Ni\textsuperscript{II} molecular complex with a tetradeinate aminoguanidine-derived Schiff base ligand: structural, spectroscopic and electrochemical studies and photoelectric response

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The new molecular nickel(II) complex, namely, \{(4-bromo-2-[(\textsuperscript{N}-[(2-oxidobenzylidene)amino]carbamimidoyl)imino)methyl]phenolato\}nickel(II)\textsubscript{2+}N\textsubscript{2}O\textsubscript{2} dimethylformamide solvate monohydrate, [Ni(C\textsubscript{15}H\textsubscript{11}BrN\textsubscript{4}O\textsubscript{2})]C\textsubscript{2}H\textsubscript{4}NO\textsubscript{2}H\textsubscript{2}O (I), crystallizes in the triclinic space group \textit{P}\textsuperscript{1} with one molecule per asymmetric unit. The guanidine ligand is a product of Schiff base condensation between aminoguanidine, salicylaldehyde and 5-bromosalicylaldehyde templated by Ni\textsuperscript{2+} ions. The chelating ligand molecule is deprotonated at the phenol O atoms and coordinates the metal centre through the two azomethine N and two phenolate O atoms in a \textit{cis}-NiN\textsubscript{2}O\textsubscript{2} square-planar configuration [average(Ni—N/O) = 1.8489 \AA, \textit{cis} angles in the range 83.08 (5)—95.35 (5)\textdegree, \textit{trans} angles of 177.80 (5) and 178.29 (5)\textdegree]. The complex molecule adopts an almost planar conformation. In the crystal, a complicated hydrogen-bonded network is formed through N—H\textsuperscript{⋯}N/O and O—H\textsuperscript{⋯}O intermolecular interactions. Complex (I) was also characterized by FT–IR and \textsuperscript{1}H NMR spectroscopy. It undergoes an Ni\textsuperscript{II} ↔ Ni\textsuperscript{III} redox reaction at \textit{E_{1/2}} = +0.295 V (vs Ag/AgCl) in methanol solution. In a thin film with a free surface, complex (I) shows a fast photoelectric response upon exposure to visible light with a maximum photovoltage of \sim 178 mV.

1. Chemical context

Guanidine, the functional group on the side chain of arginine, has attracted much attention in the fields of drug development (Santos \textit{et al.}, 2015; Hirsh \textit{et al.}, 2008) and natural product synthesis (Berlinc \\textsuperscript{ka}, 2016; Kudo \textit{et al.}, 2016). Guanidine derivatives have also been explored as catalysts and superbases (Selig, 2013; Ishikawa, 2009). Aminoguanidine (AG) is an antioxidant and nucleophilic agent with strong scavenging activities against reactive carbonyl species (RCS) – a class of byproducts originating from exogenous and endogenous oxidation. RCS react with nucleophilic targets such as nucleic acids, phospholipids and proteins to form damaging adducts (Colzani \textit{et al.}, 2016; Ramis \textit{et al.}, 2019). Diabetic and Alzheimer's disease patients were both found to have increased RCS levels in their circulatory systems (Kalousova \textit{et al.}, 2002; Picklo \textit{et al.}, 2002). Blocking RCS by carbonyl quenchers is an encouraging therapeutic strategy and the investigation of conjugates of AG and arylaldehydes as well as
their metal complexes has been at the focus of research interest for several decades (Fukumoto et al., 2002; Qian et al., 2010; Vojinović-Jesić et al., 2014).

In our previous study, the condensation reactions of aminoguanidine freshly liberated from AG/C1HCl or AG/C1HNO₃ and arylaldehydes (salicylaldehyde, 5-bromosalicylaldehyde, pyridine-2-carbaldehyde) produced the expected 1:1 Schiff base ligands isolated as protonated cations of nitrate or chloride salts as well as Cu²⁺ and Co³⁺ mononuclear complexes (Buvaylo et al., 2013, 2016, 2017). The dichloridocopper(II) complex bearing a pyridine-2-carbaldehyde aminoguanidine Schiff base ligand revealed prominent catalytic activity towards the oxidation of cyclohexane with hydrogen peroxide in the presence of various promoters (Buvaylo et al., 2017). In contrast, the interaction of AG with formaldehyde yielded a completely different compound with a high nitrogen content that had not been reported before (Buvaylo et al., 2018). 2,2'-Methylenedihydrazinecarboximidamide, which was isolated in its protonated form as the dinitrate salt, resulted from the condensation between two AG molecules and one molecule of formaldehyde.

