Journal of Chemical Crystallography, Vol. 37, No. 1, January 2007 (© 2006)
DOI: 10.1007/s10870-006-9087-3

Synthesis and crystal structure of cobalt(III) complex with a Schiff base and azide

Sreesha Sasi,(1) **M.R. Prathapachandra Kurup,**(1)* **and E. Suresh**(2)

Received September 27, 2005; accepted February 20, 2006

The cobalt(III) complex, $[Co(L)_2(N_3)_2]_2(ClO_4)_2$, L being a Schiff base *N*-[phenyl(pyridin-2-yl)methylene]aniline has been synthesized and the crystal structure determined using X-ray crystallography. The complex crystallizes in triclinic system, space group P-1 with unit cell parameters $a = 10.9367(9)$ Å, $b = 18.0817(17)$ Å, $c = 20.1629(16)$ Å, $\alpha = 111.341(2)^\circ$, $\beta = 91.622(2)^\circ$, $\gamma = 107.5030(10)^\circ$, $V = 3499.1(5)$ Å^3 and $Z = 2$. It crystallizes with two independent molecules in the asymmetric unit. The two cobalt atoms are hexa-coordinate and have a distorted octahedral geometry, satisfied by four nitrogen atoms from two molecules of the Schiff base and two nitrogen atoms from the monodentate azide group. The perchlorate ions are non-coordinating.

KEY WORDS: Cobalt(III); *N*-[phenyl(pyridin-2-yl)methylene]aniline; azide; crystal structure.

Introduction

The coordination chemistry of cobalt is of considerable interest since cobalt(II) and cobalt(III) complexes derived from Schiff bases are reported to be biologically active. Vitamin B_{12}, which is involved in the production of red blood cells is a cobalt(III) complex with a substituted corrin macrocycle.[1] Cobalt(III) complexes have shown specific hypoxic radiosensitization and thermosensitization as well as antitumor activity in vivo.[2–4] The antitumor action of cobalt(III) complexes with tetradentate Schiff bases derived from aliphatic beta-diketones and diamines was observed in the case of ascite form of Erlich carcinoma.[5] Cobalt(III)- schiff base complexes are found to be potential antiviral agents.[6,7]

Azide is a versatile ligand since it exhibits a variety of coordination modes such as monodentate, end-on bridging mode (μ-1, 1), end-to-end bridging mode (μ-1, 3) etc among many others.[8] Azide acts as an inhibitor for several enzymes like ATPases.[9] Hence the study of metal-azido complexes is very useful for the understanding of biological processes.

Cobalt(II) complex of azide anion and bis(pyrazol-1-yl)methane has been reported.[10] Cobalt(III) complexes with azide anion has been previously reported with 1,10-phenanthroline[11] and bis(2-pyridyl)amine.[12] Here we report the crystal structure of a cobalt(III) complex of *N*-[phenyl(pyridin-2-yl)methylene]aniline with azide as coligand.

---

(1) Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India.
(2) Analytical Science Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, Gujarat, India.
* To whom correspondence should be addressed; e-mail: mrp@cusat.ac.in

Experimental

Materials and physical measurements

All reagents and solvents were of AR grade and used as received. The Schiff base (L) was prepared *in situ* according to the literature method.[13] Elemental analysis was carried on a Vario III Elemental analyzer.

Caution! Although not encountered in our experiments, azido and perchlorate complexes of metal ions are potentially explosive. Only a small amount of the material should be prepared, and it should be handled with care.

Preparation of the complex

A mixture of 2-benzoylpyridine (1 mmol, 0.1832 g) and aniline (1 mmol, 0.0912 g) in 20 ml of ethanol was refluxed for 2 h to obtain a yellow solution of the Schiff base, and then an ethanolic solution of $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 0.3659 g) and NaN_3(2 mmol, 0.13 g) was added with continuous stirring. The resulting brown solution was left at room temperature for two weeks during which a brown solid separated out. This was filtered, washed with ethanol, water and ether, and dried over P_4O_{10} *in vacuo*. Brown needle-shaped single crystals suitable for X-ray diffraction were obtained by the slow evaporation of the complex from a mixture of acetone and water. Yield: 70%. Anal. Found: C, 57.34; H, 3.60; N, 18.74;. Calc. For $C_{72}H_{56}Cl_2Co_2N_{20}O_8$: C, 56.96; H, 3.72; N, 18.45%.

