Xin-Lun Li, Zhong-Ping Luo, Jun-Chao Zhang and Feng-Mei Nie*

Crystal structure of {tris((1*H*-benzo[*d*]imidazol-2-yl)methyl)amine- $\kappa^4 N, N', N'', N'''$ }- (nitrito- $\kappa^2 O, O'$)nickel(II) perchlorate – ethanol (1/1), $C_{26}H_{27}ClN_8NiO_7$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.23 × 0.21 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.85 mm ⁻¹
Diffractometer, scan mode:	XTALAB, φ and ω
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16933, 6358, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6056
$N(\text{param})_{\text{refined}}$:	389
Programs:	Olex2 [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.43233(3)	0.14083(2)	0.74578(2)	0.02002(9)
Cl1	0.25409(6)	−0.39307(5)	1.00241(5)	0.03244(14)
O1	0.50066(18)	0.00607(14)	0.65473(12)	0.0302(3)
O2	0.35826(18)	−0.04480(14)	0.81061(13)	0.0314(4)
O3	0.3721(3)	−0.3376(2)	0.91963(18)	0.0672(7)
O4	0.25618(19)	−0.37812(16)	1.10737(14)	0.0381(4)
O5	0.1256(3)	−0.3367(3)	0.9878(2)	0.1014(12)
O6	0.2615(3)	−0.5151(2)	0.9962(2)	0.0780(8)
O7	0.6033(2)	−0.32853(16)	0.67500(17)	0.0458(5)
H	0.5319	−0.2802	0.6894	0.055*
N2	0.24016(18)	0.19413(15)	0.72507(14)	0.0225(3)
N3	0.03104(18)	0.29489(16)	0.77405(14)	0.0237(4)
H3	−0.0382	0.3412	0.8096	0.028*
N1	0.36007(18)	0.27940(15)	0.85386(13)	0.0213(3)
N4	0.53141(19)	0.27803(16)	0.63908(14)	0.0232(4)
N5	0.5987(2)	0.46313(17)	0.60621(15)	0.0281(4)
H5	0.6075	0.5344	0.6175	0.034*
N7	0.62793(19)	0.12731(15)	0.97679(14)	0.0232(4)
H7	0.6215	0.1517	1.0370	0.028*
N6	0.57172(18)	0.10429(15)	0.83369(13)	0.0218(3)
N8	0.4357(2)	−0.07853(18)	0.72414(16)	0.0340(4)
C1	0.1619(2)	0.17750(18)	0.65931(16)	0.0220(4)
C2	0.1973(2)	0.1130(2)	0.57457(17)	0.0271(4)
H2	0.2877	0.0708	0.5520	0.032*
C3	0.0950(2)	0.1134(2)	0.52501(18)	0.0322(5)
H3A	0.1150	0.0692	0.4678	0.039*
C4	−0.0380(3)	0.1772(2)	0.55656(19)	0.0330(5)
H4	−0.1052	0.1753	0.5200	0.040*

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Abstract

$C_{26}H_{27}ClN_8NiO_7$, triclinic, $P\bar{1}$ (no. 2), $a = 9.893(2)$ Å, $b = 11.503(2)$ Å, $c = 13.295(3)$ Å, $\alpha = 78.77(3)^\circ$, $\beta = 70.52(3)^\circ$, $\gamma = 83.40(3)^\circ$, $V = 1397.0(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0423$, $wR_{\text{ref}}(F^2) = 0.1032$, $T = 153.15$ K.

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The cationic complex, which is the main part of the title salt is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tris(2-benzimidazolylmethyl)amine (*ntb*) was synthesized according to the literature method [3]. An ethanol (10 mL) solution of *ntb* (0.080 g, 0.20 mmol) was added into