In the present work, we attempted to synthesize an Ni complex with the Schiff base ligand derived from AG and salicylaldehyde. However, 5-bromosalicylaldehyde was also mistakenly introduced into the flask. As a result, the new tetradentate ligand (2-hydroxybenzylidene)(5-bromo-2-hydroxybenzylidene)aminoguanidine, H₂L, was formed from the

Table 1
Selected geometric parameters (Å, °).

| Bond                  | Distance (Å) | Angle (°) |
|----------------------|--------------|-----------|
| Ni1—N2               | 1.8383 (11)  |           |
| Ni1—O21              | 1.8515 (10)  |           |
| Ni1—N5               | 1.8494 (11)  |           |
| Ni1—O11              | 1.8562 (10)  |           |
| N2—Ni1—N5            | 83.08 (5)    |           |
| N2—Ni1—O21           | 177.80 (5)   |           |
| N5—Ni1—O21           | 95.25 (5)    |           |
| O21—Ni1—O11          | 86.30 (4)    |           |

In situ condensation of one AG molecule and two different molecules of the aldehydes in the presence of Ni²⁺ ions. Herein, the crystal structure of [NiL]-DMF-H₂O (DMF = N,N-dimethylformamide), (I), is presented along with the elemental analyses, IR, NMR and cyclic voltammetry results as well as photoelectric response characteristics.

2. Structural commentary
Compound (I), [Ni(C₁₅H₁₁BrN₄O₂)]-C₃H₇NO-H₂O, crystallizes in the triclinic space group P̅₁ and is assembled from discrete NiL molecules and solvent molecules of crystallization. The chelating ligand L⁻ is deprotonated at the phenol O atoms and coordinates the NiII ion through the two azomethine N and two phenolate O atoms in a cis-NiN₂O₂ square-planar configuration (Fig. 1). The Ni—N/O distances fall in the range 1.8383 (11)–1.8562 (10) Å, the cis angles at the metal atom vary from 83.08 (5) to 95.35 (5)° and the trans angles are equal to 177.80 (5)° and 178.29 (5)° (Table 1). The molecule is quite planar, the atoms with the largest deviations being C15 [δ = 0.059 (2) Å] and C23 [δ = 0.057 (2) Å] although there is very slight ‘bowing’ at the Ni atom. The dihedral angle between the two phenyl rings is 3.37 (5)°.

3. Supramolecular features
In the crystal, the NiL molecules form centrosymmetrically related pairs with an interplanar distance of approximately 3.32 Å and the Ni · · · Ni separation being 3.4191 (3) Å (Fig. 2). There are no hydrogen bonds between the NiL molecules and no π–π stacking is observed owing to the trans-orientation of the two paired molecules. Instead, the NiL molecule creates centrosymmetric hydrogen-bonded pairs through one H atom on the amine nitrogen N4, its other hydrogen forming a hydrogen bond to a centrosymmetrically related water molecule as shown by the N4· · ·N3 [−x + 2, −y + 2, −z + 1] and

Figure 1
Molecular structure and atom labelling of [NiL]-C₃H₇NO-H₂O (I), with displacement ellipsoids at the 50% probability level.

Figure 2
View of a pair of centrosymmetrically related trans-oriented NiL molecules showing the absence of π–π stacking.
The infrared spectrum of complex (I) in the 4000–400 cm⁻¹ range is very rich and shows all characteristic functional group peaks. A broad absorption near 3500 cm⁻¹ and multiple overlapping bands in the range 3358–3134 cm⁻¹ are attributed to ν(OH) and ν(NH) stretching vibrations, respectively. Bands arising above 3000 cm⁻¹ are due to aromatic ≡CH stretching of the ligand; alkyl CH stretching vibrations of L²⁻ and DMF solvent are seen from 2958 to 2808 cm⁻¹. Very intense overlapping signals in the 1668–1584 cm⁻¹ region represent ν(C=O) stretching of the DMF molecule, deformation vibrations of the amino group, a group mode of the CN₂ unit of the ligand, νas(CN₃), and ν(C≡N) peaks of L²⁻ that cannot be distinguished from each other. The symmetric stretching mode νs(CN₃) of the CN₃ unit falls in the 1600–1400 cm⁻¹ range of the aromatic ring vibrations. Several sharp bands of medium intensity are observed in the out-of-plane CH bending region (800–700 cm⁻¹).

The diamagnetic nature of the majority of square-planar Ni⁹⁺ complexes is helpful in their characterization by NMR spectroscopy. The ¹H NMR spectrum of (I) exhibits the expected set of signals between 8.5 and 2.5 ppm (Fig. 4). The presence of two –CH=N– protons that appear as two singlets in a 1:1 ratio at δ 8.37 and 8.05 ppm confirms the Schiff base condensation of AG with two aldehyde molecules. The signals arising above 3000 cm⁻¹ and multiple overlapping bands in the range 3358–3134 cm⁻¹ are attributed to ν(OH) and ν(NH) stretching vibrations, respectively. Bands arising above 3000 cm⁻¹ are due to aromatic ≡CH stretching of the ligand; alkyl CH stretching vibrations of L²⁻ and DMF solvent are seen from 2958 to 2808 cm⁻¹. Very intense overlapping signals in the 1668–1584 cm⁻¹ region represent ν(C=O) stretching of the DMF molecule, deformation vibrations of the amino group, a group mode of the CN₂ unit of the ligand, νas(CN₃), and ν(C≡N) peaks of L²⁻ that cannot be distinguished from each other. The symmetric stretching mode νs(CN₃) of the CN₃ unit falls in the 1600–1400 cm⁻¹ range of the aromatic ring vibrations. Several sharp bands of medium intensity are observed in the out-of-plane CH bending region (800–700 cm⁻¹).

