Acta Cryst. (1972). B**28**, 2591

Structure of a Bis-Bidentate Metal Complex, Bis-(*N*-t-butylpyrrole-2-carbaldimino)nickel(II). Analysis of Its Configurational Disorder in the Crystalline State*

BY CHIN HSUAN WEI AND J. RALPH EINSTEIN

Biology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

(*Received* 9 *February* 1972)

The crystal and molecular structure of a bis-bidentate nickel complex, $(C_9H_{13}N_2)_2Ni(II)$, has been determined from a single-crystal X-ray analysis. The unit-cell data are $a=16{\cdot}777$ (13), $b=7{\cdot}507$ (6), $c=15{\cdot}378$ (11) Å, $Z=4$, space group *Pbcn*. Counter data to $2\theta=48°$ (Mo $K\alpha$ radiation) were measured with an Oak Ridge computer-controlled diffractometer. The structure was solved by heavy-atom techniques and refined by the full-matrix least-squares method to $R(F)=0{\cdot}102$, based on 1160 independent nonzero reflections, or 0·049 for the 649 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The molecule has C_2 symmetry with a crystallographic twofold axis passing through the metal atom. The structure is partly disordered in that the t-butyl group appears to have two alternative orientations of equal occupancy. The configuration around the nickel atom is pseudo-tetrahedral with a dihedral angle of 88·7 (3)° between the plane defined by the Ni, N(1), and N(2) atoms and the plane defined by the Ni, N(1′), and N(2′) atoms. The two independent Ni–N bond distances, 2·032 (4) and 1·935 (5) Å, are distinctly different. The intrachelate N–Ni–N angle of 83·7 (4)° is much smaller than any of the interchelate N–Ni–N angles, which range from 116·7 to 132·7°. The N···N 'bite' distance in the five-membered ring NiN_2C_2 is 2·647 (7) Å. The pyrrole-2-carbaldimine ligand is nearly planar.

Introduction

Although a large number of X-ray investigations on Ni(II) complexes have been carried out, most structures obtained are either octahedral or square planar. In contrast, only a few structures are tetrahedral (Sacconi, 1968). For four-coordinate complexes the square-planar configuration is favored when the Ni–ligand bond is highly covalent, and the tetrahedral configuration is favored when the bonds have purely ionic character, or when the ligands are bulky. Bis-chelate complexes are particularly interesting since, in this group, the two tendencies may be fairly evenly balanced depending in part on the bulkiness of the ligands. Thus, the existence of the tetrahedral $\rightleftarrows$ planar equilibrium in solution has been firmly established for various complexes of Schiff bases and β-ketoamines (Holm, Everett & Chakravorty, 1966; Holm & O'Connor, 1971).

Among the best-studied salicylaldimine complexes, the three-dimensional structures of only two complexes, bis-(*N*-isopropylsalicylaldiminato)Ni(II) (Fox, Orioli, Lingafelter & Sacconi, 1964) and bis-(*N*-isopropyl-3-ethylsalicylaldiminato)Ni(II) (Braun & Lingafelter, 1967), have been shown to be tetrahedral by X-ray analyses. Further information is to be derived from crystallographic determination of the stereochemistry of complexes involving different basic ligands and containing the bulkier t-butyl group. As part of a systematic investigation of a series of monomeric bis-bidentate complexes, bis-(*N*-t-butylpyrrole-2-carbaldimino)M(II) (M = Co, Ni, Cu, and Zn) (Holm, Chakravorty & Theriot, 1966; Wei, 1972*b*), the structural analysis of the nickel complex was previously undertaken from a set of three-dimensional photographic data (Wei, unpublished work). The results showed that the overall structure of the nickel complex was similar (but not isomorphous) to that of the analogous cobalt complex (Wei, 1972*a*) except that the NiN_4 coordination was more distorted so as to be less tetrahedral. However, the unambiguous location of the three methyl carbon atoms was hampered by the presence of two extra Fourier peaks in the neighborhood of the peaks presumed to represent the methyl carbon atoms. Furthermore, the geometry of the presumed t-butyl group was quite distorted from a regular tetrahedral arrangement. Since the three methyl carbon atoms can rotate around the N(azomethine)–C(t-butyl) axis (in the absence of any appreciable steric hindrance), the extra peaks might be attributed to disorder of the t-butyl group. In order to clarify the nature of the disorder, if any, and to obtain structural parameters with more precision the nickel complex has been reinvestigated with three-dimensional counter data.

Experimental

Crystal specimen

Black plate-like crystals of $(C_9H_{13}N_2)_2Ni(II)$ were kindly supplied by Professor R. H. Holm, University of Wisconsin (now at Massachusetts Institute of Technology). A single crystal of dimensions $0{\cdot}10 \times 0{\cdot}12 \times 0{\cdot}38$ mm, selected for cell determination and data collection, was mounted inside a thin-walled glass capillary so that the longest dimension, corresponding

* Research supported by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation. This work was presented in part at the Winter Meeting of the American Crystallographic Association, Tulane Univeristy, New Orleans, La., March 1–5, 1970.

to the c axis, was nearly coincident with the φ axis of the diffractometer.

Unit cell and space group

On the basis of earlier Weissenberg and precession photographs, it had been established that the crystals were orthorhombic. Six strong reflexions in the 2θ range 29 to 34° were centered with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) using Mo $K\alpha_1$ radiation ($\lambda=$ 0·7093 Å), and the cell parameters together with the orientation parameters of the crystal were refined by the method of least-squares.

The crystals have cell parameters $a=16{\cdot}777$ (13), $b=7{\cdot}507$ (6), and $c=15{\cdot}378$ (11) Å. The volume of the unit cell is 1936·8 Å^3. The observed density of 1·20 (2) g.cm^{-3} (by flotation) agrees with the calculated value of $1{\cdot}22_5$ g.cm^{-3} based on four formula weights per unit cell. The total number of electrons per cell, $F(000)$, is 760. Systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for $h+k$ odd are uniquely characteristic of the space group *Pbcn* (D_{2h}^{14}, No. 60) (see *International Tables for X-ray Crystallography*, 1969). This choice was confirmed by a satisfactory refinement of the solved structure.

X-ray intensity data

A set of three-dimensional data for $2\theta\leq 48°$ was recorded with the automatic diffractometer, using Nb-filtered Mo $K\alpha$ radiation, by the θ–2θ step-scan technique. The scan width was 1·5° plus the separation of the $K\alpha_1$–$K\alpha_2$ doublet. The step width was 0·05°; step times ranged from 2 sec at low 2θ to 6 sec at high 2θ; and background counts for periods ranging from 20 to 180 sec were measured at the beginning and end of each scan. Since some background measurements at low 2θ showed errors due to the effect of the absorption edge of the β filter, the reflections for $2\theta\leq 35°$ were also measured by an ω step-scan technique without filter (H. A. Levy, unpublished work; Brown, 1969), in which three scans were run for each reflection: a main scan with the detector set at the computed 2θ, and two background scans with the detector offset lower and higher in 2θ. The scan width was 0·75° in ω, the step width was 0·025°, and the time per step was 2 sec. The detector slit width and the 2θ offset were adjusted for different ranges of 2θ in a manner similar to that described by Brown (1969). Throughout the process of data collection (both θ–2θ and ω scans), a reference reflection was recorded following every 25 reflections. The intensity of the standard reflection remained constant to within ± 3% throughout the run.