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Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C5	−0.0733(2)	0.2426(2)	0.63934(18)	0.0295(5)
H5A	−0.1627	0.2865	0.6603	0.035*
C6	0.0290(2)	0.24072(19)	0.69031(17)	0.0238(4)
C7	0.1581(2)	0.26406(18)	0.79134(16)	0.0222(4)
C8	0.2024(2)	0.3019(2)	0.87704(17)	0.0254(4)
H8A	0.1767	0.3875	0.8785	0.030*
H8B	0.1512	0.2570	0.9488	0.030*
C9	0.4435(2)	0.38625(19)	0.79463(17)	0.0265(4)
H9A	0.3768	0.4575	0.7968	0.032*
H9B	0.5122	0.3968	0.8314	0.032*
C10	0.5238(2)	0.37549(19)	0.67955(17)	0.0242(4)
C11	0.6149(2)	0.3037(2)	0.53035(16)	0.0246(4)
C12	0.6528(2)	0.2349(2)	0.44874(18)	0.0286(5)
H12	0.6213	0.1568	0.4618	0.034*
C13	0.7386(2)	0.2860(2)	0.34737(18)	0.0345(5)
H13	0.7655	0.2422	0.2894	0.041*
C14	0.7864(2)	0.4006(3)	0.32859(19)	0.0377(6)
H14	0.8475	0.4315	0.2586	0.045*
C15	0.7476(3)	0.4700(2)	0.4086(2)	0.0354(5)
H15	0.7796	0.5480	0.3953	0.043*
C16	0.6590(2)	0.4197(2)	0.50992(18)	0.0277(5)
C17	0.3994(2)	0.23089(18)	0.95308(16)	0.0230(4)
H17A	0.3216	0.1831	1.0066	0.028*
H17B	0.4141	0.2964	0.9861	0.028*
C18	0.5346(2)	0.15523(17)	0.92095(16)	0.0200(4)
C19	0.6985(2)	0.03809(18)	0.83292(16)	0.0214(4)
C20	0.7843(2)	−0.0344(2)	0.76110(18)	0.0279(5)
H20	0.7589	−0.0469	0.7013	0.033*
C21	0.9078(2)	−0.0877(2)	0.7801(2)	0.0326(5)
H21	0.9687	−0.1372	0.7320	0.039*
C22	0.9457(2)	−0.0703(2)	0.8690(2)	0.0355(5)
H22	1.0323	−0.1074	0.8789	0.043*
C23	0.8597(2)	−0.0005(2)	0.9420(2)	0.0322(5)
H23	0.8841	0.0102	1.0028	0.039*
C24	0.7357(2)	0.05330(19)	0.92230(17)	0.0234(4)
C25	0.6876(4)	−0.3348(3)	0.7436(3)	0.0638(10)
HA	0.6401	−0.3826	0.8149	0.077*
HB	0.6970	−0.2540	0.7551	0.077*
C26	0.8322(3)	−0.3899(3)	0.6938(4)	0.0834(14)
HC	0.8750	−0.3468	0.6204	0.125*
HD	0.8234	−0.4730	0.6906	0.125*
HE	0.8936	−0.3862	0.7376	0.125*

an ethanol (20 mL) solution of Ni(ClO₄)₂·6H₂O (0.074 g, 0.20 mmol) and sodium nitrite (0.014 g, 0.20 mmol), forming a clear green solution. The solution was stirred for one hour and then filtered. The filtrate was evaporated for three days to form green crystals.

Experimental details

The methyl groups were idealized and refined using rigid groups allowed to rotate about the N—C bond. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 $U_{\text{eq}}(\text{C})$

and the U_{iso} values of all other hydrogen atoms were set to 1.2 $U_{\text{eq}}(\text{C})$.

Comment

The nitrite anion is an ambidentate ligand which can form linkage isomers [4]. It can coordinate to metal ions in various ways. In the mononuclear complex, three coordination modes can often be observed, as unidentate *N*-(nitro) and *O*-(nitrito) coordination or as bidentate *O,O*-(nitrito) coordination [5]. It is known that the coordination mode of nitrite is mainly influenced by the steric hindrance imposed by the ancillary ligands. Tris(2-benzimidazolylmethyl)amine (*ntb*) is such a rigid tripodal tetradentate ligand [6–8]. In order to see how the ancillary ligand may influence the coordination mode of nitrite, a new complex [Ni(*ntb*)(NO₂)]ClO₄·CH₃CH₂OH was prepared and characterized.

The title compound consists of a discrete [Ni(*ntb*)(NO₂)]⁺ cation, a perchlorate anion and a non-coordinated solvent molecule of ethanol. In the complex cation, the nickel(II) ion is coordinated by four N atoms from *ntb* and two O atoms from nitrite, forming a distorted octahedral geometry (as shown in the figure, 50° displacement ellipsoids, hydrogen atoms omitted for clarity). The tertiary amine N1, two benzimidazole N2, N6, and the oxygen O1 atoms define the equatorial plane. Equatorial bond angles are in the range of 78.25(7)°–102.05(7)°, deviating from 90° remarkably [9]. Axial positions are occupied by O2 and N4 with a bond angle O2–Ni1–N4 of 158.66(7)°, showing a serious distorted octahedral environment. As expected, the tripodal *ntb* ligand coordinates to the nickel(II) ion with the three benzimidazole groups in a T shape. The plane of the nitrite is coplanar with one of them. The three Ni–N_{benzimidazole} distances are from 2.005(2) Å to 2.0481(18) Å. The distance between Ni1 and tertiary amine N1 is 2.2498(18) Å, significantly longer than the Ni–N_{benzimidazole} bond lengths, which is attributed to the steric requirement of the tripodal tetradentate ligand *ntb* [6, 7].

It is worth noting that the nitrite exhibits an asymmetrical bidentate chelating mode with two obvious different Ni–O bond lengths, Ni1–O1 [2.0663(17) Å], Ni1–O2 [2.2497(18) Å]. The same asymmetrical bidentate chelating mode was also observed in a ferrous complex [Fe(*ntb*)(κ²-O₂N)]BF₄ (2.104(4) Å and 2.338(4) Å for Fe1–O1 and Fe1–O2) [10]. But in [Cu(*ntb*)(NO₂)]NO₂, only mono-coordination of nitrite can be observed [a mixture of both κ¹-NO₂ and κ¹-ONO linkage isomers] [11].

In the complex, two of the [Ni(*ntb*)(NO₂)]⁺ cations are interlinked anti-symmetrically by hydrogen bonds to form a dimolecular unit. These dimolecular units are further interacted to form 1D chain structure by hydrogen bonds through the perchlorate anion and benzimidazole groups of *ntb*.

The 1D chains are further expanded into 2D network structure by weak π – π stacking interactions.

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