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of seven aromatic protons in the range 7.57–6.58 ppm observed as one singlet, four doublets and two triplets evidence the presence of two chemically inequivalent rings. A broad singlet at δ 7.25 ppm is due to the NH₂ group adjacent to the carbon atom of the guanidine moiety. The absence of the phenolic OH singlets detected at δ 11.55 ppm in the ¹H NMR spectrum of (5-bromosalicylidene)aminoguanidine·HNO₃ (Buvaylo et al., 2016) points out the deprotonation of H₂L upon coordination to the Ni²⁺ centre in (I). Three sharp singlets in a 1:3:3 ratio at 7.94, 2.88 and 2.72 ppm were attributed to the CH and two CH₃ groups of DMF, respectively.

6. Cyclic voltammetry

The electrochemical features of complex (I) were studied in methanol in the presence of 0.1 M acetate buffer (pH 4) and NaClO₄ (70:28:2) as supporting electrolyte by using a three-electrode setup (glassy carbon working electrode, platinum auxiliary electrode and Ag/AgCl reference electrode) in the potential range +1.0 to −1.0 V at a scan rate of 100 mV s⁻¹. The anodic scan, starting from the open circuit potential (0.24 V vs Ag/AgCl), displays an oxidation wave at Eₚₐ = +0.42 V coupled with a corresponding reduction wave at Eₚₑ = +0.17 V (Fig. 5). A large separation between the cathodic and anodic peak potentials (250 mV) indicates a quasi-reversible redox process which can be assigned to Ni²⁺/Ni³⁺ couple with E₁/₂ = +0.295 V (vs Ag/AgCl). The non-equivalent current intensity of cathodic and anodic peaks (iᵢᵣ = 0.551) suggests that the Ni³⁺ complex generated by oxidation of Ni²⁺ is not stable.

7. Electro-optical measurements

The ability of (I) to form thin films on its own when cast from methanol solution prompted us to examine its photoelectric response under illumination with visible light. The thin film of the complex with estimated thickness of about 1.5 μm was obtained by drop casting of a methanol solution of (I) on an electroconductive ITO (SnO₂: In₂O₃) layer of a standard glass slide and subsequent drying. A Kelvin probe technique was employed to track the contact potential difference between the free surface of the film and the probe with a BM8020 USB oscilloscope according to Davidenko et al. (2016). A 4 mm diameter aluminium plate placed ~50 μm above the surface with a vibration frequency of 4 kHz was used as the reference probe. A white-light-emitting diode (LED) with power density I ≃ 40 W m⁻² was used to illuminate the film from the ITO substrate side.

The thin-film sample of (I) showed a rather fast photoelectric response upon exposure to visible light with the surface potential Vᵣₑₚ reaching its maximum value of ~178 mV within 6 s. Then the potential diminished slightly to stay nearly constant until the light was turned off at t = 100 s (Fig. 6). The Vᵣₑₚ relaxation in the film occurred almost as fast as its growth. The free surface of the film acquired a positive charge under illumination meaning the photogenerated electrons transfer to the ITO substrate. The fast kinetics of the surface photovoltage growth and decay indicates a high mobility of the photogenerated charge carriers in (I).
8. Synthesis and crystallization
A mixture of salicylaldehyde (0.20 g, 2 mmol), 5-bromo-salicylaldehyde (0.40 g, 2 mmol), Ag·HCl (0.22 g, 2 mmol) and NiCl₂·6H₂O (0.24 g, 1 mmol) in DMF (5 mL) in a conical flask was heated at 323 K under magnetic stirring for 1.5 h with its green colour deepening. Then the solution was filtered and allowed to stand at room temperature. It changed colour to brown upon filtration. After a week, diethyl ether (2 mL) was added to the clear solution to initiate precipitation. Red shiny plate-like crystals of the title compound formed over a month. They were filtered off, washed with diethyl ether and dried in air (yield based on NiCl₂·6H₂O: 69%). Analysis calculated for C₁₈H₂₀BrN₅NiO₄ (509.01): C, 42.48; H, 3.96; N, 13.70%; found: C, 42.55; H, 3.74; N, 13.76%. ¹HN M R Water and NH₂ hydrogen atoms were refined without restraints. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

9. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms bound to carbon were included in calculated positions and refined using a riding model with isotropic displacement parameters based on those of the parent atom (C—H = 0.95 Å, Uiso(H) = 1.2Ueq(C) for CH, C—H = 0.98 Å, Uiso(H) = 1.5Ueq(C) for CH₂). Water and NH₂ hydrogen atoms were refined without restraints. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Funding information
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References
Berlink, R. G. & Romminger, S. (2016). Nat. Prod. Rep. 33, 456–490.
Buvaylo, E. A., Kasyanova, K. A., Vassilyeva, O. Y. & Skelton, B. W. (2016). Acta Cryst. E72, 907–911.
Buvaylo, E. A., Kokozay, V. N., Strutyńska, N. Y., Vassilyeva, O. Y. & Skelton, B. W. (2018). Acta Cryst. C74, 152–158.
Buvaylo, E. A., Kokozay, V. N., Vassilyeva, O. Y. & Skelton, B. W. (2013). Acta Cryst. E69, m165–m166.
Buvaylo, E. A., Kokozay, V. N., Vassilyeva, O. Y., Skelton, B. W., Nesterova, O. V. & Pombeiro, A. J. (2017). Inorg. Chem. Commun. 78, 85–90.

Table 3

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References
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Buvaylo, E. A., Kasyanova, K. A., Vassilyeva, O. Y. & Skelton, B. W. (2016). Acta Cryst. E72, 907–911.
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Ramis, R., Casasnovas, R., Mariño, L., Frau, J., Adrover, M., Vilanova, B., Mora–Diez, N. & Ortega–Castro, J. (2019). *Int. J. Quantum Chem.* **119**, e25911.

Rigaku OD (2016). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, England.

Santos, M. F., Harper, P. M., Williams, D. E., Mesquita, J. T., Pinto, G., da Costa-Silva, T. A., Hajdu, E., Ferreira, A. G., Santos, R. A., Murphy, P. J., Andersen, R. J., Tempone, A. G. & Berlinck, R. G. S. (2015). *J. Nat. Prod.* **78**, 1101–1112.

Selig, P. (2013). *Synthesis*, **45**, 703–718.

Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.

Starikova, Z. A., Yanovsky, A. I., Struchkov, Yu. T., Zubkov, S. V. & Seifullina, I. I. (1996). *Russ. Chem. Bull.* **45**, 2157–2162.

Vojinović-Ješić, L. S., Radanović, M. M., Rodić, M. V., Jovanović, L. S., Češljević, V. I. & Joksović, M. D. (2014). *Polyhedron*, **80**, 90–96.
Ni(II) molecular complex with a tetradsentate aminoguanidine-derived Schiff base ligand: structural, spectroscopic and electrochemical studies and photoelectric response

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2016); cell refinement: CrysAlis PRO (Rigaku OD, 2016); data reduction: CrysAlis PRO (Rigaku OD, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: WinGX (Farrugia, 2012).

(4-Bromo-2-[(N'-[(2-oxidobenzylidene)amino]carbamimidoyl]imino)methyl]phenolato)nickel(II) N,N-dimethylformamide monosolvate monohydrate

Crystal data

[Ni(C_{15}H_{11}BrN_{4}O_{2})]·C_{3}H_{7}NO·H_{2}O

Z = 2

\( M_r = 509.01 \)

Triclinic, \( P\bar{1} \)

Hall symbol: -P 1

\( a = 8.3057 \text{ (4) Å} \)

\( b = 9.2300 \text{ (4) Å} \)

\( c = 14.3970 \text{ (7) Å} \)

\( \alpha = 95.338 \text{ (4)}^\circ \)

\( \beta = 104.493 \text{ (4)}^\circ \)

\( \gamma = 112.592 \text{ (5)}^\circ \)

\( V = 964.23 \text{ (9) Å}^3 \)

Cell parameters from 11025 reflections

\( \theta = 3.4–37.3^\circ \)

\( \mu = 3.12 \text{ mm}^{-1} \)

\( T = 100 \text{ K} \)

Plate, red

0.32 × 0.26 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur diffractometer

Graphite monochromator

Detector resolution: 16.0009 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: analytical

(CrysAlis Pro; Rigaku OD, 2016)

\( T_{\text{min}} = 0.484, T_{\text{max}} = 0.721 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.036 \)

\( wR(F^2) = 0.083 \)

\( S = 1.04 \)

9442 measured reflections

28563 independent reflections

7711 reflections with \( I > 2\sigma(I) \)
280 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

\[ w = \frac{1}{[\sigma^2(F_{o}^2) + (0.0353P)^2 + 0.1785P]} \]
where \( P = (F_{c}^2 + 2F_{c}^2)/3 \)

\( \Delta/\sigma_{\text{max}} = 0.002 \)
\( \Delta \rho_{\text{max}} = 0.73 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.39 \text{ e Å}^{-3} \)

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Water molecule and NH\(_2\) hydrogen atoms were refined without restraints.

