

Cobalt(II) and cobalt(III) complexes with 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine

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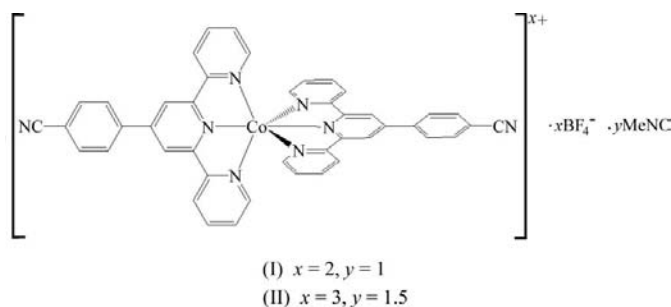
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4'-Cyanophenyl-2,2':6',2''-terpyridine (cptpy) was employed as an *N,N',N''*-tridentate ligand to synthesize the compounds bis[4'-(4-cyanophenyl)-2,2':6',2''-terpyridine]cobalt(II) bis(tetrafluoroborate) nitromethane solvate, $[\text{Co}^{\text{II}}(\text{C}_{22}\text{H}_{14}\text{N}_4)_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{NO}_2$, (I), and bis[4'-(4-cyanophenyl)-2,2':6',2''-terpyridine]cobalt(III) tris(tetrafluoroborate) nitromethane sesquisolvate, $[\text{Co}^{\text{III}}(\text{C}_{22}\text{H}_{14}\text{N}_4)_2](\text{BF}_4)_3 \cdot 1.5\text{CH}_3\text{NO}_2$, (II). In both complexes, the cobalt ions occupy a distorted octahedral geometry with two cptpy ligands in a meridional configuration. A greater distortion from octahedral geometry is observed in (I), which indicates a different steric consequence of the constrained ligand bite on the Co^{II} and Co^{III} ions. The crystal structure of (I) features an interlocked sheet motif, which differs from the one-dimensional chain packing style present in (II). The lower dimensionality in (II) can be explained by the disturbance caused by the larger number of anions and solvent molecules involved in the crystal structure of (II). All atoms in (I) are on general positions, and the F atoms of one BF_4^- anion are disordered. In (II), one B atom is on an inversion center, necessitating disorder of the four attached F atoms, another B atom is on a twofold axis with ordered F atoms, and the C and N atoms of one nitromethane solvent molecule are on a twofold axis, causing disorder of the methyl H atoms. This relatively uncommon study of analogous Co^{II} and Co^{III} complexes provides a better understanding of the effects of different oxidation states on coordination geometry and crystal packing.

Comment

$[\text{Co}(\text{tpy})_2]^{2+}$ (tpy is terpyridine) and its derivatives have been attracting much attention because of their considerable variety of spin-crossover (SCO) behaviors (Judge & Baker, 1967; Kremer *et al.*, 1982). The introduction of substituents into the 4'-position of terpyridine leads to compounds having properties with potential applications in luminescence (Alcock *et al.*, 2000), photochemistry (Yutaka *et al.*, 2003),

construction of multimetallic arrays (Mutai *et al.*, 2001) and enhancement of SCO characteristics (Gaspar *et al.*, 2001; Hayami *et al.*, 2005). We have designed the 4'-cyanophenyl-substituted ligand 4'-cyanophenyl-2,2':6',2''-terpyridine (cptpy) and prepared the first two cobalt complexes of this family, (I) and (II). These complexes could potentially be used as building blocks for new multinuclear supramolecular complexes with versatile physicochemical properties *via* bridging through the cyano groups in the molecule. Relatively few studies of Co^{III} complexes with such ligands have been carried out (Yutaka *et al.*, 2003). Figgis *et al.* (1983) observed significant differences in metal–ligand distances between Co^{II} and Co^{III} complexes of unsubstituted terpyridine, but there is no comparative information on 4'-substituted terpyridine species. The present crystallographic study is intended to contribute to a better understanding of the dependence of the coordination geometry on the oxidation state of the metal center.



The structure analysis confirms the bis-meridional configuration for both complex cations (Fig. 1). In complex (I), the Co–N distances (Table 1) are significantly longer than those observed in low-spin (LS) Co^{II} species [1.873 (11)–1.971 (13) Å (Alcock *et al.*, 2000) and 1.849 (6)–1.956 (6) Å (Galet *et al.*, 2006)] and are comparable to those of high-spin (HS) Co^{II} species [2.018 (2)–2.180 (3) Å (Galet *et al.*, 2006) and 2.075 (5)–2.189 (3) Å (Takusagawa *et al.*, 1986)], and thus (I) exhibits a characteristic feature of the HS state. The Co–N distances of (II) (Table 2) are close to those reported in $[\text{Co}(\text{tpy})_2]\text{Cl}_3$ [1.853 (7)–1.937 (7) Å; Figgis *et al.*, 1983], suggesting an LS state for (II). In both complexes, the Co–N_{central} distances are shorter than the Co–N_{terminal} distances, indicating a compression along the N2–Co–N5 central axis. This compression indicates the steric effect of the constrained cptpy ligand bite on the metal center in the two complexes.

