Tentative Assignment of Fundamental Vibrations of Thio- and Selenocarboxylates IV. Bis(*N,N*-dimethyldithiocarbamato)-nickel(II) and Bis(*N,N*-dimethyldiselenocarbamato)-nickel(II)

KAI ARNE JENSEN,[a] BRITTA MYNSTER DAHL,[a]
PER HALFDAN NIELSEN[a] and GUNNER BORCH[b]

[a]*Institute of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, and* [b]*Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark*

The infrared spectra in the range 40—4000 cm⁻¹ of bis(*N,N*-dimethyldithiocarbamato)nickel(II), and bis(*N,N*-dimethyldiseleno-carbamato)nickel(II), and the corresponding perdeuterated compounds are reported. For these compounds, the frequencies and description in symmetry coordinates of the normal vibrations of species B_{1u}, B_{2u}, and B_{3u} have been calculated using a 31-parameter force field in the generalised valence force field (GVFF) approximation. The force fields were derived by adaption of those of the free ligands and those of analogous complexes. A complete tentative assignment of the fundamentals of species B_{1u}, B_{2u}, and B_{3u} is presented for the four complexes and previous assignments are discussed.

The first normal coordinate analysis of metal complex compounds containing dithio- and diselenocarbamate ligands was reported in 1963 by Nakamoto *et al.*[1] The vibrational fundamentals of bis(dithiocarbamato)-platinum(II) and the corresponding perdeuterated complex were calculated using a Urey-Bradley force field. However, the procedure was approximative, since the calculations were performed adopting a 1:1 model, *i.e.* the complex was treated as if it consisted only of one ligand connected to the central metal atom. Furthermore, all out-of-plane vibrations were neglected and only the eleven in-plane vibrations were compared with the nine experimentally found frequencies. Recently, exploratory calculations have been published for bis-(dimethyldithiocarbamato)nickel(II) (DDTC-Ni) and the selenium analogue (DDSC-Ni)[2] using 1:1 models, but owing mainly to the lack of reliable experimental information the conclusions are still far from definitive. A preliminary account of the results obtained for metal complexes containing the

Table 1. Observed infrared spectra [a] of bis(dimethyldithiocarbamato)nickel(II), bis-(dimethyldiselenocarbamato)nickel(II) and the deuterated compounds in KBr (400—4000 cm^{-1}) and polyethylene (40—400 cm^{-1}) with a tentative assignment of the fundamentals.

$[(CH_3)_2NCSS]_2Ni$	$[(CD_3)_2NCSS]_2Ni$	$[(CH_3)_2NCSeSe]_2Ni$	$[(CD_3)_2NCSeSe]_2Ni$	Assignment [b]
3003vw	2260vw	2998vw	2253vw	
2950w	2186vw	2950w	2174vw	$\nu_{12}(B_{2u})$, $\nu_{20}(B_{3u})$
2910m	2233w	2908m	2219w	$\nu_1(B_{1u})$
	2221wsh		2207vwsh	
	2141m		2131m	
	2104w		2093w	
2849w	2061m	2848w	2053m	$\nu_2(B_{1u})$, $\nu_{21}(B_{3u})$
2776w	1949vw	2774w	1939w	
2117w	1916vw	2031vw	1760w	
1967w	1639w		1626w	
1936w	1583vw	1880vw		
1788w		1765w		
1717w		1736w		
1553vs	1500vs	1555vs	1504vs	$\nu_3(B_{1u})$
1446m	1048m	1446m	1044m	$\nu_4(B_{1u})$, $\nu_{13}(B_{2u})$, $\nu_{22}(B_{3u})$
1394s[c]	1037wsh	1401s[c]	1033w	$\nu_5(B_{1u})$
1394s[c]	1064s	1401s[c]	1059s	$\nu_{23}(B_{3u})$
		1367w		
1246s	1225s	1226m	1201s	$\nu_{24}(B_{3u})$
1150vs[c]	790w	1144vs	765w	$\nu_6(B_{1u})$
	1301vw		1298vw	
	1208msh			
	1168w		1168w	
	1098wsh		1093wsh	
1150vs[c]	977vs	1144vs	965vs	$\nu_{14}(B_{2u})$
1103w		1080vwsh		
1054m	824w	1046m	815w	$\nu_{25}(B_{3u})$
1013w		995vw		
975vs	984vs	892m	883m	$\nu_{26}(B_{3u})$
944vw	1113m		1107m	$\nu_7(B_{1u})$
	947msh			
	927wsh		926wsh	
894vw				
		870m		
	860vw			
820vw		766vw		
570w	539w	535vw	490vw[c]	$\nu_8(B_{1u})$
549w	545w	498vw	490vw[c]	$\nu_{15}(B_{2u})$
444m	414m	328s	328s	$\nu_9(B_{1u})$
414s	397s	378m	347m	$\nu_{27}(B_{3u})$
388s	363m	298w[c]	298w[c]	$\nu_{10}(B_{1u})$
376m	376m	298w[c]	298w[c]	$\nu_{28}(B_{3u})$
301m	286m	204m	204m	$\nu_{11}(B_{1u})$
273m	245m	272m	246m	$\nu_{16}(B_{2u})$
179m	175m	144vw	144vw	$\nu_{17}(B_{2u})$
104wbr	100wbr	96wbr	96wbr	
90m	85m	78m	74m	$\nu_{30}(B_{3u})$

[a] Abbreviations used: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, and sh = shoulder.

[b] The numbering of the fundamentals refer to the undeuterated compound. The counterparts of the deuterated compounds are the bands, which according to the normal coordinate analysis correspond most closely in description.

