

[2-(2-{Bis[2-(1*H*-imidazol-2-ylmethyl-eneamino)ethyl]amino}ethylimino-methyl)imidazolido]cobalt(III) bis(tetrafluoridoborate) monohydrate

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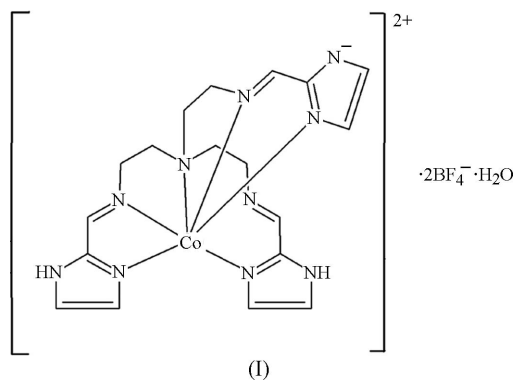
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The title compound, [Co(C₁₈H₂₃N₁₀)](BF₄)₂·H₂O, is the result of complexing a Co cation (initially in a Co^{II} state) with tris[2-(1*H*-imidazol-2-ylmethyleneamino)ethyl]amine (*L*), obtained by a condensation process involving imidazole-2-carbaldehyde and tris(2-aminoethyl)amine. Both the Co cation and the ligand were modified in the synthesis process, the cation *via* oxidation to Co^{III}, and the ligand *via* deprotonation to convert it into the 2-(2-{bis[2-(1*H*-imidazol-2-ylmethyleneamino)ethyl]amino}ethylimino-methyl)imidazolido anion (*L*⁻). The ligand chelates the metal centre in a hexadentate fashion, forming a slightly distorted octahedral CoN₆ chromophore. Packing is governed by N—H···N hydrogen bonds defining zigzag chains. A similar structure in the literature is discussed, and the wrong assignment of the oxidation state, given therein to the Co cation, is corrected.

Comment

It is well known (see *e.g.* Cotton & Wilkinson, 1988) that in the absence of complexing agents the Co^{III} species is usually not favoured in aqueous solutions containing the metal, while its stability is greatly increased when complexing agents containing nitrogen are present. Thus, it is not unusual to obtain Co^{III}N₆ chromophores *via* a synthesis procedure which starts with Co^{II} as the initial cation, and which transforms into Co^{III} through an unwitting oxidation process. Under such conditions, these transformations do not require much energy and can be spontaneous and perfectly feasible, even at room temperature. We present herein the result of one such transformation, where an intended complexation of a Co^{II} cation with tris[2-(1*H*-imidazol-2-ylmethyleneamino)ethyl]amine (*L*),

obtained by condensation of imidazole-2-carbaldehyde and tris(2-aminoethyl)amine (see *Experimental*), resulted in the generation of the [Co^{III}(*L*⁻)]²⁺ cation through the oxidation of the metal and the simultaneous loss of an imidazole H atom. The resulting ionic species was [2-(2-{bis[2-(1*H*-imidazol-2-ylmethyleneamino)ethyl]amino}ethylimino-methyl)imidazolido]cobalt(III) bis(tetrafluoridoborate) monohydrate, (I), and the structure is reported herein.



The Co^{III} centre of (I) (Fig. 1) is octahedrally surrounded by a chelating *L*⁻ ligand acting in a $\mu_1-\kappa^6 N, N', N'', N''', N''''$ mode through three imidazole and three imine N atoms. The resulting coordination polyhedron is rather regular, in spite of the restraints imposed by chelation, with *trans* angles spanning the range 173.27 (14)–176.19 (14)° and *cis* angles spanning the range 82.49 (14)–94.80 (14)° (Table 1). Co—N distances are also in a tight range, *viz.* 1.898 (3)–1.950 (3) Å, with a mean of 1.927 (24) Å, well within the expected values for Co^{III}—N distances reported in the literature [mean value in Co^{III}N₆ chromophores for 1220 cases in the 2008 version of the CSD (Allen, 2002): 1.955 (25) Å]. The cation has approximate noncrystallographic *C*₃ symmetry, as assessed by the least-squares fit between one cation and its 120° rotated image, resulting in a mean deviation of 0.12 (1) Å (Fig. 2). The structure is completed by two well resolved, though strongly

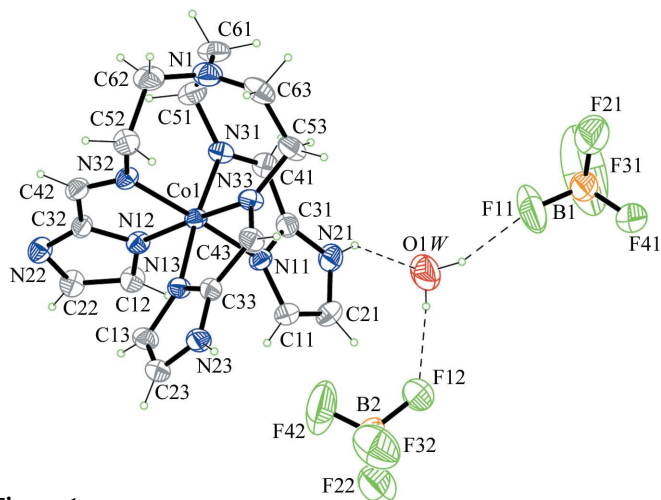


Figure 1
The asymmetric unit of (I), with displacement ellipsoids at the 30% probability level. Hydrogen bonds are shown as dashed lines.

vibrating, BF_4^- counter-anions, and a water molecule of crystallization.

