

unsym-*fac*-(*exo*-OH)-[Co(dien)(dapo)(N<sub>3</sub>)] [ZnCl<sub>4</sub>]

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## Key indicators

Single-crystal X-ray study

$T = 168\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.027

$wR$  factor = 0.061

Data-to-parameter ratio = 18.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Structural analysis of the title compound, [*N*-(2-aminoethyl)-1,2-ethanediamine]azido(2-hydroxy-1,3-propanediamine)-cobalt(III) tetrachlorozincate(II), unsym-*fac*-(*exo*-OH)-[Co(dien)(dapo)N<sub>3</sub>]ZnCl<sub>4</sub> or [Co(N<sub>3</sub>)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>O)]-[ZnCl<sub>4</sub>], confirms both the facial configuration of the *N*-(2-aminoethyl)-1,2-ethanediamine (dien) ligand and the *exo* stereochemistry of the OH substituent of the 2-hydroxy-1,3-propanediamine (dapo) ligand relative to the azide ligand.

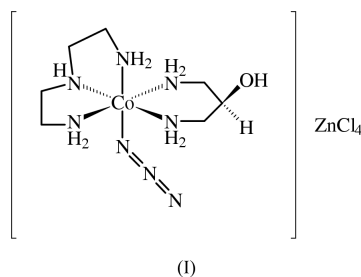
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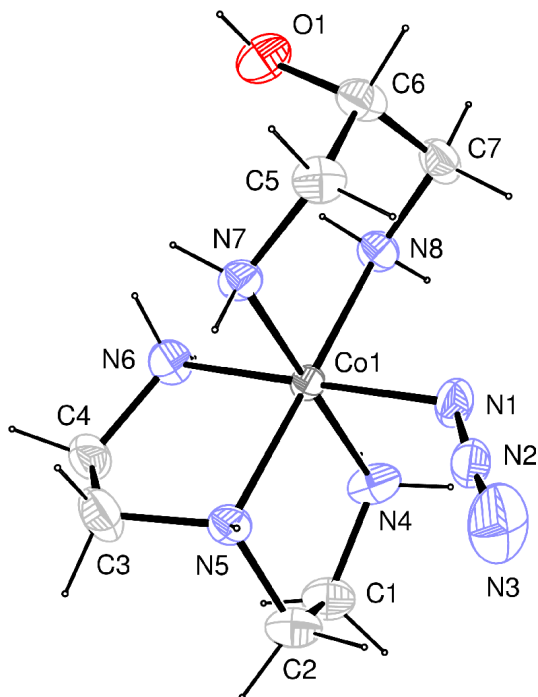
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## Comment

[Co(dien)(dapo)(N<sub>3</sub>)]<sup>2+</sup> complexes are rapidly hydrolysed in weakly alkaline solution at room temperature. The *mer*(*exo*)- and *mer*(*endo*)- forms of the [Co(dien)(dapo)OH]<sup>2+</sup> product quickly equilibrate [ $t_{1/2} = 0.20\text{ s}$ , 298 K,  $I = 1.0\text{ M}$  (NaClO<sub>4</sub>)], and at longer times (1–2 h, pH 9), significant production of unsym(*fac*) isomers occurs. The title complex, (I), was obtained by anation with azide ion, and was isolated using a combination of ion-exchange chromatography and fractional crystallization (Browne *et al.*, 2002).



The structure of the cation consists of a central Co atom coordinated to a tridentate dien ligand bound in a facial configuration, a bidentate dapo ligand, and a monodentate azide ligand. As can be seen in Fig. 1, the dapo –OH group adopts an *exo* configuration with respect to the azide ligand. The geometry about the Co atom is approximately octahedral, with the greatest deviations from 90° being found in the five-membered chelate rings of the dien ligand. The Co–N distances lie in the range 1.943 (2)–1.986 (2) Å, with the bond to the azide ligand being significantly shorter than the others. This contrasts with the three previous structurally characterized [Co(dien)(dapo)N<sub>3</sub>]<sup>2+</sup> complexes, namely  $\Lambda(-)_{436}$ -*mer*(*exo*)-[Co(dien)(dapo)N<sub>3</sub>](di-*O*-benzoyl-L-tartH)<sub>2</sub>·4H<sub>2</sub>O,  $\Lambda(-)_{436}$ - $\Lambda(-)_{436}$ -*mer*(*endo*)-[Co(dien)(dapo)N<sub>3</sub>](di-*O*-benzoyl-L-tartH)<sub>2</sub>·2.75H<sub>2</sub>O and  $\Delta(+)$ <sub>436</sub>-*mer*(*endo*)-[Co(dien)(dapo)N<sub>3</sub>](di-*O*-benzoyl-L-tartH)<sub>2</sub>·5.75H<sub>2</sub>O (Comba *et al.*, 1992), in which the bond between the Co atom and the



**Figure 1**  
The structure of the cation of (I), with displacement ellipsoids drawn at the 50% probability level (Farrugia, 1999).

secondary N atom of the dien ligand is the shortest of the Co–N distances.

