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Metal Promoted Hydrolysis of Methyl 2-(*N*-acetylhydrazono)propanoate and Crystal Structure of the Derived Ni(II) Complex*

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The new chelating ligand $CH_3C(O)NHN{=}C(CH_3)$*-*$C(O)OCH_3$*,L, obtained by condensation of* N*-acetylhydrazine and methyl pyruvate, undergoes quantitative hydrolysis of the* $-C(O)OCH_3$ *group by reacting, in hydro-alcoholic medium, with some first row transition metal acetates. Complexes of the type* ML'_2 *have been obtained and characterized, where* L' *is the derived* N*-acetylhydrazonopropanoate anion. An X-ray structural analysis carried out on the* $NiL'_2{\cdot}2H_2O$ *complex has shown a terdentate behaviour of the anionic ligand, resulting in a distorted octahedral environment around the metal. Coordination occurs through the acetyl (Ni–O = 2.094(5) Å), the iminic (Ni–N = 1.995(5) Å) and the carboxylic (Ni–O = 2.055(5) Å) donor groups. Crystals are orthorhombic, space group* Pbcn *with unit cell dimensions* a = *12.151(3),* b = *9.677(2),* c = *13.489(3) Å and Z = 4. The structure was solved by direct methods to* R = *0.0495 for 694 observed reflections.*

Introduction

There is an upsurge of interest towards the study of the chemical properties of hydrazones, owing to their coordinative capability [1], their pharmacological activity [2] and their use in analytical chemistry as metal-extracting agents [3]. In the recent years our interest in this field has been focused on the coordinative behaviour of the aroylhydrazones of hetero-aromatic aldehydes and ketones, mostly from the structural point of view [4]. In these compounds, the –CO–NH–N= group is present together with other coordinating moieties, which increase their chelating power. These investigations revealed interesting features concerning the influence coordination exerts on the ligand conformation and/or configuration [5] in connection with the nature of the metal center.

By replacing the hetero-aromatic aldehyde with an α-ketoester such as methyl pyruvate, we have obtained a new series of potentially terdentate *N*-acylhydrazones of general formula (Scheme 1)

TABLE I. Characterization Data for L[a] and the Derived Complexes ML'_2.[b]

Compound	Color	Melting Point (°C)	μ_{eff} (B.M.)	Electronic Absorption Maxima[c] (nm)	
				L–L*	d–d
L	white	175		250	
$CoL'_2{\cdot}2H_2O$	violet	>300 (dec.)	5.29	230, 280sh;	500, 1300
$NiL'_2{\cdot}2H_2O$	blue	>300 (dec.)	3.21	255, 285sh;	670, 1000
$NiL'_2{\cdot}½H_2O$	greenish blue	>300 (dec.)	3.06		
$CuL'_2{\cdot}½H_2O$	greenish blue	231 (dec.)	d	245, 285sh;	710
$ZnL'_2{\cdot}½H_2O$	pale yellow	285 (dec.)		265, 290sh;	

[a] $L = CH_3C(O)NHN{=}C(CH_3)C(O)OCH_3$. [b] $L' = CH_3C(O)NHN{=}C(CH_3)C(O)O^-$. [c] EtOH (95%) solutions. [d] Unmeasured.

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*Bis{2-(*N*-acetylhydrazono)propanoato-*ON'O'*}nickel(II) dihydrate.

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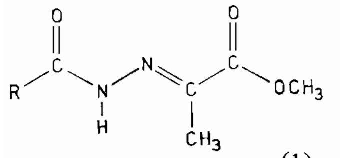
TABLE II. Characteristic IR Bands (cm^{-1}) of L and ML'_2.

