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Synthesis and crystal structures of lithium(I) and nickel(II) complexes derived from an *N*,*O*-bidentate Schiff base ligand

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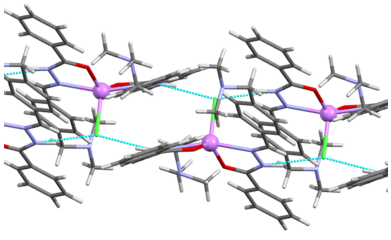
A comparative single-crystal X-ray diffraction study of two complexes derived from the same *N*,*O*-bidentate Schiff base ligand revealed distinct coordination geometries and crystal-packing arrangements for Li^{I} and Ni^{II}. In the lithium complex, chloridobis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazide)lithium(I), $[LiCl(C_{17}H_{19}N_3O)_2]$ (**2**), the Li^{I} centre adopted a five-coordinate environment defined by two *N*,*O*-chelating ligands and a chloride ion, with Li—O, Li—N and Li—Cl distances of 1.947 (3)/1.962 (3), 2.309 (4)/2.352 (4) and 2.399 (3) Å, respectively. The coordination geometry, with $\tau_5 = 0.52$, fell between the square-pyramidal and trigonal-bipyramidal limiting geometries. The coordinated chloride ion also participated in intermolecular N—H···Cl hydrogen bonding, thereby linking the complexes into one-dimensional chains. In the nickel complex, bis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazidato)nickel(II), $[Ni(C_{17}H_{18}N_3O)_2]$ (**3**), the Ni^{II} centre lies on a crystallographic inversion centre and was coordinated by two symmetry-related *N*,*O*-chelating ligands in a slightly distorted square-planar geometry, with Ni—O and Ni—N distances of 1.8408 (11) and 1.8703 (13) Å, respectively. These structures demonstrated how the metal ion controlled both the coordination geometry and the supramolecular organization of the resulting complexes.

1. Introduction

Schiff base ligands are widely used in coordination chemistry owing to their structural flexibility and ability to provide different donor sets to metal centres. Their coordination behaviour can be strongly influenced by the nature and electronic requirements of the metal ion, which may lead to significant changes in both the primary coordination sphere and the resulting supramolecular organization (Singh *et al.*, 2012; Alfonso-Herrera *et al.*, 2022).

Nickel(II) complexes supported by Schiff base ligands exhibit a broad range of coordination geometries, including square-planar, tetrahedral and octahedral arrangements, depending on the donor set and ligand architecture (Aly *et al.*, 2023). In contrast, lithium(I) generally exhibits less constrained coordination environments owing to its small ionic radius and hard Lewis acid character (Xue *et al.*, 2025). A comparison of these two metal ions with the same ligand therefore provided an opportunity to examine how differences in metal-centre preferences affected both the local coordination geometry and the organization of the crystal structure.

Despite the extensive use of Schiff base ligands in coordination chemistry, direct structural comparisons involving the same ligand coordinated to Li^{I} and Ni^{II} remain uncommon. Such comparisons are useful for assessing how metal-dependent coordination preferences influence not only the geometry



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Table 1
Experimental details.

Experiments were carried out at 120 K using a Bruker PHOTON III CPAD diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2021). H-atom parameters were constrained.

	2	**3**
Crystal data		
Chemical formula	$[Ni(C_{17}H_{18}N_3O)_2]$	$[LiCl(C_{17}H_{19}N_3O)_2]$
M_r	619.40	605.09
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	6.3619 (6), 10.7622 (13), 11.8481 (13)	11.8979 (4), 17.8064 (7), 15.6160 (6)
α, β, γ (°)	78.649 (4), 78.080 (5), 75.676 (3)	90, 93.442 (2), 90
V (Å^3)	759.91 (14)	3302.4 (2)
Z	1	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.68	1.33
Crystal size (mm)	0.16 × 0.12 × 0.10	0.14 × 0.14 × 0.12
Data collection		
T_{min}, T_{max}	0.592, 0.746	0.586, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	18991, 3631, 3275	50782, 5825, 4813
R_{int}	0.070	0.084
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.659	0.596
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.092, 1.06	0.044, 0.127, 1.04
No. of reflections	3631	5825
No. of parameters	198	401
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.43	0.30, −0.25

Computer programs: *APEX4* (Bruker, 2021), *SAINT* (Bruker, 2021), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

around the metal centre but also the organization of the resulting complexes in the solid state. Herein, we describe the crystal structures of lithium(I) and nickel(II) complexes derived from a shared *N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazide (**1**) ligand, namely, bis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazidato)nickel(II) (**2**) and chloridobis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazide)lithium(I) (**3**) (Fig. 1). In both compounds, the ligand functions as an *N*,*O*-bidentate donor. However, the two metal ions result in significantly different coordination environments.

2. Experimental

2.1. Synthesis and crystallization

2.1.1. Synthesis of *N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazide (1)

Ligand **1** was synthesized by refluxing an ethanolic mixture (10 ml) of 4-[(dimethylamino)methyl]benzaldehyde (0.440 g, 2.7 mmol), benzohydrazide (0.367 g, 2.7 mmol) and a drop of acetic acid for 24 h. After cooling to room temperature, water was added to precipitate the desired product. The resulting white solid was collected by filtration, washed with cold

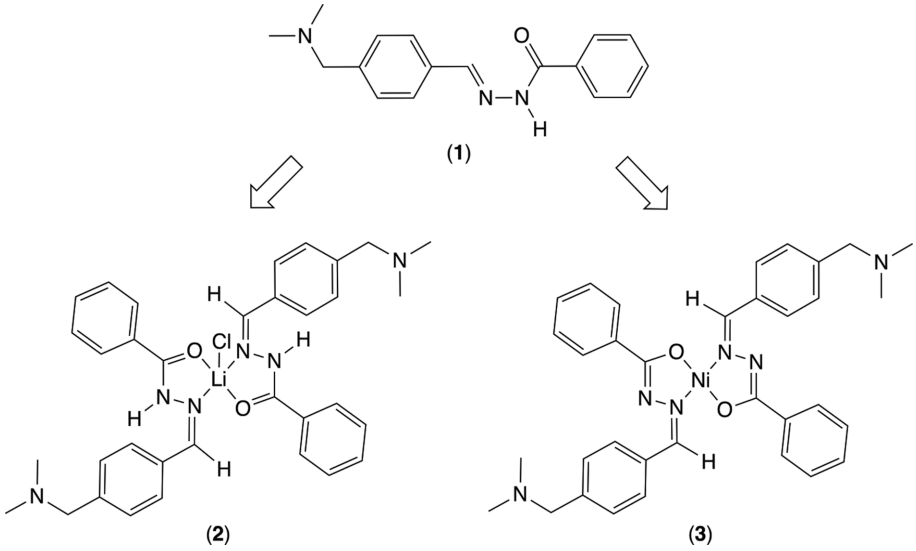


Figure 1
The synthesis of complexes **2** and **3**.

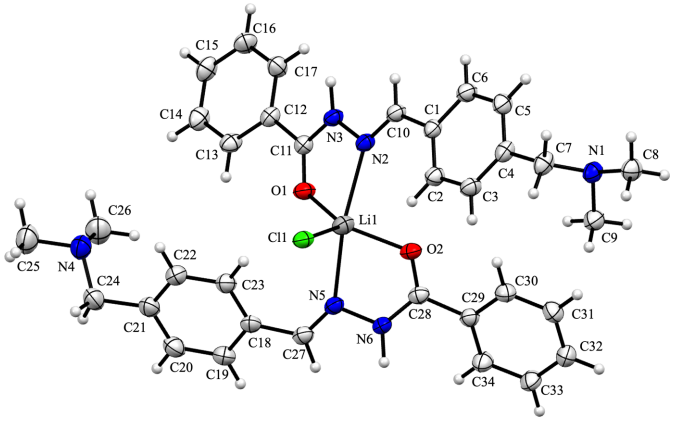


Figure 2
The molecular structure of lithium(I) complex **2**, with displacement ellipsoids drawn at the 50% probability level.

ethanol and dried under vacuum (yield: 0.340 g, 45%). FT–IR: ν(C═N and C═O) 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.33 (*s*, 1H, CH═N), 8.87 (*s*, 1H, NH), 7.87 (*br s*, 2H, arom CH), 7.74 (*br s*, 2H, arom CH), 7.57–7.45 (*m*, 3H, arom CH), 7.36 (*d*, 2H, arom CH, $^3J_{HH}$ = 8.1 Hz), 3.52 (*s*, 2H, NCH_2), 2.29 (*s*, 6H, $N(CH_3)_2$) ppm; MS (ESI–TOF): *m*/*z* = 282.16 $[M + H]^+$ (expected isotopic profiles).

