Contribution from the Todd Wehr Chemistry Building,
Marquette University, Milwaukee, Wisconsin 53233, U.S.A.

Far-infrared Spectra of Octahedral Ni^{II} Halide Complexes Containing Nitrogen and Sulfur Donors*

C. W. Schläpfer, Yutaka Saito, and K. Nakamoto**

Received January 8, 1972

Infrared spectra of trans-$Ni(L\text{-}L')_2X_2$ *type complexes where L-L' is 2,5-dithiahexane, 2-(ethylthio)-ethylamine, 2-(methylthio)-ethylamine, and N,N-dimethylethylenediamine and X is Cl, Br, I, and* NO_3 *have been measured in the 4000-50* cm^{-1} *region. Raman spectra of some of these compounds have also been measured in the crystalline state. Band assignments have been made based on observed shifts due to metal isotope* ($^{58}Ni/^{62}Ni$) *substitution, chlorine isotope (Cl/*^{37}Cl) *substitution, ligand deuteration* (NH_2/ND_2 *and* SCH_3/SCD_3) *and ligand substitution* ($Cl/Br/I/NO_3$). *The Ni-N, Ni-S, and Ni-Cl stretching bands have been assigned at* 400-360, 260-210, *and* 260-210 cm^{-1}, *respectively. The Dq and β values of these complexes have been calculated from their electronic spectra.*

Introduction

In a previous paper,[1] we have studied the far-infrared spectra of square-planar Ni^{II} and Pd^{II} complexes of mercaptoalkylamine to study the nature of the metal-sulfur(thiolato) bond. Thus far, only a few infrared studies[2] have been reported on first row transition metal complexes of thioethers. However, no definite assignments of the metal-sulfur stretching modes have been made in these previous investigations. In order to study the metal-sulfur(thioether) bond, we have studied the infrared, Raman and electronic spectra of $Ni(L{-}L')_2X_2$ type complexes where L–L' is dth(2,5-dithiahexane),[3] ete(2-(ethylthio)-ethylamine),[4] mte(2-(methylthio)-ethylamine)[5] and adimen (N,N-dimethylethylenediamine).[6] It has been established by conductivity measurements that these complexes are not ionic[3-6] in a non-coordinating solvent such as $CHCl_3$. The electronic spectra and magnetic data indicate that these complexes take a pseudooctahedral structure.[5,7] According to X-ray analysis on $Ni(adimen)_2(NO_2)_2$,[8] two adimen ligands take a *trans* square-planar structure around the central metal and two NO_2 groups occupy the 5th and 6th sites perpendicular to the square-planar plane. The trans structure is preferred in this case mainly because of steric repulsion between methyl groups of the adimen ligands. For the same reason one would predict the trans structure for the ete and mte complexes. *Cis*-halogen complexes such as $Ni(en)_2X_2$ (X = Cl and Br)[9] and $Ni(py)_2X_2$ (X = Cl and Br)[10] tend to form polynuclear species through halogen bridges. The fact that the present $Ni(L{-}L')_2X_2$ type compounds are monomeric again suggests the *trans*-halogeno structure.

In the previous papers[1,11,15] we have assigned the Ni–X, Ni–N, and Ni–S stretching vibrations of square-planar and tetrahedral Ni complexes by using the metal isotope method. If other conditions are equal, these frequencies are expected to decrease as the coordination number increases from four to six. However, no definite band assignments have yet been established for the Ni–X, Ni–N, and Ni–S stretching vibrations of octahedral Ni^{II} complexes with a mixed coordination sphere. Thus, the main purposes of this paper are to assign these vibrations based on various isotopic shifts and to elucidate the geometrical structure of these complexes from their vibrational spectra.

Experimental Section

Preparation of Compounds. 2,5-dithiahexane(CH_3-S-CH_2-CH_2-SCH_3; dth) was purchased from City Che-

---

(*) This work was supported by an ACS-PRF unrestricted research grant(3318-C3,5).
(**) Marquette University Postdoctroral Fellow. Partly supported by a grant from Stiftung für Stipendien auf dem Gebiete der Chemie, Switzerland.

[1] C. W. Schläpfer and K. Nakamoto, *Inorg. Chim. Acta*, 6, 177 (1972).

[2] C. D. Flint and D. M. Goodgame, *J. Chem. Soc.*, (*A*), 2178 (1968).

[3] R. Backhouse, M. E. Foss and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

[4] E. Uhlig, P. Schüler and D. Diehlmann, *Z. anorg. allgem. Chem.*, *335*, 156 (1965).

[5] D. H. Bush, D. C. Jicha, M. C. Tompson, J. W. Wrathall and E. Blinn, *J. Am. Chem. Soc.*, *86*, 3642 (1964).

[6] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 5909 (1963).

[7] R. L. Carlin and E. Weissberger, *Inorg. Chem.*, *3*, 611 (1964).