Compound	ν(OH)	ν(NH)	ν(CO) ester	ν_{as}(COO)	ν(CO) Amide I	δ(NH) + ν(CN) Amide II	$\delta_{as}(CH_3)$	$\delta_s(CH_3)$	ν_s(COO)
L		3200mw 3150mw	1721vs		1687vs	1610m	1425m 1445m	1390ms	
$CoL'_2\cdot 2H_2O$	3420s,br 3360sh	3120w		1627vs	1670vs	1540s	1425w	1370m	1330ms
$NiL'_2\cdot 2H_2O$	3400s,br 3320sh	3100w		1630vs	1676s	1540s	1425mw	1380mw	1345s
$NiL'_2\cdot ½H_2O$	3410w,br	3110mw		1628vs	1672vs	1545s	1430mw	1375ms	1330s
$CuL'_2\cdot ½H_2O$	3410w,br	3110mw		1620sh	1668vs,br	1540s	1420mw	1365ms	1323ms
$ZnL'_2\cdot ½H_2O$	3410w,br	3110mw		1645vs	1675vs	1540s	1425w	1370ms	1328s



$R = CH_3$ (L)
$R = C_6H_5$ (L_1)
$R = o\text{-}HOC_6H_4$ (L_2)

(1)

The present paper deals with the synthesis and the characterization of the reaction products of L with some transition metal acetates, in hydro-alcoholic medium. The X-ray structure of the dihydrate Ni(II) derivative, undertaken to confirm analytical and spectroscopic evidence, is also reported. The chemical behaviour of L_1 and L_2, which strongly differentiates from that of L, is the subject of another paper [6].

Experimental

Syntheses and Characterizations

Methyl pyruvate *N*-acetylhydrazone (L) was prepared by heating 1:1 molar ratios of acetylhydrazine and methyl pyruvate under reflux in ethanol for 30 min. The white bulky crystalline product, obtained on cooling, (–20 °C), was filtered, washed and dried *in vacuo* and identified by means of its IR, NMR and mass spectra.

L was reacted with divalent transition metal acetates (Co, Ni, Cu, Zn), 1:2 molar ratio, in boiling ethanol (95%). The limpid solutions gave, by slow evaporation, crystalline solids formulated as $ML'_2\cdot nH_2O$, which were filtered, washed with chilled ethanol and ether and dried *in vacuo* ($L' = CH_3C(O)NHN{=}C(CH_3)C(O)O^-$). Relevant characterization data are given in Table I, and Table II states the most important IR bands in the region 4000–250 cm^{-1}. All these complexes gave satisfactory elemental C, H, N analyses.

In the case of nickel, two differently coloured complexes were separated from the mother liquor, containing different amount of co-crystallized water.

Elemental C, H, N analyses were performed with a Perkin-Elmer 240 automatic analyser; IR spectra (KBr disks) were recorded on a Perkin-Elmer 283 B instrument. Electronic spectra were run on a Cary 14 and a Jasco 505 spectrophotometer. Magnetic susceptibilities were measured by the Gouy method on a Newport Instruments balance at 30 °C.

Structure Analysis

A well formed prismatic crystal of the nickel derivative, $NiL'_2\cdot 2H_2O$, of approximate dimensions 0.10 × 0.15 × 0.22 mm^3, obtained from the mother liquor without further recrystallization, was selected and mounted in a fine glass fibre. Crystal data: $C_{10}H_{18}N_4NiO_8$, $M = 380.98$, orthorhombic, space group *Pbcn*, $Z = 4$, $a = 12.151(3)$, $b = 9.677(2)$, $c = 13.489(3)$ Å, $U = 1586.1(6)$ Å^3, F(000) = 792, $Dc = 1.595$ g cm^{-3}, $Dm = 1.62$ g cm^{-3}, $\mu(Cu\text{-}K\alpha) = 21.7$ cm^{-1}.