2.1.2. Synthesis of the lithium(I) and nickel(II) complexes

In a Schlenk tube under an argon atmosphere, ligand **1** (0.170 g, 0.55 mmol) was dissolved in tetrahydrofuran (THF; 15 ml) and ^{n}BuLi (1.6 *M* in hexane, 0.3 ml, 0.55 mmol) was slowly added at −78 °C. After stirring for 1 h at −78 °C, the resulting mixture was allowed to warm to room temperature. $[NiCl(Ph)(PPh_3)_2]$ (0.423 g, 0.55 mmol) was added and the resulting mixture was stirring for 24 h. The solvent was removed under reduced pressure and the resulting solid residue was dissolved in CH_2Cl_2 (15 ml). Addition of Et_2O (30 ml) induced precipitation of a solid, which was removed by filtration. The filtrate was concentrated to approximately 1 ml and transferred to a narrow long Schlenk tube. Hexane (20 ml) was carefully layered over the solution to allow slow diffusion. Two types of single crystals suitable for X-ray diffraction analysis were obtained: colourless block-shaped crystals of lithium(I) complex **2** and orange block-shaped crystals of nickel(II) complex **3**. The two types of crystals were manually separated on the basis of their distinct colours.

For lithium(I) complex **2**, because of the instability in solution, conventional solution-phase spectroscopic characterization could not be performed. FT–IR: ν(C═N) 1647 and ν(C═O) 1608 cm^{-1}.

For nickel(II) complex **3**, FT–IR: ν(C═N—N═C) 1587 and ν(C—O) 1262 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.33 (*d*, 4H, arom CH, $^3J_{HH}$ = 7.0 Hz), 8.01 (*dt*, 4H, arom CH, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.7 Hz), 7.49–7.45 (*m*, 6H, arom CH), 7.43–7.39 (*m*, 4H, arom CH), 7.30 (*s*, 2H, CH═N), 3.50 (*s*, 4H, NCH_2), 2.28 [*s*, 12H, $N(CH_3)_2$] ppm; MS (ESI–TOF): *m*/*z* = 619.23 $[M + H]^+$ (expected isotopic profiles).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were found in a Fourier difference map.

3. Results and discussion

The lithium(I) and nickel(II) complexes **2** and **3**, respectively, derived from the same *N*,*O*-bidentate Schiff base ligand **1**, displayed distinct coordination geometries and crystal-packing arrangements. The observed structural disparities are principally attributable to the divergent coordination predilections exhibited by the two metal centres.

3.1. Lithium(I) complex

The molecular structure of lithium(I) complex **2** is shown in Fig. 2. The Li^I centre was coordinated by two *N*,*O*-chelating Schiff base ligands and one chloride ion, giving a five-coordinate environment. The Li—O distances were 1.947 (3) and

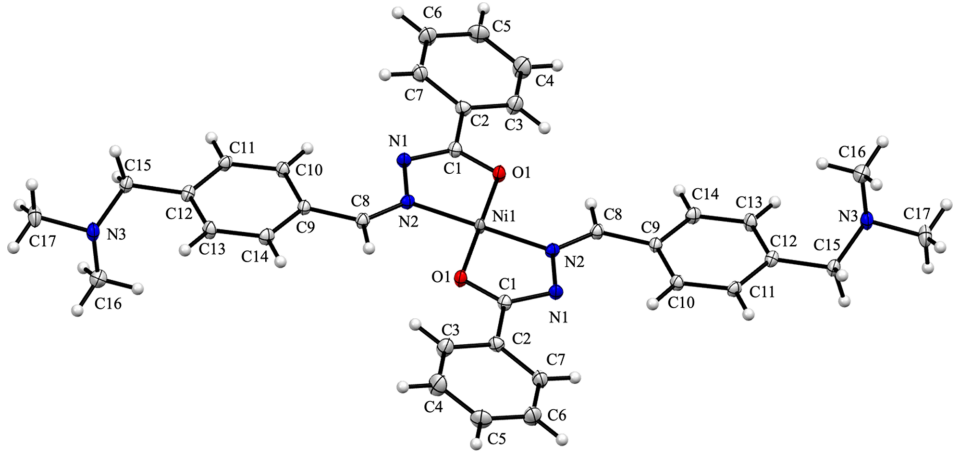


Figure 3
The molecular structure of nickel(II) complex **3**, with displacement ellipsoids drawn at the 50% probability level.

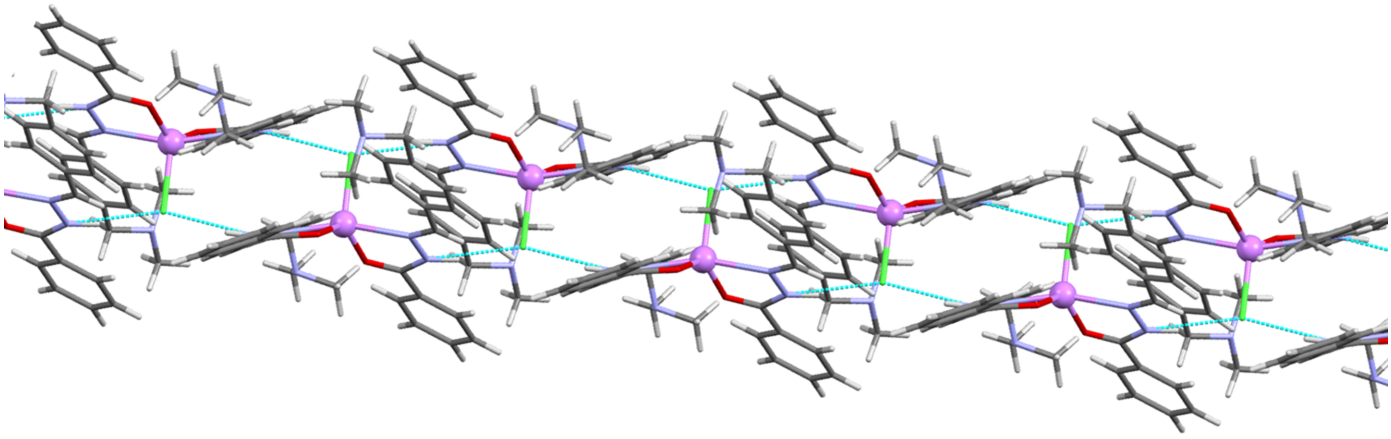


Figure 4
The crystal packing of lithium(I) complex **2**, showing the intermolecular N—H···Cl hydrogen-bonded chains.

1.962 (3) Å, while the corresponding Li—N distances were 2.309 (4) and 2.352 (4) Å, which were comparable to those reported for related lithium complexes (Specklin *et al.*, 2015). The chloride ligand completed the coordination sphere, with an Li—Cl distance of 2.399 (3) Å. Each ligand formed a five-membered chelate ring through the imine N and carbonyl O-donor atoms, with O—Li—N bite angles of 76.06 (12) and 76.61 (12)°, reflecting the geometrical constraints imposed by the chelate rings. The two ligands adopted closely similar conformations and displayed comparable bond lengths. The C═N [1.282 (2) and 1.289 (2) Å] and C═O bond lengths [1.233 (2) and 1.236 (2) Å] were consistent with delocalization within the hydrazone carbonyl fragment.

