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Bis(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4N)(μ -L-malato- $\kappa^4O^1,O^2:O^4,O^4'$)dinickel(II) bis(perchlorate) monohydrate

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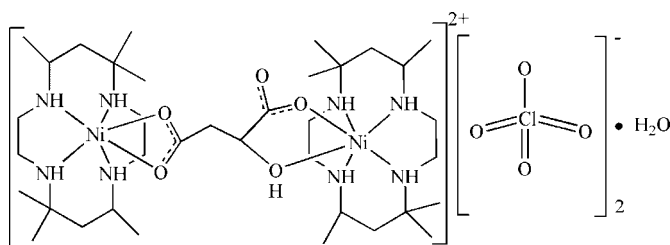
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.009$ Å; disorder in solvent or counterion; R factor = 0.043; wR factor = 0.123; data-to-parameter ratio = 17.0.

In the crystal structure of the title dinuclear compound, $[Ni_2(C_4H_4O_5)(C_{16}H_{36}N_4)_2](ClO_4)_2 \cdot H_2O$, the bridging dicarboxylate dianion O, O' -chelates to two Ni atoms, both of which are also chelated by the N-macrocylic ligand. The Ni atoms exhibit a distorted octahedral coordination. $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds link the cations and the uncoordinated water molecules into a layer structure; the perchlorate anions occupy the space between adjacent layers, and are only weakly linked to the layers. One of the perchlorate anions is disordered over two sets of sites in a 3:2 ratio.

Related literature

For the nickel phthalate perchlorate hydrate derivative of the macrocycle, see: Ou & Zhang (2009).



Experimental

Crystal data

$[Ni_2(C_4H_4O_5)(C_{16}H_{36}N_4)_2](ClO_4)_2 \cdot H_2O$ $M_r = 1035.38$
Orthorhombic, $P2_12_12_1$

$a = 13.562(2)$ Å
 $b = 18.984(2)$ Å
 $c = 19.350(3)$ Å
 $V = 4982(1)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.93$ mm⁻¹
 $T = 293$ K
 $0.48 \times 0.45 \times 0.34$ mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.605, T_{max} = 0.730$

42585 measured reflections
10997 independent reflections
7769 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.123$
 $S = 1.03$
10997 reflections
647 parameters
79 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.41$ e Å⁻³
 $\Delta\rho_{min} = -0.38$ e Å⁻³
Absolute structure: Flack (1983), 4936 Friedel pairs
Flack parameter: $-0.01(2)$

Table 1
Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------|----------|--------------|--------------|----------------|
| $N2-H2 \cdots O6^i$ | 0.84 (5) | 2.41 (2) | 3.230 (7) | 165 (6) |
| $N5-H5 \cdots O2^{ii}$ | 0.85 (5) | 2.14 (3) | 2.940 (6) | 158 (6) |
| $N7-H7 \cdots O2^{ii}$ | 0.85 (2) | 2.06 (2) | 2.869 (5) | 160 (6) |
| $O1w-H11 \cdots O5$ | 0.86 (9) | 2.09 (7) | 2.862 (9) | 149 (12) |
| $O1w-H12 \cdots O6$ | 0.86 (9) | 2.05 (8) | 2.784 (12) | 143 (13) |

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2535).

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supplementary materials

Acta Cryst. (2009). E65, m728 [doi:10.1107/S1600536809020662]

Bis(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4N)(μ -L-malato- $\kappa^4O^1,O^2;O^4,O^4'$)dinickel(II) bis(perchlorate) monohydrate

G.-C. Ou, Q. Zhou and S. W. Ng

Experimental

L-Malic acid (0.13 g, 1 mmol) was neutralized with sodium hydroxide (0.08 g, 2 mmol) in water (10 ml). To this solution was added (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel perchlorate (0.54 g, 1 mmol) dissolved in acetonitrile (10 ml). The solution was left to stand at room temperature; blue crystals formed after several weeks.

Refinement

Carbon bound H-atoms were positioned geometrically and refined using the riding model, with C—H = 0.93 to 0.98 Å and $U(H)$ set to 1.2–1.5 $U_{eq}(C)$.

H atoms attached to the N- and O-atoms were located in difference Fourier maps and were refined with a distance restraint of N—H = O—H = 0.85±0.01 Å; their temperature factors were restrained to 1.5 times $U_{eq}(N,O)$.

One of the two anions is disordered over two positions. The Cl—O distance was restrained to 1.45±0.01 Å and the O···O distance to 2.37±0.02 Å. The anisotropic temperature factors of the oxygen atoms were restrained to be nearly isotropic. The disorder refined to a 3:2 ratio.

Figures

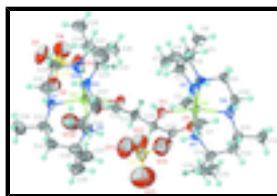


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $[\text{Ni}_2(\text{C}_{16}\text{H}_{36}\text{N}_4)_2(\text{C}_4\text{H}_4\text{O}_5)]^{2+} \cdot 2(\text{ClO}_4)^- \cdot \text{H}_2\text{O}$ showing displacement ellipsoids of the dincular salt hydrate at the 50% probability level. H-atoms are drawn as spheres of arbitrary radii. The disorder in the perchlorate is not shown.

Bis(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4N)(μ -L-malato- $\kappa^4O^1,O^2;O^4,O^4'$)dinickel(II) bis(perchlorate) monohydrate

Crystal data

$[\text{Ni}_2(\text{C}_4\text{H}_4\text{O}_5)(\text{C}_{16}\text{H}_{36}\text{N}_4)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

$M_r = 1035.38$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 13.562(2)$ Å

$F_{000} = 2208$

$D_x = 1.381$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1019 reflections

$\theta = 2.8$ – 22.5°

supplementary materials

$b = 18.984 (2) \text{ \AA}$
 $c = 19.350 (3) \text{ \AA}$
 $V = 4982 (1) \text{ \AA}^3$
 $Z = 4$

$\mu = 0.93 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
Block, blue
 $0.48 \times 0.45 \times 0.34 \text{ mm}$

Data collection

Bruker SMART area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
 $T = 293 \text{ K}$
 φ and ω scans
Absorption correction: Multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.605$, $T_{\max} = 0.730$
42585 measured reflections

10997 independent reflections
7769 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\max} = 27.2^\circ$
 $\theta_{\min} = 1.8^\circ$
 $h = -17 \rightarrow 17$
 $k = -24 \rightarrow 24$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.123$
 $S = 1.03$
10997 reflections
647 parameters
79 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 1.0201P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$
Extinction correction: none
Absolute structure: Flack (Flack, 1983), 4936 Friedel pairs
Flack parameter: $-0.01 (2)$

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|--------------|--------------|----------------------------------|------------|
| Ni1 | 0.12840 (5) | 0.77230 (3) | 0.82955 (3) | 0.03650 (16) | |
| Ni2 | 0.54780 (5) | 0.96584 (3) | 0.76686 (3) | 0.04267 (17) | |
| Cl1 | 0.82095 (12) | 0.87472 (8) | 0.96151 (9) | 0.0635 (4) | |
| Cl2 | 0.2212 (4) | 0.9094 (3) | 0.5860 (2) | 0.0694 (15) | 0.603 (15) |
| Cl2' | 0.2343 (12) | 0.8981 (10) | 0.5917 (8) | 0.184 (9) | 0.397 (15) |
| O1 | 0.2141 (2) | 0.68426 (16) | 0.81902 (18) | 0.0410 (8) | |
| O2 | 0.3574 (3) | 0.63875 (18) | 0.7861 (2) | 0.0589 (11) | |
| O3 | 0.2686 (2) | 0.81315 (17) | 0.79792 (18) | 0.0430 (8) | |
| H3O | 0.2801 | 0.8566 | 0.7964 | 0.052* | |

