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Structure and Synthesis of Bis(N^1-acetimidoylacetamidine-N^1,N^3)nickel(II) Chloride Trihydrate, $C_8H_{17.5}N_6Ni^{1.5+}.Cl^-_{1.5}.3H_2O$, at 117 K

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Abstract. $M_r = 363{\cdot}7$, triclinic, $P\bar{1}$, $a = 7{\cdot}378\,(3)$, $b = 8{\cdot}862\,(3)$, $c = 12{\cdot}813\,(3)$ Å, $\alpha = 72{\cdot}99\,(2)$, $\beta = 79{\cdot}96\,(3)$, $\gamma = 77{\cdot}27\,(4)°$, $V = 776{\cdot}0\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}557\,(1)$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 4{\cdot}4$ mm^{-1}, $F(000) = 382$, $T = 117\,(2)$ K, final $R = 0{\cdot}034$ for 1385 reflections. The crystals of the title compound, formed by evaporation of a methanolic solution of $NiCl_2$ and acetamidine, contain planar complexes of bis(N^1-acetimidoylacetamidine)nickel(II) ions. The present study thus shows that N^1-acetimidoylacetamidine can be prepared through a self-condensation reaction of acetamidine. The nickel atom is coordinated by an almost ideal square-planar arrangement of four imino nitrogen atoms. The Ni···N distances, ranging from 1·849 to 1·873 (4) Å, show that the complex is of low-spin type.

Introduction. The present study is part of a research project on synthetic and structural studies of acetamidine metal complexes. So far, only one such complex has been synthetized and characterized by single-crystal diffraction techniques, *viz* the study carried out by Stephenson (1962) on a compound expected to be bis(acetonitrile)tetraammineplatinum(II) chloride monohydrate but unexpectedly shown by the outcome of the structural investigation to be bis(acetamidine)diammineplatinum(II) chloride monohydrate. Today, with pure acetamidine available (Crossland & Grevil, 1981), the conditions for more systematic studies of metal acetamidine complexes appear promising.

The specimen used in the present study was obtained by simply evaporating a methanolic solution of stoichiometric amounts (1:4) of nickel(II) chloride hexahydrate and acetamidine. Such a synthetic procedure could possibly give somewhat unpredictable results as it is known that acetamidine, which is a strong highly hygroscopic base, when exposed to atmospheric carbon dioxide yields crystalline diacetamidinium carbonate monohydrate (Norrestam, 1984). However, in the present study it is shown that acetamidine may also undergo a self-condensation reaction, possibly under the influence of nickel(II) ions, to give the simple bidentate ligand N-acetimidoylacetamidine:

$$2\,\mathrm{NH{=}C(CH_3){-}NH_2} \rightarrow \mathrm{NH{=}C(CH_3){-}NH{-}(CH_3)C{=}NH} + \mathrm{NH_3}.$$

This reaction is analogous to the self-condensation of urea by which biuret is formed. According to Oto & Ichikawa (1973), the hydrochloride of N-acetimidoylacetamidine had been prepared earlier through the reaction between $[NH_2{-}C(CH_3){-}NH_2].Cl$ (acetamidinium chloride) and $Et{-}O{-}C(CH_3){=}NH$ in an acidic (HCl) solution.

Experimental. Green prisms from methanol at 293 K, 0·2 × 0·1 × 0·1 mm, CAD-4 diffractometer with a cryogenic device (*cf.* van Bolhuis, 1971) operated at 117 (2) K, graphite-monochromatized Cu $K\alpha$, lattice parameters from angular settings of 12 reflections with $9 < \theta < 19°$, 2117 unique reflections ($h < 5$, $|k| < 10$, $|l| < 15$) with $\theta < 74{\cdot}5°$, 1385 with $\sigma(I)/I < 0{\cdot}33$ used for refinements, no significant intensity variations in 2 standard reflections, 202 and $0\bar{2}\bar{3}$, during data collection, no corrections for absorption; Ni and one Cl atom from Patterson map, remaining atoms from subsequent $\Delta\rho$ maps, least-squares minimization of $\sum w(\Delta F)^2$, anisotropic Ni and Cl atoms, isotropic C, N

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and H atoms, occupational parameters of hydrogen atoms H(N2) and H(N2′) varied, $R = 0{\cdot}034$ and $wR = 0{\cdot}043$, $1/w \propto [\sigma^2 + 0{\cdot}0003|F_o|^2]$, (Δ/σ) max. for nonhydrogen parameters 0·14, number of refined parameters 188, $\Delta\rho$ variation $\pm 0{\cdot}3$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); programs: *SHELX*76 (Sheldrick, 1976) and *XTAPL* (Norrestam, 1982).* Table 1 gives the atomic coordinates and Table 2 the bond distances and angles.

