XAS Investigation of biorelevant cobalt complexes in aqueous media

C. Bresson,[a] S. Esnouf,[b] C. Lamouroux,[a] P. L. Solari[c] and C. Den Auwer*[d]

Received (in Montpellier, France) 12th October 2005, Accepted 9th January 2006
First published as an Advance Article on the web 25th January 2006
DOI: 10.1039/b514454j

Cobalt is an essential element of biological cycles involved in numerous metallobiomolecules, but it becomes a toxic element at high concentration or a radiotoxic element because of its use in the nuclear industry. "Molecular speciation" in biological media is an essential prerequisite to evaluate its chemical behaviour as well as its toxic or beneficial effects. In this scheme, we have focused on the coordination properties of the thiol-containing amino acid cysteine (Cys) and the pseudo-peptide *N*-(2-mercaptopropionyl)glycine (MPG) towards the Co^{2+} cation in aqueous media. XAS at the Co K edge and traditional spectroscopic techniques have been coupled in order to structurally characterize the cobalt coordination sphere. Oxidation states and geometries of the bis- and tris-cysteinato Co(III) complexes are in agreement with the literature data. In addition, bond lengths between the metallic centre and the donor atoms have been determined. The structure of a new dimeric *N*-(2-mercaptopropionyl)glycinato Co(II) complex in solution is also reported. The coordination of MPG to Co(II) through the thiolate and carboxylate functions is ascertained. This work provides fundamental structural information about biorelevant complexes of cobalt, which will contribute to our understanding of the chemical behaviour and the biological role of this radionuclide.

Introduction

Metallic compounds in biological systems have become an important field of investigation on their own due to the biochemical function of most metals in the metabolic activities of living organisms.[1,2] In addition, the bioavailability and toxicity of metallic ions are critically dependent on their chemical speciation, which is defined by IUPAC as the distribution of an element amongst defined chemical species in a system.[3] Therefore, the knowledge of the speciation of a metallic ion is an essential prerequisite to evaluate its behaviour in different media, to understand the mechanisms of its absorption and transport in living organisms, as well as its toxic or beneficial effects. Essential information on the speciation of a given metallic ion in a metal–bioligand system may be provided by solution studies. However, structures of the different species involved in a speciation pattern remain elusive. Clarification of the binding properties between the metallic centre and the donor atoms involved in the coordination of species arising from aqueous solution may promote our understanding of the chemical behaviour and the biological role of metallic ions.

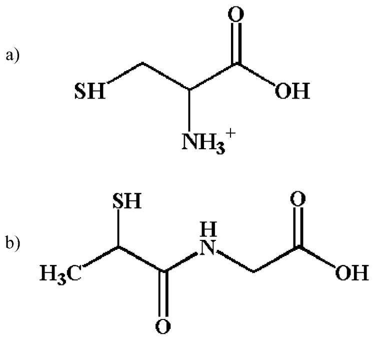
These structural investigations can involve different spectroscopic techniques such as nuclear magnetic resonance (NMR), electronic paramagnetic resonance (EPR) or infrared (IR) spectrometry. However, NMR and EPR are limited to diamagnetic and paramagnetic compounds, respectively. X-Ray absorption spectroscopy (XAS) is an ideally suited probe that allows to selectively focus on the environment and on the oxidation state of the metallic ion of interest. This technique has long been widely applied successfully to inorganic or bioinorganic systems, such as metalloproteins.[4,5]

Cobalt is a radionuclide of interest in the field of nuclear toxicological studies and particularly the ^{60}Co radioisotope, which is encountered in nuclear industry as an activation product of ^{59}Co by thermal neutrons. This radionuclide is a beta emitter producing a high energy gamma photon and has a half life time of 5.3 years. It is present at low-level aqueous radioactive waste discharges from many nuclear power and fuel-reprocessing plants[6] and has migrated more quickly than expected from disposal sites.[7] The existence of soluble, potentially available cobalt species, in biological fluids and tissues is essential to biological activities (beneficial or toxic). In case of individual contamination by cobalt, its chemical forms have to be discovered. Consequently, structural studies of cobalt complexes involving biorelevant ligands in solution represent a great interest regarding the speciation of this radionuclide in the biosphere and its removal from radioactive contaminated individuals.

In this field, we have focused our attention on building blocks of proteins, *i.e.* amino acids and small peptides, used in model studies of local metal coordination sites mimicking the naturally occurring metallobiomolecules. Cysteine (Cys), the only naturally occurring thiol-containing amino acid (Scheme 1(a)), is a major metal binding site in proteins, giving unique and important properties in enzyme activity and protein structure, especially in folding and defolding mechanisms. These crucial roles can be ascribed to the chemical reactivity of the thiol group, which is capable of both acid/base and oxidation/

---

[a] *CEA Saclay, DEN/DPC/SECR/LSRM, 91191 Gif sur Yvette, France*
[b] *Ecole Polytechnique, DSM/DRECAM/LSI, 91128 Palaiseau Cedex, France*
[c] *ESRF, BM29, 38043 Grenoble, France*
[d] *CEA Marcoule, DEN/DRCP/SCPS, 30207 Bagnols sur Cèze Cedex, France*



Scheme 1 Schematic structure of the studied ligands: (a) L-cysteine (Cys), (b) *N*-(2-mercaptopropionyl)glycine (MPG).

reduction chemistry. *N*-(2-Mercaptopropionyl)glycine (MPG) is a synthetic sulfhydryl structural analogue of glutathione (GSH), representing the right-hand portion of the latter (Scheme 1(b)). Glutathione, an important cysteine-containing tripeptide (γ-Glu-Cys-Gly), is a major intracellular reducing agent and one of the important small biomolecules present in cells of all organisms at millimolar concentrations. It possesses a multitude of physiological functions.[8,9] MPG acts as radio-protective agent by scavenging reactive oxygen species produced by irradiation[10] and has the ability to protect against drug-induced toxicity.[11]

The bis-cysteinato Co(III) complex, $[Co(Cys)_2(H_2O)_2]^{2-}$, in solution has been explored long ago by spectrophotometric studies[12,13] and the tris-cysteinato Co(III) complex, $[Co(Cys)_3]^{3-}$ by spectrophotometric, NMR and circular dichroism studies.[12–15] For these two complexes, the cobalt coordination spheres have been reported with, respectively two and three bidentate (N,S) cysteinato ligands. Studies regarding cobalt–MPG complexes are scarce and only two articles concerning determination of stability constants have been found.[16,17]

In this report, 1 : 2 and 1 : 3 Co(III)–cysteinato complexes and a 1 : 1 Co(II)–(*N*-(2-mercaptopropionyl)glycinato complex have been investigated by XAS spectroscopy (in both XANES and EXAFS regimes). Additionally, IR and EPR experiments have been performed in order to thoroughly characterize the cobalt coordination polyhedron and electronic state. For each complex the oxidation state of the metallic centre, its geometry and the distances involved in coordination are reported. Such data yield fundamental information on the structure/function of biomolecular adducts of cobalt and will contribute to the determination of the cation bioavailability. Molecular interactions and associated hazards at the cell level may be rationalised, leading to the design of efficient curative agents for the removal of radiotoxic cobalt from contaminated individuals.

