Crystal structure of (pyridine-2-carboxamide-N,O)[*tris*-(2-aminoethyl) amine-*N*,*N*',*N*'',*N*''']nickel(II) diperchlorate-monohydrate, $[Ni(C_6H_{18}N_4)(C_6H_6ON_2)][ClO_4]_2 \cdot H_2O$, $C_{12}H_{26}Cl_2N_6NiO_{10}$

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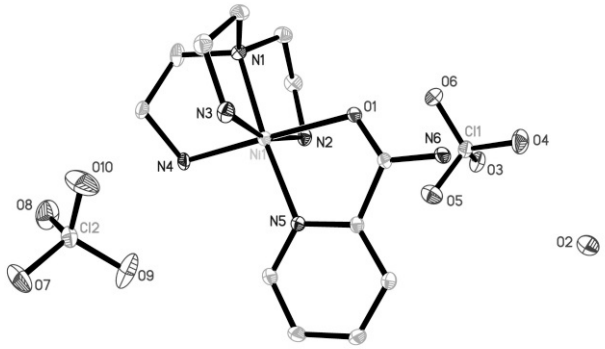

Abstract

$C_{12}H_{26}Cl_2N_6NiO_{10}$, orthorhombic, *Pbca* (no. 61), a = 12.295(3) Å, b = 11.377(2) Å, c = 30.245(6) Å, V = 4230.7 Å^3, Z = 8, $R_{gt}(F)$ = 0.0535, $wR_{ref}(F^2)$ = 0.1394, T = 153 K.

Table 1. Data collection and handling.

Crystal:	violet blocks, size 0.38×0.42×0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.33 cm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ and ω
$2\theta_{max}$:	58.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	33988, 5685
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5296
$N(param)_{refined}$:	316
Programs:	SHELXS-97, SHELXL-97, SHELXTL [6]

Source of material

To a stirred methanol solution (20 ml) containing nickel(II) perchlorate hexahydrate (0.183 g, 0.5 mmol) and *tris*-(2-aminoethyl) amine (0.073 g, 0.5 mmol), a methanol solution (20 ml) of pyridine-2-carboxamide (0.061 g, 0.5 mmol) was added dropwise. After stirring for 3 hours, the filtrate of the resulting solution was allowed to stand at room temperature for slow evaporation. Single crystals with violet colour are fromed.

Experimental details

Atoms C5, C6 and N4 are disordered with an occupancy ratio of 0.533(8) and 0.467(8).

Discussion

Tris-(2-aminoethyl)amine (tren) is a tetradentate tripodal ligand with three primary amino groups. Some transition metal complexes of it have been studied. They exhibite mononuclear [1], dinuclear [2,3], trinuclear [4] and 1-D structural features [5]. Pyridine-2-carboxamide (picolinamide) is a ligand that is similar to picolinate in its coordination mode. It can coordinate to transition metal ions via the N atom of the pyridine ring and the O atom of the formamide. Until now, nickel(II) complexes of tren using picolinamide as coligand have never been reported. In this study a nickel complex of tren containing picolinamide has been prepared and characterized.

The title complex was synthesized from the reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, tren and picolinamide. The nickel atom in the cation has a distorted octahedral environment, with tren acting in the expected quadridentate and the pyridine-2-carboxamide in a bidentate chelating mode.

The basal plane of the octahedron is defined by three primary nitrogen atoms N2, N3 and N4 of tren and O1 of picolinamide, the tertiary amine nitrogen atom N1 and the nitrogen atom N5 from pyridine occupying the apical positions. Of the three Ni–N (primary) distances, two in the basal plane are nearly equal [d(Ni1–N2) = 2.116(2) Å, d(Ni1–N3) = 2.119(3) Å], while the third is slightly shorter [d(Ni1–N4) = 2.104(3) Å] and lies *trans* to the O1 atom. The Ni1–N5 (pyridine) bond at 2.077(2) Å is the shortest and lies *trans* to the N1 atom. The Ni1–N1(tertiary) and Ni1–O1 distances are 2.082(2) Å and 2.168(2) Å respectively.

The distortions in the coordination octahedron are reflected in the N–Ni–N bite angles being all obtuse 83.27(18)° - 96.90(3)° and the O1–Ni–N5 bite angle being slightly acute [77.76(8)°]. The axial bond angle N1–Ni1–N5 is 174.81(9)°. Other significant distortions can be observed in the angles N2–Ni1–N3 [163.93(10)°] and N4–Ni1–O1 [176.6(3)°]. The bond distances and angles associated with the tren and pia are as expected.