The five-coordinate Li^{I} environment deviated from the idealized square-pyramidal and trigonal-bipyramidal geometries. The Addison τ_5 parameter (Addison *et al.*, 1984), calculated from the two largest coordination angles [161.73 (17) and 130.61 (19)°], was 0.52. This value placed the coordination geometry approximately midway between the square-pyramidal (τ_5 = 0) and trigonal-bipyramidal (τ_5 = 1) limiting geometries. The deviation from either idealized geometry was largely imposed by the small O—Li—N bite angles of the two chelating ligands. The chloride ion was directly coordinated to Li^{I}, rather than acting solely as a counter-anion, and therefore formed an integral part of the five-coordinate environment. Its structural role extended beyond the primary coordination sphere, as the coordinated chloride ion also acted as a hydrogen-bond acceptor in the intermolecular N—H···Cl interactions. The two aromatic rings of each ligand (C1–C6/C12–C17 and C18–C23/C29–C34) were nearly coplanar, with dihedral angles of 3.22 and 3.74°, respectively.

3.2. Nickel(II) complex

The molecular structure of the nickel(II) complex is shown in Fig. 3. The Ni^{II} centre lay on a crystallographic inversion centre and was coordinated by two symmetry-related *N*,*O*-chelating ligands. Consequently, the asymmetric unit contained one-half of the molecular complex. The coordination environment was essentially square planar, with Ni—O and Ni—N distances of 1.8408 (11) and 1.8703 (13) Å, respectively, which were comparable to those reported for related nickel complexes (Raj Kumar *et al.*, 2015; Yang *et al.*, 2020). The *trans* angles O1—Ni1—O1 and N2—Ni1—N2 were constrained to 180° by crystallographic inversion symmetry, while the *cis* angles of 83.61 (5) and 96.39 (5)° indicated only a modest deviation from ideal square-planar geometry. The aromatic ring bearing the dimethylamino substituent (C9–C14) was nearly coplanar with the five-membered metallacycle, with a

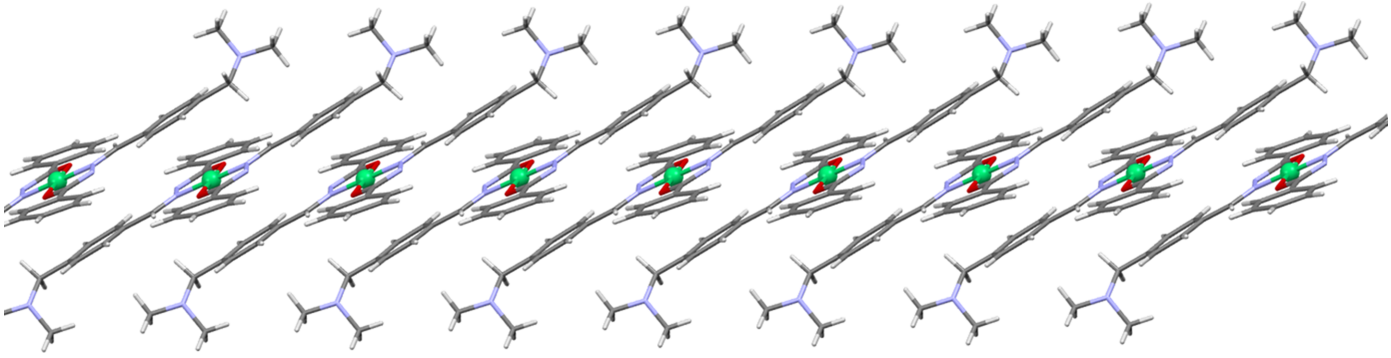


Figure 5
The crystal packing of nickel(II) complex **3**, showing the molecular columns.

dihedral angle 4.24°, whereas the second aromatic ring (C2–C7) was moderately inclined, with a dihedral angle of 13.30°.

In contrast to the lithium complex, no additional anion was coordinated to the nickel centre. Consequently, the coordination sphere comprised exclusively the two *N*,*O*-chelating ligands. The relatively short Ni—N and Ni—O distances, together with the well-defined square-planar arrangement, indicated that the ligand provided a compact coordination environment for Ni^{II}. The ligand acted exclusively as an *N*,*O*-bidentate donor in complex **3**. Although an additional donor site was present within the hydrazide fragment, the second N atom remained non-coordinating.

3.3. Supramolecular features

The crystal packing of lithium complex **2** was characterized by intermolecular N—H···Cl hydrogen bonds, with a H···Cl distance of 2.23 Å, involving the coordinated chloride ion with the N—H group of a neighbouring complex. These interactions linked the discrete lithium(I) complexes into one-dimensional chains extending through the crystal. Thus, the chloride ion fulfilled a dual structural role: it completed the coordination sphere of Li^{I} and acted as a hydrogen-bond acceptor linking neighbouring complexes. The N—H···Cl hydrogen bonds therefore played a key role in the supramolecular organization of complex **2**, assembling the individual lithium(I) complexes into chains through these intermolecular contacts. Together with the weaker interactions involving the aromatic groups, this hydrogen-bonding motif contributed to the observed crystal-packing arrangement (Fig. 4).

The crystal packing of nickel(II) complex **3** revealed an ordered arrangement of the molecules. A short intermolecular Ni···C contact of 3.2218 (18) Å was observed between the Ni^{II} centre and an aromatic C atom of a neighbouring molecule. Several short $Csp^2\cdots Csp^2$ contacts, ranging from 3.143 (2) to 3.379 (2) Å, were also observed between adjacent molecules. Collectively, these contacts contributed to the molecular packing and the formation of the observed columnar architecture (Fig. 5).

The comparison of the two crystal structures demonstrated the profound impact of the metal ion on the organization of the coordination compound. Despite the retention of the *N*,*O*-chelating mode in both complexes, Li^{I} complex **2** accommodated an additional chloride donor, resulting in a more open five-coordinate environment, whereas Ni^{II} complex **3** formed a compact square-planar complex with two chelating ligands. This disparity in the primary coordination sphere was manifested in the crystal packing: hydrogen-bonded N—H···Cl chains were observed for the lithium derivative, while the nickel complex adopted a columnar arrangement supported by short intermolecular contacts. Consequently, the metal-dependent coordination preferences were directly translated into distinct supramolecular architectures.

4. Conclusion

The crystal structures of the lithium(I) and nickel(II) complexes (**2** and **3**, respectively) demonstrated the ability of the same *N*,*O*-donor Schiff base ligand **1** to accommodate two metal centres with markedly different coordination preferences. Coordination to Li^{I} resulted in a five-coordinate environment that was distorted, with the chloride participating not only in metal coordination but also in the formation of intermolecular N—H···Cl hydrogen-bonded chains. In contrast, Ni^{II} formed a compact square-planar complex that assembled into columns through short intermolecular contacts. The structures presented demonstrate the capacity for the nature of the metal centre to regulate not only the primary coordination geometry but also the supramolecular organization of the resulting complex in the solid state.

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Synthesis and crystal structures of lithium(I) and nickel(II) complexes derived from an *N,O*-bidentate Schiff base ligand

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Computing details

Bis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazidato)nickel(II) (2)

Crystal data

$[Ni(C_{17}H_{18}N_3O)_2]$
M_r = 619.40
Triclinic, $P\overline{1}$
a = 6.3619 (6) Å
b = 10.7622 (13) Å
c = 11.8481 (13) Å
α = 78.649 (4)°
β = 78.080 (5)°
γ = 75.676 (3)°
V = 759.91 (14) Å^3
Z = 1
$F(000)$ = 326
D_x = 1.353 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6890 reflections
θ = 2.9–27.9°
μ = 0.68 mm^{-1}
T = 120 K
Block, orange
0.16 × 0.12 × 0.10 mm