Crystal structure determination and refinement

Single crystal X-ray diffraction experiments for the title compound were performed on a BRUKER SMART APEX CCD diffractometer equipped with graphite - monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K. A crystal with dimensions 0.20 mm × 0.16 mm × 0.08 mm was used. An omega-phi scan mode was employed for data collection. Crystal data and experimental details of the structure determination are given in Table 1. The collected data were reduced using SAINT.[14] The structure was solved by direct methods with the program SHELXS-97 and refined by full matrix least squares on F^2 using SHELXL-97.[15] The graphical tool used was DIAMOND.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically fixed at calculated positions.

Table 1. Crystal Data and Experimental Parameters

CCDC No	CCDC-276082
Empirical formula	$C_{36}\ H_{28}\ Cl\ Co\ N_{10}\ O_4$
Color/shape	brown/needles
Formula weight	1518.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	10.9367(9)
b (Å)	18.0817(17)
c (Å)	20.1629(16)
α (°)	111.341(2)
β (°)	91.622(2)
γ (°)	107.5030(10)
Volume	3499.1(5) Å^3
Z	2
Density (calculated)	1.441 mg/m^3
Absorption coefficient	0.623 mm^{-1}
F(000)	1560
Crystal size	0.20 mm × 0.16 mm × 0.08 mm
θ range for data collection	1.96 to 28.31°
Index ranges	$-14 \le h \le 14,\ -24 \le k \le 23,\ -26 \le l \le 26$
Reflections collected	30575
Independent reflections	15866 [R(int) $= 0.0292$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15866/0/925
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0749$, $wR_2 = 0.2011$
R indices (all data)	$R_1 = 0.1164$, $wR_2 = 0.2289$
Largest diff. peak and hole	0.907 and -0.522 eÅ^{-3}

Results and discussion

The structure of the cation is given in Fig. 1. Significant bond parameters are given in Table 2.

The compound crystallizes into the triclinic system with a space group of P-1. There are two

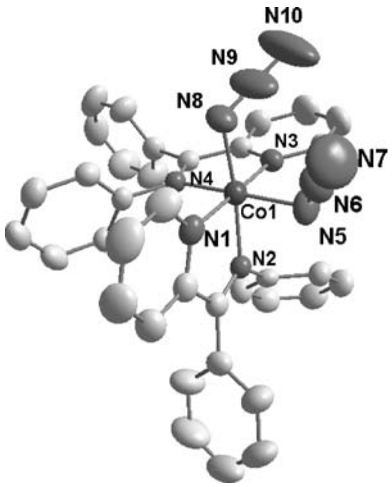

Fig. 1. Structure of the $[Co(L)_2(N_3)_2]^+$ cation, the displacement ellipsoids are drawn at 50% probability level. The hydrogen atoms and perchlorate ions are omitted for clarity.

crystallographically independent molecules in the asymmetric unit. From Table 2, it is clear that the two molecules in the asymmetric unit are almost identical. The bond angles and bond lengths in the two monomers agree with each other. So the discussion can be limited to one of the molecules. The compound consists of cobalt(III) coordinated by four nitrogen atoms from two molecules of the Schiff base and two nitrogen atoms from azide. The N_6 coordination of the cobalt(III) is completed by pairs of trans- pyridyl N, cis- azomethine N and cis- azide N to form two five membered chelate rings. The azide anions are terminal. The bond lengths and bond angles reveal significant distortion in the octahedral geometry. The rather small bite angle [N(1)–Co(1)–N(2) $= 82.26(13)^\circ$ and N(3)–Co(1)–N(4) $= 82.04(13)^\circ$] defines the largest distortion in the geometry. The azide anions which are nearly linear [N(5)–N(6)–N(7) $=$ $175.4(6)^\circ$ and N(8)–N(9)–N(10) $=$ $175.4(9)^\circ$]

Table 2. Selected bond lengths (Å) and bond angles (°)

