Articles

X-ray Absorption Spectroscopic Study of the Structure and Bonding in M[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, Where M is Fe, Co, Ni, Cu, and Zn

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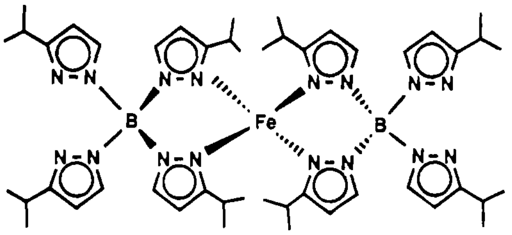
An X-ray absorption spectroscopic study of M[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, where M is Fe, Co, Ni, Cu, and Zn, has been undertaken to compare the local structure about the iron(II) ion with that of the other divalent transition metal ions. Earlier Mössbauer spectral studies have indicated the presence of an unusual displacement of the iron ion within its coordination sphere, especially at temperatures above 160 K; a displacement which might or might not occur in the cobalt complex whose X-ray structure is normal or in the remaining complexes. An extended X-ray absorption fine structure analysis of the absorption spectra reveals very similar coordination environments and metal to nitrogen bond lengths for the various complexes. The preedge X-ray absorption does reveal differences in the complexes, differences which result from electronic transitions of the metal 1s electron into the differing crystal field split states of the divalent metal ions.

Introduction

Polypyrazolylborate ligands have been used extensively to study the steric effects of ligands upon the structural and electronic properties of transition metal complexes.[6,7] They have also been useful in the study of electronic spin-state transitions induced by a temperature[8] or pressure[9,10] perturbation of the crystal field in pseudooctahedral complexes. These ligands are also of special interest because of their ability to form complexes of variable symmetry and coordination number, as has been shown for several cobalt(II) complexes.[11,12] These variations result from changes in the steric bulk of the ligands as a function of the various substituants which may be placed on the pyrazolyl ring.

The structural characterization of coordination complexes is usually performed by means of single crystal X-ray diffraction,[7] but when crystallization difficulties arise, it is necessary to use alternate experimental methods to obtain structural information. These methods often give precise structural information but usually less detail than a single-crystal study. X-ray absorption spectroscopy can provide information on the local structural order about a specific atom even in a compound for which well-defined single crystals are not available. This paper presents the structural results obtained for such a compound, Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, **I**, see the schematic structure, Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, **II**, whose single crystal structure is known,[11] and the related divalent metal complexes, Ni[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, **III**, Cu[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, **IV**, and Zn[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, **V**.



I

A Mössbauer spectroscopic study[13] of **I** has shown that there is an unusually sharp decrease in the spectral absorption area as a function of temperature, especially above 160 K. This decrease, which shows a strong variance from the Debye model of a solid, has been interpreted as resulting from the displacement of the iron atom in its coordination sphere, beginning at *ca.* 160 K and increasing with increasing temperature. Long et al.[13] have shown that the room temperature displacement must

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Table 1. The K-Edge Energies, E_0, and Relative Energies, in eV, and Intensities of the XANES Transitions

metal		E_0	*P*	*A*	*B*	*C*	*E*
Fe	energy, eV	7112	0.20, 2.00	8.9	15.0	22.7	63.8
	intensity		0.13, 0.10	0.54	1.23	1.34	1.09
Co	energy, eV	7709	0.10	9.2	15.6	23.6	65.6
	intensity		0.15	0.78	1.20	1.40	1.09
Ni	energy, eV	8333	0.12	10.5	16.7	23.3	65.9
	intensity		0.10	0.65	1.20	1.46	1.11
Cu	energy, eV	8979	−2.32	8.0	14.8	21.6	66.0
	intensity		0.04	0.51	1.22	1.47	1.12
Zn	energy, eV	9659		5.0	12.2	19.6	58.9
	intensity			1.19	1.57	1.49	1.15

