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Syntheses and Molecular Structure of Bis(1-substituted, 2.4-dithiobiuretato)-nickel(II) Complexes

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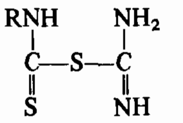
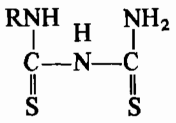
Bis(1-substituted 2,4-dithiobiuretato)nickel(II) complexes, where 1-substituted groups = C_2H_5, *n*-C_3H_7, *iso*-C_3H_7, o-*tolyl and* p-*anisidine, have been prepared and characterized on the basis of elemental analyses, magnetic moments at room temperature and electronic spectra. The crystal structure of bis(1-isopropyl-2,4-dithiobiuretato)nickel(II)·2(dimethylformamide) has been determined from 1446 X-ray diffraction data. The crystals are monoclinic, space group* $P2_1/c$, *with two formula units in a unit cell of dimensions* a = *8.008(2),* b = *14.460(5),* c = *12.059(5) Å and* $\beta = 106.45(3)^\circ$. *The structure was solved by conventional Patterson and Fourier methods, and block-diagonal least-squares refinements led to a final discrepancy index of 0.038. The structure consists of discrete bis(1-isopropyl-2,4-dithiobiuretato)nickel(II) and dimethylformamide molecules, and the former molecule is centrosymmetric with the two bidentate ligands of isopropyl-2,4-dithiobiuretato chelating to the central nickel atom through the two sulfur atoms. Examination of the bond distances and the planarity of the molecule revealed that the* π*-conjugation system extends over the 2,4-dithiobiuretato moiety.*

Introduction

Joshua *et al.* have reported that alkyl (or aryl) isothiocyanates react with thiourea in the presence of sodium or potassium hydroxide in a water-miscible organic solvent to give compounds which have been assigned a S-(N-substituted thiocarbamyl)isothiourea as shown in (I) on the basis of their chemical and mass spectral characteristics [1].


$\mathrm{RNH{-}C({=}S){-}S{-}C({=}NH){-}NH_2}$

(I)


$\mathrm{RNH{-}C({=}S){-}NH{-}C({=}S){-}NH_2}$

(II)

These compounds may form six-membered chelate complexes with transition metal ions through the sulfur and nitrogen atoms or through the two nitrogen atoms. In this study we prepared a series of nickel(II) complexes with these ligands (hereafter abbreviated as HL-R). In order to clarify the structure of the complexes, we applied the single-crystal X-ray technique to one of these compounds where R is isopropyl group. The result has revealed that the ligand structure corresponds to 1-substituted 2,4-dithiobiuret as shown in (II), contrary to the initial assumption, and that the nickel atom is square-planarly coordinated by four sulfur atoms. Based on the structure data we have discussed the π-conjugation of the ligand.

Experimental

Preparation

Alkyl (or aryl) isothiocyanates RNCS, where R = C_2H_5, n-C_3H_7, iso-C_3H_7, *o*-tolyl, *p*-anisidine, were prepared according to the methods of Dains *et al.* [2]. The ligands HL-R were prepared according to the method of Joshua *et al.*, by use of alkyl (or aryl) isothiocyanates, thiourea and potassium hydroxide with the mol ratio 1:1:1 [1]. The methods for the preparation of the nickel(II) complexes are practically the same as each other. The procedure is exemplified in the case of R = isopropyl; a methanol solution (50 ml) of nickel(II) acetate tetrahydrate (0.001 mol, 248 mg) was slowly added to hot methanol solution (20 ml) of the ligand HL-iso-C_3H_7 (0.002 mol, 354 mg). A dark brown solution was formed immediately. After standing for several hours at room temperature dark brown rhombic crystals were separated. They were collected, washed with a small amount of methanol and dried *in vacuo.* When this compound was recrystallized from dimethylformamide (DMF), Ni(L-iso-$C_3H_7)_2$·2DMF

TABLE I. Elemental Analyses [% found. (calc.)].