[c] Multiple assigned bands.

diethyldithiocarbamate ligand was given a short time ago by Pilipenko and Mel'nikova.[3]

The purpose of the present paper is to present a complete assignment of the infrared-active fundamentals of species B_{1u}, B_{2u}, and B_{3u} of the nickel complexes DDTC-Ni and DDSC-Ni. For this purpose a full normal coordinate analysis was performed using the actual 2:1 model of the complexes. A major part of the force fields were transferred from those derived previously for the free ligands, DDTC and DDSC.[4,5]

The infrared data for DDTC-Ni, DDSC-Ni, and the perdeuterated complexes and a tentative assignment of the fundamentals of species B_{1u}, B_{2u}, and B_{3u} are given in Table 1. A graphical representation of the infrared spectra of the complexes in the region below 1330 cm^{-1} is shown in Fig. 1. In the upper
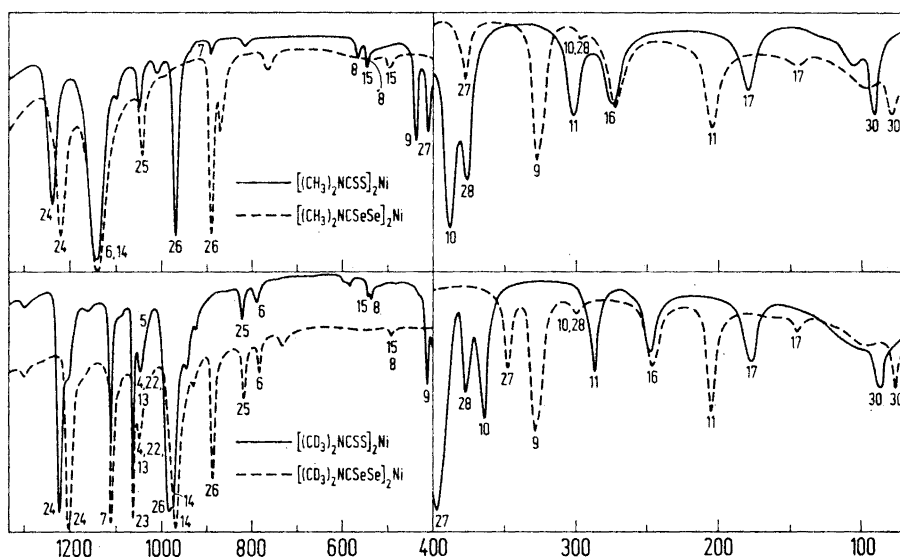

Fig. 1. The infrared spectra of bis(dimethyldithiocarbamato)nickel(II), its selenium analogue, and the perdeuterated compounds in the range $60-1333$ cm^{-1}. The numbering of the bands refers to the assigned fundamentals discussed in the text.

part the superimposed spectra of DDTC-Ni and DDSC-Ni are drawn with a full and a dashed line, respectively. In the lower part of Fig. 1 the superimposed spectra of the deuterated counterparts are shown in the same way. When arranged in this way it is immediately apparent that a number of infrared absorptions by virtue of their position, shape, and intensity appear to have common origins in the four compounds. In fact, it has often been convenient to consider the infrared spectrum of a selenium compound as DDSC-Ni to be derived from the infrared spectrum of the corresponding sulfur compound (here DDTC-Ni) by "selenation", *i.e.* the replacement of sulfur with selenium.[5] However, though it is empirically useful to say that, *e.g.*, the absorption band of DDTC-Ni, numbered 26 in Fig. 1, is "displaced from 975 cm^{-1} to 892 cm^{-1}

on selenation'', it is (1) not known to which extent this shift is due to changes in bond lengths, interbond angles, masses, or force constants when sulfur is replaced by selenium, and (2) also not known to which extent this absorption band can be described by similar symmetry coordinates and potential energy distributions in DDTC-Ni and DDSC-Ni. This problem will be discussed later on the basis of the results obtained from the vibrational analyses.

EXPERIMENTAL

The experimental details of obtaining the spectra and performing the normal coordinate analyses were described in part I of this series.[6] We thank Dr. Kjeld Rasmussen for providing us with the far-infrared data.

The complex compounds were prepared by published methods.[7] Their elemental compositions were checked by analysis. All spectra were recorded several times and with different concentrations of the complexes in the KBr-discs in order to get a reliable determination of the absorption maxima.

NORMAL COORDINATE ANALYSIS

The nickel(II) complexes in the full 2:1 model contain a total of 25 atoms assumed to be arranged according to the point group D_{2h} with the molecule in the XZ-plane and the ligands along the Z-axis. The 69 normal modes of vibration can consequently be described by the representation $11A_g + 6A_u + 5B_{1g} + 11B_{1u} + 10B_{2g} + 8B_{2u} + 7B_{3g} + 11B_{3u}$. However, only the 30 normal vibrations of the species B_{1u}, B_{2u}, and B_{3u} are infrared active, corresponding to the species A_1, B_2, and B_1 of the free ligands,[4,5] respectively. The present work is confined to the treatment of these three species.

In the absence of infrared or Raman polarisation data, there was, a priori, no way of distinguishing the fundamentals of the three species in question. Therefore, the following method was adopted. First, by comparing the spectra of the nickel(II) complexes to those of the corresponding free ligands, it was noted that many absorption bands were almost unchanged in position, shape, and strength. As a first approximation it was assumed that these bands corresponded to those ligand vibrations that were least perturbed by complex formation. A normal coordinate calculation was then carried out using the force fields previously derived for the free ligands [4,5] combined with those described for related complex compounds.[1,8] By varying the force field it proved possible to obtain agreement between most of the experimental and calculated frequencies, and a revised assignment of the fundamentals was obtained.

In the process of developing the final force field and assigning the fundamentals, several problems were encountered some of which will be mentioned here. The assignment of the bands in the CH/CD stretching and the CH_3/CD_3 deformation regions cannot be taken as decisive, and changes will undoubtedly prove necessary as the available evidence increases. Also, the assignments of the four rather closely spaced bands in the region $300-450$ cm^{-1} in DDTC-Ni and DDSC-Ni may have to be interchanged. The essential problem in assigning these bands is that only three counterparts are observed in the corresponding deuterated complex compounds. Accordingly, it has been necessary to assume

that two fundamentals are superimposed in the deuterated complexes which, however, increases the number of possible assignments of this region and leaves the results somewhat arbitrary.

