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Gas-Phase Ultraviolet Photoelectron Studies of Octahedral Tris(pyrazol-1-yl)borate Complexes of Some Divalent Transition Metals

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This paper reports the results of a study of the electronic structure of both early- and late-transition-metal 3d hydrotris(pyrazol-1-yl)borate complexes by combined He I and He II photoelectron spectroscopy. This is the first investigation of a series of analogous complexes with divalent transition metals spanning from Fe to Zn in an identical octahedral array. No gas-phase photoelectron spectra of octahedral Ni, Cu, and Zn complexes have ever been reported. In the case of Fe and Co complexes, there is evidence that the energy of the final states produced upon ionization of electrons from metal 3d subshells can be accounted for by an electrostatic model mediated by the usual Racah and ligand field parameters. As a natural consequence, the ionization energies of ligand-based molecular orbitals are no longer affected by the nature of the central metal atom. In the series of complexes from Fe to Cu, the ionization energies of the 3d subshells increase smoothly. This trend, probably, causes in the Ni and Cu complexes a better energy matching between metal 3d orbitals and combinations of ring nitrogen lone pairs of appropriate symmetry and, thence, leads to predominant, covalent metal-to-ligand bonding. A localized bonding model, reminiscent of that adopted for metallocenes, provides a good rationale for the spectra.

Introduction

The volatile metal complexes containing (pyrazol-1-yl)borate as ligands form very intriguing classes of compounds.[1] Among these compounds are complexes of divalent transition-metal ions[2] with hydrotris(pyrazol-1-yl)borate, $[HB(pz)_3]^-$, as ligand. X-ray diffraction studies have shown that each ligand is tridentate in these complexes. Each metal atom is surrounded by six nitrogen donor atoms forming a trigonally distorted octahedron[3] (Figure 1).

This group of compounds offers the rare opportunity of investigating complexes of both early and late transition metals, with an identical octahedral ligand array, which is a unique feature of metal d complexes in which $[HB(pz)_3]^-$ ligands act as coordinating groups and as anionic counterions.[4] With ligands other than $[HB(pz)_3]^-$ the complexes generally have different geometries for early- and late-transition-metal ions, the central metal atom being either in the +3 or +2 oxidation state. Little attention has been paid to the electronic structure of pyrazol-1-yl borate complexes. To date only ligand field aspects have been considered,[5] but these give little insight into the general features of metal–ligand bonding. Therefore, we have initiated photoelectron spectroscopic (PE) studies of pyrazolylborates and reported already on the electronic structure[6] of $[HB(pz)_3]^-$.

In the present paper we discuss the electronic structure of the complexes $M[HB(pz)_3]_2$ (M(II) = Fe, Co, Ni, Cu, Zn) deduced from PE spectra and describe a unitary metal–ligand bonding model, which is independent of variation of the oxidation state of the metal and/or the coordination geometries.

Experimental Section

The complexes were prepared according to literature procedures[2] and were purified first by crystallization from xylene and then by sublimation in vacuo. The complexes gave satisfactory mass-spectrometric analyses. The photoelectron spectra were run on a Perkin-Elmer PS 18 photoelectron spectrometer, modified for He II measurements by inclusion of a hollow-cathode discharge lamp (Helectros-Developments). All the spectra were calibrated by reference to peaks due to admixed noble gas, nitrogen, and He 1 s^{-1} self-ionization.

Table I. Relevant Spectral Data of Studied Complexes

compd	band label	IE	half-width	assignt
$Zn[HB(pz)_3]_2$	a	8.35	1.4	π(ring)[a]
	b	9.05		
	c	11.3	1.2	$\sigma_{BH} + \sigma_N(e_g)$
$Fe[HB(pz)_3]_2$	x	5.93		$^6A_{1g}$
	x′	6.39		$^4T_1$, $^4T_2$
	x″	7.46		$^4A_1$, $^4E_1$, $^4T_2$
	a	8.37	1.43	π(ring)[a] + $^4T_1$
	b	8.98		
	c	11.15	1.53	$\sigma_{BH} + \sigma_N(e_g,a_{2u},e_u)$
$Co[HB(pz)_3]_2$	x	7.79		$^5T_2$
	a	8.46	1.35	π(ring)[a]
	b	9.14		
	c	11.35	1.61	$\sigma_{BH} + \sigma_N(e_g,a_{2u},e_u)$
$Ni[HB(pz)_3]_2$	a	8.40	1.36	π(ring)[a]
	b	9.00		
	x	9.60		$e_g(d_{xz},d_{yz})$
	x′	10.70		$a_g(d_{z^2})$
	c	11.10	1.45	$\sigma_{BH} + \sigma_N(a_{2u},e_u) + d_{x^2-y^2}$
		11.55		
$Cu[HB(pz)_3]_2$	a	8.42	1.20	π(ring)[a]
	b	8.95		
	x	10.48		$\sigma_N(e_g)$
	c	11.51	1.19	$\sigma_{BH} + \sigma_N(a_{2u},e_u)$

