Tris(imidazolyl)phosphine cobalt complexes: structural comparisons with isoelectronic tris(pyrazolyl)hydroborato analogues

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The cobalt complexes $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{CoI}\}\mathrm{I}$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3}$ are synthesized by the reaction of the sterically demanding tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ with $\mathrm{CoI_2}$ and $\mathrm{Co(NO_3)_2}$, respectively; comparison of the structures of $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ (M = Co, Zn) with those of the structurally analogous, but neutral, tris(3-*tert*-butylpyrazolyl)hydroborato complexes $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$ illustrates that the charged complexes have a greater tendency to adopt bidentate coordination of the nitrate ligand.

We have recently described the use of the sterically demanding tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine ligand $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$[1] (see Fig. 1) for the synthesis of $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Zn(OH)}\}\mathrm{ClO_4}$,[2] the first structurally characterized monomeric zinc hydroxide complex supported by imidazole functionalities. The cation $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Zn(OH)}\}^+$ represents an excellent structural model for the active site of carbonic anhydrase, an enzyme in which the zinc centre is bound to the peptide backbone by the imidazole groups of three histidine residues.[3] Since cobalt is the only other metal which has been substituted into the apoenzyme such that significant activity ($\geqslant$50%) is still maintained,[4] we are particularly interested in comparing the coordination chemistry of zinc and cobalt complexes supported by the three imidazole functionalities of $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$. In this paper, we describe the syntheses of the cobalt complexes $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{CoI}\}\mathrm{I}$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3}$ and compare the structure of the latter to that of its zinc analogue. Furthermore, comparison of the structures of $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ (M = Zn, Co) with their structurally analogous, but neutral tris(3-*tert*-butylpyrazolyl)hydroborato counterparts $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$[5] serves to illustrate the manner by which the increased charge on a complex influences the coordination mode of nitrate ligands.

The cobalt iodide and nitrate complexes $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{CoI}\}\mathrm{I}$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3}$ are readily prepared by the reactions of the tris(imidazolyl)phosphine $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ with $\mathrm{CoI_2}$ and $\mathrm{Co(NO_3)_2}$, respectively, as illustrated in Scheme 1. The molecular structure of $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3}$ has been determined by X-ray diffraction, as shown in Fig. 2.† Of most interest to the present study is the coordination mode of the nitrate ligand in the cation $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$, and in particular its relation to that of the zinc analogue $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Zn(NO_3)}\}^+$.[2] Thus, salient bond lengths and angles for both complexes are summarized in Table 1.‡

Interest in the nitrate coordination modes in $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ (M = Co, Zn) derives from our previous study which demonstrated that, for the series of structurally related tris(3-*tert*-butylpyrazolyl)hydroborato complexes $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$

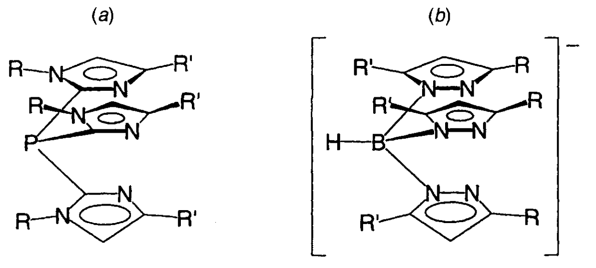
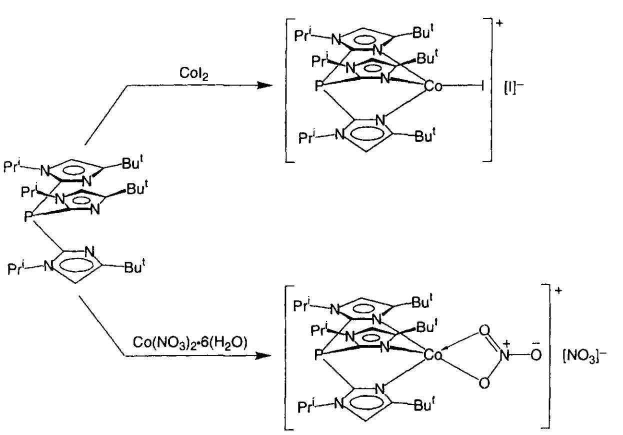