Experimental

All of the chemicals and reagents used in this study were of analytical grade. Stock solution of cobalt (0.5 mol L^{-1}) was prepared by dissolving in purified deionised water (18.2 MΩ cm), obtained with a Milli-Q system (Millipore), an appropriate amount of cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$ (Sigma–Aldrich). Required masses of L-cysteine (Fluka, puriss) and *N*-2-mercaptopropionylglycine (Sigma–Aldrich) were dissolved in Milli-Q water and constantly degassed by bubbling of N_2 to prepare stock solutions (0.6 and 0.5 mol L^{-1}, respectively) stored at −18 °C. A solution of NaOH (1 mol L^{-1}) was obtained by dissolving an appropriate mass of NaOH (Aldrich) in Milli-Q water. $[Co(NH_3)_6]Cl_3$, as a model compound, was obtained from Sigma–Aldrich.

Synthesis

Bis(cysteinato)diaquacobalt(III), Co:2Cys. The sample was prepared at ambient temperature by mixing suitable volumes of the $CoCl_2 \cdot 6H_2O$ and L-cysteine stock solutions to obtain a 1 : 2 metal-to-ligand ratio with a final concentration of cobalt at 0.1 M. By adding 4 equivalents of NaOH, the solution colour turned immediately from pink to dark brown and the final pH of the solution was around 12.

Tris(cysteinato)cobalt(III), Co:3Cys. The sample was prepared at ambient temperature by mixing suitable volumes of the $CoCl_2 \cdot 6H_2O$ and L-cysteine stock solutions to obtain a 1 : 4 metal-to-ligand ratio with a final concentration of cobalt at 0.05 M. By adding 8 equivalents of NaOH, the colour of the solution turned immediately from pink to dark green, and the final pH of the solution was around 12.

Bis(*N*-(2-mercaptopropionyl)glycinato)triaquacobalt(II)), Co:1MPG. The sample was prepared at ambient temperature by mixing suitable volumes of the $CoCl_2 \cdot 6H_2O$ and MPG stock solutions to obtain a 1 : 1 metal-to-ligand ratio with a final concentration of cobalt at 0.05 M. By adding 2 equivalents of NaOH, the colour of the solution turned immediately from pink to brown-reddish and the final pH of the solution was around 7.

X-Ray absorption spectroscopy

XAS data have been recorded at the LURE and ESRF facilities. LURE (Orsay, France): DCI ring operated at 1.8 GeV with a nominal current of 300 mA, D44 beam line. ESRF (Grenoble, France): ring operated at 6 GeV with nominal current at 200 mA, BM29 beam line. The D44 beam line was equipped with a double-crystal Si(111) (for EXAFS measurements) or Si(311) (for XANES measurements) monochromator. High harmonic rejection was achieved by 30% detuning of the crystals. The BM29 beam line was equipped with a double-crystal fixed exit Si(111) helium gas cooled monochromator. High harmonic rejection was achieved with a double Si mirror and a detuning of the monochromator of 10%. Monochromator calibration was done at the Co K edge of a Co metallic foil (7713.6 eV at the edge shoulder). Data were recorded in transmission mode with air/nitrogen filled ionization chambers. For XANES online calibration, a third detection device (diode) was position after the second ionization chamber, besides a Co metallic foil. Energy resolution at 7700 eV: D44 = 1.5 eV.

XANES data were energy calibrated using the Co metallic foil and normalized with the Athena code[18] using the

AUTOBK algorithm. EXAFS data were extracted using the Athena code.

All the data were fitted using the Artemis code.[18] EXAFS spectra were fitted in $k^3\chi(k)$ with no prior Fourier filtering. Fitting was carried out in R space between 0 and 4.0 Å. Phases, amplitudes and electron mean free path were obtained with Feff82 code[19] with a model complex of $[Zn(Cys)_2]Na_2$.[20] In order to validate the Feff calculation on this model complex, the experimental EXAFS spectrum of $[Zn(Cys)_2]Na_2$ has been fitted with phases, amplitudes and electron mean free path obtained from the Feff calculation and structural parameters matching the crystallographic ones (R factor of the fit = 0.5%). For the Co adducts, $Z = 30$ (Zn) has been replaced by $Z = 27$ (Co) in the Feff input file. During the fits, the global inelastic loss factor S_0 was adjusted and the number of first coordination sphere neighbours was fixed to six according to the Co symmetry (O_h) postulated from XANES. Only one energy threshold shift parameter was used for all the scattering paths. N and O neighbours were not distinguished in the fit (written N/O in the following) due to their similar number of electrons and comparable backscattering phases and amplitudes. The following paths were included in the fitting procedure: two single scattering paths from S and N/O neighbours with one Debye–Waller factor each. For the cysteinato series: two single scattering paths from the two C in α position of S and N with one Debye–Waller factor, two triple scattering paths from the two C–N and C–S bonds with one Debye–Waller factor. All single and multiple scattering paths including the C atom were linked to the S and N position according to the crystal structure of $[Zn(Cys)_2]Na_2$. This approximation assumes that the intramolecular distortion of the cysteine ligand is negligible from $[Zn(Cys)_2]Na_2$ to the Co compounds. For the MPG complex, although the same cluster of $[Zn(Cys)_2]Na_2$ was used for phase and amplitude calculations, the ligand conformation is supposed to be significantly different from that of the cysteine. Therefore one single independent shell of carbon atoms was added with corresponding single and triple scattering paths as described above. An additional Co–Co contribution was needed in the fit. Phases and amplitudes of this contribution were calculated using the $[Zn(Cys)_2]Na_2$ cluster with an additional Co cation positioned artificially in the cluster.

FT-IR Spectroscopy and electron paramagnetic resonance

FT-IR data were recorded at atmospheric conditions with a Brüker Equinox55 spectrometer with an ATR diamond crystal. Concerning the EPR experiments, 80 μL of solution was placed in a 4 mm OD quartz tube which was positioned in an OXFORD helium flow cryostat. The cryostat temperature was set at 4.5 K. EPR spectra were recorded at the X band (9.4 GHz) on a Brüker ER-200D ESR spectrometer. The concentration of Co(II) was calculated from a set of $CoCl_2 \cdot 6H_2O$ frozen solutions of known concentration (10^{-3}–10^{-1} mol L^{-1}).

Results

XANES

In Fig. 1, the Co K-edge XANES spectra of **Co:1MPG**, **Co:2Cys** and **Co:3Cys** are compared to those of the reference compounds aqueous $Co(II)(H_2O)_6$ (**I**) and solid $[Co(III)(NH_3)_6]Cl_3$ (**II**). In complex **I**, the Co atom is in an octahedral environment with six water molecules at 2.07 Å.[21] In complex **II**, the Co atom lies in a nearly perfect octahedron with six amine molecules in the first coordination sphere at an average distance of 1.97 Å.[22] The absorption ramp of all the spectra corresponds to the formally dipole allowed 1s → 4p transition. The spectrum of **I** has already been described in the literature.[23] It is in agreement with an octahedral or distorted octahedral Co environment as described below. The spectrum of **II** is more complex and still a matter of debate[24] although various interpretations have been proposed. Similar spectra of Co(III) have also been reported for the acetylacetonate complex,[25] or cobalamines.[26] In the following, the edge features are described in a phenomenological approach according to the literature. Consequently, the Co formal oxidation state and its coordination sphere geometry are determined. Attempts towards a quantitative analysis of the edges is currently under progress by the authors and will be the subject of a future communication.

