metal-organic compounds

cis-Bis(2,2′-bipyridine-κ²*N*,*N*′)dichlorido-cobalt(II) trihydrate

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In the title complex, $[CoCl_2(C_{10}H_8N_2)_2]\cdot 3H_2O$, the Co(II) ion is situated on a twofold rotation axis and exhibits a slightly distorted octahedral geometry and is chelated by four N atoms of the two bidentate 2,2′-bipyridine ligands and two Cl⁻ ions. The crystal packing is stabilized by hydrogen bonding formed between chloride ions and adjacent water molecules. One of the two independent water molecules in the asymmetric unit is disordered over two sets of sites, each on a twofold rotation axis, in a 0.734 (17):0.269 (17) ratio.

Related literature

For the antibacterial activity of similar complexes, see: Senthilkumar & Arunachalam (2008). For similar complexes applied in the immunoassay of carcinoma antigen-125, see: Shihong *et al.* (2009). For the application of similar complexes as biosensors, see: Ying *et al.* (2006).
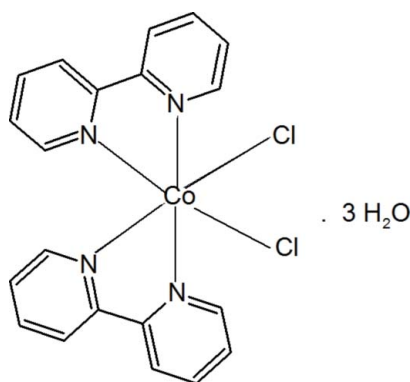
Experimental

Crystal data

$[CoCl_2(C_{10}H_8N_2)_2]\cdot 3H_2O$ M_r = 496.25

Monoclinic, $C2/c$
a = 18.3644 (8) Å
b = 13.1902 (8) Å
c = 10.8854 (6) Å
β = 120.030 (4)°
V = 2282.8 (2) Å³

Z = 4
Mo $K\alpha$ radiation
μ = 1.01 mm⁻¹
T = 293 K
$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.721, T_{max} = 0.823

18022 measured reflections
2123 independent reflections
1731 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.143
S = 1.19
2123 reflections
152 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.67 e Å⁻³
$\Delta\rho_{min}$ = −0.65 e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1*A*···Cl1	0.86 (6)	2.43 (5)	3.250 (4)	160 (5)
O1—H1*B*···Cl1ⁱ	0.85 (3)	2.37 (4)	3.218 (4)	172 (4)

Symmetry code: (i) $x, -y, z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2009).

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cis-Bis(2,2′-bipyridine-*κ²N,N′*)dichloridocobalt(II) trihydrate

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S1. Comment

2,2-Bipyridine and 1,10-phenanthroline have been extensively used to form different complexes with transition metal ions in their various oxidation states. Tris(2,2′-bipyridine)cobalt(III) complexed with bovine serum albumin has been reported as biosensors (Ying *et al.*, 2006). Bipyridine cobalt complexes were found to have considerable antibacterial activities (Senthilkumar & Arunachalam, 2008). The use of tris(bipyridine)cobalt(II) for immunoassay of carcinoma antigen-125 has been reported recently (Shihong *et al.*, 2009).

The cobalt(II) ion has site symmetry 2 and assumes octahedral geometry with two symmetry related 2,2′- bipyridine ligands and two chloride ions. Cobalt(II) is linked to two 2,2′- bipyridine bidentate ligands *via* four nitrogen atoms and two chloride ions. The two 2,2′- bipyridine ligands are in *cis* position with mutually perpendicular to each other. The hydrated water molecules in the crystal packing helps the stabilization of crystal packing by forming hydrogen bonding between adjacent chloride ions.

S2. Experimental

The complex was prepared by adding a solution of 2,2′- bipyridine (0.01 mole) in 60 ml of acetone, to a solution of cobalt(II) chloride (0.005 mole) in 60 ml of acetone. The resulting solution was stirred for two hours, filtered and dried over vacuum desiccator to get red colour complex (yield 90%). The dark red colored crystals, suitable for x-ray analysis, were obtained by slow evaporation from alcoholic solution.