[a] In the D_{3d} symmetry, ligand combinations of the π pyrazole MO's (3a″ and 2a″ in ref 20) belong to the following irreducible representations: $2a_{2g}$, $2e_g$, $2a_{1u}$, $2e_u$.

Results and Discussion

The He I and He II PE spectra of the $[HB(pz)_3]^-$ complexes of divalent Fe, Co, Ni, Cu, and Zn are all similar in their general features. They consist of three main bands (labeled a, b, c in Figures 2–4) in the 8–12-eV region.

In the He II spectra bands c are less intense than in the He I spectra.

The spectra of the Fe and Co complexes have some low-intensity onset structures below 8 eV (labeled x in Figure 3). The integrity of these structures has been thoroughly checked.[7]

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(1) (a) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 479. (b) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, *17*.

(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

(3) (a) Churchill, M. R.; Gold, K.; Maw, C. E. *Inorg. Chem.* **1970**, *9*, 1597. (b) Murphy, A.; Hataway, B. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1646. (c) Oliver, J. D.; Mullica, D. F.; Hutchinson, B. B.; Milligan, W. O. *Inorg. Chem.* **1980**, *19*, 165.

(4) Most "octahedral" metal d complexes have stoichiometries expressed by the formula ML_nX_m (L = unidentate or bidentate neutral ligand; X = anionic counterion). These complexes are insufficently volatile and/or thermally unstable for photoelectron studies.

(5) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3148.

(6) Bruno, G.; Ciliberto, E.; Fragalà, I.; Granozzi, G. *Inorg. Chim. Acta* **1981**, *48*, *61*.

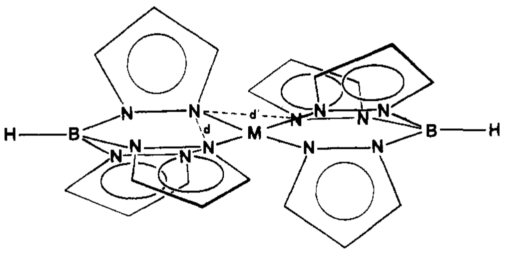

Figure 1. Geometry of hydrotris(pyrazol-1-yl)borate complexes.

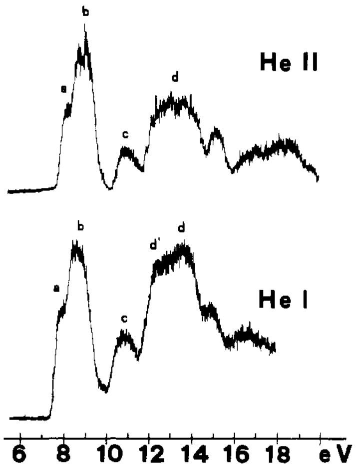

Figure 2. He I and He II spectra of Zn[HB(pz)$_3$]$_2$.

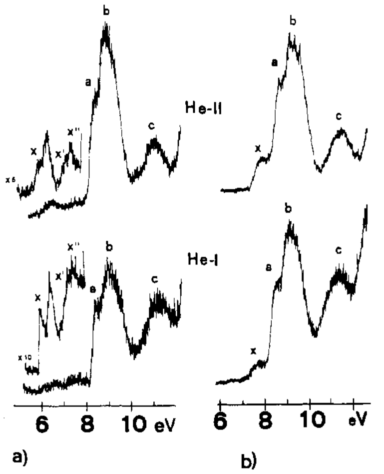

Figure 3. He I and He II spectra of (a) Fe[HB(pz)$_3$]$_2$ and (b) Co[HB(pz)$_3$]$_2$.

