

Diaquatetrakis(*tert*-butyl isocyanide)-cobalt(II) bis(perchlorate): an example of cobalt(II) coordinated by only four alkyl isocyanide ligands

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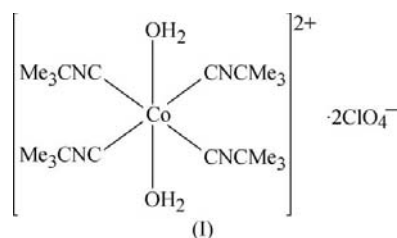
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The title compound, $[\text{Co}(\text{C}_4\text{H}_9\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, crystallizes in the monoclinic space group $C2/m$. The cation has space-group-imposed $2/m$ symmetry, while the perchlorate ion is disordered about a mirror plane. The two slightly non-equivalent Co—C bonds [1.900 (3) and 1.911 (3) Å] form a rectangular plane, with a C—Co—C bond angle of 86.83 (11)°, and the linear O—Co—O C_2 axis is perpendicular to this plane. The C≡N bond lengths are 1.141 (4) Å and the Co—C≡N and C≡N—C angles average 175.5 (4)°. The perchlorate counter-ions are hydrogen bonded to the water molecules. The title compound is the first example of four alkyl isocyanide ligands coordinating Co^{II} upon initial reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ /EtOH with alkyl isocyanide. In all other known examples, five alkyl isocyanide molecules are coordinated, as in $[(\text{RNC})_5\text{Co}—\text{Co}(\text{CNR})_5](\text{ClO}_4)_4$ ($R = \text{Me}, \text{Et}, \text{CHMe}_2, \text{CH}_2\text{Ph}, \text{C}_4\text{H}_9\text{-}n$ or C_6H_{11}) or $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{-}t)_5](\text{ClO}_4)_2$. This complex, therefore, is unique and somewhat unexpected.

Comment

Reactions of Co^{II} perchlorate with alkyl isocyanide ligands have been shown to produce metal–metal bonded diamagnetic dimeric complexes in the solid state, of general formula $[\text{Co}_2(\text{CNR})_{10}](\text{ClO}_4)_4$ and maroon–red in colour, dissociating into dark-blue one-electron paramagnetic monomeric complexes in solution. The crystallographic structure of $[(\text{MeNC})_5\text{Co}—\text{Co}(\text{CNMe})_5](\text{ClO}_4)_4$ has been determined (Cotton *et al.*, 1964), and structures with $\text{CNR} = \text{CNEt}$ (Boorman *et al.*, 1970), CNCHMe_2 (Becker, 1993) and CNCH_2Ph (Becker & Malete, 2003) were assumed to be analogous. Complexes with $\text{CNR} = \text{CNC}_4\text{H}_9\text{-}n$ and $\text{CNC}_6\text{H}_{11}$ (Becker, 1993, 1994) have not been satisfactorily isolated, but appear to exhibit analogous behaviour. The *tert*-butyl isocyanide ligand (CNCMe_3),

however, has been unique in forming low-spin monomeric Co^{II} complexes with only four alkyl isocyanide ligands (Becker *et al.*, 1986; Becker, 1993). Even recent work with the *tert*-octyl isocyanide ligand ($\text{CNC}_8\text{H}_{17}\text{-}t$, *i.e.* 1,1,3,3-tetramethylbutyl isocyanide) has also produced low-spin monomeric Co^{II} complexes but with the usual 5:1 alkyl isocyanide– Co^{II} molar ratio, *i.e.* $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{-}t)_5](\text{ClO}_4)_2$ and $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{-}t)_5](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ (Becker *et al.*, 2008). The unique composition of the title complex, (I), especially when initially reported as $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$, prompted a crystallographic investigation to determine if possible aspects such as steric crowding of the relatively bulky *tert*-butyl isocyanide ligands or unusually strong coordination of the water molecule(s) may be favouring this particular stereochemistry.