Complexes	C	H	N
$Ni(L\text{-}C_2H_5)_2$	24.98(25.07)	4.18(4.20)	21.75(21.93)
$Ni(L\text{-iso-}C_3H_7)_2$	29.52(29.20)	5.02(5.02)	20.23(20.43)
$Ni(L\text{-n-}C_3H_7)_2 \cdot 3/2CH_3OH$	30.07(30.07)	5.80(5.80)	18.09(18.30)
$Ni(L\text{-}o\text{-tol})_2$	42.39(42.26)	4.17(4.17)	16.18(16.56)
$Ni(L\text{-}p\text{-ani})_2$	40.21(39.95)	3.78(3.78)	15.16(15.52)
$Ni(L\text{-iso-}C_3H_7)_2 \cdot 2DMF$	34.13(34.47)	6.09(6.14)	20.14(20.10)
$Ni(L\text{-n-}C_3H_7)_2 \cdot 2DMF$	34.47(34.47)	6.07(6.14)	20.15(20.10)
$Ni(L\text{-}o\text{-tol})_2 \cdot 2DMF$	43.96(44.10)	5.24(5.24)	17.17(17.14)

TABLE II. Crystal Data (Numbers in parentheses here and elsewhere in this paper are the e.s.d.s in the least significant digits).

Formula unit	$Ni(S_2N_3C_5H_{10})_2 \cdot (C_3H_7NO)_2$	Cell dimensions	
Formula weight	557.5	a	= 8.008(2) Å
Space group	$P2_1/c$	b	= 14.460(5) Å
Density:		c	= 12.059(5) Å
	D_m = 1.382 g cm^{-3}	β	= 106.45(3)°
	D_x = 1.382 g cm^{-3}	V	= 1339.2(9) Å^3
Number of formulas per unit cell:		Z	= 2
Linear absorption coefficient:		μ	= 10.4 cm^{-1}
(Mo K_α radiation)			

was obtained as dark brown rhombic prisms. The results of elemental analysis are listed in Table I.

Physical Measurements

Magnetic moments were measured by the Faraday method at room temperature. Electronic spectra were measured with a Shimazu Multipurpose Spectrophotometer Model MSP-5000.

X-ray Diffraction

X-ray photographs obtained by the Weissenberg technique showed the systematic absences 0k0 with k odd and h0l with l odd, indicating the space group $P2_1/c$. The unit cell parameters were obtained from a least-squares procedure using values of 2θ of 15 reflections measured on a Syntex P$\bar{1}$ automated four-circle diffractometer with monochromated Mo K_α radiation (λ = 0.71073 Å). The crystal was ground to a sphere of radius 0.16 mm. The density was measured by flotation in a mixed solution of bromobenzene and benzene. The crystal data are given in Table II.

Intensity data were collected by the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0° min^{-1} on the Syntex diffractometer with monochromated MoK_α radiation. 1446 independent reflections with $2\theta < 42°$ were collected. Of these, intensities of 105 reflections were less than $\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects, but no corrections for absorption and extinction were made because of the low absorption coefficient and the small crystal size. An initial scale factor and over-all temperature factor were obtained by the Wilson statistics.

Structure Determination and Refinement

The Ni atoms must lie on a set of twofold special positions since there are only two formula units in a unit cell. The complex is thus required to have a center of symmetry. The non-hydrogen atoms except for the two methyl C atoms of DMF were located from a Patterson synthesis, and the missing two C atoms were located from the subsequent Fourier synthesis. Refinement was carried out by the block-diagonal least-squares method. After eight cycles of refinement with isotropic temperature factors, a discrepancy index R was reduced to 0.134 for all reflections with unit weight for $|F_o| > 3.0$ (corresponding to $I > \sigma(I)$) and zero otherwise, where $|F_o|$ is the observed structure factor multiplied by a scale factor to be refined. At the subsequent refinements with anisotropic temperature factors, the following weighting schemes were employed: $\omega = 200/(0.33|F_o|^2 - 6.7\ |F_o| + 175)$ for $|F_o| >$ 3.0 and $\omega = 0.6\ |F_o|$ otherwise. The five cycles of refinement reduced the R value to 0.066. At this

