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$H_3O_2^-$, O_2^{2-} and $O_2^{\bullet -}$ bridging ligands in cobalt(III) complexes of an acyclic phenolate-hinged dinucleating ligand†

Morten Ghiladi,[a] Jonnes T. Gomez,[a] Alan Hazell,[b] Pauli Kofod,*[c] Jan Lumtscher[a] and Christine J. McKenzie*[a]

[a] *Department of Chemistry, University of Southern Denmark, Odense Campus, 5230 Odense M, Denmark*

[b] *Department of Chemistry, Aarhus University, 8000 Århus C, Denmark*

[c] *Department of Life Sciences and Chemistry, Roskilde University, 4000 Roskilde, Denmark*

Received 14th October 2002, Accepted 14th February 2003
First published as an Advance Article on the web 3rd March 2003

The dicobalt(III) complex, $[Co_2(bpbp)(\mu\text{-}H_3O_2)_2](ClO_4)_3$ ($bpbp^-$ = 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-*tert*-butylphenolate), obtained by reaction of cobalt(II) perchlorate with Hbpbp under ambient conditions contains two $\mu\text{-}H_3O_2^-$ bridging ligands. The H-bonded O ··· O distances in this motif are 2.437(3) and 2.456(4) Å, respectively, with a Co ··· Co separation of 3.601(1) Å. The structurally precedented peroxo bridged complexes, $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}RCO_2)](ClO_4)_2$ (R = CH_3 or C_6H_5), are formed if a carboxylate is present. The X-ray crystal structure showed O–O and Co ··· Co distances of 1.422(3) and 3.168(1) Å, respectively, in the case of R = CH_3. ESI-MS shows that the bridging peroxo ligand is easily eliminated from $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$, *m*/*z* 390.0, as implicated by the observation of $[Co_2(bpbp)(\mu\text{-}CH_3CO_2)]^{2+}$, *m*/*z* 374.1, corresponding to loss of the mass equivalent of dioxygen. The superoxo complex $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{3+}$ can be prepared by Ce(IV) oxidation of $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$. Reaction of $[Co_2(bpbp)(\mu\text{-}H_3O_2)_2]^{3+}$ with hydrazine in air gives the dicobalt(II) complex $[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4$. In this complex the two exogenous hydrazinecarboxylato ligands are bound to individual metal ions with weak H-bonding between them as shown by X-ray structure analysis.

Introduction

The dinuclear peroxo bridged $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ can be cyclized in the presence of base to give $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{3+}$. The former singly-bridged complex shows an *anti* coordination of the peroxo ligand while the latter doubly-bridged complex is a classic example of *syn* coordination of O_2.[1] Enforcement of *syn* coordination of O_2 by the presence of a second bridging ligand has similarly been demonstrated in the dicobalt(III) complexes of the dinucleating ligand 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenolate, $bpmp^-$ (Fig. 1).[2] The dicobalt(II) complexes of this ligand are capable of reversible dioxygen binding (eqn. (1)) with O_2 being

$$[Co_2(bpmp)(\mu\text{-}CH_3CO_2)]^{2+} + O_2 \rightleftharpoons [Co_2(bpmp)(\mu\text{-}CH_3CO_2)(\mu\text{-}O_2)]^{2+} \quad (1)$$

removed by warming the solution or by purging with dinitrogen.[2] $[Co_2(bpmp)(\mu\text{-}O_2)(\mu\text{-}C_6H_5CO_2)](BF_4)_2\cdot 2H_2O$, in which an exogenous bridging benzoato ligand is present, was characterised by X-ray crystallography although the structure suffered from disorder.[2b] Furthermore, Suzuki *et al.* reported that a complex formulated as $[Co_2(bpmp)(OH)]^{2+}$ could also bind dioxygen to give $[Co_2(bpmp)(OH)(O_2)]^{2+}$.[2] Neither the former hydroxo-dicobalt(II) complex nor the latter hydroxo-μ-peroxo-dicobalt(III) complex was crystallographically characterised. Chin and co-workers[3] have demonstrated that in $[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)_2]^+$ a hydroxo ligand may attack the bridging phosphate monoester resulting in an intramolecular hydrolysis reaction (eqn. (2)) which may be relevant to the hydrolysis of phosphate esters by dimetallic enzymes.

$$[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)_2]^+ \rightleftharpoons [Co_2(bpmp)(\mu_3\text{-}PO_4)(OH)]^+ + PhOH \quad (2)$$

A common feature of both $[Co_2(bpmp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$ and $[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)_2]^+$ is the presence of an auxillary bridging weakly basic oxoanion. These bridging ligands may for electronic or steric reasons facilitate reactions such as dioxygen binding and intramolecular hydrolysis. On the other hand the bridging oxoanions block access to the metal ions by other molecules. Our aim at the outset of the present work was to study the dicobalt complexes in the absence of the auxillary bridging oxoanions. For example, trapping and fully characterising species like the proposed $[Co_2(bpmp)(OH)(O_2)]^{2+}$ would be interesting in the context of exploring the requirements for reversible *syn* coordination of O_2. In the present work we have used a dinucleating ligand homologous to $bpmp^-$, namely 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-*tert*-butylphenolate, $bpbp^-$ (Fig. 1). We were unable to prepare $[Co_2(bpbp)(OH)(O_2)]^{2+}$. Instead $[Co_2(bpbp)(OH)_2(H_2O)_2]^{3+}$, which contains two $\mu\text{-}H_3O_2^-$ bridging ligands, was isolated and structurally characterised. The crystal structures of $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)](ClO_4)_2$ and $[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4$ are also reported and discussed in terms of steric flexibility of the dinucleating ligand.

