

with change of relative orientation is expected to be small, as pointed out in a previous paper. Hence the relative orientation could naturally be affected by various factors such as the molecular packing and the dispersion and repulsion forces.

The computer used in this work was the HITAC 5020E in the Computer Centre, University of Tokyo. The UNICS computer programs were used in this work (the Universal Crystallographic Computing System, Japanese Crystallographic Association).

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#### References

- BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.
- BOEYENS, J. C. A. & HERBSTEIN, F. H. (1965). *J. Phys. Chem.* **69**, 2160.
- CAMERMAN, A. & TROTTER, J. (1964). *Proc. Roy. Soc. A* **279**, 129.
- HANSON, A. W. (1963). *Acta Cryst.* **16**, 1147.
- IKEMOTO, I. & KURODA, H. (1967). *Bull. Chem. Soc. Japan*, **40**, 2009.
- IKEMOTO, I. & KURODA, H. (1968). *Acta Cryst.* **B24**, 383.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- KURODA, H., AMANO, T., IKEMOTO, I. & AKAMATU, H. (1967). *J. Amer. Chem. Soc.* **89**, 6056.
- OKAYA, Y. & ASHIDA, T. (1967). *HBLIS IV, The Universal Crystallographic Computing System* (I), p. 65. Japanese Crystallographic Association.
- PROUT, C. K. & WRIGHT, J. D. (1968). *Angew. Chem.* **80**, 688.
- ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
- WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **22**, 899.

*Acta Cryst.* (1970). **B26**, 806

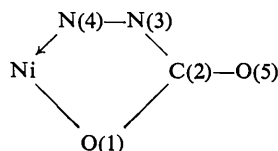
## The Crystal and Molecular Structure of Bis(hydrazinecarboxylato-*N'*,*O*)-nickel Dihydrate and Comparisons with other Complexes of the Ligand

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Bis(hydrazinecarboxylato-*N'*,*O*)-nickel dihydrate is monoclinic, space group *C2/c*, with unit-cell constants:  $a=11.78$  (1),  $b=6.95$  (1),  $c=10.54$  (1) Å,  $\beta=111.55$  (10)°. The structure determination shows how the complex around the metal is a *trans*(O), *trans*(N), *trans*(L)-octahedral chelate, with L=OH<sub>2</sub>. The chelate ring



is not planar. The atoms N(3), C(2), O(5), O(1) however, which probably form a conjugate system, deviate only slightly from a common plane. The statistical significance of the deviations from this plane is discussed in comparison with the deviations and the  $\chi^2$  significance tests as calculated for other chelate rings formed by the same ligand. The nickel-oxygen bond in the ring is shorter (2.038 Å) than the nickel-nitrogen bond (2.092 Å) and this is probably related to the negative charge on O(1). Other characteristics of the chelate ring and of the octahedral complex are discussed. The structure is held together by a network of hydrogen bonds. The hydrogen atoms, as determined by difference synthesis, are slightly off the line joining the two atoms involved in each hydrogen bond. The water molecule at O(6) forms two dative hydrogen bonds and behaves as acceptor in a third, the latter bond implying one lone pair of electrons on O(6). The second lone pair on O(6) forms a bond with the nickel atom.

#### Introduction

As part of a programme of study of the structures and related properties of the complexes of hydrazinecar-

boxylic acid, H<sub>2</sub>N'-NH-COOH (abbreviated to hycH), the structure of bis(hydrazinecarboxylato-*N'*, *O*)-nickel dihydrate, Ni(hyc)<sub>2</sub>.2H<sub>2</sub>O, has been investigated. The octahedral complexes which have been

found in bis-chelates of hycH with bivalent metals  $M^{II}$  are *trans*(O), *cis*(N'), *cis*(L) (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1968; Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967; Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli, 1969) and *trans*(O), *trans*(N'), *trans*(L) (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965c), where L is a ligand and N' and O are the donor atoms of the chelating hyc. It is worth noting that the former complex has been found in the orthorhombic compound  $Mn(hyc)_2 \cdot 2H_2O$  (Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967), which is isomorphous with the compounds  $Mg(hyc)_2 \cdot 2H_2O$  and  $Co(hyc)_2 \cdot 2H_2O$  (to be published) but not with the present compound  $Ni(hyc)_2 \cdot 2H_2O$ . In all the bis-chelates the oxygen atoms of the carboxylate groups are *trans* to one another. The same ligand also forms octahedral tris-chelates  $[M^{II} hyc_3]^-$  in *cis* configuration (Braibanti, Manotti Lanfredi & Tiripicchio, 1967).

### Experimental

#### Preparation

Crystals of the compound were obtained by very slow hydrolytic transformation of  $(N_2H_5)[Ni(hyc)_3] \cdot H_2O$  dissolved in water.

#### Crystal data

Compound: bis(hydrazinecarboxylato-*N',O*)-nickel dihydrate,  $Ni(NH_2-NH-COO)_2 \cdot 2H_2O$ ; F.W. 244.84

Crystal habit: thin plates, nearly rectangular

Crystal class: monoclinic prismatic

Unit cell: (Cu  $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ )

$a = 11.78(1)$   $b = 6.95(1)$   $c = 10.54(1) \text{ \AA}$

$\beta = 111.55(10)^\circ$ ;  $V = 802.3 \text{ \AA}^3$ ;  $Z = 4$  stoichiometric units

$D_m = 2.038$   $D_x = 2.026 \text{ g.cm}^{-3}$

$\mu = 35.98 \text{ cm}^{-1}$  (Cu  $K\alpha$ )

Possible space groups:  $C2/c$  (No. 15,  $C_{2h}^2$ ) or  $Cc$  (No. 9,  $C_s^2$ )

$C2/c$  was chosen and subsequently confirmed by the structure determination.

