EXAFS of Poly[μ-hexakis(2-methylimidazolato-N,N′)triiron(II)]: Implications for Metalloprotein Studies

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Abstract: EXAFS data at the Fe K-edge of the coordination compound poly[μ-hexakis(2-methylimidazolato-N,N′)triiron(II)] are presented. Single-scattering analysis of the EXAFS gives good agreement with the crystallographic data for the first two shells of atoms around the iron, but beyond that, multiple-scattering simulations are needed. The EXAFS data do not unambiguously indicate the presence of the methyl substituent, and upon refinement of the multiple-scattering simulation, artificially large spreads between atoms occurring at similar distances are observed. These findings imply that, in the analysis of metalloprotein EXAFS data, it is not possible to probe the difference between *pros* and *tele* coordination of imidazoles, while the potential to obtain information on possible tilting of the imidazole ring relative to the metal–N1 bond is weak.

The technique of extended X-ray absorption fine structure (EXAFS)[2] is often used to probe metals in metalloproteins. The wiggles after the edge step in the X-ray absorption or fluorescence spectrum of the metal of interest can be explained by backscattering of the photoelectron wave, leaving the excited metal atom, by the metal ligands. This leads to interference effects on the central absorber metal atom and hence corresponding oscillations in its absorption coefficient. The resulting fine structure, or EXAFS, can be analyzed to determine ligand distances with high accuracy (± 0.02 Å) and coordination numbers to within 20%. It can be used to refine structural parameters already available from crystallographic work, as in the case of hemoglobin,[3] but it can also be successfully applied to metalloproteins for which only limited structural information exists.[2] There is increasing interest in coordination compounds mimicking metalloprotein active sites.[4] For the interpretation of EXAFS of metalloproteins by the plane wave approximation, EXAFS data of crystallographically well-characterized model compounds are needed.[2b] Even when rapid curved-wave analysis, using phase shifts derived from ab initio calculations, is relied upon, the results are usually checked against the data of such compounds.[2c]

The analysis of the EXAFS of metalloproteins where the imidazole moiety of the amino acid histidine is coordinated to the metal poses specific problems,[5] including unexpected amplitude enhancements and short distances for distant shells. Recently,

various authors have started to appreciate that these phenomena are due to the multiple scattering effects, caused by the geometry of the imidazole moiety.[6] As can be seen in Figure 1, several multiple scattering pathways metal–atom A–atom B–metal exist in which the angle metal–A–B approaches 180°, the most favorable angle for forward scattering of the electron wave by atom A on to atom B.

Some years ago, we started EXAFS studies of the iron site in soybean lipoxygenase-1 and model compounds.[7] Lipoxygenases catalyze the dioxygenation of polyunsaturated fatty acids containing a (1Z,4Z)-pentadiene system, e.g. the first steps in the biosynthesis of leukotrienes and lipoxins.[8] The soybean enzyme, which is the best characterized, has a non-heme iron site with unique spectroscopic characteristics.[9] Preliminary EXAFS results pointed to the presence of imidazole ligands,[7a] and appropriate models were called for. The synthesis of a variety of iron imidazole compounds has been reported,[10] and the structure of poly[μ-hexakis(2-methylimidazolato-N,N′)triiron(II)][10a] (I) has been analyzed by X-ray crystallography[7b] (Figure 2). We report here the analysis of the EXAFS of I, establishing the presence of multiple scattering effects, but also noting possible artifacts of the multiple scattering approach with implications for the studies of metalloproteins.

Experimental Section

I was synthesized from ferrocene and 2-methylimidazole as described earlier.[10a] For EXAFS measurements, it was finely powdered and packed into a sample cell under nitrogen atmosphere. The EXAFS was recorded

