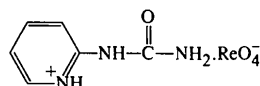


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protonation of the *endo*-N atom in the pyridyl ring favours the formation of an intramolecular N—H···O hydrogen bond which is crucial for the planarity and conformation of the molecule. The *N*-(pyridinium)urea cation is planar, with the largest deviation of 0.085 (9) Å at the amino N3 atom. The overall conformation of the molecule can be described as *s-cis-s-cis* with respect to the C1—N2—C2 imino bonds, in contrast to the *s-trans-s-cis* conformation found in *N*-(2-pyridyl)urea (Velikova, Angelova & Kossev, 1997).



(I)

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N-(2-Pyridinium)urea Perrhenate†

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Abstract

The *N*-(2-pyridinium)urea cation of the title compound, C₆H₈N₃O⁺·ReO₄⁻, is planar to within 0.085 (9) Å and adopts an *s-cis-s-cis* conformation with respect to the imino C—N bonds. The structure consists of columns of centrosymmetric dimeric plane-to-plane stacked cations and hydrogen-bonded anions. The distance between the anti-parallel carbonyl groups in the dimer is 3.16 (5) Å. An extensive network of hydrogen bonds stabilizes the ordering of the ions within the columns, which are held together by weaker hydrogen bonds and van der Waals interactions.

Comment

This work is part of an investigation of adducts of unsymmetrically substituted urea derivatives and inorganic salts with potential as non-linear optical materials. We combined *N*-(2-pyridyl)urea and perrhenic acid, assuming that the anionic host sub-network would affect the molecular geometry and arrangement of the cations.

Bond lengths and angles in the title compound, (I), compare well with the values found for other *N*-(2-pyridyl)urea derivatives (Velikova, Angelova & Kossev, 1997; Le Magueres, Ouahab, Hocquet & Fournier, 1994) and for ReO₄ tetrahedra (Lock & Turner, 1975; Macíček & Todorov, 1992; Macíček & Angelova, 1995). The

The structure contains centrosymmetric dimers of plane-to-plane stacked cations and hydrogen-bonded anions. The stacking of the cations embraces carbonyl groups which are only 3.16 (5) Å apart. In addition, the two coupled cations are captured by two ReO₄⁻ anions, forming a six-membered hydrogen-bonded ring through O12 and a relatively short, though bifurcated, hydrogen bond through O14 (Table 2). These dimers are ordered in columns along the *a* axis and interlinked by centrosymmetric eight-membered hydrogen-bonded rings formed by pairs of cations, similar to those in the structure of *N*-(2-pyridyl)urea, and by the HN31···O11 branches of the bifurcated hydrogen bond to HN31. The columns are held together by weak bifurcated hydrogen bonds [HN2···O12(1 - *x*, -*y*, 1 - *z*)] along the *b* axis, as well as by van der Waals interactions along the *c* axis.

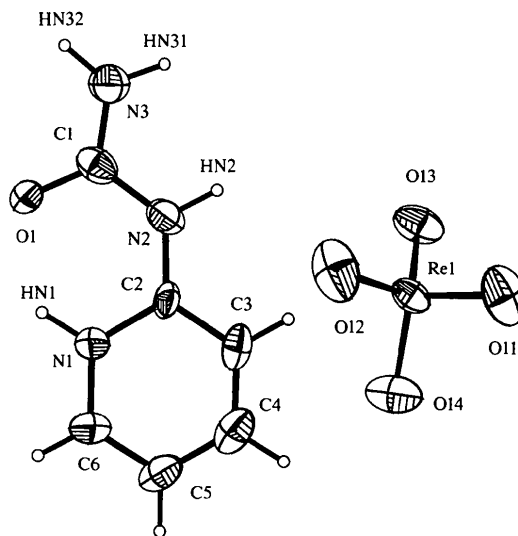


Fig. 1. The ions of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are arbitrarily reduced.

† Alternative name: 2-ureidopyridinium tetraoxorhenate.

