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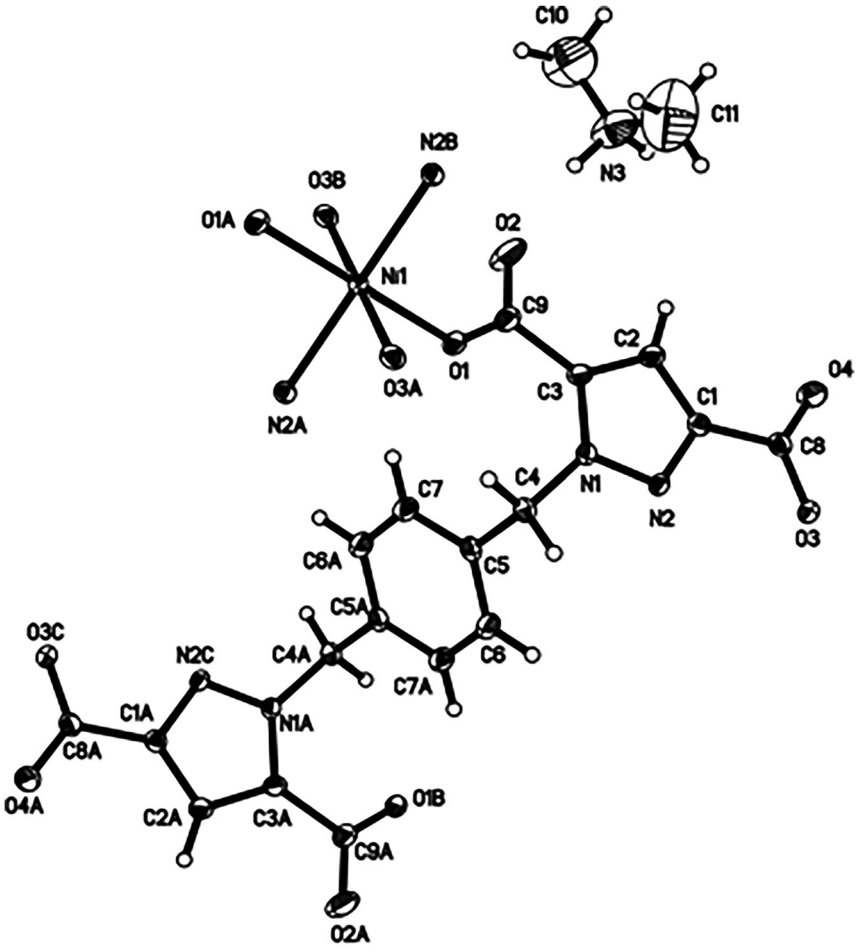
Crystal structure of bis(dimethylammonium) poly[(μ_4-1,1′-(1,4-phenylenebis(methylene)) bis(1H-pyrazole-3,5-dicarboxylato))-κ^6O^1, N^2:O^2:O^3:$O^{1'}$,$N^{2'}$]nickel (II)], $C_{22}H_{26}N_6NiO_8$



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Abstract

$C_{22}H_{26}N_6NiO_8$, monoclinic, $P2_1/n$ (no. 14), a = 10.9372(7) Å, b = 10.4567(6) Å, c = 11.7618(7) Å, β = 116.5552(19)°, V = 1203.25(13) Å^3, Z = 2, $R_{gt}(F)$ = 0.0406, $wR_{ref}(F^2)$ = 0.1089, T = 297(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

All chemicals were of analytical reagent grade and used without further purification. A mixture of $Ni(NO_3)_2{\cdot}6H_2O$ (47.4 mg), 1,1′-(1,4-phenylenebis(methylene))bis-(1*H*-pyrazole-3,5-dicarboxylic acid) (20.7 mg) and acetonitrile/DMF/water

