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The Crystal and Molecular Structure of Bis(acetophenone thioacethydrazonato)nickel(II)

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The crystal structure of bis(acetophenone thioacethydrazonato)nickel(II) has been determined by X-ray diffraction methods. The crystals are monoclinic, space group $C2/c$, $Z=4$, with unit cell dimensions: $a=21.071(8)$ Å, $b=8.537(3)$ Å, $c=13.269(5)$ Å, $\beta=118°36(2)'$. The reflection data were measured on an automated equi-inclination diffractometer. The 2271 reflections with intensities greater than their standard deviation were used to solve and refine the structure including all hydrogen atoms by Patterson, difference Fourier, and least squares procedures to final unit weighted and weighted residuals of 0.045 and 0.0[illegible] respectively.

The nickel atom is in the special position having the point symmetry of the twofold axis. The molecular geometry of the inner complex can be described as a tetrahedrally distorted *cis*-planar isomer with the phenyl groups in a *syn*-configuration. The chelate rings are planar and the angle between the two planes is 19°. The Ni-atom is displaced 0.60 Å from the ligand planes.

Structural studies of many nickel thiosemicarbazide complexes have been carried out during the last decade.[1-5] Recently, the synthesis and crystal structure of bis(thioacethydrazidato)-nickel(II) were reported, although the free ligand, which differs only at the methyl-group from thiosemicarbazide, is too unstable to be isolated.[6] It is also possible to synthesize diamagnetic thioacethydrazonate complexes of nickel(II) [7] similar to the thiosemicarbazonate complexes first prepared by Ablov and Gerbeleu.[8] The structure determinations of chlorobis(acetone thiosemicarbazone)nickel(II) chloride monohydrate and nitratobis(acetone thiosemicarbazone)nickel(II) nitrate monohydrate [9] showed that these paramagnetic nickel thiosemicarbazone complexes have the configuration of a trigonal bipyramid.

Since information about the structures of the diamagnetic inner-complexes of nickel with molecules of thioacethydrazones of various ketones could not be obtained from the results of related thiosemicarbazone complexes, it was decided to undertake a crystal structure analysis of one of these compounds. The complexes derived from unsymmetrical ketones have the possibility of a *syn-anti-amphi* configuration of the two ketone parts in addition to the *cis-trans* isomerism.

The compound chosen for this investigation was bis(acetophenone thioacethydrazonato)nickel(II) as it has been shown from thin layer and column chromatography that only a single isomer is formed.[7] Schematical drawings of the six possible isomers, assuming a planar configuration, are shown in Fig. 1. However, ^{1}H NMR spectra of the complex in common solvents [7] indicated that it possesses a twofold axis of symmetry, which would exclude isomers III and IV.

EXPERIMENTAL

Bis(acetophenone thioacethydrazonato)nickel(II) crystallized from a mixture of heptane and dichloromethane was supplied by Erik Larsen. The crystals are irregularly shaped polyhedra and prismatic needles, which exhibit pleochroism with colour changes from red to green. Preliminary oscillation, Weissenberg, and precession photographs showed that the crystals are monoclinic with the crystallo-

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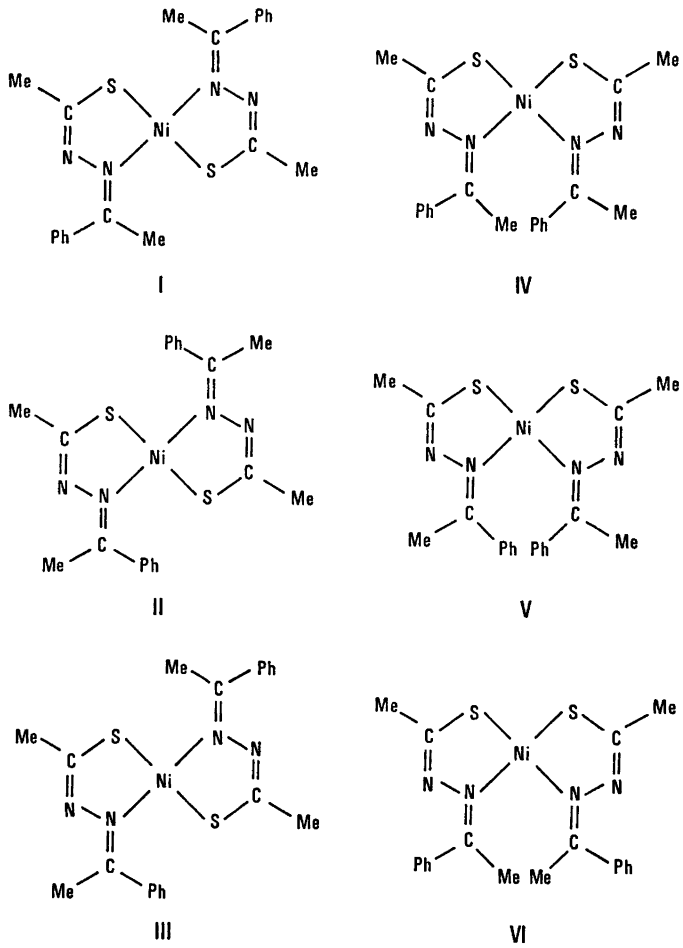