Two perchlorate anions and the water molecule, link [Ni(tren)-(pia)]$^{2+}$ cations to form a 1-D chain. Each [Ni(tren)(pia)]$^{2+}$ cation is cross-linked through two perchlorate anions and one water by N–H–O intermolecular hydrogen bonds through the two nitrogen atoms N3, N4 of tren and N6 of picolinamide. The hydrogen bonds are 2.956(2) Å [N6–H6–O3 = 158.91(2)°] for N6–O3, 3.208(1) Å [N4–H4–O7 = 148.10(2) °] for N4–O7 and 3.035(4) Å [N3–H3–O2 = 166.25(2)°] for N3–O2. While each water molecular associates with two perchlorate anions by O–H–O intermolecular hydrogen bond. [d(O2–O4) = 2.907(7) Å, O2–H2–O4 = 163.22(2) °; d(O2–O6) = 2.980(5) Å, O2–H2–O6 = 151.86(9) °].

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2E)	8*c*		0.2903	0.9009	0.5281	0.058
H(2F)	8*c*		0.2603	0.7929	0.5487	0.058
H(2A)	8*c*		0.3109	0.5349	0.3931	0.027
H(2B)	8*c*		0.3045	0.5466	0.3440	0.027
H(3A)	8*c*		0.7132	0.5299	0.3478	0.032
H(3B)	8*c*		0.7004	0.5254	0.3968	0.032
H(1A)	8*c*		0.4056	0.3109	0.4123	0.033
H(1B)	8*c*		0.3843	0.2194	0.3729	0.033
H(2C)	8*c*		0.2892	0.3593	0.3320	0.035
H(2D)	8*c*		0.2394	0.3635	0.3810	0.035
H(3C)	8*c*		0.6087	0.2122	0.3781	0.032
H(3D)	8*c*		0.5849	0.3078	0.4158	0.032
H(4A)	8*c*		0.7600	0.3472	0.3903	0.034
H(4B)	8*c*		0.7217	0.3412	0.3397	0.034
H(5A)	8*c*	0.533	0.4357	0.2827	0.2994	0.036
H(5B)	8*c*	0.533	0.5554	0.2321	0.3077	0.036

Table 2. continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(6A)	8*c*	0.533	0.6362	0.4063	0.2857	0.031
H(6B)	8*c*	0.533	0.5428	0.3831	0.2496	0.031
H(4C)	8*c*	0.533	0.4314	0.5142	0.2843	0.028
H(4D)	8*c*	0.533	0.5383	0.5763	0.2821	0.028
H(5'1)	8*c*	0.467	0.4560	0.2353	0.3089	0.029
H(5'2)	8*c*	0.467	0.5785	0.2811	0.3047	0.029
H(6'1)	8*c*	0.467	0.4849	0.3805	0.2504	0.036
H(6'2)	8*c*	0.467	0.3864	0.4118	0.2832	0.036
H(4'1)	8*c*	0.467	0.4912	0.5767	0.2812	0.023
H(4'2)	8*c*	0.467	0.5953	0.5100	0.2864	0.023
H(7)	8*c*		0.5150	0.7611	0.3135	0.030
H(8)	8*c*		0.5094	0.9606	0.3303	0.032
H(9)	8*c*		0.4975	1.0187	0.4045	0.032
H(10)	8*c*		0.4946	0.8737	0.4601	0.028
H(0A)	8*c*		0.517(3)	0.597(4)	0.509(1)	0.03(1)
H(0B)	8*c*		0.522(3)	0.730(4)	0.502(1)	0.04(1)