Co(1)–N(1)	1.921(3)	Co(2)–N(11)	1.922(3)
Co(1)–N(3)	1.927(3)	Co(2)–N(13)	1.929(3)
Co(1)–N(2)	1.962(3)	Co(2)–N(12)	1.966(3)
Co(1)–N(4)	1.964(3)	Co(2)–N(14)	1.957(3)
Co(1)–N(5)	1.941(3)	Co(2)–N(15)	1.944(4)
Co(1)–N(8)	1.944(4)	Co(2)–N(18)	1.972(4)
N(5)–N(6)	1.189(5)	N(15)–N(16)	1.187(6)
N(6)–N(7)	1.145(6)	N(16)–N(17)	1.137(7)
N(8)–N(9)	1.133(6)	N(18)–N(19)	1.158(6)
N(9)–N(10)	1.172(7)	N(19)–N(20)	1.151(7)
N(1)–Co(1)–N(3)	177.51(13)	N(11)–Co(2)–N(13)	177.24(14)
N(2)–Co(1)–N(4)	89.32(12)	N(12)–Co(2)–N(14)	88.59(12)
N(5)–Co(1)–N(8)	94.68(17)	N(15)–Co(2)–N(18)	89.0(2)
N(2)–Co(1)–N(5)	87.58(15)	N(12)–Co(2)–N(15)	92.77(17)
N(1)–Co(1)–N(8)	90.70(16)	N(11)–Co(2)–N(18)	91.69(16)
N(3)–Co(1)–N(4)	82.04(13)	N(13)–Co(2)–N(14)	81.86(13)
N(3)–Co(1)–N(8)	89.78(15)	N(13)–Co(2)–N(18)	89.55(16)
N(1)–Co(1)–N(4)	95.53(12)	N(11)–Co(2)–N(14)	95.67(13)
N(1)–Co(1)–N(5)	90.19(15)	N(11)–Co(2)–N(15)	90.81(18)
N(3)–Co(1)–N(5)	92.21(15)	N(13)–Co(2)–N(15)	91.68(18)
N(4)–Co(1)–N(8)	89.16(15)	N(14)–Co(2)–N(18)	90.33(15)
N(4)–Co(1)–N(5)	173.08(15)	N(14)–Co(2)–N(15)	173.51(17)
N(1)–Co(1)–N(2)	82.26(13)	N(11)–Co(2)–N(12)	82.27(13)
N(2)–Co(1)–N(3)	97.17(13)	N(12)–Co(2)–N(13)	96.41(14)
N(2)–Co(1)–N(8)	172.62(15)	N(12)–Co(2)–N(18)	173.72(16)
N(5)–N(6)–N(7)	175.4(6)	N(15)–N(16)–N(17)	177.3(6)
Co(1)– N(5)–N(6)	118.9(3)	Co(2)–N(15)–N(16)	117.8(4)
N(8)–N(9)–N(10)	175.4(9)	N(18)–N(19)–N(20)	177.3(6)
Co(1)–N(8)–N(9)	119.4(4)	Co(2)–N(18)–N(19)	117.5(3)

are coordinated with a N(6)–N(5)–Co(1) angle of 118.9(3)° and N(9)–N(8)–Co(1) angle of 119.4(4)°. The N–N bond lengths in the azide group are almost equal, with the longer N–N bonds involving the N atoms coordinated to the metal centre. However, in N(8)–N(9)–N(10), the N(8)–N(9) bond [1.133(6) Å] is much shorter than N(9)–N(10) bond [1.172(7) Å]. This may be attributed to the stronger C–H $\cdots \pi$ interaction in N(8)–N(9)–N(10), which is not significant in N(5)–N(6)–N(7). The Co(III)–N bond distances in the complex is in the range 1.921(3)–1.972(4) Å. This is in agreement with the previous reports.[11,12,17–19] The Co(III)–N distance is shorter for the pyridyl nitrogen atoms indicating their stronger coordination than azomethine and azide nitrogens. The perchlorate ions remain non-coordinating.

The mean plane deviation calculations show that the metal chelate rings are somewhat planar. Ring puckering analysis reveals that the ring Cg(9) comprising of Co(2), N(11), C(41), C(42) and N(12) adopts an envelope conformation on Co(2). The dihedral angle formed by the mean planes of the chelate systems are 88.90(17)° and 85.58(17)° respectively in the two units. The two pyridyl rings make a dihedral angle of 86.39(23)° and 78.15(26)° in the two monomers respectively.

The packing diagram of the molecule in the crystal lattice is given Fig. 2. In the crystal lattice, the molecules are arranged in a 'head to tail' manner. There are no classical hydrogen bonds seen in