[8] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman and D. Rogers, *Proc. Chem. Soc.*, 363 (1964).

[9] A. S. Antsyshkina and M. A. Porai-Koshits, *Proc. Acad. Sci. USSR., Chem. Sect.*, *142*, 143 (1962).

[10] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, *4*, 350 (1965).

[11] K. Nakamoto, K. Shobatake and B. Hutchinson, *Chem. Comm.*, 1451 (1969); B. Hutchinson, J. Takemoto and K. Nakamoto, *J. Am. Chem. Soc.*, *92*, 3335 (1970). K. Shobatake and K. Nakamoto, *ibid.*, *92*, 3339 (1970). K. Nakamoto, C. Udovich and J. Takemoto, *ibid.*, *92*, 3973 (1970). N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, *10*, 798 (1971).

[12] B.M. Gatehouse, S.E. Livingston and R.S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

[13] N. Tanaka, N. Sato and J. Fujita, *Spectrochim. Acta.*, *22*, 577 (1966).

[14] R.J.H. Clark and C.S. Williams, *J. Chem. Soc.*, *A*, 1425 (1966).

[15] K. Shobatake and K. Nakamoto, *J. Am. Chem. Soc.*, *92*, 3332 (1970).

mical Corp., New York, N. Y. 2-(Ethylthio)-ethylamine hydrochloride(C_2H_5S-CH_2-CH_2-$NH_2 \cdot HCl$; ete-HCl), asym-N,N-dimethylethylenediamine ($(CH_3)_2N$-CH_2-CH_2NH_2, adimen) and ethanol-d (C_2H_5OD) were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. Methyl iodide-d_3 (CD_3I) was purchased from Stohler Isotope Chemicals, Rutherford, N. J. ete · HCl was dissolved in 2N NaOH and the free base was extracted with ether. After drying the ether solution with sodium sulfate, it was evaporated in vacuo and the oily residue was used immediately to prepare the metal complexes.

$Ni(dth)_2X_2$,[3] $Ni(ete)_2X_2$,[4] and $Ni(adimen)_2X_2$[6] were prepared by reacting nickel halide or nitrate with the ligand according to literature methods. Deuteration of the NH_2 groups in the ete and adimen complexes was accomplished by using ethanol-d as the solvent instead of ethanol. $Ni(ete)_2I_2$ was also prepared by the alkylation of $Ni(mercaptoethylamine)_2$ as described by Busch and co-workers.[5] An attempt to prepare $Ni(mte)_2I_2$ by the same method was not successful. $Ni(mte)_2I_2$ was prepared by the following method: $Ni(mercaptoethylamine)_2$ (95 mg; 0.5 mmol) was suspended in 5 ml nitromethane containing CH_3I (264 mg; 2.0 mmol) and heated for 48 hours to 60°C in a sealed glass tube. During the reaction, a part of the product crystallized out. $Ni(mte)_2I_2$ was filtered off after cooling. $Ni(mte\text{-}d_2)_2I_2$ was prepared by the methylation of $Ni(mercaptoethylamine\text{-}d_2)_2$. Deuteration of the CH_3S group in $Ni(mte)_2I_2$ was carried out by using CD_3I instead of CH_3I.

All complexes containing metal isotopes and ^{37}Cl were prepared on a milligram scale using stable isotopes purchased from Oak Ridge National Laboratory. The purity of the isotopes was: ^{58}Ni (99.98%), ^{62}Ni (99.02%), and ^{37}Cl (96.05%). The nickel isotopes (metallic form) were dissolved in hydrogen halide to obtain isotopic nickel halides which were used to prepare the complexes. Metal complexes containing ^{37}Cl were prepared by using $Ni^{37}Cl_2$ which was prepared from $Na^{37}Cl$. A $Na^{37}Cl$ solution was converted to a $H^{37}Cl$ solution through a cation exchange column (AG 50W-X10(hydrogen form)). The eluate (20 ml) was reacted with an excess of $NiCO_3$ at 60° C. After ca. 10 ml of water was evaporated, the excess $NiCO_3$ was filtered off and the remaining solution was evaporated to dryness to yield $Ni^{37}Cl_2$.

The purity of the compounds prepared on a small scale was checked by comparing their infrared spectra with those prepared on a large scale.. The latter were identified by comparing their infrared and electronic spectra with published data[5-7].

Spectroscopic Measurements. Infrared spectra were measured on a Beckman IR-12(4000-250 cm^{-1}) and a Hitachi-Perkin-Elmer FIS-3(410-33 cm^{-1}) infrared spectrophotometer. The KBr pellet technique was used for the 4000-300 cm^{-1} region, and Nujol mull technique with polyethylene plates was used for the 410-33 cm^{-1} region. To observe small shifts due to metal isotope substitution, the spectra were run on an expanded scale with a scanning speed of 2-4 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency range. Calibration of the frequency reading was made by recording the spectra of polystyrene, indene, and water vapor.