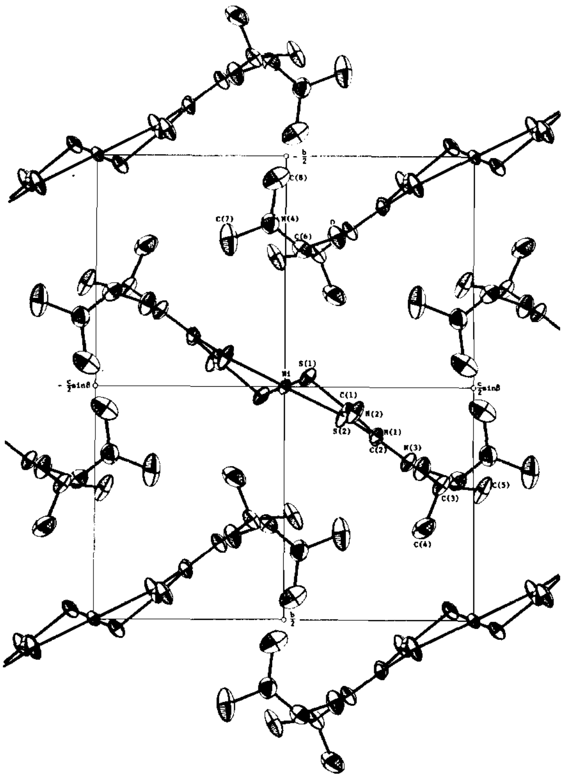


Figure 1. Projection of the crystal structure along the *a* axis. Atom shapes represent the thermal motion ellipsoids scaled to enclose 30% probability, and the H atoms have been omitted for clarity.

stage a difference Fourier synthesis revealed all H atoms except those bonded to C(8). Including these H atoms in the refinement, the R value was reduced to 0.042. The successive difference Fourier synthesis revealed the remaining three H atoms around C(8), although these positions were ambiguous and were distorted tetrahedral. The coordinates of these H atoms were modified slightly so as to fit the plausible positions. The refinement was terminated when the shifts of the parameters for the non-hydrogen atoms became less than 0.45σ. The final R value was 0.038 for all reflections. The final difference Fourier synthesis showed no significant features in the undulations within ±0.3eÅ^{-3} except for one peak of 0.65eÅ^{-3} in the vicinity of S(1). A list of observed and calculated structure factors is available from the Editor. The atomic scattering factors for Ni^{2+}, S, N, C$_{\text{cov}}$ and O, and also the anomalous dispersion corrections for the first two atoms were taken from International Tables for X-ray Crystallography [3]. Those for H atoms were adopted from the table of Stewart *et al.* [4]. All the calculations were carried out on the FACOM M-190 computer in the Computer Center of Kyushu University by use of the UNICS-II program system [5]. The drawings were made by use of ORTEP program [6]. The final atomic parameters are listed in Table III with their estimated standard deviations.