The relative intensities of the onset bands are somewhat higher in the He II than in the He I spectra (Figure 3). Onset bands below 8 eV are absent in the spectra of the Ni and Cu complexes. These complexes give, however, new bands or shoulders in the 10–11-eV region (bands x and x′, Figure 4).

The spectra in the higher region (12–18 eV) consist of diffuse and ill-resolved bands analogous to those in the spectra of the Na(I) or Tl(I) complexes[6] with [HB(pz)$_3$]$^-$. These bands are caused by ejection of electrons from inner π or σ ligand-based molecular orbitals (MO's). These orbitals are not involved in the formation of metal–ligand bonds and, therefore, will not be further discussed.

Relevant spectral data are collected in Table I.

The electronic structure of [HB(pz)$_3$]$^-$ complexes can be qualitatively described by using as bases for MO's the relevant valence orbitals of the ligand which, to some extent, reproduce the various bonds.

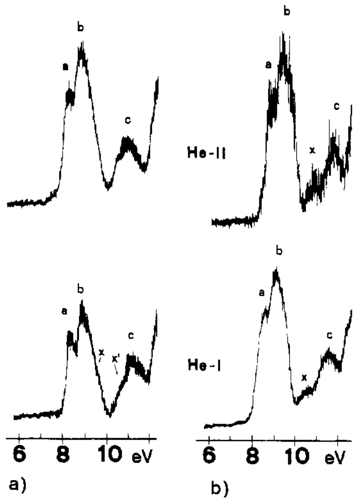

Figure 4. He I and He II spectra of (a) Ni[HB(pz)$_3$]$_2$ and (b) Cu[HB(pz)$_3$]$_2$.

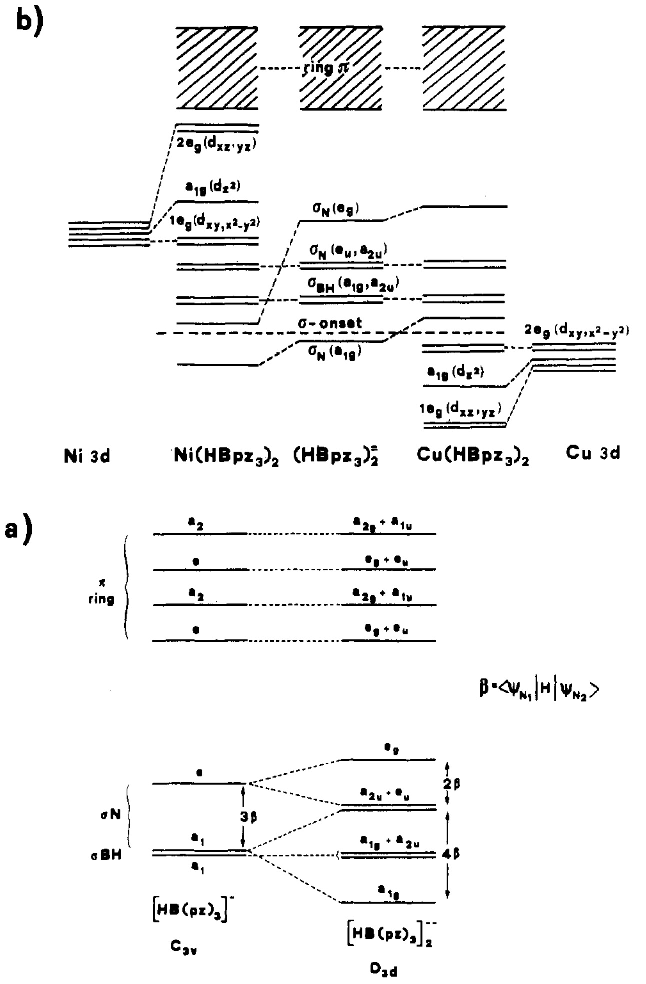

Figure 5. (a) Energy ordering of valence ligand symmetry orbitals. (b) MO qualitative scheme of Ni(II) and Cu(II) complexes.

