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

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In the title complex, $[Ni(C_4H_4O_5)(C_3H_4N_2)_3]$, the Ni^{II} atom is coordinated by one tridentate malate dianion and three imidazole molecules with a distorted octahedral geometry. The imidazole H atom links with both carboxyl O atoms of the neighboring complex to form a three-centered hydrogen bond, which results in a long centroid–centroid distance of 4.447 (2) Å between neighboring parallel imidazole rings.

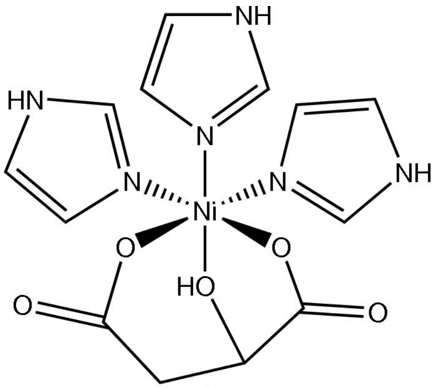
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.089
Data-to-parameter ratio = 15.6

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

Comment

Recently, we have paid much attention to the nature of π–π stacking in metal complexes (Pan & Xu, 2004), as π–π stacking between aromatic rings plays an important role in the electron transfer process in some biological system (Deisenhofer & Michel, 1989). The crystal structures of several metal complexes incorporating the imidazole ligand show the existence of π–π stacking between imidazole rings (Xu & Xu, 2004; Lin *et al.*, 2005). As part of an ongoing investigation into π–π stacking, the title Ni^{II} complex, (I), has recently been prepared and its crystal structure is presented here.



(I)

The molecular structure of (I) is illustrated in Fig. 1. The Ni^{II} atom is coordinated by one tridentate malate dianion and three imidazole molecules with a distorted octahedral geometry (Table 1). The structure is similar to that found in the Co^{II} analog (Jin *et al.*, 2003). While the carboxyl groups coordinate to the Ni^{II} atom in a monodentate mode, the hydroxy group of the malate coordinates to the Ni^{II} atom to form one five-membered and one six-membered chelate ring. The five-membered ring displays an envelope conformation, with the Ni^{II} atom in the flap position and deviating from the mean plane formed by the other four atoms by 1.019 (3) Å. In the five-membered chelate ring, the $Ni-O_{hydroxy}$ bond distance is identical to the $Ni-O_{carboxyl}$ distance. The two carboxyl planes of the malate anion are nearly perpendicular

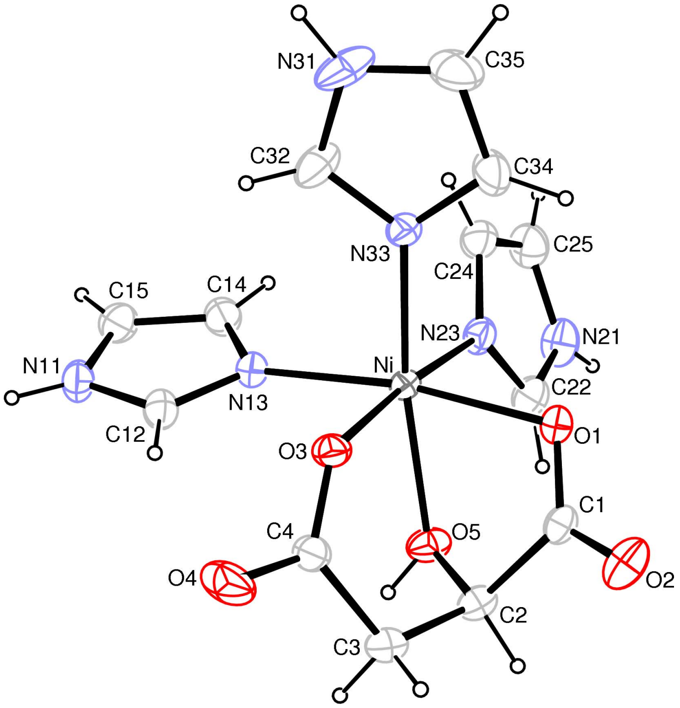


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids.