S3. Refinement

There is 1.5 water molecules per asymmetric unit. The H atoms of water oxygen O1 could be located in difference Fourier map. These H atoms were restrained to be at a distance of 0.85 Å from O1. The inter hydrogen distance was restrained to be 1.388 Å so as to retain the tetrahedral H—O—H angle. The other half molecule was disordered in two positions (O2 and O3). Their occupancies were refined initially as free variables and later the sum of the occupancies restrained as 0.5. The H atoms of disordered water molecules could not be located. The aromatic H atoms were constrained as riding atoms with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2U_{equ}(C).
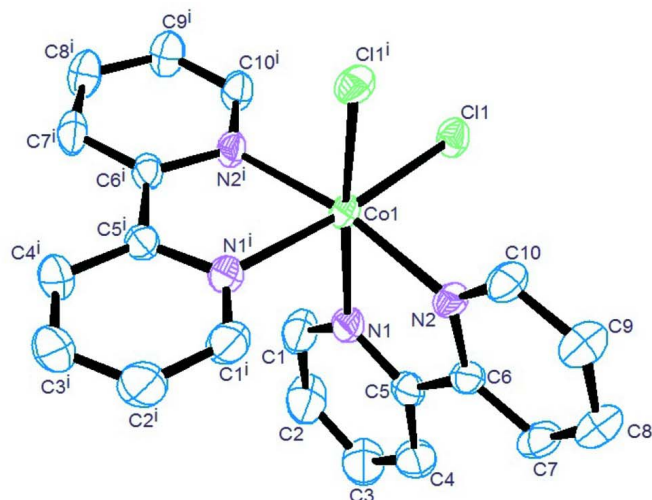
Figure 1

ORTEP of [Co(bpy)₂(Cl)₂].3H₂O drawn with 50% displacement ellipsoid level. Water molecules have been omitted for clarity.
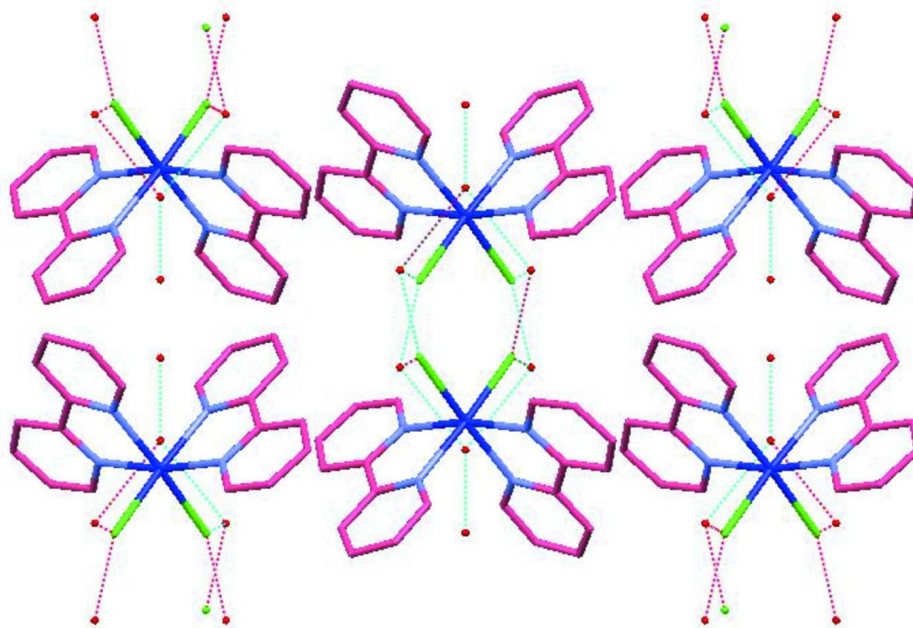
Figure 2

The crystal packing of [Co(bpy)₂(Cl)₂].3H₂O viewed along the *c* axis.