Raman spectra were recorded on a Spex model 1401 Raman spectrophotometer equipped with an Argon-ion laser(Coherent Radiation Laboratories, Model 54). Samples used for measurements were either in a powder or a pellet form. The green (19435 cm^{-1}) or blue (20492 cm^{-1}) excitation line was used depending upon the electronic spectrum of a complex (Fig. 4). It was necessary to reduce the intensity of the exciting line to ca. 30 mW to prevent decomposition of the samples. The slit width used was 225 μ. The reproducibility of the spectra was checked by repeated scans over the desired frequency regions and found to be better than 1 cm^{-1}. The frequency reading calibration was made by using the known spectra of CCl_4 and indene. It was not possi-

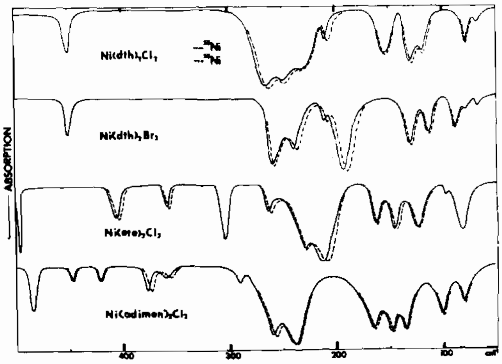

Figure 1. Far-infrared spectra and nickel isotope shifts of the $Ni(L\text{-}L')_2X_2$ type complexes.

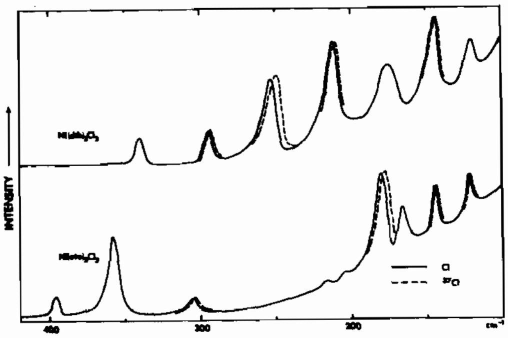

Figure 2. Raman spectra and chlorine isotope shifts of the $Ni(L\text{-}L')_2Cl_2$ type complexes.

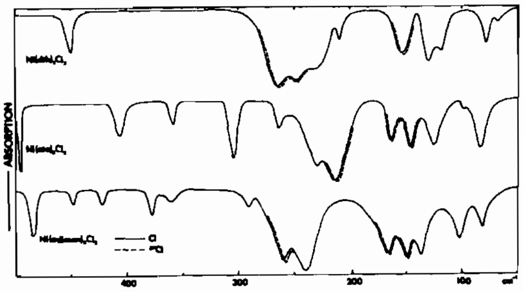

Figure 3. Far-infrared spectra and chlorine isotope shifts of the $Ni(L\text{-}L')_2Cl_2$ type complexes.

Table I. Classification of Skeletal Vibrations of $Ni(L\text{-}L')_2X_2$ Type Molecule.

D_{2h} (L=L')		C_{2h} (L≠L')	
A_g (Raman)	ν(MX)	A_g(Raman)	ν(MX)
	ν(ML)		ν(ML)
	δ(LML)		δ(LML')
	ring def (A')		ring def(A')
B_{1g} (Raman)	ν(ML)		ν(ML')
B_{2g} (Raman)	δ_s(XML)	B_g(Raman)	δ_s(XML)
B_{3g} (Raman)	δ_s(XML)		δ_s(XML')
A_u (inactive)	π(skeletal)	A_u(IR)	ν(MX)
B_{1u} (IR)	ν(MX)		π(skeletal)
	π(skeletal)		π(skeletal)
	ring def(A)		ring def(A)
B_{2u} (IR)	ν(ML)	B_u(IR)	ν(ML)
	δ(LML), ring def(B)		δ(LML'), ring def(B)
	δ_a(XML)		δ_a(XML)
B_{3u} (IR)	ν(ML)		ν(ML')
	δ(LML), ring def(C)		δ(LML'), ring def(C)
	δ_a(XML)		δ_a(XML')

ν, stretching; δ, in-plane bending (relative to the NiLL' plane); π, out-of-plane bending; a, asymmetric; s, symmetric. The ring deformation modes(A and A') (ligand vibration) were included in this table because they appear in the low frequency region and are slightly metal isotope sensitive. The ring deformation mode(B) involves a change of the LML or LML' angle inside the chelate ring whereas the ring deformation mode(C) involves a change of these angles between two chelate rings.

Table II. Observed Infrared Frequencies, Isotopic Shifts and Band Assignments for the $Ni(dth)_2X_2$ Type Compounds(cm^{-1}).