The bond distances and the interbond angles have been assumed unchanged from those used for the free ligands [4,5] as regards the $(CH_3)_2NC$ group. The remaining bond distances and angles, including those of the dithio- or diseleno-carboxylate groups and around the nickel atom, were assumed identical with those estimated by Durgaprasad et al.[2] on the basis of X-ray determinations on the diethyl analogues. The internal coordinates are shown in Fig. 2, and

Fig. 2. Internal coordinates for bis(di-methyldithiocarbamato)nickel(II), also used for the selenium substituted analogue. Additional coordinates are: torsions of methyl groups τ_1 and τ_2, out-of-plane NCSS wagging, ω_2 and out-of-plane $(CH_3)_2N$ wagging, ω_1. Bending around the S···S line, b_1, has been defined by simultaneous torsion around the two CS bonds. Bending of the two ligands around a line ($\times \cdots \times$) through the nickel atom as indicated on the figure, b_2, has been defined by simultaneous torsion around the four NiS bonds. The internal coordinates of the other ligand are identical with those shown on the figure, except that each coordinate obtained by reflection in the mirror plane (through the line $\times \cdots \times$) has been marked with a prime.
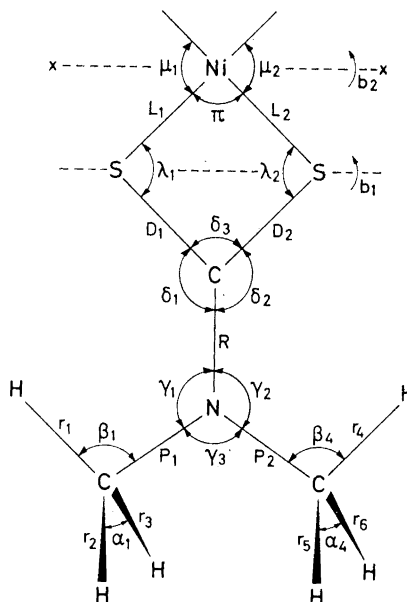
express the changes in distances and angles. The symmetry coordinates listed in Table 2 were constructed from the internal coordinates in the usual way (*cf.* Ref. 4). Normalisation of the symmetry coordinates and removal of the redundant ones were made automatically by the program used in the calculations.

The final force field is given in Table 3 and includes 31 force constants which are only seven more than those necessary to calculate the vibrational spectrum of the ligands. Six of these are simple stretching and bending force constants applying to the new bonds with the nickel atom. The additional force constant was necessary to adjust the frequency of the vibration in which the two ligands rock in-plane around the nickel atom (ϱ Lig). It was chosen as an interaction constant between deformation of angles which are not contiguous (δ and μ) as the simplest solution even though it is physically not the most probable.

Table 2. Symmetry coordinates for bis(dimethyldithiocarbamato)nickel(II).

Symmetry coordinate (unnormalized)	Symbol	Description
Species B_{1u}		
$S_1 = 2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6 - (2r_1' - r_2' - r_3' + 2r_4' - r_5' - r_6')$	$\nu_{as}CH$	Asym. CH stretch
$S_2 = r_1 + r_2 + r_3 + r_4 + r_5 + r_6 - (r_1' + r_2' + r_3' + r_4' + r_5' + r_6')$	ν_sCH	Sym. CH stretch
$S_3 = P_1 + P_2 - (P_1' + P_2')$	ν_sCNC	Sym. CNC stretch
$S_4 = R - R'$	νCN	CN stretch
$S_5 = D_1 + D_2 - (D_1' + D_2')$	ν_sCSS	Sym. CSS stretch
$S_6 = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6 - (2\alpha_1' - \alpha_2' - \alpha_3' + 2\alpha_4' - \alpha_5' - \alpha_6')$	$\delta_{as}CH_3$	Asym. CH_3 deformation
$S_7 = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 - (\alpha_1' + \alpha_2' + \alpha_3' + \alpha_4' + \alpha_5' + \alpha_6')$	δ_sCH_3	Sym. CH_3 deformation
$S_8 = 2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6 - (2\beta_1' - \beta_2' - \beta_3' + 2\beta_4' - \beta_5' - \beta_6')$	ϱCH_3	In-plane CH_3 rock
$S_9 = \beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 - (\beta_1' + \beta_2' + \beta_3' + \beta_4' + \beta_5' + \beta_6')$	–	Redundant
$S_{10} = \delta_1 + \delta_2 - (\delta_1' + \delta_2')$	δCSS	CSS deformation
$S_{11} = \delta_3 - \delta_3'$	–	Redundant
$S_{12} = \lambda_1 + \lambda_2 - (\lambda_1' + \lambda_2')$	δ_sCSNi	Sym. CSNi deformation
$S_{13} = \pi - \pi'$	$\delta SNiS$	SNiS deformation
$S_{14} = \gamma_1 + \gamma_2 - (\gamma_1' + \gamma_2')$	δCNC	$(CH_3)_2N$ deformation
$S_{15} = \gamma_3 - \gamma_3'$	–	Redundant
$S_{16} = L_1 + L_2 - (L_1' + L_2')$	ν_sNiS	Sym. NiS stretch
Species B_{2u}.		
$S_1 = r_2 - r_3 + r_5 - r_6 + (r_2' - r_3' + r_5' - r_6')$	νCH	CH stretch
$S_2 = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6 + (\alpha_2' - \alpha_3' + \alpha_5' - \alpha_6')$	δCH_3	CH_3 deformation
$S_3 = \beta_2 - \beta_3 + \beta_5 - \beta_6 + (\beta_2' - \beta_3' + \beta_5' - \beta_6')$	ϱCH_3	CH_3 rock
$S_4 = \tau_1 + \tau_2 + \tau_1' + \tau_2'$	τCH_3	CH_3 torsion
$S_5 = \omega_1 + \omega_1'$	ωCNC	$(CH_3)_2N$ out-of-plane wag
$S_6 = \omega_2 + \omega_2'$	ωCSS	CSS out-of-plane wag
$S_7 = b_1 + b_1'$	bSS	S$\cdots$S bending
$S_8 = b_2$	bLig	Out-of-plane bending of both ligands relative to the nickel atom
Species B_{3u}		
$S_1 = 2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6 + (2r_1' - r_2' - r_3' - 2r_4' + r_5' + r_6')$	$\nu_{as}CH$	Asym. CH stretch
$S_2 = r_1 + r_2 + r_3 - r_4 - r_5 - r_6 + (r_1' + r_2' + r_3' - r_4' - r_5' - r_6')$	ν_sCH	Sym. CH stretch
$S_3 = P_1 - P_2 + (P_1' - P_2')$	$\nu_{as}CNC$	Asym. CNC stretch
$S_4 = D_1 - D_2 + (D_1' - D_2')$	$\nu_{as}CSS$	Asym. CSS stretch
$S_5 = 2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6 + (2\alpha_1' - \alpha_2' - \alpha_3' - 2\alpha_4' + \alpha_5' + \alpha_6')$	$\delta_{as}CH_3$	Asym. CH_3 deformation
$S_6 = \alpha_1 + \alpha_2 + \alpha_3 - \alpha_4 - \alpha_5 - \alpha_6 + (\alpha_1' + \alpha_2' + \alpha_3' - \alpha_4' - \alpha_5' - \alpha_6')$	δ_sCH_3	Sym. CH_3 deformation
$S_7 = 2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6 + (2\beta_1' - \beta_2' - \beta_3' - 2\beta_4' + \beta_5' + \beta_6')$	ϱCH_3	In-plane CH_3 rock
$S_8 = \beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6 + (\beta_1' + \beta_2' + \beta_3' - \beta_4' - \beta_5' - \beta_6')$	–	Redundant
$S_9 = \delta_1 - \delta_2 + (\delta_1' - \delta_2')$	ϱCSS	In-plane CSS rock
$S_{10} = \lambda_1 - \lambda_2 + (\lambda_1' - \lambda_2')$	$\delta_{as}CSNi$	Asym. CSNi deformation
$S_{11} = \gamma_1 - \gamma_2 + (\gamma_1' - \gamma_2')$	ϱCNC	In-plane $(CH_3)_2N$ rock
$S_{12} = L_1 - L_2 + (L_1' - L_2')$	$\nu_{as}NiS$	Asym. NiS stretch
$S_{13} = \mu_1 - \mu_2$	ϱLig	In-plane rocking of both ligands relative to the nickel atom