be *ca.* 0.36 Å in order to explain the deviation from normal Debye law behavior. This room temperature displacement is approximately twice that predicted by the Debye model. A structural analogy between **I** and the related cobalt complex, **II**, has been proposed.[13] A single-crystal study[11] of **II** at room temperature has found that the cobalt(II) ion is in a pseudotetrahedral, D_{2d}, structural environment with the four coordinated nitrogen atoms at an average bond distance of 1.98 Å from the cobalt. Long et al.[13] have concluded that a reduced steric constraint on the iron in this complex may result in "nonideal" bonding between the iron and its coordinated ligands. If this is the case, a large displacement of the atom in its coordination sphere, unusual bond lengths, and an anomalous Debye−Waller factor might be expected. In order to confirm this we have carried out an X-ray absorption spectroscopic study followed by an extended X-ray absorption fine structure (EXAFS) analysis to determine the structural parameters around the divalent metal ion in **I**−**V** at both 77 and 300 K.

Experimental Methods

The complexes were prepared as described earlier[11] and are the same samples as used in our earlier studies.[11,13]

The X-ray absorption spectra have been measured with the synchrotron radiation provided by the DCI storage ring of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) in Orsay, France. The iron and cobalt complexes were measured at the D42 experimental station, which uses a channel cut silicon (331) crystal monochromator. The nickel, copper, and zinc complexes were measured at the D13 experimental station which uses a double crystal silicon (311) monochromator. All X-ray absorption measurements were carried out in the transmission mode using ion chambers in front and behind the sample. An oblong pellet of the material with a surface of 1 cm^2 and a mass of 20 to 30mg was pressed to yield the absorbers. The EXAFS spectra were recorded with a 2 eV step over an energy range starting at 1000eV above the metal K-edge, E_0, whose values are given in Table 1. The X-ray absorption near-edge spectra (XANES) were recorded with a 0.25 eV step over an energy range starting at 125 eV above the metal K-edge.

During the processing of the XANES data, a linear background was subtracted from the experimental spectrum by extrapolating a least-squares fit of the preedge experimental data points. The maximum of the first derivative of a metallic foil spectrum, corresponding to the first inflection point in the absorption curve, was used as the metal K-edge reference energy. For energy calibration, the spectrum of a thin metallic foil was recorded both immediately before and after each XANES measurement. K-edge spectra were normalized by taking as unit absorbance the intersection point between the atomic background and the first EXAFS oscillation.

X-ray Absorption Near-Edge Spectral Results

The XANES results for **I** at 77 and 300 K are shown in Figure 1. It is apparent that the change in temperature has little effect on the absorption in **I**, a conclusion which holds for all the complexes. Consequently, in the following we will concentrate on the XANES measurements at 77 K. Figure 2 shows the XANES spectra for complexes **I**−**V** at 77 K plotted relative to the metallic K-edge energy scale. The K-edge energies, E_0, the relative absorption energies, and the normalized intensities of the main spectral features are given in Table 1. The XANES spectra of these complexes exhibit three edge transitions, labeled A, B, and C, respectively, which appear at virtually the same relative energy for the iron, cobalt, nickel, and copper complexes, **I**−**IV**, with $E_A = 9.2 \pm 1.2$, $E_B = 15.7 \pm 1.0$, and $E_C = 22.8 \pm 0.8$ eV. The spectrum of the zinc complex, **V**, has the same three transitions, but they are shifted to lower energy. It should be noted that in the edge region, the spectra of the iron and cobalt complexes are the most similar of the series. For the other complexes, with the exception of the zinc complex, the major differences are observed in the relative intensity of the A, B, and C edge transitions. Furthermore, a clear difference is observed in the region of the preedge structure, labeled P in Figure 2.