#### Intensities

The photographs for intensity measurement were taken with an integrating Weissenberg camera using the multiple-film technique. The intensities of reflexions  $h0l$ ,  $h1l \dots h6l$  and  $hk0$ ,  $hk1 \dots hk9$  were measured by a microdensitometer. The absorption correction was applied as for cylindrical specimens ( $\mu \bar{R}_{[001]} = 0.54$ ;  $\mu \bar{R}_{[010]} = 0.18$ ).

#### Determination and refinement of the structure

The structure was solved by three-dimensional Patterson and Fourier syntheses. The atomic positional parameters were refined by differential syntheses. The corrections to the thermal parameters were obtained by the method of Nardelli & Fava (1960). The atomic form factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for C, N and O, those of Thomas & Umeda (1957) for  $Ni^{2+}$ , and those of McWeeny (1951) for H.

The hydrogen atoms were located fairly well by difference synthesis (Fig. 1). The final agreement index was  $R = 8.9\%$  for observed reflexions ( $R = 9.2\%$  without hydrogen atoms). The final results are reported in Tables 1-4.

Table 1. Final atomic coordinates with e.s.d.'s ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	5000 (0)	5000 (0)	5000 (0)
O(1)	3545 (6)	4753 (4)	5597 (6)
C(2)	2519 (8)	5267 (7)	4675 (9)
N(3)	2520 (7)	5854 (7)	3434 (8)
N(4)	3671 (7)	6343 (5)	3338 (7)
O(5)	1513 (8)	5170 (5)	4811 (9)
O(6)	5507 (6)	7649 (5)	6034 (7)
H(7)*	2006	7067	2835
H(8)*	3798	7900	3531
H(9)*	3750	5817	2583
H(10)*	6017	8233	5687
H(11)*	4716	8432	6093

\* The e.s.d.'s for hydrogen atoms from differential syntheses are approximately  $\sigma_x = 38 \cdot 10^{-4}$ ,  $\sigma_y = 2 \cdot 10^{-4}$ ,  $\sigma_z = 67 \cdot 10^{-4}$  but they are probably over optimistic.

Table 2. Anisotropic thermal parameters ( $\text{\AA}^2$ )\*

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Ni	1.572	2.077	1.810	0.094	0.565	0.017
O(1)	1.066	1.530	1.329	0.210	0.525	0.197
C(2)	0.984	0.748	1.350	0.126	0.380	0.076
N(3)	0.609	2.287	0.970	0.278	0.118	0.227
N(4)	0.965	1.658	0.929	-0.034	0.435	-0.124
O(5)	1.453	2.000	2.957	0.524	1.142	0.559
O(6)	1.002	1.273	1.035	0.141	0.374	-0.091
H(7)	1.2	} Isotropic for hydrogen atoms				
H(8)	1.2					
H(9)	1.2					
H(10)	1.1					
H(11)	1.1					

\* Average and maximum shifts in the last cycle:

Ni	$  \Delta  _{av} = 0.025$	$  \Delta  _{max} = 0.056$
Light atoms	$  \Delta  _{av} = 0.052$	$  \Delta  _{max} = 0.179$

Table 3. Observed and calculated structure factors = after F<sub>0</sub> indicates an unobserved reflexion.

Table with multiple columns of h, k, l, F<sub>o</sub>, F<sub>c</sub> values for various reflections. The table is organized into several groups of reflections, with some values in italics. The data represents observed and calculated structure factors for the compound.

### Discussion

The structure (Fig. 2) consists of octahedral chelates (Fig. 3) *trans*(O),*trans*(N),*trans*(OH<sub>2</sub>). The main intra-

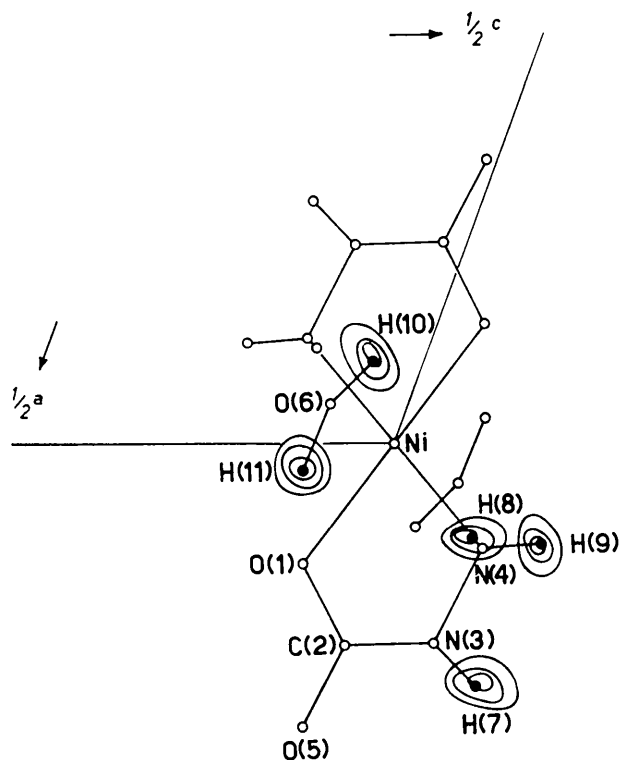
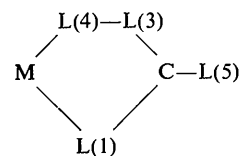


Fig. 1. Difference synthesis to locate the hydrogen atoms.

molecular bond distances and angles are reported in Tables 5 & 6. The bond lengths around the metal atom are Ni-O(1)=2.038, Ni-N(4)=2.092 and Ni-O(6)=2.111 Å. The first two bonds obey the rule that in complexes of hydrazinecarboxylic acid the metal-oxygen bond of the chelate ring is always shorter than the metal-nitrogen bond.