In an earlier investigation[6] we established the sequence of MO's in [HB(pz)$_3$]$^-$ (Figure 5a). The complexes M[HB(pz)$_3$]$_2$ possess a trigonally distorted octahedral structure of D_{3d} symmetry.[3,5] In this point group the basis orbitals of the ligands produce the symmetry combinations shown in Figure 5a. These combinations belong to one of three categories: (i) MO's formed by combining π orbitals of the pyrazole rings, (ii) MO's formed from the lone pairs of the nitrogen donor

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(7) These bands cannot be shadows excited by parasitic β or γ radiations that always accompany the emission of the main He I and He II radiations because the bands appear at the same binding energies in the He I and He II spectra.

Table II. Electrostatic Energies of Final States Produced upon Ionization of One d Electron from the Ground State of Studied Complexes

compd	ground state	ion confign	ion states	intensities	electrostatic energies[13]
$Fe[HB(pz)_3]_2$	$^5T_2(t_2{}^4e^2)$	$t_2{}^4e$	$^4T_1$	1	$10A - 25B + 6C$
			$^4T_2$	1	$10A - 17B + 6C$
		$t_2{}^3e^2$	$^6A_1$	$^6/_5$	$10A - 35B + \Delta$
			$^4A_1$	$^2/_{15}$	$10A - 25B + 5C + \Delta$
			^4E	$^2/_3$	$10A - 22B + 5C + \Delta$
			$^4T_1$	1	$10A - 16B + 7C + \Delta$
			$^4T_2$	1	$10A - 22B + 5C + \Delta$
$Co[HB(pz)_3]_2$	$^4T_1(t_2{}^5e^2)$	t^5e	$^3T_1$	1	$15A - 17B + 13C$
			$^3T_2$	1	$15A - 19B + 13C$
		t^4e^2	$^5T_2$	$^5/_2$	$15A - 35B + 7C + \Delta$
			$^3A_2$	$^1/_3$	$15A - 16B + 14C + \Delta$
			^3E	$^2/_3$	$15A - 25B + 11C + \Delta$
			$^3T_1$	1	$15A - 25B + 11C + \Delta$
			$^3T_2$	$^1/_2$	$15A - 27B + 11C + \Delta$
$Ni[BH(pz)_3]_2$	$^3A_2(t_2{}^6e^2)$	t^6e	^2E	2	$21A - 20B + 20C$
		t^5e^2	$^4T_1$	4	$21A - 30B + 14C + \Delta$
			$^2T_1$	2	$21A - 30B + 17C + \Delta$
$Cu[HB(pz)_3]_2$	$^2E(t_2{}^6e^3)$	t^6e^2	$^3A_2$	$^3/_2$	$28A - 50B + 21C$
			$^1A_1$	$^1/_2$	$28A - 34B + 25C$
			^1E	1	$28A - 42B + 23C$
		t^5e^3	$^3T_1$	$^9/_4$	$28A - 38B + 21C + \Delta$
			$^3T_2$	$^9/_4$	$28A - 50B + 21C + \Delta$
			$^1T_1$	$^3/_4$	$28A - 38B + 23C + \Delta$
			$^1T_2$	$^3/_4$	$28A - 42B + 23C + \Delta$

atoms (σ_N), and (iii) MO's formed from combinations of the two terminal σ_{BH} orbitals. Symmetry-allowed off-diagonal mixing may play a role but was found to have little effect even in $[HB(pz)_3]^-$.[6] Therefore, the energy ordering among each group of symmetry combinations is mediated by the repulsion integrals, which depend also on interligand group overlaps. However, the large distance[3] between the two ligands makes the repulsion between MO's vanish. Their final sequence in the $[HB(pz)_3]_2{}^{2-}$ framework is, therefore, analogous to that of a given ligand unit. By contrast, interligand interactions between σ_N orbitals are expected to be significant because of the particular geometry of the complexes, which have the metal ion sandwiched between two triangular arrays formed by nitrogen atoms. The triangles are rotated by 60° with respect to each other. The inter- and intraligand distances d and d' (Figure 1) between vicinal nitrogen atoms are approximately equal. The evaluation of appropriate terms for an ideal triangular, antiprismatic structure leads to the MO order given in Figure 5a. An important feature of such a description is the degeneracy of the combinations of ungerade type (e_u, a_{2u}) and coincidence of their energy with that of an unperturbed nitrogen lone pair in a simple pyrazolyl moiety.[8] Moreover, the separation between the e_g and a_{1g} orbitals, which represents the total energy dispersion of the σ_N combinations, can be estimated to be around 1.2 eV, approximately twice the value between the σ_N combinations of e and a_1 symmetry in the simple anion $[HB(pz)_3]^-$ of C_{3v} symmetry.[6] On the basis of the proposed ordering of ligand MO's in the complexes, we can postulate a qualitative bonding scheme for all the complexes by considering interactions between relevant ligand MO's and the appropriate set of metal valence orbitals. Such interactions can involve only σ_N combinations because geometrical factors preclude significant overlap with either π(ring) or σ_{BH} orbitals.

