons. High-resolution UV PE spectra were recorded in the 210–290 °C temperature range. Measurements below and beyond this range are precluded because of either an insufficient (<10 cps) count rate or incipient decomposition processes, respectively. Measurements were made using an IBM AT computer directly interfaced with a modified PS18 Perkin-Elmer spectrometer, equipped with an He I, He II source (Helectros Development). Resolution measured on the Ar $^2p_{3/2}$ line was always around 18–20 meV. The band intensities in the He II spectrum were corrected only for the He IIβ "satellite" contributions (9% on the reference N_2 spectrum).

Results

The He I and He II PE spectra of $Fe[B(pz)_4]_2$ are reported in Figure 1. In the region below 8 eV, they consist of some well-resolved, low-intensity, onset structures (labeled x), whose integrities have been carefully checked. Two main band envelopes (labeled a, b) follow in the 8–12-eV region. Finally, some diffuse and ill-resolved structures are found in the higher ionization energy

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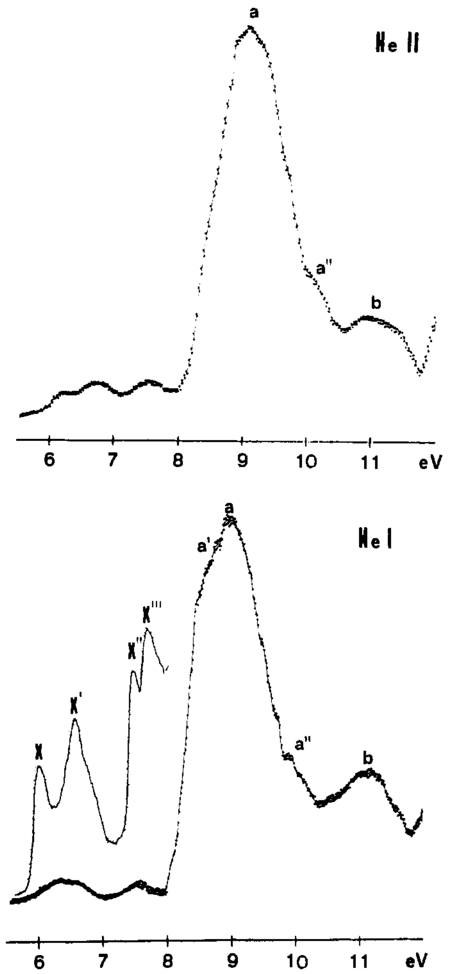

Figure 1. He I and He II PE spectra of the $Fe[B(pz)_4]_2$ complex (5.5–12 eV).

Table I. Relevant PE Data for the $Fe[HB(pz)_3]_2$[a] and $Fe[B(pz)_4]_2$[b] Complexes

$Fe[B(pz)_4]_2$			$Fe[HB(pz)_3]_2$		
band label	IE, eV	assgnt	band label	IE, eV	assgnt
x	6.06	$^6A_1$	x	5.93	$^6A_1$
x′	6.41	$^4T_1, ^4T_2$	x′	6.39	$^4T_1, ^4T_2$
x″	7.39	$^4A_1, ^4E_1$	x″	7.46	$^4A_1, ^4E_1, ^4T_2$
x‴	7.65	$^4T_2$			
a′	8.75	π(ring) + $^4T_1$	a	8.37	π(ring) + $^4T_1$
a	9.05		b	8.98	
a″	9.93	π(ring)			
b	11.12	σ_N	c	11.15	$\sigma_{BH} + \sigma_N$

[a] See ref 7a. [b] See Figure 1.

(IE) region beyond the range of Figure 1. In the He II spectrum, relative intensities of the x features increase[7a,9] compared to all the bands which follow. The spectra are strongly reminiscent of those of thermally activated high-spin $Fe[HB(pz)_3]_2$ complex[7a] even though different intensity ratios between the various bands are observed, either because of the absence of ionizations related to B–H bonds or because of the presence of the fourth pyrazolyl ring.

Relevant spectral data are collected in Table I.

Discussion

The metal–ligand bonding of $Fe[B(pz)_4]_2$ closely resembles that encountered in the parent $Fe[HB(pz)_3]_2$ complex.[7a] The $[B(pz)_4]^-$ ligand remains basically tridentate,[3a,8a,10] and therefore, the three coordinated and the single uncoordinated pyrazolyl groups maintain separate identities.[3a,8a,10]

Table II. Electrostatic Energies of Final States Produced upon Ionization of One d Electron from the d^6 $^5T_2$ Ground State of $Fe[B(pz)_4]_2$

ion confign	ion states	intensities	electr energ
t_2^4e	$^4T_1$	1	$10A - 25B + 6C$
	$^4T_2$	1	$10A - 17B + 6C$
	$^6A_1$	6/5	$10A - 35B + \Delta$
	$^4A_1$	2/15	$10A - 25B + 5C + \Delta$
$t_2^3e^2$	^4E	2/3	$10A - 22B + 5C + \Delta$
	$^4T_1$	1	$10A - 16B + 7C + \Delta$
	$^4T_2$	1	$10A - 22B + 5C + \Delta$

