Open-shell nitrene- and carbene-complexes of cobalt

Characterisation and reactivity

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Chapter 3

Geometry and spectroscopic metal oxidation state of mono- and bis-nitrene radical complexes based on the cobalt-porphyrin platform; An X-ray Absorption Spectroscopy (XAS) study.*

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Introduction

In the previous chapter the electronic structure of the porphyrin-Cobalt(III)-‘nitrene radical’ was fully described. They are the reactive intermediates in the various nitrene transfer reactions catalysed by cobalt(II) porphyrins. By combining different nitrene transfer reagents together with cobalt(II) porphyrins and probing the thus obtained reaction mixtures with different spectroscopic techniques (EPR, UV-vis and UHR-ESI-MS), we could confirm the formation of porphyrin-cobalt(III)-‘nitrene radicals’. Depending on the type of the nitrene transfer reagent, two different types of nitrene radical species were observed. For the milder reagents like organic azides mono-nitrene species were formed with a single nitrene radical attached to the central cobalt atom of the cobalt porphyrin. On the other hand upon using more oxidising nitrene transfer reagents like the N-nosyl iminoiodane (PhI=NNs) bis-nitrene species with two nitrene radicals attached to cobalt were formed. The first nitrene radical is formed due to formal oxidation of cobalt from +II to +III. Conversion of the mono-nitrene species to the bis-nitrene species is associated with a second oxidation step. This second oxidation takes place on the porphyrin ligand leading to a porphyrin cation radical. The species on the whole, thus, has three unpaired electrons of which two are anti-ferromagnetically coupled. As a result, just as the mononitrene system the bis-nitrene also was a spin=1/2 system. All the spectroscopic techniques used thus far helped us describe the electronic structures of these intermediates in great detail, but did not give us any information about their geometry, nor any direct spectroscopic evidence for the cobalt(III) oxidation state of the metal in these complexes. X-ray absorption spectroscopy (XAS) studies can be used to gain this information. A further question one might ask is, whether or not the mono-nitrene complex has an additional ligand Y (in case of the mono-nitrene) and if so, what is the nature of that ligand. While the coordination geometry of the bis-nitrene species is expected to be octahedral (6-coordinate), the geometry of the mono-nitrene species is less clear. In the absence of X-ray structures of these intermediates, these questions are not easily answered. To shine more light on this matter, the coordination geometry of the intermediates was probed by the aid of X-ray Absorption Spectroscopy (XAS). Detailed analysis of the features in the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) could help us pin-point the coordination mode of these two types of nitrene-radical species.

Figure 1. Left: The mono-nitrene species of the type obtained from and organic azide . Right: The six-coordinate bis-nitrene species obtained from and N-nosyl-iminoiodane .
Results and discussion

For the XAS studies, samples were prepared in Mössbauer/XAS cups made from Delrin® and the window side was sealed with Kapton® tape. All probes were made in benzene solution with a concentration of 10 mM and immediately frozen and stored at 77 K when the desired intermediate was formed in maximum yield, following reaction kinetics previously investigated by UV/vis and EPR spectroscopy. The temperature was kept below the melting point during storage and transfer. A He Displex cryostat was used for temperature control during the measurement, with typical sample temperatures of ~20K. Data were collected as fluorescence spectra using a 31 element solid-state Ge detector (Canberra), over an energy range of 7508 – 8328 eV (k ~ 12 Å⁻¹). Each scan required approximately 40 minutes. A Co foil spectrum was collected simultaneously using a PMT for energy calibration; the first inflection point of the metal foil reference was set to 7709 eV.

The thus obtained XANES of species 3⁰¹Ns and 5⁰¹Ns (Figure 1) are shown in Figure 2. Electronically the XANES was in excellent agreement with the electronic structures proposed thus far using other complimentary spectroscopic techniques (EPR, UV-vis and UHR-ESI-MS spectroscopy) as described in Chapter 2. The XANES part of the XAS spectra showed pre-edge signals corresponding to cobalt(III) species for both mono- and bis-nitrene species. This is in line with other experimental data (see Chapter 2 of this thesis). The starting [Co²⁺(TPP)] complex 1⁰¹ exhibited an edge inflection energy of ca. 7720.7 eV. A shoulder feature along the rising edge at 7715.4 eV corresponds to a 1s to 4p + LMCT shakedown transition, in accord with the observed 4-coordinate square planar structure of this complex. This transition is strongest in 4-coordinate square planar Co complexes, but is also observed in 5-coordinate square pyramidal geometries (it is not present in either Td or Oh geometries). Finally, a broad 1s to 3d pre-edge peak was observed at 7708.9 eV, with preliminary peak fitting analysis indicating a peak area of approximately 8.1 units. The energies of the edge and 1s→3d pre-edge transitions are in accord with the reported values for other cobalt(II) complexes.¹

