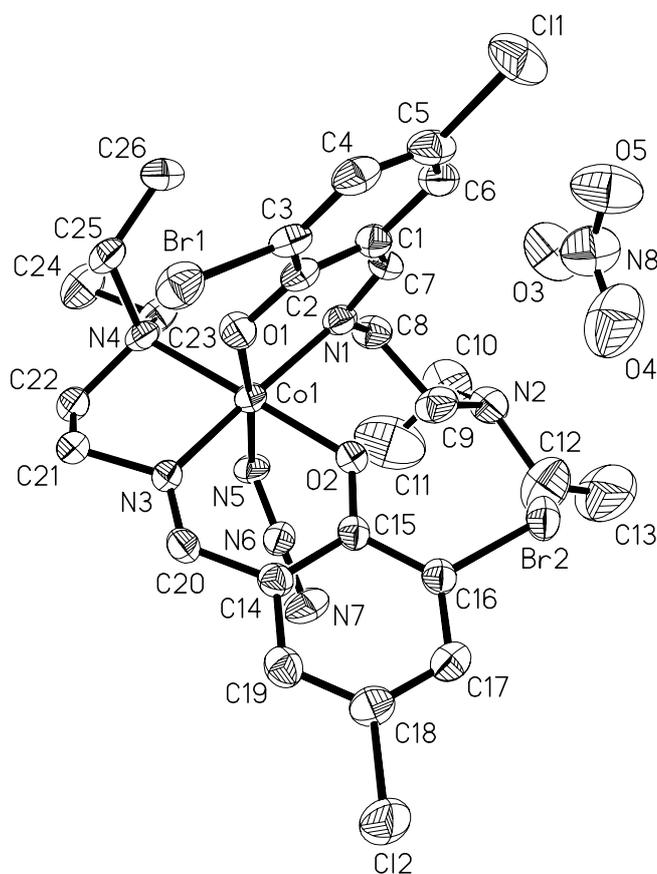


# Crystal structure of azido(2-bromo-4-chloro-6-((2-diethylaminoethyl-imino)methyl)phenolato)(2-bromo-4-chloro-6-((2-diethylhydrogen-aminoethylimino)methyl)phenolato)cobalt(III) nitrate, $[\text{Co}(\text{C}_{13}\text{H}_{17}\text{BrClN}_2\text{O})(\text{C}_{13}\text{H}_{18}\text{BrClN}_2\text{O})(\text{N}_3)][\text{NO}_3]$

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## Abstract

$\text{C}_{26}\text{H}_{35}\text{Br}_2\text{Cl}_2\text{CoN}_8\text{O}_5$ , orthorhombic, *Pbca* (no. 61),  $a = 14.331(1)$  Å,  $b = 19.392(2)$  Å,  $c = 25.521(2)$  Å,  $V = 7092.6$  Å<sup>3</sup>,  $Z = 8$ ,  $R_{\text{gt}}(F) = 0.062$ ,  $wR_{\text{ref}}(F^2) = 0.189$ ,  $T = 298$  K.

## Source of material

All the chemicals used were of AR grade. *N,N*-diethyl-1,2-diaminoethane (23.2 mg, 0.2 mmol) and 3-bromo-5-chlorosalicylaldehyde (47.0 mg, 0.2 mmol) were refluxed in 10 ml methanol for 30 min. To the above solution was added  $\text{NaN}_3$  (6.5 mg, 0.1 mmol) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29.0 mg, 0.1 mmol) in 10 ml methanol. The mixture was refluxed for 1 h. The mixture was filtered after cooling to room temperature. After keeping the filtrate in air for 7 d, brown crystals were formed.

## Experimental details

H2 was located from a Fourier difference map and refined isotropically, with N—H distance restrained to 0.90(1) Å. Other H atoms were positioned geometrically and constrained as riding atoms, with C—H distances of 0.93–0.97 Å, and  $U_{\text{iso}}(\text{H})$  set to 1.2 or 1.5  $U_{\text{eq}}(\text{C})$ .

