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Hydronium tris(oxamide dioxime-κ^2N,N')nickel(II) triiodide

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The title compound, $(H_3O)[Ni(C_2H_6N_4O_2)_3]I_3$ or (H_3O)-$[Ni(H_2oxado)_3]I_3$, where H_2oxado = oxamide dioxime, contains six $[Ni(H_2oxado)_3]^{2+}$ cations, six H_3O^+ cations and eighteen I^- anions in the unit cell. The Ni atom lies on a position of site symmetry 32 and the hydronium cation is disordered on a position of site symmetry $\overline{3}$. The crystal packing is consolidated by O—H···O hydrogen bonds that link the cations along *c* into positively charged pillars. The proton balancing the charge of the iodide ions is attached to the water molecule of crystallization, thus forming a hydronium ion.

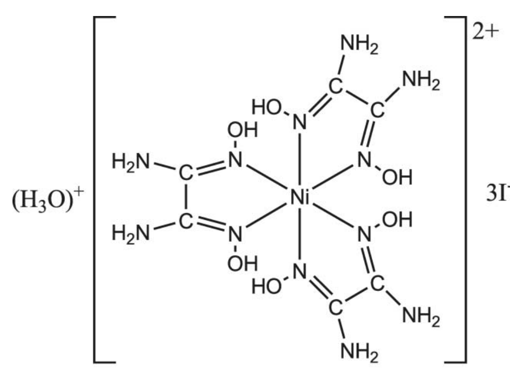
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.027
wR factor = 0.059
Data-to-parameter ratio = 26.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Transition metal complex cations of the form $[M(H_2oxado)_3]^{n+}$, where M = metal(II) or metal(III), n = 2 or 3, and H_2oxado = oxamide dioxime, are not commonplace in the literature, yet they have great potential as starting blocks that may combine with a wide range of anions to generate interesting multifunctional crystalline materials. Only three salts based on these cations (Bekaroglu *et al.*, 1978; Bélombé *et al.*, 1993; Endres & Jannack, 1980) appear to have been well characterized so far.



(I)

Our research is aimed at constructing material architectures likely to exhibit combined functionalities such as molecule-based magnetism, optical activity, nanoscale porosity and extended hydrogen bonding within the same system (Bélombé *et al.*, 2003). Thus, we prepared $[Co(H_2oxado)_3]I_3$ (Bélombé *et al.*, 1993) – which crystallizes with the same structure as the present material – and two isomorphous salts, $[Ni(H_2oxado)_3](ClO_4)_2$ and $[Ni(H_2oxado)_3](BF_4)_2$. We used these salts as a source of complex cations, and we produced the first salt of the series with linear chains of alternating $[M(H_2oxado)_3]^{3+}$ cations and $[M'(C_2O_4)_3]^{3-}$ anions, *viz.* $[Co(H_2oxado)_3]$-

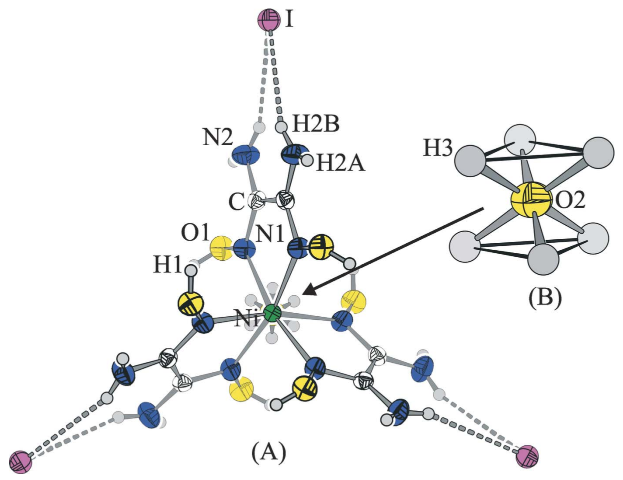


Figure 1
(A) The molecular formula unit of (I) with atom numbering, showing hydrogen bonding (dashed lines) of I atoms to the amino groups of the ligands, with atom O2 on a site of symmetry $\overline{3}$ (95% displacement ellipsoids, spheres of arbitrary radii for the H atoms). (B) Environment of O2 sites.