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Table I. Crystallographic (R in Å, Fe–N1–x Bond Angles in deg) and EXAFS (R in Å, Debye–Waller-type Factors, as $2\sigma^2$, in Å², in Parentheses) Structural Parameters of **I**[a]

atom[7b]	cryst struct (Figure 1)		EXAFS single scatt (Figure 3)	EXAFS mult scatt (Figure 5)	EXAFS mult scatt (Figure 6)	EXAFS mult scatt (Figure 7)
N1	2.03		2.01 (0.008)	2.02 (0.008)	2.01 (0.008)	2.02 (0.008)
C1	3.05	−128	8 at 3.05 ⎫	3.05 (0.015)	2.99 (0.015)	3.05 (0.015)
C2	3.04	127	(0.020) ⎬	3.04 (0.015)	3.04 (0.012)	3.04 (0.015)
C3	3.45	−98	3.35 (0.008)			3.33 (0.053)
N1[iv]	4.21	−161	4.38 (0.011)	4.21 (0.040)	4.27 (0.037)	4.23 (0.019)
C1[iv]	4.17	161	3.92 (0.011)	4.17 (0.040)	4.20 (0.039)	4.54 (0.094)
ΔE_0, eV			15.73	16.00	17.46	16.18
range, eV			25–445	0–505	0–505	0–505
fit index (k^3-wt)			0.59927	1.72550	1.21730	1.08355

[a] All occupancies are 4 unless indicated otherwise. The crystallographic angles were used in the multiple-scattering EXAFS calculations.
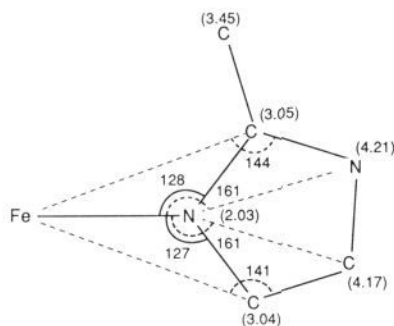
Figure 1. Geometry of the imidazole moiety in **I**, with distances of the atoms to the iron (Å) in parentheses. Hydrogen atoms are omitted for clarity.
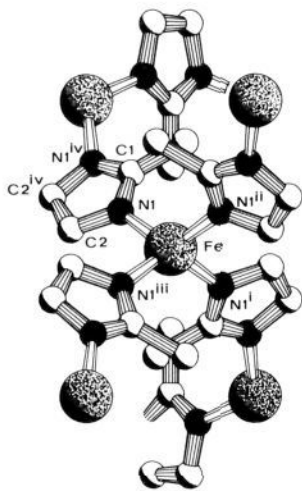
Figure 2. PLUTO drawing of the crystal structure of **I**[7b] showing the adopted numbering scheme.

in transmission mode on station 7.1 of the SERC Synchrotron Radiation Source at the Daresbury Laboratory[11] at ambient temperature. Three scans were taken, during which no signs of sample deterioration were noticed, and averaged. Data of other imidazole compounds were provided by various other users of the SRS and contributed to a data base.[12]

Data analysis and simulations employed the Daresbury Laboratory analysis package, including the background subtraction program EX-BACKI, the ab initio phase shift calculation program MUFPOT and the fast curved-wave EXAFS simulation and fitting program EXCURVE,[13] allowing

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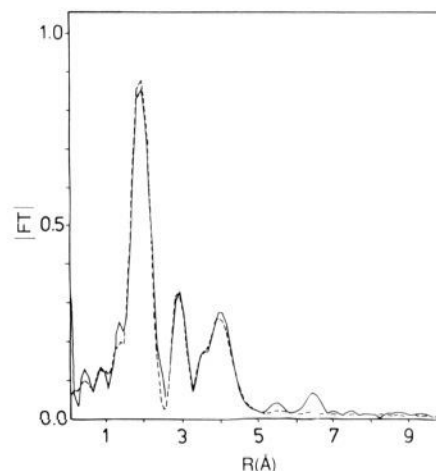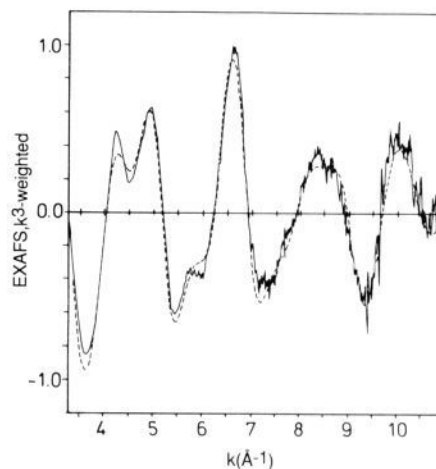

Figure 3. Fe K-edge k^3-weighted EXAFS (upper panel) and its phase-corrected Fourier transform (lower panel) of **I**: solid line, experiment; dashed line, refined single-scattering simulation with the parameters in Table I, second column.

calculations of multiple scattering up to third order. Fits were obtained by simulating the EXAFS with models based on the crystal structure and iteratively refining the shell radii and Debye–Waller-type factors to a minimum in the fit index.