Three dimensional intensity data were collected on a Siemens AED computer controlled diffractometer, using the Ni-filtered Cu-Kα radiation and the ω–2θ technique. All intensities were corrected for Lorentz and polarization, but not for absorption effects. The structure was solved by direct methods [7]. Least-squares refinement of scale factor, atomic coordinates, anisotropic (non-hydrogen atoms) and isotropic (hydrogen atoms) thermal parameters gave the final $R = 0.0495$ and Rw 0.0465 for 694 observed reflections. The weighting scheme in the final stage was $1/(\sigma^2(F_o) + 0.003F_o^2)$.

TABLE III. Atomic Fractional Coordinates (×10^4), Thermal Parameters (×10^4 Å^2) with their E.S.D.s.

	X/A	Y/R	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	5000(0)	3243(2)	2500(0)	185(6)	283(8)	294(7)	0	0	0
O1	4509(3)	1783(5)	3514(3)	283(21)	362(30)	398(27)	51(23)	−34(20)	125(28)
C1	3471(5)	1682(7)	3619(5)	361(33)	257(35)	267(32)	3(34)	−24(28)	50(36)
O2	3002(4)	889(5)	4198(4)	463(28)	398(31)	421(26)	−50(26)	−7(25)	203(28)
C2	2771(4)	2651(6)	2971(5)	208(29)	193(31)	282(31)	−7(27)	17(28)	−14(30)
C3	1549(5)	2697(8)	3093(6)	225(30)	386(41)	463(44)	2(32)	19(36)	50(38)
N1	3365(4)	3352(5)	2391(4)	236(22)	232(26)	273(29)	19(22)	−59(24)	32(29)
N2	3000(5)	4348(6)	1751(4)	218(27)	247(28)	319(28)	−43(24)	−87(25)	62(26)
C4	3814(5)	5042(7)	1257(5)	338(33)	245(42)	256(32)	−59(29)	−26(29)	−24(29)
O3	5212(3)	4783(5)	3574(3)	215(26)	308(26)	369(25)	25(19)	−13(19)	−77(22)
C5	3468(6)	6119(8)	515(5)	454(40)	300(37)	310(37)	−58(36)	−48(33)	154(32)
O4	927(5)	4652(7)	1003(5)	414(31)	556(41)	411(34)	254(29)	−75(27)	−12(30)
H31	1316(5)	1730(8)	3432(6)	899(160)					
H32	1164(5)	2783(8)	2375(6)	899(160)					
H33	1285(5)	3543(8)	3557(6)	899(160)					
H1N2	2412(75)	4315(88)	1532(70)	276(340)					
H51	4049(6)	6963(8)	492(5)	899(160)					
H52	2645(6)	6526(8)	596(5)	899(160)					
H53	3522(6)	5533(8)	−164(5)	899(160)					
H1O4	1067(60)	4690(88)	409(69)	495(265)					
H2O4	599(65)	5417(94)	1081(66)	473(291)					

The positions of H(1N2), H(1O4) and H(2O4) were determined from a difference map, whereas the positions of the methyl hydrogens were put in calculated positions.

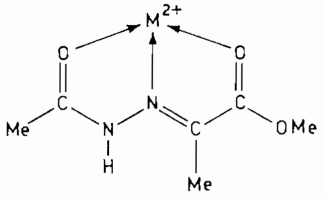
Scattering factors were those of Cromer and Mann (1968) for Ni, C, N, O and of Stewart, Davidson and Simpson (1965) for H [8].

Atomic coordinates and thermal parameters with the corresponding e.s.d.'s are given in Table III. Observed and calculated structure factors can be obtained from the authors on request.

All calculations were performed on the computer of Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord Orientale with the financial support of the University of Parma.