| | | | | | |
|------|-------------|--------------|-------------|-------------|------------|
| O4 | 0.4208 (3) | 0.89861 (18) | 0.7931 (2) | 0.0483 (9) | |
| O5 | 0.5716 (3) | 0.85639 (19) | 0.7953 (2) | 0.0520 (9) | |
| O6 | 0.8605 (4) | 0.8321 (3) | 0.9084 (3) | 0.1028 (18) | |
| O7 | 0.8598 (5) | 0.9427 (3) | 0.9528 (4) | 0.120 (2) | |
| O8 | 0.8508 (5) | 0.8471 (4) | 1.0255 (3) | 0.121 (2) | |
| O9 | 0.7173 (3) | 0.8767 (3) | 0.9558 (3) | 0.0895 (16) | |
| O10 | 0.1180 (7) | 0.9240 (9) | 0.6026 (8) | 0.145 (6) | 0.603 (15) |
| O11 | 0.2768 (10) | 0.8832 (8) | 0.6437 (6) | 0.130 (5) | 0.603 (15) |
| O12 | 0.2533 (11) | 0.9786 (6) | 0.5709 (8) | 0.159 (6) | 0.603 (15) |
| O13 | 0.2280 (19) | 0.8633 (11) | 0.5287 (9) | 0.254 (12) | 0.603 (15) |
| O10' | 0.237 (3) | 0.9458 (18) | 0.6497 (14) | 0.29 (2) | 0.397 (15) |
| O11' | 0.2788 (14) | 0.9246 (12) | 0.5304 (10) | 0.131 (8) | 0.397 (15) |
| O12' | 0.281 (2) | 0.8324 (15) | 0.6114 (19) | 0.30 (2) | 0.397 (15) |
| O13' | 0.1331 (14) | 0.8814 (14) | 0.5764 (12) | 0.153 (9) | 0.397 (15) |
| O1W | 0.7584 (7) | 0.7864 (6) | 0.7920 (5) | 0.147 (3) | |
| H11 | 0.701 (5) | 0.800 (8) | 0.778 (7) | 0.221* | |
| H12 | 0.762 (11) | 0.804 (8) | 0.833 (3) | 0.221* | |
| N1 | 0.0790 (3) | 0.7848 (2) | 0.7234 (2) | 0.0475 (10) | |
| H1 | 0.132 (3) | 0.796 (3) | 0.703 (3) | 0.071* | |
| N2 | 0.0713 (3) | 0.8748 (2) | 0.8429 (2) | 0.0434 (10) | |
| H2 | 0.015 (2) | 0.872 (3) | 0.861 (3) | 0.065* | |
| N3 | 0.1520 (3) | 0.7656 (2) | 0.9405 (2) | 0.0411 (10) | |
| H3 | 0.200 (5) | 0.736 (3) | 0.948 (3) | 0.062* | |
| N4 | 0.0065 (3) | 0.7076 (2) | 0.8493 (2) | 0.0441 (10) | |
| H4 | -0.042 (3) | 0.735 (3) | 0.851 (3) | 0.066* | |
| N5 | 0.4683 (3) | 1.0599 (2) | 0.7605 (2) | 0.0481 (11) | |
| H5 | 0.508 (4) | 1.092 (2) | 0.748 (3) | 0.072* | |
| N6 | 0.5049 (4) | 0.9492 (3) | 0.6629 (2) | 0.0558 (12) | |
| H6 | 0.454 (3) | 0.922 (3) | 0.661 (4) | 0.084* | |
| N7 | 0.6895 (3) | 0.9928 (2) | 0.7340 (2) | 0.0421 (9) | |
| H7 | 0.690 (4) | 1.0362 (10) | 0.723 (3) | 0.063* | |
| N8 | 0.5986 (3) | 0.9947 (2) | 0.8667 (2) | 0.0456 (10) | |
| H8 | 0.610 (5) | 0.9529 (14) | 0.880 (3) | 0.068* | |
| C1 | 0.0142 (5) | 0.8480 (3) | 0.7268 (3) | 0.0592 (15) | |
| H1A | -0.0499 | 0.8349 | 0.7450 | 0.071* | |
| H1B | 0.0048 | 0.8670 | 0.6807 | 0.071* | |
| C2 | 0.0603 (5) | 0.9028 (3) | 0.7724 (3) | 0.0547 (14) | |
| H2A | 0.1244 | 0.9158 | 0.7543 | 0.066* | |
| H2B | 0.0192 | 0.9446 | 0.7733 | 0.066* | |
| C3 | 0.1289 (5) | 0.9216 (3) | 0.8894 (3) | 0.0486 (12) | |
| H3a | 0.1979 | 0.9196 | 0.8745 | 0.058* | |
| C4 | 0.0963 (6) | 0.9980 (3) | 0.8861 (4) | 0.0730 (19) | |
| H4A | 0.1147 | 1.0176 | 0.8422 | 0.109* | |
| H4B | 0.1276 | 1.0241 | 0.9225 | 0.109* | |
| H4C | 0.0260 | 1.0006 | 0.8914 | 0.109* | |
| C5 | 0.1246 (4) | 0.8945 (3) | 0.9628 (3) | 0.0496 (13) | |
| H5A | 0.0560 | 0.8849 | 0.9735 | 0.059* | |
| H5B | 0.1454 | 0.9325 | 0.9930 | 0.059* | |
| C6 | 0.1849 (4) | 0.8283 (3) | 0.9827 (3) | 0.0475 (13) | |

supplementary materials

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|------|-------------|------------|------------|-------------|
| C7 | 0.2919 (4) | 0.8393 (4) | 0.9707 (3) | 0.0617 (16) |
| H7A | 0.3030 | 0.8502 | 0.9229 | 0.093* |
| H7B | 0.3272 | 0.7971 | 0.9826 | 0.093* |
| H7C | 0.3149 | 0.8775 | 0.9989 | 0.093* |
| C8 | 0.1688 (5) | 0.8155 (4) | 1.0609 (3) | 0.0663 (17) |
| H8A | 0.1966 | 0.7708 | 1.0736 | 0.099* |
| H8B | 0.0995 | 0.8154 | 1.0708 | 0.099* |
| H8C | 0.2004 | 0.8522 | 1.0868 | 0.099* |
| C9 | 0.0614 (4) | 0.7314 (3) | 0.9669 (3) | 0.0479 (12) |
| H9A | 0.0098 | 0.7663 | 0.9724 | 0.057* |
| H9B | 0.0744 | 0.7104 | 1.0117 | 0.057* |
| C10 | 0.0286 (4) | 0.6755 (3) | 0.9168 (3) | 0.0476 (13) |
| H10A | 0.0802 | 0.6405 | 0.9116 | 0.057* |
| H10B | -0.0298 | 0.6521 | 0.9345 | 0.057* |
| C11 | -0.0160 (4) | 0.6528 (3) | 0.7949 (3) | 0.0508 (13) |
| H11A | 0.0440 | 0.6251 | 0.7871 | 0.061* |
| C12 | -0.0966 (6) | 0.6027 (4) | 0.8186 (4) | 0.081 (2) |
| H12A | -0.1108 | 0.5697 | 0.7824 | 0.121* |
| H12B | -0.1550 | 0.6291 | 0.8294 | 0.121* |
| H12C | -0.0748 | 0.5778 | 0.8590 | 0.121* |
| C13 | -0.0437 (4) | 0.6878 (3) | 0.7277 (3) | 0.0582 (14) |
| H13A | -0.0940 | 0.7225 | 0.7380 | 0.070* |
| H13B | -0.0745 | 0.6522 | 0.6989 | 0.070* |
| C14 | 0.0346 (4) | 0.7242 (3) | 0.6839 (3) | 0.0547 (14) |
| C15 | -0.0159 (6) | 0.7498 (4) | 0.6154 (3) | 0.081 (2) |
| H15A | -0.0742 | 0.7763 | 0.6264 | 0.122* |
| H15B | -0.0336 | 0.7098 | 0.5878 | 0.122* |
| H15C | 0.0291 | 0.7791 | 0.5901 | 0.122* |
| C16 | 0.1187 (5) | 0.6740 (3) | 0.6648 (3) | 0.0664 (16) |
| H16A | 0.1491 | 0.6565 | 0.7061 | 0.100* |
| H16B | 0.1667 | 0.6988 | 0.6377 | 0.100* |
| H16C | 0.0929 | 0.6353 | 0.6385 | 0.100* |
| C17 | 0.4060 (5) | 1.0505 (4) | 0.6974 (3) | 0.0677 (18) |
| H17A | 0.3508 | 1.0198 | 0.7079 | 0.081* |
| H17B | 0.3801 | 1.0958 | 0.6828 | 0.081* |
| C18 | 0.4658 (5) | 1.0195 (3) | 0.6410 (3) | 0.0686 (18) |
| H18A | 0.5202 | 1.0506 | 0.6299 | 0.082* |
| H18B | 0.4255 | 1.0140 | 0.6000 | 0.082* |
| C19 | 0.5745 (6) | 0.9148 (4) | 0.6122 (3) | 0.073 (2) |
| C20 | 0.5342 (7) | 0.9181 (5) | 0.5379 (4) | 0.103 (3) |
| H20A | 0.5351 | 0.9660 | 0.5219 | 0.154* |
| H20B | 0.4677 | 0.9007 | 0.5371 | 0.154* |
| H20C | 0.5746 | 0.8897 | 0.5082 | 0.154* |
| C21 | 0.5837 (7) | 0.8374 (4) | 0.6313 (4) | 0.096 (3) |
| H21A | 0.6043 | 0.8333 | 0.6786 | 0.144* |
| H21B | 0.6316 | 0.8153 | 0.6019 | 0.144* |
| H21C | 0.5210 | 0.8146 | 0.6255 | 0.144* |
| C22 | 0.6739 (5) | 0.9521 (4) | 0.6130 (3) | 0.0643 (16) |
| H22A | 0.7134 | 0.9318 | 0.5763 | 0.077* |