X=Cl			Br		I	NO_3	
$\nu(^{58}Ni)$	Δν[a]	Δν[b]	$\nu(^{58}Ni)$	Δν[a]	ν	ν	Assignment
450	0	0	450	0	450	450	Ligand
266.7	5.0	3.0	192.6	3.5	150	333	ν(MX)
247.8	1.8	1.2	258.7	1.0	258	264	ring def(A)
232	[c]	[c]	238.9	2.5	242	241	ν(MS)
209.6	4.0	0	209.7	3.0	205	210	ν(MS)
154.2	0.8	1.5	113.4[d]	1.5	90[d]	158	δ_a(XMS)
130.8	1.5	0	130.5	1.0	132	126	ring def(B)
118.1	0.5	0.7	113.4[d]	1.5	110	112	π(skeletal)
79.0	0.5	0	88.7	1.0	90[d]	96	ring def(C)
68.0	0	0	68.0	0	68	69	lattice?

[a] $\Delta\nu = \nu(^{58}Ni)-\nu(^{62}Ni)$. [b] $\Delta\nu = \nu(Cl)-\nu(^{37}Cl)$. [c] Too broad to observe isotopic shifs. [d] Overlapped band.

ble to observe the Raman spectra of the adimen complexes below 400 cm^{-1} because of strong background scattering in the low frequency region. The Raman spectra of all the iodo complexes could not be observed because of the decomposition of the compounds due to absorption of the blue and green excitation lines. These compounds are also decomposed by absorbing the red excitation lines such as that of 15454 cm^{-1} (Kr) and 15802 cm^{-1} (He-Ne) (See Fig. 4).

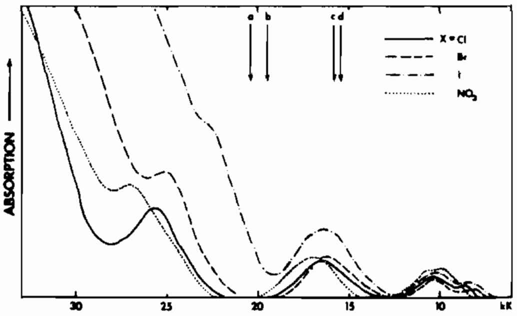

Figure 4. Electronic absorption spectra of the $Ni(ete)_2X_2$ type complexes. a,b,c and d indicate the frequencies of the blue(Ar-ion laser, 20492 cm^{-1}), green(Ar-ion laser, 19435 cm^{-1}), red(He-Ne laser, 15802 cm^{-1}) and red(Kr laser, 15454 cm^{-1}) excitation lines, respectively.

The electronic absorption spectra of the solid samples in Nujol mulls were recorded on a Cary Model 14 recording double beam spectrophotometer.

Results and Discussion

As stated in the introduction, the structure of the $Ni(L\text{-}L')_2X_2$ type compounds studied is probably *trans*. This has been confirmed by the facts that the mutual exclusion rule holds between infrared and Raman spectra (For example, compare Tables II and III and that no metal isotopic shifts have been observed in Raman spectra. In the following vibrational analysis, we consider a trans-octahedral seven-atom skeleton since our main interest is in the skeletal vibrations. The symmetry of such a model is D_{2h} for L=L' and C_{2h} for L≠L'.

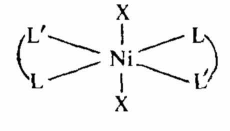

Table I gives the classification of the 15 skeletal vibrations and 2 ligand vibrations (ring def. A and A') of such a model under the D_{2h} and C_{2h} symmetry.

In order to assign the observed infrared and Raman spectra, we have studied band shifts due to the following substitutions:

(1) *Metal isotope substitution.* All metal-ligand stretching modes are expected to give a shift of 10∼2 cm^{-1} by the ^{58}Ni-^{62}Ni substitution.[11] Metal isotope shifts of ring deformation and other bending modes (2∼0 cm^{-1}) are much smaller than those of stretching modes.[11] Figure 1 shows the far-infrared spectra of four ^{58}Ni complexes and their ^{62}Ni analogs studied in this paper. No metal isotope shifts are expected for the Raman spectra of mononuclear metal complexes having a center of symmetry.

(2) *Chlorine isotope substitution.* The Ni-Cl stretching, Cl-Ni-S, Cl-Ni-N and other bending modes involving the displacement of the Cl atom should be shifted by the Cl-^{37}Cl substitution. As are shown in Figs. 2 and 3, the Cl isotope shifts are observed both in infrared and Raman spectra.

(3) *Ligand deuteration.* In the ete and adimen complexes, deuteration of the NH_2 hydrogens causes the low-frequency shifts of the Ni-NH_2 stretching and ring deformation bands (A, B and C). Among the latter, the ring deformation mode (B) gives a large shift relative to others.[1] In the mte complex, deuteration of the SCH_3 hydrogens causes the large shifts of the ring deformation modes (B) and (C) since they involve a change in the CH_3S-Ni-NH_2 angle.