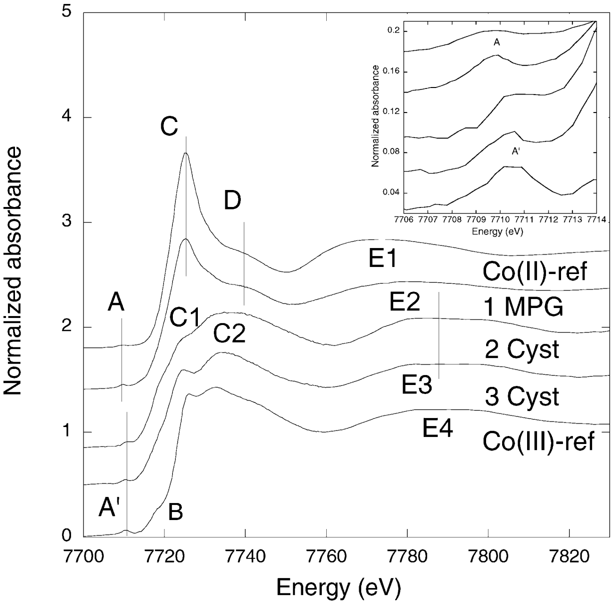


Fig. 1 Cobalt K-edge XANES spectra of complexes **Co:3Cys**, **Co:2-Cys** and **Co:1MPG**. Spectra of aqueous $Co(II)(H_2O)_6$ (Co(II)-ref, **I**) and the solid compound $[Co(NH_3)_6]Cl_3$ (Co(III)-ref, **II**) are also presented. For clarity, the XANES spectra have been shifted in ordinates. The inset shows an energy enlarged section of the XANES spectra centred on the pre-edge feature.

Pre-edge. The pre-edge features, A and A′, are described in the literature as a formal 1s → 3d transition.[27,28] They are presented in the inset of Fig. 1. The weakness of A, A′ intensity in all spectra (less than 5% of the absorption jump) suggests that in all cases the Co atom lies in an octahedral or pseudo-octahedral symmetry.[29] This transition is well known to be weak but not absent for centrosymmetric (here O_h) compounds due to quadrupole or vibronically allowed dipole coupling. The cross section of A in **I** (FWHM × intensity = 0.024) is roughly three times smaller than that of A′ in **II** (FWHM × intensity = 0.070). This corresponds to the conjugated effects: (i) an increase of the transition cross section from **I** to **II** due to a decrease of the 3d orbital population from $3d^6$ for **I** to $3d^5$ for **II**, (ii) in the high-spin configuration of **I** two badly resolved transitions towards the t^5_{2g} and e^2_g states are present whereas the low-spin configuration of **II** leads to a unique transition towards the empty e_g state.[30] The 0.7 eV high energy shift between A in **I** and A′ in **II** corresponds to the usual trend upon increase of the absorbing cation formal oxidation state from (II) in **I** to (III) in **II**. A direct comparison of the pre-edge position with **Co:1MPG**, **Co:2Cys** and **Co:3Cys** shows that Co is at oxidation state (II) in the MPG adduct and (III) in the cysteine adducts.

Edge ramp. Shoulder B in **II** is controversial. It has been described as a 1s → 4s transition,[31] a 1s → ($3d_M$–π_L*) when the ligand bears some π and π* molecular orbitals (as for cyano ligands)[21] or a 1s → $4p_z$ + LMCT transition.[28,32,33] This is equivalent to the fully relaxed final state configuration $1s^1 3d^{n+1} L^o 4p^1$ (where L^o corresponds to the charge transfer from the ligand p orbitals to the metal 3d orbitals) in agreement with the picture of a two electron transition 1s → 4p + shake down.[29] Shoulder B is also present, at the same energy, in the spectra of **Co:2Cys** and **Co:3Cys**. On the contrary, it is absent of the spectra of **I** and **Co:1MPG**. One can assume that the ligand crystal field combined with the cobalt oxidation state allows to turn on the shake down process, although the precise description of the electronic interactions is still unknown at this point. Furthermore, in the specific case of the Co(III) species debated here, this agrees with the need of interaction of configuration in the simulation of low-spin Co(III) species at the Co $L_{2,3}$ edges.[34] Similar reasons are also invoked for the appearance of peak C_1 as described below.

Edge maximum. The edge maximum corresponds to the 1s → 4p transition in the dipolar approximation. In the low-spin configuration of **II**, the shortening of the metal–ligand distances induces a destabilization of the antibonding 4p states (hybridized in the molecular picture with the ligand 2p orbitals) and consequently a decrease of the 4p participation to the molecular orbital.[35] The high intensity of peak C for complex **I** compared to peaks C_1 and C_2 for complex **II** accounts for this trend. In the multiple scattering picture, the high intensity of C is ascribed to in-phase contributions from single scattering and collinear multiple scattering paths originating from the octahedral symmetry.[36] The XANES spectrum of **Co:1MPG** is comparable to that of **I**, suggesting a similar environment for the cation. The white line splitting into peaks C_1 and C_2 for complex **II** as well as for **Co:2Cys** and **Co:3Cys** has not been clearly addressed in the literature. For instance, it has been attributed in the case of cobalamine to the *z*-polarized transitions (axial ligand) for C_1 and *xy* polarized transition (equatorial ligand) for C_2 in case of tetragonal distortion of the octahedron.[26,29,37] However the EXAFS data reported for **I**[23] and the crystal structure of **II** show that the tetragonal distortion is negligible in both reference compounds. Furthermore, all the ligands (NH_3) are equivalent in **II** and this precludes the influence of the apical ligand electronegativity to account for the white line splitting. Recently, in the case of the Cu(II)–tetrammine complex,[38] such splitting of the white line has been explained in terms of superposition of two excitation channels corresponding to the final state electronic configurations $1s^1 3d^{10} L^o 4p^1$ and $1s^1 3d^9 L 4p^1$ as described before. Tentatively, in this picture, C_2 corresponds to the dipolar 1s → 4p transition while C_1 is ascribed to the $1s^1 3d^{6+1} L^o 4p^1$ configuration and B to the $1s^1 3d^{6+2} L^{oo} 4p^1$ configuration. Feature B is positioned at the lowest energy which corresponds to an increase of the screening effect from $3d^{6+1} L^o$ to $3d^{6+2} L^{oo}$. The slight intensity and position discrepancies between C_1 and C_2 in **II** on the one hand and in **Co:2Cys** and **Co:3Cys** on the other suggest a modification of the Co coordination sphere. Above the edge maximum, feature D in **I** arises from scattering contributions.[36] The comparable position but different intensity of D in **I** and in **Co:1MPG** confirms that both coordination spheres are octahedral but not identical. Finally, features E_1, E_2, E_3 and E_4 are shape resonances related to the average distance in the first Co coordination sphere (modulated by the phase and amplitude functions associated to the backscatters). From complex **I** to **II**, the average Co–ligand distance goes from 2.07 to 1.97 Å and this global shortening of the coordination sphere is in agreement with the high energy shift of E_4 with respect to E_1, given that H_2O and NH_3 are similar backscatters. Direct comparison between E_1 and E_4 in the one hand and E_2 and E_3 On the other is impossible because the backscatters differ largely. However the similar position of E_2 with respect to C and E_3 with respect to C_2 (if C_2 is considered as the main transition channel as suggested previously) indicates that all the cobalt coordination spheres in **Co:3Cys**, **Co:2Cys** and **Co:1MPG** are comparable.

