DALTON
FULL PAPER

Synthesis and molecular structures of a pair of tris(imidazolyl)phosphine cobalt–perchlorate complexes, $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OClO_3)}\}[\mathrm{ClO_4}]$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}[\mathrm{ClO_4}]$

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The cobalt–perchlorate complexes, $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OClO_3)}\}(\mathrm{ClO_4})$ and $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}(\mathrm{ClO_4})$, have been synthesized *via* the reaction of tris[2-(1,4-diisopropylimidazolyl)]phosphine $[\mathrm{Pim}^{\mathrm{Pr^i}_2}]$ with $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$; the isolation of these species, as opposed to a hydroxide derivative $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{CoOH}\}^+$, demonstrates the important role that steric interactions play in generating synthetic analogues for metal-substituted carbonic anhydrases.

Introduction

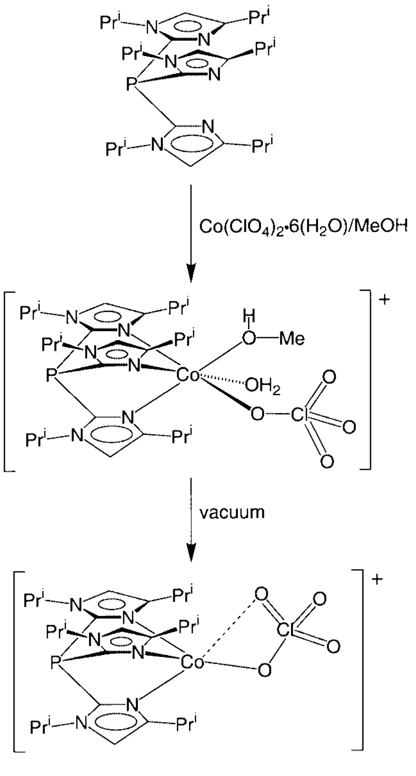
Our previous studies have described the use of the sterically demanding tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine ligand $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$[1] to prepare $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{ZnOH}\}(\mathrm{ClO_4})$. As the first structurally characterized monomeric zinc hydroxide complex supported by imidazole functionalities, $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{ZnOH}\}^+$ is an excellent structural model for the active site of carbonic anhydrase.[2] An important attribute of the $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ ligand that permits isolation of a four-coordinate zinc hydroxide complex is the sterically protective environment that is provided by the three *tert*-butyl substituents. In this paper, we describe related cobalt chemistry using the less sterically demanding ligand, $[\mathrm{Pim}^{\mathrm{Pr^i}_2}]$,[3] which provides an indication of the complexities that may arise in modeling metalloenzymes when steric constraints do not impose an appropriate coordination environment.

Results and discussion

In addition to $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{ZnOH}\}^+$,[2] structurally characterized mononuclear tetrahedral zinc hydroxide complexes have also been obtained using bulky tris(pyrazolyl)borate ligands, *e.g.* $[\mathrm{Tp}^{\mathrm{Bu^t,Me}}]\mathrm{ZnOH}$[4] and $[\mathrm{Tp}^{\mathrm{Ar,Me}}]\mathrm{ZnOH}$ ($\mathrm{Ar} = p\text{-}\mathrm{C_6H_4Pr^i}$).[5] Sterically demanding tris(pyrazolyl)borate ligands have also allowed isolation of terminal hydroxide complexes of other metals, such as the iron and cobalt complexes $[\mathrm{Tp}^{\mathrm{Bu^t,Pr^i}}]\mathrm{FeOH}$[6] and $[\mathrm{Tp}^{\mathrm{Bu^t,Me}}]\mathrm{CoOH}$.[7] However, reducing the steric demands of the $[\mathrm{Tp}^{\mathrm{RR'}}]$ ligand results in the formation of dinuclear complexes with bridging hydroxide ligands. Thus, dinuclear complexes, such as $\{[\mathrm{Tp}^{\mathrm{Pr^i}_2}]\mathrm{Fe}(\mu\text{-OH})\}_2$ and $\{[\mathrm{Tp}^{\mathrm{Pr^i}_2}]\mathrm{Co}(\mu\text{-OH})\}_2$, are obtained if the 3-pyrazolyl substituent is $\mathrm{Pr^i}$ rather than $\mathrm{Bu^t}$.[8,9] The coordination chemistry of cobalt supported by [NNN] tripodal imidazolyl ligands is of particular interest since cobalt is the only other metal which has been substituted for Zn in carbonic anhydrase such that significant activity is retained.[10] For this reason, it is pertinent to explore the coordination chemistry of cobalt using the di-isopropyl substituted tris(imidazolyl)phosphine, $[\mathrm{Pim}^{\mathrm{Pr^i}_2}]$,[3] a ligand which is structurally related to the aforementioned tris(pyrazolyl)hydroborato ligand $[\mathrm{Tp}^{\mathrm{Pr^i}_2}]$.