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$M_r = 496.25$	$b = 13.1902\,(8)$ Å
Monoclinic, $C2/c$	$c = 10.8854\,(6)$ Å
Hall symbol: -C2yc	$\beta = 120.030\,(4)°$

$V = 2282.8$ (2) Å^3

$Z = 4$

$F(000) = 1020$

$D_x = 1.444$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6958 reflections

$\theta = 2.4–25.4°$

$\mu = 1.01$ mm^{-1}

$T = 293$ K

Block, red

$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2004)

$T_{min} = 0.721$, $T_{max} = 0.823$

18022 measured reflections

2123 independent reflections

1731 reflections with $I > 2\sigma(I)$

$R_{int} = 0.051$

$\theta_{max} = 25.6°$, $\theta_{min} = 2.0°$

$h = -22 \rightarrow 19$

$k = -15 \rightarrow 15$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.143$

$S = 1.19$

2123 reflections

152 parameters

4 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 3.251P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.67$ e Å^{-3}

$\Delta\rho_{min} = -0.65$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0015 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.9376 (3)	0.3673 (3)	0.5122 (5)	0.0632 (11)	
H1	0.9858	0.3506	0.5089	0.076*	
C2	0.8848 (3)	0.4410 (4)	0.4210 (6)	0.0774 (14)	
H2	0.8973	0.4740	0.3583	0.093*	
C3	0.8134 (3)	0.4643 (4)	0.4254 (6)	0.0772 (14)	
H3	0.7768	0.5140	0.3658	0.093*	
C4	0.7964 (3)	0.4142 (3)	0.5176 (5)	0.0610 (11)	
H4	0.7476	0.4288	0.5202	0.073*	
C5	0.8517 (2)	0.3418 (2)	0.6070 (4)	0.0428 (8)	

C6	0.8377 (2)	0.2843 (2)	0.7097 (3)	0.0394 (8)	
C7	0.7668 (2)	0.2959 (3)	0.7214 (4)	0.0518 (9)	
H7	0.7247	0.3408	0.6623	0.062*	
C8	0.7588 (2)	0.2405 (4)	0.8212 (5)	0.0599 (10)	
H8	0.7120	0.2486	0.8319	0.072*	
C9	0.8211 (2)	0.1730 (3)	0.9046 (4)	0.0576 (10)	
H9	0.8171	0.1344	0.9725	0.069*	
C10	0.8893 (2)	0.1635 (3)	0.8859 (4)	0.0472 (8)	
H10	0.9310	0.1172	0.9419	0.057*	
N1	0.92249 (18)	0.3194 (2)	0.6043 (3)	0.0449 (7)	
N2	0.89867 (17)	0.2174 (2)	0.7915 (3)	0.0392 (6)	
O1	0.8926 (3)	−0.0960 (3)	0.7511 (4)	0.0902 (12)	
Cl1	0.92474 (5)	0.07552 (7)	0.56901 (9)	0.0448 (3)	
Co1	1.0000	0.20323 (5)	0.7500	0.0367 (3)	
O2	1.0000	−0.2593 (12)	0.7500	0.169 (6)	0.734 (17)
O3	1.0000	−0.4227	0.7500	0.174 (19)	0.269 (17)
H1A	0.911 (4)	−0.046 (3)	0.724 (5)	0.11 (2)*	
H1B	0.904 (4)	−0.085 (4)	0.836 (3)	0.11 (2)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.043 (2)	0.068 (3)	0.071 (3)	−0.0005 (18)	0.023 (2)	0.021 (2)
C2	0.061 (3)	0.076 (3)	0.083 (3)	0.003 (2)	0.027 (2)	0.042 (3)
C3	0.057 (3)	0.062 (3)	0.088 (3)	0.011 (2)	0.018 (2)	0.036 (2)
C4	0.046 (2)	0.050 (2)	0.070 (3)	0.0110 (17)	0.016 (2)	0.0131 (19)
C5	0.0330 (17)	0.0354 (17)	0.0441 (18)	−0.0011 (13)	0.0074 (14)	−0.0034 (14)
C6	0.0301 (17)	0.0368 (17)	0.0399 (17)	0.0027 (12)	0.0089 (14)	−0.0068 (14)
C7	0.0332 (19)	0.059 (2)	0.051 (2)	0.0130 (15)	0.0122 (16)	−0.0016 (17)
C8	0.045 (2)	0.077 (3)	0.064 (2)	0.014 (2)	0.032 (2)	0.001 (2)
C9	0.049 (2)	0.074 (3)	0.053 (2)	0.0112 (19)	0.0282 (19)	0.007 (2)
C10	0.0359 (18)	0.055 (2)	0.0461 (19)	0.0082 (16)	0.0174 (15)	0.0074 (17)
N1	0.0331 (15)	0.0416 (16)	0.0487 (16)	−0.0004 (12)	0.0120 (13)	0.0027 (13)
N2	0.0265 (14)	0.0427 (16)	0.0394 (14)	0.0044 (11)	0.0098 (11)	0.0005 (12)
O1	0.101 (3)	0.110 (3)	0.064 (2)	−0.057 (2)	0.044 (2)	−0.018 (2)
Cl1	0.0335 (5)	0.0513 (6)	0.0415 (5)	−0.0071 (3)	0.0128 (4)	−0.0062 (3)
Co1	0.0238 (4)	0.0402 (4)	0.0382 (4)	0.000	0.0097 (3)	0.000
O2	0.133 (10)	0.217 (14)	0.117 (8)	0.000	0.032 (7)	0.000
O3	0.20 (3)	0.28 (5)	0.11 (2)	0.000	0.12 (2)	0.000