## Discussion

The condensation reaction of aromatic aldehydes with primary amines has been shown to offer an easy and inexpensive way of forming a variety of Schiff bases. These Schiff bases exhibit a wide range of biological activities and applications [1–7]. Cobalt is an important life-required element. Many cobalt complexes were prepared and structurally determined by single-crystal X-ray analysis [6–8]. We have reported the structure of a mononuclear Schiff base cobalt(III) complex [9] and a mononuclear Schiff base nickel(II) complex [10]. As an extension of the work, we synthesized a further Schiff base cobalt(III) complex.

The asymmetric unit of the crystal structure of the title compound is composed of the cationic mononuclear complex molecule  $[\text{Co}(\text{C}_{13}\text{H}_{17}\text{BrClN}_2\text{O})(\text{C}_{13}\text{H}_{18}\text{BrClN}_2\text{O})(\text{N}_3)]^+$  and a nitrate anion. The Co(III) atom in the complex is coordinated by two Schiff base ligands and one azide ligand, forming an octahedral coordination. One Schiff base ligand coordinates to the metal through one phenolic O, one imine N, and one amine N atoms, while the other one coordinates to the metal through phenolic O and imine N atoms. The azide acts as a terminal ligand and coordinates to the metal through one terminal N atom. The Co—O and Co—N bond lengths are comparable to the values in other similar complexes [11,12]. The N3—Co1—N4 bond angle deviates from the ideal value of 90° by 3.9(2)°, which is due to the strain created by the five-membered chelate ring Co1/N3/C21/C22/N4.

**Table 1.** Data collection and handling.

Crystal:	red block, size 0.27 × 0.28 × 0.32 mm
Wavelength:	Mo $K_{\alpha}$ radiation (0.71073 Å)
$\mu$ :	29.33 cm <sup>-1</sup>
Diffractometer, scan mode:	Siemens P4, $\omega$
$2\theta_{\text{max}}$ :	55°
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ :	57603, 8045
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ , 3385
$N(\text{param})_{\text{refined}}$ :	405
Program:	SHELXTL [13]

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**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	U <sub>iso</sub>
H(4)	8c	0.6180	1.1680	0.7254	0.085
H(6)	8c	0.6183	1.0603	0.5931	0.078
H(7)	8c	0.4996	0.9836	0.5721	0.070
H(8A)	8c	0.3985	0.9188	0.5354	0.079
H(8B)	8c	0.3127	0.8887	0.5665	0.079
H(9A)	8c	0.4966	0.8446	0.5937	0.100
H(9B)	8c	0.4037	0.8059	0.6074	0.100
H(10A)	8c	0.3444	0.8254	0.4851	0.163
H(10B)	8c	0.3808	0.7530	0.4669	0.163
H(11A)	8c	0.2396	0.7389	0.4981	0.350
H(11B)	8c	0.2648	0.7785	0.5498	0.350
H(11C)	8c	0.3088	0.7060	0.5386	0.350
H(12A)	8c	0.5533	0.7334	0.5752	0.173
H(12B)	8c	0.4584	0.6940	0.5767	0.173
H(13A)	8c	0.5419	0.6285	0.5327	0.342
H(13B)	8c	0.5926	0.6890	0.5036	0.342
H(13C)	8c	0.4898	0.6696	0.4887	0.342
H(17)	8c	0.6272	0.7527	0.7877	0.076

**Table 2.** Continued.

Atom	Site	x	y	z	U <sub>iso</sub>
H(19)	8c	0.4075	0.8319	0.8631	0.080
H(20)	8c	0.2981	0.9050	0.8209	0.073
H(21A)	8c	0.2184	1.0181	0.7670	0.088
H(21B)	8c	0.1668	0.9506	0.7853	0.088
H(22A)	8c	0.0980	0.9992	0.7089	0.086
H(22B)	8c	0.1295	0.9224	0.7004	0.086
H(23A)	8c	0.1704	0.9196	0.6111	0.096
H(23B)	8c	0.2143	0.9842	0.5840	0.096
H(24A)	8c	0.0326	0.9820	0.6261	0.168
H(24B)	8c	0.0554	0.9789	0.5661	0.168
H(24C)	8c	0.0767	1.0461	0.5980	0.168
H(25A)	8c	0.1593	1.0881	0.6685	0.089
H(25B)	8c	0.2543	1.0814	0.6983	0.089
H(26A)	8c	0.3328	1.0840	0.6175	0.126
H(26B)	8c	0.2760	1.1519	0.6274	0.126
H(26C)	8c	0.2368	1.0954	0.5894	0.126
H(2)	8c	0.485(3)	0.816(3)	0.515(2)	0.06(2)

