The *trans*-chloro-coordinated water molecule forms an intermolecular hydrogen bond with the Cl atom of a second unit of the complex [O(*W*2)···Cl(1)($x-1,y,z$) 3·144 (2), H(*W*2)···Cl(1) 2·63 (5) Å, O(*W*2)—H(*W*2)···Cl(1) 166 (7)°]. Both coordinated water and Cl atoms are involved in intra- and intermolecular hydrogen bonds. The lattice H_2O and Cl counterion also contribute to the packing in this form. Table 3 (deposited) shows the hydrogen-bond parameters. The distortion from octahedral towards trigonal-prismatic geometry was calculated by quantification of the Muetterties & Guggenberger (1974) model (Cortés, Arriortua, Rojo, Solans & Beltran, 1985). The value obtained was $\Delta = 0{\cdot}06$, close to octahedral ($\Delta = 0$). In Table 4 are shown the distortions observed for selected hexacoordinated terpyridine compounds.

As expected, distortion in bis(terpyridine) species is greater than for monoterpyridine ones. In the case of the nitrito complex the distortion is increased by hydrogen bonds between H_2O and NO_2.

Variable-temperature (70–300 K) magnetic-susceptibility data show a paramagnetic behavior (Curie–Weiss law, $\theta = -5$ K) in the complex. The magnetic moment ($\mu_{\rm eff}$) at room temperature is 3·21 BM (1 BM $= 9{\cdot}27 \times 10^{-24}$ JT^{-1}). The ESR spectrum shows a quasi-isotropal signal with a g value of 2·15. The results are in good agreement with an octahedral stereochemistry for the Ni atom.

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Structure of Bis(*N*-isopropylidene-1*H*-imidazole-4-ethylamine)nickel(II) Diperchlorate, a Ni^{II}–Schiff-Base Complex Derived from Histamine and Acetone

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Abstract. $[Ni(C_8H_{13}N_3)_2](ClO_4)_2$, $M_r = 560{\cdot}04$, monoclinic, $P2_1/n$, $a = 9{\cdot}471$ (2), $b = 10{\cdot}270$ (1), $c = 12{\cdot}651$ (2) Å, $\beta = 107{\cdot}08$ (2)°, $V = 1176{\cdot}2$ (6) Å^3, $Z = 2$, $D_m = 1{\cdot}57$ (1), $D_x = 1{\cdot}581$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) $= 1{\cdot}11$ mm^{-1}, $F(000) = 580$, $T = 297$ (1) K, $R_F = 0{\cdot}045$ for 1382 reflections. The structure contains L_2Ni^{II} cations with site symmetry $\bar{1}$. Each Ni^{II} ion is coordinated by two imidazole and two imine N donor atoms to give an approximately square-planar coordination geometry. The Ni—N(imidazole) and Ni—N(imine) distances are 1·881 (3) and 1·911 (4) Å, respectively. The strictly planar NiN_4 unit makes an angle of 42·8 (8)° with the imidazole plane.

Introduction. We have been interested in the electronic, spectroscopic and EPR properties of model Cu^{II}–imidazole chromophores that are useful spectroscopic models for imidazole-containing Cu^{II} protein-binding sites (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). Because the imidazole π-electron system as well as the N donor ligand lone pair are involved in metal–ligand bonding, there are spectroscopic consequences of the imidazole-ring orientation relative to that of the Cu^{II} d vacancy (Schugar, 1983). This orientation may be defined precisely only in the solid state. To determine the effects of ligand orientation on the N EPR superhyperfine parameters,

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diamagnetic host lattices that preserve approximately the geometries of the neat model Cu^{II} complexes are required. We report here the synthesis and structure of a diamagnetic host lattice in which the dihedral angle between the imidazole ligands and planar NiN_4 units is approximately 45°.

Experimental. *Preparation of the title complex.* A suspension of histamine.2HCl (0·740 g, 4·0 mmol) in 35 ml of absolute ethanol was stirred with 0·465 g (8·3 mmol) of KOH, then warmed at 323 K for 30 min. After removal of the KCl precipitate by filtration, the histamine solution was added to a solution of $Ni(ClO_4)_2.6H_2O$ (0·720 g, 1·96 mmol) in 10 ml of ethanol and 15 ml of 2,2-dimethoxypropane. The resulting blue solution turned green following gentle heating (25 min, 338–343 K) and, upon standing for 1 h, deposited small, yellow crystals which were washed with ethanol. A second crop was obtained by treating the supernatant liquid with 5 ml of 2,2-dimethoxypropane and heating as above. Yield: 0·77 g, 70%. Crystals suitable for diffraction were obtained by vapor diffusion of tetrahydrofuran into a solution of the solid in approximately 15:1 (v/v) nitromethane/2,2-dimethoxypropane.

