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Structure of a Seven-Coordinated Complex of Nickel, Diaqua[2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone)]nickel(II) Nitrate Sesquihydrate*

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Abstract. $[Ni(H_2O)_2(C_{23}H_{21}N_5O_4)](NO_3)_2.1\cdot5H_2O$, $M_r = 677\cdot22$, orthorhombic, *Pbca*, $a = 17\cdot297$ (6), $b = 13\cdot614$ (5), $c = 24\cdot266$ (11) Å, $V = 5714$ (4) Å^3, $Z = 8$, $D_x = 1\cdot574$ g cm^{-3}, D_m not measured, λ(Mo $K\alpha$) $= 0\cdot71707$ Å, $\mu = 7\cdot57$ cm^{-1}, $F(000) = 2808$, $T = 295$ K, final $R = 0\cdot0578$ for 2277 unique observed reflections. The structure consists of pentagonal-bipyramidal $[Ni(H_2daps)(OH_2)_2]^{2+}$ cations [H_2daps = 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone)], NO_3^- anions and uncoordinated H_2O molecules held together by a three-dimensional network of hydrogen bonds. The H_2daps molecule functions as an N_3O_2 quinquedentate ligand defining the equatorial plane of the bipyramid, the apices of which are occupied by two H_2O molecules.

Introduction. This work is part of a programme of research into the coordinating properties of 2,6-diacetylpyridine bis(acylhydrazones). These molecules form an interesting class of compounds because of their ability to form stable metal complexes, their versatility as chelating agents, their flexibility in assuming different conformations, and their tendency to act as approximately planar quinquedentate ligands, so favouring seven-coordinate pentagonal-bipyramidal structures (Pelizzi, Pelizzi & Predieri, 1984). As an extension, we report here the crystal and molecular structure of the seven-coordinated $[Ni(H_2daps)(OH_2)_2](NO_3)_2.\frac{3}{2}H_2O$ complex, which was determined in order to provide structural data for comparison with previous X-ray work on the ligand behaviour of hydrazones towards different transition- or non-transition-metal ions. This study also provides the opportunity to supply some information about seven coordination for the Ni^{2+} ion.

Experimental. Brown-green crystals prepared by reacting equimolar amounts of 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone) and $Ni(NO_3)_2.6H_2O$ in ethanol. Parallelepipedal crystal, dimensions $0\cdot33 \times 0\cdot49 \times 0\cdot52$ mm. Siemens AED three-circle diffractometer, General Automation Jumbo 220 computer, room temperature, Nb-filtered Mo $K\alpha$ radiation. Unit-cell dimensions determined from least-squares refinement of θ values of 26 centred high-angle reflections, θ range: 12·8–18·7°. Space group inferred from systematic extinctions ($hk0$ with $h = 2n + 1$, $h0l$ with $l = 2n + 1$, and $0kl$ with $k = 2n + 1$). Intensity data collected by θ–2θ scans to $\theta_{max} = 26°$; range of hkl: h 0 to 21, k 0 to 14, l 0 to 29. A standard reflection every 50 measurements: no intensity change. 5994 reflections collected, 5417 unique and allowed by symmetry, 2283 with $I > 2\sigma(I)$. Data corrected for Lorentz, polarization and background effects. No correction for absorption or extinction. Structure solved by *MULTAN*74

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* IUPAC name: diaqua[2'-(1-{6-[1-(salicyloylhydrazono)ethyl]-pyrid-2-yl}ethylidene)salicylohydrazide]nickel(II) nitrate sesquihydrate.