![Figure 2. K-pre edge XAS data of 1⁰¹ ([Co²⁺(TPP)], green), 3⁰¹Ns (mono-nitrene, blue) and 5⁰¹Ns (bis-nitrene, red).](image-url)
The XANES of \(5^{\text{P1}}_{\text{Ns}}\) showed a +1.9 eV blue-shift of the edge inflection energy to 7722.56 eV, relative to complex \(1^{\text{P1}}\), supporting metal-centred oxidation from cobalt(II) to cobalt(III). The 1s→3d pre-edge transition was also blue-shifted by −1.0 eV to 7710.2 eV and the pre-edge increased in intensity (peak-area of 12.0 units). Most notably, \(5^{\text{P1}}_{\text{Ns}}\) lacks the diagnostic 1s→4p (+ LMCT shakedown) transition shoulder on the rising edge, providing strong evidence for a 6-coordinate \(O_h\) cobalt site. Finally, the XANES data on \(3^{\text{P1}}_{\text{Ns}}\) revealed the existence of edge and 1s→3d pre-edge transitions at nearly identical positions (7722.8 and 7710.2 eV, respectively) relative to \(5^{\text{P1}}_{\text{Ns}}\). Again no clear 1s to 4p + LMCT shakedown transition seems to be visible, suggesting that also \(3^{\text{P1}}_{\text{Ns}}\) is 6-coordinate. However, this transition could also be hidden underneath the rising edge and as such we cannot fully exclude this species being 5-coordinate. Comparison of experimental and TD-DFT calculated (Orca) K-edge XAS data of of 5-coordinate mono-nitrene \(3^{\text{P1}}_{\text{Ns}}\) and 6-coordinate bis-nitrene \(5^{\text{P1}}_{\text{Ns}}\) showed this discrepancy in the K-edge XAS data. The mono-nitrene species is predicted to have a higher intensity band at 7712 eV, which is missing in the experimental spectrum of the mono-nitrene species.

Consequently, this initially led us to believe that a sixth ligand binds to the mono-nitrene species, trans to the nitrene radical moiety. This ligand was so far not detected using EPR, UV-vis and UHR-ESI-MS. As such we wondered if a 6th ligand is really bound to \(3^{\text{P1}}_{\text{Ns}}\) or not, and if so what is the nature of this ligand. In an attempt to gain more information about this assumed 6th ligand, we decided to take up more DFT calculations to simulate the XANES part of the XAS spectra. Initially, we considered coordination of a neutral unreacted nosyl azide ligand under the conditions of the EXAFS measurements. However, DFT geometry optimizations and calculation of the Co K–edge features of the optimized structures with DFT methods revealed that such nosyl azide species have too long Co–N distances to explain the experimental XAS data. The same holds for the aqua adduct of \(3^{\text{P1}}_{\text{Ns}}\). The Ns-NH\(_2\) amine and ammonia (NH\(_3\)) adducts of \(3^{\text{P1}}_{\text{Ns}}\) have shorter Co–N bond distances, which substantially decreases the calculated intensity of the pre-edge transitions in the Co K–edge region.

\[\text{Figure 3. Comparison of experimental data (solid lines) and TD-DFT calculated (Orca) K-edge XAS data (dotted lines) of 5-coordinate mono-nitrene } 3^{\text{P1}}_{\text{Ns}} \text{ (blue) and 6-coordinate bis-nitrene } 5^{\text{P1}}_{\text{Ns}} \text{ (red).} \]
Figure 4. TD-DFT calculated (Orca) K-edge XAS data comparing five-coordinate mono-nitrene $3^{P1}_{Ns}$ with six-coordinate bis-nitrene $5^{P1}_{Ns}$ and some six-coordinate adducts of mono-nitrene $3^{P1}_{Ns}$ based on possible neutral ligands $NsN_3$, $H_2O$, $NsNH_2$, and $NH_3$. 
Figure 5. TD-DFT calculated (Orca) K-edge XAS data comparing five-coordinate mono-nitrene $3^{\pi}_{Ns}$ with six-coordinate bis-nitrene $5^{\pi}_{Ns}$ and some six-coordinate adducts of mono-nitrene $3^{\pi}_{Ns}$ based on plausible anionic ligands $N\textsubscript{3}^{-}$, $O\textsubscript{H}^{-}$, $Ns(NH)^{-}$, and $NH_{2}^{-}$.