(4) *Ligand substitution.* All the modes involving the motion of the anion (X) should be shifted markedly when X is changed from Cl to Br, for example. Thus, the Ni-X stretching, X-Ni-N and X-Ni-S bending modes should be markedly sensitive to the anion (X) substitution. All the nitrate complexes studied exhibit bands typical of the unidentate nitrato group (1480, 1270, 1015 and 800 cm^{-1})[12].

(5) *Vibraional coupling.* Vibrational coupling may occur between two modes if they belong to the same symmetry species and if their frequencies are relatively close to each other. In such a case, a mode which is not expected to be isotope-sensitive may show a small isotopic shift due to vibrational coupling with an isotope-sensitive band.

$Ni(dth)_2X_2$. Figure 1 shows the far-infrared spectra of $Ni(dth)_2X_2$ (X=Cl and Br) and Table II lists the observed infrared frequencies, isotopic shifts and band assignments of all the dth complexes studied. As is shown in Table I, two Ni-S and one Ni-X stretching modes are infrared active in trans-$Ni(dth)_2X_2$ (D_{2h} symmetry). In the ^{58}Ni-bromo complex, three bands at 238.9, 209.7 and 192.6 cm^{-1} give large shifts relative to other bands (Table II). However, the 192.6 cm^{-1} band is shifted to 150 cm^{-1} when Br is substituted by I. Thus, two bands at 238.9 and 209.7 cm^{-1} are assigned to the Ni-S stretching while the 192.6 cm^{-1} band is assigned to the Ni-Br stretching mode. The band at 258.7 cm^{-1} is assigned to the ring deformation (A). This band is slightly sensitive to the metal-isotope substitution and appears consistently in all the dth compounds studied.

The spectrum of the chloro complex is complicated because the Ni-Cl stretching, ring deformation (A) and two Ni-S stretching bands are located closely. The nickel isotope data show that two bands at 266.7 and 209.6 cm^{-1} of the ^{58}Ni-chloro complex give large shifts relative to others. The former gives a marked shift of 3.0 cm^{-1} by the Cl–^{37}Cl substitution, and is assigned to the Ni-Cl stretching mode. Then, the 209.6 cm^{-1} band must be assigned to the Ni-S stretching mode. Two shoulder bands at 247.8 and 232 cm^{-1} are assigned to the ring deformation (A) and Ni-S stretching modes respectively, although their metal isotope shifts could not be observed clearly. It is interesting to note that the ring deformation mode (A) of the chloro complex shows a shift of 1.2 cm^{-1} by the Cl-^{37}Cl substitution indicating the presence of vibrational coupling between this and the Ni-Cl stretching modes in the B_{1u} species (Table 1). Previously, vibrational coupling similar to this was noted in a polarized infrared study of trans-$[Co(en)_2Cl_2]^+$ ion[13]. Each complex exibits five bands below 200 cm^{-1}. These bands are much more difficult to assign than those above 200 cm^{-1}. In Table II, we have made tentative assignments by considering the criteria mentioned above. The spectra of the iodo and nitrato complexes have been assigned based on theri similarity to those of the chloro and bromo complexes.

Table III lists the observed Raman frequencies of the $Ni(dth)_2X_2$ type complexes. In agreement with the D_{2h} symmetry, no metal isotope shifts have been observed in the Raman spectra of these complexes. Both Fig. 2 and Table III show that $Ni(dth)_2Cl_2$ exhibits four bands which are shifted by the Cl-^{37}Cl substitution. The 252.8 cm^{-1} band which gives the largest Cl isotopic shift (2.0 cm^{-1}) can be assigned to the Ni-Cl stretching mode of the A_g species. As is seen in Table I, the Ni-Cl stretching, Ni-S stretching and ring deformation modes (A') belong to the same symmetry species. Furthermore, their frequencies are close to each other. Thus, all these three modes seem to couple strongly to cause chlorine isotopic shifts. All the band assignments given for the chloro complex have been confirmed by comparing its Raman spectrum with those of the bromo and nitrato complexes.

$Ni(ete)_2X_2$. Figure 1 illustrates the infrared spectra of $Ni(ete)_2Cl_2$ (^{58}Ni and ^{62}Ni) and Table IV lists the observed infrared frequencies and band assignments of the $Ni(ete)_2X_2$ type complexes. Band assignments of the chloro complex have been made based on the observed shifts due to metal isotope substitution, chlorine isotope substitution and ligand (NH_2 group) deuteration. The M-N stretching bands are expected to show relatively large shifts by the NH_2 group deuteration and metal isotope substitution but small shifts by the chlorine isotope substitution. Thus, the band at 405.8 cm^{-1} of $^{58}Ni(ete)_2Cl_2$ has been assigned to this mode. The M-Cl stretching mode is expected to be most sensitive to the chlorine isotope substitution and fairly sensitive to the

