Crystal structure of tris(1,10-phenanthroline-5,6-dione)nickel(II) diperchlorate, $[Ni(C_{12}H_6N_2O_2)_3][ClO_4]_2$

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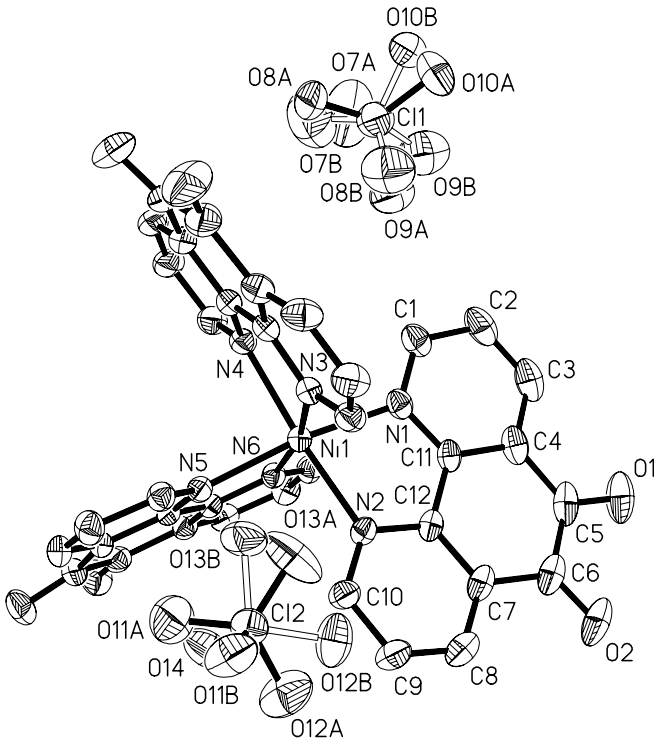

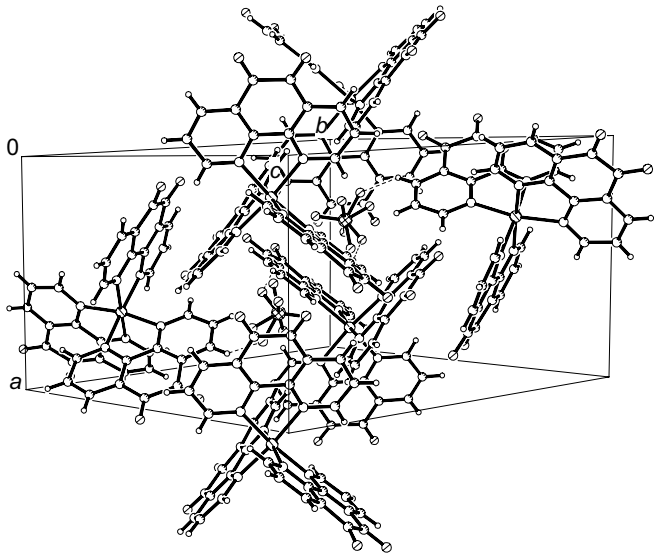

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Abstract

$C_{36}H_{18}Cl_2N_6NiO_{14}$, monoclinic, $P12_1/n1$ (no. 14), a = 10.5035(9) Å, b = 17.892(2) Å, c = 18.737(2) Å, β = 93.383(1)°, V = 3515.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.168, T = 273 K.

Source of material

The ligand 1,10-phenanthroline-5,6-dione was synthesized by the procedure described previously [1]. A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.266 g, 1.0 mmol), 1,10-phenanthroline-5,6-dione (0.224 g, 1 mmol), H_2O (15 ml) was sealed in a 25 mL Teflon-lined bomb at 160 °C for 7 days then slowly cooled to room temperature. Orange block-like crystals were collected by filtration, washed by distilled water, and air-dried in a yield of 25 % based on the initial $Ni(ClO_4)_2 \cdot 6H_2O$ input.