The tris(imidazolyl)phosphine $[\mathrm{Pim}^{\mathrm{Pr^i}_2}]$ reacts with $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ in methanol to yield the six-coordinate aqua–methanol–perchlorate complex $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}(\mathrm{ClO_4})$ (Scheme 1), the molecular structure of which has been determined by X-ray diffraction (Fig. 1). The nature of $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$ differs considerably from $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{ZnOH}\}^+$,[2] the product of the reaction between $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ and $\mathrm{Zn(ClO_4)_2{\cdot}6H_2O}$ in methanol. For example, two notable differences are that the cobalt complex is octahedral and contains an aqua rather than hydroxide ligand. In this regard, $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$ bears a closer resemblance to the cadmium aqua complex $\{[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]\mathrm{Cd(OH_2)(OClO_3)}\}^+$ which is obtained from the reaction of $[\mathrm{Pim}^{\mathrm{Pr^i,Bu^t}}]$ with $\mathrm{Cd(ClO_4)_2{\cdot}6H_2O}$,[11] the only significant difference being that the cadmium center does not bind an additional methanol ligand. It is also worth noting that the coordinated methanol in $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$ participates in a hydrogen bond interaction with an additional molecule of methanol [$d(\mathrm{O} \cdots \mathrm{O}) = 2.62$ Å].[12]

Interestingly, the methanol and water ligands in $\{[\mathrm{Pim}^{\mathrm{Pr^i}_2}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$ are not bound strongly to cobalt, such that removal of the volatile components and crystallization from $\mathrm{CHCl_3}$ yields the blue "tetrahedral" perchlorate



Scheme 1

Table 1 Comparison of Co–OH$_2$, Co–O(H)Me, and Co–OClO$_3$ bond lengths

	d[Co–OH$_2$]/Å	d[Co–O(H)Me]/Å	d[Co–OClO$_3$]/Å	Reference
$\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}^+$	—	—	1.999(3)	This work
$\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$	2.083(2)	2.095(2)	2.266(2)	This work
trans-$\{[\mathrm{N_4}]\mathrm{Co(OH_2)(HOMe)}\}^{2\,a}$	2.22(2)	2.19(2)	—	21*a*
trans-$\{[\mathrm{N_3O_2}]\mathrm{Co(OH_2)(HOMe)}\}^{2+\,a}$	2.119(4)	2.103(4)	—	21*b*
trans-$\{[\mathrm{N_4O}]\mathrm{Co(OH_2)(HOMe)}\}^{2+\,a}$	2.183(8)	2.209(9)	—	21*c*
trans-$\{[\mathrm{N_2O_2}]\mathrm{Co(OH_2)(OClO_3)}\}^{2+\,a}$	2.115(4)	—	2.220(4)	[b]
trans-$[\mathrm{N_4}]\mathrm{Co(OClO_3)_2}^{a}$	—	—	2.21(1), 2.32(1)	15*a*
CSD mean [range]	2.08 [0.43]	2.13 [0.20]	2.32 [0.25]	

[a] For brevity, only the coordinating atoms of the supporting ligands are indicated. [b] D. Luneau, F. M. Romero and R. Ziesel, *Inorg. Chem.*, 1998, **37**, 5078.

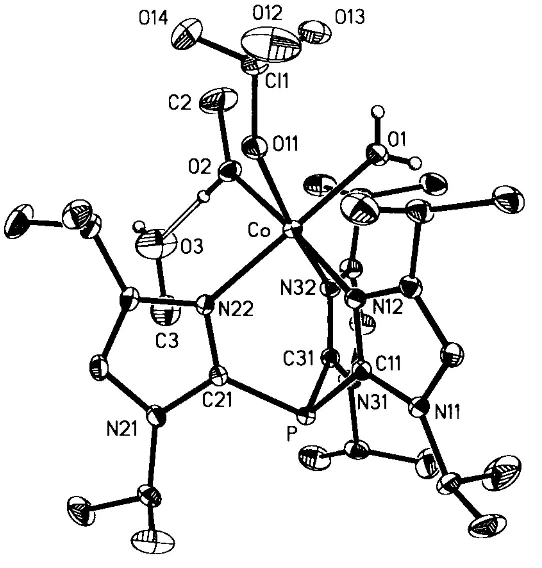


Fig. 1 Molecular structure of the cation $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$. Selected bond lengths (Å): Co–O(1) 2.083(2), Co–O(2) 2.095(2), Co–O(11) 2.266(2), Co–N(12) 2.133(2), Co–N(22) 2.139(2), Co–N(32) 2.155(2), O(2) ··· O(3) 2.62.

