

Ricky B. Nellas, Frank R. Fronczek, George R. Newkome,† Steven F. Watkins\* and Yuanjiao Xia

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

† Current address: Departments of Chemistry and Polymer Science, The University of Akron, 170 University Circle, Goodyear Polymer Center, Akron, Ohio 44325-4717, USA.

Correspondence e-mail: swatkins@lsu.edu

#### Key indicators

Single-crystal X-ray study

$T = 105$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å

$R$  factor = 0.030

$wR$  factor = 0.065

Data-to-parameter ratio = 33.3

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

## [6,6'-Bis(chloromethyl)-2,2'-bipyridyl]dichlorocobalt(II)

The title compound,  $[\text{CoCl}_2(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2)]$ , contains a Co atom coordinated in a quasi-tetrahedral manner by two Cl atoms and two N atoms of the bipyridyl group. The five-membered  $\text{CoN}_2\text{C}_2$  metallocycle has a slightly twisted envelope conformation with the Co atom at the flap.

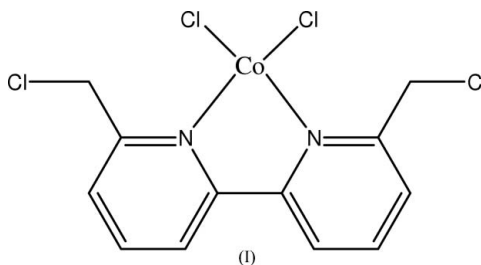
Received 24 April 2006

Accepted 6 June 2006

#### Comment

Transition metal complexes act as catalysts in Fenton-type reactions, serve as cofactors of metalloenzymes, exhibit antimicrobial and fungicidal activity (Okide *et al.*, 2000), and are often toxic or carcinogenic (Kasprzak, 2002). Organocobalt complexes, in particular  $\text{Co}^{\text{II}}$  Schiff bases, act as catalysts for the oxidation of organic molecules (Fiammengo *et al.*, 2002). This catalytic activity is affected by the formal potential of  $\text{Co}^{\text{II}}$  (Forster *et al.*, 1996), and by the electronic and steric effects of the substituents on the Schiff base ligand (Hirotsu *et al.*, 1994).

In the title compound, (I), the Co atom is coordinated by two Cl atoms and two N atoms (Table 1 and Fig. 1). The five-membered  $\text{CoN}_2\text{C}_2$  metallocycle has a slightly twisted envelope conformation with the Co atom at the flap. The dihedral angle between the  $\text{N1/C1/C7/N2}$  and  $\text{N1/Co1/N2}$  planes is  $7.7$  ( $2$ )°, and the  $\text{N}-\text{C}-\text{C}-\text{N}$  torsion angle is  $1.74$  ( $14$ )°. This structure is consistent with the structures of three variously substituted bipyridyl  $\text{Co}^{\text{II}}$ -dichloride complexes previously reported (Baker *et al.*, 1988; Bolm *et al.*, 1990; Lotscher *et al.*, 2001).



In the uncomplexed ligand (Lindoy *et al.*, 2004), the orientation of the chloromethyl group is nearly perpendicular to the bipyridyl ring plane [ $\text{N}-\text{C}-\text{C}-\text{Cl} = 86.7$  ( $1$ )°]. In (I), one chloromethyl group is nearly parallel to the ring plane and pointed away from the  $\text{CoCl}_2$  unit [ $\text{N2}-\text{C11}-\text{C12}-\text{Cl4} = -174.23$  ( $11$ )°], while the other chloromethyl group is tilted toward the  $\text{CoCl}_2$  unit [ $\text{N1}-\text{C5}-\text{C6}-\text{Cl1} = -59.16$  ( $15$ )°]. As a result,  $\text{Cl3}$  bends away from contact with  $\text{Cl1}$  [ $\text{Cl1}\cdots\text{Cl3} = 3.560$  ( $1$ ) Å;  $\text{Cl3}-\text{Co1}-\text{N1} = 125.52$  ( $3$ )°;  $\text{Cl3}-\text{Co1}-\text{N2} = 102.96$  ( $3$ )°]. In contrast, the two  $\text{Cl}-\text{Co}-\text{N}$  angles for  $\text{Cl2}$  are more nearly equal,  $114.32$  ( $3$ ) and  $108.95$  ( $3$ )°.

## Experimental

A stirred mixture of 6,6'-bis(chloromethyl)-2,2'-bipyridine (101.29 mg, prepared following Newkome *et al.*, 1982) with cobalt dichloride hexahydrate (47.6 mg) in ethanol (20 ml) was heated to 323 K. After several hours, the mixture was cooled and the solid filtered. The product was recrystallized from acetone giving (I) as blue needles (m.p. > 568 K).