Data collection

Bruker PHOTON-III CPAD diffractometer
Radiation source: Mo-ImuS 3.0 microfocus tube
φ and ω shuterless scans
Absorption correction: multi-scan (SADABS; Bruker, 2021)
T_{min} = 0.592, T_{max} = 0.746
18991 measured reflections
3631 independent reflections
3275 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 27.9°, θ_{min} = 2.9°
h = −7→8
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.06
3631 reflections
198 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.3146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 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. The samples were studied on Bruker PHOTON-III CPAD using Cu *Kα* (radiation λ = 1.54178 Å) for complex 2 and Cu *Kα* (radiation λ = 0.71073 Å) for complex 3, at T = 120 (2) K. The structures were solved with SHELXT2018 (Sheldrick, 2015a), which revealed the positions of the non-H atoms. The structures were refined with SHELXL2019/3 (Sheldrick, 2015b) by the full-matrix least-square techniques (use of F square magnitude; x, y, z, βij for C, Cl, N, O, Li and Ni atoms; x, y, z in riding mode for H atoms).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.000000	0.500000	1.000000	0.01082 (10)
O1	0.00603 (19)	0.34089 (11)	0.96262 (10)	0.0149 (2)
C1	0.1871 (3)	0.30108 (15)	0.89332 (13)	0.0133 (3)
C2	0.2126 (3)	0.17730 (15)	0.85013 (14)	0.0146 (3)
C3	0.0310 (3)	0.12157 (17)	0.86466 (16)	0.0218 (4)
H3	−0.107151	0.161473	0.904661	0.026*
C4	0.0517 (3)	0.00791 (18)	0.82078 (19)	0.0277 (4)
H4	−0.072583	−0.029656	0.830890	0.033*
C5	0.2528 (3)	−0.05127 (17)	0.76219 (17)	0.0245 (4)
H5	0.265940	−0.128403	0.731319	0.029*
C6	0.4351 (3)	0.00320 (17)	0.74900 (17)	0.0241 (4)
H6	0.573347	−0.037517	0.709746	0.029*
C7	0.4160 (3)	0.11648 (16)	0.79283 (15)	0.0197 (3)
H7	0.541182	0.152880	0.783938	0.024*
N1	0.3458 (2)	0.36588 (13)	0.85804 (12)	0.0141 (3)
N2	0.2786 (2)	0.48036 (13)	0.90710 (11)	0.0125 (3)
C8	0.4045 (3)	0.56331 (15)	0.88475 (13)	0.0134 (3)
H8	0.346776	0.637317	0.922938	0.016*
C9	0.6184 (3)	0.56316 (15)	0.81164 (13)	0.0123 (3)
C10	0.7390 (3)	0.46820 (15)	0.74290 (14)	0.0136 (3)
H10	0.685370	0.392837	0.744586	0.016*
C11	0.9370 (3)	0.48485 (15)	0.67247 (14)	0.0142 (3)
H11	1.016369	0.420476	0.625849	0.017*
C12	1.0221 (3)	0.59352 (15)	0.66846 (13)	0.0131 (3)
C13	0.9049 (3)	0.68606 (16)	0.73924 (14)	0.0153 (3)
H13	0.961455	0.759859	0.739392	0.018*
C14	0.7067 (3)	0.67079 (15)	0.80921 (14)	0.0147 (3)
H14	0.629075	0.734782	0.856579	0.018*
C15	1.2403 (3)	0.60672 (15)	0.59348 (14)	0.0146 (3)
H15A	1.359947	0.556141	0.636400	0.018*
H15B	1.255809	0.568848	0.521748	0.018*
N3	1.2662 (2)	0.74089 (14)	0.56043 (12)	0.0171 (3)
C16	1.1257 (3)	0.81237 (18)	0.47536 (17)	0.0241 (4)
H16A	1.139695	0.903121	0.457822	0.036*

H16B	0.972321	0.808433	0.507607	0.036*
H16C	1.170941	0.773515	0.403579	0.036*
C17	1.4957 (3)	0.74511 (19)	0.51409 (16)	0.0229 (4)
H17A	1.587888	0.696397	0.571901	0.034*
H17B	1.511621	0.835506	0.496922	0.034*
H17C	1.541821	0.706262	0.442307	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00893 (15)	0.01154 (15)	0.01268 (15)	−0.00433 (10)	0.00288 (10)	−0.00573 (10)
O1	0.0125 (5)	0.0152 (5)	0.0175 (5)	−0.0054 (4)	0.0030 (4)	−0.0065 (4)
C1	0.0127 (7)	0.0145 (7)	0.0131 (7)	−0.0036 (6)	−0.0012 (6)	−0.0032 (6)
C2	0.0163 (8)	0.0133 (7)	0.0147 (7)	−0.0040 (6)	−0.0011 (6)	−0.0037 (6)
C3	0.0163 (8)	0.0202 (8)	0.0308 (9)	−0.0054 (7)	0.0010 (7)	−0.0115 (7)
C4	0.0223 (9)	0.0230 (9)	0.0426 (11)	−0.0099 (7)	−0.0014 (8)	−0.0140 (8)
C5	0.0288 (10)	0.0157 (8)	0.0307 (10)	−0.0050 (7)	−0.0019 (8)	−0.0105 (7)
C6	0.0225 (9)	0.0181 (8)	0.0294 (9)	−0.0038 (7)	0.0060 (7)	−0.0095 (7)
C7	0.0180 (8)	0.0163 (8)	0.0237 (8)	−0.0063 (6)	0.0026 (7)	−0.0038 (6)
N1	0.0139 (6)	0.0110 (6)	0.0178 (6)	−0.0036 (5)	0.0017 (5)	−0.0061 (5)
N2	0.0124 (6)	0.0123 (6)	0.0131 (6)	−0.0024 (5)	−0.0001 (5)	−0.0047 (5)
C8	0.0125 (7)	0.0141 (7)	0.0138 (7)	−0.0034 (6)	0.0003 (6)	−0.0044 (6)
C9	0.0108 (7)	0.0136 (7)	0.0124 (7)	−0.0033 (6)	0.0000 (5)	−0.0027 (6)
C10	0.0129 (7)	0.0132 (7)	0.0161 (7)	−0.0046 (6)	−0.0006 (6)	−0.0048 (6)
C11	0.0120 (7)	0.0140 (7)	0.0162 (7)	−0.0017 (6)	0.0009 (6)	−0.0064 (6)
C12	0.0100 (7)	0.0168 (7)	0.0124 (7)	−0.0030 (6)	−0.0010 (6)	−0.0033 (6)
C13	0.0142 (8)	0.0156 (7)	0.0187 (8)	−0.0072 (6)	0.0000 (6)	−0.0069 (6)
C14	0.0149 (8)	0.0151 (7)	0.0147 (7)	−0.0033 (6)	0.0006 (6)	−0.0069 (6)
C15	0.0110 (7)	0.0169 (8)	0.0167 (7)	−0.0045 (6)	0.0012 (6)	−0.0059 (6)
N3	0.0142 (7)	0.0185 (7)	0.0195 (7)	−0.0083 (5)	0.0030 (5)	−0.0054 (5)
C16	0.0169 (8)	0.0214 (9)	0.0300 (10)	−0.0033 (7)	−0.0002 (7)	0.0005 (7)
C17	0.0156 (8)	0.0303 (10)	0.0232 (9)	−0.0120 (7)	0.0018 (7)	−0.0016 (7)

Geometric parameters (Å, º)

Ni1—O1^{i}	1.8408 (11)	C9—C14	1.400 (2)
Ni1—O1	1.8408 (11)	C9—C10	1.406 (2)
Ni1—N2^{i}	1.8703 (13)	C10—C11	1.390 (2)
Ni1—N2	1.8703 (13)	C10—H10	0.9500
O1—C1	1.2992 (19)	C11—C12	1.394 (2)
C1—N1	1.319 (2)	C11—H11	0.9500
C1—C2	1.480 (2)	C12—C13	1.398 (2)
C2—C3	1.395 (2)	C12—C15	1.508 (2)
C2—C7	1.398 (2)	C13—C14	1.386 (2)
C3—C4	1.388 (2)	C13—H13	0.9500
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.389 (3)	C15—N3	1.461 (2)
C4—H4	0.9500	C15—H15A	0.9900

C5—C6	1.392 (3)	C15—H15B	0.9900
C5—H5	0.9500	N3—C17	1.459 (2)
C6—C7	1.386 (2)	N3—C16	1.460 (2)
C6—H6	0.9500	C16—H16A	0.9800
C7—H7	0.9500	C16—H16B	0.9800
N1—N2	1.3990 (18)	C16—H16C	0.9800
N2—C8	1.297 (2)	C17—H17A	0.9800
C8—C9	1.454 (2)	C17—H17B	0.9800
C8—H8	0.9500	C17—H17C	0.9800