Fig. 1. Schematic drawings of the six isomers of planar bis(acetophenone thioacethydrazonato)-nickel(II).

graphic two-fold axis parallel to the needle axis. The possible space groups were determined from systematically absent reflections. The test for the piezoelectric effect on a sample of relatively large crystals (2 – 3 mm) was negative.

A single crystal of dimensions $0.30 \times 0.15 \times 0.25$ mm^3 was selected for data collection and the determination of cell constants. This crystal was mounted so that the two-fold axis was parallel to the rotation axis of the goniometer head. The unit cell dimensions were determined on a four-circle Picker FACS-1 diffractometer using Mo$K\alpha$ radiation. 30 reflections in the region of 2θ between 30° and 38° were used in a least squares refinement of the unit cell dimensions and the orientation matrix. The density of the crystals was measured by flotation in an aqueous solution of zinc chloride.

Intensity data were collected on a STOE automatic Weissenberg diffractometer using Mo$K\alpha$ radiation obtained by a graphite monochromator. Harmonics were excluded by proper settings of the pulse height discriminator. The relative intensities were measured by an ω-scan technique for all reflections included in reciprocal space between a hemisphere ($k \geq 0$) with $\sin \theta/\lambda \leq 0.7044$ and a cylinder parallel to the rotation axis with radius $\sin \theta/\lambda = 0.073$. The scans were performed at a constant rate of 1°/min and with the ω-scan range increasing from 2° to 4° with layer number. Background counts were made at both ends of each ω-scan range, each count being for half of the scan count time. A standard reflection on each individual layer line was measured for every 75 reflections, and an equator standard reflection was monitored twice between the layer lines.

These measurements of intensities of the standard reflections showed that no deterioration or misalignment of the crystal had occurred during data collection.

The intensities of symmetry related reflections were averaged. Corrections for Lorentz and polarisation effects but not for absorption were applied. Of the 2956 independent reflections so obtained, 685 had net intensities less than twice their standard deviation, $\sigma(I) = \{\sum_{i=1}^{n} \sigma_i^2\}^{\frac{1}{2}}/n$, where σ_i is the standard deviation of an individual observation based on counting statistics and n is the total number of measurements.

The following computer programs were employed in this work: V-72 (an algol 5 program for calculating diffractometer setting angles), a locally written Fortran program (for data reduction), ORTEP II [10] (the thermal ellipsoid plotting program by C. K. Johnson for illustrations), and the X-Ray System (the crystallographic program package by Stewart *et al.*[11] for the crystal structure analysis).

The X-ray atomic scattering factors used in these calculations were taken from Cromer and Mann [12] for Ni, S, C, and N and from Stewart *et al.*[13] for H. The anomalous dispersion corrections of Cromer [14] were applied to Ni and S.

The computations were performed at the Technical University of Denmark; the algol 5 program on the RC 4000 computer and Fortran programs on the IBM 370/165 computer.

CRYSTAL DATA

Bis(acetophenone thioacethydrazonato)nickel(II). $NiS_2C_{20}N_4H_{22}$; M = 441.01. Monoclinic (b unique), a = 21.071(8) Å, b = 8.537(3) Å, c = 13.269(5) Å, β = 118°36(2)′; V = 2096 Å^3; d_{obs} = 1.409 g/cm^3; Z = 4; d_{cal} = 1.399 g/cm^3. Linear absorption coefficient for X-rays (λ(Mo$K\alpha$) = 0.71069 Å), μ = 11.31 cm^{-1}. Number of electrons in the unit cell, $F(000)$ = 920. Systematically absent reflections; hkl when $h+k$ odd, $h0l$ when h and l odd, $0k0$ when k odd; space groups Cc or $C2/c$ (No. 9, C_s^4 or No. 15, C_{2h}^6). Developed faces are {100}, {001}, {101} and {111} for the prismatic needles.