Compound (I) is observed to crystallize in the monoclinic space group $C2/m$. The molecular structure is shown in Figs. 1 and 2. The Co^{II} atom is at a site with point-group symmetry of $2/m$ (C_{2h}) and is at the centre of a rectangular bipyramid. The CoC_4 moiety is strictly planar, with the linear O—Co—O C_2 axis perpendicular to this plane, but the two non-equivalent Co—C bonds [1.900 (3) and 1.911 (3) Å] form a rectangular, but not square, plane, with the unique C—Co—C bond angle being 86.83 (11)°. The Co—C bond lengths are sufficiently

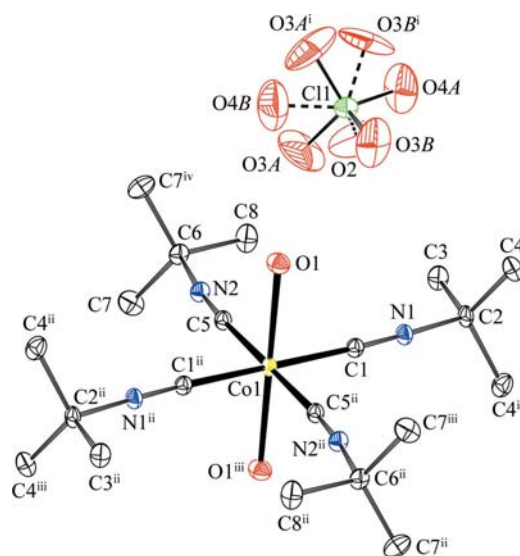


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x, -y, z$; (ii) $1-x, y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, 1-y, z$.]

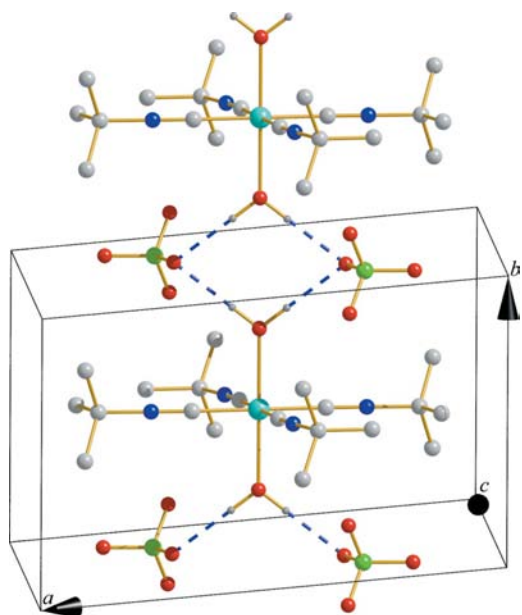


Figure 2

A packing diagram for (I), displaying the infinite hydrogen-bonded chain along the *b* axis. Hydrogen bonds are shown as dashed lines.

short to justify the $d\pi \rightarrow \pi^*$ back-bonding expected from organo isocyanide ligands, and the $\text{C}\equiv\text{N}$ bonds [both 1.141 (4) Å] are just slightly shorter than that in the free $\text{C}\equiv\text{NCH}_3$ molecule (1.166 Å; Costain, 1958). The $\text{Co}-\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{N}-\text{C}$ bond angles average 175.5 (4)°, approximately equal to, but slightly less than, the theoretically expected value of 180.0°.

The unique coordinated water molecule is orientated so that the H atoms are staggered by only 15° from being directly over the $\text{Co}-\text{C}_1$ bonds, *i.e.* the shorter $\text{Co}-\text{C}$ bonds. The H-atom locations of the coordinated water were constrained according to interatomic attraction. These assigned locations are probably the result of attraction to the perchlorate anions, rather than any interaction with the $\text{Co}-\text{C}\equiv\text{N}$ bonds. The unique water H atom takes part in an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond with an adjacent perchlorate O2 atom, with dimensions $\text{H1W}\cdots\text{O2} = 2.04$ Å, $\text{O1}\cdots\text{O2} = 2.993$ (5) Å and $\text{O1}-\text{H1W}\cdots\text{O2}$ 180°, leading to an infinite hydrogen-bonded chain in the *b* direction, as shown in Fig. 2. The perchlorate ion is disordered, which is not atypical for these anions.