O1^{i}—Ni1—O1	180.0	C10—C9—C8	126.46 (14)
O1^{i}—Ni1—N2^{i}	83.61 (5)	C11—C10—C9	119.86 (14)
O1—Ni1—N2^{i}	96.39 (5)	C11—C10—H10	120.1
O1^{i}—Ni1—N2	96.39 (5)	C9—C10—H10	120.1
O1—Ni1—N2	83.61 (5)	C10—C11—C12	121.75 (14)
N2^{i}—Ni1—N2	180.0	C10—C11—H11	119.1
C1—O1—Ni1	110.86 (10)	C12—C11—H11	119.1
O1—C1—N1	123.70 (14)	C11—C12—C13	118.30 (14)
O1—C1—C2	117.60 (14)	C11—C12—C15	120.33 (14)
N1—C1—C2	118.69 (14)	C13—C12—C15	121.31 (14)
C3—C2—C7	119.42 (15)	C14—C13—C12	120.40 (15)
C3—C2—C1	119.70 (14)	C14—C13—H13	119.8
C7—C2—C1	120.86 (15)	C12—C13—H13	119.8
C4—C3—C2	120.10 (16)	C13—C14—C9	121.47 (14)
C4—C3—H3	119.9	C13—C14—H14	119.3
C2—C3—H3	119.9	C9—C14—H14	119.3
C3—C4—C5	120.43 (17)	N3—C15—C12	113.47 (13)
C3—C4—H4	119.8	N3—C15—H15A	108.9
C5—C4—H4	119.8	C12—C15—H15A	108.9
C4—C5—C6	119.56 (17)	N3—C15—H15B	108.9
C4—C5—H5	120.2	C12—C15—H15B	108.9
C6—C5—H5	120.2	H15A—C15—H15B	107.7
C7—C6—C5	120.37 (16)	C17—N3—C16	110.43 (14)
C7—C6—H6	119.8	C17—N3—C15	110.56 (13)
C5—C6—H6	119.8	C16—N3—C15	110.95 (14)
C6—C7—C2	120.10 (16)	N3—C16—H16A	109.5
C6—C7—H7	120.0	N3—C16—H16B	109.5
C2—C7—H7	120.0	H16A—C16—H16B	109.5
C1—N1—N2	107.52 (13)	N3—C16—H16C	109.5
C8—N2—N1	120.14 (13)	H16A—C16—H16C	109.5
C8—N2—Ni1	125.57 (11)	H16B—C16—H16C	109.5
N1—N2—Ni1	114.28 (10)	N3—C17—H17A	109.5
N2—C8—C9	131.45 (14)	N3—C17—H17B	109.5
N2—C8—H8	114.3	H17A—C17—H17B	109.5
C9—C8—H8	114.3	N3—C17—H17C	109.5
C14—C9—C10	118.19 (14)	H17A—C17—H17C	109.5
C14—C9—C8	115.33 (14)	H17B—C17—H17C	109.5

N2^{i}—Ni1—O1—C1	178.65 (10)	O1—Ni1—N2—C8	179.56 (14)
N2—Ni1—O1—C1	−1.35 (10)	O1^{i}—Ni1—N2—N1	−179.03 (10)
Ni1—O1—C1—N1	1.68 (19)	O1—Ni1—N2—N1	0.97 (10)
Ni1—O1—C1—C2	−176.97 (11)	N1—N2—C8—C9	1.1 (3)
O1—C1—C2—C3	12.7 (2)	Ni1—N2—C8—C9	−177.41 (13)
N1—C1—C2—C3	−166.00 (16)	N2—C8—C9—C14	−179.61 (16)
O1—C1—C2—C7	−168.50 (15)	N2—C8—C9—C10	1.9 (3)
N1—C1—C2—C7	12.8 (2)	C14—C9—C10—C11	−1.9 (2)
C7—C2—C3—C4	−1.1 (3)	C8—C9—C10—C11	176.60 (15)
C1—C2—C3—C4	177.72 (17)	C9—C10—C11—C12	0.6 (2)
C2—C3—C4—C5	0.0 (3)	C10—C11—C12—C13	1.1 (2)
C3—C4—C5—C6	0.9 (3)	C10—C11—C12—C15	178.36 (14)
C4—C5—C6—C7	−0.7 (3)	C11—C12—C13—C14	−1.5 (2)
C5—C6—C7—C2	−0.4 (3)	C15—C12—C13—C14	−178.73 (14)
C3—C2—C7—C6	1.3 (3)	C12—C13—C14—C9	0.2 (2)
C1—C2—C7—C6	−177.53 (16)	C10—C9—C14—C13	1.5 (2)
O1—C1—N1—N2	−0.9 (2)	C8—C9—C14—C13	−177.14 (15)
C2—C1—N1—N2	177.76 (13)	C11—C12—C15—N3	156.52 (15)
C1—N1—N2—C8	−179.04 (14)	C13—C12—C15—N3	−26.3 (2)
C1—N1—N2—Ni1	−0.37 (15)	C12—C15—N3—C17	165.82 (14)
O1^{i}—Ni1—N2—C8	−0.44 (14)	C12—C15—N3—C16	−71.31 (17)

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.

Chloridobis(*N*′-{4-[(dimethylamino)methyl]benzylidene}benzohydrazide)lithium(I) (3)

Crystal data

[LiCl($C_{17}H_{19}N_3O$)$_2$]
M_r = 605.09
Monoclinic, $P2_1/c$
a = 11.8979 (4) Å
b = 17.8064 (7) Å
c = 15.6160 (6) Å
β = 93.442 (2)°
V = 3302.4 (2) Å^3
Z = 4
$F(000)$ = 1280
D_x = 1.217 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9978 reflections
θ = 3.7–66.3°
μ = 1.33 mm^{-1}
T = 120 K
Block, colourless
0.14 × 0.14 × 0.12 mm

Data collection

Bruker PHOTON-III CPAD diffractometer
Radiation source: Cu-ImuS Diamond microfocus tube
φ and ω shuterless scans
Absorption correction: multi-scan (SADABS; Bruker, 2021)
T_{min} = 0.586, T_{max} = 0.746
50782 measured reflections
5825 independent reflections
4813 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 66.7°, θ_{min} = 3.7°
h = −13→14
k = −21→21
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.127
S = 1.04
5825 reflections
401 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.8747P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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. The samples were studied on Bruker PHOTON-III CPAD using Cu *Kα* (radiation λ = 1.54178 Å) for complex 2 and Cu *Kα* (radiation λ = 0.71073 Å) for complex 3, at T = 120 (2) K. The structures were solved with SHELXT2018 (Sheldrick, 2015a), which revealed the positions of the non-H atoms. The structures were refined with SHELXL2019/3 (Sheldrick, 2015b) by the full-matrix least-square techniques (use of F square magnitude; x, y, z, βij for C, Cl, N, O, Li and Ni atoms; x, y, z in riding mode for H atoms).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.04097 (15)	0.35446 (10)	0.61277 (12)	0.0282 (4)
C2	0.13953 (15)	0.32917 (10)	0.57806 (12)	0.0310 (4)
H2	0.191837	0.364131	0.557454	0.037*
C3	0.16063 (16)	0.25289 (10)	0.57384 (13)	0.0321 (4)
H3	0.227950	0.236065	0.550246	0.039*
C4	0.08574 (16)	0.20028 (10)	0.60328 (12)	0.0315 (4)
C5	−0.01246 (16)	0.22555 (10)	0.63781 (13)	0.0341 (4)
H5	−0.064438	0.190374	0.658460	0.041*
C6	−0.03486 (16)	0.30167 (10)	0.64226 (13)	0.0331 (4)
H6	−0.102462	0.318286	0.665588	0.040*
C7	0.10925 (18)	0.11714 (10)	0.59864 (13)	0.0357 (5)
H7A	0.039218	0.090535	0.579231	0.043*
H7B	0.165738	0.107994	0.555789	0.043*
N1	0.15095 (13)	0.08679 (8)	0.68139 (10)	0.0323 (4)
C8	0.14305 (18)	0.00531 (11)	0.68176 (14)	0.0375 (5)
H8A	0.189497	−0.015401	0.637701	0.056*
H8B	0.064475	−0.009750	0.669663	0.056*
H8C	0.169861	−0.013852	0.738174	0.056*
C9	0.26634 (17)	0.11037 (11)	0.70253 (14)	0.0379 (5)
H9A	0.290834	0.091630	0.759637	0.057*
H9B	0.270407	0.165341	0.702166	0.057*
H9C	0.315507	0.090039	0.660034	0.057*
C10	0.00945 (15)	0.43323 (10)	0.61920 (12)	0.0292 (4)
H10	−0.063748	0.444298	0.636898	0.035*
N2	0.07376 (13)	0.48900 (8)	0.60261 (10)	0.0274 (3)
N3	0.02133 (12)	0.55821 (8)	0.61111 (10)	0.0289 (3)
H3A	−0.060800	0.556200	0.609800	0.035*
C11	0.08387 (15)	0.62077 (10)	0.60577 (11)	0.0271 (4)
O1	0.18565 (10)	0.61795 (7)	0.59432 (9)	0.0331 (3)