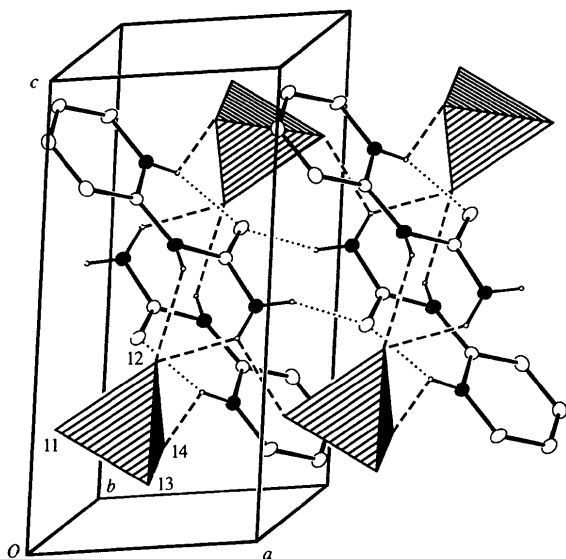


Fig. 2. A view of the structure down the *b* axis. Dotted and dashed lines denote hydrogen bonds between the organic and inorganic parts, respectively. N atoms are represented by shaded circles.

Experimental

The preparation of *N*-(2-pyridyl)urea has been described by Velikova, Angelova & Kossev (1997). Single crystals of *N*-(2-pyridinium)urea perrhenate were obtained by slow evaporation of equimolar solutions of *N*-(2-pyridyl)urea and perrhenic acid in isopropanol.

Crystal data

(C₆H₈N₃O)[ReO₄]

M_r = 400.35

Triclinic

P $\bar{1}$

a = 5.215 (1) Å

b = 9.167 (3) Å

c = 10.597 (4) Å

α = 74.61 (3)°

β = 84.65 (2)°

γ = 86.42 (5)°

V = 486.0 (7) Å³

Z = 2

D_x = 2.735 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 22 reflections

θ = 19.99–21.63°

μ = 12.68 mm⁻¹

T = 292 K

Prismatic

0.396 × 0.231 × 0.165 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/θ scans

Absorption correction:

empirical based on ψ

scans (North, Phillips & Mathews, 1968)

T_{min} = 0.104, *T_{max}* = 0.123

3110 measured reflections

2825 independent reflections

2604 reflections with *I* > 2σ(*I*)

R_{int} = 0.050

θ_{\max} = 30.0°

h = 0 → 7

k = -12 → 12

l = -14 → 14

3 standard reflections

frequency: 120 min

intensity decay: 6.8%

Refinement

Refinement on *F*²

R = 0.045

wR = 0.081

S = 1.180

2604 reflections

136 parameters

H atoms constrained

w = 1/[σ²(*F*) + (0.065*F*)²]

(Δ/σ)_{max} = 0.036

Δρ_{max} = 2.3 e Å⁻³

Δρ_{min} = -2.3 e Å⁻³

Extinction correction: Stout & Jensen (1968), formula 17.16

Extinction coefficient:

0.17783 × 10⁻⁵

Scattering factors as

coded in *SDP/PDP User's Guide* (Enraf–Nonius, 1985)

Table 1. Selected geometric parameters (Å, °)

Re1—O11	1.745 (8)	N2—C1	1.386 (11)
Re1—O12	1.657 (9)	N2—C2	1.341 (11)
Re1—O13	1.709 (8)	N3—C1	1.319 (12)
Re1—O14	1.699 (8)	C2—C3	1.368 (11)
O1—C1	1.247 (13)	C3—C4	1.353 (13)
N1—C2	1.392 (12)	C4—C5	1.391 (17)
N1—C6	1.364 (12)	C5—C6	1.358 (14)
O11—Re1—O12	108.8 (4)	O1—C1—N3	121.8 (9)
O11—Re1—O13	107.8 (4)	N2—C1—N3	118.4 (9)
O11—Re1—O14	108.6 (5)	N1—C2—N2	118.8 (7)
O12—Re1—O13	110.9 (5)	N1—C2—C3	117.4 (7)
O12—Re1—O14	109.2 (5)	N2—C2—C3	123.7 (9)
O13—Re1—O14	111.5 (4)	C2—C3—C4	121.3 (9)
C2—N1—C6	120.9 (8)	C3—C4—C5	121.2 (9)
C1—N2—C2	127.5 (9)	C4—C5—C6	117.5 (9)
O1—C1—N2	119.6 (8)	N1—C6—C5	121.3 (11)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—HN1...O14 ⁱ	2.10 (1)	2.81 (1)	130.2 (5)	
N1—HN1...O1	1.88 (1)	2.58 (1)	128.2 (5)	100.3 (3)
N2—HN2...O12	2.17 (1)	2.96 (1)	140.2 (5)	
N2—HN2...O12 ⁱⁱ	2.71 (1)	3.49 (1)	139.8 (5)	79.9 (3)
N3—HN31...O11 ⁱⁱⁱ	2.31 (1)	2.96 (1)	125.0 (6)	
N3—HN31...O12	2.33 (1)	3.10 (2)	138.5 (6)	87.9 (3)
N3—HN32...O1 ^{iv}	2.05 (1)	2.98 (1)	163.9 (6)	

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) 1 - *x*, -*y*, 1 - *z*; (iii) 1 + *x*, *y*, *z*; (iv) 2 - *x*, 1 - *y*, 1 - *z*.