In conclusion, the above XANES spectra indicate that to different oxidation states are encountered for these cobalt species, depending on the nature of the ligand. In all cases, the cation lies in an octahedral or pseudo-octahedral symmetry. Although both Cys and MPG ligands have comparable donor groups (S, N, O), the data suggest that cobalt–ligand orbital hybridization must be taken into account for the Co(III)/Cys complexes. This might also account for the difference in oxidation state between both systems. The quantitative analysis of the XANES spectra coupled to quantum chemical calculations should allow to fully understand the electronic interactions in these species.

EXAFS

The Co K-edge EXAFS spectra of **Co:3Cys**, **Co:2Cys** and **Co:1MPG** are presented in Fig. 2(a). The related Fourier transforms (FTs) are presented in Fig. 2(b). The best fit results are summarized in Table 1. The FTs in Fig. 2(b) all exhibit a strong contribution, F, which corresponds to the Co first coordination sphere. It has been fitted considering the cysteine ligand as a bidentate chelate with S(thio), N(amino) ligation and the MPG ligand as a bidentate chelate with S(thio) and O(carboxy) ligation. The non-coordination of the amido group is further detailed in the Discussion section based on IR data. According to the XANES spectra, the Co coordination sphere is octahedral and the coordination numbers have been fixed to six according to the general formula: Co(III)$(Cys)_2L_2$ for **Co:2Cys**; Co(III)Cys_3 for **Co:3Cys**; and [Co_2(II) MPG_2L_6] for **Co:1MPG** (the dimeric character of **Co:1MPG** is

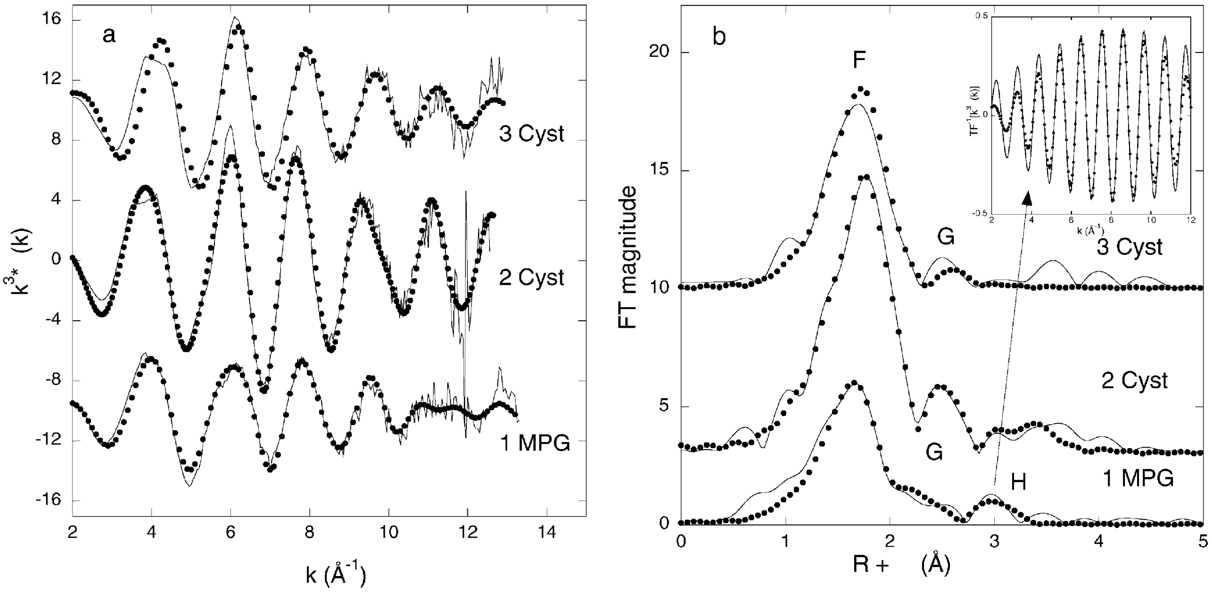


Fig. 2 Cobalt K-edge EXAFS spectra (a) of complexes **Co:3Cys**, **Co:2Cys** and **Co:1MPG** and corresponding Fourier transforms (b). For clarity, the EXAFS spectra and FT have been shifted in energy.

discussed below) where L is assumed to be an exogenous ligand coming from the aqueous solution, *i.e.* H_2O. Due to their comparable number of electrons, N and O give similar backscattering functions and cannot be distinguished in the EXAFS fit. As explained in the discussion section, coordination numbers and modes have been determined from the literature and IR data.

The two distances included in peak F and given in Table 1 are related to: $d_{Co–S}$ and $d_{Co–N}$ for **Co:3Cys**; $d_{Co–S}$ and $\{1/4(2d_{Co–N} + 2d_{Co–L})\}$ for **Co:2Cys**. The higher value of the Debye-Waller factor related to the O/N shell with regards to the S shell (Table 1) reflects the presence of several N and O(water) contributions at comparable but non-identical distances. The shorter Co–N distance in **Co:3Cys** compared to Co–N/O in **Co:2Cys** confirms the effect of the additional water molecules in the coordination sphere. In all cases, as expected from the nature of the sulfur bond, the Co–S bond is about 0.2 Å larger that the Co–O/N bond. The second, small contribution, G, corresponds to the carbon atoms adjacent to the sulfur and nitrogen ones, respectively. These contributions have been included but not fitted, as explained in the experimental section. Addition of the distal non coordinating carboxylate contributor of cysteine in the fits of **Co:3Cys** and **Co:2Cys** did not improve the fit of G.

In the FT spectrum of the **Co:1MPG** adduct (Fig. 2(b)), the presence of peak H suggests a long range contribution from a heavy scattering atom, as occurring in dimeric species. Indeed, although of small intensity, peak H can be fitted with addition of one Co atom at 3.35 Å. The nature of peak H has been also validated by Fourier back filtering analysis, and shows unambiguously that it accounts for a Co contribution (shown in inset of Fig. 2(b)). In this frame, the two sulfur atoms coming from the two MPG ligands are assumed to be bridging. In order to complete the octahedral Co coordination sphere, four additional neighbours are needed. The IR data (see Discussion section) suggest the MPG to be bidentate with thio and carboxy coordination to Co, resulting in the formula: $[Co_2(\text{II})(MPG)_2L_6]$, where L might be H_2O. Surprisingly, the Co–S and Co–O distances reported in Table 1 compare to the cysteinato series although the cobalt cation is at oxidation state (II). As for the cysteinato series, peak G is related to the carbon atoms of the MPG adjacent to the coordinating atoms.