Results

The EXAFS of **I** (Figure 3, 5–7, upper panels) shows a beating pattern indicating the presence of more than one shell, as can be seen from the Fourier transforms (same figures, lower panels). The "camel back" feature at 4–5 Å⁻¹ was considered a marker

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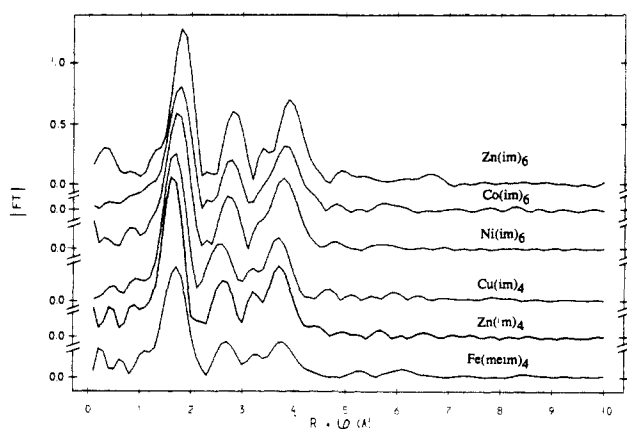
Figure 4. Fourier transform of the EXAFS of hexakis(imidazole)zinc(II) dichloride tetrahydrate,[14a] hexakis(imidazole)cobalt(II) diacetate,[14b] hexakis(imidazole)nickel(II) diperchlorate,[14c] tetrakis(imidazole)copper(II) dinitrate (II),[6b,c] tetrakis(imidazole)zinc(II) diperchlorate (III),[5b,c,6a] and poly[μ-hexakis(2-methylimidazolato-N,N')triiron(II)] (I).

for imidazole coordination in a study of Zn in insulin and model compounds.[5c] The interpretation of the EXAFS of I started by simulating the data with single-scattering theory, using a model based on the crystallographic structure parameters (Table I, first column), conceiving the carbon shells at 3.04 and 3.05 Å as a single shell. Discarding the low-k data range up to 25 eV, the so-called near-edge region (XANES) where single-scattering theory is known to be inadequate, and refining the distances and Debye–Waller-type factors, the fit presented in Figure 3, with a fit index of 0.599 27, was obtained (parameters in Table I, second column).

The agreement between EXAFS and crystal structure parameters is good for the first two shells, but beyond that it deteriorates. Omission of the methyl group in the simulations (not shown) led to a poorer fit at 3.5 Å in the Fourier transform and in the region 5.5–6.0 Å^{-1} in the EXAFS. When included, its distance to Fe is too short by approximately 0.1 Å (cf. Table I, first and second columns). Furthermore, the features it accounts for are also found in the Fourier transforms of the EXAFS of coordination compounds with unsubstituted imidazoles[6] (Figure 4).

Therefore, some doubt exists as to whether these features in the Fourier transform of the EXAFS of I are really due to the methyl group. Some improvement to the single-scattering fit could be made by allowing the occupancies to float together with the other parameters (not shown), but the result did not affect the good agreement for the first two shells nor did it improve the situation with regard to the methyl group. As far as the imidazole ring atoms N1^{iv} and C1^{iv} at approximately 4.2 Å from Fe are concerned, some authors[5b,c] observed a significant apparent shortening of their distances to the metal. We find that contributions at longer as well as shorter distances than 4.2 Å are needed for a good single-scattering fit of this shell (cf. Table I, first and second column).