Results and discussion

Syntheses

Fig. 1 depicts a summary of the series of dicobalt complexes charaterised. Reaction of Hbpbp with cobalt(II) perchlorate in acetone in the presence of carboxylate and air give the μ-peroxo complexes $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}RCO_2)](ClO_4)_2$ (R = CH_3 (**1**), C_6H_5 (**2**)) analogous to $[Co_2(bpmp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$ characterised by Suzuki and co-workers.[2] It is noteworthy that all carbons atoms in **1** shows separate ^{13}C resonance frequencies at 75.5 MHz (with the exception of the signal at 140.6 ppm where two pyridyl-C3 resonance signals are unresolved) (see Experimental section). This is a consequence of the Co–O–O–

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† Electronic supplementary information (ESI) available: Fig. S1: Raman spectra of $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$ (top) and the superoxo-bridged complex $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{3+}$ (bottom). Fig. S2: ESI-MS spectra of the peroxo bridged $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{2+}$. Fig. S3: ESI-MS spectrum of the superoxo bridged $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{3+}$. See http://www.rsc.org/suppdata/dt/b2/b210091f/

DOI: 10.1039/b210091f

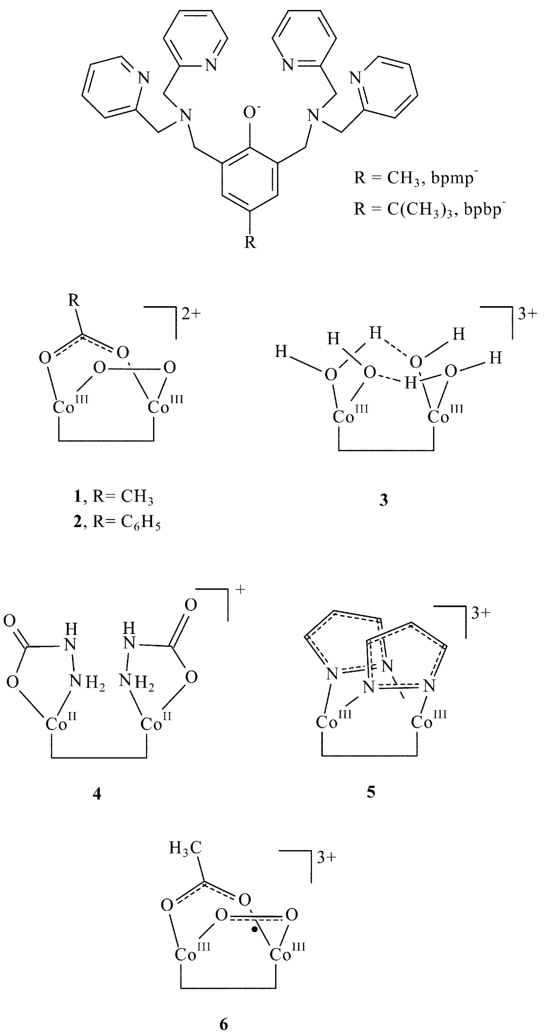

Fig. 1 Bridging motifs in dicobalt complexes of bpbp⁻. For simplicity the dinucleating ligand is represented by a line connecting the two cobalt ions.

Co torsion angle, which enforces a lack of a plane of symmetry in this cation. The observation of separate ^{13}C resonance lines also implicates that flipping of the Co–O–O–Co moiety is slow on the NMR time scale.

The reaction of Hbpbp with cobalt(II) perchlorate in aqueous acetone or methanol yields, after several days of standing, the dark brown [Co_2(bpbp)(μ-H_3O_2)$_2$](ClO_4)$_3$ (**3**). The ^{13}C NMR spectrum of **3** in CD_3CN solution showed that this cation has a plane of symmetry perpendicular to the plane of the phenolate ring (see Experimental section). There were no indications of ligand exchange with the solvent. The coordination of a single acetonitrile ligand would have broken the symmetry. Furthermore **3**·CH_3CN·H_2O was grown from acetonitrile solution with CH_3CN only being present as a solvent of crystallization. Therefore both μ-$H_3O_2^-$ bridges presumably persist in acetonitrile solution with each μ-$H_3O_2^-$ bridge being symmetrical as judged by ^{13}C NMR spectroscopy. Addition of dihydrogen peroxide to the dicobalt(II) complex of bpbp⁻ leads to recovery of the same product (**3**) with crystallisation occurring in a few hours. **3** is reduced by hydrazine and when the reaction is carried out in air the dicobalt(II) complex [Co_2(bpbp)(NH_2-$NHCO_2$)$_2$]ClO_4 (**4**) can be isolated.

