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{2,6-Bis[(4*R*)-(+)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl]pyridine-κ^3N}trinitrocobalt(III) monohydrate

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Key indicators

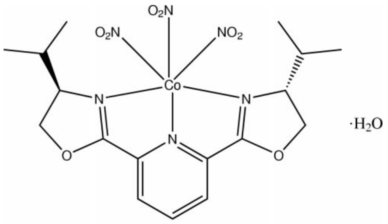
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
R factor = 0.067
wR factor = 0.153
Data-to-parameter ratio = 16.1

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

In the title compound, $[Co(NO_2)_3(C_{17}H_{25}N_3O_6)]\cdot H_2O$ or $[Co^{III}(NO_2)_3(pybox)]\cdot H_2O$, where pybox is 2,6-bis[(4*R*)-(+)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl]pyridine, the coordination geometry is distorted octahedral. This is the first reported complexation of the pybox molecule to a Co^{III} atom. The pybox ligand exhibits tridentate coordination to Co^{III} in a 1:1 ratio and the nitro anions occupy the remaining meridional positions of the octahedron. Molecules are linked, *via* solvent water molecules, into O—H···O—N hydrogen-bonded chains.

Comment

Pyridine-2,6-bis(oxazolines) are extremely useful ligands in asymmetric catalysis (Desimoni *et al.*, 2003). Since their first reported syntheses (Nishiyama *et al.*, 1989), pyridine-2,6-bis(oxazolines) have been extensively studied as chiral ligand catalysts with a variety of metals (Desimoni *et al.*, 2003). Due to our continuous interest in amino acid recognition (Chin *et al.*, 1999), we became interested in this C_2-symmetric ligand for its potential as a chiral receptor for this important class of natural products. Although pyboxes usually behave as tridentate ligands (Cuervo *et al.*, 2002; Evans, Burgey *et al.*, 1999; Evans, Kozlowski *et al.*, 1999; Nishiyama *et al.*, 1996; Nishiyama *et al.*, 1989, 1991, 1995), examples of monodentate and bidentate coordination have been reported. Monodentate pybox with Rh^I (Cuervo *et al.*, 2002), and bidentate pybox with Re^I (Heard & Jones, 1997) and Mo^0 (Heard & Tocher, 1998) clearly illustrate the other coordination modes of pybox. In addition, pybox complexes can exist either in 2:1 stoichiometric ratio, where two pybox units coordinate to the same metal, or in 1:1 pybox–metal ratio. The two reported crystal structures of a pybox coordinated to Co^{II} revealed the formation of both the complex in 2:1 stoichiometric ratio (Provent *et al.*, 2001) and the complex in 1:1 ratio (Jouaiti *et al.*, 2002) complexes. We report here the first crystal structure of a pybox with Co^{III}, (I), *viz.* 2,6-bis[(4*R*)-(+)-isopropyl-2-oxazolin-2-yl]pyridine complexed with Co^{III} in a 1:1 ratio, and crystallized as the monohydrate.



(I)

The coordination geometry of (I) is distorted octahedral, where the ligand is complexed in the more common tridentate

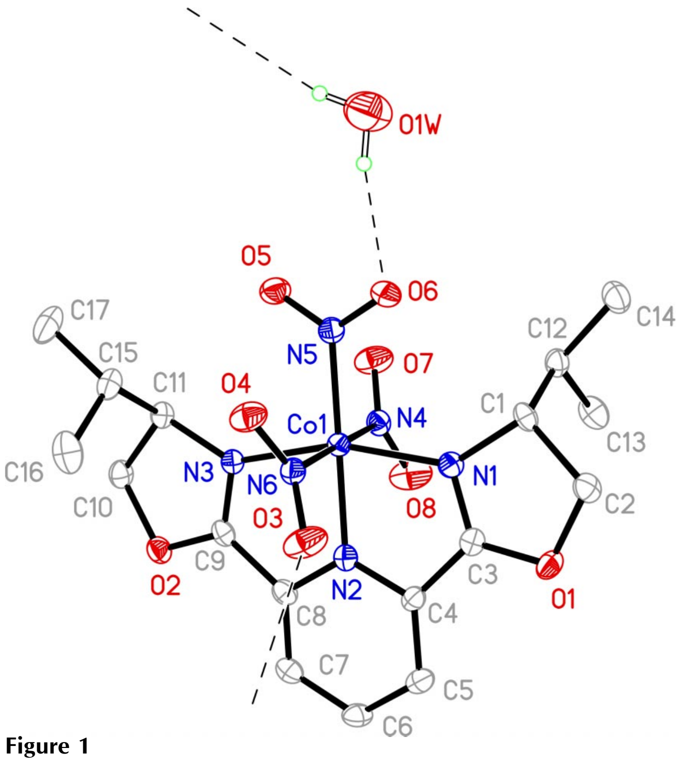


Figure 1
View of molecule (I) with the crystallographic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are indicated by dashed lines.