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(Main, Woolfson, Lessinger, Germain & Declercq, 1974) with 300 E values $\geq 1\cdot87$. The phase set with the highest combined figure of merit produced an E map which yielded part of the molecule. All other non-H atoms located from subsequent difference Fourier maps. Full-matrix least-squares refinement based on F. All non-H atoms except those of the nitrate ions and the uncoordinated waters refined using anisotropic temperature factors. 17 of the 29 H atoms located from difference synthesis and refined isotropically, eight H-atom positions generated geometrically, H atoms of the uncoordinated H_2O ignored. Six suspect reflections with bad agreement between F_o and F_c removed from last refinement cycle. $\sum w|\Delta F|^2$ minimized, where $w = 0\cdot3159/[\sigma^2(F_o) + 0\cdot014115F^2]$. Final discrepancy indices $R = 0\cdot0578$, $wR = 0\cdot0811$, $S = 0\cdot343$. 436 parameters varied in all; data-to-variable ratio 5·2/1. $(\Delta/\sigma)_{\max} = 0\cdot71$. Final ΔF map revealed several peaks, 0·65–0·45 e Å^{-3}, in vicinity of nitrate-atom positions, an indication of disorder; largest hole $-0\cdot60$ e Å^{-3}. Neutral-atom scattering factors and effects for anomalous dispersion (both real and imaginary) from *International Tables for X-ray Crystallography* (1974). Calculations carried out on a Gould SEL 32/77 computer. Major programs used: *SHELX*76 (Sheldrick, 1976), *PARST* (Nardelli, 1983) and *PLUTO* (Motherwell, 1976).

Atomic coordinates and equivalent isotropic thermal parameters varied in all; data-to-variable ratio 5·2/1. distances and angles involving non-H atoms.*

Discussion. The structure of the title compound contains $[Ni(H_2daps)(OH_2)_2]^{2+}$ cations, NO_3^- anions and H_2O molecules of crystallization. As shown in Fig. 1, the cation can be described as a distorted pentagonal bipyramid, whose base is formed by two O and three N of H_2daps and the apices by two H_2O molecules. The metal binding by the hydrazone is the same as in the

Table 1. *Fractional atomic coordinates* (× 10^5 *for* Ni *and* × 10^4 *for* O, N *and* C) *and isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Ni	11004 (4)	64689 (7)	50334 (4)	376 (3)
O(1)	−273 (3)	6419 (5)	4572 (2)	483 (20)
O(2)	233 (3)	6165 (4)	5701 (2)	468 (20)
O(3)	−225 (4)	7085 (6)	2911 (3)	618 (26)
O(4)	1108 (3)	5605 (5)	7257 (2)	692 (24)
O(5)	1082 (4)	5041 (5)	4833 (3)	448 (22)
O(6)	896 (5)	7900 (6)	5207 (4)	583 (27)
N(1)	449 (4)	6870 (7)	3850 (4)	467 (30)
N(2)	1097 (4)	6837 (5)	4153 (3)	413 (25)
N(3)	2224 (4)	6646 (5)	4816 (3)	388 (25)
N(4)	1708 (4)	6176 (5)	5755 (3)	376 (22)
N(5)	1310 (4)	5921 (5)	6204 (3)	389 (27)
C(1)	−1647 (5)	6536 (6)	3980 (4)	448 (29)
C(2)	−2318 (5)	6592 (7)	3679 (4)	540 (36)
C(3)	−2283 (6)	6802 (8)	3133 (4)	612 (42)
C(4)	−1598 (5)	6961 (8)	2870 (4)	559 (36)
C(5)	−904 (4)	6908 (7)	3171 (3)	426 (29)
C(6)	−924 (4)	6698 (6)	3730 (3)	362 (27)
C(7)	−237 (5)	6652 (5)	4088 (3)	368 (28)
C(8)	1749 (4)	7007 (6)	3927 (3)	408 (29)
C(9)	1878 (6)	7289 (9)	3342 (4)	733 (39)
C(10)	2414 (5)	6934 (6)	4315 (3)	426 (31)
C(11)	3174 (5)	7119 (7)	4169 (4)	526 (34)
C(12)	3730 (6)	6977 (9)	4573 (5)	652 (46)
C(13)	3531 (5)	6645 (7)	5085 (4)	523 (34)
C(14)	2768 (4)	6496 (7)	5204 (4)	435 (30)
C(15)	2452 (5)	6169 (6)	5743 (3)	397 (29)
C(16)	2978 (5)	5878 (7)	6194 (4)	587 (38)
C(17)	523 (5)	5957 (6)	6145 (3)	395 (30)
C(18)	42 (4)	5727 (5)	6639 (3)	420 (25)
C(19)	−747 (4)	5657 (6)	6555 (3)	488 (28)
C(20)	−1250 (6)	5443 (8)	6967 (4)	645 (41)
C(21)	−950 (5)	5323 (7)	7492 (4)	684 (41)
C(22)	−173 (6)	5393 (7)	7594 (4)	639 (35)
C(23)	323 (4)	5578 (5)	7164 (3)	445 (27)
O(7)	1522 (4)	234 (5)	3198 (3)	766 (19)
O(8)	5109 (8)	4297 (11)	4072 (6)	936 (46)
N(6)	2879 (4)	696 (5)	−535 (3)	561 (18)
O(9)	2714 (4)	853 (5)	−60 (3)	903 (21)
O(10)	2383 (4)	411 (5)	−858 (3)	925 (21)
O(11)	3544 (5)	838 (6)	−698 (3)	1042 (24)
N(7)	4736 (4)	3293 (5)	6617 (3)	650 (20)
O(12)	4658 (4)	3709 (6)	6170 (3)	1062 (23)
O(13)	4208 (4)	2933 (5)	6862 (3)	954 (22)
O(14)	5396 (3)	3246 (4)	6833 (2)	646 (16)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(*a*) In the coordination polyhedron