In this context the electronic structures of both the $[B(pz)_4]^-$ and $[HB(pz)_3]^-$ anion[7] ligands must be similar as far as the electronic system mostly involved in the metal–ligand bonding is concerned. Previous studies[7a] on the simpler $Fe[HB(pz)_3]_2$ have shown that the ligation of the tris(pyrazol-1-yl)borate anion is similar to that encountered in cyclopentadienyl complexes,[2a,10c] since each ligand supplies six electrons to the metal–ligand bonding in a three-coordinated environment around the metal.[10c] In addition, the central metal ion is similarly sandwiched between two triangular arrays which are formed by the coordinated nitrogen atoms with the σ N_{2p} lone pairs pointing toward the metal. This particular geometry leaves the π system on each pyrazolyl ring almost unaffected by the coordination with the metal center.[7a] In contrast the σ lone pairs of coordinated nitrogen atoms are remarkably perturbed upon coordination.[7a]

The energy sequences of the upper-filled MOs in both the $[HB(pz)_3]^-$ anion and the $Fe[HB(pz)_3]_2$ complex have been established previously.[7] Extrapolation of these results to the present case suggests that the lower-lying metal and ligand-based MOs can be grouped in three categories: (1) MOs associated with metal 3d subshells in the 6–8-eV region;[6d,7a] (2) MOs which represent the almost unperturbed π systems of all the pyrazolyl rings;[7,11a] (3) MOs representing the σ_N lone pairs of the nitrogen donor atoms in the 10–12-eV region,[7,11a] as well as the unique σ_N lone pairs belonging to the uncoordinated pyrazolyl rings. The latter must be slightly lower-lying in energy because of both charge arguments and the absence of any stabilizing effect due to coordination with the metal center.

In this perspective the assignment of PE data becomes a straightforward matter. Therefore, in an analogy with $Fe[HB(pz)_3]_2$,[7a] the band envelope a (Figure 1) represents the ionizations of π MOs of the coordinated pyrazolyl rings.[7,11a] In particular the higher IE feature a″, absent in the spectrum of the $Fe[HB(pz)_3]_2$ parent, can be associated with the π MOs of the uncoordinated pyrazolyl rings.[11a] Band b can be assigned to the ionization of the σ_N lone pairs of both coordinated and uncoordinated rings.[7a] Finally, the low-intensity onset features x, almost identical with those found at the onset of the spectrum of the thermally activated, high-spin $Fe[HB(pz)_3]_2$ parent complex,[7a] can be assigned to d^{-1} ionizations. In this context, these multiplet structures are completely incompatible with the $^1A_1$ ground state since, upon ionization, this can result in one final ion state[6] only and, hence, in a singular PE band. In contrast, several ion states are obtained upon removal of one electron from the d^6 $^5T_2$ ground state.[6,7a] Their electrostatic energies are reported in Table II in terms of Racah parameters (A, B, C)[6] and of crystal field splitting (Δ). On the basis of these considerations, band x represents the $^6A_1$ ion state, band x′ must be associated with the $^4T_1$ and $^4T_2$

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states, band x″ corresponds to the two ion states $^4A_1$ and ^4E, and band x‴ may be consistent with the $^4T_2$ ion state.[7a] Finally the remaining $^4T_1$ ion state is likely to be hidden under envelope a.[7a] We note that the ^4E and $^4T_2$ ion states must be degenerated in energy under the O_h symmetry. Nevertheless, the energy splitting presently found may be due to trigonally distorted coordination in the $Fe[B(pz)_4]_2$ complex. The PE relative energies (Table I) associated with the mentioned ion states have been used to fit the corresponding Racah equations for the electrostatic energies with the Fletcher–Powell method.[12a] The fitting *A*–*C* and Δ values are 0.53, 2.0×10^{-2}, 0.28, and 1.53 eV, respectively.[12b] These values are entirely in accordance with previous literature data[3a] as well as with the 1.41-eV Δ value found for the $Fe[HB(pz)_3]_2$ complex.[7a]

There is, therefore, evidence that the present $Fe[B(pz)_4]_2$ complex possesses a $^5T_2$ high-spin state in the gas phase and in the selected temperature range. This observation contrasts with the low-spin $^1A_1$ state found in the solid state and in the entire temperature range previously investigated (<67 °C).[3a] No data have been reported beyond this temperature value, with the obvious consequence that spin crossover phenomena must occur in a higher (67–210 °C) temperature range than found in the $Fe[HB(pz)_3]_2$ parent complex.[3a,13] As a matter of fact, the presence of additional uncoordinated pyrazolyl rings in the $Fe[B(pz)_4]^-$ complex certainly causes a greater sterical congestion, hence a greater trigonal distortion relative to the $Fe[HB(pz)_3]^-$ parent complex. This effect results in a more pronounced antibonding character of Fe 3d subshells of e_g symmetry[7a] and in a greater ligand field Δ value. This observation is entirely in accord with present PE data which have provided a 1.53-eV Δ value greater than 1.41 eV found in the $Fe[HB(pz)_3]_2$ parent complex.[7a] A greater thermal activation energy is, therefore, required for the $^1A_1 \rightarrow {}^5T_2$ process.

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