## Experimental

A solution of *mer-(exo)-* and *mer-(endo)-*[Co(dien)(dapo)N<sub>3</sub>]ZnCl<sub>4</sub> (1.1 g) in water (5 ml) containing NaN<sub>3</sub> (0.55 g) was allowed to stand for 1 h at pH 7.85, then for a further 1 h at pH 9.3. Precipitated Zn(OH)<sub>2</sub> was removed by filtration, the filtrate was acidified (HOAc, pH 4.5) and complexes separated by ion-exchange chromatography (Dowex 50Wx2, 1 M NaCl, pH 4.2). The slower moving of the two major bands was collected and evaporated to near dryness at room temperature. MeOH was added and solid NaCl removed by filtration. This treatment was repeated until all the NaCl was removed. The final filtrate was evaporated to dryness, and the residue in water (4 ml) was treated with aqueous Li<sub>2</sub>ZnCl<sub>4</sub> (2 M, 1 ml). The first two fractions to crystallize (ice cooling) deposited rapidly and consisted mainly of *mer-(exo)-*[Co(dien)(dapo)N<sub>3</sub>]ZnCl<sub>4</sub>. The third fraction, which was obtained on storage overnight at 277 K (0.3 g, unsym-*fac(exo-OH)* plus *endo-OH*)-[Co(dien)(dapo)N<sub>3</sub>]ZnCl<sub>4</sub>, was dissolved in the minimum volume of hot water to give large rhombohedral crystals of the unsym-*fac(exo-OH)*- isomer on slow cooling at room temperature.

### Crystal data

[Co(N<sub>3</sub>)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>O)]<sup>+</sup>  
[ZnCl<sub>4</sub>]<sup>−</sup>  
*M<sub>r</sub>* = 501.43  
Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 8.119 (3) Å  
*b* = 21.373 (6) Å  
*c* = 10.249 (3) Å  
*β* = 98.071 (4)°  
*V* = 1760.8 (9) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.891 Mg m<sup>−3</sup>  
Mo *K*α radiation  
Cell parameters from 3138 reflections  
*θ* = 2.2–26.5°  
*μ* = 2.92 mm<sup>−1</sup>  
*T* = 168 (2) K  
Irregular, red  
0.79 × 0.30 × 0.21 mm

### Data collection

Bruker CCD area-detector diffractometer  
*φ* and *ω* scans  
Absorption correction: multi-scan (SADABS; Bruker, 1997)  
*T*<sub>min</sub> = 0.843, *T*<sub>max</sub> = 1  
22443 measured reflections

3600 independent reflections  
3138 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.032  
*θ*<sub>max</sub> = 26.5°  
*h* = −10 → 10  
*k* = −20 → 26  
*l* = −12 → 12

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.027  
*wR* (*F*<sup>2</sup>) = 0.061  
*S* = 1.10  
3600 reflections  
200 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 1.8355P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
(Δ/σ)<sub>max</sub> = 0.001  
Δρ<sub>max</sub> = 0.58 e Å<sup>−3</sup>  
Δρ<sub>min</sub> = −0.41 e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co1–N1	1.943 (2)	N5–C3	1.505 (3)
Co1–N4	1.970 (2)	N6–C4	1.481 (3)
Co1–N5	1.966 (2)	N7–C5	1.497 (3)
Co1–N6	1.984 (2)	N8–C7	1.477 (3)
Co1–N7	1.986 (2)	C1–C2	1.491 (4)
Co1–N8	1.961 (2)	C3–C4	1.491 (4)
N1–N2	1.185 (3)	C5–C6	1.503 (4)
N2–N3	1.162 (3)	C6–O1	1.433 (3)
N4–C1	1.481 (4)	C6–C7	1.506 (4)
N5–C2	1.497 (3)		
N1–Co1–N4	86.44 (10)	N5–Co1–N7	91.76 (9)
N1–Co1–N5	95.59 (9)	N6–Co1–N7	91.31 (9)
N1–Co1–N6	177.91 (9)	N8–Co1–N4	91.23 (9)
N1–Co1–N7	90.12 (9)	N8–Co1–N5	175.34 (9)
N1–Co1–N8	87.71 (9)	N8–Co1–N6	90.73 (9)
N4–Co1–N6	92.21 (10)	N8–Co1–N7	91.52 (9)
N4–Co1–N7	175.51 (9)	N2–N1–Co1	125.99 (18)
N5–Co1–N4	85.71 (9)	N3–N2–N1	174.5 (3)
N5–Co1–N6	85.90 (9)		

H atoms were included in calculated positions and refined in the riding approximation with individual (or group, if appropriate) isotropic displacement parameters.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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