Table 3. Final valence force constants for bis(dimethyldithiocarbamato)nickel(II) and bis(dimethyldiselenocarbamato)nickel(II), $[(CH_3)_2NCXX]_2Ni$, $X = S$ or Se.

| Force constant	Group	Coordinates involved	Atoms common to interacting coordinates	Value [a] for $X = S$	Value [a] for $X = Se$
			Stretch		
K_r	CH_3	$C - H$	—	4.699	4.699
K_P	$CH_3 - N$	$C - N$	—	4.60	4.37
K_R	$N - C^*X_2$	$N - C^*$	—	6.50	6.47
K_D	C^*X_2	$C^* - X$	—	3.95	4.45
K_L	NiX_2	$Ni - X$	—	0.90	0.80
			Stretch-stretch		
F_r	CH_3	$C - H, C - H$	C	0.043	0.043
F_P	$CH_3 - N - CH_3$	$C - N, C - N$	N	0.80	1.01
F_D	$X - C^* - X$	$C^* - X, C^* - X$	C^*	0.55	2.00
F_{PR}	$CH_3 - N - C^*X_2$	$C - N, N - C^*$	N	0.178	0.178
F_{RD}	$N - C^* - X$	$N - C^*, C^* - X$	C^*	0.234	0.234
			Bend		
H_α	CH_3	$\angle HCH$	—	0.54	0.54
H_β	$CH_3 - N$	$\angle HCN$	—	0.73	0.73
$H_{\gamma_1} = H_{\gamma_2}$	$CH_3 - N - C^*X_2$	$\angle CNC^*$	—	0.60	1.20
H_{γ_3}	$CH_3 - N - CH_3$	$\angle CNC$	—	1.00	0.60
$H_{\delta_1} = H_{\delta_2}$	$N - C^* - X$	$\angle NC^*X$	—	1.40	1.30
H_{δ_3}	$X - C^* - X$	$\angle XC^*X$	—	1.20	0.60
H_λ	$C^* - X - Ni$	$\angle C^*XNi$	—	1.20	1.11
H_π	$X - Ni - X$	$\angle XNiX$	—	1.20	1.04
H_μ	$X - Ni - X^*$	$\angle XNiX^*$	—	1.00	1.00
H_{ω_1}	$(CH_3)_2N - C^*$	$\angle C_2NC^*$	—	0.158	0.177
H_{ω_2}	$N - C^*X_2$	$\angle NC^*X_2$	—	0.40	0.422
H_{b_1}	C^*X_2Ni	$\angle C^*X_2Ni$	—	0.35	0.335
H_{b_2}	$X_2NiX_2^*$	$\angle X_2NiX_2^*$	—	0.35	0.335
			Stretch-bend		
$F_{P\beta}$	$CH_3 - N$	$C - N, \angle HCN$	$C - N$	0.318	0.318
$F_{P\gamma}$	$CH_3 - N - C^*X_2$	$C - N, \angle CNC^*$	$C - N$	0.347	0.347
$F_{R\gamma}$	$CH_3 - N - C^*X_2$	$C^* - N, \angle CNC^*$	$C^* - N$	0.283	0.283
$F_{R\delta}$	$N - C^* - X$	$N - C^*, \angle NC^*X$	$N - C^*$	0.283	0.283
			Bend-bend		
F_β	$CH_3 - N$	$\angle HCN, \angle HCN$	$C - N$	− 0.04	− 0.04
$F_{\omega_1\omega_2}$	$C_2N - C^*X_2$	$\angle C_2NC^*, \angle NC^*X_2$	$N - C^*$	0.10 [b]	0.10 [b]
$F_{\delta\mu}$	$NC^*X_2NiX_2^*$	$\angle NC^*X, \angle XNiX^*$	X	0.20	0.20
			Torsion		
H_τ	$CH_3 - N$	$C - N$	—	0.0335	0.0335

[a] In units of mdyn/Å (stretch constants), mdyn/rad (stretch-bend interaction constants), and mdyn Å/(rad)² (bending and torsion constants).