Many known structures for CNCMe_3 complexes with cobalt are for multiple mixed-ligand complexes, usually of Co^{I} or Co^{III} . Compounds most relevant for comparison with (I) would appear to be the other Co^{II} complexes of the form $[\text{Co}(\text{CNPh})_5](\text{ClO}_4)_2 \cdot 0.5\text{ClCH}_2\text{CH}_2\text{Cl}$, especially when viewed as $[\text{Co}(\text{CNPh})_5(\text{ClO}_4)]\text{ClO}_4 \cdot 0.5\text{ClCH}_2\text{CH}_2\text{Cl}$, (II) (Jurnak *et al.*, 1975), $[\text{Co}(\text{CNC}_6\text{H}_4\text{Me-}p)_4\text{I}_2]$, (III) (Gilmore *et al.*, 1969), $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2-2,6)_4(\text{ClO}_4)_2]$, (IV) (Becker & Cooper, 1991), $[\text{Co}(\text{CNC}_6\text{H}_4\text{CO}_2\text{Me-}4)_4\text{I}_2]$, (V) (Squires & Mayr, 1997), *trans*- $[\text{Co}(\text{CNC}_6\text{H}_4\text{OSiMe}_3-2)_4\text{I}_2]$, (VI) (Hahn & Lügger, 1994), and *trans*- $[\text{Co}(\text{CNC}_6\text{H}_2\text{Pr}_2-2,6-4-\text{C}\equiv\text{CH})_4\text{I}_2]$, (VII) (Lu *et al.*, 1999). Structural comparisons based on these compounds are shown in Table 1.

The $\text{Co}-\text{O}$ bond length of 2.245 (2) Å is definitely rather long, since a $\text{Co}-\text{O}$ single-bond length of about 1.97 Å should be expected (Slade *et al.*, 1971), although this bond is known over the rather wide range of about 1.75–2.40 Å, with 1.85–2.20 Å being most common (Cambridge Structural Database, Version 5.30 of November 2008; Allen, 2002). However, the $\text{Co}-\text{I}$ bonds in (III), (V), (VI) and (VII) are also consistently elongated, while the $\text{Co}-\text{O}$ bond in (IV) [2.266 (7) Å] would be considered long, albeit short for a coordinated perchlorate bond. In none of the Co^{II} complexes considered does it appear that the CoC_4 moiety is actually square planar. The CoC_4 unit may be planar, having equal [in (VII)] or unequal [in (IV), (V) or (VI)] $\text{Co}-\text{C}$ bond lengths, but it also has unequal $\text{C}-\text{Co}-\text{C}$ bond angles, *i.e.* forming a rectangular plane. Alternatively, as in (III), there is a C_2/S_4 axis because alternating $\text{Co}-\text{C}$ bonds are bent above and below the Co centre ($\sim 5^\circ$). Complex (IV) would appear to approximate most closely the coordination structure for $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

Once tetragonal coordination is recognized for (I), analogy with addition complexes of selected nitrogen bases, $[\text{Co}(\text{CNCMe}_3)_4\text{L}_2](\text{ClO}_4)_2$ (Becker, 1992), becomes apparent. The N-base complexes are blue in colour, due to a crystal field band at 630–670 nm, while (I) is beige to light pink, with a comparable band at 814 nm. This underscores the higher position in the spectrochemical series of N-ligands over O-ligands (Wulfsberg, 2000). However, the diffuse reflectance electronic spectrum for (IV) ($\lambda_{\text{max}} = 875$ nm; Becker & Cooper, 1991) is similar to that for (I).

The coordination structure in (I) has thus been shown to be analogous to known $[\text{Co}(\text{CNR})_4\text{X}_2]$ complexes with aryl isocyanide ligands. The *t*-butyl substituents are not seen to be sterically crowded to the extent of precluding coordination of a fifth alkyl isocyanide ligand, and the relatively long $\text{Co}-\text{O}$ bond lengths contradict the possibility of particularly strong water-molecule coordination, so except for a rather unconvincing argument of strong hydrogen bonding between the coordinated water molecules and the anionic perchlorates, there appears to be no crystallographic explanation as to why a dimeric structure, or at least pentakis-alkyl isocyanide coordination, has not been observed for the title complex.

Experimental

Complex (I), $[\text{Co}(\text{C}_5\text{H}_9\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, initially reported as $[\text{Co}(\text{C}_5\text{H}_9\text{N})_4(\text{H}_2\text{O})](\text{ClO}_4)_2$, was synthesized and routinely characterized by Becker and co-workers (Becker *et al.*, 1986; Becker, 1993) by reaction of excess and/or stoichiometric amounts of CNCMe_3 with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol solution (94% yield). The complex can be recrystallized from CH_3CN and diethyl ether (85% recovery) [m.p. 383–385 K (decomposition)]. X-ray quality crystals of (I) were obtained by slow diffusion of Et_2O into a CH_3CN solution at room temperature. Elemental analysis calculated for $\text{C}_{20}\text{H}_{40}\text{Cl}_2\text{CoN}_{10}\text{O}_{10}$: C 38.35, H 6.44, N 8.94, Cl 11.32%; found: C 37.89, H 6.47, N 8.94, Cl 11.64%. IR spectrum (Nujol mull, ν , cm^{-1}): $-\text{N}\equiv\text{C}$ 2214 (*vs*), ~ 2185 (*vw*, *sh*), 2031 (*w*); $\text{O}-\text{H}$ 3448 (*s*), ~ 3500 (*m*, *sh*); diffuse reflectance electronic spectrum (nm): ~ 814 (*br*, $A = 0.289$), ~ 525 (*sh*), 462 (0.338), ~ 276 (*sh*), 263 (1.54), 216 (1.32); magnetic susceptibility: $\chi_g = 3.74$ (7) $\times 10^{-6}$ cgs, $\mu_{\text{eff}} = 2.52$ (5) BM.