**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Co(1)	8c	0.33794(6)	0.93853(4)	0.68109(3)	0.0547(5)	0.0362(4)	0.0621(6)	0.0003(4)	0.0074(4)	0.0008(4)
Br(1)	8c	0.45614(6)	1.12179(4)	0.78531(3)	0.1045(6)	0.0663(5)	0.0757(6)	0.0098(4)	-0.0068(5)	-0.0153(4)
Br(2)	8c	0.62059(5)	0.80585(4)	0.68172(3)	0.0575(4)	0.0719(5)	0.0886(6)	0.0037(4)	0.0124(4)	-0.0140(4)
Cl(1)	8c	0.7306(2)	1.1623(1)	0.6364(1)	0.084(1)	0.128(2)	0.128(2)	-0.056(1)	-0.006(1)	0.015(2)
Cl(2)	8c	0.5555(2)	0.7431(1)	0.88839(8)	0.105(2)	0.126(2)	0.077(1)	0.029(1)	-0.018(1)	0.017(1)
O(1)	8c	0.3928(3)	1.0203(2)	0.7069(2)	0.066(3)	0.050(3)	0.065(3)	-0.009(2)	0.010(2)	-0.011(2)
O(2)	8c	0.4477(3)	0.8889(2)	0.6970(2)	0.050(2)	0.052(2)	0.058(3)	0.002(2)	0.010(2)	0.004(2)
O(3)	8c	0.5481(6)	0.8884(5)	0.4787(3)	0.140(6)	0.189(8)	0.108(6)	-0.046(6)	0.012(5)	0.028(5)
O(4)	8c	0.6489(8)	0.8626(6)	0.5390(6)	0.20(1)	0.164(8)	0.27(1)	0.028(7)	0.008(9)	0.08(1)
O(5)	8c	0.6633(7)	0.9598(5)	0.5063(3)	0.209(9)	0.135(7)	0.155(7)	-0.069(6)	0.036(6)	-0.015(6)
N(1)	8c	0.3981(4)	0.9473(2)	0.6120(2)	0.064(3)	0.041(3)	0.055(3)	0.004(3)	0.001(3)	0.002(2)
N(2)	8c	0.4474(5)	0.7877(3)	0.5333(3)	0.102(5)	0.050(4)	0.081(5)	-0.013(4)	0.020(4)	-0.020(3)
N(3)	8c	0.2899(4)	0.9312(2)	0.7496(2)	0.056(3)	0.043(3)	0.067(4)	0.008(2)	0.016(3)	0.005(3)
N(4)	8c	0.2149(4)	0.9914(2)	0.6632(2)	0.061(3)	0.041(3)	0.079(4)	0.009(2)	0.002(3)	0.010(3)
N(5)	8c	0.2734(4)	0.8540(2)	0.6613(2)	0.066(3)	0.033(3)	0.081(4)	-0.006(3)	0.004(3)	0.005(3)
N(6)	8c	0.2952(3)	0.8006(3)	0.6813(2)	0.046(3)	0.043(3)	0.079(4)	-0.005(2)	0.002(3)	-0.004(3)
N(7)	8c	0.3125(5)	0.7465(3)	0.6972(3)	0.101(5)	0.046(4)	0.111(5)	-0.001(3)	-0.013(4)	0.007(4)
N(8)	8c	0.620(1)	0.9055(7)	0.5065(5)	0.15(1)	0.14(1)	0.116(9)	-0.012(9)	0.047(8)	-0.007(8)
C(1)	8c	0.5084(4)	1.0351(3)	0.6405(3)	0.056(4)	0.047(4)	0.063(5)	-0.003(3)	0.002(4)	0.002(3)
C(2)	8c	0.4685(5)	1.0492(3)	0.6893(3)	0.067(5)	0.036(3)	0.067(5)	0.004(3)	-0.006(4)	-0.001(3)
C(3)	8c	0.5125(5)	1.1007(3)	0.7209(3)	0.073(5)	0.038(3)	0.063(4)	0.002(3)	-0.010(4)	0.005(3)
C(4)	8c	0.5911(6)	1.1340(3)	0.7046(3)	0.075(5)	0.048(4)	0.088(6)	-0.003(4)	-0.024(5)	0.002(4)