[b] The out-of-plane wagging coordinates have been defined in such a way, that displacements to the same side of the ligand correspond to identical signs of the wagging coordinates.

The force field for the internal coordinates around the nickel atom was initially estimated from several published UBFF values.[1,2,8–10] A Ni − S stretching force constant between 1.4 and 2.0 mdyn/Å and a S − Ni − S bending force constant somewhere below 0.65 mdyn Å/(rad)^2 were selected as a first approximation. The omission of the repulsive terms of the UBFF and the introduction of the GVFF interaction terms must necessarily have a large influence on these values. The results of the present calculations (where the number of interaction constants has been held as low as possible) give a Ni − S stretching force constant of 0.90 mdyn/Å and a S − Ni − S bending force constant of 1.0 − 1.2 mdyn Å/(rad).^{2} As expected, the values of the selenium complex tend to be somewhat smaller.

On comparing the results listed in Table 3 with those previously given for the ligands [4,5] it can be seen that most of the force constants have been almost directly transferred. However, several changes occur, which can be related to the influence of the nickel atom and interpreted in conventional terms. The most striking change is that of the force constant of the central CN bond, which increases from 4.80/5.35 in the DDTC/DDSC ligands to around 6.50 mdyn/Å in the complexes. This is satisfactory, since complex formation will be followed by an increased weight of the resonance structure [11]

$$CH_3 \quad \quad \quad X^-$$
$$\diagdown \overset{+}{N} = C \diagup$$
$$\diagup \quad \quad \quad \diagdown$$
$$CH_3 \quad \quad \quad X^- \quad (X = S, Se)$$
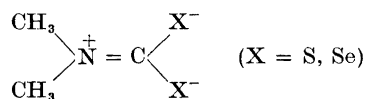
and the increased double bond character of the central CN bond is properly reflected in an increased force constant for stretching of this bond.

The changes in force field on substituting selenium for sulfur in the DDTC ligand have previously been discussed [5] and comprise, apart from the changes discussed above, a decrease in K_P and an increase in F_P and F_D, as well as several changes in the bending force constants. The stretching force constants K_P, F_P, and F_D show a similar trend for the complex compounds, but the changes in K_P and F_D appear to be greater in the complex compounds, indicating that the force field is not wholly correct. The changes in the bending force constants are not consistent, but this may depend on the assumption of identical interbond angles in the thio and the seleno compounds and is not considered serious.

The calculated fundamentals and an approximate description in symmetry coordinates are listed in Table 4 for DDTC-Ni and DDSC-Ni. The deviation of the frequencies originating mainly from the ligand vibrations is generally similar to that found for the free ligands.[4,5] For the several new modes of vibration introduced by complex formation with nickel the agreement between calculated and experimental values is considered satisfactory in view of the very simplified GVFF used in the calculations.

DISCUSSION

A description of the infrared spectra of the complex compounds is now possible by comparing the spectra in three different ways. First, the spectrum

of a compound can be compared to the spectrum of the corresponding perdeuterated compound, which gives the familiar effect of deuteration. Second, the spectrum of a certain ligand can be compared to the spectrum of the corresponding (nickel) complex, *i.e.* we can discuss the effect of complex formation. Third, the spectrum of a compound containing sulfur can be compared to the spectrum of the corresponding compound in which sulfur has been replaced by selenium, indicating the effect of selenation.

The experimental spectra of the free ligands are shown in a previous paper [5] while those of the complex compounds are reproduced in Fig. 1 of this paper, all in the region below 1330 cm^{-1}. The description of the fundamentals is based on the potential energy distributions (Table 4) and the calculated L-matrices (which are not reproduced to save space). A description of the fundamentals of the ligands has been given in previous papers.[4,5]

The most characteristic band of the complex compounds is $\nu_3(B_{1u})$, a very strong, broad band in the region 1500 − 1600 cm^{-1}. The counterparts in the spectra of the free ligands are found at somewhat lower frequencies and have been shown to originate mainly in an out-of-phase combination of νCN and ν_sCNC (more or less coupled to internal modes of the methyl groups). A quite similar description applies to the complex compounds, although the contribution from νCN has increased relative to that of ν_sCNC. In the case of the selenium-containing complexes this vibration is coupled also to ν_sCSeSe, so that a more appropriate description is an out-of-phase combination of νCN, ν_sCNC, and ν_sCSeSe. On deuteration, the frequency of the internal modes of the methyl groups is lowered and the contribution to this absorption drops almost to zero; accordingly, $\nu_3(B_{1u})$ is displaced towards lower frequencies on deuteration. According to Durgaprasad's results,[2] in DDTC-Ni this band arises from νCN weakly coupled (out-of-phase?) to ν_sCNC and ν_sCSS, in fair agreement with the results of the present calculation. To summarise, the strong, broad band in the region 1400 − 1600 cm^{-1} can be generally described as due to out-of-phase skeletal stretching, however, with varying contributions from internal modes of the methyl groups.

Both descriptions of $\nu_3(B_{1u})$ compare favourably to empirical evidence, which is best rationalised by treating this band as due to stretching of the central CN bond, *i.e.* νCN. Thus, when the importance of the resonance structure $R_2N^+ = CX_2^{2-}$ (X = S, Se) is expected to increase (by complex formation; introducing electron donating groups on nitrogen) the frequency of this band also increases.[12−18]

In the frequency range 1300 − 1500 cm^{-1} in DDTC-Ni and DDSC-Ni the deformational modes of the methyl groups occur. On deuteration they are displaced to the region 1000 − 1100 cm^{-1}. In the frequency range 1000 − 1200 cm^{-1} in DDTC-Ni and DDSC-Ni the rocking modes of the methyl groups are found. The band near 1150 cm^{-1} is the strongest of these, probably because the B_{1u} fundamental, ν_6, containing the skeletal ν_sCXX (X = S, Se) symmetrical stretching mode, is a component of this absorption. Some authors have assigned this band to one of the CNC stretching frequencies,[13,19] probably because it was observed only in dialkyldithiocarbamates and not in dithiocarbamates lacking alkyl substituents. Obviously, the present assignment may also explain this experimental result.