Discussion. In the course of the structure determination, it soon became evident that the acetamidine molecules had condensed to give bidentate N^1-acetimidoylacetamidine ligands. The nickel(II) ions are coordinated by two such ligands forming a square-planar complex, as shown in Fig. 1. There are three chloride ions per unit cell, *i.e.* one and a half chloride ions per nickel(II) ion. In order to maintain electroneutrality there must be another effective charge of −0·5 per nickel(II) ion. During the least-squares refinements the isotropic thermal parameter of the hydrogen H(N2) at the central nitrogen atom N(2) of one of the ligands had an unreasonably high value. This could indicate that this hydrogen position is not fully occupied. Furthermore, the angle C(1′)—N(2′)—C(3′) is significantly larger, 3·2 (4)°, than the corresponding angle in the other ligand. Such an angular difference should be expected due to the influence of a higher occupancy of an electron-donating substituent such as hydrogen at N(2′) (Bent, 1961; Singh, 1965). Both these observations indicate that one of the ligands (the unprimed one) could have an effective charge of −0·5 instead of being electroneutral. Allowing the occupancies of the hydrogens at N(2) and N(2′) to vary yielded least-squares refined values of 0·60 (8) and 0·98 (8), respectively.

Both the ligand molecules are roughly planar with r.m.s. deviations of the nonhydrogen atoms from the molecular planes of 0·029 and 0·014 Å for the ligands with unprimed and primed labels, respectively. The nickel atom deviates by 0·003 (4) and 0·063 (4) Å, respectively, and the dihedral angle between the planes is 176·2 (3)°. The six-membered ring formed by the atoms Ni, N(1′), C(1′), N(2′), C(3′) and N(3′) is slightly distorted towards a boat conformation with the Ni and the N(2′) atoms as the apex atoms [deviating 0·054 (4) and 0·042 (6) Å, respectively]. The bond distances in the ligands are very similar to those observed for the simple acetamidine molecule (Norrestam, Mertz & Crossland, 1983).

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10⁴) *estimated as* 1/3 *trace* **U**

	x	y	z	U_{eq}
Ni	1451 (2)	308 (1)	1036 (1)	126 (4)
Cl(1)	1712 (2)	5237 (2)	1135 (1)	171 (5)
Cl(2)	5000	5000	5000	270 (7)
N(1)	657 (7)	−1457 (5)	2045 (3)	145 (8)
N(2)	−717 (7)	−373 (4)	3521 (3)	160 (8)
N(3)	510 (7)	1527 (5)	2034 (3)	136 (8)
C(1)	−160 (8)	−1603 (5)	3029 (4)	162 (9)
C(2)	−591 (12)	−3191 (6)	3760 (4)	214 (11)
C(3)	−340 (8)	1123 (5)	3011 (4)	149 (9)
C(4)	−1099 (11)	2331 (6)	3671 (4)	168 (10)
N(1′)	2219 (7)	2093 (5)	14 (3)	146 (8)
N(2′)	3782 (7)	956 (4)	−1377 (3)	138 (8)
N(3′)	2480 (6)	−934 (4)	46 (3)	139 (8)
C(1′)	3137 (8)	2233 (5)	−934 (4)	156 (9)
C(2′)	3683 (12)	3798 (6)	−1643 (4)	194 (11)
C(3′)	3408 (8)	−567 (5)	−902 (3)	142 (9)
C(4′)	4217 (11)	−1735 (6)	−1575 (4)	183 (10)
O(w1)	4143 (6)	−1584 (4)	3392 (3)	214 (8)
O(w2)	3270 (7)	604 (5)	4629 (3)	203 (8)
O(w3)	3494 (7)	3599 (4)	3395 (3)	284 (9)

Table 2. *Bond distances* (Å) *and bond angles* (°) *between the nonhydrogen atoms*

The right column is calculated for the primed atoms (*cf.* Table 1).

Ni—N(1)	1·849 (4)	1·861 (4)
Ni—N(3)	1·858 (4)	1·873 (3)
C(1)—N(1)	1·282 (6)	1·270 (5)
C(1)—N(2)	1·367 (5)	1·369 (5)
C(1)—C(2)	1·510 (6)	1·514 (6)
C(3)—N(2)	1·362 (5)	1·376 (5)
C(3)—N(3)	1·285 (6)	1·276 (5)
C(3)—C(4)	1·508 (5)	1·497 (5)
N(1)—Ni—N(3)	89·9 (2)	89·8 (2)
N(1)—Ni—N(3′)	90·3 (2)	90·1 (2)
Ni—N(1)—C(1)	129·9 (3)	130·6 (3)
N(1)—C(1)—N(2)	124·4 (4)	122·3 (4)
N(1)—C(1)—C(2)	122·1 (4)	123·0 (4)
C(2)—C(1)—N(2)	113·5 (4)	114·6 (4)
C(1)—N(2)—C(3)	121·7 (4)	124·9 (4)
Ni—N(3)—C(3)	129·7 (3)	130·4 (3)
N(3)—C(3)—N(2)	124·3 (4)	121·7 (4)
N(3)—C(3)—C(4)	121·5 (4)	123·8 (4)
C(4)—C(3)—N(2)	114·2 (4)	114·5 (4)