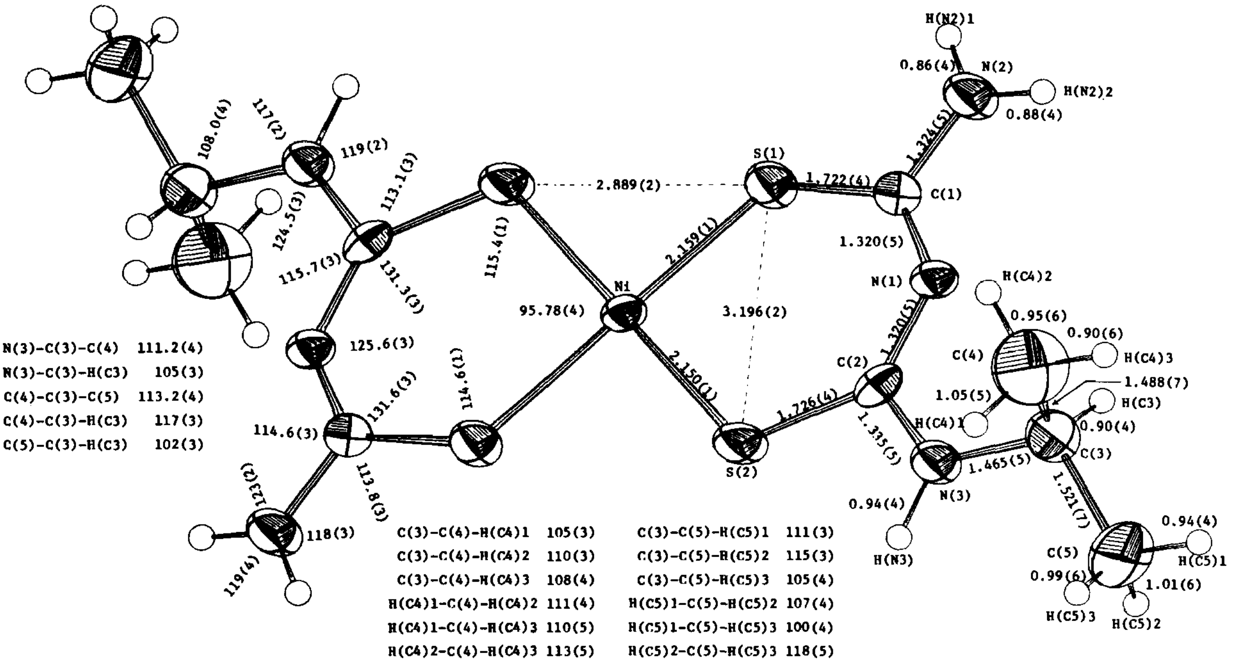


Figure 2. Bond lengths (Å) and angles (°) of the complex molecule. The H atoms are shown as open circles of arbitrary size, and the shapes of the other atoms represent the thermal motion ellipsoids scaled to enclose 50% probability.

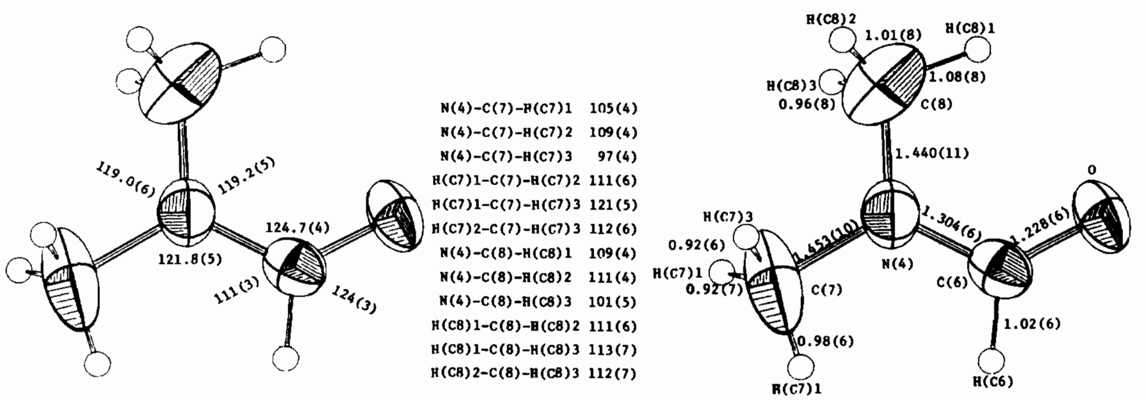


Figure 3. Bond lengths (Å) and angles (°) of the DMF molecule. The H atoms are shown as open circles of arbitrary size, and the shapes of the other atoms represent the thermal motion ellipsoids scaled to enclose 50% probability.