The best agreement between the calculated and experimental pre-edge intensities seems, however, to be obtained for anionic ligand adducts of mono-nitrene $3^{\pi}_{Ns}$. The optimized geometries of $NsNH^{-}$, $NH_{2}^{-}$ and $OH^{-}$ adducts of $3^{\pi}_{Ns}$ species have comparable Co–N and Co–X distances for the nitrene radical ligand and the 6th ligand $L_2$ (Figure 2), respectively. Hence, similar pre-edge intensities are also computed as obtained for bis-nitrene species $5^{\pi}_{Ns}$. Considering the detection of the Na$^+$ adduct of NO$_2$PhSO$_2$NHD as mentioned earlier in the ESI-MS studies in combination with the abovementioned calculated pre-edge intensities, the $NsNH^{-}$ amido ligand is a likely candidate occupying the sixth coordination site of the mono-nitrene species. Notably, the DFT calculated geometrical parameters for $3^{\pi}_{Ns}(NsNH^{-})$ is in reasonable agreement with the EXAFS data (see additional information Table 3). This would mean, however, that $3^{\pi}_{Ns}$ is anionic (perhaps containing an $NsNH_{2}^{+}$ counter ion). Formation of such a charged species in benzene is unexpected, and as such we cannot exclude the 6th ligand being the neutral $NsNH_{2}$ amine donor (despite a better agreement between the calculated and experimental XAS pre-edge intensities for the $NsNH^{-}$ amido ligand). It is further worth mentioning that
this sixth ligand $L_2$ does not prevent conversion of mono-nitrene species $3^{P_1}_{Ns}$ to bis-nitrene species $5^{P_1}_{Ns}$ upon treatment with the strongly oxidizing $N$-nosyl iminoiodane $4_{Ns}$. On adding an excess of $4_{Ns}$ to a solution of previously formed mono-nitrene species $3^{P_1}_{Ns}$, clear EPR signals corresponding to bis-nitrene species $5^{P_1}_{Ns}$ appeared, once again displaying the strongly oxidizing nature of $N$-nosyl iminoiodane. Apparently, the ligand $L_2$ can be replaced or converted to a nosyl nitrene radical moiety upon reaction of mono-nitrene $3^{P_1}_{Ns}$ with iminoiodane $4_{Ns}$. At this point, purely looking at the intensity of the DFT simulated XANES spectra of various contenders an anionic ligand seemed to be a more plausible candidate for the 6th ligand. These were ligands like $NH_2$, $OH$ or the $NsNH^-$. Because, we detected the mass of the corresponding amine for the azide during all mass measurements, we initially proposed this sixth ligand to be the anionic ligand $NsNH^-$. However, considering the ionic nature of such species, formation of which we considered rather unlikely in the apolar solvent benzene used in both these experiments and in catalysis, we started to reconsider our initial interpretations. Hence, as a follow-up of these studies we decided to perform XAS on two other very related and well-defined neutral cobalt(III) complexes. These were $[Co^{II}(TPP)(Cl)]$ and $[Co^{II}(TPP)(CF_3)]$. From the crystal structure ($[Co^{III}(TPP)(CF_3)]^3$ and X-ray powder diffraction studies ($[Co^{II}(TPP)(Cl)]$) (see Figure 14, additional information) we could confirm the geometry of these two complexes. Both of these complexes are five-coordinate with no axial ligand occupying the 6th position. Thus, pre-edge X-ray absorption features (XANES) of these complexes would give us a more realistic picture of how much the intensities of these transitions are affected by the geometry of the complexes. Based on the conclusions we drew from the observations with the nitrene radical species, these two new five-coordinate species should display distinct Co K-edge features. The corresponding experimental spectra are shown in Figure 6.

Once again, the two complexes were ascertained to be cobalt(III) complexes, but with different pre-edge intensities with respect to each other. The $[Co^{II}(TPP)(CF_3)]$ showed a higher intensity of the diagnostic pre-edge feature compared to the coordinative identical $[Co^{III}(TPP)(Cl)]$ complex. More interestingly, the definite five-coordinate $[Co^{III}(TPP)(Cl)]$ actually displays a weak pre-edge intensity, of almost comparable low intensity as that of the previously measured mono-nitrene species (which was so far considered to be six-coordinate). Apparently, π-donor ligands like $Cl^-$ (and nitrene/imido ligands) lower the intensity, even for 5-coordinate species. σ-donating ligands like $CF_3$ give rise to higher pre-edge intensities. This prompted us to also calculate these intensities using ORCA as we did for the various mono-nitrene complexes. The results are shown in Figure 7.
Figure 6. Experimental XANES spectra of the five-coordinate $[\text{Co}^{III}(\text{TPP})(\text{Cl})]$ and $[\text{Co}^{III}(\text{TPP})(\text{CF}_3)]$ complexes overlaid also with the experimental spectra of the mono-nitrene species $3^{p1}_{Ns}$.

Figure 7. TD-DFT calculated (Orca) K-edge XANES data comparing the five-coordinate mono-nitrene species $3^{p1}_{Ns}$, $[\text{Co}^{III}(\text{TPP})(\text{Cl})]$ and $[\text{Co}^{III}(\text{TPP})(\text{CF}_3)]$ and some of their adducts with neutral ligands.
Figure 8. Some six-coordinate adducts of [Co\textsuperscript{II}(TPP)](CI) and [Co\textsuperscript{III}(TPP)](CF\textsubscript{3}) based on a plausible neutral ligand like H\textsubscript{2}O.

Analysis of the transitions that give rise to the observed bands showed that in the [Co\textsuperscript{III}(TPP)](CI) complex, the pre-edge is the lowest energy transition at ~7694 eV. This arises from a core-to-valence d-shell transition (transition to d\textsubscript{z\textsuperscript{2}}, with some mixing with the p\textsubscript{z} orbital). The second band at ~7704 eV has contributions from transitions between the core 1s orbitals to the \pi* orbitals of the porphyrin ring. The metal valence d-orbitals and the 4p-orbitals seem to play a minor role in all of these transitions. This could well be caused by lowering the symmetry on going from 4- to 5-coordination, leading to stronger mixing of the p/d-orbitals with the porphyrin \pi* orbitals. As mentioned above, this second band could well be hidden underneath the rising edge in the experimental spectra (both for the 5- and 6-coordinate complexes). Thus, unlike the [Co\textsuperscript{II}(TPP)] complex, for the [Co\textsuperscript{III}(TPP)](CI) complex the pre-edge does not seem to be a pure 1s to 4p + LMCT shakedown transition. So while for the 4-coordinated [Co\textsuperscript{II}(TPP)] the band at ~7702 eV has a major contribution from a "1s to 4p" transition, the band at ~7702 eV is in fact constructed from a collection of transitions, some of them being a transition from the core 1s orbital to a porphyrin ring \pi* orbital, with minor involvement of metal d- or p-orbitals.