From a crystallographic point of view, the most interesting feature of the structure is the formation of strong $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds between adjacent imidazole groups, which involves the deprotonated N22 atom as acceptor and one of the protonated atoms, *viz.* N23, as donor, and which appears as a distinctive feature for the presence of Co^{III} (see discussion below). Fig. 3 shows the way in which this interaction threads a zigzag chain along [001]. The remaining imidazole N atom (N12), in turn, interacts with the pendent ‘water molecule and two BF_4^- counter-anions’ hydrogen-bonded system shown in Fig. 1; the counter-ions stretch out at both sides of the [001] chains and their F atoms have weak $\text{C}-\text{H}\cdots\text{F}$ interactions (Table 2) between chains.

While searching the literature for related structures, we came across a very similar Co compound (He, 2007) reported as a Co^{II} complex with the fully protonated tris(2-aminoethyl)amine (ligand *L*) in the scheme, but reported in the crystal data text as $[\text{Co}(\text{C}_{18}\text{H}_{23}\text{N}_{10})_2](\text{ClO}_4)_2\cdot 0.5\text{H}_2\text{O}$, hereafter (II). This was described in the title, scheme and text as a Co^{II} complex having two independent $[\text{Co}^{\text{II}}\text{L}]^{2+}$ cationic groups in the asymmetric unit with charge balance provided by four perchlorate counter-anions; there was also one water molecule in the asymmetric unit. To our surprise, the reported $\text{Co}-\text{N}$ distances and angles in this (He, 2007) structure were in complete agreement with those in (I) and in principle totally ascribable to a Co^{III} cationic centre instead of the reported Co^{II} structure. This misfit was also apparent in the reported formula, *ORTEP* plots and CIF coordinates, all of which confirmed that only two imidazole groups in the presumed *L* ligand were protonated, thus turning it into a L^- anion and thus enforcing the need for a 3+ cation at the central core. All

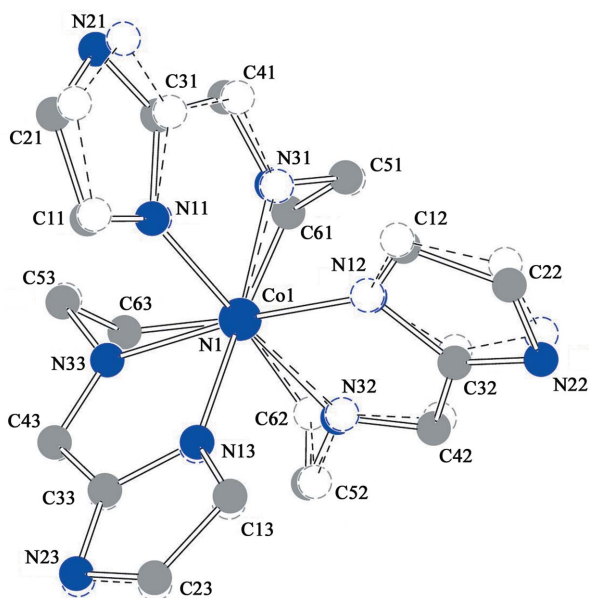


Figure 2
A least-squares fit between one cation and its 120° rotated image, showing the noncrystallographic pseudo- C_3 symmetry, viewed down the pseudo- C_3 axis.

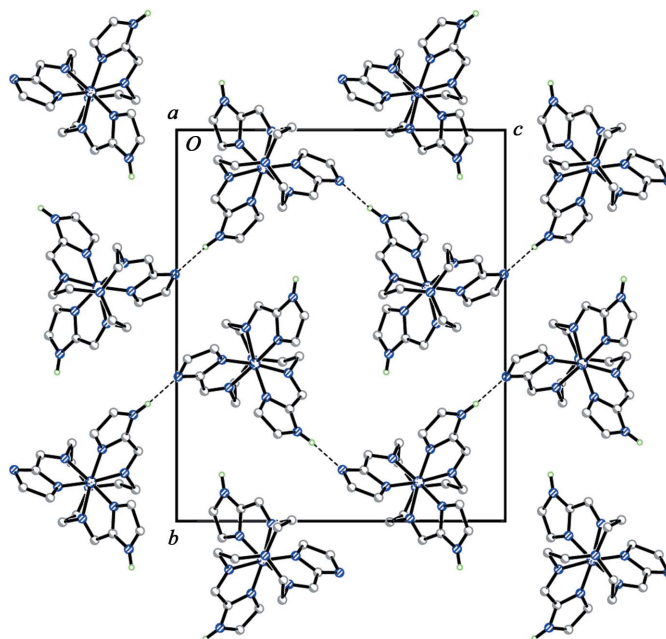


Figure 3
Packing view of (I) projected down [100]. For clarity, only the zigzag chains running along [001] are shown (without counter-ions and solvates). $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds are shown as dashed lines.

these facts support the contention that the composite cationic groups in both compounds are completely equivalent, and should have been reported as $[\text{Co}^{\text{III}}(\text{L}^-)]^{2+}$ in the He (2007) paper.