Reduction of intensity data was carried out in a manner similar to that described elsewhere (Brown, 1969). Variances $\sigma^2(F_o^2)$ for use in least-squares weighting were estimated according to the expression $\sigma^2(F_o^2)=K^2[G+(t_G/t_B)^2B]/(\mathrm{Lp})^2$, in which G is the gross intensity count, B the background count, t_G/t_B the ratio of the counting times of gross intensity and background, K the appropriate scaling constant, and Lp the Lorentz–polarization factor. An empirical quantity $(0{\cdot}03F_o^2)^2$ was then added to the variance of the averaged F_o^2. Absorption corrections, calculated by the method of Busing & Levy (1957), were applied using a linear absorption coefficient of 10·1 cm^{-1} for Mo $K\alpha$ radiation. The calculated transmission coefficient ranged from 0·925 to 0·853. Of 1385 independent reflections measured, 1160 had intensities greater than zero, and 649 had $F_o^2\geq 3\sigma(F_o^2)$.

Solution and refinement of the structure

The close similarity of the diffraction pattern of the present compound with that of the analogous cobalt complex (Wei, 1972) suggested that as in the latter, the metal atoms are on the twofold axes at the fourfold set of special positions 4(c) (see *International Tables for X-ray Crystallography*, 1969).

The y coordinate of the crystallographically independent nickel atom was obtained from a three-dimensional Patterson function (Blount, 1965) and refined by a full-matrix least-squares program (Busing, Martin & Levy, 1962) for the 700 reflections with $h+k$ even.† The subsequent three-dimensional Fourier synthesis, phased on the nickel atoms and using only the reflec-

† Since the nickel atoms are at the fourfold set of special positions 4(c), they contribute only to structure factors for reflections with $h+k$ even.

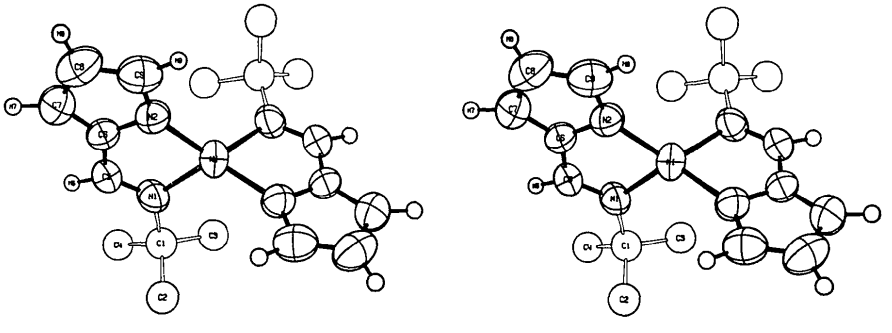

Fig. 1. Stereoscopic view of the molecule along the twofold axis showing one orientation of the t-butyl group as obtained from the rigid-group refinement. The nonhydrogen, nongroup atoms are shown with the 50% probability thermal ellipsoids.

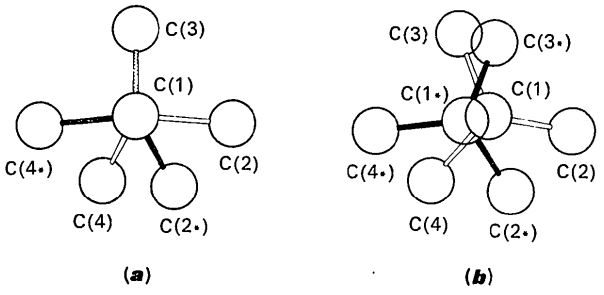

Fig. 2. View down the N(1)–C(1) bond direction showing the conformation of the t-butyl group (*a*) before and (*b*) after the rigid-group disorder treatment. In (*b*) the closed bonds are associated with one orientation of the t-butyl group and the open bonds with the other orientation.

tions with $h+k$ even, unambiguously indicated all nitrogen and carbon atomic positions except those of the three methyl carbons attached to C(1) (for numbering scheme, see Fig. 1). There were five peaks of high density on a plane approximately perpendicular to the N(1)–C(1) vector and at the expected distance of $\sim 1{\cdot}5$ Å from atom C(1). The arrangement of the peaks is shown in Fig. 2(*a*) in projection along the bond N(1)–C(1). Attempts to refine as an ordered model (with isotropic thermal motions) by choosing the combination C(2), C(3), C(4) or C(2*), C(3), C(4*) [Fig. 2(*a*)] and ignoring the two remaining peaks in each case invariably led to unreasonable bond distances and angles for the t-butyl group. Furthermore, the conventional $R(F)$ value remained at about 0·15, a value rather high for counter data. It thus became apparent that the t-butyl group was disordered. From three-dimensional difference Fourier maps at this stage, four hydrogen peaks attached to the pyrrole-2-carbaldehyde moiety were identified.

An assumption was made that the t-butyl group occupies two alternative sets of atomic sites, but that the two sites for both C(1) and C(3) are sufficiently close to have given a single peak for each of these atoms in the Fourier, so that approximate positions for the two sets are those of C(1), C(2), C(3), C(4) and C(1), C(2*), C(3), C(4*) [Fig. 2(*b*)]. With the use of a rigid-group least-squares refinement program kindly supplied by Professor L. F. Dahl of the University of Wisconsin, refinement was carried out for the disordered model including one nickel, two nitrogen, five 'full' carbon and four hydrogen atoms, and two fractional t-butyl groups (carbon atoms only) constrained to have C–C bond lengths of 1·55 Å and C–C–C bond angles of 109°28′. In order to decrease computer time, only the 649 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were utilized at this stage. The thermal motions of the nonhydrogen, nongroup atoms were treated anisotropically, and the hydrogen atoms and the group carbon atoms were assigned individual isotropic temperature factors. The occupancy factor m for each partially occupied t-butyl group was fixed as 0·5.† During the course of the refinement, reflection 102 was removed from the data set because of apparent extinction. At the end of the refinement, the values of $R(F)$ and $R_w(F)$ [the latter defined as $(\sum w|\Delta F|^2/\sum wF_o^2)^{1/2}$] stood at 0·071 and 0·080, respectively. The parameter shifts in the last cycle were all less than one third of the corresponding standard deviations. Parameters for the two half-occupancy t-butyl groups together with the derived parameters for the group carbon atoms are shown in Table 1. The arrangement of the t-butyl groups viewed down the N(1)–C(1) direction is shown in Fig. 2(*b*).

† Assignment was based on an intermediate refinement in which m was varied, with the result $m = 0{\cdot}51$ (2).

Table 1. *t-Butyl group parameters and derived parameters for group carbon atoms*

Standard deviations of the least significant figures are given in parentheses in all tables and in the text.

x_c, y_c, and z_c are the fractional coordinates of the origins for the rigid t-butyl groups *TBG*1 and *TBG*2. The rigid-body positional coordinates are defined relative to right-handed orthogonal axes x', y', and z'. In *TBG*1, the origin is at C(2); the $+x'$ direction is the C(4) → C(2) vector; and $+z'$ direction is the vector product of $\mathbf{x}'$ and the vector C(4) → C(3). The definitions for *TBG*2 are analogous, with C(2*) replacing C(2). For each group, the three angular parameters, φ, θ, and ϱ (in radians) define the orientation of the rigid-body axial system with respect to an orthogonal set of crystal axes a_o, b_o, and c_o, where $a_o = a$, $b_o = c_o \times a_o$, and $c_o = a \times b$. Three successive rotations bring the crystal axes into parallel coincidence with the rigid-body axes as follows. A positive rotation φ about c_o brings a_o to a_1 and b_o to b_1; next, a positive rotation θ about a_1 brings b_1 to b' and c_o to c_1; finally, a positive rotation ϱ about b' brings a_1 to a' and c_1 to c' (Scheringer, 1963; Watkins, 1966).