STRUCTURE DETERMINATION AND REFINEMENT

Due to the negative test for the piezoelectric effect and the statistical distribution of E-values, it was assumed that the compound being investigated crystallized in the centric space group $C2/c$. From the unit cell volume, density and the possible symmetry of the ligand, it was concluded that in this space group the Ni atom has to be in the special position $(0,y,1/4)$ with the point symmetry of a two-fold axis. As mentioned in the introduction, the ^{1}H NMR spectrum of the complex in solution indicates the presence of a two-fold axis of symmetry.

The Harker line $(0,v,\frac{1}{2})$ in the Patterson map revealed the y coordinate for the Ni atom, and a Fourier map phased on the nickel atom showed the position of the sulfur, carbon, and two nitrogen atoms of the ligand ring. The positions of the rest of the non-hydrogen atoms in the complex were located in the Fourier synthesis phased from these five atoms.

This structure was refined by full matrix least squares method using all the 2271 reflections with intensities greater than their standard deviation. The scale factor, the atomic parameters and individual temperature factors were varied in a refinement using unit weights. In the initial stage, isotropic temperature factors were used, later anisotropic temperature factors were employed. After a refinement using anisotropic temperature factors with the conventional residual of $R = 0.06$, a difference Fourier synthesis showed only 11 peaks outside the region of the Ni atom. These were in positions to be expected for the hydrogen atoms of the structure. The hydrogen atoms of the methyl groups were localized to peaks where the maximum density was only two-thirds of the corresponding density of the hydrogen atoms of the phenyl groups. This indicates larger temperature factors for the methyl groups.

The coordinates and individual temperature factors of the hydrogen atoms were also included in the final cycles of the full matrix least squares refinement, minimizing $\sum w(|F_o| - k|F_c|)^2$. The weights used in the final refinement were of the form

$$w = 1/\{2[\sigma(F)]^2 + 0.01|F| + 0.001F^2\}.$$

During the last cycle of least squares refinement no parameter shifted more than 0.138σ, the average shift being 0.012σ. The corresponding residuals were

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.044 \text{ and}$$
$$R_w = \{\sum w||F_o| - |F_c||^2/\sum w|F_o|^2\}^{\frac{1}{2}} = 0.052.$$

Table 1. Final atomic coordinates in fractions for the heavier atoms in bis(acetophenone thioacethydrazonato)nickel(II). Standard deviations $\times 10^4$ in parentheses. The other half of the molecule can be generated by the symmetry operation $(1-x,y,\frac{1}{2}-z)$.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ni	0.500	(0)	0.4071	(0.4)	0.2500	(0)
S	0.4228	(0.5)	0.2316	(1)	0.2351	(1)
C1	0.3546	(1)	0.3634	(3)	0.2135	(2)
N2	0.3649	(1)	0.5111	(2)	0.2334	(2)
N1	0.4395	(1)	0.5503	(2)	0.2792	(2)
C11	0.2794	(2)	0.3005	(5)	0.1704	(3)
C2	0.4582	(1)	0.6773	(2)	0.3404	(2)
C3	0.4049	(2)	0.7835	(4)	0.3496	(4)
C21	0.5363	(1)	0.7148	(2)	0.4076	(2)
C22	0.5602	(2)	0.8684	(3)	0.4125	(2)
C23	0.6330	(2)	0.9032	(4)	0.4753	(3)
C24	0.6820	(2)	0.7883	(4)	0.5368	(3)
C25	0.6586	(2)	0.6360	(4)	0.5345	(2)
C26	0.5857	(2)	0.6001	(3)	0.4706	(2)