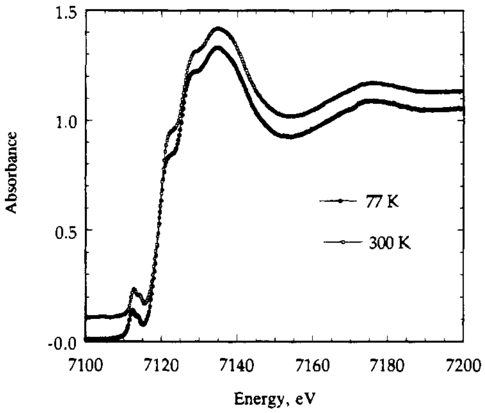

Figure 1. Near-edge X-ray absorption spectra of **I** measured at 77 (top) and 300 K at the iron K-edge.

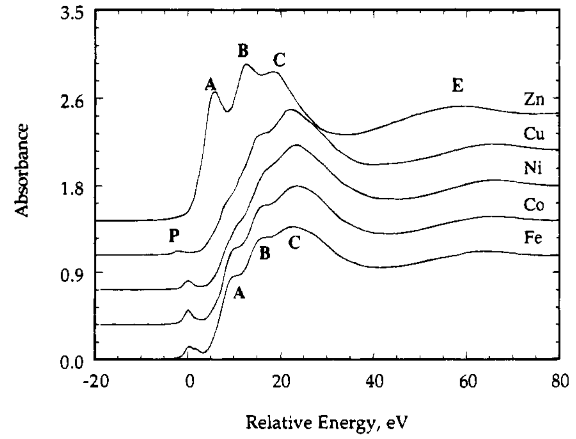

Figure 2. Near-edge X-ray absorption spectra of **I**−**V** measured at 77K at the metal K-edges.

Extended X-ray Absorption Fine Structural Results

We have performed an EXAFS analysis[14] of the extended energy range spectra in order to extract the structural parameters of the near-neighbor atoms about the metal in complexes **I**−**V**. The analysis was optimized by a comparison with the known X-ray structural parameters of the cobalt complex.[11] This permits both an evaluation of the quality of the electronic parameters, based on the tabulations of Teo and Lee,[15,16] and a further evaluation of the influence of temperature upon the Debye−Waller factor.

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Table 2. Structural Parameters Obtained from the EXAFS Analysis of the Metal K-Edge Spectra

	T, K	Fe	Co	Ni	Cu	Zn
metal–nitrogen bond length, Å	77	2.00(2)	1.97(2)	1.95(2)	1.93(2)	1.97(2)
	300	2.01(2)	1.98(2)	1.95(2)	1.94(2)	1.98(2)
Debye–Waller factor, Å	77	0.055	0.045	0.048	0.071	0.047
	300	0.062	0.055	0.056	0.083	0.055
Γ factor,[a] Å^{-2}	77	0.85	0.74	0.66	0.67	0.67
	300	0.85	0.74	0.67	0.65	0.70
quality factor, %	77	0.97	0.28	0.48	0.91	0.42
	300	0.92	0.50	0.35	0.42	0.50
effective metal ionic radii, Å[b]	300	0.77	0.72	0.69	0.71	0.74
change in ionic radii, Å, expected	300	0.00	−0.05	−0.08	−0.06	−0.03
change in ionic radii, Å, observed	300	0.00	−0.03	−0.06	−0.07	−0.03

[a] Related to the electron mean free path by the relationship $\lambda(k) = k/\Gamma$. [b] The Shannon and Prewitt effective metal ionic radii for a tetrahedral coordination environment obtained from refs 17 and 18.

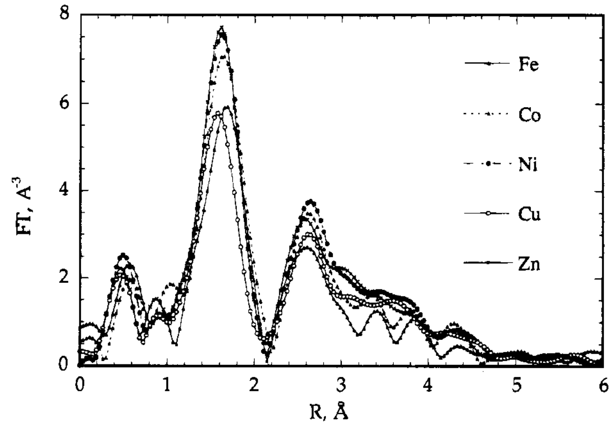

Figure 3. Fourier transforms of the EXAFS oscillations in complexes **I**–**V** observed at 77 K at the metal K-edges.