Table 1

Selected geometric parameters (Å, °) for [Co(CNCMe₃)₄(H₂O)₂](ClO₄)₂ and six analogous Co^{II}-aryl isocyanide complexes.

Compound	Co—C	C≡N	Co—C≡N	C≡N—C
(I)	1.900 (3)/1.911 (3)	1.141 (4)– 1.142 (4)	175.1 (2)– 175.8 (2)	173.3 (3)– 177.7 (3)
(II)	1.84 (2)	1.16 (1)	174.6 (6)	173.5 (10)– 179.0 (13)
(III)	1.81 (4)	1.14 (4)	178.8 (42)	174.4 (40)
(IV)	1.896 (9)/1.887 (9)	1.152 (12)	175.3 (7)	174.0 (7)– 177.2 (9)
(V)	1.865 (10)/1.835 (15)	1.15 (3)	173 (1)– 178 (1)	166 (1)– 178 (1)
(VI)	1.858 (2)/1.866 (2)	1.137 (3)– 1.148 (3)	174.6 (2)– 175.9 (2)	173.6 (2)– 174.7 (2)
(VII)	1.850 (7)	1.139 (7)	175.6 (6)	

References: (I) is [Co(CNCMe₃)₄(H₂O)₂](ClO₄)₂ (this work); (II) is [Co(CNPh)₅(ClO₄)]·ClO₄·0.5ClCH₂CH₂Cl (Jurnak *et al.*, 1975); (III) is [Co(CNC₆H₄Me-*p*)₄I₂] (Gilmore *et al.*, 1969); (IV) is [Co(C₆H₃Et₂-2,6)₄(ClO₄)₂] (Becker & Cooper, 1991); (V) is [Co(CNC₆H₄-CO₂Me-4)₂I₂] (Squires & Mayr, 1997); (VI) is [Co(CNC₆H₄OSiMe₃-2)₄I₂] (Hahn & Lügger, 1994); (VII) is [Co(CNC₆H₂Pr₂-2,6-4-C≡CH)₄I₂] (Lu *et al.*, 1999).

Crystal data

[Co(C₅H₉N)₄(H₂O)₂](ClO₄)₂
M_r = 626.39
 Monoclinic, *C*2/*m*
a = 15.8300 (10) Å
b = 8.1176 (5) Å
c = 13.8319 (9) Å
 β = 122.0130 (10)°
V = 1507.12 (17) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.80 mm⁻¹
T = 173 K
 0.73 × 0.33 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: integration (*XPREP*; Bruker, 1999)
T_{min} = 0.595, *T_{max}* = 0.939
 6901 measured reflections
 1949 independent reflections
 1867 reflections with *I* > 2σ(*I*)
R_{int} = 0.018

Refinement

R [*F*² > 2σ(*F*²)] = 0.039
wR (*F*²) = 0.106
S = 1.04
 1949 reflections
 112 parameters
 30 restraints
 H-atom parameters constrained
 Δρ_{max} = 0.72 e Å⁻³
 Δρ_{min} = -0.88 e Å⁻³

All H atoms were refined using a riding model, with C—H = 0.98 Å and O—H = 0.95 Å, and with *U*_{iso}(H) = 1.5*U*_{eq}(C) or 1.5*U*_{eq}(O). The highest residual peak was 1.412 Å from atom Cl1. Perchlorate disorder was apparent in the structure, hence atoms O3A and O3B, and atoms O4A and O4B, were refined with complementary occupancies, respectively. The orientational disorder of the anion was refined over two positions using SIMU, DELU and ISOR restraints (*SHELXTL*; Bruker, 1999); the final occupancies were 0.737 (11) for O3A/O4A and 0.263 (11) for O3B/O4B.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-NT* (Bruker, 2005); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3104). Services for accessing these data are described at the back of the journal.

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