

Experimental

For the preparation of (I), tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.13 mmol) and 2,6-bis(1,3-dimethyl-4,5-diphenylimidazolidin-2-yl)pyridine (0.15 mmol) were dissolved in dry methylene chloride. The resulting orange solution turned green on exposure to air. Removal of solvent and recrystallization from neat methanol after an unsuccessful attempt using chloroform/methanol resulted in a 20% yield of deep-blue crystals.

Crystal data

[CuCl(C ₃₉ H ₄₁ N ₅)]PF ₆ ·0.5CH ₄ O	Mo K α radiation $\lambda = 0.71069 \text{ \AA}$
$M_r = 839.75$	Cell parameters from 25 reflections
Orthorhombic	$\theta = 9.00\text{--}20.25^\circ$
$P2_12_12_1$	$\mu = 0.720 \text{ mm}^{-1}$
$a = 14.636 (2) \text{ \AA}$	$T = 293 \text{ K}$
$b = 15.185 (3) \text{ \AA}$	Rectangular prism
$c = 17.928 (2) \text{ \AA}$	$0.35 \times 0.21 \times 0.18 \text{ mm}$
$V = 3984.4 (10) \text{ \AA}^3$	Deep blue
$Z = 4$	
$D_x = 1.40 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	$h = -18 \rightarrow 0$
ω - 2θ scans	$k = -18 \rightarrow 0$
Absorption correction: none	$l = 0 \rightarrow 22$
4490 measured reflections	3 standard reflections
4490 independent reflections	frequency: 30 min
2291 reflections with $I > 2\sigma(I)$	intensity decay: none
$\theta_{\max} = 26.31^\circ$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R(F) = 0.059$	$\Delta\rho_{\max} = 0.475 \text{ e \AA}^{-3}$
$wR(F^2) = 0.179$	$\Delta\rho_{\min} = -0.622 \text{ e \AA}^{-3}$
$S = 1.007$	Extinction correction: none
4490 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
500 parameters	Absolute configuration: Flack (1983)
H atoms: see below	Flack parameter = 0.01 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 1.9156P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—N1	1.927 (6)	Cu—N4	2.116 (7)
Cu—N3	2.114 (7)	Cu—Cl	2.173 (2)
N1—Cu—N3	80.9 (3)	N1—Cu—Cl	172.7 (3)
N1—Cu—N4	81.2 (3)	N3—Cu—Cl	101.7 (2)
N3—Cu—N4	161.6 (3)	N4—Cu—Cl	96.6 (2)

All non-H atoms were refined anisotropically. The methanol solvent molecule was included in the refinement with half occupancy (based on chemical analysis). The H atoms were refined using a riding model, including torsional freedom for methyl and OH groups, with $U(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, $1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C})$ for others.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1995). Cell refinement: CAD-4 EXPRESS. Data reduction: DATAP

(Coppens, Leiserowitz & Rabinovich, 1965). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEPII (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1153). Services for accessing these data are described at the back of the journal.

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[6,6'-Bis(benzimidazol-2-yl-N³)-2,2'-bipyridine]dichlorocobalt(II)-Dimethylformamide (1/2)

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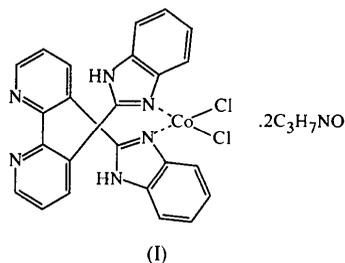
(Received 18 July 1995; accepted 12 December 1996)

Abstract

The title complex, [CoCl₂(C₂₄H₁₆N₆)]·2C₃H₇NO, has been prepared from cobalt chloride and 6,6'-dibenzimidazolyl-2,2'-bipyridine (DBBP). The metal center is coordinated in a distorted tetrahedral configuration to two Cl⁻ ions and to two N donor atoms of the DBBP ligand which acts bidentately. The Co—N distances are 2.033 (4) \AA and the Co—Cl distances are 2.2300 (18) \AA . The coordination angles lie between 102.61 (13) and 118.13 (18)°. The complex has C₂ symmetry.

Comment

Knapp *et al.* (1987) described the bidentate bis(imidazole) donor ligand, 2,2'-bis(2-imidazolyl)biphenyl, which reacted with $\text{Cu}^{\text{I,II}}$, Ni^{II} and Co^{II} ions to form pseudo-tetrahedral complexes. The ligand 6,6'-dibenzimidazolyl-2,2'-bipyridine (DBBP) was expected to form tetrahedral complexes in a similar manner. Reaction of DBBP with Co^{II} leads to formation of the title complex, (I), which is a 1:1 complex and is different from that of bis[2,2'-bis(imidazole)biphenyl]copper dperchlorate which is a 1:2 complex (Knapp *et al.*, 1987).