In the presence of two equivalents of pyrazole the reaction of Hbpbp with cobalt(II) perchlorate in acetone under reflux under air affords the bispyrazolato bridged complex [Co_2(bpbp)(μ-$C_3H_3N_2$)$_2$](ClO_4)$_3$ (**5**). The ^{13}C NMR spectrum of **5** in CD_3CN solution showed that this cation has a plane of symmetry (see Experimental section). The two bridging pyrazolato ligands show ^{13}C resonance signals at slightly different frequencies, namely at 144.7 and 145.4 ppm assigned the to C1 carbon atom of the pyrazolato ring (see Experimental section). The resonances of the two C2 carbon atoms of the two pyrazolato ligands are however not resolved. Both were found at 113.0 ppm.

Description of the crystal structures

The structure of the cation in **1** is shown in Fig. 2 and selected bond distances are given in Table 1. The two cobalt(III) ions are bridged by three ligands, namely the μ-peroxo, μ-acetato, and μ-phenolato ligands. These ligands occupy one face of the approximately octahedral cobalt(III) ion. The other face is occupied be three neutral nitrogen donor atoms from bpbp⁻. The metal ligand bond lengths in the two metal sites of the dinucleating ligand are slightly different as imposed by the structure of the μ-peroxo ligand. The O2–O4 distance is 1.422(3) Å and the Co–O–O–Co torsion angle is 52.1(2)°. In [Co_2(bpmp)(μ-O_2)(μ-$C_6H_5CO_2$)](BF_4)$_2$·2H_2O the corresponding values were 1.43(2) Å and 51°, respectively.[2b] The O–O distances in μ-peroxo-dicobalt(III) complexes with various ligands has been found to span a quite large range, namely 1.308–1.488 Å.[1b] The Co ··· Co distance is 3.168(1) Å, which is significantly shorter than in **3** and **4** (see below).

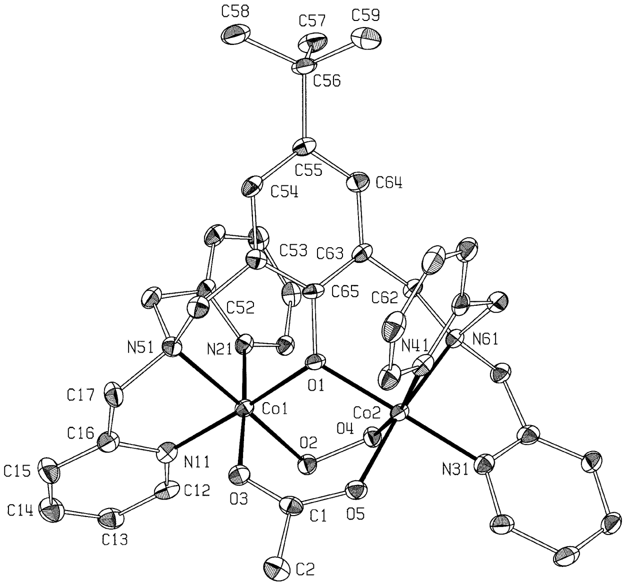

Fig. 2 X-Ray structure of the cation in **1**.

The structure of the cation in **3**·CH_3CN·H_2O is shown in Fig. 3. The metal–ligand bond lengths are almost the same in the two halves of the dinucleating ligand. Terminal aqua and hydroxo ligands complete the coordination sphere of each metal ion. The hydroxo ligand on one metal ion is strongly hydrogen bonded to the aqua ligand on the adjacent metal ion. The two H-bonded O–H ··· O distances are 2.437(3) and 2.456(4) Å (Table 2). These distances are typical for μ-$H_3O_2^-$ bridging ligands.[4] The metal–metal distance of 3.601(1) Å is much larger than for **1** but only 0.07 Å greater than for[Co_2(bpmp)(μ-$PhOPO_3$)(OH)(H_2O)](ClO_4)$_2$.[3] The X-ray crystal structure of [Co_2(bpbp)(μ-H_3O_2)$_2$](ClO_4)$_3$·2H_2O (not shown) is similar to that of **3**·CH_3CN·H_2O (Tables 1 and 2). The hydrogen atoms of the μ-$H_3O_2^-$ bridging ligands were located on electron density difference maps.

The structure of the cation in **4** is shown in Fig. 4. The two hydrazinecarboxylato ligands are bound to individual metal ions with H-bonding between them. The two N–H ··· O distances are 2.957(6) and 2.989(6) Å (Table 2), that is, not much shorter than the sum of the van der Vaals radii of nitrogen and oxygen. The hydrogen atoms of the two hydrazinecarboxylato

Table 1 Selected bond distances (Å) and angles (°) for $[Co_2(bpbp)(O_2)(CH_3CO_2)](ClO_4)_2$ **1**, $[Co_2(bpbp)(H_2O)_2(OH)_2](ClO_4)_3$ **3** and $[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4$ **4**