Furthermore, the N_{terminal}–Co–N_{terminal} bite angles for the terpyridyl chelates in (I) (Table 1) fall in the range reported for the Co^{II} complexes of 4'-aryl-substituted terpyridines (Yutaka *et al.*, 2003; Alcock *et al.*, 2000; Whittle *et al.*, 1998) and deviate considerably from ideal octahedral geometry. In (II), the bite angles are about 10° larger (Table 2). The terpyridyl units of the ligands are approximately planar. The N–C–C–N torsion angles of the two pyridyl rings of (I) [3.8 (7)–9.5 (6)°] are markedly larger than those observed for (II) [1.2 (5)–5.1 (6)°]. Thus, it can be seen that the coordination environment around the Co^{III} ion has a more ideal octahedral geometry than that observed in the Co^{II} complex.

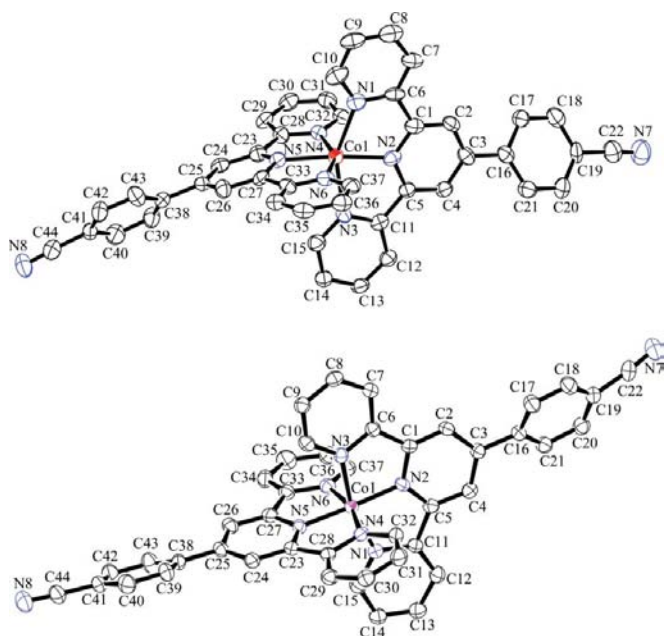


Figure 1
The molecular structures of the cobalt complex cations in (I) (top) and (II) (bottom), showing the atom-labeling schemes and 50% probability displacement ellipsoids. For clarity, H atoms, BF_4^- anions and CH_3NO_2 molecules are not shown.

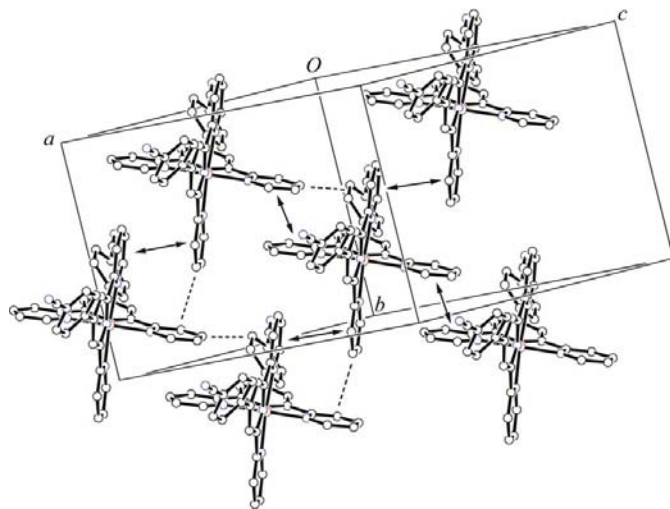


Figure 2
The intermolecular interaction scheme of the $[\text{Co}(\text{cptypy})_2]^{2+}$ complex cations in (I). π - π interactions are indicated by double-headed arrows and C-H... π interactions are indicated by dashed lines.

The benzene rings of the cptypy ligands in each case are twisted significantly with respect to the terpyridyl units. The dihedral angles between the mean planes of the benzene ring and the terpyridyl unit are $33.8(1)$ and $46.3(2)^\circ$ in (I) versus the much lower values of $18.8(2)$ and $26.3(1)^\circ$ in (II). Since such twisting is especially sensitive to intermolecular interactions (Brock & Minton, 1989), it reveals the influence of crystal packing effects in (I) and (II).