For multiple-scattering simulations, the low-k data range was included in the fits. The approach started by taking crystallographic structure parameters (atom types, distances, bond angles) for imidazole ring atoms only and adjusting the ΔE_0 value, the main-shell distance, and the Debye–Waller-type factors for all shells until good agreement with the Fourier transform was obtained, giving satisfactory agreement for the EXAFS with a fit index of 1.725 50 (Figure 5a; parameters in Table I, third column). This result indicates that multiple scattering is present in the imidazole group, contributing to the EXAFS even at high k, and
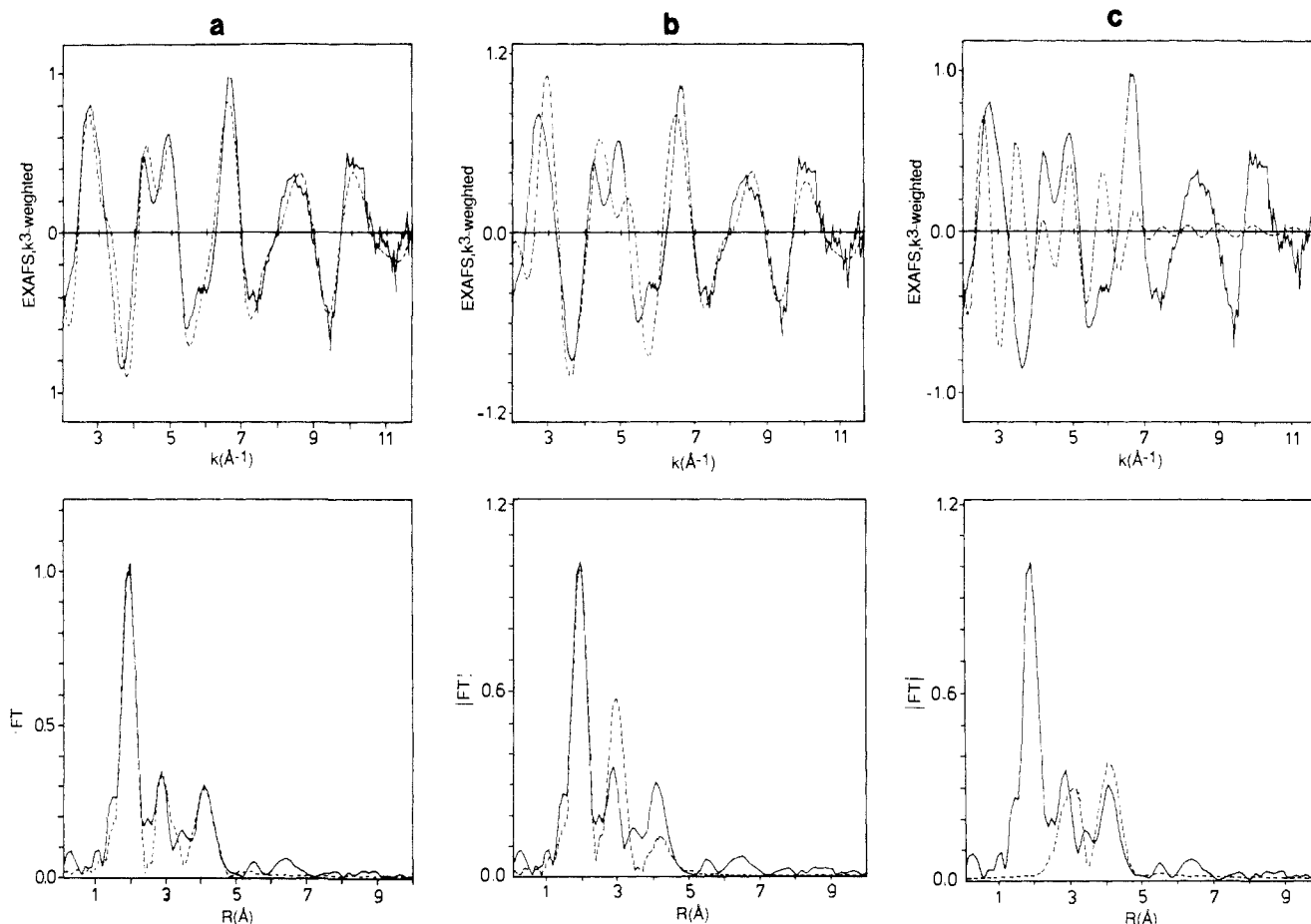
Figure 5. (a) Full-range Fe K-edge k^3-weighted EXAFS (upper panel) and its phase-corrected Fourier transform (lower panel) of I: solid line, experiment; dashed line, multiple-scattering simulation with parameters close to the crystal structure values (Table I, second column). (b) As in (a), but with the dashed line representing the single-scattering contribution only. (c) As in (a) but with the dashed line representing the multiple-scattering contribution only.
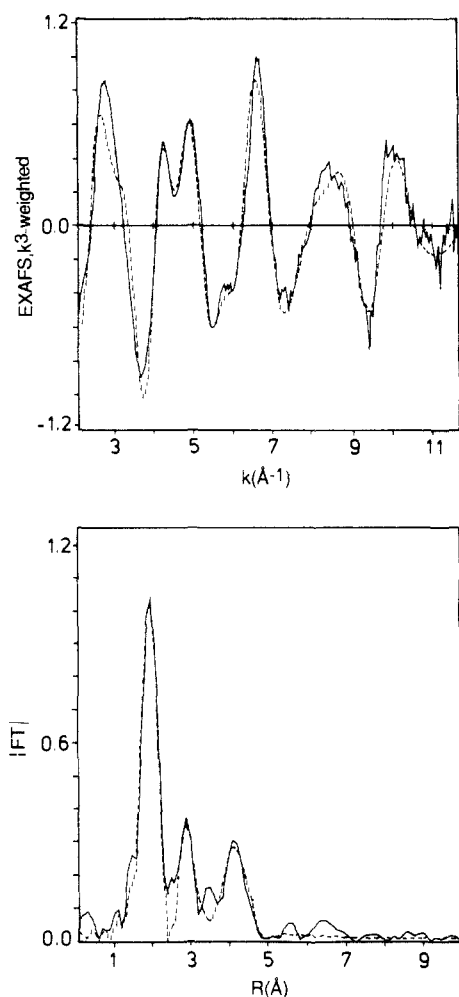
Poly[μ-hexakis(2-methylimidazolato-N,N')triiron(II)]