All the Fourier transforms of the EXAFS oscillations, shown in Figure 3, are composed of a well resolved peak in the range of 1.3 to 2.2 Å which corresponds to the first coordination shell of four nitrogen atoms. The peaks located above 2.3 Å are due to coordination shells at longer distances and to multiple scattering. Unfortunately, a multiple scattering analysis did not yield a significantly better transform nor did it provide further details of the coordination environment. As a result no multiple scattering analysis is reported herein. The Fourier transform is carried out while simultaneoulsy optimizing the electronic and structural parameters. The same optimization procedure has been applied to all the spectra at 77 and 300 K and the resulting parameters are given in Table 2.

There is very good agreement between the results given in Table 2 and the values obtained from a single-crystal X-ray diffraction study[11] of the cobalt complex. Both experimental methods give the same number of coordinated nitrogen atoms and the 1.98 Å cobalt to nitrogen bond distance agrees well with the 1.975 Å average value obtained from the single crystal study.[11] Decreasing the temperature from 300 to 77 K has no significant influence on this bond length.

As expected on the basis of the Shannon and Prewitt[17,18] effective ionic radii, see Table 2, the observed 2.01 Å room temperature iron to nitrogen bond length is somewhat longer than the 1.98 Å cobalt to nitrogen bond length. It is also longer than the 1.97 Å bond length found[19] in octahedral low-spin Fe[HB(pyrazolyl)$_3$]$_2$. However, as expected, it is shorter than the 2.17 Å bond length found[19] in octahedral high-spin Fe[HB(3,5-(CH$_3$)$_2$-pyrazolyl)$_3$]$_2$ and the average 2.25 Å bond length found[20] in Fe[HB(3-phenylpyrazolyl)$_3$]$_2$. As revealed at the bottom of Table 2, the variation in the room temperature metal-nitrogen bond lengths is essentially that expected on the basis of the variation in the Shannon and Prewitt[17,18] effective metallic ionic radii.

It is interesting both that the increase in temperature from 77 to 300 K has no significant effect on the bond length in the iron complex and that the Debye–Waller factor associated with this bond length shows upon warming a 13% increase, an increase which is smaller than the 22% increase found for the cobalt complex but similar to the 17% increase found for the nickel, copper, and zinc complexes. In view of these changes it is difficult to understand the anomalous behavior observed in the Mössbauer spectra of the iron complex.

We conclude that the influence of temperature on the iron, nickel, copper, and zinc complexes is similar and presumably normal. In contrast, the temperature variation of the Debye–Waller factor for the cobalt complex is somewhat larger than might be expected. This observation provides little support for our earlier work[13] which proposed either a variation in the local order around the iron atom or an enhancement of the amplitude of vibration of the iron atom in the coordination sphere of **I**. In either case, this should be observed as either a variation of the iron–nitrogen bond length or a larger than expected variation in the Debye–Waller factor, only the second of which is observed and only for the cobalt complex. It would thus appear that whatever causes the unusual displacement of the iron ion in **I**, as evidenced by the Mössbauer spectral work,[13] may also be operative in the cobalt complex, **II**. Thus a cobalt-57 emission Mössbauer effect study of **II** might reveal a similar unusual decrease in its spectral absorption area with increasing temperature. It is indeed surprising, in view of the Mössbauer spectral work, to find that both complexes have normal bond lengths. At this point the fundamental cause of the unusual decrease in the Mössbauer spectral absorption area of **I** above 160 K is obscure. However, a second Mössbauer spectral study of a completely new preparation of **I** has completely confirmed the earlier work.[13]