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.15 × 0.10 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.87 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8833, 2113, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 1744
$N(param)_{refined}$:	172
Programs:	Bruker [1], SHELX [2–4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.0000	0.0177 (2)
O1	0.5908 (2)	0.3932 (2)	0.1646 (2)	0.0281 (5)
O2	0.4348 (3)	0.3483 (3)	0.2317 (3)	0.0672 (11)
O3	0.8762 (2)	−0.0936 (2)	0.5639 (2)	0.0250 (5)
O4	0.6731 (3)	−0.0846 (3)	0.5641 (3)	0.0454 (7)
N1	0.7751 (3)	0.2178 (2)	0.3484 (2)	0.0217 (6)
N2	0.8274 (3)	0.1169 (2)	0.4248 (2)	0.0205 (6)
C1	0.7262 (3)	0.0684 (3)	0.4468 (3)	0.0231 (7)
C2	0.6078 (3)	0.1396 (3)	0.3832 (3)	0.0288 (8)
H2	0.5235	0.1256	0.3826	0.035*
C3	0.6406 (3)	0.2353 (3)	0.3212 (3)	0.0257 (7)
C4	0.8675 (3)	0.2956 (3)	0.3171 (3)	0.0251 (7)
H4A	0.8163	0.3326	0.2333	0.030*
H4B	0.9377	0.2409	0.3142	0.030*
C5	0.9352 (3)	0.4021 (3)	0.4119 (3)	0.0260 (7)
C6	1.0686 (4)	0.3876 (3)	0.5069 (4)	0.0360 (9)
H6	1.1156	0.3121	0.5119	0.043*
C7	0.8682 (4)	0.5159 (3)	0.4063 (3)	0.0352 (9)
H7	0.7793	0.5276	0.3432	0.042*
C8	0.7603 (3)	−0.0458 (3)	0.5310 (3)	0.0257 (7)
C9	0.5479 (4)	0.3355 (3)	0.2314 (3)	0.0318 (8)
C10	0.0973 (8)	0.2709 (9)	0.1756 (8)	0.123 (3)
H10A	0.0849	0.3310	0.1096	0.184*
H10B	0.1088	0.3163	0.2507	0.184*
H10C	0.0186	0.2164	0.1480	0.184*
N3	0.2193 (5)	0.1928 (5)	0.2041 (5)	0.0853 (17)
H3A	0.2520	0.1588	0.2845	0.128*
H3B	0.2827	0.2498	0.2028	0.128*
C11	0.2124 (12)	0.0857 (9)	0.1203 (8)	0.157 (4)
H11A	0.1378	0.0305	0.1095	0.236*
H11B	0.2964	0.0384	0.1577	0.236*
H11C	0.1983	0.1183	0.0391	0.236*

(10 mL, 3/3/4, *v*/*v*/*v*) was placed in a 15 mL of Teflon-lined stainless steel autoclave. The mixture was heated under autogenous pressure at 433 K for 72 h and then cooled to room temperature. Green block crystals were collected by filtration, washed with H_2O, and dried in air with 72 % yield.

2 Experimental details

The Multi-scan program SADABS [1] was used for absorption correction. The structures were solved by Direct Methods and refined using the SHELXS-97 [2,3] and SHELXL-2014/7, respectively [4]. Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C–H = 0.96 Å and U_{iso} (H) = 1.2 U_{eq} (C).

3 Comment

Polycarboxylate based pyrazoles have great benefits for the formation 2*D* or 3*D* metal–organic frameworks [5,6]. Among them, flexible multicarboxylate ligands have remarkable advantages because their conformational freedom and flexibility can be fine-tuned by themselves to match with the coordination preference of metal ions and lower the energetic arrangement in the self-assembly process. Many tetracarboxylate ligands have been utilized to create coordination polymers [7,8]. We recently studied the self-assembly reaction of 1,1′-(1,4-phenylenebis(methylene)) bis(1H-pyrazole-3,5-dicarboxylate).

The asymmetric unit of the title complex **1**, consists of a half Ni^{2+} ion, a half of a fully deprotonated 1,1′-(1,4-phenylenebis(methylene))bis-(1H-pyrazole-3,5-dicarboxylate) anion, one noncoordinated dimethylammonium cation by hydrolysis of DMF. As can be deduced from the charge balance, the framework is anionic having a (−2) charge, and the electroneutrality is achieved by the incorporation of the protonated amine in the voids of the net. In **1**, the Ni (II) ion is surrounded by four oxygen atoms from four 1,1′-(1,4-phenylenebis(methylene))bis-(1H-pyrazole-3,5-dicarboxylate) ligands and two nitrogen atoms of two ligands to present an octahedral geometry with separate *cis* and *trans* angles at the metal being 79.39(8)°–180.0°. The Ni–O and Ni–N bond lengths are in the range of 2.064(2)–2.0648(2) Å and 2.085(2) Å, respectively. These values are within the normal ranges [9,10] and close to those reported in other Ni(II) complexes [11]. In the polymer **1**, two carboxyl groups of pyrazole are fully deprotonated, each ligand bridges two Ni (II) ions through chelating N, O atoms of the pyrazole ring and monodentate O atom of the same pyrazole ring, forming ⋯Ni–L–Ni–L⋯ chains parallel to the crystallographic *b* direction. The Ni⋯Ni distance separated by a μ-pyrazole-carboxylate bridge is 7.942(1) Å. The dihedral angle between the planes of

the benzene ring and pyrazole rings is 71.07(3)°. The one-dimensional chains intersect to form an infinite two-dimensional network which contain nearly square $[Ni_4(L)_4]$ units. For each unit, four 1,1′-(1,4-phenylenebis(methylene)) bis-(1H-pyrazole-3,5-dicarboxylate anions act as the four edges, and four Ni (II) ions represent the four vertices. The lengths of the diagonals are 10.457 Å and 11.956 Å, and the interior angles are 82.68° and 97.32°. The ligand 1,1′-(1,4-phenylenebis(methylene))bis(1H-pyrazole-3,5-dicarboxylate)) is the same as the Cd compound $\{[Cd_2L(H_2O)_2]\cdot DMF\cdot H_2O\}_n$ [12], however, it exhibits different coordination mode.

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