Fig. 1 Tris(imidazolyl)phosphine (*a*) and tris(pyrazolyl)hydroborato ligands (*b*)



Scheme 1

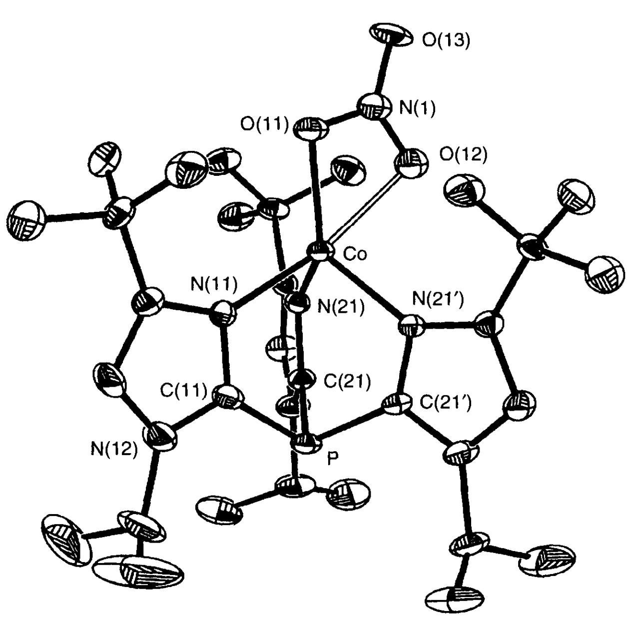


Fig. 2 Molecular structure of $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3}$. Selected bond lengths (Å) and angles (°): Co–N(11) 2.074(10), Co–N(21) 2.084(6), Co–O(11) 2.019(8), Co–O(12) 2.289(10), N(1)–O(11) 1.303(20), N(1)–O(12) 1.242(16), N(1)–O(13) 1.210(16); N(11)–Co–N(21) 92.8(2), N(21)–Co–N(21′) 104.1(3), N(11)–Co–O(11) 110.1(4), N(11)–Co–O(12) 169.2(4), N(21)–Co–O(11) 124.0(2), N(21)–Co–O(12) 93.8(2), O(11)–Co–O(12) 59.1(4).

Table 1 Comparison of nitrate coordination modes in $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ and $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$ (M = Co, Zn)

	$\mathrm{M{-}O_1}$/Å[a]	$\mathrm{M\cdots O_2}$/Å[a]	$\mathrm{M{-}O_1{-}N}$/°	$\mathrm{M{-}O_2{-}N}$/°	Δ(M–O)/Å	Δθ/°	Assignment	Ref.
$\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Zn(NO_3)}\}^+$	1.986(4)	2.518(8)	106.8(4)	82.4(8)	0.53	24.4	anisobidentate	3
$\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$	2.109(8)	2.289(10)	98.8(7)	88.0(9)	0.18	10.8	bidentate	This work
$[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{Zn(NO_3)}$	1.978(3)	2.578(5)	109.4(2)	79.8(4)	0.60	29.6	unidentate	6
$[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{Co(NO_3)}$	2.001(3)	2.339(3)	101.4(2)	85.6(2)	0.34	15.8	anisobidentate	6

[a] $\mathrm{M{-}O_1}$ refers to the primary interaction, while $\mathrm{M\cdots O_2}$ refers to the secondary interaction.

(M = Co, Ni, Cu, Zn), the preference for bidentate coordination increases in the sequence Zn < Co ≪ Cu, Ni.[5,6] Since such structural preferences correlate with the activity of metal-substituted carbonic anhydrases[5] (*i.e.* zinc, the metal with the greatest tendency to exhibit unidentate coordination of the nitrate ligand is the most active), it was suggested that the reduced activity of the metal-substituted enzymes may in part be due to stronger binding of the bicarbonate moiety to the respective metal centres, assuming that the bicarbonate ligand exhibits a similar trend in coordination modes to its isoelectronic nitrate counterpart.