While a table of hydrogen-bond data is provided in the He (2007) paper, there is no discussion or description of the hydrogen bonding in the structure of (II). Inspection of the CIF for (II) shows that the packing is defined by parallel chains extending along [100] [in this case of two different types, corresponding to the two independent cation moieties in (II)], organized through the characteristic $\text{N}-\text{H}\cdots\text{N}$ synthon, a fingerprint disclosing the presence of the L^- ligand (and concomitantly, the Co^{III} cation) in these types of structures.

Experimental

Tris(2-aminoethyl)amine (0.0748 ml, 0.5 mmol) and imidazole-2-carbaldehyde (0.14135 g, 1.5 mmol) were dissolved in methanol (10 ml) and the solution kept under reflux while stirring for half an hour. A solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.11897 g, 0.5 mmol) in water (10 ml) was added to this mixture, and the composite became deep red. Finally, NH_4BF_4 (0.15726 g, 1.5 mmol) was added to the solution which was kept under reflux for another 7 h. Slow evaporation at room temperature for two weeks yielded single crystals suitable for X-ray diffraction. For an alternative synthesis, see He *et al.* (2004).

Crystal data

$[\text{Co}(\text{C}_{18}\text{H}_{23}\text{N}_{10})](\text{BF}_4)_2\cdot\text{H}_2\text{O}$
 $M_r = 630.03$
 Monoclinic, $P2_1/c$
 $a = 9.1704$ (9) Å
 $b = 18.2328$ (19) Å
 $c = 15.3594$ (15) Å
 $\beta = 93.843$ (2)°

$V = 2562.3$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.76$ mm⁻¹
 $T = 298$ (2) K
 $0.44 \times 0.31 \times 0.11$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS in SAINT; Bruker, 2002)
 $T_{\min} = 0.70$, $T_{\max} = 0.92$

21379 measured reflections
5778 independent reflections
3528 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.194$
 $S = 0.93$
5778 reflections

361 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Co1–N12	1.898 (3)	Co1–N32	1.946 (3)
Co1–N13	1.901 (3)	Co1–N33	1.948 (3)
Co1–N11	1.918 (3)	Co1–N31	1.950 (3)
N12–Co1–N13	91.13 (14)	N11–Co1–N33	89.03 (14)
N12–Co1–N11	93.33 (14)	N32–Co1–N33	94.79 (14)
N13–Co1–N11	91.50 (14)	N12–Co1–N31	90.27 (14)
N12–Co1–N32	82.88 (13)	N13–Co1–N31	173.63 (14)
N13–Co1–N32	89.10 (14)	N11–Co1–N31	82.21 (14)
N11–Co1–N32	176.18 (14)	N32–Co1–N31	97.24 (14)
N12–Co1–N33	173.26 (14)	N33–Co1–N31	96.31 (14)
N13–Co1–N33	82.49 (14)		

All H atoms were found in a difference Fourier map and positioned afterwards at their expected positions, while allowed for riding [$\text{C}–\text{H} = 0.93–0.97 \text{ \AA}$, $\text{N}–\text{H} = 0.86 \text{ \AA}$ and $\text{O}–\text{H} = 0.85 \text{ \AA}$, and $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{host})$].

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D–H \cdots A$	$D–H$	$H \cdots A$	$D \cdots A$	$D–H \cdots A$
O1W–H1WA···F11	0.85	2.01	2.814 (6)	157
O1W–H1WB···F12	0.85	2.09	2.934 (6)	170
N21–H21N···O1W	0.86	2.05	2.779 (5)	142
N23–H23N···N22 ⁱ	0.86	1.92	2.770 (5)	170
C23–H23···F41 ⁱⁱ	0.93	2.40	3.181 (6)	142
C41–H41···F21 ⁱⁱⁱ	0.93	2.51	3.166 (6)	127
C42–H42···F21 ^{iv}	0.93	2.47	3.197 (6)	136
C43–H43···F22 ⁱⁱ	0.93	2.54	3.248 (7)	133
C61–H61A···F42 ^v	0.97	2.27	3.213 (8)	164

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x + 1, y, z$.

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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Bruker (2001). SMART. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2002). SAINT (including SADABS). Version 6.22a. Bruker AXS Inc., Madison, Wisconsin, USA.
Cotton, F. A. & Wilkinson, G. (1988). In *Advanced Inorganic Chemistry*. New York: John Wiley.
He, H.-S. (2007). *Acta Cryst.* **E63**, m1933–m1934.
He, H., Rodgers, K. R. & Arif, A. M. (2004). *J. Inorg. Biochem.* **98**, 667–676.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.