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**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))**

|    | x    | y    | z    | \( U_{\text{iso}}^{*}/U_{\text{eq}} \) |
|----|------|------|------|---------------------------------|
| Ni1 | 0.71284 (2) | 0.50588 (2) | 0.54926 (2) | 0.01171 (4) |
| Br1 | 0.78673 (2) | -0.02916 (2) | 0.16762 (2) | 0.02100 (4) |
| C11 | 0.59223 (17) | 0.53634 (16) | 0.71522 (10) | 0.0144 (2) |
| O11 | 0.61079 (14) | 0.44311 (12) | 0.64783 (8) | 0.01633 (18) |
| C12 | 0.65390 (17) | 0.70528 (16) | 0.72467 (10) | 0.0145 (2) |
| C13 | 0.62837 (19) | 0.79600 (18) | 0.79975 (11) | 0.0183 (3) |
| H13 | 0.670747 | 0.908793 | 0.805476 | 0.022* |
| C14 | 0.5434 (2) | 0.72456 (19) | 0.86487 (11) | 0.0203 (3) |
| H14 | 0.528595 | 0.787163 | 0.915561 | 0.024* |
| C15 | 0.4794 (2) | 0.55819 (19) | 0.85484 (11) | 0.0205 (3) |
| H15 | 0.418098 | 0.507219 | 0.898316 | 0.025* |
| C16 | 0.5039 (2) | 0.46680 (18) | 0.78260 (11) | 0.0182 (3) |
| H16 | 0.460325 | 0.354169 | 0.778076 | 0.022* |
| C1 | 0.73956 (18) | 0.78904 (17) | 0.65882 (10) | 0.0150 (2) |
| H1 | 0.776971 | 0.901853 | 0.668905 | 0.018* |
| N2 | 0.76894 (15) | 0.71997 (13) | 0.58640 (9) | 0.01352 (19) |
| N3 | 0.85703 (16) | 0.82274 (14) | 0.53203 (9) | 0.0156 (2) |
| C4 | 0.88158 (18) | 0.74226 (16) | 0.46136 (10) | 0.0142 (2) |
| N4 | 0.96020 (18) | 0.81776 (15) | 0.39828 (10) | 0.0179 (2) |
| N5 | 0.81845 (15) | 0.57454 (13) | 0.45334 (8) | 0.01256 (19) |
| C6 | 0.83447 (17) | 0.48570 (16) | 0.38291 (10) | 0.0134 (2) |
| H6 | 0.887782 | 0.537164 | 0.336972 | 0.016* |
| C21 | 0.69562 (17) | 0.22941 (16) | 0.43607 (10) | 0.0135 (2) |
| O21 | 0.66497 (14) | 0.29247 (12) | 0.51103 (8) | 0.01554 (18) |
| C22 | 0.77713 (17) | 0.31744 (15) | 0.37102 (10) | 0.0129 (2) |
| C23 | 0.80347 (18) | 0.23840 (16) | 0.29043 (10) | 0.0145 (2) |
| H23 | 0.85878 | 0.297919 | 0.247395 | 0.017* |
| C24 | 0.75004 (18) | 0.07631 (17) | 0.27528 (11) | 0.0158 (2) |
| C25 | 0.67098 (19) | -0.01344 (17) | 0.33888 (11) | 0.0175 (2) |
| H25 | 0.635444 | -0.126036 | 0.327557 | 0.021* |
| C26 | 0.64509 (19) | 0.06105 (16) | 0.41707 (11) | 0.0168 (2) |
| H26 | 0.592223 | -0.001036 | 0.459596 | 0.02* |
C101 1.2835 (2) 0.7674 (2) 1.04820 (14) 0.0279 (3)
H10A 1.320626 0.688278 1.021153 0.042*
H10B 1.303048 0.771121 1.106951 0.045*
H10C 1.356958 0.873448 1.108389 0.042*
C102 1.0013 (2) 0.8037 (2) 1.109651 0.045*
H10D 1.008633 0.783988 1.109651 0.045*
H10E 0.872272 0.762914 1.109651 0.045*
H10F 1.062839 0.919340 1.109651 0.045*
N10 1.09055 (17) 0.72197 (16) 1.01985 (10) 0.0211 (2)
C10 0.9998 (2) 0.6113 (2) 0.91592 (12) 0.0240 (3)
H10 0.873871 0.587458 0.88718 0.029*
O10 1.06542 (18) 0.53699 (16) 0.87336 (9) 0.0302 (3)
O1 0.8463 (2) 0.27288 (17) 0.72054 (11) 0.0263 (2)
H4A 1.011 (3) 0.919 (3) 0.4152 (17) 0.032 (6)*
H4B 1.005 (3) 0.780 (3) 0.3645 (18) 0.036 (6)*
H1A 0.773 (4) 0.281 (3) 0.686 (2) 0.054 (9)*
H1B 0.911 (4) 0.349 (3) 0.764 (2) 0.044 (7)*