Group	x_c	y_c	z_c	φ	θ	ϱ
*TBG*1	0·130 (1)	0·091 (3)	0·062 (1)	−1·29 (1)	−3·26 (1)	−2·52 (2)
*TBG*2	0·189 (1)	−0·025 (3)	0·103 (2)	−1·85 (1)	−2·74 (1)	−2·48 (1)

Group	Atom	x	y	z	B, Å^2
	C(1)	0·1084	−0·0245	0·1426	6·7 (9)
*TBG*1	C(2)	0·1298	0·0907	0·0623	7·4 (6)
	C(3)	0·0275	−0·1191	0·1267	7·4 (7)
	C(4)	0·1743	−0·1659	0·1574	11·5 (9)
	C(1*)	0·1124	−0·0711	0·1553	7·0 (9)
*TBG*2	C(2*)	0·1887	−0·0251	0·1032	9·4 (7)
	C(3*)	0·0394	−0·0681	0·0935	9·0 (9)
	C(4*)	0·1210	−0·2592	0·1958	6·4 (5)

Since the bond distances and bond angles at the sites of attachment of both alternative t-butyl groups to N(1) were reasonably normal (Table 2), the disordered model appeared to be justified. The distances C(1)···C(1*) and C(3)···C(3*) were only 0·41 and 0·67 Å respectively, as compared to 1·46 Å for C(2)···C(2*) and 1·28 Å for C(4)···C(4*). It was therefore considered adequate in the subsequent refinements without rigid-group constraints to use the weighted average positions with an occupancy factor of 1·0 for C(1) and C(3), and independent positions with an occupancy factor 0·5 for C(2), C(2*), C(4) and C(4*). A full-matrix least-squares refinement was performed with the thermal motions of all nonhydrogen atoms treated anisotropically and those of four hydrogen atoms treated isotropically. Of the 649 reflections with $F_o^2 \geq 3\sigma(F_o^2)$, three reflections (102, 110, and 214) giving poor agreement were removed from the data set. The refinement converged to give $R(F)$ and $R_w(F)$ values of 0·049 and 0·043 respectively. Comparison of the refined parameters with those obtained with the rigid-group model showed no significant differences except for the z coordinate of atom N(1) (which differed by 3 e.s.d.'s) and for the parameters of the t-butyl carbon atoms. The refinement was continued with all 1160 observed reflections excepting the three reflections giving poor agreement. The final $R(F)$ and $R_w(F)$ values were 0·102 and 0·051 respectively. The standard deviation of an observation of unit weight, defined as $[\sum w|\Delta F|^2/(n-p)]^{1/2}$, where n is the number of observations and p the number of parameters fitted to the data set, was 1·71. The maximum parameter shift in the last cycle was 28% [for C(4)] of the corresponding standard deviation. The positional e.s.d.'s were about three-fourths as large as those obtained in the refinement with the smaller data set, and both sets of refined parameters agreed to within their estimated standard deviations. The scattering factors used were those of Thomas & Umeda (1957) for nickel, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and nitrogen, and those tabulated by Ibers (1962) for hydrogen. The anomalous scattering corrections (Templeton, 1962) $\Delta f' = 0{\cdot}4$ and $\Delta f'' = 1{\cdot}2$ were employed for the nickel scattering factors.

Table 2. *Molecular parameters resulting from the rigid-group refinement*

For each of the two t-butyl groups, C-C bond lengths of 1.55 Å and C-C-C bond angles of 109°28′ were assumed in the rigid-group refinement.

Distances		Angles	
N(1)–C(1)	1·46 Å	N(1)–C(1)—C(2)	112·5°
N(1)–C(1*)	1·55	N(1)–C(1)—C(3)	107·1
Average	1·51 Å	N(1)–C(1)—C(4)	108·8
		N(1)–C(1*)–C(2*)	106·8
C(1)···C(1*)	0·41	N(1)–C(1*)–C(3*)	106·5
C(2)···C(2*)	1·46	N(1)–C(1*)–C(4*)	115·0
C(3)···C(3*)	0·67	Average	109·5°
C(4)···C(4*)	1·28		
N(1)···C(2)	2·50		
N(1)···C(3)	2·42		
N(1)···C(4)	2·45		
N(1)···C(2*)	2·49		
N(1)···C(3*)	2·48		
N(1)···C(4*)	2·61		
Average	2·49 Å		

The final values of the atomic parameters and their estimated standard deviations are given in Table 3. The observed and calculated structure amplitudes are listed in Table 4. The interatomic distances and intramolecular bond angles, calculated by means of the Busing, Martin & Levy (1964) program *ORFFE* and based on the parameters of Table 3, are given in Table 5. 'Best' planes formed by sets of specified atoms, and perpendicular distances of these and other atoms from these planes, were calculated by a weighted least-squares program (Smith, 1962). All figures were prepared by the use of the *ORTEP* program (Johnson, 1970).

Table 3. *Positional and thermal parameter* ($\times 10^4$) *for* $(C_9H_{13}N_2)_2Ni(II)$

The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	2223 (1)	$\frac{1}{4}$	38 (0·4)	370 (3)	63 (0·6)	0	−6 (0·5)	0
N(1)	994 (3)	803 (6)	2201 (3)	39 (2)	306 (12)	56 (3)	−5 (4)	−0 (2)	−14 (5)
N(2)	675 (3)	3257 (7)	3386 (3)	48 (2)	249 (12)	54 (3)	13 (5)	−5 (2)	−14 (5)
C(1)	1128 (4)	−511 (11)	1482 (4)	71 (4)	485 (26)	68 (4)	−22 (9)	8 (4)	−120 (10)
C(2)	1299 (12)	903 (26)	662 (9)	140 (14)	518 (60)	32 (7)	−30 (22)	33 (8)	−17 (16)
C(2*)	1906 (18)	−260 (39)	1073 (20)	154 (20)	671 (115)	173 (27)	−180 (41)	142 (21)	−224 (42)
C(3)	300 (4)	−971 (10)	1121 (5)	100 (5)	484 (22)	129 (6)	−21 (8)	−34 (4)	−113 (10)
C(4)	1803 (18)	−1562 (37)	1539 (20)	150 (22)	599 (110)	204 (32)	251 (40)	−92 (21)	−263 (46)
C(4*)	1196 (11)	−2589 (19)	1948 (12)	94 (10)	124 (31)	112 (10)	6 (13)	−7 (8)	−33 (14)
C(5)	1559 (4)	1255 (9)	2724 (4)	35 (3)	334 (17)	53 (4)	4 (6)	−1 (3)	6 (7)
C(6)	1429 (4)	2556 (8)	3366 (4)	47 (3)	268 (15)	47 (3)	−7 (6)	−1 (3)	−26 (7)
C(7)	1907 (4)	3319 (10)	3984 (5)	55 (4)	354 (20)	62 (4)	−21 (8)	−10 (4)	−13 (8)
C(8)	1430 (6)	4543 (11)	4392 (5)	98 (5)	312 (21)	58 (5)	−27 (9)	−0 (5)	−35 (8)
C(9)	681 (5)	4491 (9)	4019 (5)	72 (5)	262 (19)	65 (5)	11 (8)	5 (4)	−0 (8)
H(5)	2077 (24)	660 (51)	2756 (25)	1·8 (11)					
H(7)	2492 (33)	3050 (66)	4077 (30)	4·5 (15)					
H(8)	1489 (26)	5270 (57)	4909 (35)	2·5 (13)					
H(9)	138 (35)	5014 (73)	4108 (34)	5·1 (17)					

Description and discussion of the structure

The crystal structure of $(C_9H_{13}N_2)_2Ni(II)$ is made up of monomeric molecular units in which the nickel atom is coordinated to two bidentate ligands of *N*-substituted pyrrole-2-carbaldimine. Since the crystallographic twofold axis passes through the nickel atom, the configuration has C_2 symmetry. One of the two orientations for the t-butyl groups, obtained from the rigid-group refinement, was found to be similar to that for the cobalt analog (Wei, 1972). A stereoscopic view of the molecule with the other orientation for the t-butyl groups is shown in Fig. 1.