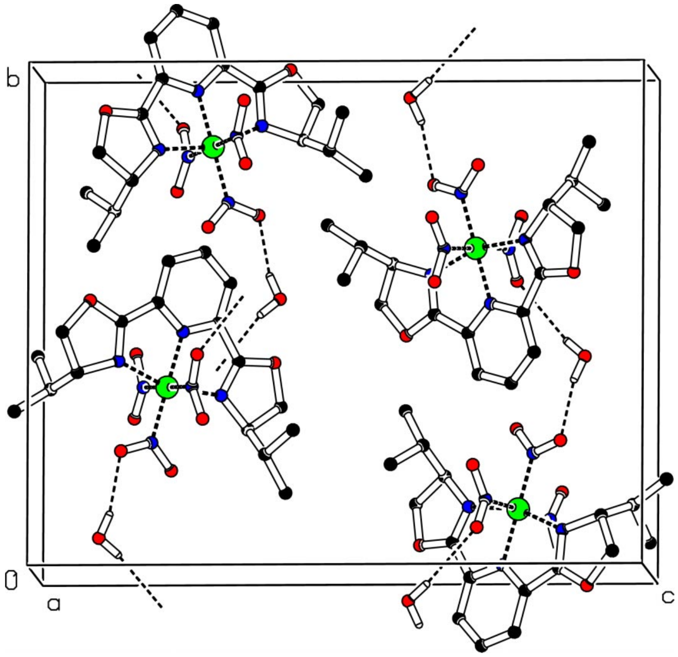


Figure 2
Packing diagram (Spek, 2002) of (I), showing the hydrogen bonding with dashed lines. Colour codes: green Co, red O, blue N, black C, white H. View along the *a* axis.

coordination and the three N atoms from pybox are in the meridional position. Nitro groups occupy the three remaining positions of the octahedron, and provide the charge balance needed for stabilizing the complex. We think the nitro groups are crucial in preventing the complexation of an additional pybox unit to form the complex in 2:1 stoichiometric ratio. The metallacycle angle N_{ox}—Co—N_{py} (ox is oxazoline and py is pyridine), average 80.78 (18)°, is slightly larger than previously reported pybox—Co^{II} values (Jouaiti *et al.*, 2002; Provent *et al.*, 2001), but is significantly smaller than the ideal octahedral angle of 90°. The length of the two Co—N_{ox} bonds, average 1.960 (4) Å, is somewhat longer than the Co—N_{py} bond length [1.905 (4) Å]. The Co—N_{py} bond length [1.905 (4) Å] in (I) is comparable to the corresponding bond lengths in other tridentate ligands with pyridine complexed to Co^{III} (Figgis *et al.*, 1983; Ziener *et al.*, 2000).

The complex molecules are linked into extended hydrogen-bonded chains through 2_1 screw axes, in the *b* direction, by virtue of the O—H···O hydrogen bonds formed between solvent water molecules and nitro groups of the complex molecules (see Table 2 and Fig. 2).

Experimental

2,6-Bis(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)pyridine (0.021 g, 0.069 mmol) was dissolved in 1.5 ml of diethyl ether with the aid of sonication. This organic solution was added to a solution of $Na_3Co(NO_2)_6$ (0.177 g, 0.437 mmol) in 1.5 ml of water. After standing overnight at room temperature, brown–red crystals were obtained in the interface of the two-phase mixture. The crystals were separated by filtration, washed with small quantities of water, followed by diethyl ether, and dried in air (0.033 g, 96%). ^{1}H NMR, 300 MHz (DMSO): 8.73 (*t*, *J* = 7.7 Hz, 1H), 8.53 (*d*, *J* = 7.7 Hz, 2H), 5.15 (dd, *J* = 9.3, 4.4 Hz, 2H), 4.95 (*t*, *J* = 9.8 Hz, 2H), 4.41 (*m*, 2H), 2.52 (*m*, 2H), 0.90 (*d*, *J* = 7.1 Hz, 6H), 0.54 (*d*, *J* = 6.6 Hz, 6H). ^{1}H NMR, 300 MHz (acetone): 8.81 (*t*, *J* = 8.2 Hz, 1H), 8.47 (*d*, *J* = 8.2 Hz, 2H), 5.17 (*dd*, *J* = 9.3, 4.4 Hz, 2H), 5.00 (*t*, *J* = 9.3 Hz, 2H), 4.55 (*m*, 2H), 2.47 (*m*, 2H), 0.97 (*d*, *J* = 7.1 Hz, 6H), 0.64 (*d*, *J* = 6.6 Hz, 6H).