Table 4. Calculated (ν_{calc}, cm⁻¹) and observed (ν_{obs}, cm⁻¹) frequencies and potential energy distribution for bis(N,N-dimethyldithio-carbamato)nickel(II), bis(N,N-dimethyldiselenocarbamato)nickel(II), and the corresponding perdeuterated compounds, using a 31-parameter generalized valence force field.

No.	[(CH₃)₂NCSS]₂Ni ν_{calc}	ν_{obs}	Description [a]	[(CD₃)₂NCSS]₂Ni ν_{calc}	ν_{obs}	Description [a]	[(CH₃)₂NCSeSe]₂Ni ν_{calc}	ν_{obs}	Description [a]	[(CD₃)₂NCSeSe]₂Ni ν_{calc}	ν_{obs}	Description [a]
B_{1u} ν_1	2964	2910	ν_{as}CH(99)	2218	2233	ν_{as}CD₃(96)	2963	2908	ν_{as}CH(99)	2217	2219	ν_{as}CD(97)
ν_2	2884	2849	ν_sCH(100)	2081	2061	ν_sCD(96)	2884	2848	ν_sCH(100)	2081	2053	ν_sCD(98)
ν_3	1534	1553	νCN(57), νCNC(14), ϱCH₃(14)	1510	1500	νCN(70), ν_sCNC(14)	1539	1555	νCN(58), νCNC(13), νCH₃(13), ν_sCSeSe(11)	1518	1504	νCN(70), ν_sCNC(13), ν_sCSeSe(15)
ν_4	1452	1446	δ_{as}CH₃(84)	1050	1048	δ_{as}CD₃(94)	1453	1446	δ_{as}CH₃(84)	1050	1044	δ_{as}CD₃(93)
ν_5	1387	1394	δ_sCH₃(95)	1001	1037	δ_sCD₃(46)	1387	1401	δ_sCH₃(100)	1001	1033	δ_sCD₃(49)
ν_6	1147	1150	ϱCH₃(45), ν_sCSS(16)	767	790	ϱCD₃(57), ν_sCNC(25)	1153	1144	ϱCH₃(45), ν_sCSeSe(20)	766	765	ϱCD₃(58), ν_sCNC(26)
ν_7	946	944	ν_sCNC(47), ϱCH₃(33)	1137	1113	ν_sCNC(37), δCD₃(50)	947	—	ν_sCNC(47), ϱCH₃(34)	1142	1107	ν_sCNC(39), δCD₃(48)
ν_8	568	570	ν_sCSS(45), νCN(17), ν_sCNC(22)	541	539	ν_sCSS(49), νCN(16), ν_sCNC(16)	524	535	ν_sCSeSe(33), νCN(20), ν_sCNC(27)	484	490	ν_sCSeSe(35), νCN(23), ν_sCNC(23)
ν_9	453	444	δCSS(30), ν_sCSNi(19), δCNC(18)	438	414	δCSS(36), δ_sCSNi(16), δCNC(9)	335	328	δCNC(48), δ_sCSeNi(11), δSeNiSe(11)	316	328	δCNC(19), δ_sCSeNi(16), δSeNiSe(20)
ν_{10}	379	388	ν_sNiS(54)	365	363	ν_sNiS(51)	300	298	ν_sNiSe(66)	290	298	νNiSe(37), νNiSe(40), δCNC(31)
ν_{11}	292	301	δCNC(39), δ_sCSNi(15)	267	286	δCNC(53), δ_sCSNi(10)	228	204	δCSeSe(35), δ_sCSeNi(34)	218	204	δCSeSe(30), δ_sCSeNi(28), δCNC(25)

Table 4. Continued.

B_{2u}

	obs	calc	Assignment	obs	calc	Assignment	obs	calc	Assignment	obs	calc	Assignment
ν_{12}	2961	2950	νCH(99)	2209	2186	νCD(98)	2960	2950	νCH(99)	2209	2174	νCD(98)
ν_{13}	1464	1446	δCH$_3$(87)	1050	1048	δCD$_3$(90)	1464	1446	δCH$_3$(87)	1049	1044	δCD$_3$(90)
ν_{14}	1120	1150	ϱCH$_3$(85)	895	977	ϱCD$_3$(84)	1120	1144	ϱCH$_3$(85)	895	965	ϱCD$_3$(85)
ν_{15}	549	549	ωCSS(80)	546	545	ωCSS(79)	497	498	ωCSeSe(76)	492	490	ωCSeSe(77)
ν_{16}	271	273	ωCNC(72)	247	245	ωCNC(71)	271	272	ωCNC(76)	246	246	ωCNC(77)
ν_{17}	177	179	bLig(60), bSS(36)	176	176	bLig(61), bSS(34)	144	144	bLig(58), bSeSe(40)	144	144	bLig(60), bSeSe(39)
ν_{18}	121	—	τCH$_3$(81)	89	—	τCD$_3$(82)	123	—	τCH$_3$(81)	88	—	τCD$_3$(83)
ν_{19}	49	—	bLig(30), bSS(29), ωCNC(37)	46	—	bLig(29), bSS(28), ωCNC(37)	45	—	bLig(29), bSeSe(33), ωCNC(34)	41	—	bLig(28), bSeSe(32), ωCNC(35)