Geometric parameters (Å, °)

C1—N1	1.327 (5)	C8—C9	1.373 (6)
C1—C2	1.381 (6)	C8—H8	0.9300
C1—H1	0.9300	C9—C10	1.373 (5)
C2—C3	1.370 (7)	C9—H9	0.9300
C2—H2	0.9300	C10—N2	1.329 (5)
C3—C4	1.362 (6)	C10—H10	0.9300

C3—H3	0.9300	N1—Co1	2.151 (3)
C4—C5	1.379 (5)	N2—Co1	2.132 (3)
C4—H4	0.9300	O1—H1A	0.86 (6)
C5—N1	1.348 (4)	O1—H1B	0.85 (3)
C5—C6	1.476 (5)	Cl1—Co1	2.4298 (9)
C6—N2	1.351 (4)	Co1—N2^i	2.132 (3)
C6—C7	1.378 (5)	Co1—N1^i	2.151 (3)
C7—C8	1.377 (6)	Co1—Cl1^i	2.4298 (9)
C7—H7	0.9300		
N1—C1—C2	122.8 (4)	C8—C9—H9	120.6
N1—C1—H1	118.6	N2—C10—C9	123.1 (3)
C2—C1—H1	118.6	N2—C10—H10	118.4
C3—C2—C1	118.2 (4)	C9—C10—H10	118.4
C3—C2—H2	120.9	C1—N1—C5	118.7 (3)
C1—C2—H2	120.9	C1—N1—Co1	125.8 (3)
C4—C3—C2	119.5 (4)	C5—N1—Co1	115.4 (2)
C4—C3—H3	120.2	C10—N2—C6	118.2 (3)
C2—C3—H3	120.2	C10—N2—Co1	125.5 (2)
C3—C4—C5	119.8 (4)	C6—N2—Co1	116.2 (2)
C3—C4—H4	120.1	H1A—O1—H1B	109 (5)
C5—C4—H4	120.1	N2—Co1—N2^i	169.92 (15)
N1—C5—C4	120.9 (4)	N2—Co1—N1^i	96.14 (11)
N1—C5—C6	116.1 (3)	N2^i—Co1—N1^i	76.58 (11)
C4—C5—C6	123.0 (3)	N2—Co1—N1	76.58 (11)
N2—C6—C7	121.4 (3)	N2^i—Co1—N1	96.14 (11)
N2—C6—C5	115.7 (3)	N1^i—Co1—N1	89.19 (16)
C7—C6—C5	122.9 (3)	N2—Co1—Cl1	91.72 (8)
C8—C7—C6	119.5 (3)	N2^i—Co1—Cl1	95.26 (8)
C8—C7—H7	120.2	N1^i—Co1—Cl1	171.64 (8)
C6—C7—H7	120.2	N1—Co1—Cl1	89.88 (8)
C9—C8—C7	118.9 (3)	N2—Co1—Cl1^i	95.26 (8)
C9—C8—H8	120.6	N2^i—Co1—Cl1^i	91.72 (8)