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|------|------------|------------|------------|-------------|
| H22B | 0.6623 | 1.0009 | 0.6007 | 0.077* |
| C23 | 0.7364 (5) | 0.9517 (3) | 0.6780 (3) | 0.0576 (15) |
| H23 | 0.7438 | 0.9029 | 0.6936 | 0.069* |
| C24 | 0.8386 (5) | 0.9808 (5) | 0.6604 (4) | 0.083 (2) |
| H24A | 0.8750 | 0.9886 | 0.7022 | 0.124* |
| H24B | 0.8317 | 1.0246 | 0.6359 | 0.124* |
| H24C | 0.8732 | 0.9476 | 0.6319 | 0.124* |
| C25 | 0.7485 (4) | 0.9935 (3) | 0.7985 (3) | 0.0495 (13) |
| H25A | 0.8109 | 1.0169 | 0.7903 | 0.059* |
| H25B | 0.7621 | 0.9455 | 0.8129 | 0.059* |
| C26 | 0.6935 (4) | 1.0309 (3) | 0.8540 (3) | 0.0519 (13) |
| H26A | 0.7323 | 1.0314 | 0.8961 | 0.062* |
| H26B | 0.6814 | 1.0792 | 0.8402 | 0.062* |
| C27 | 0.5318 (4) | 1.0307 (3) | 0.9167 (3) | 0.0549 (13) |
| C28 | 0.4578 (5) | 0.9774 (3) | 0.9420 (3) | 0.0734 (18) |
| H28A | 0.4230 | 0.9579 | 0.9032 | 0.110* |
| H28B | 0.4118 | 1.0000 | 0.9725 | 0.110* |
| H28C | 0.4914 | 0.9405 | 0.9663 | 0.110* |
| C29 | 0.5892 (6) | 1.0587 (4) | 0.9801 (4) | 0.085 (2) |
| H29A | 0.6321 | 1.0963 | 0.9659 | 0.127* |
| H29B | 0.6276 | 1.0213 | 0.9998 | 0.127* |
| H29C | 0.5434 | 1.0760 | 1.0139 | 0.127* |
| C30 | 0.4802 (5) | 1.0937 (3) | 0.8827 (3) | 0.0613 (16) |
| H30A | 0.4424 | 1.1177 | 0.9182 | 0.074* |
| H30B | 0.5308 | 1.1262 | 0.8673 | 0.074* |
| C31 | 0.4119 (4) | 1.0802 (3) | 0.8222 (3) | 0.0563 (15) |
| H31 | 0.3682 | 1.0410 | 0.8345 | 0.068* |
| C32 | 0.3483 (6) | 1.1456 (5) | 0.8105 (5) | 0.098 (3) |
| H32A | 0.3125 | 1.1407 | 0.7679 | 0.147* |
| H32B | 0.3898 | 1.1865 | 0.8081 | 0.147* |
| H32C | 0.3026 | 1.1507 | 0.8480 | 0.147* |
| C33 | 0.3003 (4) | 0.6883 (2) | 0.7964 (3) | 0.0396 (11) |
| C34 | 0.3416 (3) | 0.7616 (2) | 0.7795 (3) | 0.0398 (11) |
| H34 | 0.3525 | 0.7643 | 0.7295 | 0.048* |
| C35 | 0.4385 (3) | 0.7751 (3) | 0.8153 (3) | 0.0430 (11) |
| H35A | 0.4858 | 0.7399 | 0.8006 | 0.052* |
| H35B | 0.4293 | 0.7700 | 0.8648 | 0.052* |
| C36 | 0.4800 (4) | 0.8474 (3) | 0.8008 (3) | 0.0435 (12) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|-------------|-------------|-------------|--------------|--------------|
| Ni1 | 0.0370 (3) | 0.0302 (3) | 0.0422 (3) | 0.0003 (3) | 0.0024 (3) | -0.0010 (3) |
| Ni2 | 0.0445 (4) | 0.0362 (3) | 0.0472 (4) | -0.0054 (3) | -0.0047 (3) | 0.0082 (3) |
| Cl1 | 0.0550 (9) | 0.0606 (9) | 0.0750 (10) | 0.0010 (7) | -0.0042 (8) | 0.0111 (8) |
| Cl2 | 0.065 (3) | 0.087 (3) | 0.056 (2) | -0.024 (2) | -0.0080 (18) | 0.0161 (18) |
| Cl2' | 0.131 (11) | 0.207 (17) | 0.213 (18) | -0.036 (10) | -0.047 (11) | 0.041 (14) |
| O1 | 0.0395 (19) | 0.0307 (16) | 0.053 (2) | 0.0006 (14) | 0.0074 (16) | -0.0038 (15) |

