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Key indicators

Single-crystal X-ray study

$T = 296\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.036

wR factor = 0.095

Data-to-parameter ratio = 12.6

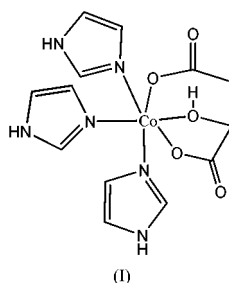
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tris(1*H*-imidazole- κN^3)(DL-malato- $\kappa^3\text{O},\text{O}',\text{O}''$)-cobalt(II)

In the title compound, $[\text{Co}(\text{C}_4\text{H}_4\text{O}_5)(\text{C}_3\text{H}_4\text{N}_2)_3]$, the cobalt(II) cation is located at the center of a distorted octahedron, being coordinated by three N atoms from three imidazole ligands and three O atoms from a malate ion. In the crystal structure, enantiomers are linked by pairs of bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form racemic dimers.

Comment

Nitrogen heterocycles are extremely important fungicides (Berger *et al.*, 1986). Imidazole derivatives have been extensively studied since the discovery of the broad-spectrum antimycotic activity of chemotherapeutic agents, such as bifonazole, clotrimazole, econazole, isoconazole, ketoconazole, miconazole and ticonazole. Malic acid is a natural constituent and common metabolite of plants and animals, being involved in the Krebs cycle and in the glyoxylic acid cycle. As part of a search for a potential fungicide, in the form of a coordination compound, (I), was synthesized and subjected to X-ray analysis.



The molecular structure of (I) is shown in Fig. 1 with the atom numbering. The title compound has $\text{Co}-\text{N}$ bond lengths ranging from 2.101 (2) to 2.127 (2) \AA and $\text{Co}-\text{O}$ bond lengths varying between 2.110 (2) and 2.141 (2) \AA . The bond angles between neighbouring atoms round the Co^{II} atom range from 74.92 (9) to 97.43 (9) $^\circ$. Therefore, the coordination geometry formed by the N and O atoms round the Co^{II} cation is that of a distorted octahedron. Three O atoms of the malate ion are involved in the coordination. Such a pattern was also found in calcium L-(–)-malate (Devatine *et al.*, 2003), but the pattern is different from the situation found in a nickel complex of malate (Zhou *et al.*, 2002).

The malate ion shows different sets of bond lengths in the carboxylate groups, *viz.* $\text{O}4-\text{C}4$ [1.265 (4) \AA] and $\text{O}5-\text{C}4$ [1.225 (4) \AA], and $\text{O}1-\text{C}1$ [1.252 (3) \AA] and $\text{O}2-\text{C}1$ [1.252 (4) \AA]. This difference may be due to the different hydrogen bonding in which the two carboxylate groups are

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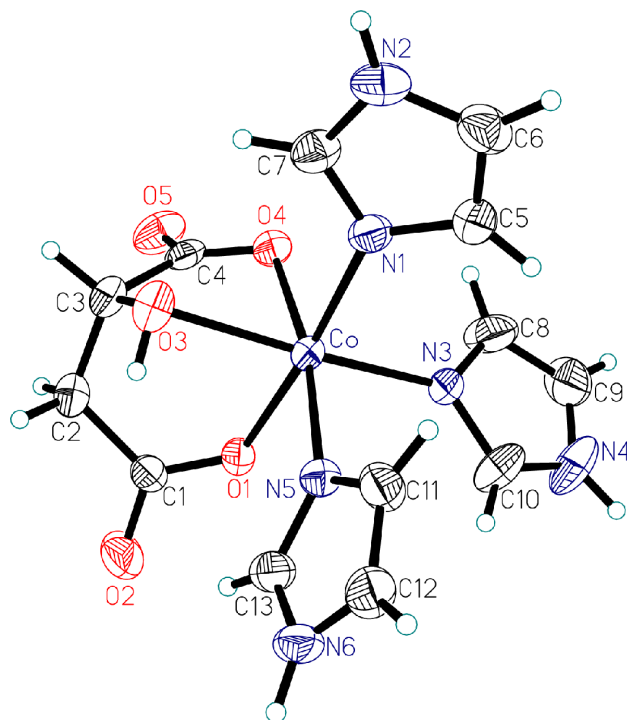


Figure 1
The structure of the title compound, showing 40% probability displacement ellipsoids and the atom-numbering scheme.

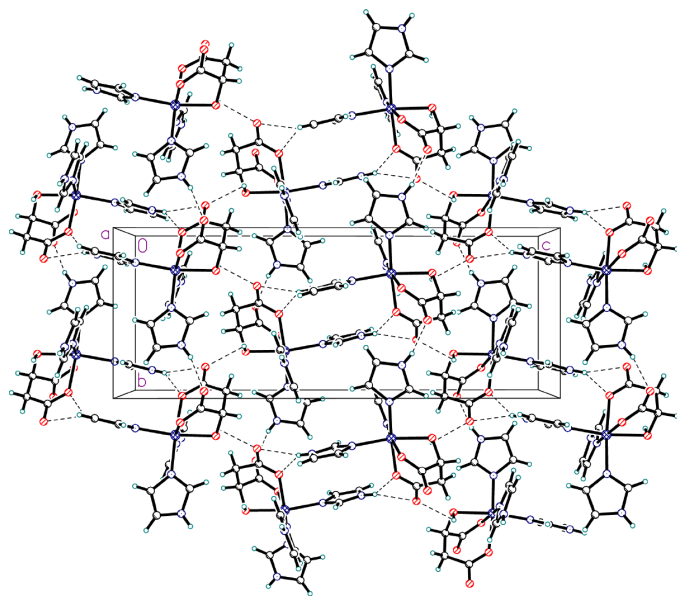


Figure 2
The packing, viewed down the *a* axis, with hydrogen bonds indicated by dashed lines.