In the title complex (Fig. 1), the Co^{II} ion is four-coordinated by two N atoms from the DBBP ligand and two Cl^- ions. The Co atom lies on a crystallographic twofold axis. The Co—N distances are 2.033 (4) Å and the Co—Cl distances are 2.2300 (18) Å. The Co—N distances are longer than those in both bis[2,2'-bis(imidazole)biphenyl]copper dperchlorate [1.949 (8)–1.980 (7) Å; Knapp *et al.*, 1987] and tetrakis(1,2-dimethylimidazole)cobalt dperchlorate [1.988 (3)–2.002 (3) Å; Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983].

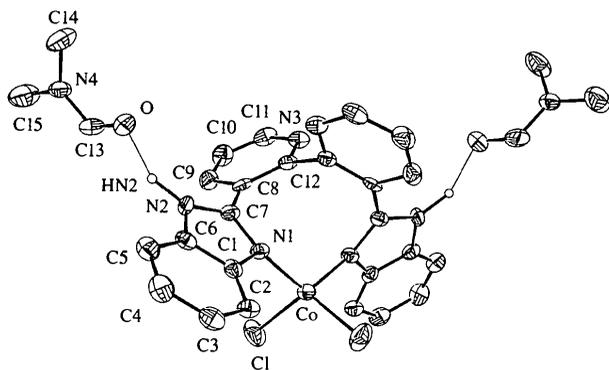


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with displacement ellipsoids for non-H atoms shown at the 30% probability level.

The geometry of the Co^{II} center is described as a distorted tetrahedron with angles ranging from 102.61 (13) to 118.13 (18) Å. The two benzimidazolyl moieties of the DBBP ligand are not coplanar, the dihedral angle between them being 73.5°. Geometrical constraints within

the nine-membered chelate ring causes the intra-ligand N1—Co—N1 angle to exceed 109°. As the two benzimidazolyl rings exhibit considerable steric hindrance, the bipyridine unit of the DBBP ligand does not bond to the metal; the dihedral angle between the benzimidazole and pyridine planes is 48.8°. The dihedral angle of the two pyridine planes in the bipyridine unit is 94.6°. There is one DMF (*N,N'*-dimethylformamide) solvent molecule in the asymmetric unit. There are strong hydrogen bonds between the N2 proton and the O atom of DMF [HN2···O 1.654 (4) Å].

Experimental

The DBBP ligand was prepared from 2,2'-bipyridyl-6,6'-dicarboxylic acid and 1,2-diaminobenzene (Cheng, 1989). A methanol solution of the ligand (0.268 g, 1 mmol) was mixed with cobalt(II) chloride (0.467 g, 2 mmol) and stirred for 3 h at room temperature. A blue precipitate was obtained. Crystals of the title compound were obtained by slow diffusion of diethyl ether into a DMF solution of the title complex.

Crystal data

[$\text{CoCl}_2(\text{C}_{24}\text{H}_{16}\text{N}_6)$].-

$2\text{C}_3\text{H}_7\text{NO}$

$M_r = 664.46$

Monoclinic

$I2/c$

$a = 17.977 (4) \text{ \AA}$

$b = 11.819 (7) \text{ \AA}$

$c = 14.696 (2) \text{ \AA}$

$\beta = 90.775 (15)^\circ$

$V = 3122 (2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.414 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 6.3\text{--}9.9^\circ$

$\mu = 0.76 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate

$0.32 \times 0.25 \times 0.05 \text{ mm}$

Blue

Data collection

Enraf–Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

empirical ψ scans (North, Phillips & Mathews, 1968)

$T_{\text{min}} = 0.86$, $T_{\text{max}} = 0.96$

2118 measured reflections

2029 independent reflections

All reflections observed

$R_{\text{int}} = 0.063$

$\theta_{\text{max}} = 22.5^\circ$

$h = -19 \rightarrow 19$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 15$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F

$R = 0.149$

$wR = 0.048$

$S = 1.08$

2029 reflections

196 parameters

H atoms: see below

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.005$

$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.23 \text{ e \AA}^{-3}$

Extinction correction:

Larson (1970)

Extinction coefficient:

$8 (3) \times 10^2$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Co	1/2	0.70161 (10)	1/4	0.0415 (7)
Cl	0.43316 (10)	0.60460 (17)	0.14763 (13)	0.0823 (13)
N1	0.4208 (2)	0.7900 (4)	0.3173 (3)	0.036 (3)
N2	0.3132 (2)	0.8848 (4)	0.3152 (3)	0.042 (3)
N3	0.5023 (3)	1.0632 (4)	0.1401 (3)	0.045 (3)
C1	0.3755 (3)	0.7485 (4)	0.3856 (4)	0.039 (3)
C2	0.3905 (3)	0.6643 (5)	0.4509 (4)	0.043 (4)
C3	0.3351 (3)	0.6440 (5)	0.5111 (4)	0.055 (4)
C4	0.2676 (3)	0.7022 (6)	0.5082 (4)	0.064 (5)
C5	0.2531 (3)	0.7834 (5)	0.4444 (4)	0.055 (4)
C6	0.3083 (3)	0.8057 (5)	0.3849 (4)	0.041 (4)
C7	0.3812 (3)	0.8747 (4)	0.2779 (4)	0.039 (3)
C8	0.4067 (3)	0.9453 (4)	0.2027 (4)	0.037 (3)
C9	0.3621 (3)	0.9624 (5)	0.1256 (4)	0.052 (4)
C10	0.3899 (3)	1.0302 (5)	0.0583 (4)	0.061 (4)
C11	0.4579 (4)	1.0785 (5)	0.0673 (4)	0.055 (4)
C12	0.4763 (3)	0.9994 (4)	0.2069 (4)	0.039 (4)
C13	0.1790 (4)	1.0639 (5)	0.2097 (5)	0.070 (5)
C14	0.1332 (4)	1.2463 (6)	0.2501 (5)	0.089 (6)
C15	0.0777 (4)	1.1432 (6)	0.1186 (6)	0.105 (6)
N4	0.1315 (3)	1.1478 (4)	0.1919 (3)	0.053 (3)
O	0.2255 (2)	1.0618 (3)	0.2701 (3)	0.069 (3)