supplementary materials

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|------|-------------|-------------|------------|--------------|--------------|--------------|
| O2 | 0.048 (2) | 0.0317 (18) | 0.097 (3) | 0.0023 (17) | 0.015 (2) | -0.0147 (19) |
| O3 | 0.0387 (18) | 0.0281 (16) | 0.062 (2) | 0.0007 (14) | 0.0060 (16) | 0.0005 (15) |
| O4 | 0.047 (2) | 0.0347 (18) | 0.063 (2) | -0.0022 (16) | -0.0028 (17) | 0.0084 (16) |
| O5 | 0.044 (2) | 0.042 (2) | 0.070 (2) | -0.0066 (16) | 0.0000 (18) | 0.0012 (18) |
| O6 | 0.071 (3) | 0.131 (5) | 0.107 (4) | 0.019 (3) | 0.005 (3) | -0.024 (4) |
| O7 | 0.099 (4) | 0.085 (4) | 0.175 (6) | -0.032 (3) | -0.040 (4) | 0.030 (4) |
| O8 | 0.140 (6) | 0.131 (5) | 0.090 (4) | 0.010 (5) | -0.022 (4) | 0.038 (4) |
| O9 | 0.054 (3) | 0.081 (3) | 0.133 (5) | 0.011 (2) | 0.011 (3) | 0.016 (3) |
| O10 | 0.139 (9) | 0.161 (10) | 0.135 (9) | -0.027 (8) | -0.001 (7) | 0.032 (8) |
| O11 | 0.141 (9) | 0.141 (9) | 0.107 (8) | -0.011 (7) | -0.045 (7) | 0.047 (7) |
| O12 | 0.152 (9) | 0.151 (10) | 0.175 (11) | -0.035 (8) | -0.022 (8) | 0.048 (9) |
| O13 | 0.260 (16) | 0.253 (16) | 0.249 (15) | 0.024 (12) | -0.024 (12) | -0.043 (11) |
| O10' | 0.29 (3) | 0.29 (3) | 0.30 (3) | -0.018 (13) | 0.009 (13) | -0.009 (13) |
| O11' | 0.134 (11) | 0.146 (12) | 0.114 (11) | -0.023 (9) | 0.038 (9) | 0.044 (9) |
| O12' | 0.31 (3) | 0.30 (3) | 0.29 (3) | 0.013 (13) | 0.002 (13) | 0.007 (13) |
| O13' | 0.144 (13) | 0.164 (13) | 0.152 (13) | -0.055 (11) | 0.002 (10) | 0.011 (10) |
| O1W | 0.132 (6) | 0.163 (8) | 0.147 (7) | 0.045 (6) | 0.011 (5) | -0.018 (6) |
| N1 | 0.048 (3) | 0.049 (3) | 0.045 (3) | -0.001 (2) | -0.004 (2) | -0.002 (2) |
| N2 | 0.048 (3) | 0.0305 (19) | 0.051 (3) | 0.0031 (18) | 0.000 (2) | -0.0006 (18) |
| N3 | 0.040 (2) | 0.042 (2) | 0.041 (2) | 0.0061 (19) | 0.0043 (18) | -0.0029 (18) |
| N4 | 0.039 (2) | 0.037 (2) | 0.056 (3) | -0.0009 (18) | 0.005 (2) | -0.0022 (19) |
| N5 | 0.041 (2) | 0.041 (2) | 0.062 (3) | -0.0029 (18) | -0.004 (2) | 0.013 (2) |
| N6 | 0.066 (3) | 0.058 (3) | 0.043 (2) | -0.023 (2) | -0.010 (2) | 0.009 (2) |
| N7 | 0.045 (2) | 0.034 (2) | 0.047 (2) | -0.0017 (18) | 0.001 (2) | 0.005 (2) |
| N8 | 0.051 (3) | 0.038 (2) | 0.048 (3) | 0.000 (2) | -0.003 (2) | 0.003 (2) |
| C1 | 0.075 (4) | 0.047 (3) | 0.056 (3) | 0.010 (3) | -0.013 (3) | 0.004 (3) |
| C2 | 0.070 (4) | 0.040 (3) | 0.054 (3) | 0.013 (3) | -0.004 (3) | 0.007 (2) |
| C3 | 0.058 (3) | 0.037 (3) | 0.051 (3) | 0.002 (3) | 0.002 (3) | -0.007 (2) |
| C4 | 0.111 (6) | 0.040 (3) | 0.067 (4) | 0.002 (3) | 0.005 (4) | -0.011 (3) |
| C5 | 0.054 (3) | 0.047 (3) | 0.048 (3) | 0.003 (3) | 0.004 (3) | -0.011 (2) |
| C6 | 0.058 (3) | 0.047 (3) | 0.038 (3) | -0.002 (3) | -0.003 (2) | -0.009 (2) |
| C7 | 0.053 (3) | 0.074 (4) | 0.059 (4) | -0.008 (3) | -0.002 (3) | -0.011 (3) |
| C8 | 0.090 (5) | 0.063 (4) | 0.046 (3) | 0.010 (3) | 0.002 (3) | -0.004 (3) |
| C9 | 0.044 (3) | 0.050 (3) | 0.049 (3) | 0.006 (3) | 0.008 (2) | 0.000 (2) |
| C10 | 0.044 (3) | 0.042 (3) | 0.057 (3) | -0.002 (2) | 0.011 (3) | 0.006 (2) |
| C11 | 0.049 (3) | 0.040 (3) | 0.062 (3) | -0.005 (2) | 0.001 (3) | -0.009 (3) |
| C12 | 0.085 (5) | 0.071 (4) | 0.086 (5) | -0.036 (4) | 0.012 (4) | -0.020 (4) |
| C13 | 0.052 (3) | 0.054 (3) | 0.068 (4) | -0.006 (3) | -0.009 (3) | -0.015 (3) |
| C14 | 0.057 (3) | 0.056 (3) | 0.051 (3) | -0.004 (3) | -0.008 (3) | -0.011 (3) |
| C15 | 0.107 (6) | 0.076 (5) | 0.061 (4) | -0.005 (4) | -0.021 (4) | -0.008 (3) |
| C16 | 0.077 (4) | 0.062 (4) | 0.059 (4) | 0.002 (3) | 0.006 (4) | -0.019 (3) |
| C17 | 0.056 (4) | 0.077 (4) | 0.070 (4) | 0.001 (3) | -0.020 (3) | 0.026 (4) |
| C18 | 0.070 (4) | 0.073 (4) | 0.063 (4) | -0.011 (3) | -0.019 (3) | 0.029 (3) |
| C19 | 0.105 (6) | 0.072 (4) | 0.044 (3) | -0.015 (4) | 0.003 (4) | 0.000 (3) |
| C20 | 0.124 (7) | 0.134 (7) | 0.050 (4) | -0.035 (6) | -0.009 (4) | -0.011 (4) |
| C21 | 0.143 (8) | 0.068 (5) | 0.076 (5) | -0.019 (5) | 0.015 (5) | -0.012 (4) |
| C22 | 0.074 (4) | 0.070 (4) | 0.049 (3) | -0.005 (3) | 0.009 (3) | 0.003 (3) |
| C23 | 0.074 (4) | 0.046 (3) | 0.053 (3) | 0.014 (3) | 0.006 (3) | 0.006 (3) |
| C24 | 0.063 (4) | 0.118 (6) | 0.067 (4) | 0.017 (4) | 0.007 (3) | 0.009 (4) |

| | | | | | | |
|-----|-----------|-----------|-----------|------------|------------|------------|
| C25 | 0.040 (3) | 0.051 (3) | 0.058 (3) | -0.003 (2) | -0.004 (3) | -0.003 (3) |
| C26 | 0.049 (3) | 0.048 (3) | 0.058 (3) | -0.001 (3) | -0.014 (3) | -0.003 (3) |
| C27 | 0.065 (4) | 0.055 (3) | 0.045 (3) | 0.002 (3) | -0.001 (3) | -0.003 (3) |
| C28 | 0.090 (5) | 0.067 (4) | 0.063 (4) | -0.002 (4) | 0.027 (4) | 0.003 (3) |
| C29 | 0.087 (5) | 0.100 (6) | 0.067 (4) | 0.012 (4) | -0.004 (4) | -0.022 (4) |
| C30 | 0.065 (4) | 0.047 (3) | 0.072 (4) | -0.001 (3) | 0.005 (3) | -0.006 (3) |
| C31 | 0.043 (3) | 0.048 (3) | 0.078 (4) | -0.002 (2) | -0.003 (3) | 0.007 (3) |
| C32 | 0.081 (5) | 0.104 (6) | 0.108 (6) | 0.040 (5) | -0.005 (5) | -0.005 (5) |
| C33 | 0.042 (3) | 0.030 (2) | 0.047 (3) | 0.001 (2) | 0.001 (2) | -0.010 (2) |
| C34 | 0.039 (3) | 0.035 (2) | 0.045 (3) | 0.000 (2) | 0.005 (2) | -0.002 (2) |
| C35 | 0.041 (3) | 0.033 (2) | 0.055 (3) | 0.001 (2) | 0.002 (2) | 0.005 (2) |
| C36 | 0.045 (3) | 0.037 (3) | 0.049 (3) | -0.004 (2) | 0.001 (2) | 0.000 (2) |

Geometric parameters (Å, °)

| | | | |
|-----------|------------|----------|------------|
| Ni1—O1 | 2.046 (3) | C8—H8A | 0.9600 |
| Ni1—N4 | 2.094 (4) | C8—H8B | 0.9600 |
| Ni1—N2 | 2.110 (4) | C8—H8C | 0.9600 |
| Ni1—O3 | 2.142 (3) | C9—C10 | 1.505 (8) |
| Ni1—N1 | 2.174 (4) | C9—H9A | 0.9700 |
| Ni1—N3 | 2.173 (4) | C9—H9B | 0.9700 |
| Ni2—N7 | 2.087 (4) | C10—H10A | 0.9700 |
| Ni2—N5 | 2.090 (4) | C10—H10B | 0.9700 |
| Ni2—N6 | 2.117 (5) | C11—C13 | 1.508 (8) |
| Ni2—N8 | 2.122 (5) | C11—C12 | 1.519 (8) |
| Ni2—O5 | 2.174 (4) | C11—H11A | 0.9800 |
| Ni2—O4 | 2.203 (4) | C12—H12A | 0.9600 |
| Ni2—C36 | 2.516 (5) | C12—H12B | 0.9600 |
| C11—O8 | 1.405 (6) | C12—H12C | 0.9600 |
| C11—O7 | 1.405 (6) | C13—C14 | 1.524 (9) |
| C11—O9 | 1.411 (5) | C13—H13A | 0.9700 |
| C11—O6 | 1.414 (6) | C13—H13B | 0.9700 |
| C12—O13 | 1.416 (10) | C14—C16 | 1.531 (9) |
| C12—O11 | 1.435 (9) | C14—C15 | 1.570 (9) |
| C12—O12 | 1.415 (10) | C15—H15A | 0.9600 |
| C12—O10 | 1.463 (10) | C15—H15B | 0.9600 |
| C12'—O12' | 1.446 (12) | C15—H15C | 0.9600 |
| C12'—O11' | 1.424 (11) | C16—H16A | 0.9600 |
| C12'—O10' | 1.443 (12) | C16—H16B | 0.9600 |
| C12'—O13' | 1.439 (12) | C16—H16C | 0.9600 |
| O1—C33 | 1.250 (6) | C17—C18 | 1.481 (10) |
| O2—C33 | 1.234 (6) | C17—H17A | 0.9700 |
| O3—C34 | 1.438 (6) | C17—H17B | 0.9700 |
| O3—H3O | 0.8400 | C18—H18A | 0.9700 |
| O4—C36 | 1.270 (6) | C18—H18B | 0.9700 |
| O5—C36 | 1.257 (6) | C19—C22 | 1.523 (9) |
| O1W—H11 | 0.86 (9) | C19—C21 | 1.522 (10) |
| O1W—H12 | 0.86 (9) | C19—C20 | 1.540 (10) |
| N1—C1 | 1.489 (7) | C20—H20A | 0.9600 |