The very weak pre-edge band at ~7694 eV computed for [Co\textsuperscript{II}(TPP)] is again dominated by 1s-to-metal-d-orbital transitions, but it now involves the d\textsubscript{z\textsuperscript{2}-\gamma\textsuperscript{2}} orbital instead of the d\textsubscript{z\textsuperscript{2}} orbital. This is in line with the fact that the only completely empty d-orbital in this complex is the d\textsubscript{z\textsuperscript{2}-\gamma\textsuperscript{2}} orbital. The p-d mixing in the d\textsubscript{z\textsuperscript{2}-\gamma\textsuperscript{2}} orbital can be expected to be small in the square planar [Co\textsuperscript{II}(TPP)]. Such mixing becomes much stronger for the d\textsubscript{z\textsuperscript{2}}-orbital of 5-coordinate complexes like [Co\textsuperscript{III}(TPP)](CI) and [Co\textsuperscript{III}(TPP)](CF\textsubscript{3}). Hence, this leads to an increase in the pre-edge intensity. For the 6-coordinate complex this intensity drops as compared to a 5-coordinate complex, but not so much as in the case of with an empty d\textsubscript{z\textsuperscript{2}} orbital. In this case the empty d\textsubscript{z\textsuperscript{2}} involved must always be quite strongly mixed with the 4p\textsubscript{z} (and the 4s) orbital (to even allow the binding of a 5\textsuperscript{th} or 6\textsuperscript{th} donor to the axial position). So the intensity remains relatively strong compared to the 4-coordinate cobalt(II) complex [Co\textsuperscript{II}(TPP)]. Additionally, the drop in intensity of the second band for the 5-coordinate complexes can also be reasoned based on the fact that on going from 4-coordination to 5-coordination, due to a change in symmetry, the 1s-to-4p transition is mostly removed but transitions from the core 1s orbitals to the \pi* orbitals of the porphyrin ring still remain.
On comparing the experimental pre-edge (~7694 eV) intensities of the 5-coordinate chlorido complex [CoIII(TPP)(Cl)] with that of the mono-nitrene species 3\(^{+}\)\(Ns\), one could perhaps conclude that the latter is also 5-coordinate. However, the DFT computed pre-edge intensities of [CoIII(TPP)(Cl)] and 3\(^{+}\)\(Ns\) do not match up, with [CoIII(TPP)(Cl)] having a much lower intensity than the 5-coordinate 3\(^{+}\)\(Ns\) (factor 3 roughly). The computed intensity of 6-coordinate 3\(^{+}\)\(Ns\) with a neutral NH:Ns amine donor at the 6\(^{th}\) coordination site, however, closely matches that of [CoIII(TPP)(Cl)]. Based on this DFT comparison, and experimental detection of NH:Ns in the catalytic reaction mixtures, we are tempted to conclude that 3\(^{+}\)\(Ns\) is indeed a 6-coordinate species, but with a neutral NH:Ns donor coordinated rather to cobalt(III) than an anionic NsNH\(^{+}\) ligand.

Summary and conclusions

Based on the XAS data on the cobalt(III) complexes [CoIII(TPP)(Cl)] and [CoIII(TPP)(CF\(_3\))] presented in this chapter it can be concluded that the relative intensities of the XANES features cannot always be straightforwardly correlated to the coordination numbers around the metal centre. The use of XANES as a diagnostic tool to distinguish reliably between 5- and 6-coordinate [CoIII(Por)] species is complicated by several contributing factors. Pre-edge intensities are influenced by \(\pi\)-donation and higher energy transitions (in all cases) between 7713-7720 eV are not purely 1s to 4p + LMCT shakedown transitions, but largely 1s to porphyrin \(\pi^*\) transitions for many of the [CoIII(Por)] species. Furthermore, these transitions can be hidden underneath the rising edge. While for the mono-nitrene species the absence of a shakedown transition and the weak pre-edge intensity initially led us to believe that an anionic donor binds to the 6\(^{th}\) coordination site of 3\(^{+}\)\(Ns\), it is now safe to conclude that this is not the case. This is also in line with the experimental observations from catalysis, where reactions are performed in apolar solvents and the use of additives does not have a dramatic effect in nitrene-transfer reactions catalysed by cobalt(II) porphyrins.\(^4\) The sixth ligand in the mono-nitrene species is therefore most likely a neutral amine donor (derived from the azide), rather than an anionic (amido) ligand.