involved. Atoms O4 and O5 are acceptors of two strong hydrogen bonds, *viz.* N6—H6'···O4ⁱⁱⁱ and N2—H2'···O5ⁱ, while O1 and O2 are acceptors in a weaker bifurcated interaction, *viz.* N4—H4'···O1ⁱⁱⁱ and N4—H4'···O2ⁱⁱ (symmetry codes are in Table 2). As for the imidazole ligands, the N3=C10 bond length [1.302 (4) Å] is slightly shorter than those of N5=C13 [1.321 (4) Å] and N1=C7 [1.317 (4) Å], and comparable with the corresponding bond length

[1.308 (2) Å] observed in hexakis(imidazole)nickel(II) disalicylate (Jian *et al.*, 1999).

A molecular packing diagram is given in Fig. 2. In the crystal structure, enantiomers are linked by pairs of bifurcated hydrogen bonds, N4—H4'···O1ⁱⁱⁱ and N4—H4'···O2ⁱⁱ, to form dimers. Such dimers are further linked by N2—H2'···O5ⁱ, N6—H6'···O4ⁱⁱⁱ and O3—H3O···O2^{iv} hydrogen bonds (Table 2).

Experimental

DL-Malic acid and Co(NO₃)₂ in a 1:1 molar ratio were mixed together with water and heated to afford a clear solution. Dilute NaOH (0.05 *N*) was used to adjust the pH to approximately 7. Imidazole (in a 3:1 molar ratio of imidazole/DL-malic acid) was added to the solution while maintaining the temperature at 353 K. Crystals of the title compound were formed by slow evaporation of water at 293 K for a week.

Crystal data

[Co(C₄H₄O₅)(C₃H₄N₂)₃]
M_r = 395.25
 Monoclinic, *P*₂₁/*c*
a = 8.482 (1) Å
b = 8.597 (1) Å
c = 22.489 (4) Å
 β = 90.71 (1)°
V = 1639.8 (4) Å³
Z = 4

D_x = 1.601 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 29 reflections
 θ = 3.0–15.7°
 μ = 1.09 mm⁻¹
T = 296 (2) K
 Prism, pink
 0.52 × 0.52 × 0.44 mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.575, *T_{max}* = 0.620
 3099 measured reflections
 2890 independent reflections
 2392 reflections with *I* > 2σ(*I*)

R_{int} = 0.012
 θ_{\max} = 25.0°
h = 0 → 10
k = 0 → 10
l = -26 → 26
 3 standard reflections
 every 97 reflections
 intensity decay: 1.4%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.036
wR(*F*²) = 0.095
S = 1.08
 2890 reflections
 230 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 1.2283P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.51 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0066 (7)

Table 1

Selected geometric parameters (Å, °).

Co—N3	2.101 (2)	O2—C1	1.252 (4)
Co—O4	2.110 (2)	O3—C3	1.451 (4)
Co—N1	2.114 (3)	O4—C4	1.265 (4)
Co—O3	2.120 (2)	O5—C4	1.225 (4)
Co—N5	2.127 (2)	N1—C7	1.317 (4)
Co—O1	2.141 (2)	N3—C10	1.302 (4)
O1—C1	1.252 (3)	N5—C13	1.321 (4)
N3—Co—O4	93.18 (9)	N1—Co—N5	94.50 (10)
N3—Co—N1	94.26 (10)	O3—Co—N5	97.43 (9)
O4—Co—N1	91.33 (9)	N3—Co—O1	89.73 (8)
O4—Co—O3	74.92 (9)	O4—Co—O1	85.21 (8)
N1—Co—O3	91.33 (9)	O3—Co—O1	84.11 (8)
N3—Co—N5	93.85 (9)	N5—Co—O1	88.45 (9)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2'\cdots O5^i$	0.86	1.99	2.828 (4)	165
$N4-H4'\cdots O1^{ii}$	0.86	2.13	2.907 (4)	150
$N4-H4'\cdots O2^{ii}$	0.86	2.25	3.025 (4)	149
$N6-H6'\cdots O4^{iii}$	0.86	1.91	2.755 (3)	168
$O3-H3O\cdots O2^{iv}$	0.88 (4)	2.27 (4)	2.572 (3)	100 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $-1-x, 1-y, -1-z$; (iii) $x-1, y, z$; (iv) $-1-x, y-\frac{1}{2}, -\frac{1}{2}-z$.

The hydroxy H atom was located in a difference Fourier map and refined isotropically. All the other H atoms were placed in calculated positions ($N-H = 0.86$ and $C-H = 0.93-0.98$ Å) and refined in the riding mode, with isotropic displacement parameters 1.2 times U_{eq} of the parent atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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