Results and Discussion

Crystal Structure

A projection of the crystal structure along the *a* axis is shown in Fig. 1. The crystal consists of discrete Ni(L-iso-C_3H_7)$_2$ and DMF molecules. The former molecules lie on the crystallographic inversion centers having their major axis roughly parallel to the ⟨121⟩ axes, and the latter lie approximately on the {400} planes. The DMF molecules do not coordinate to the Ni atom, but are centrosymmetrically connected to the isothiocyanate groups of the Ni(L-iso-C_3H_7)$_2$ molecules in a side slip fashion by two weak hydrogen bonds with N(3) distance of 2.997(6), H(N3)- - -O 2.06(5) Å and N(3)–H(N3)- - -O angle of 173(4)°. All the other intermolecular contacts are of the van der Waals type.

Molecular Structure

The molecular structures of the Ni(L-iso-C_3H_7)$_2$ and DMF are shown in Figs. 2 and 3 respectively with the bond lengths and angles. The Ni(L-iso-C_3H_7)$_2$ molecule is formed by two bidentate ligands of 1-isopropyl-2,4-dithiobiuretato chelating to the central Ni atom through the four S atoms, and is described as bis(1-isopropyl-2,4-dithiobiuretato)nickel(II). This structure implies that Joshua's assignment of chemical structure of the free ligand to structure (I) is not correct, since the structural change from (I) to (II) in the process of complexation is unlikely to occur under this mild reaction condition.

The final difference Fourier synthesis showed that the ligand molecule of 1-isopropyl-2,4-dithiobiuret loses a central H atom in forming the neutral complex Ni(L-iso-C_3H_7)$_2$. The central NiS_4 moiety is perfectly planar (coordination plane), since the complex molecule has a crystallographic center of symmetry. This is compatible with the fact that all the compounds are diamagnetic.

The Ni–S bond lengths of 2.159(1) and 2.150(1) Å are considerably shorter than the sum of Pauling's covalent radii (2.33 Å) [7], and there must be appreciable covalency in their bonds. These bond lengths are comparable with the values found in the four-coordinate Ni(II) complexes in which Ni–S bond lengths fall in the range 2.1–2.3 Å pointed out by Lopez-Castro *et al.* as a range of Ni–S bond lengths of such complexes [8], for example, Ni(xan)$_2$, Ni(dtc)$_2$, Ni(mnt)$_2$, Ni(qdt)$_2$ and Ni(HQS_2)$_2$ [9–13], where xan = xanthate, dtc = diethyldithiocarbamate, mnt = maleonitrildithionate, qdt = 2,3-quinoxalinedithiolato and HQS_2 = quinoxaline-2,3-dithiolato.

The two S–C bond lengths of 1.722(4) and 1.726(4) Å show a partial double bond character. These values are closer to those of the neutral Ni(II) complexes than to those of the cationic or anionic ones [11–14]. The four N–C bond lengths in the 2,4-dithiobiuretato moiety range from 1.320(4) to 1.335(5) Å and these bonds have a high double bond character, while the N(3)–C(3) length of 1.465(5) Å is characterized as a single bond. The bond lengths and angles of isopropyl group are of generally acceptable values.

The analysis of the planarity for 2,4-dithiobiuretato moiety, shown in Table IV together with the least-squares planes for the other moieties, indicates that this moiety is planar within the maximum deviation of 0.047 Å. The Ni atom lies 0.51 Å from this plane and this corresponds to a dihedral angle of 159° between this plane and the coordination plane. Thus, judging from the bond lengths and the planarity, the 2,4-dithiobiuretato moiety may be considered to form a π-conjugation system.

The inter- and intra-chelate S- - -S distances of 2.889(2) and 3.196(2) Å are far shorter than the van der Waals contacts of 3.70 Å [7]. The former is somewhat shorter than the range of 3.04–3.17 Å suggested by Stiefel *et al.* as indication of some residual S- - -S bonding [15], though the latter is longer than one. Thus, it may be assumed that there is some residual S- - -S bonding in this complex.

TABLE III. Fractional Atomic Coordinates and Temperature Factors.