While studying the structural questions through the above EXAFS analysis, an interesting feature was noted in the XANES spectra. As indicated above, the XANES spectra of the complexes are very similar except in the preedge region, which is shown in detail in Figure 4. A clear doublet is visible in the case of the iron complex, whereas only a single line of decreasing intensity is observed for the cobalt, nickel, and copper complexes, and no absorption is found for the zinc complex. The splitting between the two lines in the iron complex is *ca.*

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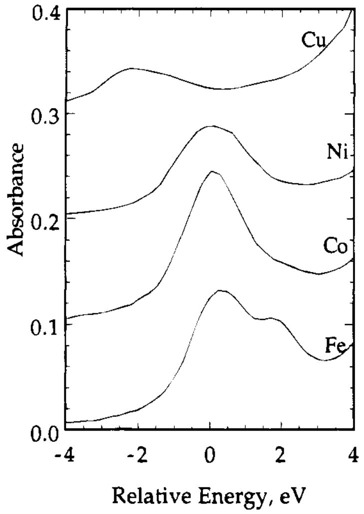

Figure 4. Expansion of the near-edge X-ray absorption spectra of **I**–**V** measured at 77 K.

1.5 eV or 12 000 cm^{-1}. These low intensity absorption lines, found below the optically allowed s- to p-orbital electronic transitions, are well-known in X-ray absorption spectroscopy[21–23] and correspond to the excitation of the metal 1s electron into an unoccupied molecular orbital composed predominantly of metal 3d atomic orbitals, as is discussed below.

Discussion

The transitions occuring in the preedge region of the K-edge absorption are firmly established[24] as transitions of the 1s electron to bound HOMO states composed of 3d and 4p metal atomic orbitals and 2p ligand orbitals. In the near-edge region, the transitions are of the 1s electron to an empty p orbital.

The interpretation of the XANES structure is based on the Fermi–Golden rule

$$\sigma(E) \approx |\langle\Psi_f|\overline{\epsilon\cdot r}|\Psi_i\rangle|^2 N(E)\,\delta(h\nu - (E_f - E_i)) \qquad (1)$$

in which the photoabsorption cross section, $\sigma(E)$, is proportional to the vacant state density, N(E), and to the square of the transition moment, $|\langle\Psi_f|\overline{\epsilon\cdot r}|\Psi_i\rangle|$, where $\overline{\epsilon\cdot r}$ is the electric dipole transition operator, Ψ_f and Ψ_i are the final and initial states of energy E_f and E_i, and δ is the Dirac function. For this work E_i is the binding energy of the 1s electron, the K-edge energy, E_0, given in Table 1. This expression indicates that X-ray absorption spectroscopy is sensitive to the valence shell occupancy and the site symmetry. Indeed a transition of a 1s electron into a molecular orbital is allowed if the molecular orbital is unoccupied or partially occupied and if the transition moment, $|\langle\Psi_f|\overline{\epsilon\cdot r}|\Psi_i\rangle|$, is nonzero. This condition[25] is equivalent to the requirement that the direct product, $\Gamma_f \times \Gamma_{dip} \times \Gamma_i$, of the applicable irreducible representations, contains the totally symmetric, A_1, irreducible representation.

Table 3. Preedge Absorption Band Assignments

metal	3d^n	electronic transition[a]	*N*(*E*)	obsd intens
Fe	3d^6	$1s^2 + e^3t_2{}^3 \rightarrow 1s^1 + e^4t_2{}^3$ $\rightarrow 1s^1 + e^3t_2{}^4$	3	0.149
Co	3d^7	$1s^2 + e^4t_2{}^3 \rightarrow 1s^1 + e^4t_2{}^4$	3	0.144
Ni	3d^8	$1s^2 + e^4t_2{}^4 \rightarrow 1s^1 + e^4t_2{}^5$	2	0.103
Cu	3d^9	$1s^2 + e^4t_2{}^5 \rightarrow 1s^1 + e^4t_2{}^6$	1	0.058
Zn	3d^{10}	$1s^2 + e^4t_2{}^6 \rightarrow$ [forbidden]	0	0.000