The dihedral angle between the coordination plane defined by atoms Ni, N(1), and N(2) and the coordination plane defined by atoms Ni, N(1′), and N(2′) (primes refer to atoms related to the corresponding independent atoms by the twofold symmetry) is 88·7 (3)°, a value slightly different from the corresponding value of 89·6 (4)° obtained for the cobalt complex; it is appreciably larger than the equivalent values of 81·5 and 85·3°, respectively, in the distorted tetrahedral complexes bis-(*N*-isopropylsalicylaldiminato)Ni(II) (Fox *et al.*, 1964) and bis-(*N*-isopropyl-3-ethylsalicylaldiminato)Ni(II) (Braun & Lingafelter, 1967), which contain less bulky sec-alkyl groups attached to the ligand parts. Among the class of *N*-substituted Schiff base and β-ketoaminine nickel(II) complexes, the present compound possesses the maximum molecular tetrahedrality yet determined by X-ray diffraction – a tetrahedrality which seems to persist in solution (Holm & O'Connor, 1971), in contrast with those complexes having less bulky ligands such as *N*-sec-alkylsalicylaldimine. For the latter complexes, the existence of both tetrahedral and planar configurations in *solution* has been widely recognized (Sacconi, Paoletti & Ciampolini, 1963; Sacconi, Ciampolini & Nardi, 1964; Sacconi, Ciampolini & Campigli, 1965).

It has been frequently reported (Braun & Lingafelter, 1966; Braun & Lingafelter, 1967; Sacconi, 1968; Everett & Holm, 1968) that for a given type of ligand in four-coordinate complexes, the nickel-donor atom bond distances increase as the structure goes from low-spin square-planar form to high-spin tetrahedral form, because of the decreased strength of the σ bonds and possibly because of less favourable d_π–p_π interaction in the latter form (Braun & Lingafelter, 1966; Braun & Lingafelter, 1967). The Ni–N bond distances

Table 4. *Observed and calculated structure amplitudes* ($\times 10$) *for* $(C_9H_{13}N_2)_2Ni(II)$