	1	**3**·$2H_2O$	**3**·$CH_3CN·H_2O$	**4**·$3.875H_2O$
Co1–Co2	3.168(1)	3.601(1)	3.601(1)	3.873(1)
Co1–O1	1.895(2)	1.977(3)	1.970(2)	2.116(3)
Co1–N11	1.921(3)	1.908(4)	1.908(3)	2.204(4)
Co1–N21	1.922(3)	1.925(4)	1.923(3)	2.104(4)
Co1–N51	2.026(2)	1.976(4)	1.959(3)	2.160(3)
Co2–O1	1.896(2)	1.980(3)	1.983(2)	2.134(3)
Co2–N31	1.929(2)	1.915(4)	1.910(3)	2.215(4)
Co2–N41	2.024(2)	1.926(4)	1.920(3)	2.094(3)
Co2–N61	1.968(3)	1.960(5)	1.960(3)	2.148(3)
Co1–O2/N1	1.875(2)	1.882(5)	1.896(2)	2.138(4)
Co1–O3	1.916(2)	1.910(4)	1.903(3)	2.074(3)
Co2–O4	1.873(2)	1.903(4)	1.903(2)	2.045(4)
Co2–O5/N3	1.908(2)	1.894(4)	1.886(3)	2.156(3)
Co1–O1–Co2	113.4(1)	131.0(2)	131.2(1)	131.3(1)
Co1–O1–C65	118.3(2)	114.6(3)	114.4(2)	113.8(2)
Co2–O1–C65	122.8(2)	114.5(3)	114.4(2)	114.9(2)

Table 2 Hydrogen bond bridging in $[Co_2(bpbp)(H_2O)_2(OH)_2](ClO_4)_3$ **3** and in $[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4$ **4**

D–H ··· A	Compound	D–H/Å	H ··· A/Å	D ··· A/Å	D–H ··· A/°
O3–H3a ··· O5	**3**·$2H_2O$	1.19(6)	1.26(6)	2.446(5)	170(4)
O4–H4a ··· O2	**3**·$2H_2O$	0.87(7)	1.60(7)	2.427(5)	158(6)
O3–H3a ··· O5	**3**·$CH_3CN·H_2O$	1.14(8)	1.32(7)	2.456(4)	172(6)
O2–H2a ··· O4	**3**·$CH_3CN·H_2O$	1.10(6)	1.35(6)	2.437(3)	170(5)
N1–HN1a ··· O4	**4**·$3.875H_2O$	0.99(5)	2.01(5)	2.957(5)	158(4)
N3–HN3a ··· O3	**4**·$3.875H_2O$	0.84(5)	2.24(5)	2.989(6)	149(5)

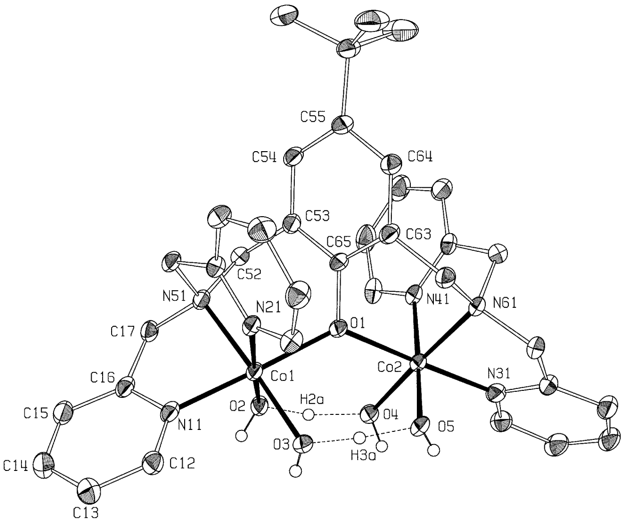

Fig. 3 X-Ray structure of the cation in **3**·$CH_3CN·H_2O$.

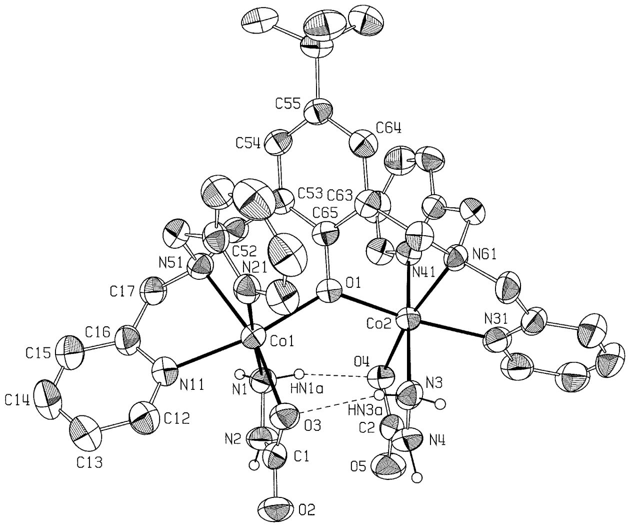

Fig. 4 X-Ray structure of the cation in **4**·$3.875H_2O$.

ligands were located on electron density difference maps. The Co1–N1 and Co2–N3 bond distances are 2.138(4) and 2.156(3) Å, respectively. They are thus slightly shorter than those in the mononuclear $[Co(N_2H_4)_2(NH_2NHCO_2)_2]$ (Co–N 2.198(2) Å).[6] The Co1–O3 (2.074(3) Å) and Co2–O4 (2.045(4) Å) bond distances are similar to that in $[Co(N_2H_4)_2(NH_2NHCO_2)_2]$ (Co–O 2.064(2) Å).[6] The Co1 ··· Co2 distance is 3.873(1) Å while the Co1–O1–Co2 angle (131.3(1)°) is essentially identical to that in **1**, **3**·$CH_3CN·H_2O$ and **3**·$2H_2O$. The metal–metal distances in this small series of complexes span a relatively large range from 3.168(1) to 3.873(1) Å thereby demonstrating the flexibility of $bpbp^-$ in adopting to alterations in steric requirements.