Table 2. Thermal parameters for the heavier atoms in bis(acetophenone thioacethydrazonate)nickel(II). The expression for the temperature factor is exp $\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*\}$. The anisotropic temperature factor constants. U_{ij}, are in units of Å$^2 \times 10^{-4}$. The estimated standard deviations from the least squares refinement are given in parentheses in units of the last significant figure in the parameter value.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	443(3)	259(2)	541(3)	0	309(2)	0
S	701(5)	323(3)	1035(7)	−112(3)	541(5)	− 47(3)
C1	470(14)	509(12)	478(14)	−115(11)	260(12)	3(11)
N2	359(10)	453(10)	480(12)	− 40(8)	218(9)	25(9)
N1	352(9)	315(8)	421(10)	6(7)	219(8)	39(7)
C11	546(18)	792(22)	621(21)	−275(17)	260(16)	− 47(18)
C2	433(12)	323(9)	457(13)	26(9)	271(11)	18(9)
C3	587(19)	487(15)	929(28)	76(14)	473(20)	−120(16)
C21	449(13)	357(10)	377(12)	14(9)	237(11)	− 36(9)
C22	518(15)	373(11)	520(15)	− 28(11)	193(13)	− 19(11)
C23	594(17)	560(15)	615(18)	−174(15)	226(15)	− 88(14)
C24	476(16)	823(21)	514(17)	− 92(16)	194(14)	−122(15)
C25	523(16)	639(16)	456(15)	156(14)	146(13)	6(13)
C26	548(15)	419(12)	424(13)	44(11)	244(12)	20(10)

The final atomic parameters are listed in Tables 1 – 3. The labelling of the non-hydrogen atoms is given in Fig. 2, which also contains bond lengths and angles, except for the benzene ring and the carbon hydrogen bonds. The rule used in the numbering scheme for the hydrogen atoms is such that the first two numbers indicate to which carbon atom it is bonded and the third distinguishes between hydrogen atoms attached to the same carbon atom.

A list of observed structure amplitudes and calculated structure factors may be obtained from the author upon request.

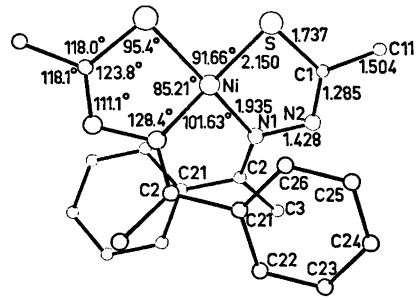

Fig. 2. A perspective view of bis(acetophenone-thioacethydrazonato)nickel(II) showing the labels of the atoms and part of the bond lengths and angles.

Table 3. Refined parameters for the hydrogen atoms in bis(acetophenone thioacethydrazonato)nickel(II). The temperature factor is expressed as exp $(-8\pi^2 U \sin^2 \theta/\lambda^2)$. The standard deviations in units of the last significant figure in the parameter value are given in parentheses.

Atom	x	y	z	$U \times 10^2$
H111	0.276(2)	0.223(5)	0.218(3)	10(1)
H112	0.262(2)	0.255(5)	0.094(4)	10(1)
H113	0.253(3)	0.375(6)	0.178(4)	11(2)
H31	0.355(3)	0.755(7)	0.306(5)	16(2)
H32	0.407(3)	0.867(7)	0.330(5)	13(2)
H33	0.420(3)	0.973(6)	0.420(5)	12(2)
H22	0.528(2)	0.946(4)	0.373(3)	5.6(8)
H23	0.649(2)	1.014(4)	0.472(3)	8.3(10)
H24	0.732(2)	0.816(5)	0.580(3)	8.5(11)
H25	0.689(2)	0.552(4)	0.571(3)	7.3(10)
H26	0.571(2)	0.504(4)	0.472(2)	5.2(8)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The molecular structure of bis(acetophenone thioacethydrazonato)nickel(II) can be described as a *cis-syn* configuration indicating that the sulfur atoms are *cis* and that phenyl groups are *syn*. The structure is illustrated by V in Fig. 1. From the schematic drawings one would imagine this structure to be one of the least likely due to the bulkiness of the phenyl groups.

However, Fig. 3, which is an ORTEP [10] plot of the molecule viewed down the two-fold axis shows it is possible for this diamagnetic inner complex to have the *cis-syn* configuration and not have any close contacts. The arrangement of the two sulfur atoms and the two coordinating nitrogen atoms, which form a tetrahedrally distorted planar configuration, is also seen from this drawing.

Using the coordinates in Table 1, mean planes for characteristic groups of atoms within the molecule were calculated, in order to describe the non-planarity of this complex. The equations defining these planes and the distances of the atoms to the planes are listed in Table 4.