In a general chelate ring,



not necessarily pentatomic (Table 7), the values  $\Delta_1 = [M-L(1)] - [M-L(4)]$  and  $\Delta_2 = [C-L(1)] - [C-L(5)]$  are correlated at a very high level of probability, with the exception of two values out of sixteen. The correlation coefficient (Cramér, 1954) is found to be,  $\rho = 4.18$  for  $n = 14$ , and the correlation can be accepted at a very high probability level ( $P > 99\%$ ). If the regression of  $\Delta_1$  on  $\Delta_2$  is calculated, the regression curve (Fig. 4)  $\Delta_c = -0.01685 - 0.750 \Delta_2 + 3.25 \Delta_2^2$  is obtained, where  $\Delta_c$  is the calculated value of  $\Delta_1$ . The regression curve can also be accepted at a very high probability level, being  $F = 6.41$  against  $F_{2,11,0.05} = 3.98$ . The correlation can be explained if  $\Delta_2$  is assumed to indicate the excess negative charge on L(1) with a corresponding lengthening of C-L(1). In other compounds, such as the 8-hydroxyquinolines (Palenik, 1964*a,b*) an excess negative charge can be assigned to the oxygen atom corresponding to L(1); in fact, in the copper complex

Table 4. Atomic peak heights ( $e \cdot \text{\AA}^{-3}$ ), curvatures ( $e \cdot \text{\AA}^{-5}$ ) and *e.s.d.*'s

		$\rho$	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	$A_{hk}$	$A_{hl}$	$A_{kl}$	
Ni	Obs	77.4	855	798	895	42	333	3	
	Calc	78.7	843	794	888	39	329	3	
O(1)	Obs	19.3	214	198	219	8	94	5	
	Calc	19.4	207	196	213	7	90	4	
C(2)	Obs	13.9	164	149	141	7	63	-6	
	Calc	13.9	160	145	141	6	62	-6	
N(3)	Obs	14.6	149	131	140	10	43	3	
	Calc	14.4	143	133	137	10	43	1	
N(4)	Obs	15.7	159	153	167	9	59	8	
	Calc	15.4	155	154	162	9	57	7	
O(5)	Obs	16.1	171	163	154	12	73	8	
	Calc	16.3	164	160	155	9	70	6	
O(6)	Obs	19.0	186	197	186	9	69	-5	
	Calc	18.9	182	195	183	9	67	-4	
$\sigma$		0.3	4	3	4	2	3	2	
		$\rho$							
H(7)	Obs	1.2							
	Calc	0.9							
H(8)	Obs	1.2							
	Calc	1.3							
H(9)	Obs	1.0							
	Calc	0.9							
H(10)	Obs	1.2							
	Calc	1.1							
H(11)	Obs	1.3							
	Calc	1.3							

it has been found that Cu-O=1.925 Å compared with Cu-N=1.972 Å and Cu-O=1.935 Å compared with Cu-N=1.972 Å (Palenik, 1964a) and in the zinc complex Zn-O=2.066 compared with Zn-N=2.099 Å (Palenik, 1964b). Therefore it can be inferred that the shortening of the M-O(1) bond is probably a result of the attractive force of the excess negative charge localized on O(1). The third bond in the complex between the nickel atom and the water molecules, Ni-O(6)=2.111 Å, is of the same length as Ni-N(4). The angles between the bonds radiating from the metal atom in-

dicate that the complex is not appreciably distorted, except for the angle N(4)-Ni-O(1) which is of course conditioned by the 'biting' distance of the chelating group, O(1)···N(4)=2.678 Å.

The bond lengths in the chelate group are as expected: C(2)-O(1)=1.291 Å is longer than C(2)-O(5)=1.246 Å, as it should be if the excess negative charge were on O(1). The bond C(2)-N(3)=1.371 Å falls within the range for carbon-nitrogen bonds in amides: C-N=1.319 (Hughes & Small, 1962), 1.345 (Bracher & Small, 1967), 1.385 (Braibanti, Manotti Lanfredi &

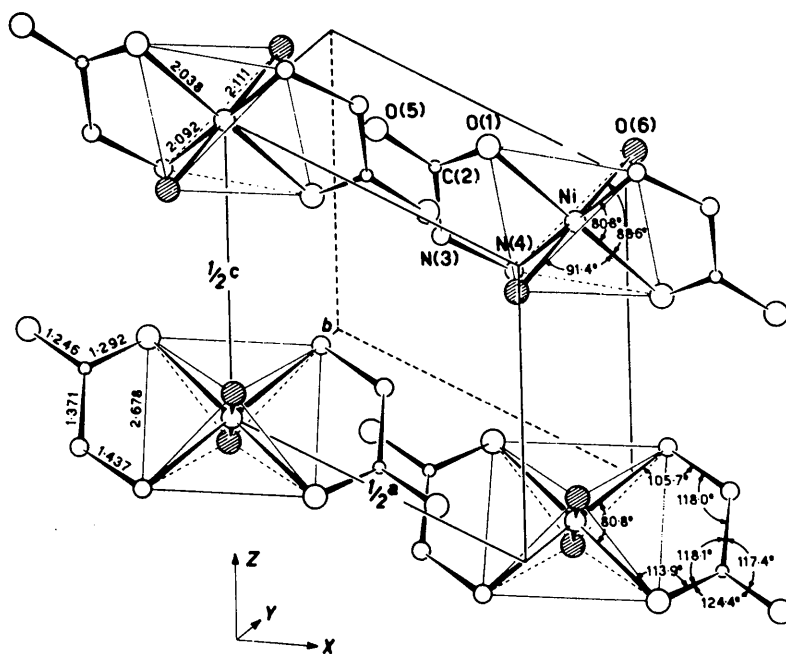


Fig. 2. The structure of bis(hydrazinecarboxylato-*N',O*)-nickel dihydrate, Ni(N'H<sub>2</sub>-NH-COO)<sub>2</sub>·2H<sub>2</sub>O.