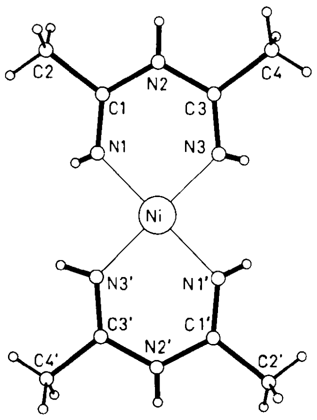

Fig. 1. The structure of the bis(N^1-acetimidoylacetamidine)-nickel(II) ion and the atomic labels used.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39261 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The four coordinating nitrogens and the nickel ion are almost coplanar, with deviations less than 0·02 Å and, as the angles N—Ni—N deviate by less than 0·2° from the ideal value, the square-planar geometry is almost perfect. The average Ni—N bond length of 1·86 (1) Å indicates that the compound is a low-spin complex (see *e.g.* Ito & Toriumi, 1981; Madaule-Aubry, Busing & Brown, 1968). The overall geometry of the complex resembles that of anionic bis(biuretato)-metal complexes. In these complexes the biuret molecules act as bidentate ligands through their deprotonated amide nitrogen atoms (see *e.g.* Birker, Freeman, Guss & Watson, 1977; Siegel & Martin, 1982, and references therein).

The structure is held together by *inter alia* an extensive net of hydrogen bonds. Thus, the imino nitrogens N(1), N(3), N(1′) and N(3′) participate as donors in hydrogen bonds to the chlorine atom Cl(1), [N···Cl ranging from 3·351 (4) to 3·414 (4) Å]. The amino nitrogens N(2) and N(2′) form hydrogen bonds to two water molecules O(*w*2) and O(*w*1) [N···O distances 2·746 (6) and 2·734 (6) Å respectively]. Other hydrogen bonds occur between the water molecules [O···O from 2·686 (6) to 2·759 (6) Å] and between the chlorine atoms and the water molecules [O···Cl from 3·125 (4) to 3·201 (4) Å].

The square-planar complexes are stacked along the **a** direction (Fig. 2) but with the molecular planes inclined in such a way that the complexes are parallel to the $(10\bar{1})$ planes, yielding a very strong $20\bar{2}$ reflexion. The chlorine atoms and the water molecules occupy the space between the molecular stacks.

The author is indebted to Dr I. Crossland, Department of Organic Chemistry, The Technical University of Denmark, for his generous supply of acetamidine and for stimulating discussions.

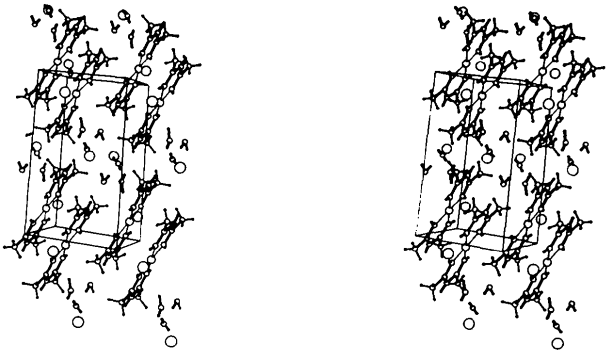

Fig. 2. Packing diagram of the crystal structure with *c* vertical, *a* horizontal and *b* out of the plane of the paper. The larger circles represent the chlorine atoms.

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Structure of Bis(isothiocyanato)tetrakis(pyridine)nickel(II), $C_{22}H_{20}N_6NiS_2$, a Redetermination

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Abstract. $M_r = 491{\cdot}28$, monoclinic, $C2/c$, $a = 12{\cdot}434\,(4)$, $b = 12{\cdot}944\,(5)$, $c = 16{\cdot}461\,(6)$ Å, $\beta = 118{\cdot}78\,(2)°$, $V = 2322{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}39$, $D_x = 1{\cdot}41$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}03$ mm^{-1}, $F(000) = 1016$, $T = 298$ K. Final $R = 0{\cdot}063$ for 1300 observed reflections. The structure consists of close-packed units. The Ni$^{\rm II}$ atoms are pseudo-octahedrally *trans*-coordinated by two N atoms