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Bis{2,6-bis[3-(2,4,6-trimethylphenyl)-pyrazol-1-yl-*κN*^{2}]pyridine-*κN*}-cobalt(II) dinitrate at 290 and 150 K

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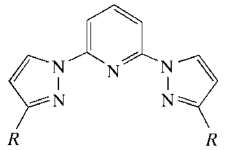
The title compound, $[\mathrm{Co(C_{29}H_{29}N_5)_2](NO_3)_2}$, contains a six-coordinate high-spin $\mathrm{Co^{II}}$ ion with approximate local D_{2d} symmetry. The bond lengths and angles at cobalt undergo only small changes between the two temperatures, which confirms that the $\mathrm{Co^{II}}$ ion does not undergo a spin-state transition over this temperature range.

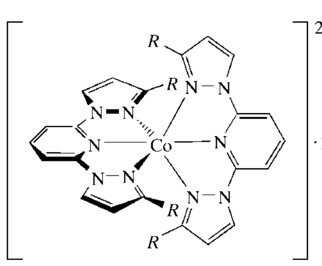
Comment

We have recently reported a synthetic and structural study of a series of complexes denoted $[\mathrm{Co}(L^R)_2]^{2+}$ [R is H, ^{i}Pr, Ph or mesityl (Mes); Holland *et al.*, 2001]. As part of this study, we described the crystal structure of $[\mathrm{Co}(L^{\mathrm{Mes}})_2](\mathrm{ClO_4})_2\cdot 2\mathrm{CH_3NO_2}$, which we obtained at 150 K to prevent desolvation of the crystals. Unfortunately, it was not possible to interpret this structure meaningfully because, although the complex is in a high-spin form at 290 K, in the absence of variable-temperature magnetic data, it was unclear whether the Co ion had undergone a spin-state transition upon cooling (see, for example, Figgis *et al.*, 1983; Gaspar *et al.*, 2001). We now report structure determinations of the title unsolvated salt, $[\mathrm{Co}(L^{\mathrm{Mes}})_2](\mathrm{NO_3})_2$, (I), at 290 and 150 K, which are intended to address this ambiguity.

Compound (I) crystallizes in the orthorhombic space group $Pca2_1$, with one complex dication and two anions per asymmetric unit, all of which lie on general positions. The $\mathrm{Co^{II}}$ ion has a distorted octahedral stereochemistry with approximate D_{2d} local symmetry, which resembles those of other $[M(L^R)_2]^{2+}$ (M is Fe, Co, Ni, Cu or Zn) complexes that we have characterized crystallographically (Solanki *et al.*, 1998, 2001; Halcrow *et al.*, 2000; Holland *et al.*, 2001, 2002). As in these other compounds, the coordination sphere at cobalt in (I) is substantially distorted from an ideal octahedron by the restricted bite angle of the L^{Mes} ligand; the average of the four angles N2—Co1—N9, N2—Co1—N23, N36—Co1—N43 and N2—Co1—N57 is 77.09 (13)° at 150 K, compared with the ideal octahedral angle of 90°. While five of the six Co—N bonds in (I) are identical at the two temperatures to within experimental error, the Co1—N36 bond is 0.013 (2) Å longer at 150 K than at 290 K. This cannot reflect the existence of a partial spin-state transition upon cooling, since that would give rise to a shortening of this bond at lower temperature (Figgis *et al.*, 1983; Holland *et al.*, 2001), the opposite trend to that observed. Hence, the origin of this effect is uncertain, although librational shortening of the Co—N bonds at 290 K may contribute to it. All the N—Co—N angles in the two structures are identical to within three s.u.'s, except for N9—Co1—N57, which is 0.44 (8)° larger at 150 K than at 290 K, and N23—Co1—N57, which has contracted by 0.63 (8)° in the low-temperature structure. The significance of these small differences is also unclear.



