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Crystal structure of bis(2-hydroxy-2,2-bis(pyridin-2-yl)acetato)nickel(II) methanol solvate, $Ni[(C_5H_4N)_2C(OH)COO]_2 \cdot CH_3OH$

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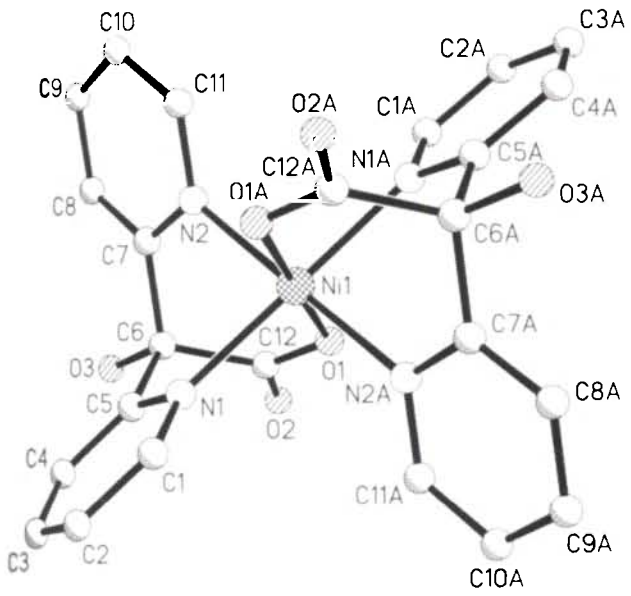

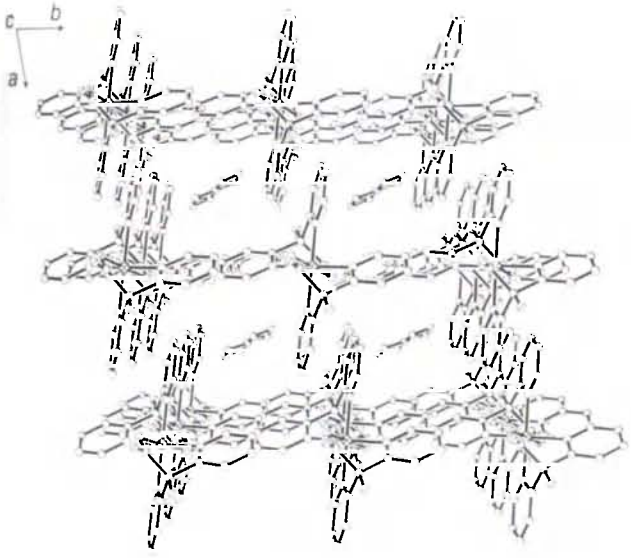

Abstract

$C_{25}H_{22}N_4Ni_1O_7$, triclinic, $P\bar{1}$ (no. 2), a = 8.462(2) Å, b = 8.514(2) Å, c = 10.467(2) Å, α = 79.823(4)°, β = 74.813(4)°, γ = 76.791(4)°, V = 703.1 Å^3, Z = 1, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.144, T = 296 K.

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Source of material

The title complex was synthesized by mixed solution method. A solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.106 g, 0.5 mmol) in 10 ml methanol was added to a solution of α-pyridoin (0.115 g, 0.5 mmol) in 10 ml of methanol. The reaction mixture was stirred for 2 h at room temperature and then filtered. The filtrate was kept to diffuse in ether. After two weeks, blue block crystals were obtained.

Elemental analysis: found – C, 54.63 %; H, 3.99 %; N, 10.17 %; calc. for $C_{25}H_{22}N_4Ni_1O_7$ – C, 54.68 %; H, 4.04 %; N, 10.20 %.

Experimental details

The methanol H atoms could neither be located from Fourier difference maps nor added geometrically due to the strong disorder of the solvent molecule over probably eight positions. The occupancy factors for C and O atoms are 0.25 or 0.50. The other H atoms were located from Fourier difference maps and refined using riding rigid body model.

Discussion

Coordination complexes of the first transition metal are known to provide the driving force for rearrangement by stabilizing the products, which is very important in multiple biological processes [1,2]. 2,2′-pyridoin molecules have been well-investigated by crystallography [3-5]. However, studying on α-pyridoin molecule, a ligand similar to 2,2′-pyridyl molecule, is still rare. Herein, we present the synthesis and crystal structure of the rearrangement product of α-pyridoin with $Ni(CH_3COO)_2 \cdot 4H_2O$.