supplementary materials

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|-----------|-------------|-------------|-----------|
| N1—C14 | 1.506 (7) | C20—H20B | 0.9600 |
| N1—H1 | 0.85 (5) | C20—H20C | 0.9600 |
| N2—C2 | 1.471 (7) | C21—H21A | 0.9600 |
| N2—C3 | 1.487 (7) | C21—H21B | 0.9600 |
| N2—H2 | 0.84 (5) | C21—H21C | 0.9600 |
| N3—C9 | 1.480 (6) | C22—C23 | 1.517 (8) |
| N3—C6 | 1.513 (7) | C22—H22A | 0.9700 |
| N3—H3 | 0.88 (6) | C22—H22B | 0.9700 |
| N4—C10 | 1.472 (7) | C23—C24 | 1.531 (9) |
| N4—C11 | 1.511 (7) | C23—H23 | 0.9800 |
| N4—H4 | 0.85 (5) | C24—H24A | 0.9600 |
| N5—C31 | 1.471 (8) | C24—H24B | 0.9600 |
| N5—C17 | 1.494 (8) | C24—H24C | 0.9600 |
| N5—H5 | 0.85 (5) | C25—C26 | 1.487 (8) |
| N6—C18 | 1.496 (8) | C25—H25A | 0.9700 |
| N6—C19 | 1.510 (9) | C25—H25B | 0.9700 |
| N6—H6 | 0.85 (5) | C26—H26A | 0.9700 |
| N7—C23 | 1.478 (7) | C26—H26B | 0.9700 |
| N7—C25 | 1.483 (7) | C27—C28 | 1.508 (9) |
| N7—H7 | 0.85 (2) | C27—C30 | 1.534 (8) |
| N8—C26 | 1.478 (7) | C27—C29 | 1.547 (9) |
| N8—C27 | 1.491 (7) | C28—H28A | 0.9600 |
| N8—H8 | 0.85 (5) | C28—H28B | 0.9600 |
| C1—C2 | 1.501 (8) | C28—H28C | 0.9600 |
| C1—H1A | 0.9700 | C29—H29A | 0.9600 |
| C1—H1B | 0.9700 | C29—H29B | 0.9600 |
| C2—H2A | 0.9700 | C29—H29C | 0.9600 |
| C2—H2B | 0.9700 | C30—C31 | 1.514 (9) |
| C3—C4 | 1.518 (7) | C30—H30A | 0.9700 |
| C3—C5 | 1.512 (7) | C30—H30B | 0.9700 |
| C3—H3a | 0.9800 | C31—C32 | 1.529 (9) |
| C4—H4A | 0.9600 | C31—H31 | 0.9800 |
| C4—H4B | 0.9600 | C32—H32A | 0.9600 |
| C4—H4C | 0.9600 | C32—H32B | 0.9600 |
| C5—C6 | 1.548 (8) | C32—H32C | 0.9600 |
| C5—H5A | 0.9700 | C33—C34 | 1.536 (7) |
| C5—H5B | 0.9700 | C34—C35 | 1.507 (7) |
| C6—C7 | 1.484 (8) | C34—H34 | 0.9800 |
| C6—C8 | 1.548 (8) | C35—C36 | 1.510 (7) |
| C7—H7A | 0.9600 | C35—H35A | 0.9700 |
| C7—H7B | 0.9600 | C35—H35B | 0.9700 |
| C7—H7C | 0.9600 | | |
| O1—Ni1—N4 | 89.28 (15) | C10—C9—H9B | 109.8 |
| O1—Ni1—N2 | 166.91 (15) | H9A—C9—H9B | 108.2 |
| N4—Ni1—N2 | 103.22 (17) | N4—C10—C9 | 109.8 (4) |
| O1—Ni1—O3 | 76.30 (13) | N4—C10—H10A | 109.7 |
| N4—Ni1—O3 | 164.72 (15) | C9—C10—H10A | 109.7 |
| N2—Ni1—O3 | 91.55 (15) | N4—C10—H10B | 109.7 |
| O1—Ni1—N1 | 99.79 (15) | C9—C10—H10B | 109.7 |

| | | | |
|----------------|-------------|---------------|-----------|
| N4—Ni1—N1 | 89.60 (17) | H10A—C10—H10B | 108.2 |
| N2—Ni1—N1 | 84.37 (17) | C13—C11—N4 | 110.4 (4) |
| O3—Ni1—N1 | 87.94 (16) | C13—C11—C12 | 110.9 (5) |
| O1—Ni1—N3 | 88.08 (15) | N4—C11—C12 | 111.5 (5) |
| N4—Ni1—N3 | 84.36 (17) | C13—C11—H11A | 108.0 |
| N2—Ni1—N3 | 89.29 (17) | N4—C11—H11A | 108.0 |
| O3—Ni1—N3 | 99.94 (15) | C12—C11—H11A | 108.0 |
| N1—Ni1—N3 | 170.03 (16) | C11—C12—H12A | 109.5 |
| N7—Ni2—N5 | 104.33 (16) | C11—C12—H12B | 109.5 |
| N7—Ni2—N6 | 90.01 (18) | H12A—C12—H12B | 109.5 |
| N5—Ni2—N6 | 85.9 (2) | C11—C12—H12C | 109.5 |
| N7—Ni2—N8 | 85.12 (18) | H12A—C12—H12C | 109.5 |
| N5—Ni2—N8 | 90.06 (18) | H12B—C12—H12C | 109.5 |
| N6—Ni2—N8 | 172.74 (18) | C11—C13—C14 | 120.3 (5) |
| N7—Ni2—O5 | 100.08 (15) | C11—C13—H13A | 107.2 |
| N5—Ni2—O5 | 155.28 (16) | C14—C13—H13A | 107.2 |
| N6—Ni2—O5 | 98.00 (17) | C11—C13—H13B | 107.2 |
| N8—Ni2—O5 | 88.17 (16) | C14—C13—H13B | 107.2 |
| N7—Ni2—O4 | 158.72 (15) | H13A—C13—H13B | 106.9 |
| N5—Ni2—O4 | 96.04 (15) | N1—C14—C13 | 110.1 (4) |
| N6—Ni2—O4 | 85.28 (16) | N1—C14—C16 | 107.4 (5) |
| N8—Ni2—O4 | 101.17 (16) | C13—C14—C16 | 111.8 (5) |
| O5—Ni2—O4 | 60.25 (13) | N1—C14—C15 | 111.4 (5) |
| N7—Ni2—C36 | 129.40 (16) | C13—C14—C15 | 107.8 (5) |
| N5—Ni2—C36 | 126.19 (17) | C16—C14—C15 | 108.2 (5) |
| N6—Ni2—C36 | 90.80 (17) | C14—C15—H15A | 109.5 |
| N8—Ni2—C36 | 96.45 (17) | C14—C15—H15B | 109.5 |
| O5—Ni2—C36 | 29.99 (15) | H15A—C15—H15B | 109.5 |
| O4—Ni2—C36 | 30.30 (15) | C14—C15—H15C | 109.5 |
| O8—C11—O7 | 110.0 (4) | H15A—C15—H15C | 109.5 |
| O8—C11—O9 | 111.4 (4) | H15B—C15—H15C | 109.5 |
| O7—C11—O9 | 109.9 (4) | C14—C16—H16A | 109.5 |
| O8—C11—O6 | 108.5 (4) | C14—C16—H16B | 109.5 |
| O7—C11—O6 | 107.2 (4) | H16A—C16—H16B | 109.5 |
| O9—C11—O6 | 109.7 (4) | C14—C16—H16C | 109.5 |
| O13—C12—O11 | 111.1 (11) | H16A—C16—H16C | 109.5 |
| O13—C12—O12 | 113.1 (11) | H16B—C16—H16C | 109.5 |
| O11—C12—O12 | 108.8 (8) | C18—C17—N5 | 109.8 (5) |
| O13—C12—O10 | 110.5 (11) | C18—C17—H17A | 109.7 |
| O11—C12—O10 | 113.5 (8) | N5—C17—H17A | 109.7 |
| O12—C12—O10 | 99.4 (9) | C18—C17—H17B | 109.7 |
| O12'—C12'—O11' | 109.9 (16) | N5—C17—H17B | 109.7 |
| O12'—C12'—O10' | 108.9 (16) | H17A—C17—H17B | 108.2 |
| O11'—C12'—O10' | 114.5 (16) | C17—C18—N6 | 109.9 (5) |
| O12'—C12'—O13' | 106.2 (15) | C17—C18—H18A | 109.7 |
| O11'—C12'—O13' | 108.1 (13) | N6—C18—H18A | 109.7 |
| O10'—C12'—O13' | 108.9 (16) | C17—C18—H18B | 109.7 |
| C33—O1—Ni1 | 121.1 (3) | N6—C18—H18B | 109.7 |
| C34—O3—Ni1 | 115.8 (3) | H18A—C18—H18B | 108.2 |