B_{3u}

	obs	calc	Assignment	obs	calc	Assignment	obs	calc	Assignment	obs	calc	Assignment
ν_{20}	2961	2950	ν_{as}CH(99)	2210	2186	ν_{as}CD(98)	2962	2950	ν_{as}CH(99)	2212	2174	ν_{as}CD(98)
ν_{21}	2883	2849	ν_sCH(100)	2076	2061	ν_sCD(99)	2882	2848	ν_sCH(100)	2074	2053	ν_sCD(99)
ν_{22}	1462	1446	δ_{as}CH$_3$(88)	1045	1048	δ_{as}CD$_3$(71)	1461	1446	δ_{as}CH$_3$(88)	1052	1044	δ_{as}CD$_3$(67)
ν_{23}	1383	1394	δ_sCH$_3$(98)	1066	1064	δ_sCD$_3$(67), ν_{as}CNC(37)	1385	1401	δ_sCH$_3$(96)	1041	1059	δ_sCD$_3$(78)
ν_{24}	1246	1246	ν_{as}CSS(35), ϱCSS(36), ν_{as}CNC(16), δ_{as}CSNi(13)	1248	1225	ν_{as}CSS(39), ϱCSS(40), ν_{as}CNC(10), δ_{as}CSNi(14)	1222	1226	aCSeSe(28), δ_{as}CSeNi(28), ν_{as}CNC(24), ν_{as}CSeSe(13)	1215	1201	εCSeSe(37), δ_{as}CSeNi(33), ν_{as}CNC(18), ν_{as}CSeSe(18)
ν_{25}	1080	1054	ϱCH$_3$(66)	793	824	ϱCD$_3$(78)	1040	1046	ϱCH$_3$(66)	783	815	ϱCD$_3$(66)
ν_{26}	957	975	ν_{as}CNC(87), ν_{as}CSS(18)	962	984	ν_{as}CNC(50), ν_{as}CSS(17)	883	892	ν_{as}CNC(85), ν_{as}CSeSe(15)	888	883	ν_{as}CNC(43), ν_{as}CSeSe(25)
ν_{27}	416	414	ν_{as}CSS(30), ϱCSS(30), δ_{as}CSNi(24)	398	397	ν_{as}CSS(26), ϱCSS(32), δ_{as}CSNi(20)	373	378	ν_{as}CSeSe(33), δ_{as}CSeNi(43)	346	347	ν_{as}CSeSe(26), δ_{as}CSeNi(35)
ν_{28}	376	376	ν_{as}NiS(62)	375	376	ν_{as}NiS(61)	301	298	ν_{as}NiSe(56)	298	298	ν_{as}NiSe(51)
ν_{29}	192	—	ϱLig(40)	181	—	ϱLig(43)	166	—	ϱCSeSe(54), ϱLig(22), δ_{as}CSeNi(28)	157	—	ϱCSeSe(50), ϱLig(26), δ_{as}CSeNi(31)
ν_{30}	82	90	ϱLig(44), δ_{as}CSNi(22)	76	85	ϱLig(39), δ_{as}CSNi(26)	72	78	ϱLig(59)	68	74	ϱLig(55)

^{a} Abbreviations used (*cf.* Table 2): ν = stretching, δ = deformation, ϱ = rocking, ω = wagging, τ = torsion, and, as subscripts, s = symmetric, as = antisymmetric. The rounded potential energy distribution values are shown in parenthesis; small values have been neglected. In cases where several vibrations contribute significantly, the most important is printed in italics.

In the region between 1240 and 1260 cm^{-1} in DDTC and DDTC-Ni there is observed $\nu_{24}(B_{3u})$, a band of medium strength, which is displaced by about 20 cm^{-1} on deuteration or by selenation. This band is due to an out-of-phase combination of ν_{as}CNC and ν_{as}CXX (X = S, Se) coupled to skeletal angle deformation. In the case of the free ligands the latter component was mainly ϱCNC, but in the case of the complex compounds this has been replaced by ϱCXX (X = S, Se) and ϱ_{as}CXNi. According to the calculations by Durgaprasad et al. on DDTC-Ni [2] it should be described as due mainly to ν_{as}CNC, but with small contributions from ϱCNC and ϱCSS. The use of this absorption in empirical work has turned out to be of doubtful value.[17],[18]

In the infrared region between 950 and 1000 cm^{-1} a strong broad band is observed in both DDTC and DDTC-Ni. Since it is almost unchanged by deuteration, but displaced by about 100 cm^{-1} towards lower frequencies on selenation, a tentative empirical conclusion is that it can be described as mainly ν_{as}CXX (X = S, Se) (see references in part I of this series.[6]) The calculations indicate that this band should be assigned to $\nu_{26}(B_{3u})$ which originates from ν_{as}CXX coupled in-phase with ν_{as}CNC in various proportions. Since the potential energy distributions (Table 4) are almost identical in DDTC-Ni and DDSC-Ni it is obviously correct to say that this band has the same origin in both complexes. This is also approximately true for the deuterated complexes.

The reason for the shift of this absorption towards lower frequencies on selenation can now be summarised as follows. (1) Probably the geometry of the CXX group differs for the two complexes, but this effect has not been explored and will be neglected in the present discussion. (2) The increased mass of selenium relative to sulfur can account only for ca. 30 cm^{-1} of the 100 cm^{-1} shift actually found (cf. Ref. 3). (3) The remaining shift is due partly to the lowered force constant for asymmetrical CNC stretching, partly to the lowered force constant for asymmetrical CXX stretching on selenation. It has been proposed that this frequency could be used to estimate stability of complex compounds,[14] but in the light of our calculations the use of $\nu_3(B_{1u})$ in the 1500 cm^{-1} region seems much more attractive for this purpose.

In the region between 500 and 600 cm^{-1} the two fundamentals $\nu_8(B_{1u})$ and $\nu_{15}(B_{2u})$ are found. Both behave in the same way as the infrared counterparts $\nu_8(A_1)$ and $\nu_{28}(B_2)$ in the spectra of the free ligands, and have a similar origin.[5] The former is the in-phase combination of ν_sCXX, νCN, and ν_sCNC (X = S, Se), i.e. the skeletal breathing vibration. The latter is due to the CXX wagging motion.