(a) Non-hydrogen Atoms

All values have been multiplied by 10^4. The anisotropic temperature factors are expressed in the form: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Atoms	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	99(1)	35(1)	39(1)	−6(1)	31(1)	−10(1)
S(1)	2780(1)	−210(1)	607(1)	109(2)	49(1)	64(1)	2(1)	30(1)	−23(1)
S(2)	−235(1)	631(1)	1563(1)	114(2)	85(1)	64(1)	−20(1)	44(1)	−41(1)
N(1)	3286(4)	1044(2)	2418(2)	100(5)	38(2)	47(2)	1(2)	33(3)	−10(2)
C(1)	3855(4)	521(3)	1704(3)	105(7)	41(2)	49(3)	−3(3)	24(4)	2(2)
C(2)	1653(5)	1109(2)	2442(3)	151(7)	37(2)	35(3)	4(3)	36(4)	−6(2)
N(2)	5559(4)	557(3)	1861(3)	108(6)	81(3)	73(3)	−16(3)	35(4)	−41(2)
N(3)	1382(4)	1628(2)	3289(3)	104(6)	55(2)	59(3)	−8(3)	29(3)	−24(2)
C(3)	2751(5)	2125(3)	4149(4)	140(8)	58(2)	70(4)	−6(4)	30(4)	−28(2)
C(4)	3136(8)	3031(4)	3690(5)	319(14)	68(3)	133(6)	−48(5)	63(7)	−33(4)
C(5)	2188(7)	2211(4)	5247(4)	281(12)	111(4)	77(4)	−46(6)	52(6)	−57(4)
O	2164(4)	−3231(2)	1354(3)	199(6)	87(2)	74(3)	23(3)	65(3)	20(2)
N(4)	2469(5)	−3525(3)	−405(3)	244(9)	71(2)	76(3)	11(4)	48(4)	−2(2)
C(6)	2351(5)	−2974(3)	426(4)	163(9)	55(3)	90(4)	8(4)	48(5)	13(3)
C(7)	2616(9)	−3172(6)	−1502(5)	381(17)	172(7)	73(5)	30(8)	78(7)	14(5)
C(8)	2378(13)	−4510(5)	−250(7)	698(32)	84(4)	172(9)	10(9)	102(13)	−39(5)

(b) Hydrogen Atoms

The hydrogen atoms are labelled in terms of the atom to which they are attached. The coordinate values have been multiplied by 10^3.

Atoms	x	y	z	B	Atoms	x	y	z	B
H(N2)1	598(5)	26(3)	139(3)	4.2	H(C5)3	130(7)	271(4)	508(5)	9.3
H(N2)2	628(5)	86(2)	244(3)	3.9	H(C6)	242(7)	−230(4)	20(5)	8.4
H(N3)	23(5)	170(3)	334(3)	4.3	H(C7)1	261(7)	−250(4)	−142(5)	10.1
H(C3)	364(5)	172(3)	437(3)	4.4	H(C7)2	168(8)	−337(4)	−209(5)	10.7
H(C4)1	196(6)	340(3)	352(4)	6.8	H(C7)3	361(8)	−348(4)	−150(5)	10.0
H(C4)2	348(7)	294(4)	301(5)	7.8	H(C8)1	223(10)	−465(5)	59(7)	13.6
H(C4)3	396(7)	331(4)	425(5)	8.2	H(C8)2	344(9)	−483(5)	−35(6)	13.5
H(C5)1	306(5)	249(3)	584(4)	5.1	H(C8)3	136(10)	−466(5)	−86(7)	12.4
H(C5)2	189(8)	161(4)	557(5)	9.5					

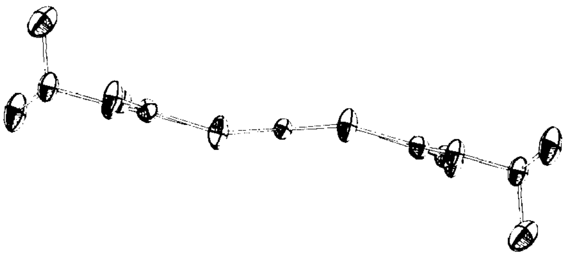


Figure 4. An edge-on view of the complex molecule, projected parallel to the coordination plane. Atom shapes represent the thermal motion ellipsoids scaled to enclose 30% probability, and the H atoms have been omitted for clarity.