Discussion

The title structure consists of $[Ni(C_{12}H_6N_2O_2)_3]^{2+}$ complex cations and perchlorate anions. The Ni atoms are coordinated pseudo-octahedrally by six nitrogen atoms of three 1,10-phenanthroline-5,6-dione ligands with the axial apical positions occupied by N2 atom and N4 atom (figure, top). The other four aromatic pyridyl N atoms reside at the equatorial plane sites. The average Ni—N length is 2.091 Å, being shorter than those in the cationic complex $[Ni(phen)_3]^{2+}$ in [2]. The *cis* bond angles at the central Ni atom from the apical N2 atom and N4 atom fall in the range from 78.6(1)° to 98.2(1)°, and the *trans* bond angle ∠N2–Ni–N4 is 173.6(1)°, suggesting a significant deviation from the value for a perfect octahedral coordination.

Hydrogen bonding and π-π stacking interactions play important roles in the supramolecular assembly and contribute to stabilize the network. The 1,10-phenanthroline-5,6-dione donor hydrogen atoms to the perchlorate anion oxygen atoms O9A, O10A, O11A, O13A and O14 to form weak intermolecular hydrogen bonding interactions (figure, bottom). The title complex molecules are stabilized by π—π stacking interactions between the 1,10-phenanthroline-5,6-dione ligands of neighboring molecules with the mean interplanar distances of 3.698 Å.

Table 1. Data collection and handling.

Crystal:	orange block, size 0.177 × 0.245 × 0.256 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.88 cm^{-1}
Diffractometer, scan mode:	Bruker SMART Apex II CCD, ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	29755, 8656
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4944
$N(param)_{refined}$:	596
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.5137	0.0976	0.0209	0.074
H(2A)	4*e*	0.5122	0.0353	–0.0874	0.093
H(3A)	4*e*	0.6745	0.0594	–0.1639	0.095
H(8B)	4*e*	1.0579	0.3489	–0.0747	0.081
H(9B)	4*e*	1.0220	0.4062	0.0326	0.079
H(10B)	4*e*	0.8824	0.3528	0.1080	0.065
H(13A)	4*e*	0.6135	0.0709	0.1939	0.066
H(14B)	4*e*	0.4501	0.0343	0.2626	0.074
H(15A)	4*e*	0.2731	0.1101	0.2676	0.075
H(20A)	4*e*	0.2691	0.4230	0.0678	0.077
H(21A)	4*e*	0.4442	0.4416	0.0013	0.076
H(22A)	4*e*	0.6154	0.3609	0.0156	0.059
H(25A)	4*e*	0.6522	0.3596	0.2006	0.055
H(26A)	4*e*	0.7164	0.4007	0.3127	0.067
H(27A)	4*e*	0.8545	0.3282	0.3842	0.064
H(32A)	4*e*	1.0507	0.0070	0.2408	0.065
H(33A)	4*e*	0.9722	–0.0186	0.1252	0.066
H(34A)	4*e*	0.8307	0.0633	0.0691	0.058