Supporting information, experimental and computational details

- **EXAFS analysis of** [CoI(TPP)] 1\(^{+}\), mono-nitrene 3\(^{+}\)\(Ns\), bis-nitrene 5\(^{+}\)\(Ns\), [CoI(TPP)(Cl)] and [CoI(TPP)(CF\(_3\))]\(^5\)

Extended X-ray absorption fine structure (EXAFS) analysis revealed further structural details (Figure 10, Figure 9, Table 1, Table 3, Table 4, Table 2). For complex 5\(^{+}\)\(Ns\), the first coordination sphere could be satisfactorily fitted by considering six N/O scatterers at a distance of 1.92 Å (Table 1). Although the additional outer-shell features could be satisfactorily accounted for by considering single scattering paths involving 8 carbons at 2.94 Å, 12 carbons at 3.35 Å, and 4 oxygen donors at 3.57 Å distance from cobalt, the fit could be significantly improved by introducing multiple-scattering pathways. The best fit for 5\(^{+}\)\(Ns\) is represented by fit 12 in Table 2 and Figure 9B. It is important to note that efforts were also made to include the effect of the sulfur scatterers originating from the two –NNs units. However, all fits (fits 9-11 in Table 1) including any kind of S-shell showed negative Debye-Waller factors in the fit parameters; and hence they were not considered in the fitting procedure.

Interestingly, consistent with the XANES data, our attempts to do a set of fits for a back transformation range limited to the first shell (\(r = 0.8 - 2.1\) Å) for 3\(^{+}\)\(Ns\) also pointed to a 6-coordinate geometry (fits 1-3; Table 2). This was thus far not identified based on the other spectroscopic techniques. The best fit to the data of the mono-nitrene species requires six N/O scatterers at ~1.95 Å distance from the
cobalt(III) centre, which is slightly longer (although almost identical within the error of measurements) than the Co–N distance of 1.92 Å obtained from the EXAFS data of bis-nitrene species $5^{P_1}_{Ns}$.

**Figure 9.** Overlaid Fourier transform EXAFS spectra for $1^{P_1}$, $3^{P_1}_{Ns}$ and $5^{P_1}_{Ns}$. All spectra are weighted by $k^3$.

**Table 1.** Summary of comparison of the EXAFS determined metrical parameters (for the first three shells) of $3^{P_1}_{Ns}$ and $5^{P_1}_{Ns}$ with that of the DFT calculated values for $3^{P_1}_{Ns}$($Ns$-$NH^-$), $3^{P_1}_{Ns}$($Ns$-$NH_2$) and $3^{P_1}_{Ns}$.

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**Figure 10.** A) XANES of [Co$^{II}$TPP] (red), $3^{P_1}_{Ns}$ (green) and $5^{P_1}_{Ns}$ (blue). Spectra are referenced to the first inflection point of a cobalt reference foil set to 7709.0 eV. B) Fourier transform EXAFS spectra of $5^{P_1}_{Ns}$ (dotted line) and the best fit (red line); the inset shows the EXAFS data on a wave vector scale weighted by $k^3$ with respective representation. C) Fourier transform EXAFS spectra of $3^{P_1}_{Ns}$ (dotted line) and the best fit (red line); the inset shows the EXAFS data on a wave vector scale weighted by $k^3$ with respective representation.
**Table 2.** Summary of the EXAFS fitting for [Co\(^n\)(TPP)]\(^1\). The best fit for the date (fit 9) is represented in bold. \(r\) is in units of Å; \(\sigma^2\) is in units of \(10^{-3}\) Å; \(\Delta E_0\) is in units of eV; R-factor represents the GOF. Fourier transform range: \(k\) 1.5-5.0 Å\(^{-1}\). The fit was optimized in \(R\) space with a \(k\)-weight of 3. The fitting range is 0.8-4.0 Å for fits 1-4 and 0.8-5.0 for fits 5-11.

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</tr>
<tr>
<td>10</td>
<td>0.042</td>
<td>-0.62</td>
<td>6  1.93 2.9</td>
<td>8  2.93 0.8</td>
<td>12  3.25 0.4</td>
<td>4  4.03 2.6</td>
<td>2  3.19 -2.9</td>
<td>16  4.19 2.7</td>
<td>32  4.52 23.3</td>
<td>24  4.77 8.8</td>
</tr>
<tr>
<td>11</td>
<td>0.052</td>
<td>-1.53</td>
<td>6  1.92 3.0</td>
<td>8  2.94 4.3</td>
<td>12  3.32 9.6</td>
<td>2  5.30 -3.8</td>
<td>1  3.73 -0.1</td>
<td>16  4.19 11.2</td>
<td>32  4.57 7.7</td>
<td>24  4.78 6.4</td>
</tr>
<tr>
<td>12</td>
<td>0.048</td>
<td>-1.21</td>
<td>6  1.92 3.0</td>
<td>8  2.94 4.5</td>
<td>12  3.35 8.7</td>
<td>4  3.57 2.2</td>
<td></td>
<td></td>
<td>16  4.23 9.4</td>
<td>32  4.55 6.1</td>
</tr>
</tbody>
</table>

* multiscattering (2 legs) with a degeneracy of 2 for the shown paths and untreated \(\sigma^2\) values.