An edge-on view of the complex molecule, as shown in Fig. 4, shows that the molecule assumes a gently sloped chair-like shape where the seat and the reasts are formed by the coordination plane and the two isopropyl-2,4-dithiobiuretato moieties respectively.

The bond lengths, the bond angles and the molecular conformation of this complex except for the isopropyl group are very similar to those published by Pignedoli *et al.* in a summary of three Ni(II) and one Pd(II) complexes in which the metal ions are square-planarly coordinated to the four S atoms by the neutral or uninegative two bidentate ligands of dithiobiuret.

None of the bond lengths and angles of DMF molecule appears to depart significantly from those reported in the other structures (for example, [16]). This molecule is planar within the maximum deviation of 0.016 Å, and makes a dihedral angle of 85° with the coordination plane.

TABLE IV. Least-squares Planes for Some Moieties.

(a) Coefficients of the Least-squares Planes
The equations are of the form $lu + mv + nw = d$, where u, v and w are in Å units referred to the crystallographic axes.

	l	m	n	d
(I) Coordination Moiety	0.2576	0.9002	−0.4097	0.0
(II) Dithiobiuretato Moiety	−0.0595	−0.7762	0.6189	0.5092
(III) DMF Molecule	0.9268	−0.0210	0.0971	1.8749

(b) Deviations in Å Units from the Least-squares Planes
Atoms with an asterisk are not included in the calculation of the planes.

	(I)		(II)		(III)
Ni	0.0	Ni*	−0.5092	O	−0.0122
S(1)	0.0	S(1)	0.0470	C(6)	0.0101
S(2)	0.0	S(2)	−0.0391	N(4)	0.0170
C(1)*	0.6320	C(1)	−0.0064	C(7)	−0.0127
C(2)*	0.5775	C(2)	−0.0098	C(8)	−0.0025
N(1)*	0.8422	N(1)	−0.0330	H(C6)*	0.0135
N(2)*	0.9530	N(2)	−0.0112		
N(3)*	0.7795	N(3)	0.0523		
		C(3)*	0.0710		
		H(N2)1*	−0.0484		
		H(N2)2*	0.0473		
		H(N3)*	0.0638		

(c) Dihedral Angles in Degrees

Coordination Moiety–Dithiobiuretato Moiety	159.14
Coordination Moiety–DMF Molecule	84.94

TABLE V. Spectral Data (in DMF) of the Complexes, Ni(L-R)$_2$.

R	C_2H_5	n-C_3H_7	iso-C_3H_7	o-tol
ν_1	18.24	18.34	18.20	18.62
(ϵ)	(91)	(95)	(82)	(119)
ν_2	21.41	21.50	21.50	21.50
(ϵ)	(137)	(140)	(126)	(176)
ν_3	27.39	27.77	27.77	27.17
(ϵ)	(967)sh	(1062)sh	(1105)sh	(1347)sh
ν_4	30.77	30.76	31.05	28.98
(ϵ)	(2077)	(2018)	(2209)	(2650)

Inspection of the figures with the thermal motion ellipsoids suggests that the molecules are librating about points close to their centroids. The terminal methyl C atoms of the complex and of the DMF have large temperature factors. Examination of the thermal motion analyses for the complex and the DMF molecules showed that the assumption of a rigid body motion is not justified, so that the thermal corrections of the bond lengths and angles were not applied in this work.

Electronic Spectra and Magnetic Moments

The band positions and their molar extinction coefficients of the electronic spectra measured in DMF are tabulated in Table V. In the solution all the complexes have similar reflectance spectra to those in the powder state, and so each molecular structure in the solution probably is the same as in the powder. There is little difference, which occurs as the 1-substituted group is varied, in the band positions and in the molar extinction coefficients. Besides, the observed values of the magnetic moments indicate that all these complexes are diamagnetic. Therefore, all the complexes of this series may be regarded as having the same square-planar coordination as the Ni(L-iso-C_3H_7)$_2$ molecule, whose structure has been confirmed as described above.

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