C12	0.02452 (15)	0.69392 (10)	0.61594 (12)	0.0285 (4)
C13	0.07886 (16)	0.75880 (10)	0.59024 (13)	0.0325 (4)
H13	0.150332	0.755344	0.566471	0.039*
C14	0.02853 (17)	0.82839 (11)	0.59939 (13)	0.0372 (5)
H14	0.065255	0.872490	0.581274	0.045*
C15	−0.07469 (18)	0.83373 (11)	0.63473 (13)	0.0386 (5)
H15	−0.108547	0.881541	0.641296	0.046*
C16	−0.12891 (18)	0.76987 (11)	0.66058 (14)	0.0391 (5)
H16	−0.200083	0.773767	0.684731	0.047*
C17	−0.07946 (17)	0.69979 (11)	0.65130 (13)	0.0353 (4)
H17	−0.116870	0.655872	0.669181	0.042*
C18	0.46867 (15)	0.68482 (10)	0.51296 (12)	0.0303 (4)
C19	0.54249 (17)	0.74601 (11)	0.51262 (14)	0.0376 (5)
H19	0.614121	0.742613	0.542689	0.045*
C20	0.51256 (18)	0.81145 (12)	0.46905 (14)	0.0409 (5)
H20	0.563067	0.852817	0.470688	0.049*
C21	0.40932 (17)	0.81713 (11)	0.42296 (13)	0.0369 (5)
C22	0.33562 (17)	0.75625 (11)	0.42411 (14)	0.0376 (5)
H22	0.264082	0.759744	0.393913	0.045*
C223	0.36407 (16)	0.69111 (11)	0.46800 (13)	0.0335 (4)
H223	0.312389	0.650432	0.467650	0.040*
C24	0.37881 (19)	0.88618 (12)	0.36930 (15)	0.0437 (5)
H24A	0.430066	0.927799	0.387381	0.052*
H24B	0.390349	0.875042	0.308342	0.052*
N4	0.26357 (16)	0.91015 (10)	0.37702 (12)	0.0430 (4)
C25	0.2291 (2)	0.96420 (14)	0.31013 (17)	0.0573 (6)
H25A	0.148579	0.975029	0.312730	0.086*
H25B	0.243187	0.943112	0.253808	0.086*
H25C	0.272257	1.010700	0.318964	0.086*
C26	0.2489 (2)	0.94207 (14)	0.46079 (16)	0.0562 (6)
H26A	0.271302	0.905177	0.505145	0.084*
H26B	0.169649	0.955566	0.465508	0.084*
H26C	0.295775	0.987101	0.468460	0.084*
C27	0.50575 (15)	0.61811 (10)	0.56097 (12)	0.0307 (4)
H27	0.582936	0.614859	0.580017	0.037*
N5	0.44096 (12)	0.56359 (8)	0.57913 (10)	0.0285 (3)
N6	0.49685 (12)	0.50579 (8)	0.62455 (10)	0.0290 (3)
H6A	0.579000	0.503800	0.619100	0.044*
C28	0.43444 (15)	0.44915 (10)	0.65463 (12)	0.0281 (4)
O2	0.33111 (10)	0.44761 (7)	0.64276 (9)	0.0334 (3)
C29	0.49709 (15)	0.38904 (10)	0.70420 (12)	0.0282 (4)
C30	0.44188 (16)	0.32142 (11)	0.71782 (12)	0.0338 (4)
H30	0.366552	0.314555	0.695461	0.041*
C31	0.49632 (17)	0.26426 (12)	0.76374 (14)	0.0394 (5)
H31	0.458086	0.218315	0.772538	0.047*
C32	0.60619 (17)	0.27338 (11)	0.79707 (13)	0.0371 (5)
H32	0.643283	0.234033	0.828637	0.044*
C33	0.66094 (17)	0.34036 (11)	0.78380 (13)	0.0388 (5)

H33	0.736248	0.346958	0.806319	0.047*
C34	0.60720 (16)	0.39817 (11)	0.73794 (14)	0.0364 (5)
H34	0.645676	0.444089	0.729544	0.044*
Cl1	0.24513 (3)	0.48191 (2)	0.42064 (3)	0.03081 (14)
Li1	0.2536 (3)	0.52092 (18)	0.5680 (2)	0.0348 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0253 (9)	0.0259 (9)	0.0326 (10)	0.0011 (7)	−0.0037 (7)	0.0013 (7)
C2	0.0272 (10)	0.0266 (9)	0.0390 (11)	0.0008 (7)	0.0017 (8)	0.0006 (8)
C3	0.0272 (10)	0.0311 (10)	0.0380 (11)	0.0048 (7)	0.0022 (8)	−0.0014 (8)
C4	0.0317 (10)	0.0271 (10)	0.0347 (10)	0.0033 (7)	−0.0063 (8)	0.0001 (7)
C5	0.0314 (10)	0.0265 (9)	0.0441 (11)	−0.0029 (7)	−0.0012 (8)	0.0029 (8)
C6	0.0263 (10)	0.0300 (10)	0.0431 (11)	0.0024 (7)	0.0025 (8)	0.0013 (8)
C7	0.0399 (11)	0.0258 (10)	0.0403 (11)	0.0023 (8)	−0.0062 (9)	−0.0028 (8)
N1	0.0326 (9)	0.0245 (8)	0.0394 (9)	0.0011 (6)	−0.0012 (7)	−0.0002 (6)
C8	0.0373 (11)	0.0276 (10)	0.0477 (12)	0.0025 (8)	0.0028 (9)	0.0006 (8)
C9	0.0323 (11)	0.0359 (11)	0.0450 (12)	0.0001 (8)	−0.0008 (9)	0.0047 (9)
C10	0.0239 (9)	0.0285 (9)	0.0351 (10)	0.0039 (7)	0.0011 (7)	0.0000 (8)
N2	0.0246 (8)	0.0243 (8)	0.0332 (8)	0.0045 (6)	0.0000 (6)	−0.0005 (6)
N3	0.0223 (8)	0.0239 (8)	0.0406 (9)	0.0040 (6)	0.0014 (6)	−0.0001 (6)
C11	0.0260 (10)	0.0272 (9)	0.0278 (9)	0.0012 (7)	0.0009 (7)	0.0014 (7)
O1	0.0227 (7)	0.0290 (7)	0.0480 (8)	0.0013 (5)	0.0052 (6)	−0.0006 (6)
C12	0.0285 (10)	0.0266 (9)	0.0298 (10)	0.0033 (7)	−0.0022 (7)	−0.0016 (7)
C13	0.0275 (10)	0.0291 (10)	0.0404 (11)	−0.0011 (7)	−0.0026 (8)	−0.0034 (8)
C14	0.0396 (11)	0.0245 (10)	0.0467 (12)	−0.0017 (8)	−0.0041 (9)	−0.0013 (8)
C15	0.0462 (12)	0.0256 (10)	0.0434 (12)	0.0080 (8)	−0.0025 (9)	−0.0040 (8)
C16	0.0382 (11)	0.0358 (11)	0.0440 (12)	0.0104 (9)	0.0095 (9)	−0.0024 (9)
C17	0.0380 (11)	0.0287 (10)	0.0399 (11)	0.0033 (8)	0.0094 (8)	0.0017 (8)
C18	0.0257 (9)	0.0332 (10)	0.0329 (10)	0.0039 (7)	0.0087 (7)	0.0014 (8)
C19	0.0277 (10)	0.0424 (11)	0.0431 (12)	−0.0013 (8)	0.0057 (8)	0.0049 (9)
C20	0.0349 (11)	0.0377 (11)	0.0513 (13)	−0.0048 (9)	0.0110 (9)	0.0054 (9)
C21	0.0342 (11)	0.0353 (11)	0.0423 (11)	0.0031 (8)	0.0127 (9)	0.0050 (9)
C22	0.0296 (10)	0.0388 (11)	0.0446 (12)	0.0034 (8)	0.0031 (8)	0.0073 (9)
C223	0.0286 (10)	0.0307 (10)	0.0417 (11)	0.0008 (8)	0.0055 (8)	0.0022 (8)
C24	0.0436 (12)	0.0392 (12)	0.0496 (13)	0.0024 (9)	0.0150 (10)	0.0097 (10)
N4	0.0474 (11)	0.0371 (9)	0.0448 (11)	0.0073 (8)	0.0065 (8)	0.0077 (8)
C25	0.0678 (17)	0.0467 (13)	0.0576 (16)	0.0122 (12)	0.0050 (13)	0.0135 (11)
C26	0.0661 (16)	0.0533 (15)	0.0507 (15)	0.0144 (12)	0.0164 (12)	0.0035 (11)
C27	0.0250 (9)	0.0339 (10)	0.0334 (10)	0.0043 (8)	0.0038 (7)	−0.0013 (8)
N5	0.0242 (8)	0.0300 (8)	0.0313 (8)	0.0054 (6)	0.0017 (6)	0.0000 (6)
N6	0.0211 (8)	0.0307 (8)	0.0350 (9)	0.0034 (6)	0.0007 (6)	0.0044 (6)
C28	0.0251 (10)	0.0316 (10)	0.0277 (9)	0.0022 (7)	0.0020 (7)	−0.0038 (7)
O2	0.0198 (7)	0.0374 (7)	0.0428 (8)	0.0017 (5)	0.0009 (5)	0.0031 (6)
C29	0.0250 (9)	0.0319 (10)	0.0279 (10)	0.0027 (7)	0.0026 (7)	0.0001 (7)
C30	0.0267 (10)	0.0392 (11)	0.0354 (11)	−0.0027 (8)	0.0001 (8)	0.0040 (8)
C31	0.0365 (11)	0.0367 (11)	0.0449 (12)	−0.0061 (9)	0.0016 (9)	0.0092 (9)