* smaller fitting range

**Table 3:** Summary of EXAFS fitting for 5\(^{2}\). Bold line represents the best fit for the system (fit 12). \(r\) is in units of Å; \(\sigma^2\) is in units of \(10^{-3}\) Å; \(\Delta E_0\) is in units of eV; R-factor represents the GOF. Fourier transform range: \(k\) 1.5-5.0 Å\(^{-1}\). The fit was optimized in \(R\) space with a \(k\)-weight of 3. The fitting range is 0.8-2.1 Å for fits 1-2 and 0.8-4.8 for fits 3-11.

<table>
<thead>
<tr>
<th>fit</th>
<th>R-factor</th>
<th>(\Delta E_0)</th>
<th>Co-N/C</th>
<th>Co-C·N</th>
<th>Co-...C/N</th>
<th>Co-...C/N</th>
<th>Co-...C/N</th>
<th>Co-...C/N</th>
<th>Co-...C/N</th>
<th>Co-...C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>0.311</td>
<td>-3.09</td>
<td>4  1.93 1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2'</td>
<td>0.136</td>
<td>0.20</td>
<td>4  1.94 1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3'</td>
<td>0.105</td>
<td>-1.01</td>
<td>4  1.94 1.7</td>
<td>8  2.97 2.7</td>
<td>4  3.32 2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4'</td>
<td>0.062</td>
<td>-0.75</td>
<td>4  1.94 1.8</td>
<td>8  2.97 2.9</td>
<td>4  3.33 1.8</td>
<td>8  4.31 1.4</td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>0.832</td>
<td>-0.78</td>
<td>4  1.94 1.8</td>
<td>8  2.97 2.9</td>
<td>4  3.33 2.0</td>
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<td>8  2.98 2.8</td>
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<td></td>
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</tr>
<tr>
<td>7</td>
<td>0.062</td>
<td>-0.27</td>
<td>4  1.94 1.8</td>
<td>8  2.98 2.9</td>
<td>4  3.32 2.0</td>
<td>8  4.11 4.9</td>
<td>4  4.93 -2.8</td>
<td>16  4.22 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
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<td>8  2.98 2.7</td>
<td>4  3.32 2.4</td>
<td>8  4.15 8.2</td>
<td>4  4.93 -2.5</td>
<td>12  4.24 3.1</td>
<td>32  3.99 54.3</td>
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</tr>
<tr>
<td>9</td>
<td>0.057</td>
<td>0.10</td>
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<td>8  2.98 2.7</td>
<td>4  3.32 2.6</td>
<td>12  4.92 2.7</td>
<td></td>
<td></td>
<td>12  4.24 5.0</td>
<td>32  4.03 33.0</td>
</tr>
</tbody>
</table>
**Table 4. Summary of EXAFS fitting for 3'^{2}Ne. Bold line represents the best fit for the system (fit 10).** \( r \) is in units of Å; \( \sigma^2 \) is in units of \( 10^{-3} \) Å; \( \Delta E_0 \) is in units of eV; R-factor represents the GOF. Fourier transform range: \( k \) 1.5-5.0 Å\(^{-1} \). The fit was optimized in R space with a \( k \)-weight of 3. The fitting range is 0.8-2.1 for fits 1-3 and 1.2-5.0 for fits 4-11.

<table>
<thead>
<tr>
<th>fit</th>
<th>R-factor</th>
<th>( \Delta E_0 )</th>
<th>Co-N/C</th>
<th>Co···C/N</th>
<th>Co···C/N</th>
<th>Co···O/N</th>
<th>Co···C/N *</th>
<th>Co···N···C *</th>
<th>Co···C···C *</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>n</td>
<td>r</td>
<td>( \sigma^2 )</td>
<td>n</td>
<td>r</td>
<td>( \sigma^2 )</td>
<td>n</td>
</tr>
<tr>
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<td>3.40</td>
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<td>1.95</td>
<td>1.5</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>5</td>
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<td>2.7</td>
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<td></td>
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<tr>
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<td>6</td>
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<td>6</td>
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<td>6.2</td>
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<td>1.95</td>
<td>3.7</td>
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<td>6.5</td>
<td>12</td>
</tr>
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<td>0.037</td>
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<td>6</td>
<td>1.95</td>
<td>3.7</td>
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</tr>
<tr>
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<td>3.6</td>
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<td>12</td>
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<td>8</td>
<td>3.00</td>
<td>6.6</td>
<td>12</td>
</tr>
</tbody>
</table>

* multiscattering (2 legs) with a degeneracy of 2 for the shown paths and untreated \( \sigma^2 \) values.

' smaller fitting range

**Figure 11.** \( k^2 \)-weighted FT of the Co K edge EXAFS data and best fit of \([\text{Co}^{III}(\text{TPP})(\text{CF}_3)]) \) (not phase corrected). Fitting was optimized for all \( k \)-weights (1-3). The inset shows the data and best fit in \( k \)-space, and presented in \( k \) space with a weighting of 3.
Table 5. Summary table of the EXAFS fitting parameters for \([\text{Co}^{III}(\text{TPP})\text{(CF}_3)]\). Fitting parameters; \(S_0^2=0.81\) (as determined by a Co foil standard), \(\Delta E_0 = +1.27\). Fitting range; \(3 < k < 14, 1 < R < 4.9\). The final \(R\)-factor was 0.031. Single scattering paths are shown in bold.