In (I), two types of interactions between terminal pyridyl rings of adjacent molecules, namely offset π - π interactions

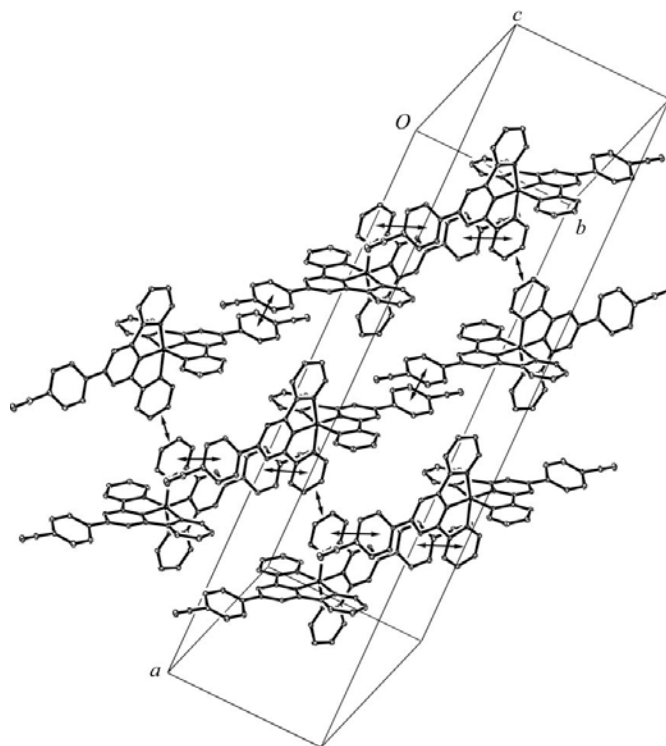


Figure 3
The packing of the $[\text{Co}(\text{cptypy})_2]^{3+}$ complex cations in (II). Double-headed arrows indicate π - π interactions.

[nearest C—C distance = $3.376(7)$ Å] and edge-to-face C—H... π interactions [$\text{C}\cdots\pi = 3.684(7)$ Å, with a dihedral angle of $89.8(1)^\circ$], operate in concert (Fig. 2). As is observed in $[\text{M}(\text{tpy})_2]^{2+}$ complexes where the anion-cation ratio is 2:1 (Scudder *et al.*, 1999), the interactions involving anions and solvent molecules do not in general disrupt the motif of (I). Each terminal pyridyl ring of a ligand participates in these interactions with the adjacent molecules, thus forming a layer of interlocked cations. The layers stack through offset π - π interactions [$3.460(9)$ and $3.618(8)$ Å] between the benzene and central pyridyl rings of adjacent molecules [dihedral angles = $3.4(2)$ and $10.2(2)^\circ$], as well as C—H... π interactions [$\text{C}\cdots\pi = 3.307(9)$ Å and C—H... $\pi = 31.9(2)^\circ$] between the benzene rings of adjacent molecules. As a result of the distortion of the benzene-terpyridyl unit, alternating layers in the stack are rotated by 45° . This packing motif is also observed in $[\text{Cu}(\text{tpy})_2](\text{PF}_6)_2$ (Scudder *et al.*, 1999).

The crystal packing of (II) is disrupted compared with that in (I) by the greater number of BF_4^- ions and CH_3NO_2 solvent molecules, which hinder the formation of C—H... π interactions between the terminal pyridyl rings. The complex cations are linked by π - π interactions to form a one-dimensional supramolecular chain similar to those seen in biphenyl-substituted species (Alcock *et al.*, 2000) (Fig. 3). A two-dimensional layer is built by π - π interactions between terminal pyridyl rings of adjacent chains [$3.199(9)$ Å] and stabilized by C—H... π interactions between terminal pyridyl and benzene rings [$3.546(8)$ Å and $46.5(2)^\circ$]. As a result, the N2—Co—N5 central axes of molecules in adjacent layers are

approximately perpendicular to one another, forming a visual crossover grid.

The difference in packing patterns between (I) and (II) may be attributed to the number of anions and solvent molecules. The larger ionic radius of Co^{II} and the greater distortion from octahedral geometry make it possible to achieve a different packing style of higher dimensionality involving fewer anions and solvent molecules compared with the situation with Co^{III} . Given the sensitivity of the crystal packing to both the number, charge and size of the constituent ions and the number of solvent molecules, it will be necessary to conduct further comparative studies of this type in order to reach more relevant and precise conclusions.