Crystal data

$[Co(NO_2)_3(C_{17}H_{25}N_3O_6)]\cdot H_2O$
$M_r = 516.36$
Orthorhombic, $P2_12_12_1$
$a = 6.7185 (3)$ Å
$b = 16.5766 (8)$ Å
$c = 20.2149 (10)$ Å
$V = 2251.33 (19)$ Å^3
$Z = 4$
$D_x = 1.523$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 2747 reflections
$\theta = 2.6–27.5°$
$\mu = 0.82$ mm^{-1}
$T = 150 (1)$ K
Needle, colourless
0.10 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.922$, $T_{max} = 0.976$
9702 measured reflections

4948 independent reflections
3621 reflections with $I > 2\sigma(I)$
$R_{int} = 0.102$
$\theta_{max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -21 \rightarrow 21$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.153$
$S = 1.06$
4948 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 0.7005P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Absolute structure: Flack (1983); 2017 Friedel pairs
Flack parameter = −0.02 (3)

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Table 1
Selected geometric parameters (Å, °).

Co1—N5	1.903 (5)	Co1—N1	1.946 (4)
Co1—N2	1.905 (4)	Co1—N6	1.960 (4)
Co1—N4	1.945 (5)	Co1—N3	1.973 (4)
N5—Co1—N2	179.0 (2)	N4—Co1—N6	178.8 (2)
N5—Co1—N4	90.5 (2)	N1—Co1—N6	89.92 (18)
N2—Co1—N4	90.5 (2)	N5—Co1—N3	99.43 (19)
N5—Co1—N1	99.03 (18)	N2—Co1—N3	80.69 (18)
N2—Co1—N1	80.86 (18)	N4—Co1—N3	88.70 (17)
N4—Co1—N1	90.71 (19)	N1—Co1—N3	161.53 (18)
N5—Co1—N6	90.45 (19)	N6—Co1—N3	90.37 (16)
N2—Co1—N6	88.55 (19)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O1W—H2$W$$\cdots$O6	0.84	2.14	2.962 (8)	165
O1W—H1$W$$\cdots$O3^{i}	0.84	2.57	3.326 (10)	150

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

All H atoms bonded to C atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 1.00 Å, and included in the refinement in the riding-model approximation, with $U_{\rm iso}$ = $1.2U_{\rm eq}$ ($1.5U_{\rm eq}$ for methyl) of the carrier atom. H atoms bonded to the water O atom were refined with an O—H distance restraint of 0.840 (1) Å. The data, being generally weak, result in a slightly higher than normal $R_{\rm int}$ value.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Chin. J., Lee, S. S., Lee, K. J., Park, S. & Kim, D. H. (1999). *Nature*, **401**, 254–257.

Cuervo, D., Diez, J., Gamasa, M. P., Garcia-Granda, S. & Gimeno, J. (2002). *Inorg. Chem.* **41**, 4999–5001.

Desimoni, G., Faita, G. & Quadrelli, P. (2003). *Chem. Rev.* In the press.

Evans, D. A., Burgey, C. S., Kozlowski, M. C. & Tregay, S. W. (1999). *J. Am. Chem. Soc.* **121**, 686–699.

Evans, D. A., Kozlowski, M. C., Murry, J. A., Burgey, C. S., Campos, K. R., Connell, B. T. & Staples, R. J. (1999). *J. Am. Chem. Soc.* **121**, 669–685.

Figgis, B. N., Kucharski, E. S. & White, A. H. (1983). *Aust. J. Chem.* **36**, 1563–1571.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Heard, P. J. & Jones, C. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1083–1091.

Heard, P. J. & Tocher, D. A. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2169–2176.

Jouaiti, A., Hosseini, M. W. & Kyritsakas, N. (2002). *Chem. Commun.* pp. 1898–1899.

Nishiyama, H., Aoki, K., Itoh, H., Iwamura, T., Sakata, N., Kurihara, O. & Motoyama, Y. (1996). *Chem. Lett.* pp. 1071–1072.

Nishiyama, H., Itoh, Y., Sugawara, Y., Matsumoto, H., Aoki, K. & Itoh, K. (1995). *Bull. Chem. Soc. Jpn*, **68**, 1247–1262.

Nishiyama, H., Kondo, M., Nakamura, T. & Itoh, K. (1991). *Organometallics*, **10**, 500–508.

Nishiyama, H., Sakaguchi, H., Nakamura, T., Horihata, M., Kondo, M., & Itoh, K. (1989). *Organometallics*, **8**, 846–848.

Nonius (1997–2002). *COLLECT*. Nonius BV, Delft, The Netherlands.

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.

Provent, C., Bernardinelli, G., Williams, A. F. & Vulliermet, N. (2001). *Eur. J. Inorg. Chem.* pp. 1963–1967.

Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.12 Windows NT Version. Bruker AXS Inc., Madison, USA.

Spek, A. L. (2002). *PLATON*. University of Utrecht, The Netherlands.

Ziener, U., Breuning, E., Lehn, J. M., Wegelius, E., Rissanen, K., Baum, G., Fenske, D. & Vaughan, G. (2000). *Chem. Eur. J.* **6**, 4132–4139.

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