Table 1 Best fit parameters from the adjustments of the raw EXAFS spectra of **Co:3Cys**, **Co:2Cys** and **Co:1MPG**. The goodness of the fit is given by the *R* factor. See the experimental section for the fitting procedure

Sample	Co–O/N	Co–S	Co–Co	
Co:2Cys	4 O/N at 2.09 Å $\sigma^2 = 0.0098$ Å^2	2 S at 2.26 Å $\sigma^2 = 0.0039$ Å^2		$R = 0.008$ $S_0 = 1.2,^a\ e_0 = -6.8$
Co:3Cys	3 N at 2.01 Å $\sigma^2 = 0.0049$ Å^2	3 S at 2.24 Å $\sigma^2 = 0.0052$ Å^2		$R = 0.010$ $S_0 = 0.7,\ e_0 = -4.6$
Co:1MPG	4 O at 2.03 Å $\sigma^2 = 0.0053$ Å^2	2 S at 2.26 Å $\sigma^2 = 0.0044$ Å^2	1 Co at 3.35 Å $\sigma^2 = 0.0068$ Å^2	$R = 0.024$ $S_0 = 0.7,\ e_0 = -5.8$

[a] This value of S_0 is surprisingly high compared to the two other samples. This discrepancy is attributed to amplitude distortion in data recording (at LURE for this sample) compared to the two other samples (both recorded at ESRF).

It has been fitted with one independent shell of three carbon atoms at 2.91 Å as explained in the Experimental section.

Discussion

Co(II) gives rise to simple salts with all the common anions which are readily obtained as hydrates from aqueous solutions, $[Co(H_2O)_6]^{2+}$ (usually written Co^{2+}). On the other hand, Co^{3+} is a strong oxidant that is rapidly reduced in water. When a ligand is present in solution, Co^{2+} may be complexed, providing a Co(II) or Co(III) complex, depending on the crystal field stabilization energy (CFSE) of the ligand and the pH of the solution. If the ligand is positioned not too high in the spectrochemical series, complexes of Co(II) can be isolated without special precautions. Cys and MPG have three potential coordination sites: carboxy, thio and amino for the cysteine; carboxy, thio and amido groups for the MPG (Scheme 1(b)). The pK_a values of the different functions have been determined for the two ligands[16,39–42] and vary between 1.82 for $pK_{a(COOHCys)}$ to 10.36 for $pK_{a(NH_3^+Cys)}$.

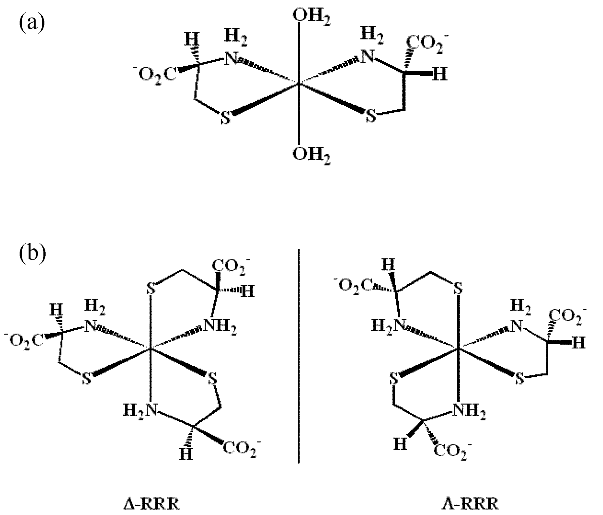
In order to render all the coordination sites of the ligands available, this work has been carried out at pH = 12 for the cysteinato series and pH = 7 for the MPG adduct. On the one hand, this avoids simultaneous presence of several complexes when adding $CoCl_2 \cdot 6H_2O$. Although Co(II) and Co(III) are, respectively classified as borderline and hard Lewis acids, they may both potentially interact with the amino, amido, thio and carboxy functions of these two ligands, resulting a variety of Co(II) and Co(III) coordination modes. The type of the coordination of the complexes is also conditioned by the metal-to-ligand ratio (M/L), determining the stoichiometries of the complexes.

Cobalt in water in the presence of two equivalents of cysteine

The brown bis-cysteinato Co(III) complex in solution has been explored long ago by spectrophotometric studies.[12,13] Coordination to the cobalt through the thiolate and amino groups of cysteine was deduced and a *cis*-diaquo structure was proposed, although five possible geometric isomers exist.[12] In our experiments, XANES data related to **Co:2Cys** reveal that the cobalt centre is in an octahedral or pseudo-octahedral environment with formal oxidation state (III). The EPR spectrum of **Co:2-Cys** shows that this complex is diamagnetic, which is consistent with the low-spin Co(III) formulation. The goodness of the EXAFS fit confirms the assumed geometry with only four of the six positions of the octahedral coordination sphere occupied by N, S cysteine donor atoms and the two remaining positions by O atoms. Averaged Co(III)–S, Co(III)–N/O distances are found to be 2.26, 2.09 Å, respectively. The only distances available in the literature are in solid crystalline cobalt(III) complexes, where compact packing is said to be governed by minimum van der Waals plus hydrogen energy, which might not be the same in solution as in the solid state. Averaged Co(III)–S bond lengths in crystalline complexes holding cysteine, penicillamine or aliphatic aminothiol as one of their ligands are 2.26–2.22 Å.[43–52] Interestingly, in *trans*(*S*)-$[Co(III)(aet)_2(en)]^-$ (en = ethylenediamine), the Co–S distances are 2.29 Å.[53,54] The lengthening of the Co–S bond lengths is due to the sulfur *trans* effect. Indeed, sulfur ligands have a tendency to labilise groups positioned in *trans* position regarding the sulfur atom in the octahedral Co(III) complexes.[49,55] By comparison with the data cited above, we can conclude that the two sulfur atoms in the aqueous bis-cysteinate Co(III) complex are not in *trans* position. Consequently, among the possible geometric isomers for the Co(III) bis-cysteinate complex, the isomers holding the sulfur atoms in *trans* position can be excluded. In crystalline Co(III) complexes with aminothiol ligands containing primary, secondary or tertiary amine, Co–N bond lengths range from 1.94 to 1.99 Å.[43,44,46,47,49,56] Averaged Co–N distances in the reference compound $Co(III)(NH_3)_6Cl_3$ are 1.97 Å.[22] Co–N distances involving the nitrogen atom bonded *trans* to the sulfur atom are lengthened and range from 2.00 to 2.02 Å.[44,47,49,51,52] From these results, the *trans*(*N*,*S*) structure is proposed for **Co:2Cys**. Tridentate (N,S,O) coordination by cysteine to cobalt is relatively uncommon and to our knowledge, only one X-ray crystallographic structure exhibits L-cysteinate acting as a tridentate-N,S,O ligand in a monomeric Co(III) complex.[44] The *S*-methylcysteine (SMC) acts also as a tridentate ligand in $[Co(III)(SMC)_2]^-$.[56] Reported Co–O distances in these complexes are 1.92 and 1.91 Å. While tridentate coordination of cysteine is scarce, the penicillamine is generally terdentately coordinated to the cobalt. In reported penicillamino–Co(III) complexes, coordinated carboxylato oxygen atoms are positioned at 1.92–1.93 Å from the Co(III) centre[46,47] (much shorter than the average Co–O/N distance proposed here). The sulfur *trans* effect has been also observed for coordinated oxygen atoms, however distances to the cobalt centre become *ca.* 0.02–0.07 Å longer than the previous distances.[45,46] The non-chelating role of the carboxylate group is further evidenced by the occurrence of its frequencies in the range of non-coordinated COO^- (**Cys**: $\nu_{as}(COO^-)$ = 1603 cm^{-1}; $\nu_s(COO^-)$ = 1400 cm^{-1}, **Co:2Cys**: $\nu_{as}(COO^-)$ = 1607 cm^{-1}; $\nu_s(COO^-)$ = 1397 cm^{-1}), in agreement with the literature.[57] This non-coordinating character of the carboxylate group can be explained by combined steric reasons and less nucleophilic character of this atom with respect to S and N. The N, S chelation mode results in a five-membered ring pattern that is well known to stabilize the complex. In conclusion, the structure of **Co:2Cys** matches with a single *trans*(*N*,*S*) structure, in which the water groups are thus in *trans* position (Scheme 2(a)), excluding the *cis* diaquo structure postulated in the literature.