J. Am. Chem. Soc., Vol. 110, No. 23, 1988 7749

Figure 6. As in Figure 5a, but with the dashed line representing a simulation with refined parameters (Table I, third column).
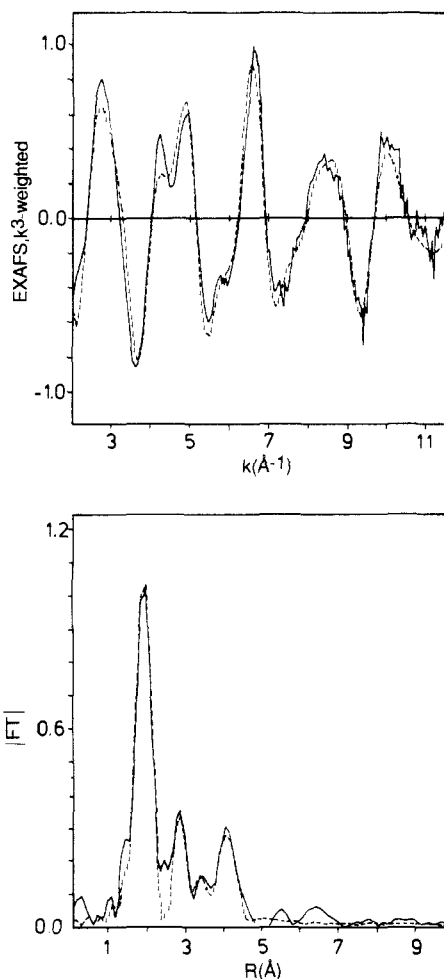

Figure 7. As in Figure 5a, but with the dashed line representing a simulation with refined parameters, including parameters for the methyl group (Table I, fourth column).