The ligand ring formed by the atoms S, C1, N1, and N2 approximately form a plane. The nickel atom is not in this plane (plane II, Table 4), but is displaced 0.60 Å from the plane. The angle between the ligand plane and its symmetry related forming the other half of the molecule is found to be 19°. This considerable deviation from planarity can also be illustrated

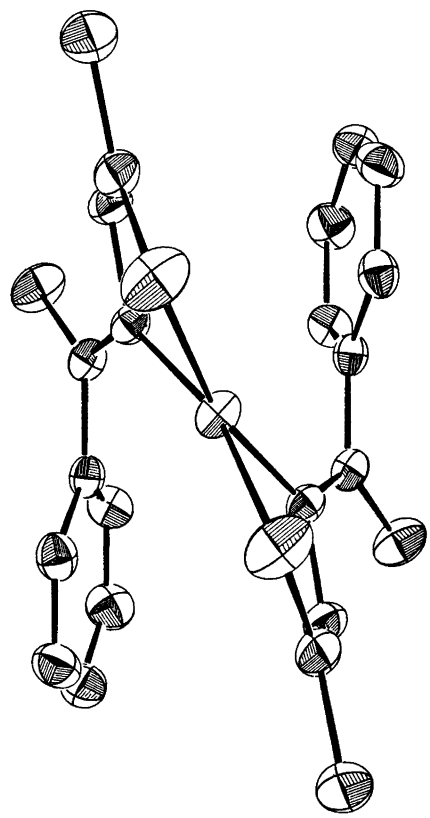

Fig. 3. A perspective view of one molecule from its two-fold axis. The thermal ellipsoids are scaled to enclose 33 % probability.

Table 4. Least squares planes calculated for some characteristic groups of atoms in bis(acetophenone thioacethydrazonato)nickel(II).

Plane	Equation for the least squares plane in direct space [a]
I	$1.5125\ x - 1.5975\ y + 10.9568\ z = 2.8451.$
II	$-7.0048\ x - 1.3949\ y + 12.9318\ z = -0.2401$
III	$-12.1877\ x + 1.6585\ y + 12.9029\ z = -0.0775$

Atom	Distances in Å of the atoms from the planes. I	II	III
Ni	0.000*	−0.597	−2.115
S	0.000*	−0.005*	−1.658
C1	−0.550	0.010*	−0.887
N2	−0.552	0.005*	−0.510
N1	0.000*	−0.010*	−0.763
C11	−1.035	0.068	−0.630
C2	0.496	0.488	0.008
C3	0.346	0.832	0.952
C21	1.290	0.758	−0.013*
C22	1.135	0.439	0.013*
C23	1.877	0.693	−0.006*
C24	2.808	1.304	−0.001*
C25	2.991	1.651	0.001*
C26	2.238	1.385	0.006*

* The starred displacements are those of the atoms used in determining the least squares plane.
[a] The equations for the least squares planes for the other half of the molecule may be generated by the symmetry operation $(1-x,\ y,\ \frac{1}{2}-z)$.

by the angle between the two coordination planes (plane I and its symmetry equivalent) defined by the two S−Ni−N1 groups. This has been calculated to 21.6°.

The phenyl groups are tilted relative to the ligand rings. The mean plane (plane III) calculated from the carbon atoms of the benzene ring form an angle of 26° with the ligand ring (plane II) to which it is attached, and an angle of 16° with the ligand plane of the other half of the molecule.

All bond lengths and angles within the molecule and their estimated standard deviations (but not corrected for the effect of thermal vibration) are listed in Table 5. The Ni−S and Ni−N1 bond lengths of 2.150 Å and 1.935 Å are similar to those found in other planar nickel complexes having thiosemicarbazide or related compounds as ligands.[1-6].

However, it should be noted that the Ni−S bond in this *cis* complex is significantly shorter than the Ni−S bond found in similar *trans* complexes. This was also noticed by R. Grønbæk Hazell in the investigation of the structures of β-Ni(tscH)$_2$SO$_4$[3] and *cis* and *trans* isomers of Ni(tscH)$_2$(NO$_3$)$_2$.[5] The structures of the *cis* and *trans* isomers of bis(thioacethydroxamato)nickel(II) [15-16] seem also to confirm the general observation that a *cis* Ni−S complex deviates more from planarity than the equivalent *trans* complex. The Ni−S bond length from 2.145 to 2.155 Å in *cis* complexes are significantly shorter than the Ni−S bonds found in similar trans complexes varying between 2.165 and 2.184 Å.

Looking at the molecular dimensions of the ligand it is remarkable that nearly all the bonds outside the phenyl group can be described as single or double bonds. The two C=N bonds do not vary much from their mean value of 1.291 Å, which is comparable to the bondlength of a C=N double bond of 1.28 Å.[17] The N−N bondlength of 1.428 Å is very similar to the magnitude of the N−N bondlength found in hydrazine derivatives. Finally, the C1−C11 and C2−C3 bondlengths of 1.504 Å and 1.493

Table 5. Bond lengths (Å) and bond angles (°) in bis(acetophenone thioacethydrazonato)nickel(II). The standard deviations in terms of the last digit are in parentheses.