Complexes of d^{10} Metal Ions: $Zn[HB(pz)_3]_2$. There is no doubt that bands a and b in Figure 2 must be related to ionizations of π MO's from the pyrazolyl ring, because the measured IE's and band shapes are almost identical with those in the spectra of the Na(I) and Tl(I) compounds.[6] This observation is in agreement with the hypothesis that the energies of π orbitals are determined only by interaction within a given ligand unit and are almost unaffected by the nature of the metal atom.

Previous results[6] suggest that ionizations from both σ_N and σ_{BH} combinations must produce bands in the 10–12-eV region. The spectrum of $Zn[HB(pz)_3]_2$ has only band c in this region (Figure 2). Therefore, this band must be produced by ionizations from both types of MO's. The measured IE (Table I) practically coincides with the value found for the corresponding σ_{BH} ionization in the Na(I) compound.[6] Furthermore, this band decreases, as expected, in relative intensity under He II radiation because of the reduced H_{1s} cross section.[6,9] The considerations developed in the previous section, however, indicate that it is hardly conceivable to locate all ionizations of the symmetry combinations of σ_N orbitals below band c because of their predicted energy dispersion (Figure 5a). Intensity arguments and the presence of a shoulder at 12.5 eV (band d′ in Figure 2), which is absent in $Na[HB(pz)_3]$, strongly suggest that only the $\sigma_N(e_g)$ combination is responsible for band c. The remaining components (a_{2u}, e_u, a_{1g}) are probably hidden under the intense, higher energy bands. On the other hand, an overall stabilization of these σ_N combinations must be expected due to specific metal–ligand interactions involving 4s and 4p (respectively a_{1g}, e_u and a_{2u} in D_{3d}) metal orbitals.

Complexes of d^6 and d^7 Metal Ions: $Fe[HB(pz)_3]_2$ and $Co[HB(pz)_3]_2$. The PE spectra of the Fe and Co complexes have low-intensity onset bands (Figure 3), which represent ionizations from partially filled metal 3d subshells. This general assignment is firmly supported by the absence of similar features in the spectra of Na(I), Tl(I), and Zn(II) complexes and by the moderately increased[10] relative intensities of these bands under He II radiation. $Fe[HB(pz)_3]_2$ has distorted-octahedral symmetry around the metal atom.[3c] The ground-state configuration of the complex in the solid state has been

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(8) These bands correspond to the t_{1u} combination of ligand bonds in a pure octahedral environment. In the present case, their energies are only affected by Coulomb integrals between σ_N lone pairs correlated by the inversion center. Geometric considerations, however, unambiguously indicate that these terms are of no importance when compared to those involving σ_N lone pairs of vicinal nitrogen atoms (those correlated by S_6 or C_3 symmetry operations).

(9) Downs, A. J.; Egdell, R. G.; Orchard, A. F.; Thomas, P. D. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1755.

(10) It is well-known that metal 3d cross sections increase moderately under He II radiation with respect to those of MO's having significant O 2p or N 2p character.

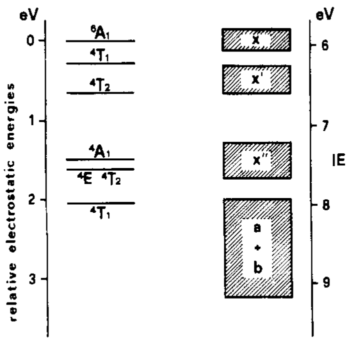

Figure 6. Comparison of relative electrostatic energies (left side) of 3d ion states for Fe[HB(pz)$_3$]$_2$ with experimental IE's (right side) of corresponding PE bands. PE bands are represented by rectangles whose widths reproduce experimental half-width values.

described as a spin equilibrium between the low-spin configuration $^1A_{1g}$, predominant below room temperature, and a high-spin $^5T_{2g}$ state, stable above 391 K.[11] Because the gas-phase spectrum was recorded in the 400 K range, a $^5T_{2g}$ ground-state configuration can be assumed.