Table 5. Main intramolecular bond distances and angles

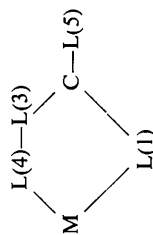
Ni—O(1)	2.038 (7) Å	O(1)—Ni—N(4)	80.8 (3)°
Ni—N(4)	2.092 (7)	O(1)—Ni—N(4) <sub>v</sub>	99.2 (3)
Ni—O(6)	2.111 (4)	O(1)—Ni—O(6)	91.4 (2)
O(1)—C(2)	1.291 (11)	O(1)—Ni—O(6) <sub>v</sub>	88.6 (2)
C(2)—N(3)	1.371 (12)	N(4)—Ni—O(6)	91.5 (2)
N(3)—N(4)	1.437 (12)	Ni—O(1)—C(2)	113.9 (6)
C(2)—O(5)	1.246 (14)	O(1)—C(2)—N(3)	118.1 (9)
N(4)—O(1)	2.678 (9)	C(2)—N(3)—N(4)	118.0 (7)
		N(3)—N(4)—Ni	105.7 (4)
		O(1)—C(2)—O(5)	124.4 (8)
		O(5)—C(2)—N(3)	117.4 (9)

Asymmetric units: V,  $\frac{1}{2} + x$ ,  $\frac{3}{2} - y$ ,  $\frac{1}{2} + z$ .

Table 6. Intramolecular bond distances and angles involving hydrogen atoms

N(3)—H(7)	1.09 (4) Å	H(7)—N(3)—C(2)	126 (3)°
N(4)—H(8)	1.10 (1)	H(7)—N(3)—N(4)	97 (3)
N(4)—H(9)	0.91 (6)	H(8)—N(4)—H(9)	120 (4)
O(6)—H(10)	0.91 (5)	H(8)—N(4)—N(3)	107 (3)
O(6)—H(11)	1.10 (5)	H(9)—N(4)—N(3)	112 (3)
		H(10)—O(6)—H(11)	120 (3)

Table 7. Regression of the single-bond character of the C-L(1) bond on the ionic character of the M-L(1) bond in the chelate rings



N	Compound	Complex	M	L(1)	L(3)	L(4)	L(5)	$d_2$ (Å)	$d_1$ (Å)	$d_6$ (Å)	Reference
1	Ni(N'H <sub>2</sub> -NH-COO) <sub>2</sub> .2H <sub>2</sub> O	octahedral	Ni	O	N	N	O	+0.046	-0.054	-0.045	1
2	Zn(N'H <sub>2</sub> -NH-COO) <sub>2</sub> .2N <sub>2</sub> H <sub>4</sub>	octahedral	Zn	O	N	N	O	+0.050*	-0.120*	—	2
3	(N <sub>2</sub> H <sub>5</sub> )Ni(N'H <sub>2</sub> -NH-COO) <sub>3</sub> .H <sub>2</sub> O	octahedral	Ni	O	N	N	O	+0.089	-0.073	-0.058	3
4	(N <sub>2</sub> H <sub>5</sub> )Ni(N'H <sub>2</sub> -NH-COO) <sub>3</sub> .H <sub>2</sub> O	octahedral	Ni	O	N	N	O	+0.038	-0.040	-0.041	3
5	(N <sub>2</sub> H <sub>5</sub> )Ni(N'H <sub>2</sub> -NH-COO) <sub>3</sub> .H <sub>2</sub> O	octahedral	Ni	O	N	N	O	+0.088	-0.042	-0.058	3
6	Mn(N'H <sub>2</sub> -NH-COO) <sub>2</sub> .2H <sub>2</sub> O	octahedral	Mn	O	N	N	O	+0.125	-0.070	-0.060	4
7	Mn(N'H <sub>2</sub> -NH-COO) <sub>2</sub> .2H <sub>2</sub> O	octahedral	Mn	O	N	N	O	+0.105	-0.044	-0.060	4
8	Cd(N'H <sub>2</sub> -NH-COO) <sub>2</sub>	octahedral	Cd	O	N	N	O	-0.050*	-0.140*	—	5
9	Cd(N'H <sub>2</sub> -NH-COO) <sub>2</sub> .H <sub>2</sub> O	octahedral	Cd	O	N	N	O	+0.030	-0.060	-0.036	6
10	ZnC <sub>5</sub> H <sub>7</sub> NO <sub>4</sub> .2H <sub>2</sub> O	pyramidal	Zn	O	C	N	O	-0.023	+0.003	+0.002	7
11	CuC <sub>5</sub> H <sub>7</sub> NO <sub>4</sub> .2H <sub>2</sub> O	pyramidal	Cu	O	C	N	O	+0.042	-0.031	-0.043	8
12	Ni(NH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -COO) <sub>2</sub> .2H <sub>2</sub> O	octahedral	Ni	O	C-C	N	O	-0.064	+0.044	+0.044	9
13	Cu(NH <sub>2</sub> -NH-CO-NH <sub>2</sub> )Cl <sub>2</sub>	octahedral	Cu	O	N	N	-NH <sub>2</sub>	†	-0.020	-0.017	10
14	Zn(NH <sub>2</sub> -NH-CO-NH <sub>2</sub> )Cl <sub>2</sub>	octahedral	Zn	O	N	N	-NH <sub>2</sub>	†	-0.010	-0.017	10
15	Ni(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> O) <sub>2</sub> .2H <sub>2</sub> O	square planar	Ni	N	C	N	O	+0.060	-0.050	-0.050	11
16	Ni(NH <sub>2</sub> -CH <sub>2</sub> -COO) <sub>2</sub> .2H <sub>2</sub> O	octahedral	Ni	O	C	N	O	+0.020	-0.020	-0.031	12

$$d_6 = -0.01685 - 0.750d_2 + 3.254d_2^2$$

$$d_1 = [M-L(1)] - [M-L(4)]$$

$$d_2 = [C-L(5)] - [C-L(1)]$$

\* Excluded from the regression.