$[Cr(C_2O_4)_3]\cdot 5H_2O$ (Bélombé *et al.*, 2006; Nenwa, 2004). We now report the structure of the title compound, (I), for which an earlier assignment of the site of the charge-balancing proton (Endres, 1985) turns out to be incorrect.

The molecular formula unit of (I) is depicted in Fig. 1, obviating the *C*3 symmetry of the lattice and involving disorder of the H_3O^+ ion, the O atom of which is located on a site of symmetry $\overline{3}$. The Ni atom lies on a position of site symmetry 32. Selected bond lengths are listed and compared with previous values in Table 1. The slight differences in the Ni—N distances in this study compared with the values in the earlier study are due to the fact that the present work was carried out at 100 K, whereas the earlier study was conducted at room temperature. Selected torsion angles summarized in Table 2 underline the non-coplanarity of the ligand atoms with the central Ni. Fig. 2 depicts the crystal packing, illustrating the stacking of the complex and the hydronium cations into positively charged pillars along *c*. It reveals a hexagonal sublattice of iodide ions 'encapsulating' each pillar. It is also seen that next-neighbour complexes are rotated by an angle of 60° relative to each other. The view along [001] of a pillar (Fig. 3) shows intermolecular O—H···O hydrogen bonds with a regular Ni···Ni spacing of 7.244 (3) Å (*c*/2).

It is worth noting that the linear-chain ordering of positive complex entities observed here is rather an unusual self-assembly mode, as such entities would normally be expected to be mutually repulsive. Obviously, however, the stabilizing effect of the long-range hydrogen bonding far overwhelms the mutual repulsion in the present case.

Experimental

Compound (I) was obtained according to the literature method of Endres (1985).

Crystal data

$(H_3O)[Ni(C_2H_6N_2O_2)_3]I_3$
M_r = 812.76
Trigonal, $R\overline{3}c$
a = 16.105 (2) Å
c = 14.488 (3) Å
V = 3254.4 (9) Å^3
Z = 6
D_x = 2.488 Mg m^{-3}
Mo *Kα* radiation
μ = 5.22 mm^{-1}
T = 100 (2) K
Hexagonal prism, pink–red
0.11 × 0.09 × 0.05 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: numerical [*X-RED32* (Stoe & Cie, 2001); crystal description using *FACEIT* (Stoe & Cie, 2002); optimization using equivalent reflections (*X-SHAPE*; Stoe & Cie, 1999)]
T_{min} = 0.450, T_{max} = 0.678
13652 measured reflections
1557 independent reflections
1461 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 35.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.059
S = 1.17
1557 reflections
60 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 30.9996P + (0.0144P)^2]$ … printed as: $w = \{1 - \exp[-10(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2) + 30.9996P + (0.0144P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.49 e Å^{-3}
$\Delta\rho_{min}$ = −1.19 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00016 (5)

Table 1
Selected bond distances (Å) involving non H atoms in (I).

Values in square brackets are from Endres (1985).

Ni—N1^{i-v}	2.044 (2)	[2.055 (5)]
N1—C	1.304 (3)	[1.293 (8)]
N1—O1	1.420 (2)	[1.416 (7)]
N2—C	1.325 (3)	[1.310 (9)]
C—C^{iii}	1.494 (4)	[1.502 (8)]

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $y, x, -z-\frac{1}{2}$; (iv) $x-y, -y, -z-\frac{1}{2}$; (v) $-x, -x+y, -z-\frac{1}{2}$.

Table 2
Selected torsion angles (°) for (I).

O1—N1—C—N2	−6.6 (3)	O1—N1—C—C^{iii}	174.4 (2)
Ni—N1—C—N2	−174.0 (2)	Ni—N1—C—C^{iii}	6.97 (3)

Symmetry code: (iii) $y, x, -z-\frac{1}{2}$.