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)	4*e*		0.68915(4)	0.21590(3)	0.10528(2)	0.0416(3)	0.0431(3)	0.0344(3)	–0.0017(2)	0.0026(2)	–0.0001(2)
Cl(1)	4*e*		0.1764(1)	0.1249(1)	0.02175(8)	0.0703(9)	0.125(1)	0.0772(9)	–0.0057(9)	–0.0035(7)	0.0292(9)
Cl(2)	4*e*		0.7750(1)	0.52093(6)	0.12995(6)	0.0708(8)	0.0484(6)	0.0680(7)	–0.0003(5)	0.0046(6)	–0.0024(5)
O(1)	4*e*		0.8751(4)	0.1268(2)	–0.2077(2)	0.143(3)	0.099(3)	0.049(2)	0.049(3)	0.015(2)	–0.014(2)
O(2)	4*e*		1.0177(4)	0.2499(2)	–0.1759(2)	0.109(3)	0.112(3)	0.061(2)	0.036(2)	0.044(2)	0.021(2)
O(3)	4*e*		0.1460(3)	0.2355(2)	0.2491(2)	0.067(2)	0.112(3)	0.107(3)	–0.008(2)	0.042(2)	0.004(2)
O(4)	4*e*		0.1369(3)	0.3575(3)	0.1649(2)	0.065(2)	0.143(4)	0.120(3)	0.046(3)	0.025(2)	0.029(3)
O(5)	4*e*		1.0233(3)	0.2243(2)	0.4076(2)	0.084(2)	0.079(2)	0.051(2)	–0.006(2)	–0.021(2)	–0.003(2)
O(6)	4*e*		1.0864(3)	0.0870(2)	0.3562(2)	0.071(2)	0.087(2)	0.064(2)	0.020(2)	–0.013(2)	0.012(2)
O(7A)	4*e*	0.608(7)	0.200(1)	0.0564(5)	0.0531(6)	0.231(9)	0.131(7)	0.149(7)	0.104(6)	0.022(7)	0.049(6)
O(8A)	4*e*	0.608	0.1167(5)	0.1726(3)	0.0778(3)	0.080(4)	0.100(4)	0.064(3)	0.005(3)	0.017(3)	–0.012(3)
O(9A)	4*e*	0.608	0.2905(8)	0.1628(6)	0.0089(5)	0.097(6)	0.216(9)	0.122(6)	–0.044(6)	0.032(5)	–0.037(6)
O(10A)	4*e*	0.608	0.0956(8)	0.1241(5)	–0.0398(4)	0.102(6)	0.103(6)	0.076(5)	0.019(5)	–0.025(4)	–0.017(4)
O(7B)	4*e*	0.392	0.191(2)	0.0930(9)	0.0869(6)	0.22(1)	0.19(1)	0.13(1)	–0.018(9)	–0.028(8)	0.018(9)
O(8B)	4*e*	0.392	0.229(1)	0.1939(5)	0.0083(8)	0.130(9)	0.097(7)	0.16(1)	–0.006(7)	0.011(8)	–0.015(7)
O(9B)	4*e*	0.392	0.264(1)	0.0759(6)	–0.0198(6)	0.115(8)	0.123(8)	0.160(9)	0.004(7)	0.007(7)	0.035(7)
O(10B)	4*e*	0.392	0.0593(9)	0.1108(9)	–0.0141(6)	0.072(6)	0.116(8)	0.079(7)	–0.007(6)	–0.001(5)	–0.013(6)
O(11A)	4*e*	0.608	0.7869(9)	0.4962(5)	0.2024(3)	0.133(6)	0.102(5)	0.087(5)	–0.013(5)	0.002(4)	0.026(4)
O(12A)	4*e*	0.608	0.9012(7)	0.5155(4)	0.1048(5)	0.102(5)	0.090(5)	0.150(6)	0.014(4)	0.062(5)	–0.018(4)
O(13A)	4*e*	0.608	0.6894(9)	0.4786(5)	0.0909(5)	0.142(7)	0.091(5)	0.156(7)	–0.006(5)	–0.072(6)	–0.037(5)
O(11B)	4*e*	0.392	0.855(1)	0.4800(6)	0.1769(6)	0.083(7)	0.084(6)	0.101(7)	–0.002(5)	–0.033(6)	0.002(6)