Results and Discussion

The reaction of methyl pyruvate *N*-acetylhydrazone, L, with some first-row transition metal acetates gives coloured crystalline solids, soluble in water and light alcohols. Analytical and spectroscopic data, together with the results of the X-ray structural analysis, carried out on the dihydrate nickel derivative, formulate these complexes as $ML'_2 \cdot nH_2O$ ($n = \frac{1}{2}, 2$) where L′ is the derived *N*-acetylhydrazonopropanoate anion. This anionic Schiff base clearly derives from the complete hydrolysis of the starting ligand, as a consequence of the polarization induced by the coordination of the ester grouping to the metal center, as depicted in the following scheme (2):



(2)

In fact the probable intermediate (2) should be prone to the nucleophilic attack of a water molecule on the ester carbon atom, as happens in the case of the metal ion-promoted hydrolysis of aminoacid esters [9]. The same reaction mechanism has been proposed for many other examples of metal-promoted or catalyzed reactions, in which esters [10], amides [10] or nitriles [11] are hydrolyzed. The formation of a chelate complex seems to be the essential condition in order that this kind of reaction takes place: indeed hydrolysis of simple esters is not catalyzed by metal ions since chelate formation does not occur and the possible intermediates cannot be stabilized [12].

It is interesting to note the different behaviour of the methyl pyruvate N-aroylhydrazones $RC(O)NHN{=}C(CH_3)C(O)OCH_3$ ($R = C_6H_5$, $o\text{-}HOC_6H_4$), described in a previous paper [6]. These ligands, by reacting with metal acetates, undergo deprotonation of the

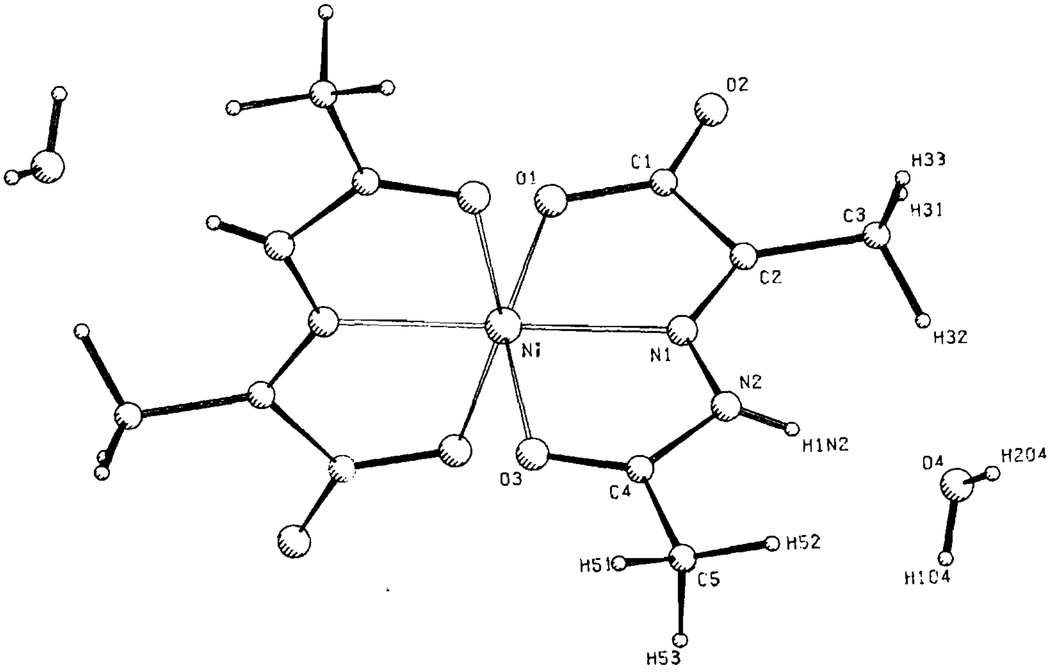


Fig. 1. Perspective view of the complex along [010].

'amidic' nitrogen to form neutral hexacoordinated metal complexes, in which the intact ester grouping participates to the chelation. This behaviour is in agreement with the results of an early work of Sacconi [13], concerning the influence of the R group on the RC(O)NHN=CR′R″ system in presence of nickel acetate. In fact the aromaticity of R is paralleled with the tendency toward enolization of the RC(O)NH–group, *i.e.* with the tendency of the carbonyl oxygen atom to assume an extra negative charge. If we assume that this negative charge is in some extent delocalized on the whole ligand, it should make the ester grouping less prone to the nucleophilic attack.