supplementary materials

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|-------------|-----------|---------------|-----------|
| C34—O3—H3O | 122.1 | N6—C19—C22 | 110.3 (5) |
| Ni1—O3—H3O | 122.1 | N6—C19—C21 | 108.1 (6) |
| C36—O4—Ni2 | 88.6 (3) | C22—C19—C21 | 111.9 (7) |
| C36—O5—Ni2 | 90.2 (3) | N6—C19—C20 | 111.6 (7) |
| H11—O1W—H12 | 103 (13) | C22—C19—C20 | 107.7 (6) |
| C1—N1—C14 | 113.7 (4) | C21—C19—C20 | 107.2 (6) |
| C1—N1—Ni1 | 103.2 (3) | C19—C20—H20A | 109.5 |
| C14—N1—Ni1 | 121.2 (3) | C19—C20—H20B | 109.5 |
| C1—N1—H1 | 109 (5) | H20A—C20—H20B | 109.5 |
| C14—N1—H1 | 107 (5) | C19—C20—H20C | 109.5 |
| Ni1—N1—H1 | 101 (5) | H20A—C20—H20C | 109.5 |
| C2—N2—C3 | 113.5 (4) | H20B—C20—H20C | 109.5 |
| C2—N2—Ni1 | 104.9 (3) | C19—C21—H21A | 109.5 |
| C3—N2—Ni1 | 115.6 (3) | C19—C21—H21B | 109.5 |
| C2—N2—H2 | 109 (4) | H21A—C21—H21B | 109.5 |
| C3—N2—H2 | 105 (5) | C19—C21—H21C | 109.5 |
| Ni1—N2—H2 | 109 (5) | H21A—C21—H21C | 109.5 |
| C9—N3—C6 | 113.8 (4) | H21B—C21—H21C | 109.5 |
| C9—N3—Ni1 | 104.2 (3) | C23—C22—C19 | 120.1 (5) |
| C6—N3—Ni1 | 122.1 (3) | C23—C22—H22A | 107.3 |
| C9—N3—H3 | 106 (4) | C19—C22—H22A | 107.3 |
| C6—N3—H3 | 101 (4) | C23—C22—H22B | 107.3 |
| Ni1—N3—H3 | 109 (4) | C19—C22—H22B | 107.3 |
| C10—N4—C11 | 111.9 (4) | H22A—C22—H22B | 106.9 |
| C10—N4—Ni1 | 104.2 (3) | N7—C23—C22 | 111.4 (5) |
| C11—N4—Ni1 | 115.9 (3) | N7—C23—C24 | 111.3 (5) |
| C10—N4—H4 | 112 (4) | C22—C23—C24 | 108.6 (5) |
| C11—N4—H4 | 108 (4) | N7—C23—H23 | 108.5 |
| Ni1—N4—H4 | 105 (4) | C22—C23—H23 | 108.5 |
| C31—N5—C17 | 113.7 (5) | C24—C23—H23 | 108.5 |
| C31—N5—Ni2 | 116.4 (3) | C23—C24—H24A | 109.5 |
| C17—N5—Ni2 | 103.8 (4) | C23—C24—H24B | 109.5 |
| C31—N5—H5 | 112 (5) | H24A—C24—H24B | 109.5 |
| C17—N5—H5 | 102 (5) | C23—C24—H24C | 109.5 |
| Ni2—N5—H5 | 108 (5) | H24A—C24—H24C | 109.5 |
| C18—N6—C19 | 115.0 (5) | H24B—C24—H24C | 109.5 |
| C18—N6—Ni2 | 103.5 (4) | N7—C25—C26 | 109.9 (4) |
| C19—N6—Ni2 | 120.7 (4) | N7—C25—H25A | 109.7 |
| C18—N6—H6 | 104 (5) | C26—C25—H25A | 109.7 |
| C19—N6—H6 | 103 (5) | N7—C25—H25B | 109.7 |
| Ni2—N6—H6 | 110 (5) | C26—C25—H25B | 109.7 |
| C23—N7—C25 | 112.9 (4) | H25A—C25—H25B | 108.2 |
| C23—N7—Ni2 | 119.4 (3) | N8—C26—C25 | 109.5 (4) |
| C25—N7—Ni2 | 104.0 (3) | N8—C26—H26A | 109.8 |
| C23—N7—H7 | 109 (4) | C25—C26—H26A | 109.8 |
| C25—N7—H7 | 101 (4) | N8—C26—H26B | 109.8 |
| Ni2—N7—H7 | 108 (4) | C25—C26—H26B | 109.8 |
| C26—N8—C27 | 115.0 (4) | H26A—C26—H26B | 108.2 |
| C26—N8—Ni2 | 104.6 (3) | N8—C27—C28 | 107.9 (5) |