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)	8*c*		0.50710(3)	0.52148(3)	0.36361(1)	0.0213(2)	0.0175(2)	0.0141(2)	–0.0001(1)	0.0010(1)	–0.0013(1)
O(1)	8*c*		0.5018(1)	0.5315(2)	0.43516(6)	0.026(1)	0.0178(9)	0.0150(8)	–0.0005(7)	–0.0017(6)	–0.0001(7)
O(2)	8*c*		0.2686(2)	0.8676(2)	0.55231(8)	0.072(2)	0.039(1)	0.035(1)	0.008(1)	–0.004(1)	0.008(1)
N(1)	8*c*		0.5021(2)	0.3390(2)	0.35867(8)	0.021(1)	0.019(1)	0.022(1)	0.0004(8)	–0.0002(8)	–0.0015(8)
N(2)	8*c*		0.3359(2)	0.5048(2)	0.36672(7)	0.022(1)	0.029(1)	0.018(1)	0.0044(9)	–0.0012(8)	–0.0019(9)
N(3)	8*c*		0.6767(2)	0.4936(2)	0.37055(8)	0.021(1)	0.030(1)	0.029(1)	–0.004(1)	0.0029(9)	–0.005(1)
N(5)	8*c*		0.5109(2)	0.7016(2)	0.37469(7)	0.022(1)	0.018(1)	0.017(1)	–0.0009(8)	0.0009(8)	–0.0010(8)
N(6)	8*c*		0.5155(2)	0.6582(2)	0.49244(8)	0.039(1)	0.020(1)	0.015(1)	–0.003(1)	–0.0029(9)	0.0001(9)
C(1)	8*c*		0.3992(2)	0.3029(3)	0.3798(1)	0.026(1)	0.025(1)	0.031(1)	–0.005(1)	0.001(1)	0.003(1)
C(2)	8*c*		0.3054(2)	0.3790(3)	0.3632(1)	0.023(1)	0.033(2)	0.032(2)	–0.004(1)	–0.001(1)	0.001(1)
C(3)	8*c*		0.5977(2)	0.2970(3)	0.3837(1)	0.027(2)	0.026(1)	0.028(1)	0.006(1)	–0.002(1)	0.006(1)
C(4)	8*c*		0.6995(2)	0.3653(3)	0.3698(1)	0.023(1)	0.033(2)	0.028(1)	0.005(1)	–0.001(1)	0.000(1)
C(5)	8*c*	0.533	0.509(2)	0.3031(8)	0.3102(4)	0.030(7)	0.041(9)	0.018(6)	–0.006(5)	–0.001(5)	–0.015(5)
C(6)	8*c*	0.533	0.5566(5)	0.4004(5)	0.2812(2)	0.032(3)	0.027(3)	0.018(2)	0.006(2)	0.003(2)	–0.005(2)
N(4)	8*c*	0.533	0.5022(9)	0.5132(5)	0.29415(9)	0.021(4)	0.028(4)	0.020(4)	0.005(2)	0.008(2)	0.001(3)
C(5')	8*c*	0.467	0.504(2)	0.3048(7)	0.3128(4)	0.05(1)	0.008(6)	0.018(7)	0.004(5)	0.006(6)	–0.001(4)
C(6')	8*c*	0.467	0.4662(6)	0.4014(5)	0.2812(2)	0.049(5)	0.026(3)	0.016(3)	–0.006(3)	–0.001(3)	–0.007(2)
N(4')	8*c*	0.467	0.5231(9)	0.5126(6)	0.2944(1)	0.019(4)	0.023(4)	0.015(4)	–0.004(2)	–0.002(2)	–0.002(3)
C(7)	8*c*		0.5116(2)	0.7845(3)	0.34357(9)	0.033(2)	0.024(1)	0.017(1)	–0.000(1)	0.002(1)	0.000(1)
C(8)	8*c*		0.5076(2)	0.9037(3)	0.3533(1)	0.036(2)	0.022(1)	0.023(1)	0.000(1)	–0.001(1)	0.005(1)
C(9)	8*c*		0.5011(2)	0.9378(3)	0.3970(1)	0.037(2)	0.018(1)	0.025(1)	–0.000(1)	–0.001(1)	–0.003(1)
C(10)	8*c*		0.4997(2)	0.8522(3)	0.42980(9)	0.028(1)	0.023(1)	0.018(1)	–0.000(1)	–0.0002(9)	–0.003(1)
C(11)	8*c*		0.5061(2)	0.7352(2)	0.41754(8)	0.018(1)	0.021(1)	0.015(1)	0.0002(9)	–0.0010(8)	–0.0005(9)
C(12)	8*c*		0.5078(2)	0.6344(2)	0.44962(8)	0.019(1)	0.021(1)	0.015(1)	–0.0009(9)	–0.0004(8)	0.0003(9)
Cl(1)	8*c*		0.21114(6)	0.60580(6)	0.47517(2)	0.0313(4)	0.0280(3)	0.0228(3)	0.0046(3)	0.0034(3)	–0.0021(2)
Cl(2)	8*c*		0.75452(6)	0.64179(7)	0.24790(2)	0.0278(4)	0.0353(4)	0.0261(3)	0.0002(3)	0.0069(3)	0.0001(3)
O(3)	8*c*		0.0955(2)	0.6192(2)	0.46904(7)	0.030(1)	0.038(1)	0.033(1)	0.0021(9)	0.0036(9)	–0.0104(9)
O(4)	8*c*		0.2376(2)	0.6284(2)	0.52088(8)	0.050(2)	0.054(2)	0.025(1)	0.006(1)	–0.007(1)	–0.010(1)
O(5)	8*c*		0.2679(2)	0.6849(2)	0.44663(8)	0.033(1)	0.038(1)	0.040(1)	–0.001(1)	0.002(1)	0.010(1)
O(6)	8*c*		0.2412(2)	0.4866(2)	0.46461(8)	0.061(2)	0.029(1)	0.038(1)	0.014(1)	0.012(1)	–0.001(1)
O(7)	8*c*		0.8369(2)	0.7036(3)	0.2245(1)	0.050(2)	0.064(2)	0.052(2)	–0.015(1)	0.019(1)	0.017(1)
O(8)	8*c*		0.6913(3)	0.5745(3)	0.21715(9)	0.061(2)	0.061(2)	0.043(2)	–0.012(2)	0.002(1)	–0.021(1)
O(9)	8*c*		0.6849(2)	0.7216(3)	0.2701(1)	0.050(2)	0.076(2)	0.067(2)	0.011(2)	0.010(2)	–0.041(2)
O(10)	8*c*		0.8043(3)	0.5660(3)	0.2794(1)	0.065(2)	0.065(2)	0.067(2)	0.001(2)	–0.008(2)	0.035(2)

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