Upon removal of one electron from the d^6 ground state $^5T_{2g}$, the ion states listed in Table II are obtained.[12] Their electrostatic energies, expressed in conventional terms[13] of crystal field splitting (Δ) and of Racah parameters B and C, are also given in Table II.

The relative energy ordering of the various states is reported in Figure 6.

Two possibilities can be considered. First, it may be assumed that the ion states $^6A_1$, $^4T_1$, and $^4T_2$ are represented by the onset bands x, x' and x''. The use of expressions listed in Table II with the assumption $C = 4B$ leads to enormously high values of $\Delta = 4.08$ eV and $B = 133$ meV, in disagreement with the values obtained[5,11] for neutral Fe[HB(pz)$_3$]$_2$.

Alternatively, band x may represent the ground ion state $^6A_1$, x' may be associated with the $^4T_2$ and $^4T_1$ states, and finally, x'' may correspond to the three states $^4A_1$, ^4E, and $^4T_2$, which lie indeed within a 3B energy range. The band associated with the remaining $^4T_1$ state is hidden under the intense band a caused by ionizations of ring MO's. This leads to a Δ value of 1.41 eV, entirely in accord with the value for the neutral Fe[HB(pz)$_3$]$_2$ even though the resulting B value of 50 meV is smaller. Nevertheless, lower B values must be expected in the d^{-1} ion state because of the smaller interelectronic repulsion within d subshells.

Within this proposed assignment, two further comments must be made. In Figure 6 the energy separations between the seven ion states are compared with experimental half-widths of the corrsponding PE bands. In contrast to bands x and x'' the half-width of the band x' is narrower than expected from the energy separation between the $^4T_1$ and $^4T_2$ states. We must, however, note that CI effects within the ^4T states may reduce the first-order energy separation.

Second, the relative intensities of the bands x, x', and x'' (1:2:2.5)[14,15] agree well with the statistical probabilities (Table II) of the corresponding ion states.[12]

In the spectrum of Co[HB(pz)$_3$]$_2$ (Figure 3b) a single low-intensity band is present at the onset. The complex possesses a high-spin configuration having the d^7 ground state $^4T_1$.[3,5] Therefore, the ionization of one electron gives rise to the states listed in Table II.[12] Most of the corresponding PE bands must be hidden under the very intense bands that follow in the spectrum. Comparison of the relative intensities as well as energy considerations suggests that the onset band is associated only with the generation of the ground $^5T_2$ ion state.

The remaining bands at IE ≤ 12 eV in the spectra of the Fe and Co complexes are similar to those in the spectrum of Zn[HB(pz)$_3$]$_2$. Therefore, we propose an analogous assignment (Table I). It is worth noting that bands c are considerably broadened in both spectra (Table I). Even though multiplet structures, which may be due to electrostatic coupling of the positive hole in the ion state with the open-shell ground configuration, may cause the observed broadening, bands from the ionizations of the σ_N combinations are, at least, partly responsible for the broadness of bands c. The shift of σ_N combinations of u symmetry toward higher IE's cannot occur, because the relevant metal valence orbitals have g symmetry. Furthermore, arguments given previously favor metal–ligand bonds of predominant ionic character in the Fe(II) and Co(II) complexes and rule out any significant overlap between metal d orbitals and σ_N combinations of g symmetry.

