

compare well with those in analogous compounds (Beauchamp, Layek & Theophanides, 1982, and references quoted therein) and are significantly different from those reported by MYK.

The values of bond distances and angles in the chelate ligands and perchlorate groups are in the same range as those reported by MYK.

The results of our analysis lead to the conclusion that the $A2_122$ space group is the one which better describes the structures of these compounds, which should therefore be considered as one-dimensionally rather than three-dimensionally ordered. Final positional parameters are given in Table 3.

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{*N*-[*N*-(3-Hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)glycyl]glycinato(2-)]nickel(II) Trihydrate, [Ni(C₁₂H₁₃N₃O₅)]·3H₂O

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Abstract. $M_r = 392.01$, triclinic, $P\bar{1}$, $a = 7.082$ (1), $b = 9.004$ (1), $c = 12.425$ (1) Å, $\alpha = 97.5$ (1), $\beta = 89.6$ (1), $\gamma = 100.1$ (1)°, $U = 773.2$ (3) Å³, $Z = 2$, $D_x = 1.68$, $D_m = 1.70$ Mg m⁻³ (by flotation method), $F(000) = 408$, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu(\text{Cu } K\alpha) = 2.2$ mm⁻¹, room temperature, final $R = 0.050$ for 1802 observed reflections. The Ni²⁺ ion is coordinated by the tetradentate ligand in a square-planar arrangement. The packing is determined by hydrogen bonds between the complex and the water molecules and by weak interactions between the stacked planar molecules of the complex.

Introduction. The Schiff-base derivatives of pyridoxal or salicylaldehyde with amino acids, in the presence of metal ions, have been used as model catalysts for a large number of biological reactions (Snell, Braunstein, Severin & Torchinskii, 1968). For this reason their properties have been extensively studied in solution (Abbott & Martell 1970; Wrobley & Long, 1977) and in the solid state (Capasso, Giordano, Mattia, Mazzarella & Ripamonti, 1974; Dawes & Waters, 1982). We have extended this study to metal complexes of pyridoxal Schiff bases containing di- and tripeptides

and in this paper we present the crystal structure of [Ni(C₁₂H₁₃N₃O₅)]·3H₂O.

Experimental. Red prisms from aqueous methanol solution, 0.55 × 0.08 × 0.04 mm, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation, lattice parameters from 20 reflections (20° < θ < 27°); data collection: ω – θ scan, 3180 independent reflections with $\theta \leq 75^\circ$, $-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $0 \leq l \leq 14$, 1805 with $I \geq 3\sigma(I)$. Three standard reflections (40 $\bar{1}$, $\bar{2}1\bar{5}$, $\bar{1}40$) monitored at intervals of 5 h (5% variation), Lp correction, absorption ignored, Patterson and Fourier methods, anisotropic full matrix (on F), H from $\Delta\rho$ synthesis isotropic, not refined. Three reflections (100, 001, $\bar{1}10$ measured improperly due to asymmetric background) excluded from final cycles of refinement. Final $R = 0.050$, $R_w = 0.056$, $w = 1/\sigma^2(F_o)$, 1802 observations, 217 variables; final $(\Delta/\sigma)_{\text{max}} = 0.41$. max. and min. heights in final $\Delta\rho$ map 0.5 and -0.4 e Å⁻³, no correction for secondary extinction; scattering factors from *International Tables for X-ray Crystallography* (1974), Enraf–Nonius SDP software and PDP 11/34 computer of the ‘Centro di Metodologie Chimico-fisiche dell’Università di Napoli’.

Discussion. Fig. 1 shows the molecular structure of the complex together with the numbering scheme used. Final positional parameters are given in Table 1,* bond lengths and angles in Table 2. The Ni²⁺ ion is square-planar coordinated by the tetradentate ligand *via* the phenolic O(1) and the carboxylic O(4) oxygens and the imino N(2) and the deprotonated N(3) nitrogens. The metal distances to the carboxylic and phenolic oxygens [1.870 (3) and 1.829 (3) Å respectively] are similar to those found in all complexes with pyridoxylidene-amino acid ligands. Distances within the peptide group show the effect of metal-ion coordination to the deprotonated N(3) atom. The metal coordination increases the double-bond character of the peptide linkage and the single-bond character of the C—O bond; consequently C(10)—N(3) = 1.317 (5) Å is shorter and C(10)—O(3) = 1.249 (5) Å is longer than the quoted values for a standard free peptide group (Freeman, 1967). Except for O(2), all the non-hydrogen atoms form an approximate extended planar system, with deviations of the single atoms from the best plane less than 0.3 Å. The molecule can be described better by four planes which are defined by the five- and six-membered rings. The chelate ring through the atoms Ni, N(3), C(10), C(9), N(2) is strictly planar, whereas the five-membered ring comprising the Ni, O(4), C(12), N(11), N(3) is considerably distorted and its conformation approaches an envelope with its apex at C(12).

In the crystal the molecules pack almost parallel to the *yz* plane, to give a substantial vertical stacking of the chelate ring (Fig. 2).