Atomic displacement parameters (Å²)

|           | U¹¹   | U¹²   | U¹³   | U²²   | U²³   | U³³   |
|-----------|-------|-------|-------|-------|-------|-------|
| Ni1       | 0.01357 (7) | 0.00904 (7) | 0.01292 (8) | 0.00464 (6) | 0.00502 (6) | 0.00230 (6) |
| Br1       | 0.02594 (7) | 0.01691 (7) | 0.02208 (8) | 0.00886 (6) | 0.01230 (6) | 0.00042 (5) |
| C11       | 0.0134 (5) | 0.0148 (6) | 0.0142 (6) | 0.0052 (4) | 0.0043 (4) | 0.0024 (5) |
| O11       | 0.0216 (4) | 0.0124 (4) | 0.0166 (5) | 0.0069 (4) | 0.0091 (4) | 0.0027 (4) |
| C12       | 0.0136 (5) | 0.0148 (6) | 0.0149 (6) | 0.0060 (4) | 0.0047 (4) | 0.0015 (5) |
| C13       | 0.0187 (6) | 0.0165 (6) | 0.0188 (6) | 0.0076 (5) | 0.0053 (5) | −0.0003 (5) |
| C14       | 0.0210 (6) | 0.0230 (7) | 0.0184 (6) | 0.0101 (5) | 0.0084 (5) | 0.0009 (5) |
| C15       | 0.0202 (6) | 0.0242 (7) | 0.0171 (6) | 0.0079 (5) | 0.0085 (5) | 0.0036 (5) |
| C16       | 0.0200 (6) | 0.0163 (6) | 0.0175 (6) | 0.0056 (5) | 0.0079 (5) | 0.0031 (5) |
| C1        | 0.0165 (5) | 0.0121 (5) | 0.0165 (6) | 0.0063 (4) | 0.0053 (4) | 0.0016 (4) |
| N2        | 0.0150 (4) | 0.0106 (5) | 0.0149 (5) | 0.0049 (4) | 0.0050 (4) | 0.0033 (4) |
| N3        | 0.0197 (5) | 0.0099 (5) | 0.0172 (5) | 0.0050 (4) | 0.0077 (4) | 0.0034 (4) |
| C4        | 0.0156 (5) | 0.0099 (5) | 0.0160 (6) | 0.0045 (4) | 0.0043 (4) | 0.0032 (4) |
| N4        | 0.0253 (6) | 0.0099 (5) | 0.0201 (6) | 0.0059 (4) | 0.0119 (5) | 0.0046 (4) |
| N5        | 0.0138 (4) | 0.0089 (4) | 0.0143 (5) | 0.0043 (4) | 0.0040 (4) | 0.0026 (4) |
| C6        | 0.0140 (5) | 0.0115 (5) | 0.0145 (5) | 0.0046 (4) | 0.0053 (4) | 0.0033 (4) |
| C21       | 0.0137 (5) | 0.0118 (5) | 0.0156 (6) | 0.0054 (4) | 0.0054 (4) | 0.0027 (4) |
| O21       | 0.0204 (4) | 0.0108 (4) | 0.0181 (5) | 0.0066 (3) | 0.0102 (4) | 0.0033 (3) |
| C22       | 0.0128 (5) | 0.0107 (5) | 0.0147 (5) | 0.0042 (4) | 0.0046 (4) | 0.0028 (4) |
| C23       | 0.0153 (5) | 0.0128 (5) | 0.0160 (6) | 0.0055 (4) | 0.0067 (4) | 0.0024 (5) |
| C24       | 0.0162 (5) | 0.0147 (6) | 0.0171 (6) | 0.0067 (5) | 0.0064 (5) | 0.0010 (5) |
| C25       | 0.0201 (6) | 0.0112 (5) | 0.0231 (7) | 0.0066 (5) | 0.0101 (5) | 0.0023 (5) |
| C26       | 0.0193 (6) | 0.0114 (5) | 0.0223 (7) | 0.0055 (5) | 0.0116 (5) | 0.0055 (5) |
| C101      | 0.0209 (7) | 0.0330 (9) | 0.0281 (8) | 0.0103 (6) | 0.0069 (6) | 0.0046 (7) |
| C102      | 0.0314 (8) | 0.0339 (9) | 0.0292 (9) | 0.0212 (7) | 0.0060 (7) | 0.0042 (7) |
| N10       | 0.0206 (5) | 0.0228 (6) | 0.0208 (6) | 0.0097 (5) | 0.0063 (5) | 0.0062 (5) |
| C10       | 0.0248 (7) | 0.0239 (7) | 0.0210 (7) | 0.0063 (6) | 0.0083 (6) | 0.0092 (6) |
|   |    |    |    |    |    |    |    |
|---|----|----|----|----|----|----|----|
| O10 | 0.0366 (6) | 0.0287 (6) | 0.0245 (6) | 0.0094 (5) | 0.0159 (5) | 0.0038 (5) |
| O1  | 0.0294 (6) | 0.0320 (7) | 0.0224 (6) | 0.0169 (6) | 0.0092 (5) | 0.0081 (5) |