Ni—O(1)	2·628 (6)	Ni—N(4)	2·081 (6)
Ni—O(2)	2·247 (6)	Ni—O(5)	2·005 (7)
Ni—N(2)	2·194 (6)	Ni—O(6)	2·024 (9)
Ni—N(3)	2·028 (6)		
O(1)—Ni—N(2)	65·7 (2)	O(5)—Ni—O(1)	81·8 (2)
O(1)—Ni—N(3)	139·3 (2)	O(5)—Ni—N(2)	89·2 (3)
O(1)—Ni—N(4)	144·1 (2)	O(5)—Ni—N(3)	93·9 (3)
O(1)—Ni—O(2)	72·5 (2)	O(5)—Ni—N(4)	91·5 (3)
O(2)—Ni—N(2)	137·9 (2)	O(5)—Ni—O(2)	89·2 (3)
O(2)—Ni—N(3)	148·2 (3)	O(6)—Ni—O(1)	87·4 (3)
O(2)—Ni—N(4)	72·2 (2)	O(6)—Ni—N(2)	88·9 (3)
N(2)—Ni—N(3)	73·9 (3)	O(6)—Ni—N(3)	96·2 (3)
N(2)—Ni—N(4)	149·8 (3)	O(6)—Ni—N(4)	95·6 (3)
N(3) Ni N(4)	76·0 (3)	O(6)—Ni—O(2)	84·9 (3)
		O(6)—Ni—O(5)	168·8 (3)

(*b*) In the hydrazone moiety

C(1)—C(2)	1·373 (12)	C(19)—C(20)	1·358 (12)
C(2)—C(3)	1·358 (15)	C(20)—C(21)	1·386 (14)
C(3)—C(4)	1·362 (14)	C(21)—C(22)	1·369 (14)
C(4)—C(5)	1·407 (12)	C(22)—C(23)	1·373 (12)
C(5)—O(3)	1·356 (10)	C(23)—O(4)	1·377 (9)
C(5)—C(6)	1·385 (11)	C(23)—C(18)	1·378 (10)
C(6)—C(1)	1·409 (11)	C(18)—C(19)	1·383 (10)
C(6)—C(7)	1·473 (11)	C(18)—C(17)	1·492 (10)
C(7)—O(1)	1·217 (10)	C(17)—O(2)	1·221 (10)
C(7)—N(1)	1·354 (11)	C(17)—N(5)	1·371 (11)
N(1)—N(2)	1·342 (10)	N(5)—N(4)	1·332 (10)
N(2)—C(8)	1·275 (10)	N(4)—C(15)	1·288 (10)
C(8)—C(9)	1·487 (13)	C(15)—C(16)	1·476 (13)
C(8)—C(10)	1·490 (11)	C(15)—C(14)	1·487 (12)
C(10)—N(3)	1·319 (11)	C(14)—N(3)	1·347 (10)
C(10)—C(11)	1·384 (12)	C(14)—C(13)	1·367 (12)
C(11)—C(12)	1·387 (14)	C(13)—C(12)	1·365 (16)