Experimental

4'-Cyanophenyl-2,2':6',2''-terpyridine was synthesized according to literature procedures (Chamchoumis & Potvin, 1998; Constable *et al.*, 1990). For the synthesis of (I), a solution of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) in methanol (20 ml) was layered over a solution of ctpy (0.2 mmol) in dichloromethane (20 ml). Red needle-shaped crystals of (I) formed after one week at 278 K. Red block-shaped crystals of (I) suitable for X-ray diffraction were obtained by recrystallization from a nitromethane/diethyl ether system after one week at 313 K. Complex (II) was prepared by adding a tetrahydrofuran solution (20 ml) of AgBF_4 (0.2 mmol) to a nitromethane solution (20 ml) of (I) (0.2 mmol). After one week at 313 K, orange crystals of (II) suitable for X-ray diffraction were obtained. Oxidation by the Ag^{I} ion resulted in the formation of the Co^{III} species from (I).

Compound (I)

Crystal data

$[\text{Co}(\text{C}_{22}\text{H}_{14}\text{N}_4)_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{NO}_2$	$V = 4118 (7) \text{ \AA}^3$
$M_r = 962.34$	$Z = 4$
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 13.304 (13) \text{ \AA}$	$\mu = 0.51 \text{ mm}^{-1}$
$b = 12.125 (12) \text{ \AA}$	$T = 120.1 \text{ K}$
$c = 27.30 (3) \text{ \AA}$	$0.20 \times 0.20 \times 0.10 \text{ mm}$
$\beta = 110.761 (12)^\circ$	

Data collection

Rigaku Mercury diffractometer	6271 reflections with $F^2 > 2\sigma(F^2)$
23489 measured reflections	$R_{\text{int}} = 0.056$
8003 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$	$\Delta\rho_{\text{max}} = 1.13 \text{ e \AA}^{-3}$
$wR(F^2) = 0.169$	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
$S = 1.04$	Absolute structure: Flack (1983),
8003 reflections	3285 Friedel pairs
632 parameters	Flack parameter: 0.026 (19)
H-atom parameters constrained	

Compound (II)

Crystal data

$[\text{Co}(\text{C}_{22}\text{H}_{14}\text{N}_4)_2](\text{BF}_4)_3 \cdot 1.5\text{CH}_3\text{NO}_2$	$V = 9123 (8) \text{ \AA}^3$
$M_r = 1079.67$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 37.80 (2) \text{ \AA}$	$\mu = 0.48 \text{ mm}^{-1}$
$b = 10.748 (6) \text{ \AA}$	$T = 110.2 \text{ K}$
$c = 22.99 (1) \text{ \AA}$	$0.30 \times 0.07 \times 0.05 \text{ mm}$
$\beta = 102.388 (9)^\circ$	

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

Co1—N1	2.132 (4)	Co1—N4	2.147 (5)
Co1—N2	2.007 (4)	Co1—N5	2.028 (4)
Co1—N3	2.146 (4)	Co1—N6	2.133 (4)
N1—Co1—N2	76.41 (17)	N2—Co1—N5	169.48 (18)
N1—Co1—N3	152.98 (16)	N4—Co1—N5	77.21 (18)
N1—Co1—N5	111.88 (17)	N4—Co1—N6	154.20 (15)
N2—Co1—N3	77.31 (16)	N5—Co1—N6	77.19 (19)

Table 2
Selected geometric parameters (\AA , $^\circ$) for (II).

Co1—N1	1.937 (4)	Co1—N4	1.944 (4)
Co1—N2	1.860 (4)	Co1—N5	1.857 (3)
Co1—N3	1.946 (4)	Co1—N6	1.927 (4)
N1—Co1—N2	82.4 (2)	N2—Co1—N5	177.4 (2)
N1—Co1—N3	164.6 (2)	N4—Co1—N5	82.6 (2)
N1—Co1—N5	100.0 (2)	N4—Co1—N6	164.4 (2)
N2—Co1—N3	82.2 (2)	N5—Co1—N6	81.9 (2)

Data collection

Rigaku Mercury diffractometer	35412 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	10280 independent reflections
$T_{\text{min}} = 0.789$, $T_{\text{max}} = 0.976$	7454 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.096$	688 parameters
$wR(F^2) = 0.238$	H-atom parameters constrained
$S = 1.17$	$\Delta\rho_{\text{max}} = 1.03 \text{ e \AA}^{-3}$
10280 reflections	$\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$

All H atoms were positioned geometrically and treated as riding [C—H = 0.95 and 0.98 \AA , and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. One BF_4^- anion (containing B2) in (I) is disordered such that three of the F atoms are each distributed over two positions with 50% occupancy. In (II), one BF_4^- anion (containing B4) is disordered, with all four F atoms statistically distributed over two sites related by inversion symmetry. The methyl H atoms of one nitromethane solvent molecule (containing N10 and C46) are statistically disordered over two sets of positions related by twofold rotation.

For (I), data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*. For (II), data collection: *CrystalClear*; cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEPII*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3135). Services for accessing these data are described at the back of the journal.

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