Cobalt in water in the presence of four equivalents of cysteine

This Co(III) tris-cysteinato complex has been widely investigated in solution and in the solid state from a spectrochemical and stereochemical point of view, providing electronic absorption (UV-visible), NMR and circular dichroism data.[12–15] It has been demonstrated that the Δ-*RRR*-*fac*(*S*)-$[Co(Cys\text{-}N,S)_3]^{3-}$ diastereoisomer is formed stereospecifically,[14,15] in which the cysteine is bonded to the Co(III) through the thiolate and amino groups (Scheme 2(b)). No X-ray crystallographic structure corresponding to the mononuclear Co(III) tris-cysteinate is available in the literature, but it is recognised that mononuclear Co(III) complexes with aminoethanethiol and Cys can serve as effective S-donating ligands toward a variety of metal ions to form S-bridged polynuclear complexes.[51,58–62]



Scheme 2 (a) Structure of the *trans*(*N*,*S*)-bis(cysteinato)diaquacobalt(III) complex and (b) structure of Δ-*RRR*-*fac*(*S*)-[Co(III)(Cys-*N*,*S*)$_3$]$^{3-}$ and Λ-*RRR*-*fac*(*S*)-[Co(III)(Cys-*N*,*S*)$_3$]$^{3-}$ diastereoisomers.

Both XANES and EXAFS data of **Co:3Cys** confirm that addition of an excess of cysteine ligand to $CoCl_2 \cdot 6H_2O$ in basic medium, leads to the formation a mononuclear complex of 1 : 3 stoichiometry as demonstrated in the literature. The EPR measurement verifies the presence of Co(III) in **Co:3Cys**. In the EXAFS fit and according to the literature, the octahedral sphere of the Co(III) is filled by three bidentate N,S-cysteine ligands and the sulfur and nitrogen atoms are positioned at 2.24 and 2.01 Å, respectively, from the metallic centre (Table 1). By comparison of these distances with those reported above it is obvious that the aqueous tris-cysteinate Co(III) complex is consistent with a *trans*(*N*,*S*) geometric isomer. The Co–N distances are shorter for **Co:3Cys** than for **Co:2Cys**. The tris-cysteinato complex, which bears a net charge of 3− might be expected to bind its ligands more tightly than the bis-cysteinate with a net charge of 1−, explaining the shortening of the distances.

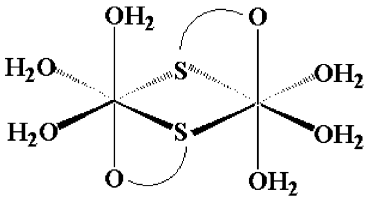
Contrarily to **Co:2Cys**, *i.e.* *trans*(*N*,*S*)-[Co(III)(Cys)$_2$(H$_2$O)$_2$]$^-$, the structure of the geometrical isomer **Co:3Cys** *i.e.* [Co(Cys-*N*,*S*)$_3$]$^{3-}$ could not be determined, as XAS is not sensitive to the Δ(*R*)/Λ(*R*) diastereoisomers, *mer* and *fac* isomers (Scheme 2(b)).

Cobalt in water in the presence of one equivalent of MPG

The reaction of one equivalent of MPG with $CoCl_2 \cdot 6H_2O$ in neutral medium leads to a brown-reddish complex. By the help of a set of $CoCl_2 \cdot 6H_2O$ frozen solutions of known concentration, EPR spectroscopy shows that cobalt in **Co:1MPG** is at oxidation state (II), consistent with a paramagnetic high-spin configuration, excluding a mixed-valence complex. This result was confirmed by XANES experiments: a direct comparison of the pre-edge position of **Co:1MPG** with **I** and **II** shows that the cobalt is at oxidation state (II) and that the local coordination around cobalt is octahedral or pseudo-octahedral.

To our knowledge, no X-ray structure of cobalt–MPG complexes is available in the literature and only three crystalline structures of Ni(II), Re(V) and V(IV) complexes have been reported:[63–65] Both rhenium and vanadium complexes are mononuclear adducts while the nickel complex forms a trimeric species in which three sulfur atoms are bridging. In all these cases, MPG is a tridentate ligand through thio, carboxy and deprotonated amido groups. In solution state, it has been observed that the thiolate anchor promotes amide deprotonation and coordination to the metallic centre at pH around 4 for V(IV)[41] and Sn(IV),[40] at pH around 6.5 and 8 for Cu(II)[66] and Ni(II).[42] However, conclusions about the ability of the thiolate to serve as an anchor for amide deprotonation is speculative: in the Fe(II)–MPG complex emerging in solution at $6 < pH < 7.8$, the amide group is not coordinated to the metallic centre;[67] there is no evidence of the peptide hydrogen ionisation in MPG solutions containing Pt(II);[42] Zn(II)[68] and Cd(II)[69] are not able to induce amide deprotonation; and contradictory results are obtained concerning Pd(II).[42,70] Concerning the cobalt–MPG system, relatively few solution studies have been performed compared to other transition metals. These latter concern potentiometric and spectrophotometric studies relative to the determination of stability constants.[16,17] It is reported that in weakly basic medium, the cobalt is at oxidation state (II) and the deprotonation/coordination of the peptidic amido group was not induced.[16] Infrared spectroscopy is an informative technique about the coordination mode of a ligand to a metallic cation. FT-IR spectra of the MPG and **Co:1MPG** have been recorded. Upon complexation, characteristic vibration of the MPG unionised carboxyl group at 1726 cm^{-1} disappears. On the other hand, the presence of two bands at 1601 and 1382 cm^{-1} in **Co:1MPG** are characteristic of the antisymmetric and symmetric stretching frequencies of a coordinated carboxylate group.[57] The spectrum of **Co:1MPG** exhibits a broad band at 1650 cm^{-1} which lies at 1654 cm^{-1} in the free ionised ligand, showing that the peptide carbonyl function is not complexed by Co(II) (the vibration of a coordinated peptide carbonyl function is typically at 1625 cm^{-1}). The vibrational band of the amide group (1557 cm^{-1}) is not shifted compared to the free ligand, suggesting that the nitrogen of the amide function of the MPG is not linked to the cobalt. These observations allow us to exclude the participation of the peptidic group –NHCO– of the MPG to the complexation of cobalt. The coordination mode of the MPG through the thiolate and carboxylate functions is thus assumed.