Table III. Observed Raman Frequencies, Isotopic Shifts and Band Assignments for the Ni(dth)$_2$X$_2$ and Ni(ete)$_2$X$_2$ Type Complexes (cm^{-1}).

dth Complexes				free	ete Complexes					
X=Cl		Br	NO$_3$	dth	X=Cl			Br	NO$_3$	
ν	$\Delta\nu^{a}$	ν	ν	ν	ν(Cl)	$\Delta\nu^{a}$	$\Delta\nu^{b}$	ν	ν	Assignment
443.0	0	443	443	443	—	—	—	—	—	Ligand(dth)
—	—	—	—	—	396.0	0	6.0	397	400	ν(MN)
341.0	0	342	338	345	—	—	—	—	—	Ligand(dth)
295.2	1.4	296	290	—	358.7	0.0	11.0	359	355	ring def (A')
252.8^{c}	2.0	196	284	—	180.1	1.5	2.0	150	200	ν(MX)
252.8^{c}	—	254	254	254	—	—	—	—	—	Ligand(dth)
212.4	1.4	215	206	—	305.6	1.5	6.0	309	305	ν(MS)
—	—	—	—	—	218.0	0	0	220	200^{c}	Ligand(ete)
—	—	—	—	—	202.0	0	3.0	202	200^{c}	Ligand(ete)
175.4	0	172	173	—	—	—	—	—	—	ν(MS)
145.2	1.0	110	147	—	145.5	1.0	5.0	123	—^{d}	δ(XML)
					124.0	1.0	2.0	112	—^{d}	δ(XML)
120.0	0	120	120	—	166.3	0	1.0	165	166	δ(LML)

^{a} ν(Cl)—ν(^{37}Cl). ^{b} ν(NH$_2$)—ν(ND$_2$). ^{c} overlapped band. ^{d} not observed.

Table IV. Observed Infrared Frequencies, Isotopic Shifts and Band Assignments for the Ni(ete)$_2$X$_2$ and Ni(mte)$_2$X$_2$ Type Complexes (cm)$^{-1}$.

Ni(ete)$_2$X$_2$							Ni(mte)$_2$I$_2$				
X=Cl				Br	I	NO$_3$					
ν(^{58}Ni)	$\Delta\nu^{a}$	$\Delta\nu^{b}$	$\Delta\nu^{c}$	ν	ν	ν	ν(^{58}Ni)	$\Delta\nu^{a}$	$\Delta\nu^{c}$	$\Delta\nu^{d}$	Assignment
496	0.0	0.0	2.0	490	490	490	480	0.0	5.0	0.0	Ligand
405.8	2.7	0.0	11.0	410	412	416	412	1.9	6.0	1.0	ν(MN)
368.1	2.2	0.0	6.0	367	363	372	495	1.0	6.0	0.0	ring def(A)
305.0	0.0	0.0	7.0	302	298	296	—	—	—	—	Ligand(ete)
263.5	2.0	0.0	3.0	268	268	260	268.3	2.0	1.0	2.9	ν(MS)
229.4	1.5	0.5	9.0	226	230	224	250.1	1.3	6.3	7.3	ring def(B)
212.3	4.5	1.9	4.0	154	132	240	140.0	1.0	0.0	1.5	ν(MX)
163.1	1.2	0.0	3.0	165	163	163	225.5	1.5	1.1	12.0	ring def(C)
149.5	1.4	1.2	1.0	126	112	148	128.7	1.5	2.0	0.0	δ_a(XMN)
126.8	1.0	1.5	0.0	98^{e}	84	128	89	0.0	0.0	0.0	δ_a(XMS)
98	0.0	0.0	0.0	98^{e}	98	100	102.1	0.0	0.0	0.0	π(skeletal)
84	0.0	0.0	0.0	76	68	—	75	0.0	0.0	0.0	

^{a} $\Delta\nu$ = ν(^{58}Ni)—ν(^{62}Ni). ^{b} $\Delta\nu$ = ν(Cl)—ν(^{37}Cl) ^{c} $\Delta\nu$ = ν(NH$_2$)—ν(ND$_2$). ^{d} $\Delta\nu$ = ν(SCH$_3$)—ν(SCD$_3$). ^{e} overlapped band.

metal isotope substitution. Thus, the band at 212.3 cm^{-1} has been assigned to this mode. The M-S stretching band should be sensitive to the metal isotope substitution but not sensitive to the chlorine isotope substitution. Thus, the band at 263.5 cm^{-1} has been assigned to this mode. These band assignments have also been confirmed by the results obtained for Ni(mte)$_2$I$_2$ shown in Table IV.