<table>
<thead>
<tr>
<th>Scattering path (path indicator, see Figure 12)</th>
<th>N</th>
<th>(\sigma^2) (Å(^2))</th>
<th>(\Delta R) (Å)</th>
<th>(R_{\text{eff}}) (Å)</th>
<th>(R_{\text{fitted}}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N</td>
<td>4</td>
<td>0.0021</td>
<td>-0.018</td>
<td>1.963</td>
<td>1.945</td>
</tr>
<tr>
<td>Co-C (CF3)</td>
<td>1</td>
<td>0.0020</td>
<td>0.179</td>
<td>1.896</td>
<td>2.075</td>
</tr>
<tr>
<td>Co-F</td>
<td>3</td>
<td>0.0025</td>
<td>0.034</td>
<td>2.734</td>
<td>2.767</td>
</tr>
<tr>
<td>Co-C (C14.1)</td>
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<td>0.0020</td>
<td>-0.004</td>
<td>3.001</td>
<td>2.997</td>
</tr>
<tr>
<td>Co-N-C (N1.1 C4.1)</td>
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<td>0.0031</td>
<td>-0.041</td>
<td>3.171</td>
<td>3.130</td>
</tr>
<tr>
<td>Co-C (C20.1)</td>
<td>4</td>
<td>0.0020</td>
<td>-0.019</td>
<td>3.424</td>
<td>3.405</td>
</tr>
<tr>
<td>Co-C (C19.1 C20.1)</td>
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<td>0.0020</td>
<td>0.029</td>
<td>3.908</td>
<td>3.937</td>
</tr>
<tr>
<td>Co-C (C5.2)</td>
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<td>0.060</td>
<td>4.203</td>
<td>4.263</td>
</tr>
<tr>
<td>Co-N-C (N1.1 C3.1)</td>
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<td>0.0031</td>
<td>0.091</td>
<td>4.241</td>
<td>4.332</td>
</tr>
<tr>
<td>Co-C-C (C19.1 C18.1)</td>
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<td>0.0020</td>
<td>0.014</td>
<td>4.317</td>
<td>4.331</td>
</tr>
<tr>
<td>Co-C (C33.1)</td>
<td>4</td>
<td>0.0020</td>
<td>-0.006</td>
<td>4.915</td>
<td>4.909</td>
</tr>
</tbody>
</table>
Figure 13. $k^3$-weighted FT of the Co K edge EXAFS data and best fit of [Co$^{III}$TPP](Cl) (not phase corrected). Fitting was optimized for all $k$-weights (1-3). The inset shows the data and best fit in $k$-space, and presented in $k$ space with a weighting of 3.

Table 6. Summary table of the EXAFS fitting parameters for [Co$^{III}$TPP](Cl). Fitting parameters; $S_0^2=0.81$ (as determined by a Co foil standard), $\Delta E_0 = -0.16$. Fitting range; $3 < k < 14, 1 < R < 4.9$. The final R-factor was 0.022. Single scattering paths are shown in bold.

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>$\sigma^2$ ($\text{Å}^2$)</th>
<th>$\Delta R$ (Å)</th>
<th>$R_{\text{eff}}$ (Å)</th>
<th>$R_{\text{fitted}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N</td>
<td>4</td>
<td>0.0011</td>
<td>0.003</td>
<td>1.963</td>
<td>1.966</td>
</tr>
<tr>
<td>Co-Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-C (C14.1)</td>
<td>8</td>
<td>0.0024</td>
<td>0.000</td>
<td>3.001</td>
<td>3.002</td>
</tr>
<tr>
<td>Co-N-C (N1.1 C4.1)</td>
<td>16</td>
<td>0.0017</td>
<td>0.006</td>
<td>3.171</td>
<td>3.177</td>
</tr>
<tr>
<td>Co-N-C-N (N4.1 C19.1 N4)</td>
<td>8</td>
<td>0.0046</td>
<td>-0.131</td>
<td>3.337</td>
<td>3.206</td>
</tr>
<tr>
<td>Co-C (C20.1)</td>
<td>4</td>
<td>0.0024</td>
<td>-0.012</td>
<td>3.424</td>
<td>3.412</td>
</tr>
<tr>
<td>Co-C-C (C19.1 C20.1)</td>
<td>14</td>
<td>0.0024</td>
<td>-0.002</td>
<td>3.908</td>
<td>3.906</td>
</tr>
<tr>
<td>Co-C-C (C19.1 C18.1)</td>
<td>12</td>
<td>0.0024</td>
<td>-0.183</td>
<td>4.317</td>
<td>4.134</td>
</tr>
<tr>
<td>Co-N-C (N1.1 C3.1)</td>
<td>10</td>
<td>0.0023</td>
<td>0.012</td>
<td>4.241</td>
<td>4.253</td>
</tr>
<tr>
<td>Co-C (C5.2)</td>
<td>6</td>
<td>0.0024</td>
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<td>4.376</td>
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<td>Co-C (C33.1)</td>
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<td>0.0024</td>
<td>-0.018</td>
<td>4.915</td>
<td>4.897</td>
</tr>
</tbody>
</table>
- Powder XRD data of [CoIII(TPP)(Cl)] sample used for XAS experiments

![Figure 14](image-url)