The pyridoxal group is not fully involved in the overlap, but each molecule has another above and below it, related by centers of symmetry and separated by ~3.5 Å. The Ni—Ni line is approximately normal to the molecular planes; however, the distances between the Ni atoms [3.676 (2) and 3.903 (2) Å] do not suggest direct axial interaction. An intermolecular hydrogen bond between O(2) and O(4) at *x*, 1+*y*, *z* directly connects molecules belonging to different stacks, successively translated along the *b* direction, thus forming, together with the stacking interactions, layers parallel to the *ab* plane. The molecules are elongated approximately normal to the layers, exposing alternately on either side of the layer the positively charged (protonated) N(1) and the partially negatively charged O(3). The water molecules lie between the layers and are bonded to each other and to adjacent layers by a network of hydrogen bonds. Specifically O(W2) is tetrahedrally surrounded by O(W1), two

O(W3) (of symmetry-related water molecules) and O(2) of the complex molecule, whereas O(W1) and O(W3) are involved in only three hydrogen bonds. The hydrogen-bond scheme together with the geometrical parameters are reported in Table 3.

Table 1. *Positional parameters* (×10⁴) *and equivalent isotropic temperature factors* (Å²)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j b_{ij} a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Ni	2422 (1)	4271 (1)	100 (1)	2.32 (2)
O(1)	2508 (5)	4643 (3)	1584 (3)	2.87 (8)
O(2)	1627 (5)	10568 (4)	1836 (3)	2.97 (7)
O(3)	2271 (6)	4720 (4)	-2990 (3)	3.65 (9)
O(4)	2296 (5)	2189 (3)	148 (3)	2.80 (8)
O(5)	2499 (5)	35 (3)	-909 (3)	3.42 (8)
N(1)	3210 (6)	7323 (4)	3925 (3)	2.77 (9)
N(2)	2598 (6)	6250 (4)	-146 (3)	2.35 (8)
N(3)	2274 (6)	3792 (4)	-1358 (3)	2.36 (8)
C(1)	2874 (7)	5991 (5)	3292 (4)	2.50 (10)
C(2)	2775 (7)	5973 (5)	2142 (4)	2.30 (10)
C(3)	2927 (7)	7379 (5)	1729 (4)	2.14 (9)
C(4)	3278 (7)	8758 (5)	2460 (4)	2.30 (10)
C(5)	3402 (8)	8688 (5)	3547 (4)	2.60 (10)
C(6)	2649 (9)	4565 (6)	3784 (4)	3.70 (10)
C(7)	2792 (7)	7438 (5)	573 (4)	2.20 (10)
C(8)	3486 (7)	10299 (5)	2086 (4)	2.50 (10)
C(9)	2531 (8)	6432 (5)	-1310 (4)	3.00 (10)
C(10)	2353 (7)	4882 (5)	-1977 (4)	2.40 (10)
C(11)	2105 (7)	2185 (5)	-1773 (4)	2.40 (10)
C(12)	2312 (7)	1373 (5)	-801 (4)	2.40 (10)
O(W1)	3189 (6)	7333 (4)	-3921 (3)	3.42 (8)
O(W2)	456 (6)	9112 (4)	-3680 (3)	3.82 (9)
O(W3)	1860 (7)	1887 (5)	-4475 (3)	5.40 (10)

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

Ni—O(1)	1.829 (3)	N(2)—C(9)	1.478 (5)
Ni—O(4)	1.870 (3)	N(3)—C(10)	1.317 (5)
Ni—N(2)	1.830 (4)	N(3)—C(11)	1.455 (5)
Ni—N(3)	1.806 (4)	C(1)—C(2)	1.430 (6)
O(1)—C(2)	1.287 (5)	C(1)—C(6)	1.476 (6)
O(2)—C(8)	1.424 (5)	C(2)—C(3)	1.413 (6)
O(3)—C(10)	1.249 (5)	C(3)—C(4)	1.424 (6)
O(4)—C(12)	1.306 (5)	C(3)—C(7)	1.449 (6)
O(5)—C(12)	1.225 (5)	C(4)—C(5)	1.364 (6)
N(1)—C(1)	1.330 (5)	C(4)—C(8)	1.503 (6)
N(1)—C(5)	1.357 (5)	C(9)—C(10)	1.513 (6)
N(2)—C(7)	1.289 (5)	C(11)—C(12)	1.512 (6)
O(1)—Ni—O(4)	90.9 (1)	C(2)—C(3)—C(4)	119.4 (4)
O(1)—Ni—N(2)	96.9 (1)	C(2)—C(3)—C(7)	121.0 (4)
O(4)—Ni—N(3)	86.1 (1)	C(4)—C(3)—C(7)	119.6 (4)
N(2)—Ni—N(3)	86.2 (2)	C(3)—C(4)—C(5)	119.1 (4)
Ni—O(1)—C(2)	125.0 (3)	C(3)—C(4)—C(8)	122.7 (4)
Ni—O(4)—C(12)	114.6 (3)	C(5)—C(4)—C(8)	118.2 (4)
C(1)—N(1)—C(5)	123.8 (4)	N(1)—C(5)—C(4)	120.4 (4)
Ni—N(2)—C(7)	127.0 (3)	N(2)—C(7)—C(3)	123.5 (4)
Ni—N(2)—C(9)	113.6 (3)	O(2)—C(8)—C(4)	108.4 (4)
C(7)—N(2)—C(9)	119.4 (4)	N(2)—C(9)—C(10)	108.8 (3)
Ni—N(3)—C(10)	119.6 (3)	O(3)—C(10)—N(3)	126.6 (4)
Ni—N(3)—C(11)	116.3 (3)	O(3)—C(10)—C(9)	121.7 (4)
C(10)—N(3)—C(11)	124.1 (4)	N(3)—C(10)—C(9)	111.8 (4)
N(1)—C(1)—C(2)	119.0 (4)	N(3)—C(11)—C(12)	106.3 (3)
N(1)—C(1)—C(6)	119.7 (4)	O(4)—C(12)—O(5)	122.7 (4)
C(2)—C(1)—C(6)	121.3 (4)	O(4)—C(12)—C(11)	115.9 (4)
O(1)—C(2)—C(1)	115.2 (4)	O(5)—C(12)—C(11)	121.4 (4)
O(1)—C(2)—C(3)	126.5 (4)	C(1)—C(2)—C(3)	118.2 (4)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances involving H atoms and least-squares-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38694 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