L^R



$R = -\mathrm{C_6H_2(CH_3)_3}$-2,4,6
(I)

The effective magnetic moment of (I) at 290 K is 4.2 μ_{B}, which is identical, within experimental error, to that exhibited by $[\mathrm{Co}(L^{\mathrm{Mes}})_2](\mathrm{ClO_4})_2$ (Holland *et al.*, 2001), and is consistent

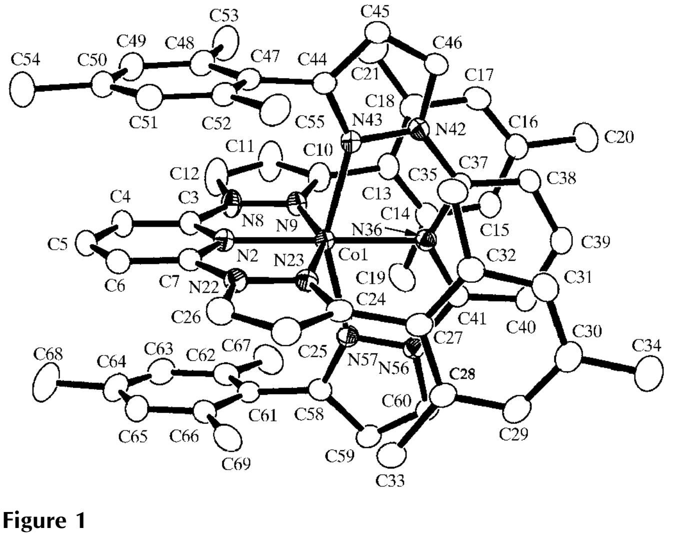


Figure 1
A view of the molecular structure of the $[\mathrm{Co}(L^{\mathrm{Mes}})_2]^{2+}$ dication in (I) at 150 K, showing 35% probability displacement ellipsoids and the atom-numbering scheme employed. H atoms have been omitted for clarity.

with (I) being completely high-spin at this temperature (O'Connor, 1982). The almost identical molecular structures of (I) at 290 and 150 K also demonstrates that (I) is still in a high-spin state at 150 K. That being the case, it is interesting that all the Co—N bonds in (I) are shorter than the corresponding bonds in $[Co(L^{Mes})_2](ClO_4)_2\cdot 2CH_3NO_2$ at 150 K, by between 0.017 (2) and 0.035 (2) Å. Despite this, the Co—N distances in (I) are within the range previously observed for high-spin Co^{II} complexes with an N_6 donor set (tabulated in Holland *et al.*, 2001). In particular, the Co—N(pyridine) bond lengths, which are the most sensitive to the spin state of a Co^{II} ion in this type of complex (Figgis *et al.*, 1983), are within the range expected from a high-spin Co^{II} compound. Hence, this study emphasizes that the coordination sphere in six-coordinate high-spin Co^{II} complexes is rather plastic, and that structural data can only be related to the spin state in these compounds with care (Holland *et al.*, 2001).

Experimental

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.16 g, 0.55 mmol) and L^{Mes} (0.50 g, 1.11 mmol) in MeCN (50 ml) was stirred at 323 K until all the solid had dissolved. The resultant orange solution was filtered and then concentrated *in vacuo* until orange–yellow microcrystals began to form. After overnight storage of the mixture at 243 K, the product was filtered off, washed with Et_2O and dried *in vacuo*. Diffusion of Et_2O vapour into a dilute MeCN solution of the sparingly soluble complex yielded small strongly diffracting rectangular prisms of (I). The same crystal was used for data collection at both 290 and 150 K.

Compound (I) at 290 K

Crystal data

$[Co(C_{29}H_{29}N_5)_2](NO_3)_2$
$M_r = 1078.09$
Orthorhombic, $Pca2_1$
$a = 22.3350$ (1) Å
$b = 10.9094$ (2) Å
$c = 22.1061$ (2) Å
$V = 5386.40$ (11) Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 59 607 reflections
$\theta = 2.6$–27.5°
$\mu = 0.38$ mm^{-1}
$T = 290$ (2) K
Rectangular prism, orange
0.45 × 0.35 × 0.28 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.847$, $T_{max} = 0.901$
59 607 measured reflections
11 975 independent reflections
10 665 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.5°$
$h = -29 \rightarrow 27$
$k = -12 \rightarrow 14$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.104$
$S = 1.04$
11 975 reflections
721 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2 + 0.6652P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0083 (8)
Absolute structure: Flack (1983), with 5661 Friedel pairs
Flack parameter = −0.004 (9)

Table 1
Selected geometric parameters (Å, °) for (I) at 290 K.