(*c*) In the nitrate groups

N(6)—O(9)	1·208 (10)	N(7)—O(12)	1·231 (11)
N(6)—O(10)	1·224 (10)	N(7)—O(13)	1·194 (11)
N(6)—O(11)	1·232 (11)	N(7)—O(14)	1·259 (10)

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* Lists of observed and calculated structure factors, H coordinates, anisotropic thermal parameters and angles in the hydrazone moiety and in the nitrate groups have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42896 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

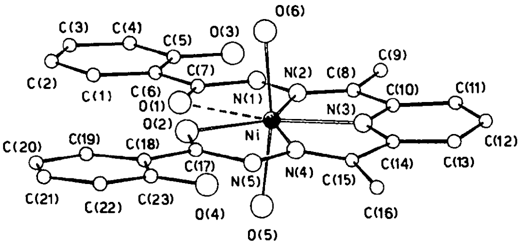

Fig. 1. A perspective view of the $[Ni(H_2daps)(OH_2)_2]^{2+}$ cation.

structure of two previously reported pentagonal-bipyramidal Ni^{II} cations, namely diaqua[2,6-diacetylpyridine bis(semicarbazone)]nickel (Wester & Palenik, 1974) and diaqua[2,6-diacetylpyridine bis(benzoic acid hydrazone)]nickel (Giordano, Palenik, Palenik & Sullivan, 1979). In this compound, H_2daps encircles the Ni^{II} ion in an unsymmetrical quinquedentate fashion, this being mainly associated with the non-equivalence of the two Ni—O bonds, which are notably different at 2·628 (6) and 2·247 (6) Å. This disparity, which explains the splitting of the CO frequency value observed in the infrared spectrum, has already been observed, even if to a lesser extent, in both the aforementioned compounds and has been attributed to Jahn–Teller distortions. It can be added that in our compound only the O atom that is bonded more weakly to Ni is involved in an intermolecular hydrogen bond with a water molecule.

The five interior angles in the pentagon range from 65·7 (2) to 76·0 (3)° with an average of 72°, which is the expected value for an idealized pentagon. The N_3O_2 donor set of atoms that forms the pentagon is not completely planar, with maximum atom deviations of 0·09 Å. The angle between the apical ligands is 168·8 (3)° and those between apical and equatorial atoms are close to 90°, their range being 81·8 (2)–96·2 (3)°.

The molecule contains two intramolecular hydrogen bonds which occur between the hydrazidic N atoms, N(1) and N(5), and the hydroxyl O atoms, O(3) and O(4) [N(1)···O(3) 2·58 (1); N(5)···O(4) 2·62 (1) Å]. As regards the crystal packing, the structure is stabilized by an extensive network of hydrogen bonds, which involve the complex cations, through the hydroxyl and the water O atoms, the nitrate anions and the uncoordinated water molecules.

In summary, from this and the preceding studies of 2,6-diacetylpyridine bis(acylhydrazones) it appears that, among the different conformations the ligand can assume in coordinating to metal ions, the quinquedentate planar conformation is the favoured one.

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Reactions of Coordinated Molecules. 48. The Structure of a Pt–W Cluster Containing a Bridging η^1,η^3-*p*-Tolylmethylene Ligand

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Abstract. μ-Carbonyl-2-carbonyl-2-η-cyclopentadienyl-μ-[σ:η^3-*p*-tolylmethylene-C^{α}(Pt,W)$C^{1,2}$(W)]-1,1-bis(triethylphosphine)platinumtungsten(1+)(*Pt–W*) tetrafluoroborate, $[(\eta\text{-}C_5H_5)(OC)_2W\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4\text{-}CH_3\text{-}p)(H)\}Pt\{P(CH_2CH_3)_3\}_2]BF_4$: $M_r = 927·33$, orthorhombic, $Pca2_1$, $a = 18·240\ (4)$, $b = 11·231\ (3)$, $c = 15·817\ (4)$ Å, $V = 3240$ Å^3, $Z = 4$, $D_x = 1·901$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu =$

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