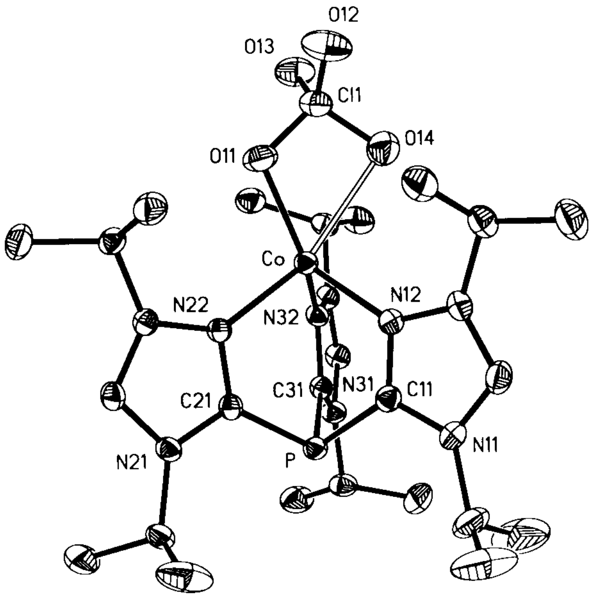


Fig. 2 Molecular structure of the cation $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}^+$. Selected bond lengths (Å): Co–O(11) 1.999(3), Co ··· O(14) 2.50, Co–N(12) 2.024(3), Co–N(22) 2.033(3), Co–N(32) 2.023(3).

complex $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}[\mathrm{ClO_4}]$ which is devoid of any additional ligands.[13] An X-ray diffraction study (Fig. 2) reveals that the "tetrahedral" cobalt center in $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}^+$ does interact with a second oxygen atom of the perchlorate ligand, but indicates that the interaction is very long [2.50 Å] compared to the primary interaction [1.999(3) Å]. The ligand is, therefore, better described as adopting a unidentate rather than bidentate coordination mode.[14,15] The latter observation is in accord with the notion that perchlorate is a weakly coordinating ligand.[16,17] For example, the more strongly bonding nitrate ligand in $\{[\mathrm{Pim^{Pr^i,Bu^t}}]\mathrm{Co(NO_3)}\}^+$ binds in a bidentate rather than unidentate manner, in spite of the fact that it is a derivative of the more sterically demanding $[\mathrm{Pim^{Pr^i,Bu^t}}]$ ligand.[18,19] Interestingly, the Co–OClO$_3$ bond length in $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}^+$ is not only significantly shorter than that in six-coordinate $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$ [2.266(2) Å], but is also substantially shorter than for any other complex listed in the Cambridge Structural Database (CSD),[20] as summarized in Table 1.

There are no examples of structurally characterized octahedral cobalt complexes with an aqua–methanol–perchlorate combination of ligands listed in the CSD to provide a comparison with $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$. Aqua–methanol complexes are, nevertheless, known (Table 1),[21] and such species also exist with perchlorate as a counterion,[21a,b] but the latter does not interact significantly with the cobalt center. The molecular structure of $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$, therefore, presents a unique opportunity to compare the three Co–O bond lengths, *i.e.* Co–OH$_2$, Co–O(H)Me, and Co–OClO$_3$, in a single compound (Table 1). Examination of Table 1 indicates that the Co–OClO$_3$ bond is the longest of the three, and that it is also 0.27 Å longer than the Co–OClO$_3$ bond in $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}^+$. Evidently, the Co–OClO$_3$ interaction must be regarded as rather pliable. In this regard, the Cd–OClO$_3$ [2.203(8) Å] and Cd–OH$_2$ [2.297(9) Å] bond lengths in the related cadmium complex $\{[\mathrm{Pim^{Pr^i,Bu^t}}]\mathrm{Cd(OH_2)(OClO_3)}\}^+$ exhibit the opposite trend to that in $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$, with the Cd–OClO$_3$ bond being shorter than the Cd–OH$_2$ bond. It is also noteworthy that, despite the three different Co–O bond lengths in $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}^+$, the three Co–N bond lengths are very similar, indicating that there are no significant differences in the *trans* influences of H$_2$O, MeOH and $[\mathrm{OClO_3}]^-$ in this system.