Table 3
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···I^{vi}	0.92 (2)	2.83 (3)	3.717 (2)	164 (4)
N2—H2*B*···I	0.91 (3)	2.78 (3)	3.639 (2)	158 (4)
O2—H3···O1^{vii}	0.89 (3)	1.64 (6)	2.400 (2)	142 (9)

Symmetry codes: (vi) $-y+\frac{2}{3}, x-y+\frac{1}{3}, z+\frac{1}{3}$; (vii) $-x+y, -x, z$.

The H atoms attached to O2 are disordered over two sites of equal occupancy. All H atoms were initially located in a difference Fourier map and were refined using distance restraints of N—H = 0.95 (3) Å

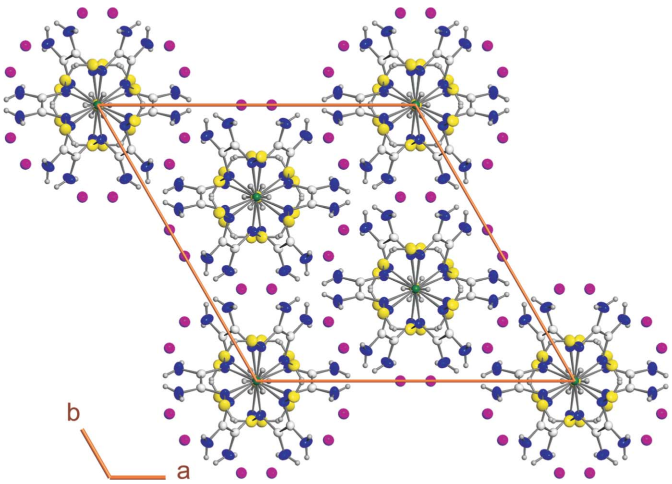


Figure 2
A projection of the structure of (I) down [001], illustrating the stacking of complexes into pillars. Ni atoms are green, I atoms purple, N atoms blue, O atoms yellow, C atoms white and H atoms grey.

and O—H = 0.84 (3) Å. H-atom coordinates refined to the values reported in the archived CIF, with $U_{iso}(H) = 1.2U_{eq}(N)$ for H2*A* and H2*B*, and $U_{iso}(H) = 1.5U_{eq}(O)$ for H1 and H3. The highest peak and deepest hole in the final difference map are 1.46 Å from atom H2*B* and 1.26 Å from N1, respectively.

Data collection: *WinXpose* (Stoe & Cie, 2002); cell refinement: *RECIPE* (Stoe & Cie, 2002); data reduction: *INTEGRATE* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97* and *DIAMOND*.

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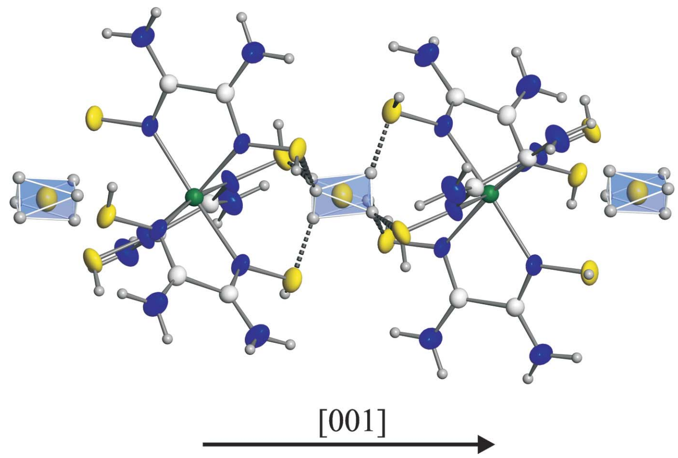

Figure 3
A view of a pillar, perpendicular to [001], showing O—H···O hydrogen bonds (dashed lines) between H_3O^+ and adjacent $[Ni(H_2oxado)_3]^{2+}$ ions.

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