Infrared Spectra

The IR spectrum of the ligand L (Table II) exhibits two very intense carbonyl bands at 1721 and 1687 cm^{-1}, attributable to the ester and hydrazide ν(CO) respectively. In the IR spectra of the complexes the former is replaced by the typical bands (ν_{as} and ν_s) of the coordinated carboxylic group, derived from the hydrolysis of the ester. The values of these latters are comparable with the corresponding ones observed for metal glycino complexes [14], showing the same slight dependence of the frequency on the nature of the metal center.

The frequency of the amide I band in the complexes undergo a small lowering (10–20 cm^{-1}) due to coordination effects; more pronounced (80 cm^{-1}) is the lowering of this band in metal complexes of deprotonated *N*-aroylhydrazones, where abstraction of the 'amidic' proton strongly modifies the structural parameters in the hydrazidic group [6, 15]. Coordination also affects the amide II band, mainly due to ν(CN) and δ(NH), as it has been observed in other *N*-acylhydrazones with coordinated azomethyne groups [16].

The infrared data strongly suggest a terdentate behaviour of the anionic ligand, requiring an octahedral coordination for the metals, which has been confirmed by the X-ray structural analysis carried out on the dihydrate Ni complex.

X-ray Structure

The molecular complex is depicted in Fig. 1, where the atom numbering scheme used in the tables is defined. Bond distances and angles are listed in Table IV, and Table V contains deviations of atoms from and dihedral angles between certain least-squares planes within the molecule.

Two ligand ions, related by a two-fold axis parallel to [010] through the nickel, are coordinated to it in a distorted octahedral environment involving O(3) and N(1) from the hydrazidic moiety and O(1) from the carboxylic group. The ligand is therefore terdentate and forms two pentatomic, practically co-planar chelation rings, the dihedral angle they form being only 0.9° (Table V).

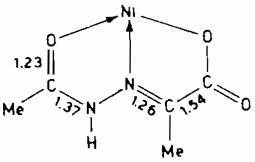
TABLE IV. Bond Distances (Å) and Angles (°) with e.s.d.'s in Parentheses.

Ni–O(1)	2.055(5)	C(2)–C(3)	1.495(8)
Ni–N(1)	1.995(5)	C(2)–N(1)	1.262(8)
Ni–O(3)	2.094(5)	N(1)–N(2)	1.368(8)
O(1)–C(1)	1.273(7)	N(2)–C(4)	1.369(9)
O(2)–C(1)	1.234(8)	C(4)–O(3)	1.231(7)
C(1)–C(2)	1.538(9)	C(4)–C(5)	1.505(9)
N(1)–Ni–O(3)	77.8(2)	O(2)–C(1)–C(2)	118.9(5)
O(1)–Ni–O(3)	156.1(2)	C(1)–C(2)–N(1)	111.3(5)
O(1)–Ni–N(1)	78.3(2)	C(1)–C(2)–C(3)	120.3(5)
O(3)–Ni–$O(3^{i})$	89.3(2)	C(3)–C(2)–N(1)	128.3(6)
O(3)–Ni–$O(1^{i})$	93.7(2)	Ni–N(1)–C(2)	119.7(4)
N(1)–Ni–$O(1^{i})$	106.1(2)	C(2)–N(1)–N(2)	125.8(5)
O(3)–Ni–$N(1^{i})$	97.8(2)	Ni–N(1)–N(2)	114.0(4)
N(1)–Ni–$N(1^{i})$	173.9(2)	N(1)–N(2)–C(4)	114.8(5)
O(1)–Ni–$O(1^{i})$	93.1(2)	N(2)–C(4)–C(5)	117.5(6)
Ni–O(1)–C(1)	114.5(1)	N(2)–C(4)–O(3)	120.3(6)
O(1)–C(1)–C(2)	116.0(5)	O(3)–C(4)–C(5)	122.2(6)
O(1)–C(1)–O(2)	125.1(6)	Ni–O(3)–C(4)	113.0(4)