H	L	10F0	10FC
****	K = 0	****	
0	2	1732	1845
0	4	789	234
0	6	1026	967
0	8	452	475
0	10	462	455
0	12	414	405
0	14	81	94
0	16	62	19
1	2	166	443
1	4	293	300
1	6	41	16
1	8	54	55
1	10	72	95
1	12	29	37
1	14	103	104
1	16	104	97
2	0	1315	1286
2	2	1455	1495
2	4	592	598
2	6	527	526
2	8	479	521
2	10	368	384
2	12	264	264
2	14	136	163
2	16	65	81
3	2	37	93
3	4	131	130
3	6	287	259
3	8	320	327
3	10	243	242
3	12	73	73
3	14	67	67
3	16	38	37
4	0	782	701
4	2	310	307
4	4	469	502
4	6	759	779
4	8	730	747
4	10	137	136
4	12	166	149
4	14	244	278
4	16	158	138
5	2	52	56
5	4	69	58
5	6	243	235
5	8	111	111
5	10	137	150
5	12	97	98
6	0	667	689
6	2	534	543
6	4	713	708
6	6	730	727
6	8	414	419
6	10	309	310
6	12	202	240
6	14	170	157
7	2	326	326
7	4	298	279
7	6	160	157
7	8	106	93
7	10	61	86
7	12	64	98
7	14	93	36
8	0	562	558
8	2	214	205
8	4	810	826
8	6	326	341
8	8	240	236
8	10	407	418
8	12	122	135
8	14	39	30
9	2	33	118
9	4	113	128
9	6	201	206
9	8	74	57
9	12	127	93
10	0	410	422
10	2	542	550
10	4	440	439
10	6	422	435
10	8	399	399
10	10	102	121
10	12	52	42
11	2	400	412
11	4	241	234
11	6	50	59
11	10	46	76
11	12	95	115
12	0	431	435
12	2	464	464
12	4	431	452
12	6	345	344
12	8	249	224
12	10	160	157
13	2	161	201
13	4	138	138
13	8	59	14
13	12	4	54
14	0	356	367
14	2	264	287
14	4	224	216
14	6	151	137
14	8	157	142
14	10	159	199
14	12	146	142
15	2	69	58
15	4	43	62
15	6	84	29
15	8	46	62
15	10	40	24
16	0	205	194
16	2	131	118
16	4	102	55
16	6	126	120
16	8	171	117
17	2	45	47
17	8	30	21
18	0	136	142
18	2	183	177
18	4	140	123
18	6	129	121
19	2	43	11
****	K = 1	****	
0	1	756	551
1	1	1511	1601
1	2	766	831
1	3	897	906
1	4	322	347
1	5	768	749
1	6	140	132
1	7	493	428
1	8	249	259
1	9	416	419
1	10	94	120
1	11	422	410
1	12	40	59
1	13	240	234
1	17	14	14
2	1	820	883
2	2	1625	1526
2	3	1329	1051
2	4	342	319
2	5	92	75
2	6	10	46
2	7	243	222
2	8	43	56
2	9	182	178
2	10	106	99
2	11	81	77
2	12	78	87
2	13	79	75
2	15	122	123
2	16	30	11
2	17	24	1
3	0	208	194
3	1	414	381
3	2	429	441
3	3	1041	1018
3	4	18	34
3	5	478	487
3	6	131	122
3	7	369	355
3	8	14	7
3	9	419	417
3	10	45	13
3	11	256	259
3	13	193	177
3	14	104	82
3	15	148	133
3	16	83	64
4	0	109	116
4	1	77	76
4	2	338	354
4	4	334	338
4	5	29	47
4	6	79	75
4	7	240	240
4	8	130	136
4	9	200	197
4	10	78	101
4	11	76	37
4	12	67	55
4	14	87	84
4	16	69	28
5	0	82	26
5	1	602	622
5	2	86	98
5	3	680	653
5	4	95	81
5	5	684	697
5	6	130	103
5	7	613	558
5	8	95	80
5	9	295	293
5	11	195	194
5	12	111	84
5	13	231	216
5	14	102	94
5	15	128	135
6	1	220	198
6	2	161	122
6	3	37	18
6	5	60	43
6	5	308	317
6	6	287	304
6	8	124	124
6	9	132	120
6	10	43	45
6	11	3	37
6	14	140	150
6	14	67	36
7	0	330	338
7	1	584	582
7	2	232	236
7	3	707	709
7	4	89	103
7	5	647	672
7	6	93	97
7	7	385	392
7	8	140	126
7	9	353	348
7	10	48	18
7	11	284	284
7	12	55	104
7	13	101	120
7	14	64	43
8	1	114	104
8	2	94	73
8	3	158	152
8	4	332	323
8	5	120	117
8	6	76	73
8	7	59	69
8	8	78	73
8	10	138	153
8	11	83	48
8	12	63	69
9	0	448	441
9	1	304	301
9	2	156	151
9	3	511	517
9	4	57	58
9	5	550	547
9	6	26	5
9	7	393	393
9	8	85	80
9	9	255	239
9	10	48	73
9	11	140	123
9	12	14	10
9	13	112	95
10	1	80	72
10	2	26	19
10	3	61	45
10	4	42	13
10	5	36	14
10	6	48	32
10	7	39	49
10	8	50	49
10	9	81	29
10	12	68	37
11	0	157	165
11	1	411	412
11	2	140	132
11	3	384	384
11	4	128	138
11	5	399	419
11	6	56	53
11	7	373	374
11	8	76	54
11	9	180	148
11	10	28	42
11	11	103	82
12	1	82	52
12	2	52	55
12	3	171	166
12	4	118	106
12	5	177	173
12	7	42	35
12	8	93	102
12	9	13	18
12	10	98	118
12	11	113	60
13	0	45	43
13	1	463	458
13	2	81	93
13	3	358	354
13	4	73	75
13	5	206	210
13	6	82	85
13	7	152	156
13	8	24	45
13	9	200	199
13	10	28	19
13	11	186	180
14	1	60	43
14	2	48	54
14	3	10	9
14	4	63	37
14	5	57	49
14	6	48	30
14	7	14	33
14	8	53	47
14	9	10	8
14	10	48	32
14	11	10	9
15	1	53	47
15	2	35	29
15	3	277	276
15	4	133	133
15	5	112	97
15	6	61	7
15	7	103	130
15	8	131	134
15	9	148	137
15	10	14	9
16	1	47	6
16	2	53	37
16	3	63	26
16	4	53	37
16	5	119	130
16	6	51	5
16	7	38	18
16	8	35	24
16	9	35	36
17	0	37	11
17	1	113	128
17	2	35	35
17	3	148	137
17	4	119	130
17	8	41	4
18	1	45	13
18	2	28	26
18	4	52	1
19	1	146	143
****	K = 2	****	
0	0	379	367
0	1	106	91
0	2	1330	1248
0	3	1507	1517
0	4	605	593
0	5	1054	1029
0	6	120	127
0	7	231	210
0	8	283	296
0	9	112	109
0	10	350	350
0	11	45	20
0	12	293	313
0	13	109	103
0	14	226	226
0	15	84	44
0	16	63	42
1	1	356	360
1	2	47	16
1	3	100	94
1	4	232	239
1	5	234	228
1	6	262	254
1	7	202	202
1	8	91	81
1	9	80	90
1	12	21	29
1	13	40	36
1	14	67	11
1	15	67	11
2	0	489	481
2	1	64	54
2	2	284	295
2	3	275	252
2	4	814	803
2	5	340	335
2	6	305	320
2	7	179	171
2	8	353	354
2	9	54	84
2	10	403	400
2	11	54	36
2	12	196	189
2	14	148	102
2	16	109	107
3	1	244	229
3	2	37	35
3	3	230	239
3	4	456	460
3	5	152	157
3	6	37	12
3	7	175	156
3	8	235	243
3	9	45	39
3	10	30	10
3	11	57	49
3	12	121	132
3	13	26	57
3	14	64	50
3	15	56	52
3	16	55	52
4	0	793	810
4	1	139	113
4	2	385	412
4	3	51	28
4	4	696	685
4	5	733	735
4	6	34	29
4	7	71	25
4	8	381	398
4	9	125	122
4	10	321	319
4	11	127	126
4	12	129	12
4	13	90	123
4	14	73	73
4	15	49	58
5	1	51	24
5	2	128	126
5	3	332	323
5	4	75	66
5	5	128	135
5	6	128	135
5	7	69	67
5	8	52	50
5	9	56	53
5	10	73	68
5	11	765	753
5	12	54	53
5	13	68	81
5	14	50	53
5	15	98	83
6	1	318	306
6	2	269	264
6	3	463	454
6	4	64	79
6	5	406	406
6	6	175	175
6	7	53	53
6	8	136	159
6	9	85	81
6	11	134	138
6	13	207	207
7	1	29	1
7	2	87	78
7	3	39	32
7	4	72	85
7	5	122	133
7	6	90	71
7	7	69	71
7	8	230	233
7	9	159	161
7	10	60	32
7	11	151	151
7	12	103	107
7	13	64	50
7	14	49	45
8	1	106	103
8	2	55	49
8	3	128	130
8	4	85	65
8	5	108	98
8	6	131	134
8	7	143	130
8	8	109	96
8	9	130	126
8	10	73	75
8	11	82	60
8	12	178	172
8	13	46	51
8	14	87	71
8	15	55	63
9	1	106	106
9	2	195	193
9	3	232	221
9	4	306	340
9	5	102	108
9	6	93	98
9	7	53	53
9	8	153	146
9	9	57	69
9	10	70	105
9	11	90	87
9	12	35	29
9	13	29	29
9	14	73	73
9	15	63	67
10	1	350	346
10	2	37	32
10	3	90	60
10	4	97	103
10	5	117	107
10	6	183	196
10	7	66	66
10	8	155	115
10	9	48	35
10	10	42	52
10	11	62	55
10	12	112	117
10	13	28	28
10	14	70	105
11	1	74	93
11	2	73	72
11	3	96	114
11	4	106	103
11	5	106	103
11	6	71	75
11	7	142	154
11	8	54	38
11	9	70	70
11	10	70	70
11	11	28	11
11	12	112	104
11	13	28	28
11	14	28	28
12	1	28	28
12	2	50	33
12	3	112	112
12	4	33	33
12	5	33	33
12	6	33	33
12	7	33	33
12	8	33	33
12	9	33	33
12	10	33	33
12	11	33	33
12	12	33	33
12	13	33	33
12	14	33	33
12	15	33	33
13	1	85	68
13	2	59	2
13	3	97	102
13	4	47	42
13	5	48	16
13	6	80	49
13	7	87	81
13	8	63	76
13	9	84	102
13	10	107	92
13	11	118	125
13	12	102	105
13	13	80	91
13	14	51	53
13	15	66	52
13	16	26	32
14	1	53	3
14	2	68	6
14	3	80	7
14	4	102	97
14	5	109	128
14	6	60	95
14	7	134	117
14	8	102	97
14	9	102	97
14	10	116	116
14	11	80	80
14	12	112	97
14	13	39	27
14	14	46	54
14	15	67	35
15	1	66	16
15	2	111	88
15	3	103	98
15	4	116	116
15	5	50	24
15	6	44	19
****	K = 5	****	
0	1	74	90
1	1	175	161
1	2	91	87
1	3	101	84
1	4	187	201
1	5	267	235
1	6	162	151
1	7	157	163
1	8	126	139
1	9	95	67
1	10	70	50
1	11	66	65
1	12	97	99
1	13	79	58
1	14	46	54
2	1	118	121
2	2	84	61
2	3	33	39
2	4	56	8
2	5	68	60
2	6	73	62
2	7	44	29
2	8	50	33
2	9	121	112
2	10	60	26
2	11	84	27
2	12	65	14
2	13	37	52
2	14	58	6
3	1	206	204
3	2	181	176
3	3	256	256
3	4	162	147
3	5	206	205
3	6	232	230
3	7	232	230
3	8	114	95
3	9	151	53
3	10	64	52
3	11	49	9
3	12	46	85
3	13	48	48
4	1	85	68
4	2	59	2
4	3	97	102
4	4	47	42
4	5	48	16
4	6	80	49
4	7	87	81
4	8	63	76
4	9	84	102
4	10	107	92
4	11	118	125
4	12	102	105
4	13	80	91
4	14	51	53
4	15	66	52
4	16	26	32
5	1	206	220
5	2	51	38
5	3	213	205
5	4	101	95
5	5	113	127
5	6	95	101
5	7	95	94
5	8	69	65
5	9	99	94
5	10	27	33
5	11	25	52
5	12	42	27
5	13	112	117
5	14	136	5
5	15	59	55
5	16	122	122
****	K = 6	****	
0	0	297	287
0	1	89	68
0	2	170	148
0	3	47	47
0	4	168	165
0	5	258	274
0	6	147	133
0	7	267	259
0	8	73	92
0	9	136	146
0	10	150	142
0	11	154	148
0	12	65	53
0	14	88	62
0	15	77	62
1	1	55	36
1	2	52	44
1	3	146	142
1	4	39	26
1	5	35	50
1	6	20	22
1	7	112	112
1	8	47	40
1	9	307	301
1	10	150	142
1	11	126	120
1	12	50	22
1	13	188	123
1	14	126	120
1	15	45	22
2	0	307	301
2	1	150	142
2	2	308	306
2	3	76	66
2	4	22	22
2	5	254	267
2	6	312	305
2	7	331	330
2	8	204	205
2	9	50	51
2	10	151	125
2	11	89	87
2	12	108	112
2	14	58	10
2	15	12	49
2	16	50	52
3	1	64	64
3	2	86	75
3	3	111	99
3	4	22	22
3	5	88	88
3	6	82	84
3	7	73	71
3	8	135	135
3	9	190	190
3	10	187	175
3	11	46	85
3	12	46	85
4	1	123	124
4	2	31	1
4	3	241	231
4	4	58	67
4	5	186	188
4	6	19	11
4	7	56	16
4	8	45	16
4	9	62	45
4	10	63	76
4	11	152	154
4	12	300	309
4	13	328	339
4	14	367	351
4	15	452	454
4	16	210	222
4	17	352	356
4	18	114	99
4	19	17	42
4	20	113	72
4	21	77	79
4	22	67	62
4	23	36	49
5	1	57	57
5	2	57	30
5	3	39	37
5	4	57	51
5	5	35	15
5	6	163	169
5	7	73	117
5	8	110	126
5	9	260	266
5	10	300	304
5	11	266	266
5	12	321	319
5	13	215	213
5	14	199	212
5	15	78	85
6	1	85	82
6	2	87	54
6	3	142	149
6	4	132	132
6	5	68	101
6	6	135	135
6	7	142	157
6	8	58	8
6	9	47	42
6	10	142	7
6	11	58	8
6	12	42	2
6	13	58	3
6	14	33	9
6	15	107	103
6	16	117	117
6	17	96	87
6	18	113	112
6	19	134	150
6	20	148	122
6	21	227	228
6	22	259	259
6	23	195	145
6	24	115	117
6	25	28	35
6	26	75	101
6	27	80	85
6	28	134	150
7	1	148	122
7	2	227	228
7	3	259	259
7	4	195	145
7	5	115	117
7	6	28	35
7	7	75	101
7	8	80	85
7	9	134	150
7	10	148	122
7	11	227	228
7	12	259	259
7	13	195	145
7	14	115	117
7	15	28	35
7	16	75	101
7	17	80	85
7	18	134	150
7	19	148	122
7	20	227	228
7	21	259	259
7	22	195	145
7	23	115	117
7	24	28	35
7	25	75	101
7	26	80	85
7	27	134	150
7	28	148	122
7	29	227	228
7	30	259	259
7	31	195	145
7	32	115	117
7	33	28	35
7	34	75	101
7	35	80	85
7	36	134	150
7	37	148	122
7	38	227	228
7	39	259	259
7	40	195	145
7	41	115	117
7	42	28	35
7	43	75	101
7	44	80	85
7	45	134	150
7	46	148	122
7	47	227	228
7	48	259	259
7	49	195	145
7	50	115	117
7	51	28	35
7	52	75	101
7	53	80	85
7	54	134	150
7	55	148	122
7	56	227	228
7	57	259	259
7	58	195	145
7	59	115	117
7	60	28	35