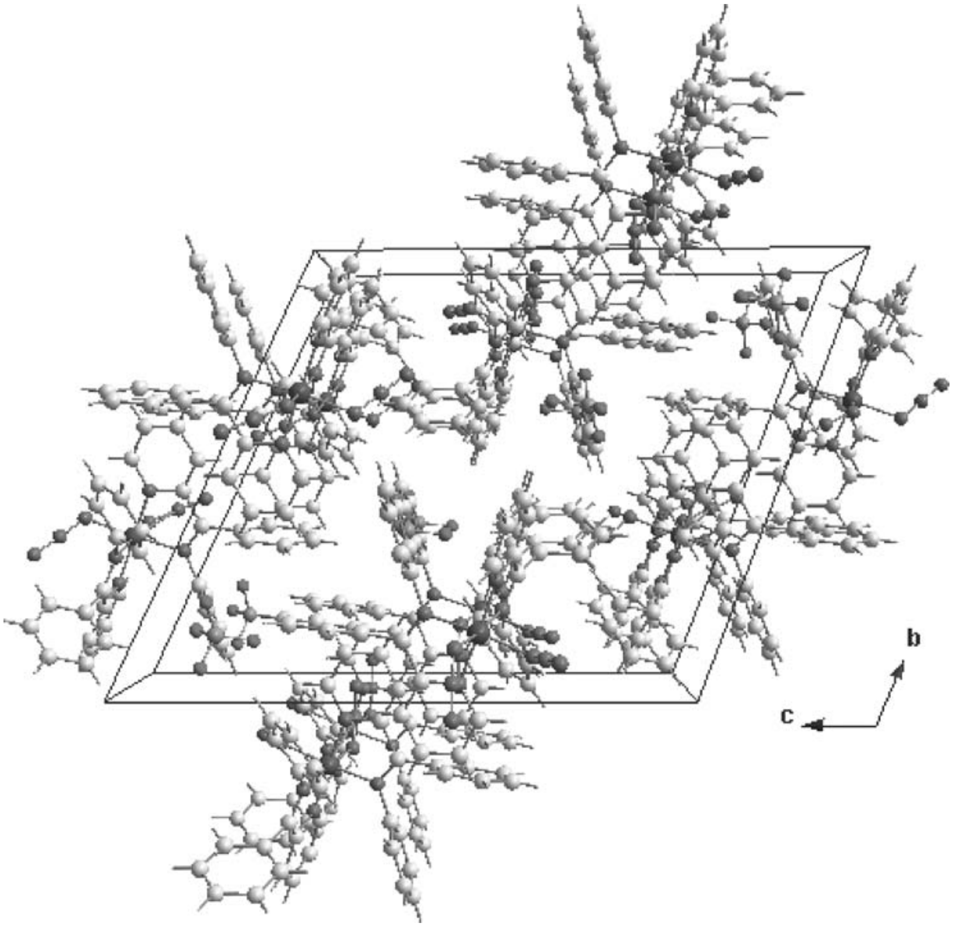

Fig. 2. Unit cell packing diagram of $[Co(L)_2(N_3)_2]_2(ClO_4)_2$ viewed along the a axis.

Table 3. Interaction parameters of the title compound

D–H···A	H···A (Å)	D···A (Å)	D–H···A(°)
C(1)–H(1)···N(8)	2.38	2.888(7)	114
C(19)–H(19)···N(5)	2.43	2.941(7)	114
C(37)–H(37)···N(18)	2.43	2.939(8)	114
C(50)–H(50)···O(1)^a	2.29	3.077(8)	141
C(55)–H(55)···N(15)	2.41	2.912(9)	114
C(64)–H(64)···O(2)^b	2.51	3.389(10)	158
C(68)–H(68)···O(1)^a	2.53	3.429(7)	163
π–π interactions Cg(I)–Res(1)–Cg(J)	Cg–Cg (Å)	α°	β°
Cg(1) [1] → Cg(8)	3.879(2)	40.13	18.13
Cg(3) [1] → Cg(8)	3.880(3)	38.40	17.73
Cg(8) [1] → Cg(1)	3.879(2)	40.13	46.78
Cg(8) [1] → Cg(3)	3.880(3)	38.40	26.21
Cg(9) [2] → Cg(16)	3.849(2)	40.11	18.67
Cg(10) [2] → Cg(14)	3.983(2)	42.99	19.82
Cg(11) [2] → Cg(16)	3.883(3)	37.76	19.19
Cg(14) [2] → Cg(10)	3.983(2)	42.99	48.61
Cg(16) [2] → Cg(9)	3.849(2)	40.11	47.16
Cg(16) [2] → Cg(11)	3.883(3)	37.76	30.36
CH – π interactions Y–X(I)- Res(I)- Cg(J)	X···Cg	Y–X···Cg	Y···Cg
N(16)–N(17)[2] → Cg(9)	3.219(7)	53.3(4)	2.697(5)
N(19)–N(20)[2] → Cg(3)	2.954(6)	117.1(6)	3.626(4)
N(19)–N(20)[2] → Cg(10)	3.080(6)	54.4(3)	2.584(4)
N(19)–N(20)[2] → Cg(12)	3.601(7)	74.7(4)	3.479(5)