Experimental section

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.[22] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on a Bruker Avance 400 DRX spectrometer. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using an electrospray ion source. $[\mathrm{Pim^{Pr^i_2}}]$ was prepared by the literature method.[3]

Synthesis of $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OH_2)(HOMe)(OClO_3)}\}[\mathrm{ClO_4}]$ and $\{[\mathrm{Pim^{Pr^i_2}}]\mathrm{Co(OClO_3)}\}[\mathrm{ClO_4}]$

$[\mathrm{Pim^{Pr^i_2}}]$ (160 mg, 0.33 mmol) was added to a stirred suspension

Table 2 Crystal, intensity collection and refinement data

	{[Pim$^{Pr^i_2}$]Co(OH$_2$(HOMe)$_2$(OClO$_3$)}[ClO$_4$]	{[Pim$^{Pr^i_2}$]Co(OClO$_3$)}[ClO$_4$]
Symmetry	Monoclinic	Monoclinic
Formula	$C_{29}H_{55}Cl_2N_6O_{11}PCo$	$C_{29}H_{47}Cl_8N_6O_8PCo$
Formula weight	824.59	981.23
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	12.6185(8)	15.3832(11)
b/Å	18.2452(11)	16.8991(12)
c/Å	17.6528(10)	17.8228(11)
α/°	90	90
β/°	90.537(1)	100.154(1)
γ/°	90	90
V/Å^3	4064.0(4)	4560.7(5)
Z	4	4
Temperature/K	233	238
Radiation (λ/Å)	0.71073	0.71073
ρ(calcd.)/g cm^{-3}	1.348	1.429
μ(Mo-Kα)/mm^{-1}	0.651	0.928
θ_{max}/°	28.3	28.3
No. of data	9302	10147
No. of parameters	522	490
$R_1{}^a$	0.0460	0.0624
$wR_2{}^a$	0.1222	0.1819
GOF	1.094	1.057

of Co(ClO$_4$)$_2$·6H$_2$O (121 mg, 0.33 mmol) in methanol (*ca.* 5 mL) giving a purple mixture. The reaction was stirred for 90 minutes, after which the mixture was filtered and the volatile components were removed *in vacuo* from the filtrate giving a purple residue. The product was washed with pentane (*ca.* 5 mL) and dried *in vacuo*, giving {[Pim$^{Pr^i_2}$]Co(OClO$_3$)}[ClO$_4$] as a bright blue–purple powder (206 mg, 84%). $m/z = 642$ (M$^+$). IR Data (cm^{-1}), KBr pellet: 2970 (w), 2958 (w), 2933 (vw), 2871 (vw), 1554 (w), 1194 (m), 1145 (s), 1117 (s), 1090 (vs), 627 (m). ^{1}H NMR (CDCl$_3$): δ −12.9, −1.7, 6.0, 12.9, 80.0 (assignments not given due to the paramagnetic nature of the compound). {[Pim$^{Pr^i_2}$]Co(OH$_2$)(HOMe)(OClO$_3$)}[ClO$_4$] is obtained as pink–purple crystals upon direct crystallization from the reaction solvent. ^{1}H NMR (CD$_3$OD): δ −87.5, −26.8, 14.5, 39.6, 51.9 (assignments not given due to the paramagnetic nature of the compound).

X-Ray structure determinations

Crystal data, data collection and refinement parameters are summarized in Table 2. X-Ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).[23] Hydrogen atoms on carbon were included in calculated positions.

CCDC reference number 186/1948.

See http://www.rsc.org/suppdata/dt/b0/b002894k/ for crystallographic files in .cif format.

Conclusion

In summary, a pair of cobalt–perchlorate complexes, {[Pim$^{Pr^i_2}$]Co(OClO$_3$)}$^+$ and {[Pim$^{Pr^i_2}$]Co(OH$_2$)(HOMe)(OClO$_3$)}$^+$, have been isolated as perchlorate salts and structurally characterized by X-ray diffraction. The isolation of these complexes, rather than the cobalt hydroxide counterpart of {[Pim$^{Pr^i,Bu^t}$]ZnOH}$^+$, underscores the complexities that arise in generating accurate synthetic analogues for metal-substituted carbonic anhydrases.

Acknowledgements

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1 Abbreviations: tris(2-imidazolyl)phosphines are represented by the abbreviation [Pim$^{R,R'}$], with the 1- and 4-alkyl substituents listed respectively as superscripts.

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both nitrate anions coordinate and the zinc center is six coordinate, $[\mathrm{Pim}^{\mathrm{Pr}^{i}_{2}}]\mathrm{Zn}(\eta^1\text{-}\mathrm{ONO_2})(\eta^2\text{-}\mathrm{O_2NO})$. See: C. Kimblin, W. E. Allen and G. Parkin, *Main Group Chem.*, 1996, **1**, 297.

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