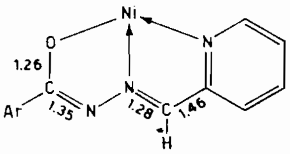
i = 1 – x, y, ½ – z

Bond angles at Ni range from 77.8 to 106.1° showing significant departures from the ideal octahedral values. A better view of the metal environment can be achieved considering the equations of the coordination planes of the octahedron: (i) O(1), N(1), O(3), $N(1^{i})$ are nearly coplanar with a maximum deviation of 0.03 Å. Ni lies almost in the mean least-squares plane through them, its displacement from it being only 0.046 Å, while $O(1^{i})$ and $O(3^{i})$ are far from it by 2.04 and –2.01 Å respectively. The axial angle ($O(1^{i})$–Ni–$O(3^{i})$, 156.1(2)°) differ notably from 180°. (ii) the $O(1^{i})$, $N(1^{i})$, $O(3^{i})$, N(1) plane is related to (i) by the twofold axis. (iii) O(1), O(3), $O(1^{i})$, $O(3^{i})$ are significantly tetrahedrally distorted; the metal lies exactly on the mean plane, while N(1) and $N(1^{i})$ are far from it by 1.99 Å. In this case the axial angle N(1)–Ni–$N(1^{i})$, 173.9(2)° is close to linearity.

Among the structures of several octahedral Ni(II) complexes, reported in the literature, one in particular, $Ni(sip)_2$ (sip = *N*′-pyridylmethylene-N″-salicyloylhydrazido(1–)-*NN*′O) [17], containing two terdentate anionic ligands related by a twofold axis, is suitable for the purpose of comparison. In fact the Ni–O(3) and Ni–N(1) distances, involving the hydrazidic moiety, compare very well with the corresponding ones found in $Ni(sip)_2$, whereas H abstraction from that group produces, in this latter complex, some significant changes into the structural parameters of the hydrazidic moiety. The major differencies are shown by the scheme (3) where



NiL'_2 (3a)



$Ni(sip)_2$ (3b)

structure (3a) represents L′, clearly in the keto form, as it is suggested by the values of the CO distances, which corresponds well with that expected for a pure double bond. The bonding situation in the sip anion is not so sharp, and it seems correct to assume that the iminol form (3b) contributes in some extent to the overall structure, even though the CO distance maintains a considerable amount of double bond character. The values of the CN double bond (1.262(8) Å) and of the C(1)–C(2) single bond

TABLE V. Deviations (Å) of Atoms from Weighted Least-Squares Planes and Dihedral Angles (°) between Them.

(1) Chelation ring: Ni, O(1), C(1), C(2), N(1)
Ni: –0.002(1), O(1): 0.017(5), C(1): –0.011(7), C(2): –0.042(6), N(1): 0.037(5), O(2): –0.027(5), C(3): –0.184(8).

(2) Chelation ring: Ni, N(1), N(2), O(3), C(4)
Ni: –0.001(1), N(1): 0.024(5), N(2): –0.023(6), O(3): 0.011(5), C(4): –0.004(7), C(5): –0.005(7).

(3) Coordination plane: O(1), N(1), O(3), $N(1^{i})$.
O(1): 0.023(6), N(1): –0.034(7), O(3): 0.024(6), $N(1^{i})$: –0.022(7), Ni: 0.046(4), $O(1^{i})$: 2.042(6), $O(3^{i})$: –2.014(6).