| | | | |
|------------|-----------|---------------|-----------|
| C27—N8—Ni2 | 120.8 (3) | N8—C27—C30 | 110.9 (4) |
| C26—N8—H8 | 109 (5) | C28—C27—C30 | 111.0 (5) |
| C27—N8—H8 | 110 (5) | N8—C27—C29 | 111.5 (5) |
| Ni2—N8—H8 | 95 (4) | C28—C27—C29 | 107.9 (5) |
| N1—C1—C2 | 109.8 (5) | C30—C27—C29 | 107.6 (5) |
| N1—C1—H1A | 109.7 | C27—C28—H28A | 109.5 |
| C2—C1—H1A | 109.7 | C27—C28—H28B | 109.5 |
| N1—C1—H1B | 109.7 | H28A—C28—H28B | 109.5 |
| C2—C1—H1B | 109.7 | C27—C28—H28C | 109.5 |
| H1A—C1—H1B | 108.2 | H28A—C28—H28C | 109.5 |
| N2—C2—C1 | 109.7 (4) | H28B—C28—H28C | 109.5 |
| N2—C2—H2A | 109.7 | C27—C29—H29A | 109.5 |
| C1—C2—H2A | 109.7 | C27—C29—H29B | 109.5 |
| N2—C2—H2B | 109.7 | H29A—C29—H29B | 109.5 |
| C1—C2—H2B | 109.7 | C27—C29—H29C | 109.5 |
| H2A—C2—H2B | 108.2 | H29A—C29—H29C | 109.5 |
| N2—C3—C4 | 113.1 (5) | H29B—C29—H29C | 109.5 |
| N2—C3—C5 | 110.2 (4) | C31—C30—C27 | 118.5 (5) |
| C4—C3—C5 | 110.7 (5) | C31—C30—H30A | 107.7 |
| N2—C3—H3a | 107.5 | C27—C30—H30A | 107.7 |
| C4—C3—H3a | 107.5 | C31—C30—H30B | 107.7 |
| C5—C3—H3a | 107.5 | C27—C30—H30B | 107.7 |
| C3—C4—H4A | 109.5 | H30A—C30—H30B | 107.1 |
| C3—C4—H4B | 109.5 | N5—C31—C30 | 110.8 (5) |
| H4A—C4—H4B | 109.5 | N5—C31—C32 | 112.6 (6) |
| C3—C4—H4C | 109.5 | C30—C31—C32 | 108.8 (6) |
| H4A—C4—H4C | 109.5 | N5—C31—H31 | 108.2 |
| H4B—C4—H4C | 109.5 | C30—C31—H31 | 108.2 |
| C3—C5—C6 | 119.3 (4) | C32—C31—H31 | 108.2 |
| C3—C5—H5A | 107.5 | C31—C32—H32A | 109.5 |
| C6—C5—H5A | 107.5 | C31—C32—H32B | 109.5 |
| C3—C5—H5B | 107.5 | H32A—C32—H32B | 109.5 |
| C6—C5—H5B | 107.5 | C31—C32—H32C | 109.5 |
| H5A—C5—H5B | 107.0 | H32A—C32—H32C | 109.5 |
| C7—C6—N3 | 108.3 (4) | H32B—C32—H32C | 109.5 |
| C7—C6—C8 | 108.2 (5) | O2—C33—O1 | 126.6 (5) |
| N3—C6—C8 | 111.2 (5) | O2—C33—C34 | 115.3 (4) |
| C7—C6—C5 | 111.4 (5) | O1—C33—C34 | 118.1 (4) |
| N3—C6—C5 | 110.4 (4) | O3—C34—C35 | 111.7 (4) |
| C8—C6—C5 | 107.2 (5) | O3—C34—C33 | 108.2 (4) |
| C6—C7—H7A | 109.5 | C35—C34—C33 | 112.0 (4) |
| C6—C7—H7B | 109.5 | O3—C34—H34 | 108.2 |
| H7A—C7—H7B | 109.5 | C35—C34—H34 | 108.2 |
| C6—C7—H7C | 109.5 | C33—C34—H34 | 108.2 |
| H7A—C7—H7C | 109.5 | C34—C35—C36 | 113.2 (4) |
| H7B—C7—H7C | 109.5 | C34—C35—H35A | 108.9 |
| C6—C8—H8A | 109.5 | C36—C35—H35A | 108.9 |
| C6—C8—H8B | 109.5 | C34—C35—H35B | 108.9 |
| H8A—C8—H8B | 109.5 | C36—C35—H35B | 108.9 |

supplementary materials

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|---------------|------------|-----------------|------------|
| C6—C8—H8C | 109.5 | H35A—C35—H35B | 107.7 |
| H8A—C8—H8C | 109.5 | O5—C36—O4 | 120.8 (5) |
| H8B—C8—H8C | 109.5 | O5—C36—C35 | 120.5 (5) |
| N3—C9—C10 | 109.4 (4) | O4—C36—C35 | 118.8 (4) |
| N3—C9—H9A | 109.8 | O5—C36—Ni2 | 59.8 (3) |
| C10—C9—H9A | 109.8 | O4—C36—Ni2 | 61.1 (2) |
| N3—C9—H9B | 109.8 | C35—C36—Ni2 | 175.7 (4) |
| N4—Ni1—O1—C33 | 170.1 (4) | Ni1—N2—C2—C1 | 44.9 (5) |
| N2—Ni1—O1—C33 | -27.0 (9) | N1—C1—C2—N2 | -61.4 (6) |
| O3—Ni1—O1—C33 | -4.8 (4) | C2—N2—C3—C4 | 47.5 (7) |
| N1—Ni1—O1—C33 | 80.6 (4) | Ni1—N2—C3—C4 | 168.7 (4) |
| N3—Ni1—O1—C33 | -105.5 (4) | C2—N2—C3—C5 | 171.9 (4) |
| O1—Ni1—O3—C34 | 6.3 (3) | Ni1—N2—C3—C5 | -66.8 (5) |
| N4—Ni1—O3—C34 | -13.4 (8) | N2—C3—C5—C6 | 74.0 (6) |
| N2—Ni1—O3—C34 | -178.7 (3) | C4—C3—C5—C6 | -160.1 (5) |
| N1—Ni1—O3—C34 | -94.3 (3) | C9—N3—C6—C7 | 157.0 (5) |
| N3—Ni1—O3—C34 | 91.8 (3) | Ni1—N3—C6—C7 | -76.7 (5) |
| N7—Ni2—O4—C36 | 21.9 (6) | C9—N3—C6—C8 | 38.2 (6) |
| N5—Ni2—O4—C36 | -174.9 (3) | Ni1—N3—C6—C8 | 164.5 (4) |
| N6—Ni2—O4—C36 | 99.7 (3) | C9—N3—C6—C5 | -80.7 (5) |
| N8—Ni2—O4—C36 | -83.6 (3) | Ni1—N3—C6—C5 | 45.5 (5) |
| O5—Ni2—O4—C36 | -2.3 (3) | C3—C5—C6—C7 | 59.7 (7) |
| N7—Ni2—O5—C36 | -169.0 (3) | C3—C5—C6—N3 | -60.8 (6) |
| N5—Ni2—O5—C36 | 20.1 (6) | C3—C5—C6—C8 | 177.9 (5) |
| N6—Ni2—O5—C36 | -77.6 (3) | C6—N3—C9—C10 | 173.3 (4) |
| N8—Ni2—O5—C36 | 106.3 (3) | Ni1—N3—C9—C10 | 38.1 (5) |
| O4—Ni2—O5—C36 | 2.3 (3) | C11—N4—C10—C9 | 173.7 (4) |
| O1—Ni1—N1—C1 | 179.2 (3) | Ni1—N4—C10—C9 | 47.8 (4) |
| N4—Ni1—N1—C1 | 90.0 (4) | N3—C9—C10—N4 | -60.8 (5) |
| N2—Ni1—N1—C1 | -13.3 (3) | C10—N4—C11—C13 | 176.8 (4) |
| O3—Ni1—N1—C1 | -105.1 (4) | Ni1—N4—C11—C13 | -63.9 (5) |
| O1—Ni1—N1—C14 | 50.5 (4) | C10—N4—C11—C12 | 53.1 (6) |
| N4—Ni1—N1—C14 | -38.7 (4) | Ni1—N4—C11—C12 | 172.4 (4) |
| N2—Ni1—N1—C14 | -142.0 (4) | N4—C11—C13—C14 | 72.6 (6) |
| O3—Ni1—N1—C14 | 126.3 (4) | C12—C11—C13—C14 | -163.4 (5) |
| O1—Ni1—N2—C2 | 92.6 (7) | C1—N1—C14—C13 | -76.0 (6) |
| N4—Ni1—N2—C2 | -104.9 (4) | Ni1—N1—C14—C13 | 47.9 (6) |
| O3—Ni1—N2—C2 | 71.1 (4) | C1—N1—C14—C16 | 162.0 (5) |
| N1—Ni1—N2—C2 | -16.7 (4) | Ni1—N1—C14—C16 | -74.1 (5) |
| N3—Ni1—N2—C2 | 171.0 (4) | C1—N1—C14—C15 | 43.6 (7) |
| O1—Ni1—N2—C3 | -33.1 (9) | Ni1—N1—C14—C15 | 167.5 (4) |
| N4—Ni1—N2—C3 | 129.3 (4) | C11—C13—C14—N1 | -62.5 (7) |
| O3—Ni1—N2—C3 | -54.7 (4) | C11—C13—C14—C16 | 56.9 (7) |
| N1—Ni1—N2—C3 | -142.4 (4) | C11—C13—C14—C15 | 175.7 (5) |
| N3—Ni1—N2—C3 | 45.3 (4) | C31—N5—C17—C18 | -171.1 (5) |
| O1—Ni1—N3—C9 | -99.3 (3) | Ni2—N5—C17—C18 | -43.8 (5) |
| N4—Ni1—N3—C9 | -9.8 (3) | N5—C17—C18—N6 | 60.1 (7) |
| N2—Ni1—N3—C9 | 93.5 (3) | C19—N6—C18—C17 | -174.9 (5) |
| O3—Ni1—N3—C9 | -175.0 (3) | Ni2—N6—C18—C17 | -41.2 (5) |