C32	0.0351 (11)	0.0371 (11)	0.0386 (11)	0.0024 (8)	−0.0004 (8)	0.0081 (8)
C33	0.0296 (10)	0.0403 (11)	0.0454 (12)	−0.0015 (8)	−0.0078 (9)	0.0078 (9)
C34	0.0291 (10)	0.0331 (10)	0.0462 (12)	−0.0038 (8)	−0.0045 (8)	0.0053 (9)
Cl1	0.0212 (2)	0.0340 (3)	0.0373 (3)	0.00187 (16)	0.00206 (17)	−0.00086 (18)
Li1	0.0289 (17)	0.0357 (18)	0.0399 (19)	0.0062 (13)	0.0016 (14)	0.0000 (14)

Geometric parameters (Å, º)

C1—C2	1.396 (3)	C18—C19	1.400 (3)
C1—C6	1.400 (3)	C18—C27	1.459 (3)
C1—C10	1.457 (2)	C19—C20	1.385 (3)
C2—C3	1.383 (3)	C19—H19	0.9500
C2—H2	0.9500	C20—C21	1.390 (3)
C3—C4	1.390 (3)	C20—H20	0.9500
C3—H3	0.9500	C21—C22	1.395 (3)
C4—C5	1.391 (3)	C21—C24	1.520 (3)
C4—C7	1.509 (3)	C22—C223	1.379 (3)
C5—C6	1.384 (3)	C22—H22	0.9500
C5—H5	0.9500	C223—H223	0.9500
C6—H6	0.9500	C24—N4	1.448 (3)
C7—N1	1.460 (2)	C24—H24A	0.9900
C7—H7A	0.9900	C24—H24B	0.9900
C7—H7B	0.9900	N4—C26	1.446 (3)
N1—C9	1.455 (2)	N4—C25	1.461 (3)
N1—C8	1.454 (2)	C25—H25A	0.9800
C8—H8A	0.9800	C25—H25B	0.9800
C8—H8B	0.9800	C25—H25C	0.9800
C8—H8C	0.9800	C26—H26A	0.9800
C9—H9A	0.9800	C26—H26B	0.9800
C9—H9B	0.9800	C26—H26C	0.9800
C9—H9C	0.9800	C27—N5	1.282 (2)
C10—N2	1.289 (2)	C27—H27	0.9500
C10—H10	0.9500	N5—N6	1.396 (2)
N2—N3	1.391 (2)	N5—Li1	2.352 (4)
N2—Li1	2.309 (4)	N6—C28	1.353 (2)
N3—C11	1.345 (2)	N6—H6A	0.9868
N3—H3A	0.9769	C28—O2	1.233 (2)
C11—O1	1.236 (2)	C28—C29	1.494 (2)
C11—C12	1.495 (2)	C28—Li1	2.783 (4)
C11—Li1	2.780 (4)	O2—Li1	1.947 (3)
O1—Li1	1.962 (3)	C29—C34	1.392 (3)
C12—C17	1.389 (3)	C29—C30	1.394 (3)
C12—C13	1.395 (3)	C30—C31	1.383 (3)
C13—C14	1.387 (3)	C30—H30	0.9500
C13—H13	0.9500	C31—C32	1.387 (3)
C14—C15	1.380 (3)	C31—H31	0.9500
C14—H14	0.9500	C32—C33	1.381 (3)
C15—C16	1.380 (3)	C32—H32	0.9500

C15—H15	0.9500	C33—C34	1.388 (3)
C16—C17	1.391 (3)	C33—H33	0.9500
C16—H16	0.9500	C34—H34	0.9500
C17—H17	0.9500	Cl1—Li1	2.399 (3)
C18—C223	1.396 (3)		

C2—C1—C6	118.95 (17)	C22—C21—C24	120.42 (19)
C2—C1—C10	124.28 (17)	C223—C22—C21	121.61 (19)
C6—C1—C10	116.75 (17)	C223—C22—H22	119.2
C3—C2—C1	119.63 (18)	C21—C22—H22	119.2
C3—C2—H2	120.2	C22—C223—C18	120.15 (18)
C1—C2—H2	120.2	C22—C223—H223	119.9
C2—C3—C4	121.61 (18)	C18—C223—H223	119.9
C2—C3—H3	119.2	N4—C24—C21	112.87 (17)
C4—C3—H3	119.2	N4—C24—H24A	109.0
C3—C4—C5	118.71 (17)	C21—C24—H24A	109.0
C3—C4—C7	121.40 (18)	N4—C24—H24B	109.0
C5—C4—C7	119.90 (18)	C21—C24—H24B	109.0
C6—C5—C4	120.33 (18)	H24A—C24—H24B	107.8
C6—C5—H5	119.8	C26—N4—C24	110.94 (19)
C4—C5—H5	119.8	C26—N4—C25	110.11 (18)
C5—C6—C1	120.76 (18)	C24—N4—C25	111.20 (19)
C5—C6—H6	119.6	N4—C25—H25A	109.5
C1—C6—H6	119.6	N4—C25—H25B	109.5
N1—C7—C4	112.01 (16)	H25A—C25—H25B	109.5
N1—C7—H7A	109.2	N4—C25—H25C	109.5
C4—C7—H7A	109.2	H25A—C25—H25C	109.5
N1—C7—H7B	109.2	H25B—C25—H25C	109.5
C4—C7—H7B	109.2	N4—C26—H26A	109.5
H7A—C7—H7B	107.9	N4—C26—H26B	109.5
C9—N1—C8	110.34 (15)	H26A—C26—H26B	109.5
C9—N1—C7	111.11 (16)	N4—C26—H26C	109.5
C8—N1—C7	110.75 (15)	H26A—C26—H26C	109.5
N1—C8—H8A	109.5	H26B—C26—H26C	109.5
N1—C8—H8B	109.5	N5—C27—C18	124.27 (17)
H8A—C8—H8B	109.5	N5—C27—H27	117.9
N1—C8—H8C	109.5	C18—C27—H27	117.9
H8A—C8—H8C	109.5	C27—N5—N6	113.35 (15)
H8B—C8—H8C	109.5	C27—N5—Li1	143.91 (15)
N1—C9—H9A	109.5	N6—N5—Li1	102.71 (13)
N1—C9—H9B	109.5	C28—N6—N5	118.12 (14)
H9A—C9—H9B	109.5	C28—N6—H6A	124.8
N1—C9—H9C	109.5	N5—N6—H6A	115.3
H9A—C9—H9C	109.5	O2—C28—N6	121.85 (16)
H9B—C9—H9C	109.5	O2—C28—C29	121.61 (17)
N2—C10—C1	124.70 (17)	N6—C28—C29	116.53 (15)
N2—C10—H10	117.7	O2—C28—Li1	37.06 (11)
C1—C10—H10	117.7	N6—C28—Li1	85.04 (12)