According to the EXAFS data, **Co:1MPG** is consistent with a dimer, in which each MPG is coordinated to the Co(II) centres through the carboxy and the thio functions, these later having a bridging role between the two Co(II) atoms. The octahedral sphere of the metallic cation is fulfilled by three water molecules. This complex has never been described in the literature and one of the possible schematic structures is drawn in Scheme 3. The first coordination shell of each Co(II) is formed by two S atoms at 2.26 Å and four oxygen atoms at *ca.* 2.03 Å. Oxygen atoms coming from the carboxylate function or water molecule cannot be distinguished by EXAFS: 2.03 Å is thus an average value. The distance between the two metallic centres is 3.35 Å. Octahedral monomeric and dimeric Co(II) complexes containing water and/or carboxylate groups as one of their ligands present a rather wide Co(II)–O distance range, spanning 2.04–2.19 Å.[71–76] In **Co:1MPG**, the lengths of the



Scheme 3 Structure of one of possible (*N*-2-mercaptopropionyl) glycinato)triaquacobalt(II) dimers.

observed Co(II)–O bonds do not differ significantly compared to the literature data. Data related to Co(II)–S distances in octahedral complexes are very scarce. In a trimeric complex of Co(II) containing an aminothiol [48] behaving as bridging and terminal ligand through the sulfur atom, the central tetrahedral Co(II)–S bond lengths (2.30–2.31 Å) are shorter than the octahedral terminal bond lengths (2.51–2.52 Å) and the distance between the cobalt centres is 3.24 Å. The bridging sulfur-to-cobalt bond length in **Co:1MPG** is about 0.04 Å shorter than the Co(II)–S central distance and about 0.25 Å shorter than the Co(II)–S terminal distance. However, it is difficult to establish a comparison since in the trimer described in the literature, the central cobalt coordinated to bridging sulfur is tetrahedral and the two others are octahedral but terminal.

In summary, the thiolato group has been demonstrated to be an anchor for many transition metals, but in neutral medium, it is not effective enough for Co(II) to promote deprotonation of the amide group and subsequent coordination to the cobalt centre. On the other hand, it has been demonstrated that the deprotonation of the amide hydrogen and concomitant coordination of the amido N to cobalt appear to be a key step toward oxidation of the metal centre,[77,78] with atmospheric oxygen being the oxidizing agent. Therefore, syntheses of amide/peptide complexes of Co(III) are performed usually in basic solutions in order to induce the deprotonation of the amide function.[77–79] With respect to these observations, it is thus worthwhile to monitor the changes in oxidation state and structural arrangement by XAS, EPR and IR as a function of pH and also the ratio M/L. These experiments are now in progress. The phenomenological comparison of the XANES spectra also suggests that a both ligands (Cys and MPG) induce different electronic properties of the cobalt cation, although the donor groups are comparable. Such behaviour should be further investigated from a combined theoretical chemical and spectroscopic approach.

Conclusion

The present work highlights the advantage of using XAS spectroscopy to structurally characterise Co(II)/(III) complexes of biorelevant ligands in aqueous solution. Mono-, bis- and tris-cysteinato Co(III) complexes have been reinvestigated by this technique and the dimeric *N*-(2-mercaptopropionyl)glycinato Co(II) complex has been reported for the first time. This work is the starting point of the investigation of cobalt–MPG complexes, by studying the effect of the metal-to-ligand ratio and the pH. In order to better define the driving forces influencing the structural properties of these complexes, further investigation of the MPG chelating effects is under progress. These studies are of interest for Co(II)/(III) active sites modelling in metalloproteins.

Acknowledgements

This work was supported by the French Nuclear and Environmental Toxicology program and CEA/DEN/DDIN/MR.

XAS Measurements were carried out at LURE, a former French user facility and at ESRF a European facility. The authors would like to thank Nathalie Boubals for her help in IR experiments.

References

1 S. J. Lippard and J. M. Berg, in *Principles of Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, 1994.
2 J. A. Cowan, in *Inorganic Biochemistry: An Introduction*, Wiley-VCH, Weinheim, 1997.
3 D. Templeton, F. Ariese, R. Cornelis, L. G. Danielsson, H. Muntau, H. P. van Leeuven and R. Lobinski, *Pure Appl. Chem.*, 2000, **72**, 1453.
4 I. Ascone, R. Fourme, S. Hasnain and K. Hodgson, *J. Synchrotron Radiat.*, 2005, **12**, 1.
5 J. E. Penner-Hahn, *Coord. Chem. Rev.*, 1999, **192**, 1101.
6 S. Szöke, G. Patzay and L. Weiser, *Radiochim. Acta*, 2003, **91**, 229.
7 T. H. Christensen, P. Kjeldsen, P. L. Bjerg, D. L. Jensen, J. B. Christensen, A. Baun, H. J. Albrechsten and G. Heron, *Appl. Geochem.*, 2001, **16**, 659.
8 H. Sies, *Free Radical Biol. Med.*, 1999, **27**, 916.
9 D. A. Dickinson and H. J. Forman, *Biochem. Pharmacol.*, 2002, **64**, 1019.
10 A. Garner, Z. Jamal and T. F. Slater, *Int. J. Biol. Relat. Stud. Phys. Chem. Med.*, 1986, **50**(2), 323.
11 W. Li, X. M. Yuan, S. Ivanova, K. J. Tracey, J. W. Eaton and U. T. Brunk, *Biochem. J.*, 2003, **371**, 429.
12 R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, 1956, **78**, 4893.
13 G. Gorin, J. E. Spessard, G. A. Wessler and J. P. Oliver, *J. Am. Chem. Soc.*, 1959, **81**, 3193.
14 A. P. Arnold and W. G. Jackson, *Inorg. Chem.*, 1990, **29**, 3618.
15 R. D. Gillard and R. Maskill, *Chem. Commun.*, 1968, 160.
16 B. Harman and I. Sovago, *Inorg. Chim. Acta*, 1983, **80**, 75.
17 M. J. Quesada, L. Sanchez and R. J. Garcia-Villanova, *ARS Pharm.*, 1982, **23**, 397.
18 B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537.
19 J. J. Rehr and R. C. Albers, *Rev. Mod. Phys.*, 2000, **72**, 621.
20 P. Bell and W. S. Sheldrick, *Z. Naturforsch., Teil B*, 1984, **39**, 1732.
21 V. Briois, C. Cartier dit Moulin, M. Momenteau, P. Maillard, J. Zarembowitch, E. Dartyge, A. Fontaine, G. Tourillon, P. Thuéry and M. Verdaguer, *J. Chim. Phys.*, 1989, **86**, 1623.
22 G. J. Kruger and E. C. Reynhardt, *Acta Crystallogr., Sect. B*, 1978, **34**, 915.
23 P. D'Angelo, M. Benfatto, S. Della Longa and N. V. Pavel, *Phys. Rev. B*, 2002, **66**, 64209.
24 A. Mimouni, J. Moscovici and A. Michalowicz, *J. Phys. IV Fr.*, 1997, **7**, 623.
25 O. Kleifeld, L. Rulisek, O. Bogin, A. Frenkel, Z. Halvas, Y. Burstein and I. Sagi, *Biochemistry*, 2004, **43**, 7151.
26 M. Giorgetti, I. Ascone, M. Berettoni, P. Conti, S. Zamponi and R. Marassi, *J. Biol. Inorg.Chem.*, 2000, **5**, 156.
27 J. E. Hahn, R. A. Scott and K. O. Hodgson, *Chem. Phys. Lett.*, 1982, **88**, 595.
28 N. Kosugi, T. Yokoyama, K. Asakura and H. Kuroda, *Chem. Phys.*, 1984, **91**, 249.
29 C. Cartier dit Moulin, M. Momenteau, E. Dartyge, A. Fontaine, G. Tourillon, A. Michalowicz and M. Verdaguer, *J. Chem. Soc., Dalton Trans.*, 1992, 609.
30 C. Roux, D. M. Adams, J.-P. Itié, A. Polian, D. N. Hendrickson and M. Verdaguer, *Inorg. Chem.*, 1996, **35**, 2846.