that the curved-wave theory adequately accounts for it. We agree with Strange et al.[6b,c] who also allowed values for the Debye–Waller-type factors that increased with the distance to the central absorber atom. It appears that in spite of the rigidity of the imidazole moiety it is possible that the atoms far away from the absorber have less correlated motion with the absorber than the atoms closer to it, as reflected in the higher value for the Debye–Waller-type factor. The relatively high Debye–Waller-type factors as compared to work on tetrakis(imidazole)copper(II) nitrate (II)[6c] are probably due to the fact that our data were taken at ambient temperature, as in the crystallographic study.[7b] We have also inspected the single- and multiple-scattering contributions to the model compound EXAFS (Figure 5, parts b and c, respectively) and found that (a) the contribution for the atoms at approximately 4.2 Å consists almost completely of multiple scattering and (b) for the atoms at approximately 3.05 Å the single-scattering contribution is about twice as large as the multiple scattering and out of phase with it.

Iterative refinement of the values of ΔE_0, distances, and Debye–Waller-type factors from the simulation in Figure 5a led to a lower fit index, 1.217 30 (Figure 6; Table I, fourth column). The improved agreement is partly due to an increased splitting occurring in two pairs of shells that were relatively close in the simulation based on crystallographic data, viz. the two shells of carbon atoms C1 and C2 at 3.04 and 3.05 Å, which are now at 2.99 and 3.04 Å, respectively, and the carbon atom C1[iv] at 4.17 and nitrogen atom N1[iv] at 4.21 Å, which refine to 4.20 and 4.27 Å, respectively. Similar apparent splittings have been observed in EXAFS studies where the single-scattering approach was used to analyze data of tetrakis(imidazole)zinc(II) diperchlorate[5b] (III), zinc in insulin,[5c] tetrakis(imidazole)copper(II) nitrate[5b] (II), and copper in superoxide dismutase[5b,15] and in multiple-scattering

studies of the latter two.[6c,16] Especially in the studies on copper, the splitting was considered significant, as a spread from 2.95 to 3.05 Å exists in the Cu–C1 and Cu–C2 bonds in the crystal structure of III,[17] and the finding of different Cu–C1 and Cu–C2 distances in superoxide dismutase was thought to reflect tilting of the imidazole ring with respect to the Cu–N1 bond.[5b,15,16] However, in the crystal structures of I and III, the metal–C1 and metal–C2 distances are within 0.01 Å, viz. 3.04–3.05 Å for I[9b] (cf. Table I) and 3.00 Å for III,[18] and even in the analysis of the EXAFS of those compounds a tendency for a spread in those distances is observed.

We have also investigated the influence of inclusion of the methyl carbon in the multiple-scattering simulations, either included in the multiple-scattering unit or as an independent additional single-scattering contribution. In order to avoid the splitting discussed above, the parameters for C1 and C2 were not refined. As expected from of the geometry of the Fe–methyl-imidazole unit (Figure 1), there are no significant multiple-scattering pathways involving the methyl group. Its inclusion as an independent single-scattering shell led, as in the case of the pure single-scattering approach, to a lower fit index but also to too short a distance to Fe for this shell (Figure 7; Table I, fifth column). In addition, a physically unrealistic splitting in the

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Fe–N1^{iv} and Fe–Cl^{iv} distances and a high Debye–Waller-type factor for the latter were observed, and the "camel back" was poorly fitted, in spite of a good agreement on the Fourier transform.

Discussion

It is now firmly established that multiple scattering in imidazole ring systems is important, even at high k.[5,6] However, the artifacts encountered in this work deserve some comment.

Our finding that the presence of the methyl substituent on the imidazole ring cannot be unambiguously established in the EXAFS of **I** has important bearing on the EXAFS analysis of metalloproteins. Imidazoles in histidine residues in metalloproteins can coordinate either with the nitrogen adjacent to the carbon to which the rest of the protein is attached (*pros* coordination) or with the nitrogen separated from it by one carbon (*tele* coordination). In **I**, the methyl carbon is in a position where a carbon would be in the case of *pros* coordination in a metalloprotein, but our present result indicates that it is not possible to unambiguously determine this with EXAFS.