The analogy between the $\{[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M^{II}}\}^+$ moieties in the aforementioned model complexes and those in the enzyme $\{\mathrm{M^{II}(His)_3}\}^{2+}$, however, is limited as a consequence of the difference in formal charge. For this reason, we wished to compare the coordination modes of mono(nitrate) complexes of cobalt and zinc supported by three neutral imidazole donors. In this regard, although structurally characterized mono(nitrate) complexes of cobalt are known,[7] we are not aware of any derivatives (other than the above) which contain only three nitrogen donors as supporting ligands.§ Thus, $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Zn(NO_3)}\}^+$ represent a unique pair of structurally characterized (mono)nitrate complexes of cobalt and zinc with a common NNN supporting ligand environment. The coordination modes of the nitrate ligands in $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ (M = Co, Zn) are summarized in Table 1,‡ from which it is evident that the nitrate ligand in $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$ exhibits significantly more bidentate character than that in the zinc analogue; the coordination modes may be classified as bidentate and anisobidentate, respectively.‡[9] For example, the difference in Co–O bond lengths is only 0.18 Å, compared to 0.53 Å for the corresponding value in the zinc system. Although such a trend parallels the differences observed previously for $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$ (M = Co, Zn), in which the difference in Co–O bond lengths (0.34 Å) is less than the difference in Zn–O bond lengths (0.60 Å), it is apparent that the charged $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ complexes show a greater tendency towards bidentate coordination than do their counterparts $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{M(NO_3)}$. Thus, whereas the nitrate ligand in $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{Co(NO_3)}$ may be classified as anisobidentate, the nitrate ligand in the charged complex $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$ is appropriately described as bidentate. However, despite the difference in nitrate coordination modes, both ligands $[\mathrm{Tp}^{\mathrm{Bu^t}}]$ and $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ bind to the cobalt with similar average bond lengths and angles: $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$, $\mathrm{Co{-}N_{av}}$ 2.08 Å, $\mathrm{N{-}Co{-}N_{av}}$ 96.6°; $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{Co(NO_3)}$, $\mathrm{Co{-}N_{av}}$ 2.06 Å, $\mathrm{N{-}Co{-}N_{av}}$ 95.2°.[5]

In summary, while the tris(imidazolyl)phosphine $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ and tris(pyrazolyl)hydroborato $[\mathrm{Tp}^{\mathrm{Bu^t}}]$ ligands possess similar steric demands, we have demonstrated that the charged complexes $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{M(NO_3)}\}^+$ exhibit a more pronounced tendency to adopt bidentate coordination of the nitrate ligand than do their neutral counterparts. In view of the structural consequences of such electronic effects, it is evident that, in addition to modelling the coordination geometry, accurate synthetic analogues of metalloenzymes should also attempt to model the charge distribution at the active site.

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Footnotes

† *Crystal data* for $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}\mathrm{NO_3{\cdot}2CHCl_3}$: orthorhombic, space group *Pnma* (no. 62), a = 20.667(7), b = 14.102(2), c = 16.809(4) Å, U = 4899(2) Å^3, Z = 4, R = 0.0686, R_w = 0.0756. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The nitrate ligand has been classified as binding to a single metal centre by three different coordination modes: (*i*) bidentate, (*ii*) anisobidentate, and (*iii*) unidentate. These coordination modes have been distinguished according to the asymmetry of the interaction. Specifically, complexes in which (*i*) the difference in M–O bond lengths Δ(M–O) is >0.6 Å, and (*ii*) the difference in bond angles at oxygen Δθ >28°, are classified as unidentate; complexes with (*i*) Δ(M–O) in the range 0.3–0.6 Å, and (*ii*) Δθ in the range 14–28°, are classified as anisobidentate; while complexes with (*i*) Δ(M–O) <0.3 Å, and (*ii*) Δθ <14°, are classified as bidentate. See: G. J. Kleywegt, W. G. R. Wiesmeijer, G. J. Van Driel, W. L. Driessen, J. Reedijk and J. H. Noordik, *J. Chem. Soc., Dalton Trans.* 1985, 2177.

§ Some structurally characterized bis(nitrate)complexes of cobalt with only three nitrogen donors as supporting ligands include $[\eta^3\text{-}fac\text{-}\mathrm{EtN(CH_2CH_2pz^{Me2})_2}]\mathrm{Co(NO_3)_2}$[7a] and $[\eta^3\text{-}mer\text{-}\mathrm{PhN(CH_2pz^{Me2})_2}]\mathrm{Co(NO_3)_2}$[7b] ($\mathrm{pz^{Me2}}$ = 3,5-dimethylpyrazolyl).

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