†  $d_2 = 0$  (assumed).Statistical test for regression curve:  $F = 6.41$ ,  $F_{2,11,0.05} = 3.98$ ,  $F_{2,11,0.01} = 7.20$ .

## References

- 1 Present work
- 2 Ferrari, Braibanti, Bigliardi & Lanfredi (1965c)
- 3 Braibanti, Manotti Lanfredi & Tiripicchio (1967)
- 4 Braibanti, Tiripicchio, Manotti Lanfredi & Camellini (1967)
- 5 Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968)
- 6 Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli (1969)
- 7 Gramaccioli (1966)
- 8 Gramaccioli & Marsh (1966)
- 9 Jose, Pant & Biswas (1964)
- 10 Nardelli, Fava Gasparri, Boldrini & Giraldi Battistini (1965)
- 11 Chang, Park & Li (1968)
- 12 Freeman & Guss (1968)

Table 8. Bond distances in the hydrazinecarboxylato group in complexes

Compound ring	Ni(hyc) <sub>2</sub> ·2H <sub>2</sub> O	Zn(hyc) <sub>2</sub> ·2N <sub>2</sub> H <sub>4</sub>	(N <sub>2</sub> H <sub>5</sub> )Ni(hyc) <sub>3</sub> ·H <sub>2</sub> O	V	VI	Mn(hyc) <sub>2</sub> ·2H <sub>2</sub> O	VII	Cd(hyc) <sub>2</sub>	VIII	Cd(hyc) <sub>2</sub> ·H <sub>2</sub> O	IX	Mean(σ <sub>m</sub> )
Ni—O(1)	2.038 (7)		2.042 (11)	2.069 (16)	2.068 (10)	1.314 (22)	1.317 (23)	1.200 (40)*	1.200 (40)*	1.280 (20)		2.047 (5)
Ni—N(4)	2.092 (7)		2.115 (12)	2.111 (13)	2.108 (17)	1.360 (23)	1.452 (25)†	1.420 (40)	1.420 (40)	1.370 (20)		2.101 (5)
O(1)—C(2)	1.292 (11)	1.300 (40)	1.274 (14)	1.338 (16)	1.249 (19)	1.326 (26)*	1.366 (26)*	1.400 (40)	1.400 (40)	1.410 (30)		1.293 (6)
C(2)—N(3)	1.371 (12)	1.390 (50)	1.398 (19)	1.326 (26)*	1.416 (25)	1.435 (23)	1.366 (26)*	1.400 (40)	1.400 (40)	1.410 (30)		1.381 (8)
N(3)—N(4)	1.437 (12)	1.390 (20)	1.440 (20)	1.423 (22)	1.422 (15)	1.209 (19)	1.192 (23)	1.250 (40)	1.250 (40)	1.250 (20)		1.425 (7)
C(2)—O(5)	1.246 (14)	1.250 (20)	1.185 (18)*	1.250 (20)	1.201 (17)							1.230 (6)

References

\* Probably different from the mean.

† Significantly different from the mean.

1 Present work

2 Ferrari, Braibanti, Bigliardi &amp; Lanfredi (1965c)

3 Braibanti, Manotti Lanfredi &amp; Tiripicchio (1967)

4 Braibanti, Tiripicchio, Manotti Lanfredi &amp; Camellini (1967)

5 Braibanti, Tiripicchio, Manotti Lanfredi &amp; Bigoli (1968)

6 Braibanti, Manotti Lanfredi, Tiripicchio &amp; Bigoli (1969)

$$\text{Mean} = \frac{\sum_i [d_i(1/\sigma_i^2)]}{\sum_i (1/\sigma_i^2)}, \quad \sigma_m = 1/\sqrt{\sum_i (1/\sigma_i^2)}$$

Tiripicchio, 1967), 1.33 (Peyronel & Pignedoli, 1967), 1.318, 1.325, 1.325 (Haas, Harris & Mills, 1965), 1.33 (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), 1.33, 1.35 (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965), 1.31, 1.34 (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), 1.335, 1.315 (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969), 1.316, 1.326 (Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969) and 1.37 Å (Fava Gasparri, Nardelli & Villa, 1967). However, the value found in the present compound indicates that here the carbon–nitrogen bond has low double-bond character.

The bond N(3)–N(4)=1.437 Å is shorter than the same bond (N–N=1.45, 1.46, 1.47 Å) in hydrazine, either free (Collin & Lipscomb, 1951; Liminga & Olovsson, 1964) or in complexes (Ferrari, Braibanti & Bigliardi, 1963; Ferrari, Braibanti, Bigliardi & Dal-

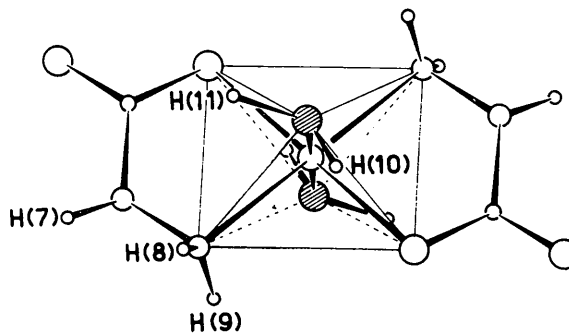


Fig. 3. Octahedral chelate with hydrogen atoms. Note the tetrahedral configuration of N(4), and the trigonal configuration of N(3).