**Geometric parameters (Å, °)**

- Ni1—N2 1.8383 (11) C6—C22 1.4176 (18)
- Ni1—N5 1.8494 (11) C6—H6 0.95
- Ni1—O21 1.8515 (10) C21—O21 1.3048 (16)
- Ni1—O11 1.8562 (10) C21—C26 1.4241 (19)
- Br1—C24 1.9044 (14) C21—C22 1.4255 (19)
- C11—O11 1.3142 (17) C21—C23 1.4208 (19)
- C11—C16 1.415 (2) C23—C24 1.3651 (19)
- C11—C12 1.4228 (19) C23—H23 0.95
- C12—C13 1.413 (2) C24—C25 1.407 (2)
- C12—C1 1.433 (2) C25—C26 1.370 (2)
- C13—C14 1.379 (2) C25—H25 0.95
- C13—H13 0.95 C26—H26 0.95
- C14—C15 1.398 (2) C101—N10 1.452 (2)
- C14—H14 0.95 C101—H10A 0.98
- C15—C16 1.382 (2) C101—H10B 0.98
- C15—H15 0.95 C101—H10C 0.98
- C16—H16 0.95 C102—N10 1.453 (2)
- C1—N2 1.2947 (18) C102—H10D 0.98
- C1—H1 0.95 C102—H10E 0.98
- N2—N3 1.3926 (16) C102—H10F 0.98
- N3—C4 1.3069 (18) N10—C10 1.327 (2)
- C4—N4 1.3423 (18) C10—O10 1.233 (2)
- C4—N5 1.4133 (17) C10—H10 0.95
- N4—H4A 0.85 (2) O1—H1A 0.72 (3)
- N4—H4B 0.81 (2) O1—H1B 0.80 (3)
- N5—C6 1.3095 (17)