The physically unreal splittings observed in the refinement of the multiple-scattering simulations are not due to the multiple-scattering approach proper, but to an important feature that is inevitably linked to it, viz. the need to simulate the data with too many parameters. The information content of an EXAFS spectrum is best assessed from its Fourier transform. Every resolved shell is determined by its position, amplitude in correlation with shell width, and its phase relationship with the nontransformed EXAFS. The position of a shell, if phase-corrected, can give information on the distance to the central atom; its amplitude, in correlation with the shell width, can give information about the occupancy in correlation with the Debye–Waller-type factor (static and/or thermal disorder), and the phase relationship with the EXAFS can give information about the atom type and presence of multiple scattering. The spectrum of **II** has been simulated with 21 highly correlated parameters,[6c] viz. ΔE_0 and five shells with distances, occupancies, Debye–Waller type factors, and bond angles. This procedure leads to splittings in the shells that are significantly larger than those found in the crystal structure.[17] However, there are only three shells, and one should attempt simulations varying only 10 parameters, viz. ΔE_0, three shells with distances, occupancies, and Debye–Waller type factors. Even under these conditions, correlations between ΔE_0 and the distances, and between the occupancies and the Debye–Waller-type factors, cannot be avoided. The futility of multiparameter approaches in EXAFS analysis has been discussed earlier.[19]

In any case where for example eight carbons occur at the same or slightly varying distances from a metal, which are represented in the EXAFS single- or multiple-scattering analysis by two groups of four, there will always be a splitting in the distances upon refinement, whether it is a physical reality or not. In the multiple-scattering approach, the representation of the 3.05- and 4.2-Å shells by pairs of contributions with equal or almost equal metal–N1– ring atom angles is obligatory, and therefore, upon refinement, the information on the true average ligand distance of these shells to the central atom is obscured. This information is valuable, because if mixed-ligand shells, where imidazole ligands coordinate to the metal in addition to other (oxygen, sulfur)

ligands, are present, the distance of the nitrogen donor atom to the metal cannot be unambiguously derived from the main shell. We conclude from our present results, in particular the good agreement with the crystallography for the first two shells of the single-scattering simulation (cf. Figure 3 and Table I, columns 1 and 2), that the position of the imidazole ring atoms at approximately 3.05 Å, as derived from single-scattering simulations, can give a reliable indication of the distance of the nitrogen donor atom to the metal. However, as the single-scattering approach may lead to anomalous occupancies for the imidazole ring atoms, because of the neglect of amplitude effects due to multiple scattering, the potential of the multiple-scattering approach to determine the number of imidazole ligands, although limited,[6c] is worthy of further exploration. As far as asymmetric imidazole coordination is concerned, theoretical calculations[6a] have shown that a rotation of 8° of the imidazole ring about an axis perpendicular to the imidazole plane, corresponding to a splitting in the metal–C1 and –C2 distances of approximately 0.2 Å, makes a substantial difference to the multiple scattering. It remains to be established whether such a tilting can be distinguished experimentally. Our results suggest that it would have to be considerable in order to be unambiguously detected in EXAFS as a physical reality.

Conclusion

A combined approach for the EXAFS analysis of systems with imidazole ligands is advocated, viz. multiple-scattering analysis to estimate the number of imidazole ligands, and single-scattering analysis to determine their position with respect to the central atom. Neither approach is expected to give information on the possibility of *pros* or *tele* coordination by histidines, while the potential of multiple-scattering simulations to establish tilting of the imidazole ligands with respect to the metal–N1 bond is weak. The interpretation of EXAFS data has been described as "the art of discerning which structural features are required by the data and which features are merely consistent with it".[2d] Our present work indicates that if an approach involving too many parameters is used, even features appearing to be required by the data, e.g. the splitting of imidazole ring atom shells, can be physically unrealistic.

Registry No. I, 61424-69-9; **II**, 26682-41-7; **III**, 33790-63-5; hexakis(imidazole)zinc(II) dichloride, 22678-31-5; hexakis(imidazole)cobalt(II) diacetate, 35848-52-3; hexakis(imidazole)nickel(II) diperchlorate, 27285-55-8.

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