D_m by flotation in heptane/CCl_4; yellow plate 0·25 × 0·28 × 0·10 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Systematic absences consistent with $P2_1/n$; cell constants from setting angles of 25 reflections with $13{\cdot}94 \leq \theta \leq 19{\cdot}12°$; data corrected for Lp and absorption (empirical) effects. Variation in intensity of 3 standard reflections <1%; 1932 unique reflections measured with $2 \leq 2\theta \leq 50°$; 1382 with $I > 3\sigma(I)$ used in refinement. Range of h,k,l: 0 to 10, 0 to 12, −14 to 14. Structure solved by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference Fourier map and at calculated positions; C—H distance 0·95 Å; H atoms not refined. Full-matrix least-squares refinement on F; all non-H atoms anisotropic; $w = 4F_o/[\sigma^2(F_o^2) + 0{\cdot}0016F_o^4]$; final $R_F = 0{\cdot}045$, $wR_F = 0{\cdot}057$, $S = 1{\cdot}74$, $\Delta_{\max}/\sigma < 0{\cdot}09$. No correction for secondary extinction. Scattering factors from *International Tables for X-ray Crystallography* (1974); programs from Enraf–Nonius (1983) *SDP*. During the structure-solution process some difficulty was encountered in locating atom C(4). Difference electron density maps showed multiple peaks and several models involving partially occupied sites were refined, but all led to unrealistic interatomic contacts. In the model reported, C(4) has relatively large thermal parameters, suggesting some positional or thermal disorder at that site. On the final difference electron density map, the two largest peaks, 0·77 and 0·58 e Å^{-3}, were located 1·26 and 0·29 Å, respectively, from C(4). The next largest peak (0·40 e Å^{-3}) was a residual of the perchlorate ion.

Table 1. *Fractional atomic coordinates and thermal parameters*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Ni	0·000	0·000	0·000	2·64 (2)
Cl	−0·2602 (1)	0·1375 (1)	−0·6346 (1)	3·78 (3)
O(1)	−0·3078 (5)	0·0596 (5)	−0·7312 (3)	6·4 (1)
O(2)	−0·2140 (6)	0·2606 (4)	−0·6621 (4)	8·5 (2)
O(3)	−0·1374 (4)	0·0735 (4)	−0·5603 (3)	5·7 (1)
O(4)	−0·3739 (5)	0·1483 (7)	−0·5851 (4)	9·6 (2)
N(1)	−0·0788 (4)	0·0066 (4)	−0·1548 (3)	3·39 (9)
N(2)	−0·1209 (6)	0·0264 (5)	−0·3317 (3)	5·5 (1)
N(3)	−0·1816 (4)	0·0747 (4)	0·0077 (3)	2·94 (8)
C(1)	−0·0192 (6)	0·0376 (5)	−0·2337 (4)	4·0 (1)
C(2)	−0·2499 (7)	−0·0183 (9)	−0·3158 (5)	7·4 (2)
C(3)	−0·2228 (6)	−0·0316 (7)	−0·2064 (5)	5·9 (2)
C(4)	−0·3114 (7)	−0·084 (1)	−0·1357 (6)	10·4 (2)
C(5)	−0·3158 (6)	−0·0034 (6)	−0·0450 (5)	4·9 (1)
C(6)	−0·1964 (5)	0·1867 (5)	0·0477 (4)	3·3 (1)
C(7)	−0·3414 (6)	0·2429 (6)	0·0487 (5)	5·0 (1)
C(8)	−0·0663 (6)	0·2708 (6)	0·0955 (5)	5·1 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ni—N(1)	1·881 (3)	N(2)—C(2)	1·374 (9)
Ni—N(3)	1·911 (4)	N(3)—C(5)	1·485 (6)
Cl—O(1)	1·419 (4)	N(3)—C(6)	1·281 (6)
Cl—O(2)	1·414 (5)	C(2)—C(3)	1·338 (8)
Cl—O(3)	1·424 (4)	C(3)—C(4)	1·50 (1)
Cl—O(4)	1·400 (6)	C(4)—C(5)	1·43 (1)
N(1)—C(1)	1·321 (7)	C(6)—C(7)	1·493 (8)
N(1)—C(3)	1·385 (6)	C(6)—C(8)	1·480 (7)
N(2)—C(1)	1·333 (6)		

N(1)—Ni—N(3)	87·2 (2)	Ni—N(3)—C(5)	115·1 (3)
N(1)—Ni—N(3′)	92·8 (2)	Ni—N(3)—C(6)	125·8 (3)
O(1)—Cl—O(2)	109·6 (3)	N(1)—C(1)—N(2)	109·2 (5)
O(1)—Cl—O(3)	107·4 (3)	N(2)—C(2)—C(3)	106·1 (5)
O(1)—Cl—O(4)	109·8 (3)	N(1)—C(3)—C(2)	108·8 (6)
O(2)—Cl—O(3)	108·9 (3)	N(1)—C(3)—C(4)	118·0 (5)
O(2)—Cl—O(4)	112·0 (4)	C(2)—C(3)—C(4)	133·2 (5)
O(3)—Cl—O(4)	109·1 (3)	C(3)—C(4)—C(5)	115·0 (7)
C(1)—N(1)—C(3)	107·0 (4)	N(3)—C(5)—C(4)	116·9 (5)
Ni—N(1)—C(1)	131·9 (3)	N(3)—C(6)—C(7)	123·9 (4)
Ni—N(1)—C(3)	121·0 (4)	N(3)—C(6)—C(8)	120·7 (5)
C(1)—N(2)—C(2)	108·9 (5)	C(7)—C(6)—C(8)	115·3 (5)
C(5)—N(3)—C(6)	118·9 (4)		