O(12B)	4*e*	0.392	0.808(1)	0.5099(6)	0.0578(4)	0.122(8)	0.087(6)	0.069(6)	0.031(6)	0.028(5)	–0.009(5)
O(13B)	4*e*	0.392	0.6499(8)	0.4871(6)	0.1310(6)	0.080(6)	0.058(5)	0.106(7)	–0.022(5)	0.005(5)	–0.013(5)
O(14)	4*e*		0.7502(4)	0.5980(2)	0.1364(2)	0.097(3)	0.049(2)	0.134(3)	–0.000(2)	0.046(2)	–0.010(2)
N(1)	4*e*		0.6634(3)	0.1603(2)	0.0080(2)	0.057(2)	0.045(2)	0.041(2)	0.001(2)	–0.006(2)	0.004(1)
N(2)	4*e*		0.8221(3)	0.2709(2)	0.0455(2)	0.045(2)	0.049(2)	0.040(2)	0.001(2)	0.009(1)	–0.001(1)
N(3)	4*e*		0.5412(3)	0.2915(2)	0.0828(2)	0.043(2)	0.049(2)	0.036(2)	–0.004(1)	–0.000(1)	–0.001(1)
N(4)	4*e*		0.5390(3)	0.1655(2)	0.1578(2)	0.041(2)	0.053(2)	0.042(2)	–0.005(2)	–0.003(1)	0.005(1)
N(5)	4*e*		0.7481(3)	0.2653(2)	0.2021(2)	0.039(2)	0.042(2)	0.038(2)	0.000(1)	0.005(1)	0.001(1)
N(6)	4*e*		0.8247(3)	0.1376(2)	0.1453(2)	0.043(2)	0.041(2)	0.038(2)	–0.001(1)	0.007(1)	–0.004(1)
C(1)	4*e*		0.5763(5)	0.1086(2)	–0.0106(2)	0.074(3)	0.054(3)	0.054(3)	–0.006(2)	–0.013(2)	0.004(2)
C(2)	4*e*		0.5752(6)	0.0704(3)	–0.0753(3)	0.107(4)	0.055(3)	0.067(3)	–0.006(3)	–0.025(3)	–0.012(2)
C(3)	4*e*		0.6705(6)	0.0859(3)	–0.1214(3)	0.115(5)	0.068(3)	0.052(3)	0.016(3)	–0.012(3)	–0.014(2)
C(4)	4*e*		0.7591(5)	0.1407(2)	–0.1040(2)	0.086(3)	0.047(2)	0.044(2)	0.020(2)	–0.005(2)	–0.006(2)
C(5)	4*e*		0.8601(5)	0.1605(3)	–0.1520(2)	0.097(4)	0.072(3)	0.039(2)	0.040(3)	0.006(2)	0.003(2)
C(6)	4*e*		0.9429(5)	0.2285(3)	–0.1339(2)	0.078(3)	0.070(3)	0.048(2)	0.031(3)	0.021(2)	0.015(2)
C(7)	4*e*		0.9269(4)	0.2666(2)	–0.0648(2)	0.064(3)	0.059(3)	0.046(2)	0.018(2)	0.019(2)	0.009(2)
C(8)	4*e*		0.9981(4)	0.3297(3)	–0.0449(3)	0.064(3)	0.072(3)	0.069(3)	0.003(3)	0.024(2)	0.015(2)
C(9)	4*e*		0.9782(4)	0.3628(3)	0.0190(3)	0.060(3)	0.065(3)	0.075(3)	–0.011(2)	0.020(2)	0.004(2)
C(10)	4*e*		0.8920(4)	0.3311(2)	0.0635(2)	0.050(2)	0.055(3)	0.059(3)	–0.005(2)	0.012(2)	–0.003(2)
C(11)	4*e*		0.7515(4)	0.1774(2)	–0.0387(2)	0.061(2)	0.044(2)	0.035(2)	0.009(2)	–0.001(2)	0.003(2)
C(12)	4*e*		0.8376(4)	0.2395(2)	–0.0186(2)	0.051(2)	0.047(2)	0.036(2)	0.012(2)	0.008(2)	0.005(2)
C(13)	4*e*		0.5422(4)	0.1015(2)	0.1958(2)	0.054(2)	0.058(3)	0.053(2)	–0.006(2)	–0.004(2)	0.012(2)
C(14)	4*e*		0.4447(4)	0.0790(3)	0.2372(2)	0.058(3)	0.070(3)	0.058(3)	–0.012(2)	0.003(2)	0.020(2)