C10—N2—N3	112.84 (15)	C29—C28—Li1	158.16 (15)
C10—N2—Li1	143.70 (15)	C28—O2—Li1	120.51 (16)
N3—N2—Li1	103.38 (13)	C34—C29—C30	118.98 (17)
C11—N3—N2	118.35 (15)	C34—C29—C28	122.79 (17)
C11—N3—H3A	125.8	C30—C29—C28	118.23 (16)
N2—N3—H3A	114.8	C31—C30—C29	120.29 (17)
O1—C11—N3	121.73 (16)	C31—C30—H30	119.9
O1—C11—C12	121.61 (16)	C29—C30—H30	119.9
N3—C11—C12	116.65 (16)	C30—C31—C32	120.64 (18)
O1—C11—Li1	38.08 (11)	C30—C31—H31	119.7
N3—C11—Li1	83.97 (12)	C32—C31—H31	119.7
C12—C11—Li1	159.01 (15)	C33—C32—C31	119.16 (18)
C11—O1—Li1	119.06 (15)	C33—C32—H32	120.4
C17—C12—C13	119.45 (17)	C31—C32—H32	120.4
C17—C12—C11	123.07 (17)	C32—C33—C34	120.75 (18)
C13—C12—C11	117.46 (17)	C32—C33—H33	119.6
C14—C13—C12	119.98 (19)	C34—C33—H33	119.6
C14—C13—H13	120.0	C33—C34—C29	120.18 (18)
C12—C13—H13	120.0	C33—C34—H34	119.9
C15—C14—C13	120.19 (19)	C29—C34—H34	119.9
C15—C14—H14	119.9	O2—Li1—O1	130.61 (19)
C13—C14—H14	119.9	O2—Li1—N2	96.12 (15)
C14—C15—C16	120.22 (18)	O1—Li1—N2	76.61 (12)
C14—C15—H15	119.9	O2—Li1—N5	76.06 (12)
C16—C15—H15	119.9	O1—Li1—N5	95.77 (14)
C15—C16—C17	120.1 (2)	N2—Li1—N5	161.73 (17)
C15—C16—H16	120.0	O2—Li1—Cl1	111.85 (15)
C17—C16—H16	120.0	O1—Li1—Cl1	117.53 (15)
C12—C17—C16	120.09 (19)	N2—Li1—Cl1	99.64 (12)
C12—C17—H17	120.0	N5—Li1—Cl1	98.60 (13)
C16—C17—H17	120.0	O2—Li1—C11	128.71 (17)
C223—C18—C19	118.44 (17)	O1—Li1—C11	22.86 (7)
C223—C18—C27	123.83 (17)	N2—Li1—C11	54.04 (8)
C19—C18—C27	117.73 (17)	N5—Li1—C11	118.35 (13)
C20—C19—C18	120.92 (19)	Cl1—Li1—C11	113.56 (12)
C20—C19—H19	119.5	O2—Li1—C28	22.43 (7)
C18—C19—H19	119.5	O1—Li1—C28	128.21 (15)
C19—C20—C21	120.59 (19)	N2—Li1—C28	118.24 (14)
C19—C20—H20	119.7	N5—Li1—C28	53.87 (8)
C21—C20—H20	119.7	Cl1—Li1—C28	108.66 (12)
C20—C21—C22	118.27 (18)	C11—Li1—C28	137.77 (14)
C20—C21—C24	121.26 (19)		

C6—C1—C2—C3	−0.3 (3)	C223—C18—C19—C20	0.2 (3)
C10—C1—C2—C3	−179.04 (17)	C27—C18—C19—C20	−179.42 (19)
C1—C2—C3—C4	0.1 (3)	C18—C19—C20—C21	−1.5 (3)
C2—C3—C4—C5	−0.1 (3)	C19—C20—C21—C22	2.0 (3)
C2—C3—C4—C7	−179.91 (17)	C19—C20—C21—C24	−175.3 (2)

C3—C4—C5—C6	0.3 (3)	C20—C21—C22—C223	−1.4 (3)
C7—C4—C5—C6	−179.92 (17)	C24—C21—C22—C223	176.0 (2)
C4—C5—C6—C1	−0.5 (3)	C21—C22—C223—C18	0.1 (3)
C2—C1—C6—C5	0.5 (3)	C19—C18—C223—C22	0.4 (3)
C10—C1—C6—C5	179.31 (17)	C27—C18—C223—C22	−179.92 (19)
C3—C4—C7—N1	101.4 (2)	C20—C21—C24—N4	−138.4 (2)
C5—C4—C7—N1	−78.4 (2)	C22—C21—C24—N4	44.4 (3)
C4—C7—N1—C9	−72.9 (2)	C21—C24—N4—C26	70.9 (2)
C4—C7—N1—C8	164.08 (17)	C21—C24—N4—C25	−166.2 (2)
C2—C1—C10—N2	−8.0 (3)	C223—C18—C27—N5	−12.2 (3)
C6—C1—C10—N2	173.21 (18)	C19—C18—C27—N5	167.49 (19)
C1—C10—N2—N3	177.92 (16)	C18—C27—N5—N6	179.13 (16)
C1—C10—N2—Li1	−6.0 (4)	C18—C27—N5—Li1	−2.8 (4)
C10—N2—N3—C11	172.02 (16)	C27—N5—N6—C28	173.31 (16)
Li1—N2—N3—C11	−5.6 (2)	Li1—N5—N6—C28	−5.55 (19)
N2—N3—C11—O1	−0.6 (3)	N5—N6—C28—O2	0.1 (3)
N2—N3—C11—C12	−179.53 (15)	N5—N6—C28—C29	−178.98 (15)
N2—N3—C11—Li1	4.55 (16)	N5—N6—C28—Li1	4.59 (16)
N3—C11—O1—Li1	8.3 (3)	N6—C28—O2—Li1	7.4 (3)
C12—C11—O1—Li1	−172.79 (17)	C29—C28—O2—Li1	−173.54 (17)
O1—C11—C12—C17	−162.01 (18)	O2—C28—C29—C34	−162.64 (19)
N3—C11—C12—C17	16.9 (3)	N6—C28—C29—C34	16.5 (3)
Li1—C11—C12—C17	−174.5 (3)	Li1—C28—C29—C34	−173.1 (3)
O1—C11—C12—C13	16.4 (3)	O2—C28—C29—C30	16.6 (3)
N3—C11—C12—C13	−164.68 (16)	N6—C28—C29—C30	−164.30 (17)
Li1—C11—C12—C13	3.9 (5)	Li1—C28—C29—C30	6.1 (5)
C17—C12—C13—C14	−0.6 (3)	C34—C29—C30—C31	−0.4 (3)
C11—C12—C13—C14	−179.02 (17)	C28—C29—C30—C31	−179.66 (18)
C12—C13—C14—C15	0.7 (3)	C29—C30—C31—C32	0.2 (3)
C13—C14—C15—C16	−0.5 (3)	C30—C31—C32—C33	−0.1 (3)
C14—C15—C16—C17	0.2 (3)	C31—C32—C33—C34	0.2 (3)
C13—C12—C17—C16	0.3 (3)	C32—C33—C34—C29	−0.4 (3)
C11—C12—C17—C16	178.62 (18)	C30—C29—C34—C33	0.5 (3)
C15—C16—C17—C12	−0.1 (3)	C28—C29—C34—C33	179.71 (19)