The crystal structure of the title compound consists of neutral $Ni[(C_5H_4N)CCO_2(OH)(C_5H_4N)]_2$ entities and uncoordinated disordered methanol molecules, indicating a metal-promoted rearrangement of α-pyridoin to form 2-hydroxy-2,2-di(pyridin-2-yl) acetic acid. Each Ni(II) atom is six-coordinated and has a approximate octahedral environment (CuN_4O_2) with the Ni(II) atom at the center of symmetry (figure, top). Within the equatorial plane, the sum of the relative bond angles (∠N1–Ni–N2 = 85.4(1)° and ∠N2–Ni–N1^i = 94.6(1)°, symmetry code i: $-x,-y,2-z$) around Ni(II) atom is 360°. The apical ∠O1–Cu1–O1^i bond angle is 180°. The two independent Ni—N bond distances are nearly equivalent (2.064(3) Å and 2.073(3) Å) and slightly longer than the stronger Ni—O bond (2.046(2) A). The pyridine rings in the same ligand are in normal *cis*-position and the dihedral angle between them is 65.4°. Interestingly, through the intermolecular C–H···O bond (3.276 Å – 3.365 A) and π-π interactions between the pyridine rings with a distance of 3.465 Å, the adjacent mononuclear units are linked into an extended grid network parallel to the *a*,*b* plane. Moreover, the intermolecular O–H···O bond (2.879 Å) further connect the planes into 3D supramolecular architecture with channel (5.625 × 7.117 Å^2; figure, bottom).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.07 × 0.20 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.36 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3601, 2458
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2146
$N(param)_{refined}$:	195
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(3)	2*i*	0.1581	0.0176	0.5219	0.063
H(1)	2*i*	−0.1121	0.3697	0.9974	0.054
H(2)	2*i*	−0.0970	0.6031	0.8528	0.064
H(3A)	2*i*	0.0334	0.5859	0.6284	0.069
H(4)	2*i*	0.1394	0.3317	0.5580	0.059
H(8)	2*i*	0.4777	−0.0851	0.6064	0.057
H(9)	2*i*	0.6855	−0.1904	0.7239	0.071
H(10)	2*i*	0.6129	−0.2156	0.9557	0.067
H(11)	2*i*	0.3378	−0.1474	1.0628	0.054

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	1*a*		0	0	0	0.0276(3)	0.0338(4)	0.0245(3)	−0.0059(2)	−0.0042(2)	−0.0004(2)
N(1)	2*i*		0.0030(3)	0.2126(3)	0.8684(3)	0.037(1)	0.037(2)	0.032(2)	−0.006(1)	−0.009(1)	−0.003(1)
N(2)	2*i*		0.2467(3)	−0.0662(3)	0.9030(3)	0.028(1)	0.043(2)	0.030(1)	−0.008(1)	−0.008(1)	−0.002(1)
O(1)	2*i*		−0.0593(3)	−0.0984(3)	0.8580(2)	0.034(1)	0.042(1)	0.028(1)	−0.0132(9)	−0.0042(9)	−0.0010(9)
O(2)	2*i*		−0.0281(3)	−0.1103(3)	0.6407(2)	0.054(2)	0.053(2)	0.030(1)	−0.021(1)	−0.014(1)	−0.001(1)
O(3)	2*i*		0.2201(3)	0.0439(3)	0.5594(2)	0.043(1)	0.062(2)	0.022(1)	−0.019(1)	−0.0021(9)	−0.001(1)
C(1)	2*i*		−0.0605(5)	0.3624(4)	0.9079(4)	0.052(2)	0.037(2)	0.045(2)	−0.004(2)	−0.014(2)	−0.005(2)
C(2)	2*i*		−0.0520(5)	0.5025(5)	0.8223(4)	0.064(2)	0.032(2)	0.067(3)	−0.004(2)	−0.028(2)	−0.003(2)
C(3)	2*i*		0.0250(6)	0.4922(5)	0.6888(4)	0.080(3)	0.036(2)	0.056(3)	−0.016(2)	−0.025(2)	0.013(2)
C(4)	2*i*		0.0886(5)	0.3411(4)	0.6473(4)	0.063(2)	0.045(2)	0.039(2)	−0.018(2)	−0.014(2)	0.009(2)
C(5)	2*i*		0.0768(4)	0.2037(4)	0.7388(3)	0.037(2)	0.038(2)	0.029(2)	−0.012(1)	−0.010(1)	0.002(1)
C(6)	2*i*		0.1498(4)	0.0330(4)	0.6984(3)	0.031(2)	0.042(2)	0.022(2)	−0.010(1)	−0.004(1)	0.001(1)
C(7)	2*i*		0.2892(4)	−0.0482(4)	0.7692(3)	0.032(2)	0.040(2)	0.032(2)	−0.012(1)	−0.006(1)	−0.001(1)
C(8)	2*i*		0.4517(4)	−0.0957(5)	0.6991(4)	0.036(2)	0.063(2)	0.035(2)	−0.006(2)	0.002(1)	−0.002(2)
C(9)	2*i*		0.5752(5)	−0.1592(6)	0.7690(4)	0.029(2)	0.085(3)	0.052(2)	0.002(2)	−0.002(2)	−0.004(2)
C(10)	2*i*		0.5319(5)	−0.1755(6)	0.9067(4)	0.033(2)	0.078(3)	0.052(2)	0.004(2)	−0.017(2)	−0.005(2)
C(11)	2*i*		0.3673(4)	−0.1315(5)	0.9701(4)	0.038(2)	0.059(2)	0.034(2)	−0.004(2)	−0.011(2)	−0.002(2)
C(12)	2*i*		0.0076(4)	−0.0677(4)	0.7352(3)	0.032(2)	0.031(2)	0.029(2)	−0.004(1)	−0.007(1)	−0.001(1)
O(4)	1*b*	0.50	½	½	½	0.16(1)	0.077(9)	0.079(8)	−0.007(7)	−0.060(8)	0.021(6)
O(5)	2*i*	0.25	0.403(3)	0.671(2)	0.328(2)	0.25(3)	0.11(2)	0.12(1)	−0.09(2)	−0.15(2)	0.08(1)
C(13)	2*i*	0.25	0.452(3)	0.636(4)	0.425(3)	0.10(2)	0.07(2)	0.14(3)	−0.05(1)	−0.03(2)	−0.04(2)
C(14)	2*i*	0.25	0.451(3)	0.550(4)	0.398(4)	0.10(2)	0.06(2)	0.17(3)	−0.05(2)	−0.02(2)	−0.02(2)

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