C(5)	8c	0.6299(5)	1.1172(4)	0.6577(4)	0.071(5)	0.057(4)	0.088(6)	-0.017(4)	-0.016(5)	0.016(4)
C(6)	8c	0.5908(5)	1.0699(3)	0.6253(3)	0.067(4)	0.057(4)	0.072(5)	-0.003(4)	0.000(4)	0.010(4)
C(7)	8c	0.4702(4)	0.9871(3)	0.6045(3)	0.057(4)	0.047(4)	0.072(5)	-0.007(3)	0.012(3)	0.009(3)
C(8)	8c	0.3789(5)	0.8989(3)	0.5685(3)	0.083(5)	0.051(4)	0.064(5)	-0.011(4)	-0.001(4)	-0.005(3)
C(9)	8c	0.4356(6)	0.8319(4)	0.5803(3)	0.121(7)	0.057(4)	0.072(5)	0.010(4)	0.005(5)	-0.007(4)
C(10)	8c	0.3634(9)	0.7802(6)	0.4973(4)	0.16(1)	0.110(8)	0.14(1)	-0.025(7)	0.012(9)	-0.065(7)
C(11)	8c	0.288(1)	0.7484(8)	0.5230(7)	0.25(2)	0.18(1)	0.27(2)	-0.10(1)	0.01(2)	0.03(1)
C(12)	8c	0.5008(9)	0.7188(5)	0.5539(5)	0.18(1)	0.098(7)	0.15(1)	0.035(7)	0.008(9)	-0.067(7)
C(13)	8c	0.534(1)	0.6730(7)	0.5169(7)	0.31(2)	0.14(1)	0.23(2)	0.07(1)	0.06(2)	-0.01(1)
C(14)	8c	0.4140(4)	0.8624(3)	0.7864(3)	0.056(4)	0.049(4)	0.055(4)	-0.003(3)	0.004(3)	0.000(3)
C(15)	8c	0.4670(4)	0.8579(3)	0.7401(3)	0.042(4)	0.044(3)	0.058(4)	-0.007(3)	0.003(3)	-0.007(3)
C(16)	8c	0.5463(4)	0.8148(3)	0.7425(3)	0.051(4)	0.046(3)	0.068(4)	-0.006(3)	0.006(3)	-0.005(3)
C(17)	8c	0.5741(5)	0.7802(3)	0.7876(3)	0.061(4)	0.053(4)	0.077(5)	-0.001(3)	-0.013(4)	-0.004(4)
C(18)	8c	0.5216(6)	0.7878(4)	0.8318(3)	0.077(5)	0.070(5)	0.065(5)	0.001(4)	-0.015(4)	0.001(4)
C(19)	8c	0.4422(5)	0.8277(4)	0.8325(3)	0.070(5)	0.067(4)	0.062(5)	-0.004(4)	0.009(4)	-0.007(4)
C(20)	8c	0.3278(5)	0.9014(3)	0.7886(3)	0.062(4)	0.054(4)	0.067(5)	-0.002(3)	0.021(4)	0.003(4)
C(21)	8c	0.2038(5)	0.9709(3)	0.7575(3)	0.081(5)	0.057(4)	0.082(6)	0.020(4)	0.030(5)	0.018(4)
C(22)	8c	0.1517(5)	0.9688(3)	0.7070(3)	0.062(4)	0.053(4)	0.099(6)	0.010(3)	0.019(4)	0.010(4)
C(23)	8c	0.1726(5)	0.9696(4)	0.6118(3)	0.079(5)	0.066(5)	0.096(6)	0.017(4)	-0.024(5)	0.003(4)
C(24)	8c	0.0753(6)	0.9967(5)	0.5993(4)	0.100(7)	0.105(7)	0.132(8)	0.033(6)	-0.023(6)	0.008(6)
C(25)	8c	0.2219(5)	1.0693(3)	0.6662(3)	0.078(5)	0.046(4)	0.098(6)	0.015(4)	0.008(4)	0.003(4)
C(26)	8c	0.2713(6)	1.1032(4)	0.6210(3)	0.103(6)	0.059(4)	0.091(6)	-0.001(4)	0.015(5)	0.020(4)