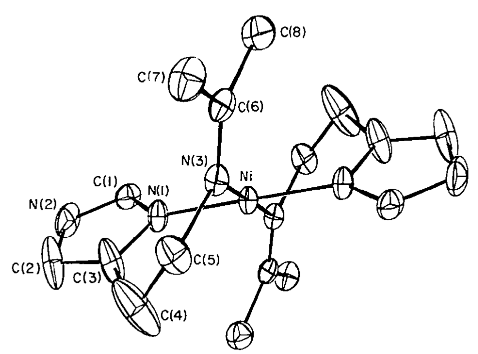

Fig. 1. View of the title complex showing the atom-numbering scheme. The perchlorate groups and H atoms have been omitted for clarity.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the title complex showing the atom-numbering scheme is given in Fig. 1 while selected bond distances and angles are given in Table 2. The structure contains discrete, centrosymmetric bis(*N*-isopropylidene-1*H*-imidazole-4-ethylamine)nickel(II) cations separated by perchlorate anions. Each Ni^{II} ion is situated on a center of symmetry and is coordinated in a distorted square-planar fashion by two imidazole and two imine N donor atoms. Axial coordination by the perchlorate anion is absent; the shortest Ni···O(perchlorate) distance is 4·048 (7) Å. As required by the center of symmetry, the NiN_4 unit is strictly planar. The imidazole group [N(1)—C(1)—N(2)—C(2)—C(3)] is planar to within ±0·01 Å and makes a dihedral angle of 42·8 (8)° with the NiN_4 unit, a value which is twice that reported for bis(histamine)copper(II) diperchlorate (21·4°, Bonnet & Jeannin, 1970) whose structure contains tetragonal Cu equatorially coordinated to four N atoms and weakly axially coordinated to two perchlorate O atoms. To date, we have not been successful in doping Cu into the title complex, and this may be related to the differences in coordination geometry and/or orientation of the imidazole rings between the Ni and Cu complexes. Both the Ni—N(imidazole) and Ni—N(imine) distances [1·881 (3), 1·911 (4) Å] are close to the value expected for square-planar Ni^{II} complexes {*cf.* 1·896 (3) Å for bis-*μ*-[1,1,1,16,16,16-hexafluoro-4,13-dimethyl-2,15-bis(trifluoromethyl)-5,12-diazahexadeca-4,12-diene-2,15-diolato]-dinickel(II) (Martin, Payne & Willis, 1978)} and shorter than most Ni—N values reported for tetrahedral Ni^{II} complexes {1·916 (4) Å for bis(*N*-methyl-1-methylimino-9-phenaleneaminato)-nickel(II) (Franz, McLaughlin, Martin & Robertson, 1982); 1·974 (4) Å for bis[*N*-(3-methoxysalicylidene)-isopropylaminato]nickel(II) (Ashida, Iwata, Yamane, Kakudo, Takeuchi & Yamada, 1976)}.

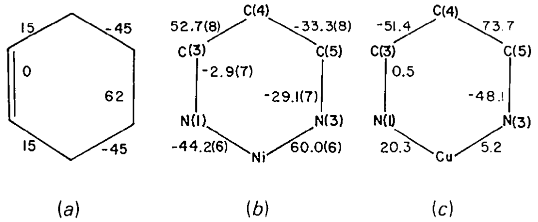

Fig. 2. Torsional angles (°) for (*a*) the half-chair form of cyclohexene (Pedone *et al.*, 1970), and the chelate rings in (*b*) the present structure, and (*c*) bis(histamine)copper(II) diperchlorate.

Coordination of Ni by N(1) and N(3) yields six-membered chelate rings. Because the imidazole ring is conjugated, flexibility of the chelate ring is limited as in cyclohexene; in particular, the Ni—N(1)—C(3)—C(4) unit is expected and found to be approximately planar [max. deviations ±0·015 Å]. Atoms C(5) and N(3) show large deviations from this plane in the same direction [−0·99 and −1·38 Å, respectively], indicating that the chelate ring has assumed a distorted boat conformation, unlike derivatives of cyclohexene which normally assume the stable half-chair conformation (Pedone, Benedetti, Immirzi & Allegra, 1970). In the comparison Cu–histamine structure, the six-membered chelate rings assume a somewhat more shallow boat conformation with C(5) and N(3) deviations of 1·13 and 0·72 Å from the Cu—N(1)—C(3)—C(4) plane. The conformational differences between these rings, which lead to the substantially different imidazole/MN_4 dihedral angles, are also evident in the ring torsional angles; these are shown in Fig. 2 along with values for the half-chair form of cyclohexane.

The perchlorate groups exhibit typical bond distances and angles, and show no signs of disorder. One O atom forms a hydrogen bond with N(2) of the imidazole ring [O(3)···N(2) 2·891 (6) Å; O(3)···H(N2)—N(2) 165°].

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42434 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.