As shown in our previous paper[1], all the three ring deformation modes (A, B and C) are shifted slightly by the metal isotope substitution. Furthermore, both ring deformation modes A and B give large shifts by the deuteration of the NH$_2$ group. These trends have also been observed for the ete and mte complexes shown in Table IV. The ring deformation modes(B and C) are sensitive to the substitution of the S-alkyl group, indicating the presence of vibrational coupling between these modes and low-frequency S-alkyl vibrations. It is interesting to note that the frequencies of three ring deformation modes of the ete and mte complexes(Table IV) are much higher than those of the dth complexes(Table II). This is mainly due to the fact that the former complexes contain the NH$_2$ group which forms a much stronger metal-ligand bond than the S(alkyl) group of the latter.

Table III lists the observed Raman frequencies, isotopic shifts and band assignments. The Raman spectrum of Ni(ete)$_2$Cl$_2$ is shown in Figure 2. No Raman bands shows metal isotope shifts, indicating the presence of a center of symmetry in this molecule. However, four bands show relatively large shifts by the chlorine isotope substitution. As is seen in Table I, vibrational coupling is expected between the MX, MN and MS stretching and other bending modes in the A$_g$ species. It is not possible, therefore, to give clear-cut assignments from the chlorine isotope experiment. The assignments listed in Table III have been made based on the results of the anion substitution studies and the infrared studies shown in Table IV.

Ni(adimen)$_2$X$_2$. Figure i shows the infrared spectra of Ni(adimen)$_2$Cl$_2$ (^{58}Ni and ^{62}Ni) and Table V lists the observed frequencies, isotopic shifts and band assignments of the Ni(adimen)$_2$X$_2$ type complexes. The iodo complex was not included in this paper because its infrared spectrum cannot be explained in terms of the theoretical analysis shown in Table I. It is highly probable that this complex is not pseudooctahedral since its electronic spectrum and magnetic property are different from those of other halogeno complexes.[6]

According to X-ray analysis on Ni(adimen)$_2$(NO$_2$)$_2$,[8]

Table V. Observed Infrared Frequencies, Isotopic Shifts and Band Assignments for the $Ni(adimen)_2X_2$ Type Complexes (cm^{-1}).

X=Cl				Br	NO_3	
$\nu(^{58}Ni)$	$\Delta\nu$ [a]	$\Delta\nu$ [b]	$\Delta\nu$ [c]	ν	ν	Assignment
484	0	0	10.0	490	490	Ligand
447	1.0	0	3.0	450	450	ring def(A)
422	1.0	0	2.0	425	425	
378.1	4.0	0	4.0	374	380	$\nu(M\text{-}NH_2)$
360.0	5.0	0	0.0	364	368	$\nu(M\text{-}N(CH_3)_2)$
290.0	0	0	0	296	300	Ligand
260.7	2.5	2.0	1.2	190	280	$\nu(M\text{-}X)$
242.8	1.2	0	10.0	245	248	ring def(B)
172.5	1.5	1.0	2.0	138 [d]	209	$\delta_a(XMNH_2)$
149.2	1.5	1.5	0.0	122	185	$\delta_a(XMN(CH_3)_2)$
137.5	1.0	0	6.0	138 [d]	148	ring def(C)
102.0	1.0	0	4.0	100	116	π(skeletal)
83.0	0	0	0	85	88	

[c] $\Delta\nu = \nu(NH_2)-\nu(NH_2)$. [b] $\Delta\nu = \nu(Cl)-\nu(^{37}Cl)$. [a] $\Delta\nu = \nu(^{58}Ni)-\nu(^{62}Ni)$. [d] Overlapped band.

two adimen ligands form a trans square-planar skeleton around the central atom. However, the $Ni-(CH_3)_2$ distance is different from the $Ni-NH_2$ distance. Thus, the symmetry of the NiN_4O_2 skeleton is approximated as C_{2h}. As is seen in Figure 1 and Table V, two bands at 378.1 and 360.0 cm^{-1} of the ^{58}Ni-chloro complex show large shifts relative to others when ^{58}Ni is substituted by ^{62}Ni. Furthermore, the former gives a large shift by the deuteration of the NH_2 group. Therefore, the 378.1 cm^{-1} band was assigned to the $Ni-NH_2$ stretching whereas the 360.0 cm^{-1} band was assigned to the $Ni-N(CH_3)_2$ stretching mode. The band at 260.7 cm^{-1} is sensitive to the chlorine isotope as well as the metal isotope substitution. This band has been assigned to the Ni–Cl stretching mode. Other bending modes have been assigned by considering their frequencies and the effects of various substitutoins on these modes.