of 2·032 (4) and 1·935 (5) Å in this structure are both longer than the Ni–N bond distances found in the following planar complexes having donor atom sets N_4 with five-membered rings: nickel dimethylglyoxime (average 1·89 Å) (Godycki & Rundle, 1953), nickel methylethylglyoxime (average 1·86 Å) (Frasson & Panattoni, 1960), nickel glyoxime (1·874 Å) (Calleri, Ferraris & Viterbo, 1967), bis-(2-amino-2-methyl-3-butanone oximato)Ni(II) chloride monohydrate (1·91 and 1·86 Å) (Schlemper, 1968), bis(pyridine-2-carboxamido)Ni(II) dihydrate (1·92 and 1·87 Å) (Chang, Park & Li, 1968), bis-(*o*-phenylenediamino)Ni (average 1·832 Å) (Hall & Soderberg, 1968) and ethylenebis-(biguanidine)Ni(II) dichloride monohydrate (average 1·865 Å) (Holian & Marsh, 1970). The present Ni–N distances may also be compared to the average values in the disorted tetrahedral complexes bis-(*N*-isopropyl salicylaldiminato)Ni(II) (1·90 Å) (Fox *et al.*, 1964) and bis-(*N*-isopropyl-3-ethylsalicylaldiminato)Ni(II) (1·974 Å) (Braun & Lingafelter, 1967), which are respectively 0·050 and 0·054 Å longer than the Ni–N distances of 1·920 Å in a related square-planar complex bis-(*N*-isopropyl-3-methylsalicylaldiminato)Ni(II) (Braun & Lingafelter, 1966).

Table 5. *Interatomic distances* (Å) *and intramolecular angles* (degrees)

Primes refer to atoms related to those in the asymmetric unit by the crystallographic twofold axis; asterisks refer to carbon atoms with the alternative orientation of the t-butyl group of the molecule.

DISTANCE		ANGLE	
Ni–N(1)	2.032(4)	N(1)–Ni–N(2)	83.7(4)
Ni–N(2)	1.935(5)	N(1)–Ni–N(1′)	116.7(2)
N(1)–C(1)	1.498(7)	N(1)–Ni–N(2′)	122.1(2)
N(1)–C(5)	1.288(6)	N(2)–Ni–N(2′)	132.7(3)
C(5)–C(6)	1.406(7)	Ni–N(1)–C(5)	108.9(4)
C(6)–C(7)	1.369(7)	Ni–N(2)–C(6)	111.7(4)
C(7)–C(8)	1.370(9)	N(1)–C(5)–C(6)	120.5(6)
C(8)–C(9)	1.381(9)	N(2)–C(6)–C(5)	115.2(6)
N(2)–C(9)	1.344(7)	C(6)–N(2)–C(9)	105.9(6)
N(2)–C(6)	1.369(6)	N(2)–C(6)–C(7)	111.4(6)
		N(2)–C(9)–C(8)	109.1(7)
C(1)–C(2)	1.67(2)	C(6)–C(7)–C(8)	104.8(6)
C(1)–C(2*)	1.46(2)	C(9)–C(8)–C(7)	108.8(7)
C(1)–C(3)	1.54(1)	Ni–N(2)–C(9)	142.3(5)
C(1)–C(4)	1.38(2)	C(5)–C(6)–C(7)	133.4(7)
C(1)–C(4*)	1.72(2)	Ni–N(1)–C(1)	129.5(4)
AVERAGE	1.55(1)	C(5)–N(1)–C(1)	121.6(5)
		N(1)–C(1)–C(2)	99.5(8)
C(5)–H(5)	0.98(4)	N(1)–C(1)–C(3)	106.2(6)
C(7)–H(7)	1.01(5)	N(1)–C(1)–C(4)	116.9(10)
C(8)–H(8)	0.97(5)	N(1)–C(1)–C(2*)	111.5(10)
C(9)–H(9)	1.00(5)	N(1)–C(1)–C(4*)	107.4(7)
AVERAGE	0.99(2)		
		C(2)–C(1)–C(3)	91.4(9)
N(1)...N(2)	2.646(7)	C(3)–C(1)–C(4)	129.5(13)
N(1)...N(1′)	3.459(8)	C(4)–C(1)–C(2)	105.6(18)
N(1)...N(2′)	3.471(7)	C(2*)–C(1)–C(3)	132.9(15)
N(2)...N(2′)	3.545(9)	C(3)–C(1)–C(4*)	90.4(8)
		C(4*)–C(1)–C(2*)	103.7(17)
N(1)...C(2)	2.42(2)		
N(1)...C(3)	2.43(1)	C(2)–C(3)–C(4)	58.7(9)
N(1)...C(4)	2.46(2)	C(3)–C(4)–C(2)	53.6(6)
N(1)...C(2*)	2.45(2)	C(4)–C(2)–C(3)	67.6(9)
N(1)...C(4*)	2.60(2)	C(2*)–C(3)–C(4*)	58.6(9)
		C(3)–C(4*)–C(2*)	69.3(10)
C(2)...C(3)	2.30(2)	C(4*)–C(2*)–C(3)	52.0(6)
C(3)...C(4)	2.64(2)		
C(4)...C(2)	2.44(3)	N(1)–C(5)–H(5)	124(2)
C(2*)...C(3)	2.75(3)	C(6)–C(5)–H(5)	115(2)
C(3)...C(4*)	2.31(2)	C(6)–C(7)–H(7)	126(3)
C(4*)...C(2*)	2.51(3)	C(8)–C(7)–H(7)	129(3)
C(2)...C(2*)	1.48(4)	C(7)–C(8)–H(8)	133(3)
C(4)...C(4*)	1.42(4)	C(9)–C(8)–H(8)	117(3)
C(2)...C(4*)	3.29(2)	C(8)–C(9)–H(9)	139(3)
C(2*)...C(4)	1.22(3)	N(2)–C(9)–H(9)	111(3)