Table 2. Selected geometric parameters (Å, °)

Co—Cl	2.2300 (18)	Co—N1	2.033 (4)
Cl—Co—Cl ⁱ	118.12 (10)	Cl ⁱ —Co—N1	108.08 (13)
Cl—Co—N1	102.61 (13)	N1—Co—N1 ⁱ	118.13 (18)

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

The title structure was solved by the heavy-atom method; subsequent Fourier syntheses based on the heavy atom revealed the positions of all the non-H atoms. Least-squares refinement including anisotropic parameters for the non-H atoms was performed. H atoms were placed at calculated positions with *U* = *U*(attached atom) + 0.01 Å².

Data collection: CAD-4-PC Software (Enraf-Nonius, 1992). Cell refinement: CAD-4-PC Software. Data reduction: NRC-VAX DATRD2 (Gabe, Le Page, White & Lee, 1987). Program(s) used to solve structure: NRCVAX SOLVER. Program(s) used to refine structure: NRCVAX LSTSQ. Molecular graphics: NRCVAX. Software used to prepare material for publication: NRCVAX TABLES.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1062). Services for accessing these data are described at the back of the journal.

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CuW(py)₂(H₂O)₂O₂F₄ and CuW(py)₄O₂F₄

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Abstract

Two new Cu^{II}/W^{VI} oxyfluorides, *catena*-poly[(trifluoro-oxotungsten)-*μ*-fluoro-[diaquabis(pyridine-*N*)copper]-*μ*-oxo] or *catena*-poly[(difluoro-*cis*-dioxotungsten)-*μ*-fluoro-[diaquabis(pyridine-*N*)copper]-*μ*-fluoro], [CuW(O₂F₄(C₅H₅N)₂(H₂O)₂], (I), and *catena*-poly[(trifluoro-oxotungsten)-*μ*-fluoro-[tetrakis(pyridine-*N*)copper]-*μ*-oxo] or *catena*-poly[(difluoro-*cis*-dioxotungsten)-*μ*-fluoro-[tetrakis(pyridine-*N*)copper]-*μ*-fluoro], [CuW(O₂F₄(C₅H₅N)₄], (II), have been synthesized. The first complex, (I), contains one-dimensional chains of alternating [Cu(py)₂(H₂O)₂(O/F)_{2/2}]^{0.66+} cations and [W(O/F)₄(O/F)_{2/2}]^{0.66-} anions. The corner-linked octahedra form infinite and parallel chains that run along the *b* axis. The second compound, (II), contains one-dimensional chains of alternating [Cu(py)₄(O/F)_{2/2}]^{0.66+} cations and [W(O/F)₄(O/F)_{2/2}]^{0.66-} anions. The corner-linked octahedra form infinite and non-intersecting chains that switch between [110] and [1 $\bar{1}$ 0] every *c*/2.

Comment

Two new complexes containing the [WO₂F₄]²⁻ anion, CuW(py)₂(H₂O)₂O₂F₄, (I), and CuW(py)₄O₂F₄, (II), have been synthesized. For (I), the Cu^{II} cation is axially Jahn–Teller distorted with four ‘short’ equatorial distances [Cu—NC₅H₅]_{ave} = 2.02 (1) and Cu—OH₂]_{ave} = 2.00 (1) Å] and two ‘long’ bonds [Cu—X1]_{ax} = 2.356 (7) and Cu—X2]_{ax} = 2.363 (7) Å], with X1 and X2 disordered 33% O/67% F. The Cu^{II} octahedra are linked to W^{VI} through the axial ligands. Each W^{VI} atom is coordinated by two O and four F atoms [W—(X3—X6)]_{eq,ave} = 1.885 (7) Å and W—(X1,X2)]_{ax,ave} = 1.866 (7) Å], with X1—X6 disordered 33% O/67% F. Inter- and intra-chain hydrogen bonding (Fig. 2) occurs between H₂O and O/F [O7—H···X5($\frac{1}{2}$ - *x*, $\frac{1}{2}$ + *y*, $\frac{3}{2}$ - *z*) = 2.61 (1) Å (inter-