Note. Equivalent position codes: $a = 1-x, 1-y, 2-z$; $b = -1+x, 1+y, z$.
Cg(1) = Co(1), N(1), C(5), C(6), N(2).
Cg(3) = N(1), C(1), C(2), C(3), C(4), C(5).
Cg(8) = C(31), C(32), C(33), C(34), C(35), C(36).
Cg(9) = Co(2), N(11), C(41), C(42), N(12).
Cg(10) = Co(2), N(13), C(59), C(60), N(14).
Cg(11) = N(11), C(37), C(38), C(39), C(40), C(41).
Cg(14) = C(49), C(50), C(51), C(52), C(53), C(54).
Cg(16) = C(67), C(68), C(69), C(70), C(71), C(72).
Cg(12) = N(13), C(55), C(56), C(57), C(58), C(59).

the crystal structure. The packing of the molecules in the crystal lattice is stabilized by some weak hydrogen bonding interactions and C–H···π interactions (Table 3). The orientation of the molecules in the crystal lattice is in such a manner that $\pi\cdots\pi$ stacking interactions involving metal chelate ring, pyridyl and phenyl rings reinforce the packing. The metal chelate ring Cg(1) and pyridyl ring Cg(3) are involved in π–π interaction with the phenyl ring Cg(8) at average distances of 3.879(2) and 3.880(3) Å. Similar interactions are observed in the second molecule also. In addition in the second molecule, there is π–π interaction between metal chelate ring Cg(10) and phenyl ring Cg(14) at average distance of 3.983(2) Å.

Supplementary material All crystallographic data for this paper are deposited with the Cambridge Crystallographic Data Centre (CCDC–276082). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223–336033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors are thankful to the Department of Science and Technology, Ministry of Science and Technology, Govt. of India for financial support (No.SR/S1/IC-31/2003). The authors thank Sophisticated Analytical Instrumentation Facility (SAIF), Cochin University of Science and

Technology, Kochi-22, Kerala, India for elemental analysis. Sreesha Sasi is thankful to the Council of Scientific and Industrial Research, New Delhi, India for financial assistance in the form of a fellowship.

References

1. Battersby, A.R. *Acc. Chem. Res.* **1993**, *26*, 15.
2. Stratford, I.J. *Int. J. Rad. Oncol. Biol. Phys.* **1992**, *22*, 529.
3. Teicher, B.A.; Abrams, M.J.; Rosbe, K.W.; Herman, T.S. *Cancer Res.* **1990**, *50*, 6971.
4. Denny, W.A.; Wilson, W.R.; Hay, M.P. *Br J Cancer Suppl* **1996**, *27*, S32.
5. Dori, Z.; Gershon, D. *US-Patent*, Pat. No. 5, 258, 403, Date of Patent. Nov 2, 1993.
6. Dunkel, E.C.; Geary, P.; Brooks, J.; Pavanlangston, D. *4th Int. Conf. on Antiviral Res.* New Orleans, **1991**, 170.
7. Devlin, H.; Geary, P.; Pavanlangston, D.; Dori, Z.; Dunkel, E.C. *Inv. Ophth-V* **1993**, *34*, 1348.
8. Ribas, J.; Escuér, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193–195*, 1027.
9. Knowles, A.F.; Nagy, A.K. Eur. J. Biochem. **1999**, *262*, 349.
10. Tang, L.-F.; Shi, H.-Q.; Wang, Z.-H.; Zhang, L. *J. Chem. Cryst.* **2000**, *30*, 159.
11. Zhao, Q.; Wang, X.; Fang, R.; Tiekink, E.R.T. *Acta Cryst.* **2003**, *E59*, m690.
12. Du, M.; Guo, Y.-M.; Leng, X.-B.; Bu, X.-H. *Acta Cryst.* **2001**, *E57*, m97.
13. Gao, E.-Q.; Bai, S.-Q.; Yue, Y.-F.; Wang, Z.-M.; Yan, C.-H. *Inorg. Chem.* **2003**, *42*, 3642.
14. Siemens, *SMART and SAINT, Area Detector Control and Integration Software*, Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA, **1996**.
15. Sheldrick, G.M. *SHELXTL Version 5.1, Software Reference Manual*, Bruker AXS Inc, Madison, Wisconsin, USA, **1997**.
16. Brandenburg, K. *Diamond Version 3.0*, **1997–2004** Crystal Impact GbR, Bonn, Germany.
17. Browne, J.B.; Buckingham, D.A.; Blackman, A.G.; Clark, C.R. *Acta Cryst.* **2002**, *E58*, m125.
18. Dong, Z.-Y.; Liu, X.-W.; Wang, X.-Q.; Wang, R.-J.; Shen, G.-Q. *Acta Cryst.* **2003**, *E59*, m260.
19. Yuan, C.-L. *Acta Cryst.* **2005**, *E61*, m2112.