The intrachelate N(1)–Ni–N(2) angle of 83·7 (4)° is much smaller than the normal tetrahedral angle of 109°28′, while the other three independent angles of 116·7 (2), 122·1 (2), and 132·7 (3)° for N(1)–Ni–N(1′), N(1)–Ni–N(2′) and N(2)–Ni–N(2′) respectively, are much larger than the tetrahedral angle. The values are attributable to the constraints imposed by the chelating five-membered ring; the intrachelate angle is comparable with the corresponding angles (range 80–86·5°) in the above-mentioned $[NiN_4]$-type complexes having five-membered rings. The chelate 'bite' distance is 2·646 (7) Å, a value not much different from that [2·70 (1) Å] in the analogous cobalt complex.

No significant deviations from normal values occur for any of the individual bond distances and angles in the pyrrole-2-carbaldimine moiety. Calculation of a weighted best plane passing through the atoms of the pyrrole-

C–N–Ni/2 moiety shows that the constituent atoms are nearly coplanar, with a maximum deviation of 0·109 Å for C(1). This is probably not significant in view of the fact that the C(1) position is the average of two atomic sites. The deviations of the remaining atoms range from 0·000 for Ni to 0·035 Å for N(2).

The existence of disorder in this crystal, in contrast with its absence in the similar crystal structure of the cobalt analog, is an interesting phenomenon and difficult to explain. The nature of the disorder is further illustrated in Fig. 3 which shows the t-butyl groups in projection along bond N(1) → C(1) [Fig. 3(*b*)] or N(1) → C(1*) [Fig. 3(*c*)], together with the corresponding view for the analogous cobalt complex [Fig. 3(*a*)]. Orientation 3(*b*) is roughly related to orientation 3(*c*) by a mirror plane passing through atoms C(5), N(1), and C(1) or C(1*), while orientations 3(*a*) and 3(*b*) are very similar.

The general validity of the model adopted here for the disorder has been established by the successful refinements of the structure. The rigid-group refinement, in which the t-butyl groups were allowed to 'float', with no constraints on their mode of attachment to N(1), resulted in reasonable geometry at these sites of attachment. As shown in Table 2, all interatomic N(1)···CH_3 distances are approximately equal (maximum difference 0·19 Å) and average 2·49 Å; and all N(1)–C–CH_3 angles conform closely to the normal tetrahedral angle of 109°28′ (average value 109·5°). Although the N(1)–C(1) bond distance is 0·09 Å shorter than the N(1)–C(1*) distance, their average value of 1·51 Å is not unreasonable. Furthermore, the shortest C···C and C···H contacts (not considering the methyl hydrogen atoms) between neighboring semi-molecular units are 3·64 Å for C(2*)···C(4) and 2·99 Å for C(3)···H(9), based on the results of the

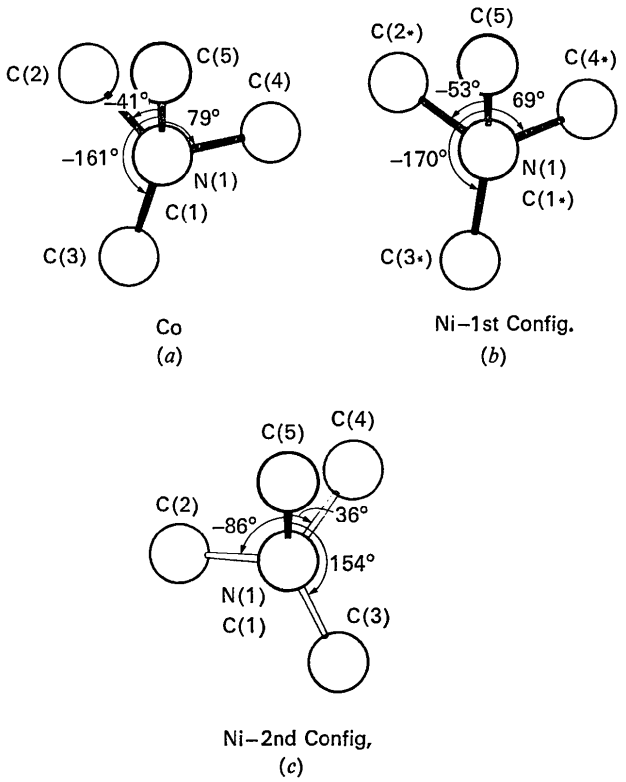

Fig. 3. Views down the N(1)–C(1) bond directions showing the conformations of the two equally-populated t-butyl groups for the nickel complex [(*b*) and (*c*)]. For comparison, the equivalent view for the cobalt complex is given in (*a*).

rigid-group refinement; or 3·59 Å for C(2*)···C(4) and 3·09 Å for C(7)···H(5), based on the final refinement. Thus, neither t-butyl group seems to be involved in any abnormal crystal packing.

In the final refinement of the structure in which C(1) and C(3) represent average atomic positions, in contrast to C(2), C(2*), C(4), and C(4*), which occupy individual partial-occupancy sites, some anomalies did appear in the thermal ellipsoids and in bond distances and angles. A projection along the bond C(5) → C(1) of the thermal ellipsoids for the t-butyl group (parameters from Table 3) is given in Fig. 4. The largest thermal displacements for C(2*) and C(4) are both 0·71 (4) Å, along directions approximately perpendicular to bonds C(1)–C(2*) and C(1)–C(4). These displacements are much larger than the largest thermal displacements for the other partial-occupancy atoms, C(2) [0·47 (2) Å] and C(4*) [0·38 (2) Å]; and all these values are considerably larger than the corresponding values (ranging from 0·29 to 0·33 Å) for the remaining nonhydrogen atoms with the exception of C(8) [0·38 (1) Å]. Elongation of individual apparent thermal ellipsoids is commonly found when an average atomic position is assumed for two atomic sites – *viz.* in the average disordered structure of triiron dodecacarbonyl (Wei & Dahl, 1969). However, the unusual elongation of the thermal ellipsoid for only one member of each pair of sites C(2) and C(4), and C(2*) and C(4*), represents an anomalous result, which may be ascribed to minor deficiencies in the disorder model and/or to the difficulties normally encountered in the refinement of disordered structures. Other abnormal molecular parameters in the t-butyl group are the C(1)–CH_3 bond distances (1·38–1·72 Å) and the N(1)–C(1)–CH_3 bond angles (91·4–132·9°) (Table 5).