Co1—N2	2.0132 (18)	Co1—N36	2.0077 (17)
Co1—N9	2.1190 (15)	Co1—N43	2.1327 (17)
Co1—N23	2.1368 (17)	Co1—N57	2.1581 (16)
N2—Co1—N9	77.42 (7)	N9—Co1—N57	93.44 (6)
N2—Co1—N23	77.03 (7)	N23—Co1—N36	102.20 (7)
N2—Co1—N36	179.08 (7)	N23—Co1—N43	93.34 (6)
N2—Co1—N43	102.21 (7)	N23—Co1—N57	92.54 (6)
N2—Co1—N57	103.69 (7)	N36—Co1—N43	77.29 (7)
N9—Co1—N36	103.34 (7)	N36—Co1—N57	76.81 (6)
N9—Co1—N23	154.45 (7)	N43—Co1—N57	154.10 (6)
N9—Co1—N43	92.04 (7)		

Compound (I) at 150 K

Crystal data

$[Co(C_{29}H_{29}N_5)_2](NO_3)_2$
$M_r = 1078.09$
Orthorhombic, $Pca2_1$
$a = 22.1974$ (2) Å
$b = 10.7761$ (1) Å
$c = 22.0365$ (1) Å
$V = 5271.16$ (7) Å^3
$Z = 4$
$D_x = 1.358$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 86 435 reflections
$\theta = 2.6$–27.5°
$\mu = 0.39$ mm^{-1}
$T = 150$ (2) K
Rectangular prism, orange
0.45 × 0.35 × 0.28 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.844$, $T_{max} = 0.899$
86 435 measured reflections
11 941 independent reflections
11 339 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$
$h = -28 \rightarrow 28$
$k = -13 \rightarrow 13$
$l = -27 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.06$
11 941 reflections
720 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 1.4056P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0124 (9)
Absolute structure: Flack (1983), with 5773 Friedel pairs
Flack parameter = 0.001 (8)

At both temperatures, one of the two nitrate ions was disordered and was modelled over three orientations. At 290 K, these were refined with occupancies of 0.40, 0.30 and 0.30, the latter two orien-

Table 2
Selected geometric parameters (Å, °) for (I) at 150 K.

Co1—N2	2.0199 (17)	Co1—N36	2.0206 (16)
Co1—N9	2.1177 (15)	Co1—N43	2.1279 (16)
Co1—N23	2.1320 (17)	Co1—N57	2.1538 (16)
N2—Co1—N9	77.41 (7)	N9—Co1—N57	93.88 (6)
N2—Co1—N23	76.99 (6)	N23—Co1—N36	102.09 (6)
N2—Co1—N36	179.02 (7)	N23—Co1—N43	93.63 (6)
N2—Co1—N43	102.41 (6)	N23—Co1—N57	91.91 (6)
N2—Co1—N57	103.68 (6)	N36—Co1—N43	77.27 (6)
N9—Co1—N23	154.39 (6)	N36—Co1—N57	76.64 (6)
N9—Co1—N36	103.52 (7)	N43—Co1—N57	153.91 (6)
N9—Co1—N43	92.04 (6)		

tations sharing a common N atom. At 150 K, three distinct partial NO_3^- moieties were detected, with occupancies of 0.40, 0.40 and 0.20. The N—O distances within the disordered anion at 290 K were restrained to 1.25 (1) Å, and non-bonded O···O distances within a given disorder orientation were restrained to 2.17 (1) Å. At 150 K, corresponding restraints of 1.26 (1) and 2.18 (1) Å, respectively, were applied. At both temperatures, all non-H atoms with occupancies of greater than 0.5 were refined anisotropically, and all H atoms were placed in calculated positions and refined using a riding model. The torsion angles of all the CH_3 groups in the molecule were allowed to refine freely except that, at both temperatures, antibumping restraints were applied to individual H atoms attached to atoms C21 and C53, and C35 and C55. Even with these restraints, there is one abnormally short intermolecular H···H contact, *viz.* H11···H35*C*$^{\rm i}$ of 2.06–2.10 Å [symmetry code: (i) x, $y-1$, z]. Introduction of additional antibumping restraints between H11 and the C35$^{\rm i}$ methyl group prevented the refinements from converging, so these were omitted from the final models. However, for this reason, the refined methyl-group torsion angles on C35 at the two temperatures probably do not correspond to the 'true' equilibrium positions. The fixed C—H distances were as follows: at 290 K, C—H(aryl) = 0.93 Å and C—H(methyl) = 0.96 Å; at 150 K, C—H(aryl) = 0.95 Å and C—H(methyl) = 0.98 Å. At both temperatures, the H-atom $U_{\rm iso}$ parameters were fixed at $1.2U_{\rm eq}$(C) for C—H(aryl), and $1.5U_{\rm eq}$(C) for C—H(methyl).

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1518). Services for accessing these data are described at the back of the journal.

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