31 F. Béland, A.-R. Badiei, M. Rönning, D. Nicholson and L. Bonneviot, *Phys. Chem. Chem. Phys.*, 1999, **1**, 605.
32 O. Haas, R. P. Struis and J. M. McBreen, *J. Solid State Chem.*, 2004, **177**, 1000.
33 S. E. Shadle, J. E. Penner-Hahn, H. J. Schugar, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 1993, **115**, 767.
34 V. Escax, G. Champion, M.-A. Arrio, M. Zacchigna, C. Cartier dit Moulin and A. Bleuzen, *Angew. Chem., Int. Ed.*, 2005, **44**, 2.
35 V. Briois, C. Cartier dit Moulin, P. Sainctavit and A.-M. Flank, *J. Am. Chem. Soc.*, 1995, **117**, 1019.
36 S. Della Longa, A. Bianconi, L. Palladino, B. Simonelli, A. Congiu Castellano, E. Borghi, M. Barteri, M. Beltramini, G. P. Rocco, B. Salvato, L. Bubacco, R. S. Magliozzo and J. Peisach, *Biophys. J.*, 1993, **65**, 2680.
37 F. Champloy, K. Gruber, G. Jogl and C. Kratky, *J. Synchrotron Radiat.*, 2000, **7**, 267.
38 J. Chaboy, A. Munoz-Paez, F. Carrera, P. Merkling and E. Sanchez Marcos, *Phys. Rev. B*, 2005, **71**, 134208.
39 P. Gockel, H. Vahrenkamp and A. D. Zuberbühler, *Helv. Chim. Acta*, 1993, **76**, 511.
40 K. Gajda-Schrantz, A. Jancso, C. Pettinari and T. Gajda, *Dalton Trans.*, 2003, 2912.
41 T. Jakusch, P. Buglyo, A. I. Tomaz, J. Costa Pessoa and T. Kiss, *Inorg. Chim. Acta*, 2002, **339**, 119.
42 Y. Sugiura, Y. Hirayama, H. Tanaka and H. Sakurai, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2367.
43 H. C. Freeman, C. J. Moore, W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 3513.
44 K. Okamoto, H. Umehara, M. Nomoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1709.
45 H. M. Helis, P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, 1977, **99**, 3309.
46 P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, 1977, **99**, 101.
47 K. Okamoto, K. Wakayama, H. Einaga, M. Ohmasa and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3473.
48 T. Kotera, A. Fujita, M. Mikuriya, H. Tsutsumi and M. Handa, *Inorg. Chem. Commun.*, 2003, **6**, 322.
49 R. C. Elder, L. R. Florian, R. E. Lake and A. M. Yacynych, *Inorg. Chem.*, 1973, **12**, 2690.
50 T. Konno, T. Yoshimura and M. Hirotsu, *Acta Crystallogr., Sect. C*, 2001, **57**, 538.
51 K. Okamoto, S. Aizawa, T. Konno, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3859.
52 M. J. Heeg, E. L. Blinn and E. Deutsch, *Inorg. Chem.*, 1985, **24**, 1118.
53 T. Yonemura, K. Okamoto, T. Ama, H. Kawaguchi and T. Yasui, *Chem. Lett.*, 1993, 1123.
54 T. Yonemura, Z.-P. Bai, K. Okamoto, T. Ama, H. Kawagushi, T. Yasui and J. Hidaka, *J. Chem. Soc., Dalton Trans.*, 1999, 2151.
55 M. H. Dickman, R. J. Doedens and E. Deutsch, *Inorg. Chem.*, 1980, **19**, 945.
56 P. de Meester and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, 1976, 618.
57 *Infrared Spectra of Inorganic and Coordination Compounds, Part B*, ed. K. Nakamoto, Wiley Interscience, New York, 1997.
58 T. Konno, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 627, and references cited herein.
59 Y. Miyashita, H. Yoshida, T. Sato, Y. Yamada, K. Fujisawa and K. Okamoto, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1191.
60 T. Yonemura, S. Nakahira, T. Ama, H. Kawaguchi, T. Yasui, K. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2859.
61 S. Aizawa, K. Okamoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1601.
62 S. Konno, K. Aizawa, K. Okamoto and J. Hidaka, *Chem. Lett.*, 1985, 1017.
63 A. J. Tasiopoulos, A. N. Troganis, Y. Deligiannakis, A. Evangelou, T. A. Kabanos, J. D. Woollins and A. Slawin, *J. Inorg. Biochem.*, 2000, **79**, 159.
64 B. Nock, T. Maina, F. Tisato, C. P. Raptopoulou, A. Terzis and E. Chiotellis, *Inorg. Chem.*, 2000, **39**, 5197.
65 N. Baidya, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 1989, **28**, 3426.
66 Y. Sugiura, Y. Hirayama, H. Tanaka and K. Ishizu, *J. Am. Chem. Soc.*, 1975, **97**, 5577.
67 G. Terzian, M. Asso, R. Panossian, M. Guiliano and D. Benlian, *J. Chim. Phys.*, 1982, **79**, 181.
68 M. Filella and D. R. Williams, *Inorg. Chim. Acta*, 1983, **106**, 49.
69 H. Kozlowski, I. Sovago, J. Spychala, J. Urbanska, K. Varnagy, A. Kiss and K. Cherifi, *Polyhedron*, 1990, **9**, 831.
70 I. Sovago and R. B. Martin, *J. Inorg. Nucl. Chem.*, 1981, **43**, 425.
71 M. Scarpellini, A. J. Wu, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 2005, **44**, 5001.
72 Z.-L. Wang, L.-H. Wei and J.-Y. Niu, *Acta Crystallogr., Sect. E*, 2005, **61**, m1907.
73 B. Barszcz, S. A. Hodorowicz, K. Stadnicka and A. Jablonska-Wawrzycka, *Polyhedron*, 2005, **24**, 627.
74 N. Kotsakis, C. P. Raptopoulou, V. Tangoulis, A. Terzis, J. Giapintzakis, T. Jakusch, T. Kiss and A. Salifoglou, *Inorg. Chem.*, 2003, **42**, 22.
75 R. Carballo, A. Castineiras, B. Covelo, E. Garcia-Martinez and E. M. Vazquez-Lopez, *Acta Crystallogr., Sect. E*, 2003, **59**, m588.
76 R. March, W. Clegg, R. A. Coxall and P. Gonzalez-Duarte, *Inorg. Chim. Acta*, 2003, **346**, 87.
77 K. Delany, S. K. Arora and P. K. Mascharak, *Inorg. Chem.*, 1988, **27**, 705.
78 H. Siegel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.
79 C. Jubert, A. Mohamadou, C. Gérard, S. Brandes, A. Tabard and J. P. Barbier, *J. Chem. Soc., Dalton Trans.*, 2002, 2660.