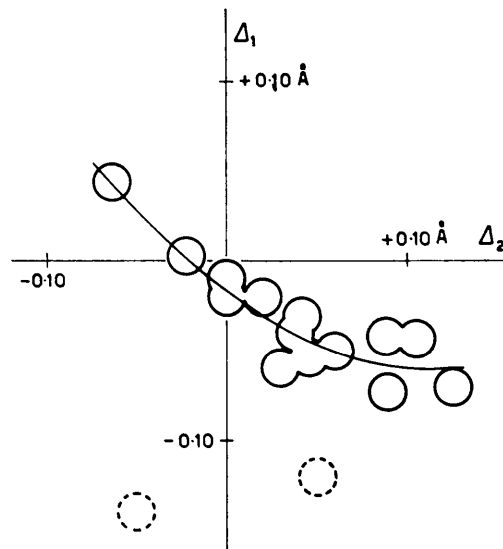


Fig. 4. Regression of  $\Delta_1 = [M-L(1)] - [M-L(2)]$  on  $\Delta_2 = [C-L(1)] - [C-L(5)]$  in the chelate rings. Dotted circles do not belong to the regression.

lavallo, 1963; Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a, b, c*).

All the distances found in nine chelate rings are compared in Table 8.

The whole chelate ring is not planar and according to the  $\chi^2$  significance test, the group N(3)-C(2)-O(5) is also probably not planar. The best plane through N(3), C(2), O(5), O(1) is  $0.00693 X + 0.94055 Y + 0.33957 Z = 4.98589 \text{ \AA}$ , where  $X, Y, Z$  are referred to orthogonal axes  $X \equiv x, Y \equiv y$  and  $Z \perp X, Y$ ; the sum of the squares of the standardized variable is  $\sum (\Delta/\sigma_\perp)^2 = 29.5$ , compared with  $\chi_{95\%}^2 = 3.841$  for one degree of freedom. This result can be compared with results obtained in nine chelate rings of the same ligand (Table 9); the results are consistent over the entire class if proper weights are given to each determination. In any case the deviations from the plane are fairly small and do not appear to contradict the assumption of conjugation between atoms N(3), C(2), O(5), O(1).

The atoms N(4) and M<sup>II</sup> are, in general, significantly out of the plane which passes approximately through the four atoms mentioned, and in any case their positions differ from those in the other rings. This means that the group N(3), C(2), O(5), O(1) rotates around the bond N(4)-N(3). This distortion can be approximately measured by the dihedral angle  $\omega = \text{M}^{\text{II}} \dots \text{N}(4) - \text{N}(3) - \text{C}(2)$  (Fig. 5). Presumably the lone pair of

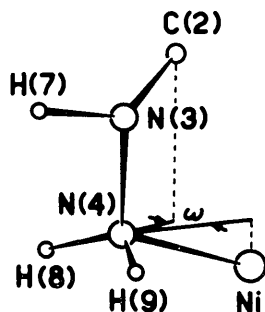


Fig. 5. The dihedral angle  $\text{M}^{\text{II}} \dots \text{N}(4) - \text{N}(3) - \text{C}(2)$ .

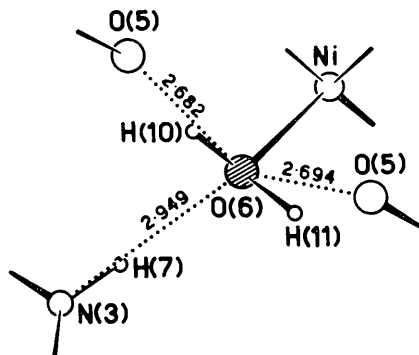


Fig. 6. Environment of the water molecule of O(6).

Table 9. Hydrazinecarboxylato group in complexes: deviations from the plane through O(1), C(2), N(3), O(5)

Compound	Ni(hyc) <sub>2</sub> ·2H <sub>2</sub> O	Zn(hyc) <sub>2</sub> ·2N <sub>2</sub> H <sub>4</sub>	(N <sub>2</sub> H <sub>5</sub> )Ni(hyc) <sub>3</sub> ·H <sub>2</sub> O	Mn(hyc) <sub>2</sub> ·2H <sub>2</sub> O	Cd(hyc) <sub>2</sub>	Cd(hyc) <sub>2</sub> ·H <sub>2</sub> O	Mean $\Delta_m(\sigma_m)$				
Ring	I	II	III	IV	V	VI	VII	VIII	IX		
$\Delta(\sigma_\perp)$ ( $\text{Å} \times 10^3$ )	+2 +21 (4) -5 (4) -6 (5) 29.5	-11 (30) +3 (30) -1 (30) -1 (30) 0.15	-3 (14) +9 (17) -3 (17) -3 (20) 0.38	O(11) O(16) O(14) O(14) 0.00	-9 (12) +29 (13) +9 (14) -10 (12) 6.63	-16 (15) +73 (18) -19 (17) -17 (14) 20.35	-5 (13) +34 (20) -12 (21) -10 (17) 3.71	-1 (22) +7 (32) -1 (28) -1 (19) 0.06	-4 (17) +10 (15) -6 (22) +3 (15) 0.62		-8 (3) +17 (3) -2 (4) -3 (4) 40.02
$\sum (\Delta/\sigma_\perp)^2$	not planar +292 (5) -26 (0)	planar +260 (17) -331 (0)	planar +260 (17) +103 (17)	not planar +160 (14) +203 (14)	not planar -4 (18) +74 (18)	planar -54 (21) -187 (21)	planar +210 (32) +717 (32)	planar +192 (22) -755 (22)	not planar		
Planarity $\Delta(\sigma_\perp)$ ( $\text{Å} \times 10^3$ )											
Reference*	1	2	3	3	3	4	5	5	6		

$\chi_{95\%}^2 = 3.841$

\* References as in Table 8.