All H atoms were placed in idealized positions [C—H (N—H) = 0.95 Å, *U*(H) = 0.0506 Å²]. The loss of intensity (6.8%) was not due to significant crystal decay or radiation damage, but rather to a power instability, laboratory air conditioning or electronic performance. High residual peaks near the Re atom are due to an underestimated absorption correction.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP User's Guide* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP User's Guide*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, unpublished).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1281). Services for accessing these data are described at the back of the journal.

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Bis[*N*-(β -naphthyl)-2-oxy-1-naphthaldiminato]nickel(II)

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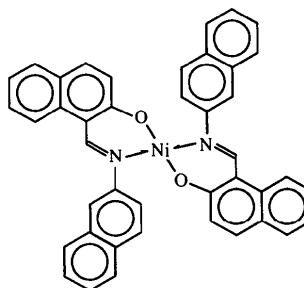
(Received 11 April 1997; accepted 12 May 1997)

Abstract

There is a remarkable stereochemical difference between the free ligand and that coordinated to the Ni atom in the title compound {systematic name: bis[1-(2-naphthyl-iminomethyl)-2-naphtholato-*N,O*]nickel(II), $[Ni(C_{21}H_{14}NO)_2]$ }. Upon coordination, the orientation of the *N*-(β -naphthyl)-2-oxy-1-naphthaldimine ligand (which is almost planar in the solid state when uncomplexed) is changed so that the plane of the *N*- β -naphthyl substituent is almost normal to the plane of the naphthaldiminato moiety. Two bidentate ligands coordinate to the Ni atom (which lies on an inversion centre) with their O and N atoms in a (necessarily) *trans* arrangement and forming a stepped conformation with a mean chelate-plane vertical separation of 0.639 (2) Å. Main dimensions are Ni—O 1.820 (2), Ni—N 1.901 (2) Å and O—Ni—N 91.75 (7)°.

Comment

We are currently studying the variation of stereochemistry as a function of ligand structure in a series of complexes with the same metal atom. The crystal structure of the title compound, (I), was determined in order to ascertain the conformational perturbations of the ligand upon coordination.



(I)

The Ni atom of compound (I) (Fig. 1) lies on an inversion centre and is coordinated to two bidentate Schiff base ligands in a characteristic square-planar manner with the coordinating O and N atoms necessarily in a *trans* arrangement (Fig. 1). The Ni^{II} square-planar geometry has normal dimensions, with Ni—O1 1.820 (2), Ni—N1 1.901 (2) Å and O1—Ni—N1 91.75 (7)°. Delocalization of the chelate-ring π -electrons accounts for both the O1—C12 [1.300 (3) Å] and N1—C1 [1.298 (3) Å] bond lengths being intermediate between single- and double-bond values (Allen *et al.*, 1987). Bond lengths in the naphthalene moieties are mostly as expected; the shortening of the C13—C14 bond length [to 1.347 (4) Å] is consistent with a quinoid effect (Exelby & Grinter, 1965).

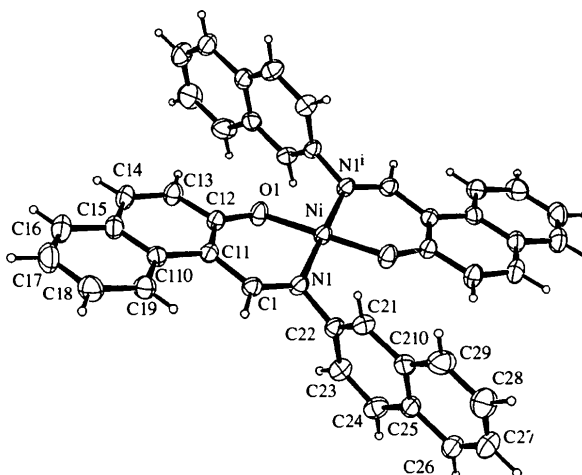


Fig. 1. ORTEP (Johnson, 1976) view of the title molecule showing 30% probability displacement ellipsoids. H atoms are plotted as circles of arbitrarily size. [Symmetry code: (i) $-x, -y, -z$].