(4) Coordination plane: O(1), O(3), $O(1^{i})$, $O(3^{i})$.
O(1): 0.43(7), O(3): 0.43(7), $O(1^{i})$: –0.43(7), $O(3^{i})$; –0.43(7), Ni: 0.0, N(1): 1.99(7), $N(1^{i})$: –1.99(7).

(1)–(2) = 0.9
(1)–(3) = 3.4
(1)–(4) = 84.8
(2)–(3) = 3.0
(2)–(4) = 85.2
(3)–(4) = 88.2

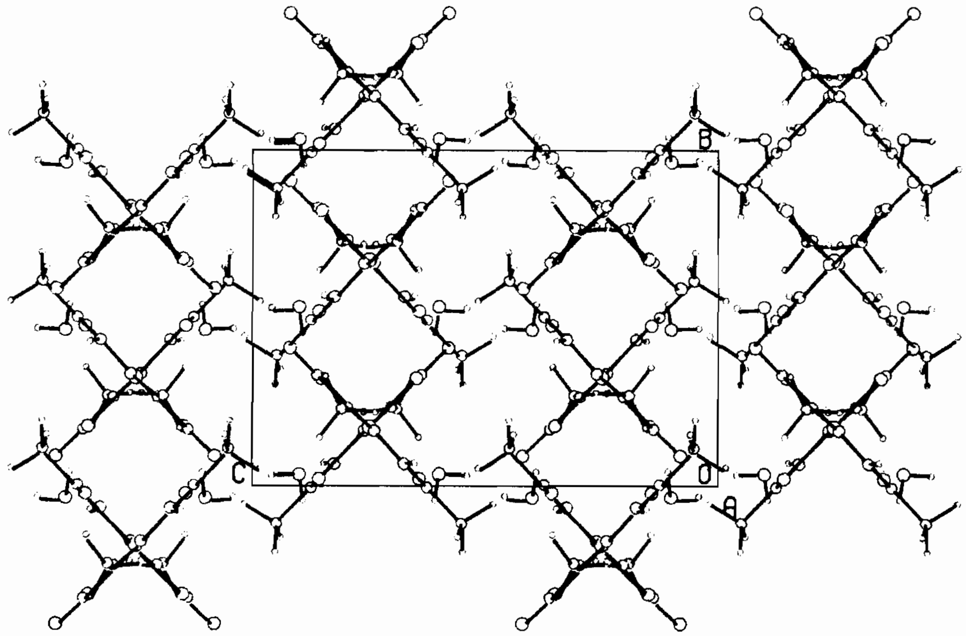


Fig. 2. Crystal packing along [100].

TABLE VI. Hydrogen Bonds and Van der Waals Interactions (<3.5 Å).

$N(2)\cdots O(4) = 2.73(1)$
$O(4)\cdots O(1^{ii}) = 2.77(1)$
$O(4)\cdots O(2^{iii}) = 2.81(1)$
$C(5)\cdots C(1^{iv}) = 3.33(1)$
$C(5)\cdots O(2^{iv}) = 3.44(1)$
$C(5)\cdots O(3^{iv}) = 3.48(1)$
$C(5)\cdots O(2^{iii}) = 3.18(1)$
$O(2)\cdots C(3^{v}) = 3.47(1)$

Roman numerals as superscripts refer to the following equivalent positions:

ii $= x - ½, ½ + y, ½ - z$
iii $= ½ - x, ½ - y, z - ½$
iv $= x, 1 - y, z - ½$
v $= ½ - x, y - ½, z$

(1.538(9) Å), which is comparable with the same distance found in the oxalate group [18], confirm the assumption that the overall structure is frozen in the canonical form (3a).

The structural parameters of the coordinated carboxylate group are in good agreement with the corresponding ones found in nickel complexes of aminoacids, *e.g.* in diaquobisglycinatonickel(II) (Ni–O = 2.06(1) Å) [19].

Packing is determined by a network of hydrogen bonds which involves the amidic nitrogen, the water molecule and both the oxygen of the carboxylic group (Table VI).

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