C7—C8—H8	120.6	N1^i—Co1—Cl1^i	89.88 (8)
C10—C9—C8	118.8 (4)	N1—Co1—Cl1^i	171.64 (8)
C10—C9—H9	120.6	Cl1—Co1—Cl1^i	92.22 (5)
N1—C1—C2—C3	−0.8 (8)	C7—C6—N2—C10	−0.9 (5)
C1—C2—C3—C4	−0.5 (8)	C5—C6—N2—C10	180.0 (3)
C2—C3—C4—C5	1.0 (8)	C7—C6—N2—Co1	176.4 (3)
C3—C4—C5—N1	−0.3 (6)	C5—C6—N2—Co1	−2.7 (4)
C3—C4—C5—C6	−180.0 (4)	C10—N2—Co1—N2^i	−136.3 (3)
N1—C5—C6—N2	1.5 (4)	C6—N2—Co1—N2^i	46.6 (2)
C4—C5—C6—N2	−178.8 (3)	C10—N2—Co1—N1^i	−93.0 (3)
N1—C5—C6—C7	−177.5 (3)	C6—N2—Co1—N1^i	89.9 (2)
C4—C5—C6—C7	2.2 (5)	C10—N2—Co1—N1	179.3 (3)
N2—C6—C7—C8	1.9 (5)	C6—N2—Co1—N1	2.2 (2)
C5—C6—C7—C8	−179.1 (3)	C10—N2—Co1—Cl1	89.8 (3)

C6—C7—C8—C9	−1.5 (6)	C6—N2—Co1—Cl1	−87.3 (2)
C7—C8—C9—C10	0.3 (7)	C10—N2—Co1—Cl1ⁱ	−2.6 (3)
C8—C9—C10—N2	0.7 (6)	C6—N2—Co1—Cl1ⁱ	−179.7 (2)
C2—C1—N1—C5	1.5 (6)	C1—N1—Co1—N2	−179.5 (3)
C2—C1—N1—Co1	179.7 (4)	C5—N1—Co1—N2	−1.3 (2)
C4—C5—N1—C1	−1.0 (5)	C1—N1—Co1—N2ⁱ	7.5 (3)
C6—C5—N1—C1	178.7 (3)	C5—N1—Co1—N2ⁱ	−174.3 (2)
C4—C5—N1—Co1	−179.3 (3)	C1—N1—Co1—N1ⁱ	83.9 (3)
C6—C5—N1—Co1	0.4 (4)	C5—N1—Co1—N1ⁱ	−97.9 (3)
C9—C10—N2—C6	−0.4 (5)	C1—N1—Co1—Cl1	−87.7 (3)
C9—C10—N2—Co1	−177.4 (3)	C5—N1—Co1—Cl1	90.5 (2)

Symmetry code: (i) −*x*+2, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯Cl1	0.86 (6)	2.43 (5)	3.250 (4)	160 (5)
O1—H1*B*⋯Cl1ⁱⁱ	0.85 (3)	2.37 (4)	3.218 (4)	172 (4)

Symmetry code: (ii) *x*, −*y*, *z*+1/2.