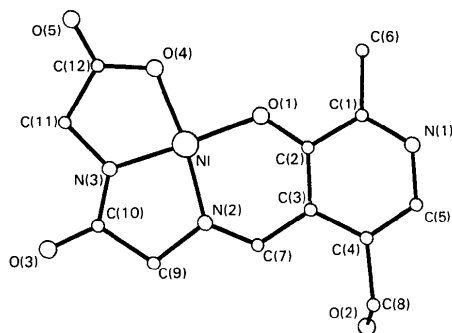
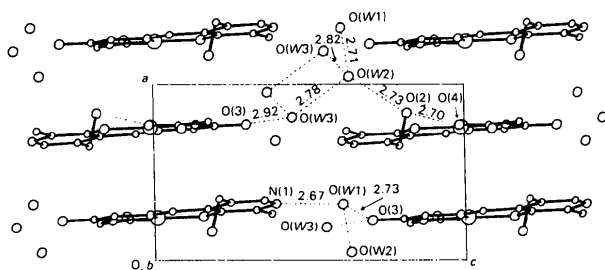


Fig. 1. The molecular structure.

Fig. 2. A view of the molecular packing parallel to *b*: only some hydrogen bonds are reported (dashed lines). (Distances in Å.)Table 3. *Hydrogen bonds*

Donor	Acceptor	at	<i>D</i> ... <i>A</i> (Å)	<i>D</i> - <i>H</i> (Å)	<i>H</i> ... <i>A</i> (°)
O(2)	O(4)	<i>x</i> , <i>y</i> +1, <i>z</i>	2.701 (4)	0.96	166
N(1)	O(W1)	<i>x</i> , <i>y</i> , <i>z</i> +1	2.675 (5)	0.98	162
O(W1)	O(3)	<i>x</i> , <i>y</i> , <i>z</i>	2.732 (4)	0.91	176
O(W1)	O(W2)	<i>x</i> , <i>y</i> , <i>z</i>	2.712 (5)	1.00	169
O(W2)	O(2)	- <i>x</i> , 2- <i>y</i> , - <i>z</i>	2.728 (4)	0.87	163
O(W2)	O(W3)	- <i>x</i> , 1- <i>y</i> , -1- <i>z</i>	2.784 (5)	0.93	170
O(W3)	O(3)	<i>x</i> , <i>y</i> , <i>z</i>	2.917 (5)	1.08	168
O(W3)	O(W2)	<i>x</i> , <i>y</i> -1, <i>z</i>	2.823 (5)	1.13	122

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The Structure of Bis(2,4-dinitrophenolato)tris(1,10-phenanthroline)barium(II), $\text{Ba}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{C}_6\text{H}_3\text{N}_2\text{O}_5)_2$

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Abstract. $M_r = 1044.18$, monoclinic, $P2_1/n$, $a = 11.244$ (3), $b = 21.23$ (1), $c = 17.935$ (5) Å, $\beta = 93.42$ (3)°, $V = 4273$ (3) Å³, $Z = 4$, $D_m = 1.62$, $D_x = 1.62$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 9.16$ cm⁻¹, $F(000) = 2096$, $T = 294$ K, $R = 0.033$ for 5640 observed reflections. Ba is bonded to six N atoms of the three phenanthrolines (phen) and to the three O atoms of the dinitrophenolates (dnp), which form a mono-capped distorted square antiprismatic coordination. The N atoms of the three phen's are pair-wise ligated, the

fourth bidentate ligand is formed by phenolic and *o*-nitro-group O atoms of dnp1 and the coordination is completed by phenolic O of dnp2. The *o*-nitro group of dnp2 is disordered over two sites with occupancies of 0.55 and 0.45.

Introduction. In a previous paper we reported the structure of the acetone solvate of bis(1,10-phenanthroline)bis(2,4,6-trinitrophenolato)barium(II) (Postma, Kanters, Duseenberg, Venkatasubramanian &