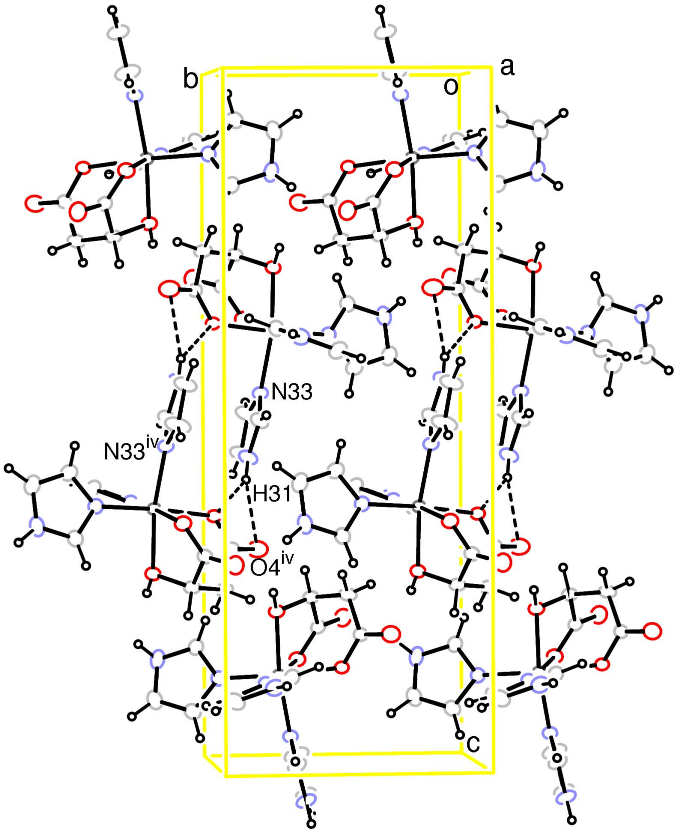


Figure 2
The packing of (I), showing the intermolecular hydrogen bonding (dashed lines) [symmetry code: (iv) $1 - x, 2 - y, 1 - z$].

to each other, the dihedral angle being 83.0 (2)°. The Ni^{II} atom lies out of the carboxyl planes by 0.800 (6) and 0.812 (5) Å.

Extensive intermolecular hydrogen bonding occurs in the crystal structure. It is notable that imidazole atom H31 links with both O atoms of the C4-carboxyl group of the neighboring complex molecule to form a three-centered hydrogen bond (Fig. 2 and Table 2); this results in a long centroid–centroid distance of 4.447 (2) Å between the neighboring parallel imidazole rings, suggesting no π–π stacking between imidazole rings in the crystal structure of (I).

Experimental

An ethanol solution (5 ml) of imidazole (2 mmol) was mixed with an aqueous solution (5 ml) of $NiCl_2\cdot6H_2O$ (1 mmol) and an aqueous solution (5 ml) containing DL-malic acid (1 mmol) and Na_2CO_3 (1 mmol). The solution was refluxed for 1 h and filtered. Blue single crystals of (I) were obtained after 20 d.

Crystal data

$[Ni(C_4H_4O_5)(C_3H_4N_2)_3]$
$M_r = 395.03$
Monoclinic, $P2_1/c$
$a = 8.4419$ (4) Å
$b = 8.5266$ (2) Å
$c = 22.3912$ (4) Å
$\beta = 90.5840$ (11)°
$V = 1611.65$ (9) Å^3
$Z = 4$

$D_x = 1.628$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7674 reflections
$\theta = 2.5$–25.0°
$\mu = 1.24$ mm^{-1}
$T = 295$ (2) K
Prism, blue
0.32 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.692$, $T_{max} = 0.805$
12885 measured reflections

3525 independent reflections
3115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -29 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.089$
$S = 1.06$
3525 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.2519P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ni—O1	2.0766 (16)	Ni—N13	2.0766 (19)
Ni—O3	2.1193 (15)	Ni—N23	2.0700 (19)
Ni—O5	2.0782 (16)	Ni—N33	2.0540 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O4^{i}	0.87	1.74	2.586 (3)	163
N11—H11···O1^{ii}	0.86	1.92	2.764 (2)	168
N21—H21···O2^{iii}	0.86	1.99	2.836 (3)	165
N31—H31···O3^{iv}	0.86	2.12	2.899 (3)	150
N31—H31···O4^{iv}	0.86	2.28	3.049 (3)	149

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

The hydroxy H atom was located in a difference Fourier map and refined as riding in its as-found position relative to atom O5, with a fixed isotropic displacement parameter of 0.05 Å^2. Other H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å and N—H = 0.86 Å, and included in the final cycles of refinement in a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier).

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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