Complexes of d^8 and d^9 Metal Ions: Ni[HB(pz)$_3$]$_2$ and Cu[HB(pz)$_3$]$_2$. The spectra of these "octahedral" d^8 and d^9 complexes (Figure 4), although similar in their general appearance to those already discussed, lack low-intensity onset bands. The 10–12-eV region has more structure with new shoulders (bands x, x' in the Ni complex) or bands (band x in the Cu complex). When dealing with the PE spectra of late 3d metals, one must expect the IE's of the metal d subshells to increase smoothly within the period.[16] This trend and the spin-averaged IE values of 3d subshells obtained from the Fe and Co complexes suggest that the bands associated with metal 3d ionizations in the d^8 and d^9 complexes should interfere with the bands a and b caused by ligand ionizations. In addition, the covalent contribution to metal–ligand bonds may be more important for Ni and Cu complexes than for the complexes of the early elements.[17] The previously adopted, purely electrostatic model may not be adequate for a treatment of metal d ionizations. An MO scheme based upon an overlap model[18] is probably more appropriate.

The analysis of the PE spectrum of Ni[HB(pz)$_3$]$_2$ indicates that the shoulders x and x' (Figure 4a) are most likely caused by metal 3d ionizations. Upon removal of one electron from the $^3A_2$ ground state of this d^8, high-spin complex[5] the ion states $^4T_1$, ^2E, and $^2T_2$ can be produced. A purely electrostatic model demands well-resolved PE bands. Unfortunately the location of the band associated with the generation of the $^4T_1$ ion ground state is uncertain. Shoulder x could be this band. However, the trend of IE's related to the production of ground ion states (Table I) in the Fe and Co complexes suggests that the corresponding band in the Ni complex may lie under the broad band a. Therefore, any crystal field analysis of 3d^{-1} ionizations will provide uncertain results.

Alternatively, if the energies of the 3d subshells were largely determined by covalent metal–ligand interactions, a bond orbital model[18] could be used.

Metal d orbitals transform in the D_{3d} point group as a$_{1g}$ + 2e$_g$. The energies of unperturbed metal orbitals relative to those of appropriate ligand MO's can be estimated on the basis of the considerations presented earlier in this paper. It is safe to assume that the metal 3d subshells are energetically comparable with the σ_N ligand MO's (Figure 5b).

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(11) (a) Hutchinson, B.; Daniels, L.; Henders, E.; Neill, P. *J. Chem. Soc., Chem. Commun.* **1979**, 1003. (b) Jesson, J. P.; Weiher, J. F.; Trofimenko, S. *J. Chem. Phys.* **1968**, *48*,2058.

(12) Cox, P. A. *Struct. Bonding (Berlin)* **1975**, *24*, 59.

(13) Griffith, J. S. "The Theory of Transition-Metal Ions"; Cambridge University Press: New York, 1971.

(14) This relative intensity ratio may be rather inaccurate because it is difficult to evaluate correctly the contribution of the low-IE tail of band a to the various onset bands.

(15) Cox, P. A.; Evans, S.; Orchard, A. F. *Chem. Phys. Lett.* **1972**, *13*, 386.

(16) Evans, S.; Hammett, A.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 227.

(17) Fragalà, I.; Costanzo, L. L.; Ciliberto, E.; Condorelli, G.; D'Arrigo, C. *Inorg. Chim. Acta* **1980**, *40*, 15.

(18) Cox, P. A.; Evans, S.; Orchard, A. F.; Richardson, N. V.; Roberts, P. J. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 26.

On the basis of energy and overlap considerations, metal–ligand bonds are expected to be formed predominantly from $\sigma_N(e_g)$ combinations and d_{xz} and d_{yz} metal orbitals. Interactions of lesser importance may involve $\sigma_N(a_{1g})$ and metal d_{z^2} orbitals. This model leads to the bonding scheme shown in Figure 5b, which correctly predicts the ^3A ground-state configuration even though it requires the partly filled metal subshells to lie among filled ligand orbitals. This situation has been treated theoretically.[19] Therefore, the shoulders x and x′ may represent ionizations from the antibonding $2e_g$ and a_{1g} metal orbitals. Bands due to ionization of the remaining nonbonding metal orbitals $1e_g$ should be hidden under the main band c. This assignment provides reasonable values for the ligand field splitting Δ ($\sim$1.5 eV) and the trigonal splitting δ ($\sim$0.5 eV). The alternative possibility of assigning bands x′ and x to $1e_g$ and a_{1g} "metal" orbitals and placing the antibonding $2e_g$ metal orbital band under the band *a* must be dismissed because such an assignment would lead to a very high trigonal splitting of $\sim$1.1 eV. Ionizations from the antibonding $2e_g$ metal orbital will give rise, under the proposed assignment, to quartet and doublet final states generated by the coupling of the positive hole with the $^3A_2$ ground state. These states should not be very different energetically because covalency effects will lead to small exchange integrals.