C(15)	4*e*		0.3401(4)	0.1241(3)	0.2401(2)	0.053(3)	0.081(3)	0.053(2)	–0.022(2)	0.007(2)	0.012(2)
C(16)	4*e*		0.3335(4)	0.1906(3)	0.2020(2)	0.045(2)	0.073(3)	0.044(2)	–0.010(2)	0.002(2)	–0.001(2)
C(17)	4*e*		0.2267(4)	0.2431(3)	0.2064(2)	0.042(2)	0.086(3)	0.059(3)	–0.010(2)	0.011(2)	–0.005(2)
C(18)	4*e*		0.2231(4)	0.3140(3)	0.1610(3)	0.046(3)	0.091(4)	0.067(3)	0.010(3)	0.000(2)	0.005(3)
C(19)	4*e*		0.3335(4)	0.3276(3)	0.1162(2)	0.044(2)	0.066(3)	0.057(3)	0.001(2)	–0.005(2)	0.000(2)
C(20)	4*e*		0.3372(4)	0.3897(3)	0.0713(3)	0.045(2)	0.063(3)	0.083(3)	0.006(2)	–0.006(2)	0.008(2)
C(21)	4*e*		0.4413(4)	0.4013(3)	0.0325(2)	0.061(3)	0.056(3)	0.071(3)	–0.004(2)	–0.009(2)	0.017(2)
C(22)	4*e*		0.5431(4)	0.3518(2)	0.0405(2)	0.049(2)	0.050(2)	0.048(2)	–0.005(2)	–0.003(2)	0.005(2)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(23)	4*e*		0.4358(4)	0.2786(2)	0.1188(2)	0.040(2)	0.055(2)	0.038(2)	–0.003(2)	–0.006(2)	–0.001(2)
C(24)	4*e*		0.4358(4)	0.2097(2)	0.1609(2)	0.040(2)	0.063(3)	0.037(2)	–0.006(2)	–0.002(2)	–0.001(2)
C(25)	4*e*		0.7082(4)	0.3303(2)	0.2289(2)	0.047(2)	0.044(2)	0.046(2)	0.002(2)	0.007(2)	–0.003(2)
C(26)	4*e*		0.7463(4)	0.3554(2)	0.2960(2)	0.065(3)	0.049(2)	0.055(2)	0.005(2)	0.008(2)	–0.012(2)
C(27)	4*e*		0.8291(4)	0.3128(2)	0.3381(2)	0.058(3)	0.063(3)	0.039(2)	–0.004(2)	0.008(2)	–0.010(2)
C(28)	4*e*		0.8746(3)	0.2463(2)	0.3110(2)	0.043(2)	0.052(2)	0.035(2)	–0.007(2)	0.003(2)	0.000(2)
C(29)	4*e*		0.9707(4)	0.2015(2)	0.3523(2)	0.052(2)	0.062(3)	0.041(2)	–0.008(2)	–0.001(2)	0.001(2)
C(30)	4*e*		1.0114(4)	0.1261(2)	0.3219(2)	0.041(2)	0.063(3)	0.049(2)	0.000(2)	0.001(2)	0.011(2)
C(31)	4*e*		0.9591(4)	0.1056(2)	0.2493(2)	0.044(2)	0.048(2)	0.042(2)	–0.000(2)	0.005(2)	0.007(2)
C(32)	4*e*		0.9951(4)	0.0401(2)	0.2167(2)	0.050(2)	0.051(2)	0.061(3)	0.005(2)	0.006(2)	0.011(2)
C(33)	4*e*		0.9478(4)	0.0245(2)	0.1485(2)	0.063(3)	0.042(2)	0.060(3)	0.010(2)	0.010(2)	–0.002(2)
C(34)	4*e*		0.8630(4)	0.0744(2)	0.1152(2)	0.055(2)	0.047(2)	0.044(2)	–0.001(2)	0.007(2)	–0.003(2)
C(35)	4*e*		0.8740(3)	0.1536(2)	0.2118(2)	0.037(2)	0.044(2)	0.036(2)	–0.003(2)	0.006(2)	0.002(2)
C(36)	4*e*		0.8311(3)	0.2239(2)	0.2434(2)	0.036(2)	0.042(2)	0.035(2)	–0.006(2)	0.008(1)	–0.001(1)

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