### Crystal data

[CoCl<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>)]  
*M<sub>r</sub>* = 382.95  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 7.4783 (10) Å  
*b* = 15.727 (2) Å  
*c* = 12.652 (2) Å  
 $\beta$  = 104.847 (6)°  
*V* = 1438.3 (4) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 1.77 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 1.92 mm<sup>-1</sup>  
*T* = 105 K  
 Fragment cut from needle, blue  
 0.27 × 0.18 × 0.12 mm

### Data collection

Nonius KappaCCD diffractometer  
 (with Oxford Cryostream)  
 $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan  
 (HKL SCALEPACK;  
 Otwinowski & Minor, 1997)  
*T<sub>min</sub>* = 0.625, *T<sub>max</sub>* = 0.802

41075 measured reflections  
 5719 independent reflections  
 4468 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.025  
 $\theta_{\max}$  = 33.7°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030  
*wR*(*F*<sup>2</sup>) = 0.065  
*S* = 1.04  
 5719 reflections  
 172 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.7315P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.67 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.60 \text{ e } \text{Å}^{-3}$

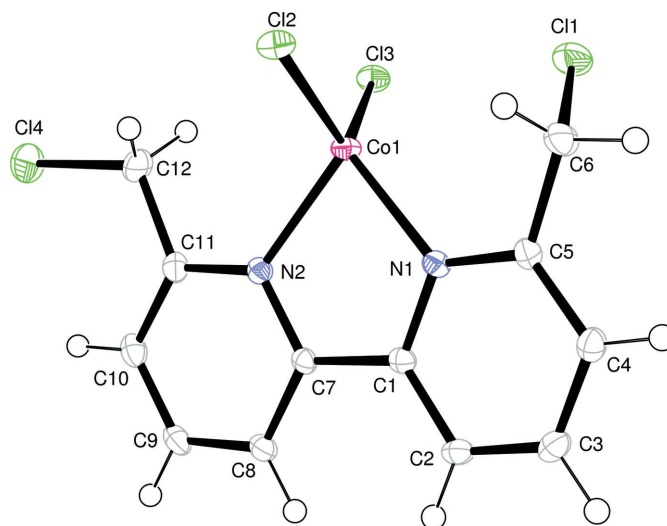
**Table 1**

Selected geometric parameters (Å, °).

C1–N1	1.3573 (17)	Cl3–Co1	2.2315 (4)
C1–C7	1.4899 (19)	Co1–N1	2.0406 (12)
C7–N2	1.3529 (17)	Co1–N2	2.0583 (12)
Cl2–Co1	2.2253 (5)		
N1–C1–C7	115.54 (11)	N1–Co1–Cl3	125.52 (3)
N2–C7–C1	115.94 (12)	N2–Co1–Cl3	102.96 (3)
N1–Co1–N2	81.18 (5)	Cl2–Co1–Cl3	117.433 (17)
N1–Co1–Cl2	108.95 (3)	C1–N1–Co1	113.64 (9)
N2–Co1–Cl2	114.32 (3)	C7–N2–Co1	112.92 (9)

H atoms were placed in calculated positions, and refined with C–H bond lengths constrained to 0.95 Å for aromatic and 0.99 Å for chloromethyl H atoms, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(carrier C atom).

Data collection: COLLECT (Nonius, 2000); cell refinement: HKL DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to



**Figure 1**

View of (I) (50% probability displacement ellipsoids for non-H atoms).

refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

The purchase of the diffractometer was made possible by grant No. LEQSF(1999–2000)-ESH-TR-13, administered by the Louisiana Board of Regents.

## References

- Baker, G. L., Fronczek, F. R., Kiefer, G. E., Marston, C. R., Modenbach, C. L., Newkome, G. R., Puckett, W. E. & Watkins, S. F. (1988). *Acta Cryst.* **C44**, 1668–1669.
- Bolm, C., Zehnder, M. & Bur, D. (1990). *Angew. Chem.* **102**, 206–208.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fiammengo, R., Bruinink, C. M., Crego-Calama, M. & Reinhoudt, D. N. (2002). *J. Org. Chem.* **67**, 8552–8557.
- Forster, S., Rieker, A., Maruyama, K., Murata, K. & Nishinaga, A. (1996). *J. Org. Chem.* **61**, 3320–3326.
- Hirotsu, M., Kojima, M., Nakajima, K., Kashino, S. & Yoshikawa, Y. (1994). *Bull. Chem. Soc. Jpn.* **69**, 2549–2557.
- Kasprzak, K. S. (2002). *Free Radical Biol. Med.* **32**, 958–967.
- Lindoy, L. F., McMurtrie, J. C. & Price, J. R. (2004). *Acta Cryst.* **E60**, o886–o888.
- Lotscher, D., Rupprecht, S., Collomb, P., Belsler, P., Viebrock, H., von Zelewsky, A. & Burger, P. (2001). *Inorg. Chem.* **40**, 5675–5681.
- Newkome, G. R., Puckett, W. E., Kiefer, G. E., Gupta, V. D., Xia, Y., Coreil, M. & Hackney, M. A. J. (1982). *Org. Chem.* **47**, 4116–4120.
- Nonius (2000). COLLECT. Nonius BV, Delft, The Netherlands.
- Okide, G. B., Adikuwu, M. & Esimone, C. O. (2000). *Biol. Pharm. Bull.* **23**, 257–258.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.