Oxidation of 1 to a μ-superoxo complex

The CV of **1** (Fig. 5) shows a reversible oxidation at 510 mV and an irreversible reduction at −845 mV. The solid line in the CV

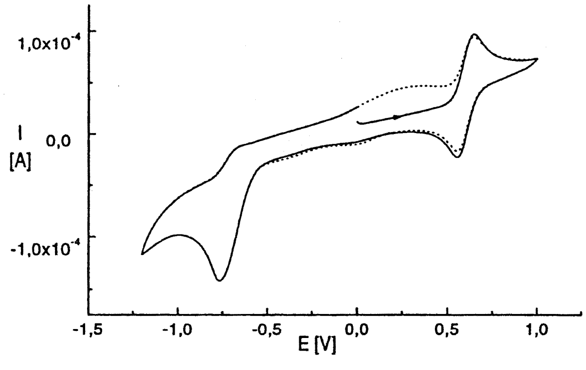

Fig. 5 Cyclic voltammogram of $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)](ClO_4)_2$ in acetonitrile.

of **1** shows the first sweep and the dotted line is the second sweep. The arrowhead indicates the direction of the sweep. The fact that the second scan shows new features is also consistent with an irreversible reduction in the first cycle. The irreversible reduction at −845 mV is assigned to a reduction of Co^{III} to Co^{II} on the basis of literature data for related μ-peroxo cobalt(III) compounds.[5f,g] The reversible redox wave at 510 mV is assigned to the coordinated $O_2^{2-}/O_2^{\bullet -}$ couple. The value is typical for this redox couple and, for example, for $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{3+}$ the corresponding redox potential has been reported to be 570 mV.[5f] Formation of the superoxo-bridged complex $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{3+}$ (**6**) is verified by EPR analysis of the product obtained by $[Ce(NO_3)_6]^{2-}$ oxidation of **1** in a mixture of aqueous nitric acid and acetonitrile. The EPR spectrum of (**6**) shows a 15 line spectrum centred at *ca.* $g = 2$ at room temperature (Fig. 6) indicating that the unpaired electron of the superoxide radical anion couples with both ^{59}Co nuclei ($I = 7/2$). The isotropic hyperfine coupling constant is 10.8 G, which is typical for dibridged dinuclear μ-superoxo complexes of cobalt.[5a] For example, the EPR spectrum of $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{4+}$ shows an isotropic hyperfine coupling constant of 12.4 G.[5b] The peroxo- and superoxo-bridged complexes are distinguished by ν(O–O) at 827.0 and 1044.0 cm^{-1} in the resonance Raman spectrum, respectively (Fig. S1, ESI†). These values are typical for dibridged dicobalt complexes with amines and related ligands.[5c] By comparison,[5d,e] solid $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4](NO_3)_3\cdot H_2O$ has ν(O–O) at 820 cm^{-1} while solid $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]Cl_4$ has ν(O–O) at 1072 cm^{-1}. In addition, the peroxo- and superoxo-bridged complexes are easily distinguished by ESI-MS by the *m*/*z* values (they have the same molecular mass but a 2+ and 3+ charge, respectively, for **1** and **6**). Tandem MS/MS (Fig. S2, ESI†) shows that the mass equivalent of O_2 is readily lost from both **1** and **6** to generate the $[Co_2(bpbp)(\mu\text{-}CH_3CO_2)]^{2+}$ and $[Co_2(bpbp)(\mu\text{-}CH_3CO_2)]^{3+}$ ions, respectively. Interestingly this loss is considerably more facile for the peroxo complex. Indeed, the molecular cation for **1** can be observed only using very mild source conditions.

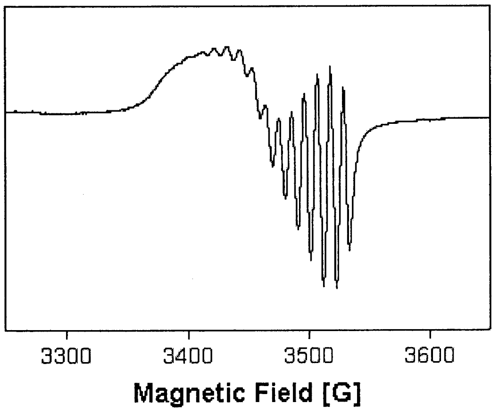

Fig. 6 EPR spectrum of the superoxo-bridged complex $[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)]^{3+}$.