N(4) lies along  $M^{II}-N(4)$  and therefore the dihedral angle  $\omega$  indicates, apart from a small distortion of the  $M^{II}-N(4)$  bond, the rotation of the tetrahedral N(4) group with respect to the line N(3)-C(2). In all the complexes two enantiomorphous ligands exist. In centrosymmetric *trans*(O), *trans*(*N'*), *trans*(L) complexes, two opposite enantiomorphs are bound to the same metal atom, while in non-centrosymmetric complexes two or three groups of the same enantiomorphous form are bound to the same metal atom. These enantiomorphs could either possess different structures or they could be obtained by free rotation of  $H_2N'$  around the bond N-N: the values of the angle  $\omega$  (Table 10) which from range 1.5 to 32° seem to indicate that the second possibility is more likely. The rotation should then be 'frozen' by complex formation or by crystallization. It is remarkable that the cobalt compound  $Co(hyc)_2 \cdot 2H_2O$ , although obtained under similar conditions to the nickel compound, is isostructural with the manganese compound  $Mn(hyc)_2 \cdot 2H_2O$  (Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967) which is a *trans*(O), *cis*(*N'*), *cis*(L) complex.

The complexes in this structure are held together by a network of hydrogen bonds (Table 11). Two weak hydrogen bonds are formed by N(3) and N(4) [ $N(3) \cdots O(6)_{IV} = 2.949$  and  $N(4) \cdots O(1)_I = 2.938$  Å].

One of the two hydrogen atoms of the tetrahedral N(4) group is not involved in hydrogen bonding. The angles  $N(3)-H(7) \cdots O(6)_{IV} = 135^\circ$  and  $N(4)-H(9) \cdots O(1)_I = 163^\circ$  indicate that the hydrogen atoms are slightly off the lines joining N(3) to  $O(6)_{IV}$  and N(4) to  $O(1)_I$ . This is in accordance with data quoted by Hamilton & Ibers (1968) and with the current view of bent hydrogen bonds. Two strong hydrogen bonds are formed by the water molecule containing O(6) [ $O(6) \cdots O(5)_{II} = 2.682$  and  $O(6) \cdots O(5)_{III} = 2.694$  Å]. Again the hydrogen atoms are off the line joining the heavy atoms [ $O(6)-H(11) \cdots O(5)_{II} = 144^\circ$  and  $O(6)-H(10) \cdots O(5)_{III} = 155^\circ$ ]. It is interesting to note that the angles  $Ni-O(6)-H(10) = 107^\circ$  and  $Ni-O(6)-H(11) = 112^\circ$  are close to the tetrahedral value so the water molecule of O(6) is in a nearly tetrahedral configuration with the Ni atom and is bound to it through one lone pair; the second lone pair of the oxygen atom is implied as acceptor in a hydrogen bond with H(7). The whole environment of O(6) therefore consists of a distorted tetrahedral structure (Fig. 6). This situation corresponds to type *H* of the classification of Chidambaram, Sequeira & Sikka (1964).

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Table 10. *Hydrazinecarboxylato group in complexes: dihedral angle*

Compound	Type of complex	Dihedral angle
Ni(hyc) <sub>2</sub> · 2H <sub>2</sub> O	<i>trans</i> (O) <i>trans</i> ( <i>N'</i> ) <i>trans</i> (L)	20.6°
Zn(hyc) <sub>2</sub> · 2N <sub>2</sub> H <sub>4</sub>	<i>trans</i> (O) <i>trans</i> ( <i>N'</i> ) <i>trans</i> (L)	21.5
(N <sub>2</sub> H <sub>5</sub> )Ni(hyc) <sub>3</sub> · H <sub>2</sub> O	<i>cis</i> (tris-chelate)	{ 14.5 4.6 7.2
Mn(hyc) <sub>2</sub> · 2H <sub>2</sub> O	<i>trans</i> (O) <i>cis</i> ( <i>N'</i> ) <i>cis</i> (L)	1.5
	<i>trans</i> (O) <i>cis</i> ( <i>N'</i> ) <i>cis</i> (L)	5.0
Cd(hyc) <sub>2</sub>	<i>trans</i> (O) <i>cis</i> ( <i>N'</i> ) <i>cis</i> (L)	3.0
Cd(hyc) <sub>2</sub> · H <sub>2</sub> O	<i>trans</i> (O) <i>cis</i> ( <i>N'</i> ) <i>cis</i> (L)	32

Table 11. *Hydrogen bonds and related angles*

N(3)-H(7) ··· O(6) <sub>IV</sub>	N(3) ··· O(6) <sub>IV</sub>	2.949 (10) Å
	H(7) ··· O(6) <sub>IV</sub>	2.07 (6)
	N(3) — H(7) ··· O(6) <sub>IV</sub>	135 (3)°
N(4)-H(9) ··· O(1) <sub>I</sub>	N(4) ··· O(1) <sub>I</sub>	2.938 (9) Å
	H(9) ··· O(1) <sub>I</sub>	2.06 (6)
	N(4) — H(9) ··· O(1) <sub>I</sub>	163 (4)°
O(6)-H(11) ··· O(5) <sub>II</sub>	O(6) ··· O(5) <sub>II</sub>	2.682 (11) Å
	H(11) ··· O(5) <sub>II</sub>	1.71 (5)
	O(6) — H(11) ··· O(5) <sub>II</sub>	144 (5)°
O(6)-H(10) ··· O(5) <sub>III</sub>	O(6) ··· O(5) <sub>III</sub>	2.694 (10) Å
	H(10) ··· O(5) <sub>III</sub>	1.84 (4)
	O(6) — H(10) ··· O(5) <sub>III</sub>	155 (4)°