**Figure 14.** Powder XRD obtained for the sample of [CoIII(TPP)(Cl)] used for the XAS measurements.

- Experimental and computational details

For samples 1P1, 3P1, and 5P1Ns, XAS measurements were performed on NSLS X3B, which is equipped with a sagitally focusing Si(111) double-crystal monochromator and a post-monochromator Ni-coated harmonic rejection mirror. Note that while the Ni mirror was in the beampath during data collection, metallic Ni contamination is not significant based on measurement of an experimental blank spectrum. Hence Cobalt EXAFS could only be collected up to the Nickel K-edge energy. The samples were prepared in Mössbauer/XAS cups made from Delrin® and the window side was sealed with Kapton tape. All probes were made in benzene solution with a concentration of 10 mM and immediately frozen and stored at 77 K when the desired intermediate was formed in maximum yield, following reaction kinetics previously investigated by UV/vis and EPR spectroscopy. The temperature was kept below the melting point for storage period and transfer. A He Displex cryostat was used for temperature control during the measurement, with typical sample temperatures of ~20 K. Data were collected as fluorescence spectra using a 31 element solid-state Ge detector (Canberra), over an energy range of 7508 – 8328 eV (k ~ 12 Å⁻¹). Each scan required approximately 40 minutes. A Co foil spectrum was collected simultaneously using a PMT for energy calibration; the first inflection point of the metal foil reference was set to 7709 eV.

For the two subsequent complexes, [CoIII(TPP)(Cl)] and [CoIII(TPP)(CF₃)], XAS measurements were performed at B18 (Diamond Light Source, beamtime SP15305-1), using a Si(111) crystal monochromator with Pt harmonic rejection mirrors. Samples were in powder form and sealed between two pieces of 13 micron Kapton® foil, and measured at room temperature as fluorescence spectra using a 36 element solid state Ge detector. Spectra was collected up to k=14 Å⁻¹, and averaged over at least 20 scans, with a total time per sample of 40 minutes. All spectra were referenced to a Co foil (EXAFS Materials), with the first peak in the first derivative set to 7709 eV.
Data averaging and processing (including background subtraction etc) was carried out using Athena from the ifeffit/Demeter package. Reference spectra for individual scans were carefully aligned to ensure that the energy scale was identical for all spectra. Sets of scans at each spot were examined for photo-reduction effects. No evidence for photo-reduction was observed based upon edge energies or spectral changes although slight burn marks were visible after the measurement.

EXAFS analysis and fitting was performed with Artemis from the ifeffit package and FEFF. The fitting process is summarized in tables for each sample showing the major fitting parameters. The goodness of the fit (GOF) is represented by the R-factor (value from ifeffit package) which is defined by

\[ R = \sum \left( \frac{\chi_{\text{dat}}(R_i) - \chi_{\text{th}}(R_i)}{(\chi_{\text{dat}}(R_i))} \right)^2. \]

Geometry optimizations were carried out with the Turbomole program package\(^6\) coupled to the PQS Baker optimizer\(^7\) via the BOpt package\(^8\) at the DFT level using the b3-lyp functional\(^9\) and def(2)-TZVP basis set\(^10\) for the geometry optimizations of all stationary points. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerically calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated.

XAS Co K-edge absorption parameters of complex \(5\,^{3}\text{P}_{1}\,^{3}\text{Ns}\), five coordinate \(3\,^{3}\text{P}_{1}\,^{3}\text{Ns}\) and several ligand adducts of \(3\,^{3}\text{P}_{1}\,^{3}\text{Ns}\) were calculated with ORCA\(^11\) using geometries obtained from Turbomole optimizations [BP86/def2-TZVP\(^9\) using Grimme’s dispersion corrections disp3\(^{12}\)]. XAS parameters were calculated with ORCA TD-DFT calculations\(^13\) at both the BP86/def2-TZVP and the b3-lyp/def2-TZVP level employing COSMO dielectric corrections.

**Acknowledgements**

We thank Dr. Erik R. Farquhar (NLS, Brookhaven) for help with XAS data collection. Dr. David J Martin and Dr. Moniek Tromp are thanked for help with XAS data collection and data interpretation of compounds \([\text{Co}^{	ext{III}}(\text{TPP})\text{CF}_3]\) and \([\text{Co}^{	ext{III}}(\text{TPP})\text{Cl}]\).
References and notes


(2) However, the absence of the 1S to 4p+LMCT shakedown transition could also be because it is hidden underneath the rising edge, and also the weak intensity of the pre-edge transitions could have a different reason than formation of 6-coordinate species.

(3) Goswami, M.; de Bruin, B.; Dzik, I. W; Chem. Commun, 2017, 53, 4382-4385. Also see chapter 7 of this thesis.


(5) (a) EXAFS analysis of $^{1}\text{P}_{1}$, $^{3}\text{P}_{2}$, and $^{5}\text{P}_{2}$ were performed by K. Ray and co-workers and S. De Beer and co-workers. (b) EXAFS analysis of $[^{1}\text{Co}(\text{TPP})(\text{Cl})]$ and $[^{1}\text{Co}(\text{TPP})(\text{CF}_{3})]$ were performed by D. J. Martin and M. Tromp.