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## References

1. Zeng, W.; Li, J.; Qin, S.: The effect of aza crown ring bearing salicylaldehyde Schiff bases Mn(III) complexes as catalysts in the presence of molecular oxygen on the catalytic oxidation of styrene. *Inorg. Chem. Commun.* **9** (2006) 10-12.
2. Lu, J.; Liu, T.; Cai, S.; Wang, X.; Liu, L.; Wang, Y.: Synthesis, structure and biological activity of cobalt(II) and copper(II) complexes of valine-derived Schiff bases. *J. Inorg. Biochem.* **100** (2006) 1888-1896.
3. Singh, K.; Barwa, M. S.; Tyagi, P.: Synthesis, characterization and biological studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with bidentate Schiff bases derived by heterocyclic ketone. *Eur. J. Med. Chem.* **41** (2006) 147-153.
4. Hothi, H. S.; Makkar, A.; Sharma, J. R.; Manrao, M. R.: Synthesis and antifungal potential of Co(II) complexes of 1-(2'-hydroxyphenyl)ethylidene-anilines. *Eur. J. Med. Chem.* **41** (2006) 253-255.
5. Offiong, O. E.; Nfor, E.; Ayi, A. A.; Martelli, S.: Synthesis, spectral and cytotoxicity studies of palladium(II) and platinum(II) amino acid Schiff base complexes. *Transition Met. Chem.* **25** (2000) 369-373.
6. Guo, H.-M.; Zhang, B.-S.: Crystal structure of bis(2,2'-bipyridine-*N,N'*) carbonatocobalt(III) hydrogencarbonate pentahydrate, [Co(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(CO<sub>3</sub>)] [HCO<sub>3</sub>] · 5H<sub>2</sub>O. *Z. Kristallogr. NCS* **221** (2006) 507-508.
7. Liu, Z.-H.; Zhang, J.-J.; Zhang, W.-J.: Crystal structure of bis(diethylenetriamine)cobalt(II) tetrahydroxypentaborate, [Co(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)<sub>2</sub>] [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub>. *Z. Kristallogr. NCS* **220** (2005) 555-556.
8. Dieng, M.; Diouf, O.; Gaye, M.; Sall, A. S.; Barry, A. H.; Weller, R.: Crystal structure of mononitratobis(1,10-phenanthroline)cobalt(II) mononitrate, [Co(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)] [NO<sub>3</sub>]. *Z. Kristallogr. NCS* **220** (2005) 399-400.
9. Peng, S.-J.; You, Z.-L.: Synthesis, characterization and crystal structure of bis{2-methoxy-6-[(2-diethylaminoethylimino)methyl]phenolato}thiocyanatocobalt(III) perchlorate. *J. Chem. Crystallogr.* **37** (2007) 415-419.
10. Peng, S.-J.; Yang, D.-W.; Xiao, Z.-L.; Wu, D.-X.; Cao, Z.: Crystal structure of methanol[4-bromo-*N*-(2-pyridylmethyl)salicylaldehyde-*N,N',O*]nickel(II) perchlorate, [Ni(CH<sub>3</sub>OH)(C<sub>14</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>2</sub>)]ClO<sub>4</sub>. *Z. Kristallogr. NCS* **220** (2005) 633-634.
11. Zakrzewski, G.; Sacconi, L.: Four-, five and six-coordinated nickel(II) and cobalt(II) complexes of Schiff bases derived from pyridine-2-carboxaldehyde and *N,N*-substituted ethylenediamines. *Inorg. Chem.* **7** (1968) 1034-1036.
12. Munro, O. Q.; Govender, S.: A new polymorph of a cobalt(III) Schiff base complex exhibits a one-dimensional C-H...O hydrogen-bonded extended structure with helical 2<sub>1</sub> symmetry. *Acta Crystallogr. C* **63** (2007) m150-m152.
13. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.0. Siemens Industrial Automation, Analytical Instrumentation, Madison, Wisconsin, USA 1995.