Asymmetric units:

I	$x$	$1-y$	$z-\frac{1}{2}$
II	$\frac{1}{2}-x$	$\frac{3}{2}-y$	$1-z$
III	$\frac{1}{2}+x$	$\frac{1}{2}+y$	$z$
IV	$x-\frac{1}{2}$	$\frac{3}{2}-y$	$z-\frac{1}{2}$

## References

- ANDRETTI, G. D., DOMIANO, P., FAVA GASPARRI, G. & NARDELLI, M. (1969). To be published.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BONAMICO, M., DESSY, G., MARIANI, C., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 619.
- BONAMICO, M., DESSY, G., MUGNOLI, A., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 886.
- BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 898.
- BRACHER, B. H. & SMALL, R. W. H. (1967). *Acta Cryst.* **23**, 410.
- BRAIBANTI, A., MANOTTI LANFREDI, A. M. & TIRIPICCHIO, A. (1967). *Z. Kristallogr.* **124**, 335.
- BRAIBANTI, A., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & BIGOLI, F. (1969). *Acta Cryst.* **B25**, 100.
- BRAIBANTI, A., TIRIPICCHIO, A., MANOTTI LANFREDI, A. M. & BIGOLI, F. (1968). *Z. Kristallogr.* **126**, 307.
- BRAIBANTI, A., TIRIPICCHIO, A., MANOTTI LANFREDI, A. M. & CAMELLINI, M. (1967). *Acta Cryst.* **23**, 248.
- BRAIBANTI, A., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1969). *Acta Cryst.* **B25**, 2286.
- CHANG, S. C., PARK, D. Y. & LI, N. C. (1968). *Inorg. Chem.* **7**, 2144.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, J. K. (1964). *J. Chem. Phys.* **41**, 3616.
- COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 10.
- CRAMÉR (1954). *The Elements of Probability Theory*. Stockholm: Almqvist & Wiskell.
- FAVA GASPARRI, G., NARDELLI, M. & VILLA, A. (1967). *Acta Cryst.* **23**, 384.
- FERRARI, A., BRAIBANTI, A. & BIGLIARDI, G. (1963). *Acta Cryst.* **16**, 498.
- FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & DALLAVALLE, F. (1963). *Z. Kristallogr.* **119**, 284.
- FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965a). *Acta Cryst.* **18**, 367.
- FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965b). *Acta Cryst.* **19**, 548.
- FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965c). *Z. Kristallogr.* **122**, 259.
- FREEMAN, H. C. & GUSS, J. M. (1968). *Acta Cryst.* **B24**, 1133.
- GRAMACCIOLI, C. M. (1966). *Acta Cryst.* **21**, 600.
- GRAMACCIOLI, C. M. & MARSH, R. E. (1966). *Acta Cryst.* **21**, 594.
- HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* **19**, 676.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- HUGHES, D. O. & SMALL, R. W. H. (1962). *Acta Cryst.* **15**, 933.
- JOSE, P., PANT, L. M. & BISWAS, A. B. (1964). *Acta Cryst.* **17**, 24.
- LIMINGA, R. & OLOVSSON, I. (1964). *Acta Cryst.* **17**, 1523.
- MCWEENEY, R. (1951). *Acta Cryst.* **4**, 513.
- NARDELLI, M. & FAVA, G. (1960). *Ric. Sci.* **30**, 898.
- NARDELLI, M., FAVA GASPARRI, G., BOLDRINI, P. & GIRALDI BATTISTINI, G. (1965). *Acta Cryst.* **19**, 491.
- PALENIK, G. J. (1964a). *Acta Cryst.* **17**, 687.
- PALENIK, G. J. (1964b). *Acta Cryst.* **17**, 696.
- PEYRONEL, G. & PIGNEDOLI, A. (1967). *Acta Cryst.* **23**, 398.
- THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

*Acta Cryst.* (1970). **B26**, 815

## The Crystal Structure of TiFeSi and Related Compounds

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TiFeSi crystallizes with an orthorhombic unit cell of space group  $Ima2$  ( $C_{2v}^{22}$ ) with lattice constants  $a = 6.997 \pm 0.002$ ,  $b = 10.830 \pm 0.005$ ,  $c = 6.287 \pm 0.002$  Å. The structure is of a new type, which is a superstructure of the ordered Fe<sub>2</sub>P-type, with 12 formula units in the orthorhombic unit-cell. TiFeSi has a strong tendency to form pseudohexagonal multiple twins with the common  $a$  axis as twin axis. The structure has been refined by the least-squares method from single-crystal X-ray data, giving a final  $R$  value of 0.094 for the 344 observed reflections. TiFeGe crystallizes with the same structure:  $a = 7.155 \pm 0.002$ ,  $b = 11.025 \pm 0.007$ ,  $c = 6.405 \pm 0.003$  Å, while TiCoGe is of the ordered Fe<sub>2</sub>P-type:  $a = 6.222 \pm 0.002$ ,  $c = 3.7267 \pm 0.0010$  Å. The coordination polyhedra in the structures TiFeSi and TiCoGe are very similar to those occurring in TiNiSi ( $E$  phase) and Nb<sub>5</sub>Cu<sub>4</sub>Si<sub>4</sub>. The interatomic distances in these structures are discussed.

### Introduction

Recent investigations on ternary systems with two transition metals and silicon or germanium showed the

existence of a large number of isotypic phases at the composition 1:1:1 which are called  $E$  phases (for a summary of references see Jeitschko, 1968; Jeitschko, Jordan & Beck, 1969), the structure of which was determined for the prototype TiNiSi to be of the ordered PbCl<sub>2</sub>-type (Shoemaker & Shoemaker, 1965). In one of these studies (Spiegel, Bardos & Beck, 1963) a

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