The $\mu\text{-}H_3O_2^-$ bridging ligand

Complex **3** is the first example of two $\mu\text{-}H_3O_2^-$ bridging ligands in cobalt(III) complexes with a dinucleating ligand. The chemistry of the $\mu\text{-}H_3O_2^-$ bridging ligand has been reviewed.[4a] Structural characterisations of $\mu\text{-}H_3O_2^-$ bridging ligands in discrete cobalt(III) complexes are however limited to *trans*-$[Co(en)_2(NO_2)]_2(H_3O_2)(ClO_4)_3\cdot 2H_2O$ and *trans*-$[Co(en)_2(NCS)]_2(H_3O_2)(CF_3SO_3)_3\cdot H_2O$.[4c] In addition the X-ray crystal structure of *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$, which contains an infinite chain of *trans*-$[Co(en)_2(H_3O_2)]_n^{2n+}$, has been reported.[4b] The $\mu\text{-}H_3O_2^-$ bridging ligand shows in these complexes O ··· O distances in the range 2.412(9)–2.441(2) Å and the hydrogen bond is classified as being "very strong". The Co–O bond distances[4b,c] are in the range 1.906(6)–1.916(1) Å and are thus significantly shorter than in $\mathbf{3}\cdot 2H_2O$ and $\mathbf{3}\cdot CH_3CN\cdot H_2O$ (Table 1). The report on the crystal structure of $[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)(H_2O)](ClO_4)_2$ does not quote the O ··· O distance.[3] However, inspection of the bond lengths deposited in Cambridge Crystallographic Database reveals an O ··· O distance of 2.452 Å, which is very close to one of the bond distances in $\mathbf{3}\cdot CH_3CN\cdot H_2O$ and thus is indicative of a very strong hydrogen bond. By use of a dinucleating ligand it is very possible that the $\mu\text{-}H_3O_2^-$ bridging ligand persists in solution. This type of structural motif is presumably highly relevant to hydrolytic oligozinc enzymes such as phospholipase C,[7a] alkaline phosphatase,[7b] and P1 nuclease.[7c] Recently two dizinc model complexes with $\mu\text{-}H_3O_2^-$ bridging ligands have been reported.[8]

One might envisage that if an aqua ligand in **3** is replaced by *e.g.* a phosphate ester, hydrolysis of the latter may be promoted by an intramolecular attack from the adjacent hydroxo ligand. As mentioned in the introduction, hydrolysis of a *coordinated* phosphate monoester in $[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)_2]^+$ has been reported.[3] Up till now, attempts to use **3** to promote hydrolysis reactions have been unsuccessful. We can conclude from this, that either the complexes are not sufficiently labile to undergo substitution of the water ligand for the substrate, or that the lack of a secondary supporting bridge in **3** means that the system is not sterically appropriate for intramolecular reaction at the bridging site. It is noteworthy that $[Co_2(bpmp)(\mu\text{-}PhOPO_3)(OH)_2]^+$ was prepared[3] by air oxidation of cobalt(II) in the presence of $bpmp^-$ and phenylphosphonate. In view of our findings, it is very likely that coordination of phenylphosphonate can only achieved starting from cobalt(II), and that the subsequent hydrolysis reaction cannot be extended to any catalytic action of the dicobalt complexes.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed at the Chemistry Department II at Copenhagen University, Denmark and Atlantic Microlab, Inc., Norcross, Georgia 30091, USA. UV/VIS spectra were recorded on a Shimadzu UV-3100 spectrophotometer. IR spectra of the complexes in KBr discs were measured using a Hitachi 270–30 IR spectrometer. Electrospray ionization mass spectra (ESI MS) were obtained using a Finnigan TSQ 700 triple quadrapole instrument equipped with a Finnigan API source in the nanoelectrospray mode. Cyclic voltammograms were recorded using an Eco Chemie Autolab potentiostat equipped with an ECD low-current auxiliary module and controlled by the General Purpose Electrochemical Systems v.3.2 software (Eco Chemie software). The all-glass cell consisted of a working and a reference compartment connected *via* a Luggin capillary. The working compartment contained a platinum disc (5 mm in diameter) working electrode and a semi-cylindrical platinum gauze auxiliary electrode. The reference compartment contained a silver wire reference electrode immersed in a 0.01 M $AgNO_3$ solution in dry acetonitrile separated from the bulk solution by a porous Vycor plug. Dry acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte was used at ambient temperature under a N_2 atmosphere. The redox potentials are reported against the ferrocenium/ferrocene couple, which was 89 mV in acetonitrile. Electron paramagnetic resonance (EPR) measurements at X-band frequency were obtained using a Bruker ESP-380E FT-EPR spectrometer. 2,6-Bis[bis(2-pyridylmethyl)aminomethyl]-4-*tert*-butylphenol (Hbpbp) was prepared as described earlier.[9]

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compounds should be prepared and handled behind suitable protective shields.