- N2—Ni1—N5 83.08 (5) N5—C6—C22 124.01 (12)
- N2—Ni1—O21 177.80 (5) N5—C6—H6 118
- N5—Ni1—O21 95.25 (5) C22—C6—H6 118
- N2—Ni1—O11 95.35 (5) O21—C21—C26 118.42 (12)
- N5—Ni1—O11 178.29 (5) O21—C21—C22 124.57 (12)
- O21—Ni1—O11 86.30 (4) C26—C21—C22 117.02 (12)
- O11—C11—C16 119.03 (13) C21—O21—Ni1 126.68 (9)
- O11—C11—C12 124.05 (12) C6—C22—C23 117.06 (12)
- C16—C11—C12 116.91 (12) C6—C22—C21 12.19 (12)
- C11—O11—Ni1 126.59 (9) C23—C22—C21 120.75 (12)
- C13—C12—C11 120.07 (13) C24—C23—C22 119.52 (13)
- C13—C12—C1 117.68 (13) C24—C23—H23 120.2
- C11—C12—C1 122.24 (12) C22—C23—H23 120.2
- C14—C13—C12 121.51 (14) C23—C24—C25 120.99 (13)
- C14—C13—H13 119.2 C23—C24—Br1 119.43 (11)
- C12—C13—H13 119.2 C25—C24—Br1 119.57 (10)
| Bond                        | Angle (°)         | Bond                        | Angle (°)         | Bond                        | Angle (°)         |
|-----------------------------|-------------------|-----------------------------|-------------------|-----------------------------|-------------------|
| C13—C14—C15                | 118.70 (14)       | C26—C25—C24                | 120.21 (13)       |
| C13—C14—H14                | 120.7             | C26—C25—H25                | 119.9             |
| C15—C14—H14                | 120.7             | C24—C25—H25                | 119.9             |
| C16—C15—C14                | 120.97 (14)       | C25—C26—C21                | 121.51 (13)       |
| C16—C15—H15                | 119.5             | C25—C26—H26                | 119.2             |
| C14—C15—H15                | 119.5             | C21—C26—H26                | 119.2             |
| C15—C16—C11                | 121.82 (14)       | N10—C101—H10A              | 109.5             |
| C15—C16—H16                | 119.1             | N10—C101—H10B              | 109.5             |
| C11—C16—H16                | 119.1             | H10A—C101—H10B             | 109.5             |
| N2—C1—C12                  | 123.84 (13)       | N10—C101—H10C              | 109.5             |
| N2—C1—H1                   | 118.1             | H10A—C101—H10C             | 109.5             |
| C12—C1—H1                  | 118.1             | H10B—C101—H10C             | 109.5             |
| C1—N2—N3                   | 115.09 (12)       | N10—C102—H10D              | 109.5             |
| C1—N2—Ni1                  | 127.91 (10)       | N10—C102—H10E              | 109.5             |
| N3—N2—Ni1                  | 116.98 (9)        | H10D—C102—H10E             | 109.5             |
| C4—N3—N2                   | 110.50 (11)       | N10—C102—H10F              | 109.5             |
| N3—C4—N4                   | 120.38 (12)       | H10D—C102—H10F             | 109.5             |
| N3—C4—N5                   | 117.40 (12)       | H10E—C102—H10F             | 109.5             |
| N4—C4—N5                   | 122.21 (12)       | C10—N10—C101               | 121.63 (14)       |
| C4—N4—H4A                  | 114.7 (15)        | C10—N10—C102               | 121.41 (14)       |
| C4—N4—H4B                  | 123.3 (17)        | C101—N10—C102              | 116.96 (14)       |
| H4A—N4—H4B                 | 115 (2)           | O10—C10—N10                | 125.34 (16)       |
| C6—N5—C4                   | 120.76 (12)       | O10—C10—H10                | 117.3             |
| C6—N5—Ni1                  | 127.20 (9)        | N10—C10—H10                | 117.3             |
| C4—N5—Ni1                  | 112.02 (9)        | H1A—O1—H1B                 | 115 (3)           |
| C16—C11—O11—Ni1            | 177.39 (10)       | N3—C4—N5—Ni1               | −0.36 (15)        |
| C12—C11—O11—Ni1            | −1.81 (19)        | N4—C4—N5—Ni1               | −178.86 (11)      |
| N2—Ni1—O11—C11             | 1.06 (12)         | N2—Ni1—N5—C6               | −178.04 (12)      |
| O21—Ni1—O11—C11            | 179.59 (11)       | O21—Ni1—N5—C6              | 3.41 (12)         |
| O11—C11—C12—C13            | −179.83 (13)      | N2—Ni1—N5—C4               | 0.59 (9)          |
| C16—C11—C12—C13            | 0.96 (19)         | O21—Ni1—N5—C4              | −177.96 (9)       |
| O11—C11—C12—C1             | 1.4 (2)           | C4—N5—C6—C22               | 178.98 (12)       |
| C16—C11—C12—C1             | −177.81 (13)      | Ni1—N5—C6—C22              | −2.50 (19)        |
| C11—C12—C13—C14            | −0.3 (2)          | C26—C21—O21—Ni1            | −178.48 (9)       |
| C1—C12—C13—C14             | 178.49 (13)       | C22—C21—O21—Ni1            | 1.61 (19)         |
| C12—C13—C14—C15            | −0.9 (2)          | N5—Ni1—O21—C21             | −2.96 (11)        |
| C13—C14—C15—C16            | 1.4 (2)           | O11—Ni1—O21—C21            | 177.76 (11)       |
| C14—C15—C16—C11            | −0.8 (2)          | N5—C6—C22—C23              | 179.74 (12)       |
| O11—C11—C16—C15            | −179.68 (13)      | N5—C6—C22—C21              | 0.0 (2)           |
| C12—C11—C16—C15            | −0.4 (2)          | O21—C21—C22—C6             | 0.4 (2)           |
| C13—C12—C1—N2              | −179.16 (13)      | C26—C21—C22—C6             | −179.48 (12)      |
| C11—C12—C1—N2              | −0.4 (2)          | O21—C21—C22—C23            | −179.27 (13)      |
| C12—C1—N2—Ni1              | −178.84 (12)      | C26—C21—C22—C23            | 0.82 (18)         |
| C12—C1—N2—Ni1              | −0.2 (2)          | C6—C22—C23—C24             | −179.73 (12)      |
| N5—Ni1—N2—C1               | −179.40 (13)      | C21—C22—C23—C24            | −0.02 (19)        |
| O11—Ni1—N2—C1              | −0.08 (13)        | C22—C23—C24—C25            | −0.7 (2)          |
| N5—Ni1—N2—N3               | −0.76 (9)         | C22—C23—C24—Br1            | −179.66 (10)      |

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O11—Ni1—N2—N3 178.56 (9)  C23—C24—C25—C26 0.5 (2)
C1—N2—N3—C4 179.55 (12)  Br1—C24—C25—C26 179.49 (11)
Ni1—N2—N3—C4  0.73 (14)  C24—C25—C26—C21 0.4 (2)
N2—N3—C4—N4  178.31 (12)  O21—C21—C26—C25 179.09 (13)
N2—N3—C4—N5 −0.22 (17)  C22—C21—C26—C25 −1.0 (2)
N3—C4—N5—C6  178.37 (12)  C101—N10—C10—O10 0.1 (3)
N4—C4—N5—C6 −0.1 (2)  C102—N10—C10—O10 179.88 (17)

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A  | D····A | D—H···A |
|-----------|------|-------|--------|---------|
| N4—H4A···N3\(^i\) | 0.85 (2) | 2.16 (2) | 3.0116 (17) | 176 (2) |
| N4—H4B···O1\(^ii\) | 0.81 (2) | 2.09 (2) | 2.8900 (19) | 169 (2) |
| O1—H1A···O11 | 0.72 (3) | 2.38 (3) | 3.0056 (17) | 146 (3) |
| O1—H1A···O21 | 0.72 (3) | 2.48 (3) | 3.0719 (18) | 141 (3) |
| O1—H1B···O10 | 0.80 (3) | 1.97 (3) | 2.772 (2) | 178 (3) |

Symmetry codes: (i) −x+2, −y+2, −z+1; (ii) −x+2, −y+1, −z+1.