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| O1—Ni1—N3—C6 | 130.3 (4) | C18—N6—C19—C22 | 73.4 (7) |
| N4—Ni1—N3—C6 | -140.3 (4) | Ni2—N6—C19—C22 | -51.8 (6) |
| N2—Ni1—N3—C6 | -36.9 (4) | C18—N6—C19—C21 | -164.0 (6) |
| O3—Ni1—N3—C6 | 54.5 (4) | Ni2—N6—C19—C21 | 70.8 (7) |
| O1—Ni1—N4—C10 | 68.1 (3) | C18—N6—C19—C20 | -46.3 (7) |
| N2—Ni1—N4—C10 | -108.0 (3) | Ni2—N6—C19—C20 | -171.5 (5) |
| O3—Ni1—N4—C10 | 87.2 (7) | N6—C19—C22—C23 | 63.5 (8) |
| N1—Ni1—N4—C10 | 167.9 (3) | C21—C19—C22—C23 | -56.9 (8) |
| N3—Ni1—N4—C10 | -20.1 (3) | C20—C19—C22—C23 | -174.5 (7) |
| O1—Ni1—N4—C11 | -55.4 (4) | C25—N7—C23—C22 | 179.9 (5) |
| N2—Ni1—N4—C11 | 128.6 (4) | Ni2—N7—C23—C22 | 57.2 (6) |
| O3—Ni1—N4—C11 | -36.2 (8) | C25—N7—C23—C24 | -58.8 (6) |
| N1—Ni1—N4—C11 | 44.5 (4) | Ni2—N7—C23—C24 | 178.6 (4) |
| N3—Ni1—N4—C11 | -143.5 (4) | C19—C22—C23—N7 | -67.2 (7) |
| N7—Ni2—N5—C31 | -129.5 (4) | C19—C22—C23—C24 | 169.9 (6) |
| N6—Ni2—N5—C31 | 141.5 (4) | C23—N7—C25—C26 | -175.7 (4) |
| N8—Ni2—N5—C31 | -44.5 (4) | Ni2—N7—C25—C26 | -44.9 (5) |
| O5—Ni2—N5—C31 | 41.2 (6) | C27—N8—C26—C25 | -174.6 (4) |
| O4—Ni2—N5—C31 | 56.7 (4) | Ni2—N8—C26—C25 | -39.8 (5) |
| C36—Ni2—N5—C31 | 53.5 (4) | N7—C25—C26—N8 | 59.7 (6) |
| N7—Ni2—N5—C17 | 104.8 (4) | C26—N8—C27—C28 | -161.0 (5) |
| N6—Ni2—N5—C17 | 15.9 (4) | Ni2—N8—C27—C28 | 72.1 (5) |
| N8—Ni2—N5—C17 | -170.2 (4) | C26—N8—C27—C30 | 77.3 (6) |
| O5—Ni2—N5—C17 | -84.4 (5) | Ni2—N8—C27—C30 | -49.7 (6) |
| O4—Ni2—N5—C17 | -68.9 (4) | C26—N8—C27—C29 | -42.6 (7) |
| C36—Ni2—N5—C17 | -72.1 (4) | Ni2—N8—C27—C29 | -169.5 (4) |
| N7—Ni2—N6—C18 | -91.2 (4) | N8—C27—C30—C31 | 62.6 (7) |
| N5—Ni2—N6—C18 | 13.1 (4) | C28—C27—C30—C31 | -57.4 (7) |
| O5—Ni2—N6—C18 | 168.6 (4) | C29—C27—C30—C31 | -175.2 (6) |
| O4—Ni2—N6—C18 | 109.5 (4) | C17—N5—C31—C30 | -176.0 (5) |
| C36—Ni2—N6—C18 | 139.4 (4) | Ni2—N5—C31—C30 | 63.5 (5) |
| N7—Ni2—N6—C19 | 39.1 (4) | C17—N5—C31—C32 | -53.9 (7) |
| N5—Ni2—N6—C19 | 143.5 (4) | Ni2—N5—C31—C32 | -174.4 (5) |
| O5—Ni2—N6—C19 | -61.1 (4) | C27—C30—C31—N5 | -71.3 (7) |
| O4—Ni2—N6—C19 | -120.1 (4) | C27—C30—C31—C32 | 164.3 (6) |
| C36—Ni2—N6—C19 | -90.3 (4) | Ni1—O1—C33—O2 | -177.9 (4) |
| N5—Ni2—N7—C23 | -127.0 (4) | Ni1—O1—C33—C34 | 2.5 (6) |
| N6—Ni2—N7—C23 | -41.2 (4) | Ni1—O3—C34—C35 | -130.4 (3) |
| N8—Ni2—N7—C23 | 144.2 (4) | Ni1—O3—C34—C33 | -6.6 (5) |
| O5—Ni2—N7—C23 | 57.0 (4) | O2—C33—C34—O3 | -176.7 (4) |
| O4—Ni2—N7—C23 | 35.8 (7) | O1—C33—C34—O3 | 2.9 (6) |
| C36—Ni2—N7—C23 | 49.9 (4) | O2—C33—C34—C35 | -53.1 (6) |
| N5—Ni2—N7—C25 | 106.1 (3) | O1—C33—C34—C35 | 126.5 (5) |
| N6—Ni2—N7—C25 | -168.1 (3) | O3—C34—C35—C36 | -57.3 (5) |
| N8—Ni2—N7—C25 | 17.3 (3) | C33—C34—C35—C36 | -178.9 (4) |
| O5—Ni2—N7—C25 | -69.9 (3) | Ni2—O5—C36—O4 | -4.0 (5) |
| O4—Ni2—N7—C25 | -91.1 (5) | Ni2—O5—C36—C35 | 175.0 (4) |
| C36—Ni2—N7—C25 | -77.0 (4) | Ni2—O4—C36—O5 | 4.0 (5) |
| N7—Ni2—N8—C26 | 11.9 (3) | Ni2—O4—C36—C35 | -175.0 (4) |

supplementary materials

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| N5—Ni2—N8—C26 | -92.5 (3) | C34—C35—C36—O5 | -144.5 (5) |
| O5—Ni2—N8—C26 | 112.2 (3) | C34—C35—C36—O4 | 34.5 (7) |
| O4—Ni2—N8—C26 | 171.3 (3) | N7—Ni2—C36—O5 | 14.0 (4) |
| C36—Ni2—N8—C26 | 141.0 (3) | N5—Ni2—C36—O5 | -169.7 (3) |
| N7—Ni2—N8—C27 | 143.4 (4) | N6—Ni2—C36—O5 | 104.7 (3) |
| N5—Ni2—N8—C27 | 39.1 (4) | N8—Ni2—C36—O5 | -74.9 (3) |
| O5—Ni2—N8—C27 | -116.3 (4) | O4—Ni2—C36—O5 | -176.1 (5) |
| O4—Ni2—N8—C27 | -57.1 (4) | N7—Ni2—C36—O4 | -169.9 (3) |
| C36—Ni2—N8—C27 | -87.4 (4) | N5—Ni2—C36—O4 | 6.3 (4) |
| C14—N1—C1—C2 | 174.7 (5) | N6—Ni2—C36—O4 | -79.2 (3) |
| Ni1—N1—C1—C2 | 41.5 (5) | N8—Ni2—C36—O4 | 101.1 (3) |
| C3—N2—C2—C1 | 172.0 (5) | O5—Ni2—C36—O4 | 176.1 (5) |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|---------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N2—H2 \cdots O6 ⁱ | 0.84 (5) | 2.41 (2) | 3.230 (7) | 165 (6) |
| N5—H5 \cdots O2 ⁱⁱ | 0.85 (5) | 2.14 (3) | 2.940 (6) | 158 (6) |
| N7—H7 \cdots O2 ⁱⁱ | 0.85 (2) | 2.06 (2) | 2.869 (5) | 160 (6) |
| O1w—H11 \cdots O5 | 0.86 (9) | 2.09 (7) | 2.862 (9) | 149 (12) |
| O1w—H12 \cdots O6 | 0.86 (9) | 2.05 (8) | 2.784 (12) | 143 (13) |

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y+1/2, -z+3/2$.

Fig. 1