Table 3 Summary of crystal data for $[Co_2(bpbp)(O_2)(CH_3CO_2)](ClO_4)_2$ **1**, $[Co_2(bpbp)(H_2O)_2(OH)_2](ClO_4)_3$ **3** and $[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4$ **4**

	1	**3**·$2H_2O$	**3**·$CH_3CN·H_2O$	**4**·$3.875H_2O$
Empirical formula	$C_{38}H_{42}N_6O_{13}Cl_2Co_2$	$C_{36}H_{49}N_6O_{19}Cl_3Co_2$	$C_{38}H_{50}N_7O_{18}Cl_3Co_2$	$C_{38}H_{48.75}N_{10}O_{12.875}ClCo_2$
M	979.60	1094.04	1117.13	1006.99
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	36.018(2)	11.7233(6)	11.906(1)	10.823(2)
b/Å	10.1931(6)	13.2960(7)	13.329(2)	12.824(2)
c/Å	21.971(1)	16.0808(8)	16.168(2)	16.787(2)
α/°	90	108.857(1)	108.359(2)	85.545(3)
β/°	94.602(1)	90.455(1)	90.173(2)	84.364(3)
γ/°	90	112.061(1)	112.728(2)	78.741(3)
V/Å^3	8040(1)	2174.5(2)	2223.3(4)	2270.0(5)
Z	8	2	2	2
D_c/g cm^{-3}	1.618	1.671	1.668	1.473
μ/mm^{-1}	1.028	1.033	1.012	0.862
T/K	120	120	120	295
2θ range/°	1.9–26.8	1.8–28.4	1.8–29.5	1.9–27.5
Reflections collected	41749	12051	17416	28542
Independent reflections	7789	8241	10910	10436
R_{int}	0.052	0.049	0.064	0.072
No. of obsd. reflections	6007	6850	7504	6233
$I > n\sigma(I)$, n	3	3	3	1.5
$R(F)$, $wR(F)$	0.039, 0.041	0.067, 0.052	0.043, 0.048	0.056, 0.052
Goodness of fit (F^2)	1.034	1.086	1.190	1.108
No. of variables	550	619	638	603

$[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}CH_3CO_2)](ClO_4)_2$ (1)

Hbpbp (0.1235 g, 0.22 mmol), sodium acetate (0.022 g, 0.27 mmol) and $Co(ClO_4)_2·6H_2O$ (0.200 g, 0.55 mmol) were mixed in 15 mL acetone and 2 mL water. The colour of the solution changed from orange–red to brown–red over a few minutes and the product crystallised as dark brown needles overnight. Yield 0.185 g, 86%. Calc. for $Co_2C_{38}H_{42}N_6O_{13}Cl_2$: C, 46.59; H, 4.32; N, 8.58; Cl, 7.24. Found: C, 46.31; H, 4.41; N, 8.47; Cl, 7.24%. ESI-MS: m/z 374 (100%, $[Co_2(bpbp)(\mu\text{-}CH_3CO_2)]^{2+}$), 847 (40%, $\{[Co_2(bpbp)(\mu\text{-}CH_3CO_2)](ClO_4)\}^+$). UV-Vis (MeOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 308 (8100, sh); 350 (7280, sh); 481 (3360, sh); 690 (370, sh). δ_C (75.5 MHz, CD_3CN) 27.4 (1 C, μ-*C*H_3CO_2), 31.5 (3 C), 35.0, 60.4, 61.4, 64.9, 65.3, 66.8, 67.5, 120.3, 121.5, 124.0, 124.9, 125.4, 126.2, 126.5, 126.8, 127.2, 128.7, 129.1, 129.7, 140.6 (2 C), 141.5, 141.7, 146.3, 150.7, 152.1, 152.6, 153.6, 155.8, 161.5, 162.5, 164.4, 165.1 and 189.3 (μ-CH_3*C*O_2).

$[Co_2(bpbp)(\mu\text{-}O_2)(\mu\text{-}C_6H_5CO_2)](ClO_4)_2·H_2O$ (2·H_2O)

Hbpbp (0.05 g, 0.09 mmol) and benzoic acid (0.016 g, 0.13 mmol) dissolved in 15 mL of acetone were mixed with $Co(ClO_4)_2·6H_2O$ (0.067 g, 0.18 mmol) in 2 mL of water. The product crystallised over 24 h. Yield 0.041 g, 45%. Calc. for $Co_2C_{43}H_{44}N_6O_{13}Cl_2·H_2O$: C, 48.72; H, 4.34; N, 7.93. Found: C, 48.47; H, 4.09, N, 7.37%.

$[Co_2(bpbp)(\mu\text{-}H_3O_2)_2](ClO_4)_3·2H_2O$ (3·$2H_2O$)