We wish to thank Professor R. H. Holm of Massachusetts Institute of Technology for kindly furnishing the sample of the compound used in this study and for his interest in this work. The rigid-group refinement program was generously made available by Professor L. F. Dahl of the University of Wisconsin. We are also grateful to Dr H. A. Levy of the Oak Ridge National Laboratory for the use of the diffractometer in his laboratory, and to Drs G. D. Brunton and J. H. Burns of the Oak Ridge National Laboratory for reading the manuscript before it was submitted for publication.

References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BLOUNT, J. F. (1965). *FOURIER, A Three-Dimensional Crystallographic Fourier Summation Program for the CDC* 1604 *Computer*. Ph. D. Thesis (Appendix), Univ. of Wisconsin, Madison, Wisconsin.

BRAUN, R. L. & LINGAFELTER, E. C. (1966). *Acta Cryst.* **21**, 546.

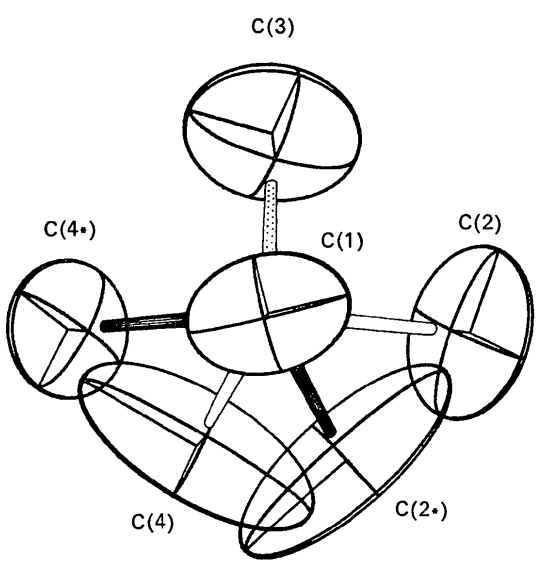

Fig. 4. The 50% probability thermal ellipsoids of the t-butyl group obtained from the anisotropic least-squares refinement based on half occupancy for C(2), C(2*), C(4), and C(4*), and whole occupancy for the averaged atoms (C1) and C(3). In the especially elongated ellipsoids for (C2*) and C(4), the largest r.m.s. thermal displacements are along directions approximately perpendicular to bonds C(1)–C(2*) and C(1)–C(4) respectively.

BRAUN, R. L. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **22**, 780.
BROWN, G. M. (1969). *Acta Cryst.* B**25**, 1338.
BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer.* Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
CALLERI, M., FERRARIS, G. & VITERBO, D. (1967). *Acta Cryst.* **22**, 468.
CHANG, S. C., PARK, D. Y. & LI, N. C. (1968). *Inorg. Chem.* **7**, 2144.
EVERETT, G. W., JR & HOLM, R. H. (1968). *Inorg. Chem.* **7**, 776.
FOX, M. R., ORIOLI, P. L., LINGAFELTER, E. C. & SACCONI, L. (1964). *Acta Cryst.* **17**, 1159.
FRASSON, E. & PANATTONI, C. (1960). *Acta Cryst.* **13**, 893.
GODYCKI, L. E. & RUNDLE, R. E. (1953). *Acta Cryst.* **6**, 487.
HALL, G. S. & SODERBERG, R. H. (1968). *Inorg. Chem.* **7**, 2300.
HOLIAN, B. L. & MARSH, R. E. (1970). *Acta Cryst.* B**26**, 1049.
HOLM, R. H., CHAKRAVORTY, A. & THERIOT, L. J. (1966). *Inorg. Chem.* **5**, 625.
HOLM, R. H., EVERETT, G. W., JR & CHAKRAVORTY, A. (1966). *Progress in Inorganic Chemistry.* Edited by F. A. Cotton. Vol. 7, pp. 83–214. New York: Interscience.
HOLM, R. H. & O'CONNOR, M. J. (1971). *Progress in Inorganic Chemistry.* Edited by S. J. LIPPARD. Vol. 14, pp. 241–401. New York: John Wiley.
IBERS, J. A. (1962). *International Tables for X-ray Crystallography.* Vol. III, p. 202. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1969). Vol. I, p. 149. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
SACCONI, L. (1968). *Transition Metal Chemistry.* Edited by R. L. CARLIN. Vol. 4, pp. 199–298. New York: Dekker.
SACCONI, L., PAOLETTI, P. & CIAMPOLINI, M. (1963). *J. Amer. Chem. Soc.* **85**, 411.
SACCONI, L., CIAMPOLINI, M. & NARDI, N. (1964). *J. Amer. Chem. Soc.* **86**, 819.
SACCONI, L., CIAMPOLINI, M. & CAMPIGLI, U. (1965). *Inorg. Chem.* **4**, 407.
SCHERINGER, C. (1963). *Acta Cryst.* **16**, 546.
SCHLEMPER, E. O. (1968). *Inorg. Chem.* **7**, 1130.
SMITH, D. L. (1962). *PLANE, A Least-Squares Plane Program for the CDC* 1604 *Computer.* Ph. D. Thesis (Appendix IV), Univ. of Wisconsin, Madison, Wisconsin.
TEMPLETON, D. H. (1962). *International Tables for X-ray Crystallography.* Vol. III, p. 214. Birmingham: Kynoch Press.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
WATKINS, S. F. (1966). *Rigid Body Mechanics.* Ph. D. Thesis (Appendix I), Univ. of Wisconsin, Madison, Wisconsin.
WEI, C. H. (1972*a*). *Inorg. Chem.* **11**, 1100.
WEI, C. H. (1972*b*). *Inorg. Chem*, In the press.
WEI, C. H. & DAHL, L. F. (1969). *J. Amer. Chem. Soc.* **91**, 1351.

Acta Cryst. (1972). B**28**, 2598

The Crystal Structure of 2-Methyl-3-phenyl-4-(*N*-methyl-*N*-hydroxyamidin)-isoxazolin-5-one Hydrobromide

BY L. FANFANI, A. NUNZI, P. F. ZANAZZI AND A. R. ZANZARI
Istituto di Mineralogia dell'Università di Perugia, Perugia 06100, *Italy*

(*Received* 7 *February* 1972)

Crystals of 2-methyl-3-phenyl-4-(*N*-methyl-*N*-hydroxyamidin)isoxazolin-5-one hydrobromide are orthorhombic, space group *Pbca*, with $a = 19{\cdot}539$ (2), $b = 10{\cdot}676$ (2) and $c = 13{\cdot}418$ (2) Å. There are eight formula units per unit cell. The structure was solved by the heavy atom method employing 2954 intensity data collected on a Weissenberg apparatus. It was refined by least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms to an R index of 0·075 for 1452 independent observed reflexions. Bond distances are in reasonable agreement with the corresponding values for related substances. The nitrogen atom of the iminic group is protonated. The planarity of the *N*-methyl-*N*-hydroxyamidin chain indicates the occurrence of two mesomeric forms for this group.

Introduction

The present X-ray study was undertaken in order to determine the molecular structure of the product of the reaction between ethyl-α-cyano-β-methoxy-β-phenyl acrylate and an excess of methylhydroxylamine because spectroscopic data and chemical behaviour did not confirm which of the two stereoisomers (I) and