The region below 500 cm^{-1} has recently been discussed by Ojima et al. for DDTC-Ni.[20] The three metal translation vibrations expected to occur in this region are (1) the symmetrical Ni$-$S stretching vibration of species B_{1u}, ν_sNiS, (2) the antisymmetrical Ni$-$S stretching vibration of species B_{3u}, ν_{as}NiS, and (3) a ring out-of-plane vibration, in which the ligands bend out-of-plane relative to the central nickel atom, bLig. In the latter vibration the ligands move up and down like the wings of a butterfly, and it may conveniently be described as a "flapping" motion of the molecule. The working hypothesis of Ojima et al. is, that since only three strong bands whose fre-

quencies change with the central metal ion were observed, these can be assigned to the vibrations described above, at 387, 300, and 179 cm^{-1}, respectively.

According to our results this treatment is not adequate. In our opinion, the resistance of the $C-S-$ metal angle to deformation is expected to depend on the strength of the bond between the sulfur atom of the ligand and the metal atom. This means that absorptions involving either (1) symmetrical deformation of the CSNi angles, δ_sCSN1, of species B_{1u}, or (2) antisymmetrical deformation of the CSNi angles, δ_{as}CSNi, of species B_{3u} are also expected to be dependent on the central metal ion. This is necessarily also true for the vibration in which the two ligands rock in-plane around the metal atom, ϱLig, of species B_{3u}.

In species B_{1u} the fundamental ν_{10} at 388 cm^{-1} can be described as ν_sNiS in agreement with Ojima et al.[20] The two fundamentals ν_9 and ν_{11} both involve δ_sCSNi, but their main components are other skeletal deformation vibrations, and their variation with the metal atom should only be small. The former band at 444 cm^{-1} is independent of the central metal, while the latter fundamental at 301 cm^{-1} changes at least 30 cm^{-1} from the nickel to the palladium complex. It seems that calculations and experiment disagree slightly here.

In species B_{3u} the fundamental ν_{28} at 376 cm^{-1} can be described as ν_{as}NiS. This means that according to our treatment ν_sNiS and ν_{as}NiS should be almost coincident, while Ojima et al. ascribe them to bands separated by ca. 75 cm^{-1}. We do not claim our assignment to be correct, but if the two vibrations are to be placed so far apart it is necessary to introduce a fairly big interaction force constant in the GVFF, and this seems rather unlikely in view of the mass of the nickel atom.

The fundamentals ν_{29} and ν_{30} of species B_{3u} arise from the strongly coupled ϱLig and δ_{as}CSNi modes. Only the latter fundamental has been assigned to the band near 90 cm^{-1}. It is displaced 8 cm^{-1} towards lower frequencies by replacing nickel with palladium.

In species B_{2u} the calculations show that the "flapping" motion of the ligands is strongly coupled to bending of the ligands around the S$\cdots$S line (see Fig. 2), giving rise to the fundamentals ν_{17} and ν_{19}. Only the former of these has been observed, at 179 cm^{-1}, in accordance with the results of Ojima et al. The fundamental ν_{16} at 273 cm^{-1} occurs in all dimethyldithiocarbamates and dimethyldiselenocarbamates irrespective of the nature of the central metal. According to the calulations it can be described as mainly ωCNC, i.e. the wagging motion of the dimethylamino group.

REFERENCES

1. Nakamoto, K., Fujita, J., Condrate, R. A. and Morimoto, Y. J. Chem. Phys. **39** (1963) 423.
2. Durgaprasad, G., Sathyanarayana, D. N. and Patel, C. C. Can. J. Chem. **47** (1969) 631.
3. Pilipenko, A. T. and Mel'nikova, N. V. Zh. Neorg. Khim. **14** (1969) 462; Russian J. Inorg. Chem. **15** (1970) 608. (English Transl.).
4. Jensen, K. A., Dahl, B. M., Nielsen, P. H. and Borch, G. Acta Chem. Scand. **25** (1971) 2029.
5. Jensen, K. A., Dahl, B. M., Nielsen, P. H. and Borch, G. Acta Chem. Scand. **25** (1971) 2039.

6. Jensen, K. A., Mygind, H., Nielsen, P. H. and Borch, G. *Acta Chem. Scand.* **24** (1970) 1492.
7. Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **21** (1967) 2904.
8. Agarwala, U., Lakshmi and Rao, P. B. *Inorg. Chim. Acta* **2** (1968) 337.
9. Siimann, O. and Fresco, J. *Inorg. Chem.* **8** (1969) 1846.
10. Barraclough, C. G., Martin, R. L. and Stewart, I. M. *Australian J. Chem.* **22** (1969) 891.
11. Jensen, K. A., Krishnan, V. and Jørgensen, C. K. *Acta Chem. Scand.* **24** (1970) 743.
12. Jowitt, R. N. and Mitchel, P. C. H. *J. Chem. Soc.* **A 1970** 1702.
13. Coutts, R. S. P., Wailes, P. C. and Kingston, J. V. *Australian J. Chem.* **23** (1970) 463.
14. Prabhakaran, C. P. and Patel, C. C. *Indian J. Chem.* **7** (1969) 1257.
15. McCormick, B. J., Stormer, B. P. and Kaplan, R. I. *Inorg. Chem.* **8** (1969) 2522.
16. Beurskens, P. T., Cras, J. A. and van der Linden, J. G. M. *Inorg. Chem.* **9** (1970) 475.
17. Honda, M., Komura, M., Kawasaki, Y., Tanaka, T. and Okawara, R. *J. Inorg. Nucl. Chem.* **30** (1968) 3231.
18. Kamitani, T., Yamamoto, H. and Tanaka, T. *J. Inorg. Nucl. Chem.* **32** (1970) 2621.
19. Smith, J. N. and Brown, T. M. *Inorg. Nucl. Chem. Lett.* **6** (1970) 441.
20. Ojima, I., Onishi, T., Iwamoto, T., Inamoto, N. and Tamaru, K. *Inorg. Nucl. Chem. Lett.* **6** (1970) 65.