Ni – S	2.150(1)	S – Ni – S′	91.66(5)
Ni – N1	1.935(2)	S – Ni – N1	85.21(7)
S – C1	1.737(3)	N1 – Ni – N1′	101.63(9)
C – N2	1.285(3)	Ni – S – C1	95.4(1)
N – N1	1.428(3)	S – C1 – C2	123.8(2)
C – C11	1.504(5)	S – C1 – C11	118.0(2)
N – C2	1.298(3)	C11 – C1 – N2	118.1(4)
C – C3	1.493(6)	C1 – N2 – N1	111.1(2)
C – C21	1.483(3)	N2 – N1 – Ni	117.6(1)
C21 – C22	1.395(3)	N2 – N1 – C2	113.9(2)
C22 – C23	1.382(4)	Ni – N1 – C2	128.4(2)
C23 – C24	1.375(4)	N1 – C2 – C3	122.9(2)
C24 – C25	1.386(5)	N1 – C2 – C21	118.3(2)
C25 – C26	1.387(4)	C3 – C2 – C21	118.7(2)
C26 – C21	1.382(3)	C2 – C21 – C22	120.2(2)
C11 – H111	0.94(5)	C2 – C21 – C26	120.6(2)
C11 – H112	0.97(5)	C22 – C21 – C26	119.1(1)
C11 – H113	0.88(5)	C21 – C22 – C23	120.2(2)
C3 – H31	0.96(6)	C22 – C23 – C24	120.4(3)
C3 – H32	0.77(6)	C23 – C24 – C25	119.9(3)
C3 – H33	0.83(6)	C24 – C25 – C26	119.9(3)
C22 – H22	0.91(3)	C25 – C26 – C21	120.5(3)
C23 – H23	1.00(4)		
C24 – H24	0.95(4)		
C25 – H25	0.93(3)		
C26 – H26	0.88(3)		

Å indicate that these bonds can be described as single C – C bonds. By comparison of these results with their analogs obtained from structures of other "planar" nickel complexes having thiosemicarbazides or related compounds as ligands,[1-6,9] one finds that the only examples having similar localized bonds are the inner complexes bis(thioacethydrazidato)nickel(II) [6] and bis(thiosemicarbazidato)nickel(II).[1] However, the C – S bond length has approximately the same magnitude in the charged and inner complexes with a value from 1.70 Å to 1.73 Å.

The relative arrangement of the molecules in the crystal is shown in Fig. 4, which is a stereo pair illustrating the packing as seen from the crystallographic *b* axis. The molecules are arranged so that the average plane between plane II in Table 4 and its symmetry equivalent is nearly parallel to the *a* – *b* plane. There are van der Waals interactions between adjacent molecules in the direction of the *c* axis. The atoms C11, C1, N2, C2, and C3 of the ligand ring of one molecule have distances between 3.28 Å and 3.82 Å to the atoms C26, C26, C24 of the phenyl group of the nearest molecule, which interacts with a phenyl group from the first molecule. All other intermolecular distances are larger than the sum of the van der Waals radii [18] of the atoms.

The strong pleochroism of the crystals can be derived from the molecular packing. The crystals are red when the electric vector of the polarized light is parallel to the two-fold axis of the crystal and the molecules and green when

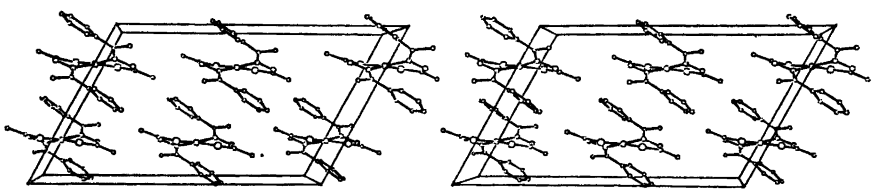

Fig. 4. An ORTEP stereo drawing of a full unit cell as viewed down the *b*-axis.

the electric vector is perpendicular to the two-fold axis.

Unfortunately, it is not possible from this single crystal structure analysis to explain why the molecular structure of bis(acetophenone thioacethydrazonato)nickel(II) approaches a *cis* configuration of the sulfur atoms and why the phenyl group does not enhance conjugation within the ligand. It is the hope, however, that structural determination of related complexes having other thiohydrazones as ligands may elucidate these problems.

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