The assignment of the ionizations of the σ_{BH} and of σ_N combinations are based on the arguments presented earlier (Table I). The more structured band c with a shoulder at 11.5 eV could be associated with an energy dispersion of the σ_N combinations different from that of previous cases. This difference can be attributed to covalent interactions between the metal and the ligands.

Finally, we examine the spectrum of Cu[HB(pz)$_3$]$_2$ (Figure 4b). In this case the band c in the 10–12-eV region now has two clearly resolved components. The component at higher energy shows a half-width (Table I) smaller than the half-widths of the corresponding bands in the previously discussed spectra (Table I).

The Cu d^9 system has a ^2E ground state. Ionizations from 3d subshells produce many ion states. A purely electrostatic model predicts that their energies are spread over a wide range (Table II). With the sole exception of band x, no such bands are evident within the windows left by the main bands. Furthermore, the narrower half-width (Table I) of the main bands a, b, c and the absence of additional side structures similar to those found for Ni[HB(pz)$_3$]$_2$ indicate that bands associated with $3d^{-1}$ ionizations lie at higher IE range, probably above 12 eV. It is likely that band x, centered at 10.5 eV, represents the ionization of a ligand-based MO destabilized, relative to the cases previously discussed, by specific metal–ligand interactions. The reduced half-width of band c in the spectrum of Cu[HB(pz)$_3$]$_2$ (Table I) compared to that in the spectrum of the nickel complex suggests that band x has shifted out of band c. This behavior can be explained with an MO model analogous to that proposed for Ni[HB(pz)$_3$]$_2$ (Figure 5b). Simple overlap considerations among bonding orbitals suggest that the interactions between the $\sigma_N(e_g)$ combination and more metal centered $d_{xy,xz}(e_g)$ orbitals are again the best source of bonding and cause the destabilization of the $\sigma_N(2e_g)$ combination. As a consequence we feel confident in assigning the band x, centered at 10.48 eV, to this σ_N combination.

Conclusion

This study provides the first example of an investigation by gas-phase PE spectroscopy of a series of coordination complexes of d^6 to d^{10} transition metals all having the same "octahedral" ligand array. Identical geometries and an identical stoichiometry of these complexes makes it possible to propose a unitary bonding model unaffected by a variation of geometries and/or changes of the formal oxidation state of the metal. In the Fe and Co complexes the metal 3d ionizations are dominated by electrostatic, Russell–Saunders couplings.

The energies of the final states produced upon removing one metal 3d electron from the ground states can be predicted by an electrostatic model employing the usual Racah and ligand field parameters. Accordingly, the binding energies of ligand-based MO's of π character are dominated, in Koopmans' approximation, by intraligand coulombic repulsion whereas the binding energies of MO's of σ_N symmetry combinations are determined by intra- and interligand coulombic repulsion and are practically independent of the central metal atoms.

Within the series of M[HB(pz)$_3$]$_2$ complexes the spin-averaged metal 3d IE's from Fe to Cu complexes increase smoothly. In this manner the energies of the appropriate symmetry combinations of σ_N lone pairs are probably better matched with metal valence orbitals, thus resulting in more covalent metal–ligand bonds. In both cases the spectral patterns can be better explained with a localized bonding model. There is evidence of a strong interaction between metal and ligand orbitals of e_g symmetry and a somewhat weaker interaction between orbitals of a_g symmetry. This bonding situation is reminiscent of that in metallocenes and agrees well with the triangular sandwich model that we have proposed for describing the valence electronic structure.

The PE data of Ni[HB(pz)$_3$]$_2$ provide a total ligand field splitting of $\Delta = 1.5$ eV with a trigonal component of 0.5 eV. The more metal-centered 3d orbitals in the Cu complex cause the corresponding PE bands to shift under the intense structure above 12 eV. Nevertheless, there is again evidence of a strong interaction involving e_g orbitals, which, due to the higher binding energies of metal $d_{xz,yz}$ orbitals, destabilize the ligand σ_N (e_g) orbitals.

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