[a] Obtained by assuming a strong mixing of the ligand p-orbitals with the metal 3d orbitals of t_2 symmetry

The use of the direct product permits the determination of the allowed transitions and their polarizations. For example, in the preedge region, for a metal in a centrosymmetric complex, the electric dipole transition to a molecular orbital composed of only 3d metal atomic orbitals is totally forbidden. In contrast, for a metal in a noncentrosymmetric complex, the transition to a molecular orbital composed of 3d metal atomic orbitals of t_2 symmetry in a tetrahedral complex, or of e and b_2 symmetry in a D_{2d} complex, are allowed. This rule reflects only the local symmetry at the absorber and whether or not there is a mixture of the 3d and ligand p atomic orbitals in the frontier molecular orbitals. When the preedge absorption is observed, and no quadrupolar contribution is expected, the observed transitions are allowed through the mixing of ligand p-orbital character into the predominantly 3d metal frontier orbitals.

If we compare quantitatively the preedge absorptions shown in Figure 4, we observe changes in the integrated intensities from the iron(II) to the zinc(II) spectra. The integrated intensity of the preedge peak is directly proportional to the number of empty states in the predominantly metal 3d character frontier orbitals for which the transitions are allowed. Hence, in Table 3, we have included the tetrahedral 3d orbital occupancy of each metal and the integrated intensity measured in the spectra. There is excellent agreement between the orbital occupancies of the final state or the vacant state density, *N*(*E*), and the observed integrated intensities. As expected the integrated intensity decreases from iron(II) to zinc(II) with a ratio close to 3:2:1:0, the zero corresponding to the totally occupied 3d^{10} electronic configuration of the Zn(II) complex. The 1.5 eV or 12 000 cm^{-1} splitting observed in the preedge bands of the iron complex corresponds to a crystal field parameter, *Dq* (tetrahedral), of 1200 cm^{-1}, a rather large but not unreasonable value.

In agreement with the distorted tetrahedral D_{2d} structure of the absorbing metals in complexes **I**–**V**, the general shape of the K-edge spectra, shown in Figure 2, is characteristic of a noncentrosymmetric environment around the metal. The three A, B, and C edge bands, shown in Figure 2, are surprisingly similar to the features observed in the spectra of coordination complexes with square-planar symmetry, such as metallic porphyrins or phthalocyanines.[26,27] In this symmetry, polarized experiments on single-crystal copper complexes[28] have clearly demonstrated that the A band is a 1s → $4p_z$ + "shake-down"

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transition with a metal to ligand charge transfer, the B band is a pure 1s → 4p$_z$ transition, whereas the C band is a 1s → 4p$_{x,y}$ transition. Because the 4p$_z$(b$_2$) molecular orbital is more stable than the 4p$_{x,y}$(e) molecular orbitals in D_{2d} symmetry, we assume that the same assignments can be made for the present spectra.

Finally, the apparent relative shift, shown in Figure 2, of the leading edge of the zinc complex to lower energy with respect to the other metals of the series occurs because the zero energy value used to place the spectra on the same relative energy scale does not correspond to the same energy level in this 3d^{10} compound as for to the other 3d^n complexes. For each transition metal, we used as zero energy the maximum of the first derivative of the metallic foil spectrum, the maximum of which corresponds to the Fermi level of the metal. But in iron, cobalt, nickel, and copper metallic foils, the Fermi level corresponds to empty 3d levels, whereas in zinc it corresponds to empty 4p levels which are at a higher energy. This accounts for the apparent relative shift observed for the zinc spectrum.

Note Added in Proof. We have just learned that the crystal structure of **I** has been solved[29] and shows a highly distorted pseudotetrahedral coordination environment for the iron(II) ion.

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