Hbpbp (0.3 g, 0.52 mmol) in 10 mL acetone was mixed with $Co(ClO_4)_2·6H_2O$ (0.4 g, 1.09 mmol) in 10 mL of water. On the dropwise addition of 35% H_2O_2 (0.5 mL, 0.2 g, 5.88 mmol) the colour of the solution changed from pink to dark brown. The reaction was stirred for further 30 min and left standing. The product crystallised over a few hours. Yield 0.47 g, 82%. Calc. for $[Co_2(bpbp)(OH)_2(H_2O)_2](ClO_4)_3·2H_2O$, $Co_2C_{36}H_{49}N_6O_{19}Cl_3$: C, 39.52; H, 4.51; N, 7.68; Cl, 9.72. Found: C, 39.28; H, 4.48; N, 7.55; Cl, 9.92%. ESI-MS, m/z: 361 (100%, $[Co_2(bpbp)(O)(OH)]^{2+}$), 429 (40%, $\{[Co_2(bpbp)(OH)_2)](ClO_4)\}^+$). UV-Vis (MeOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 253 (2790, sh); 368 (2728); 446 (1762, sh); 556 (440, sh). δ_C (75.5 MHz, CD_3CN) 31.5 (3 C), 35.0, 59.5 (2 C), 66.3 (2 C), 66.7 (2 C), 121.1 (2 C), 125.4 (2 C), 126.4 (2 C), 127.2 (2 C), 127.6 (2 C), 130.6 (2 C), 141.8 (2 C), 143.0 (2 C), 147.5, 150.7 (2 C), 153.6 (2 C), 155.2, 164.0 (2 C) and 164.6 (2 C). The same compound can be prepared without the addition of H_2O_2, however crystallization took 2 weeks.

$[Co_2(bpbp)(NH_2NHCO_2)_2]ClO_4·4H_2O$ (4·$4H_2O$)

$[Co_2(bpbp)(OH)_2(H_2O)_2](ClO_4)_3·2H_2O$ (0.1 g, 0.09 mmol) was dissolved in 25 mL of water and 10 mL of ethanol. Hydrazine hydrate (1.0 mL, 20.6 mmol) was added and the color changed from greenish to pink. The product as pink crystals deposited over 24 h (0.07 g, 78%). Calc. for $Co_2C_{38}H_{45}N_{10}O_9Cl.4H_2O$: C, 45.13; H, 5.24; N, 13.85. Found: C, 45.28; H, 5.42; N, 13.70%. IR/cm^{-1}: 1606, ν_{CO}; 1096 ν_{ClO_4}. The ClO_4 band is less intense compared to the starting material.

$[Co_2(bpbp)(\mu\text{-}C_3H_3N_2)_2](ClO_4)_3$ (5)

Hbpbp (0.27 g, 0.47 mmol) and pyrazole (0.064 g, 0.94 mmol) in 10 mL acetone was mixed with $Co(ClO_4)_2·6H_2O$ (0.43 g, 1.2 mmol) in 10 mL of water. After 1 h at reflux temperature the solution was brown–red. After the mixture was cooled, the product crystallised over a few hours. Yield 0.322 g, 61%. Calc. for $[Co_2(bpbp)(C_3H_3N_2)_2](ClO_4)_3$, $Co_2C_{42}H_{45}N_{10}O_{13}Cl_3$; C, 44.96; H, 4.04; N, 12.48; Cl, 9.47. Found: C, 44.76; H, 4.10; N, 12.10; Cl, 8.95%. δ_C (75.5 MHz, CD_3CN): 31.3 (3 C), 35.6, 61.7 (2 C), 67.4 (2 C), 68.5 (2 C), 113.0 (2 C, μ-$C_3H_3N_2$ (C2)), 122.4 (2 C), 127.3 (2 C), 127.8 (2 C), 128.3 (2 C), 129.0 (2 C), 129.9 (2 C), 142.5 (2 C), 144.0 (2 C), 144.7 (2 C, μ-$C_3H_3N_2$ (C1)), 145.4 (2 C, μ-$C_3H_3N_2$ (C1)), 149.5, 150.1, 152.1 (2 C), 155.7 (2 C), 163.5 (2 C), and 164.9 (2 C).

Crystal structure analyses

Crystals of **1**, **3**·$2H_2O$ and **3**·$CH_3CN·H_2O$ were mounted on a Bruker-Smart CCD diffractometer at 120 K and **4**·$3.875H_2O$ at 295 K. Crystal data and details of refinement are listed in Table 3. Data were collected with ω-scans and corrected for Lorentz and polarisation effects and corrected for absorption by integration.[10] The structures were solved by direct methods using SIR97[11] and refined by the method of least-squares, on F. Hydrogen atoms attached to C or N were kept fixed at calculated positions whilst those of uncoordinated water molecules were kept fixed at positions determined from difference syntheses. Hydrogen atoms of coordinated water or hydroxyl groups of **3**·$2H_2O$, and **3**·$CH_3CN·H_2O$ were refined isotropically as were those of the coordinated NH_2 groups in **4**·$3.875H_2O$. Originally the H atoms **3**·$CH_3CN·H_2O$ were modelled as in **3**·$2H_2O$, *i.e.* with a water molecule and a hydroxyl group coordinated to each cobalt atom, but on refinement one H atom moved from O4 to O2 so that there were two water molecules coordinated to Co1 and two hydroxyl groups on Co2. Solvent peaks, O14, O15 and O16, in **4** were interpreted as water molecules with site occupation factors x for O14 and O15 and $1 - x$ for O16. The sum of the site occupation factors for these was 1.875(9). Programs, other than those referenced, were from KRYSTAL.[12] Selected bond distances are listed in Table 1 and details of the bridging hydrogen bonds in Table 2.

CCDC reference numbers 195394–195397.

See http://www.rsc.org/suppdata/dt/b2/b210091f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Financial support from the Danish Natural Science Research Council is gratefully acknowledged.

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