Summary on Far-Infrared Spectra. Figure 3 shows the far-infrared spectra of the $Ni(L-L')_2Cl_2$ type complexes where L–L′ is dth, ete and adimen. The ^{37}Cl isotope spectra are shown by dotted lines only for those bands which are sensitive to such isotopic substitution. As discussed previously, the ^{58}Ni–Cl stretching mode has been assigned to the strong bands at 266.7 (dth), 212.3 (ete) and 260.7 (adimen) cm^{-1} based on the chlorine isotope and other data. In the dth complex, the band at 247.7 cm^{-1} ring deformation (A) is also shifted to a lower frequency since this mode couples with the Ni–Cl stretching mode. All three complexes exhibit chlorine-isotope sensitive bands between 170 and 120 cm^{-1}. These bands have been assigned to the Cl–Ni–S or Cl–Ni–N bending mode. This mode splits into two bands in the ete and adimen complexes since these ligands are not symmetrical. It is interesting to note that both Ni–Cl stretching and Cl–Ni–L bending frequencies depend upon the nature of the L–L′ ligand; both frequencies are higher in the dth and adimen complexes than in the ete complex. This result will be discussed later in connection with the Ni–N and Ni–S stretching frequencies. In any case, these Ni–Cl stretching frequencies of octahedral complexes are close to those already reported; monomeric $Ni(py)_4Cl_2$ (246 cm^{-1})[10], and polymeric $Ni(NH_3)_2Cl_2$ (240 cm^{-1}).[14] As expected, these frequencies are much lower than those of tetrahedral (340-300 cm^{-1}) and trans square-planar (near 400 cm^{-1}) complexes.[15]

Previously, the Ni–N stretching band of the $[Ni(NH_3)_6]^{2+}$ ion (NiN_6 skeleton) has been assigned at 330 cm^{-1}.[16] The Ni–N stretching bands of $Ni(adimen)_2Cl_2$ (N_4Cl_2 skeleton) are at 380-360 cm^{-1} and that of $Ni(ete)_2Cl_2$ ($N_2S_2Cl_2$ skeleton) is at 406 cm^{-1}. Finally, the Ni–N stretching frequency of polymeric $Ni(NH_3)_2Cl_2$ which consists of a NiN_2Cl_4 skeleton is at 435 cm^{-1}.[14] Thus the octahedral Ni–N stretching frequency increases as the nitrogen atom of the NiN_6 skeleton is replaced by another atom.

In the present work, the Ni–S(thioether) stretching bands of the dth and ete complexes have been assigned in the range between 265 and 210 cm^{-1}. These frequencies are lower than those found for Ni(mercaptoethylamine)$_2$ (377 and 330 cm^{-1}) because the latter is four-coordinate (planar) and involves the Ni–S (thiolate) bond which is expected to be stronger than the Ni–S (thioether) bond.

As stated above, the Ni–Cl stretching frequency of the ete complex is lower than that of the dth and adimen complexes. On the other hand, the Ni–S stretching frequency of the ete complex is higher than those of the dth complex and the Ni–N stretching frequency of the ete complex is higher than those of the adimen complex. These results seem to suggest that the Ni–Cl bonds of the ete complex are weaker than those of the dth and adimen complexes and that the Ni–S and Ni–N bonds of the ete complex are stronger than those of the dth and adimen complexes. The molecular models of these complexes indicate that the dth and adimen complexes are more crowded in the $Ni(L-L')_2$ plane than the ete complexes. This crowding may cause a slight expansion of the chelate ring in the former relative to the latter complexes. Thus the Ni–L(L′) stretching frequencies of the former may be lower than those of the latter whereas the Ni–Cl stretching frequencies of the former are higher than that of the latter.

Electronic Spectra. Figure 4 shows the electronic spectra of the $Ni(ete)_2X_2$ type complexes, and Table

---

(16) L. Sacconi, A. Sabatini and P. Gans, *Inorg. Chem.*, 3, 1772 (1964).

Table VI. Absorption Maxima of Electronic Spectra of $Ni(L\text{-}L')_2X_2$ Type Complexes (KK).

$^3A_{2g}\longrightarrow$					$^3T_{2g}$		10Dq		β	
		$^3T_{1g}$	$^3T_{1g}$	^1E_g	^3E_g	$^3B_{2g}$	Exp.	Theor.	Exp.	Theor.
$Ni(dth)_2X_2$	X=Cl	24.0	14.9	—	9.6	8.9	9.4	9.3	0.69	0.71
	Br	23.5	14.6	—	9.4	8.7	9.1	9.2	0.69	0.70
	I	22.2	14.9	—	9.0	8.4	8.9	9.1	0.67	0.68
	NO_3	26.0	16.6	—	10.7	9.9	10.4	10.1	0.73	0.75
$Ni(ete)_2X_2$	X=Cl	25.6	16.2	—	10.6	8.4	9.9	9.4	0.78	0.76
	Br	25.2	16.0	—	10.7	8.2	9.9	9.3	0.78	0.75
	I	23.0	16.4	—	10.4	8.1	9.6	9.3	0.74	0.74
	NO_3	27.4	16.9	—	10.8	10.0	10.5	10.4	0.82	0.80
$Ni(adimen)_2X_2$	X=Cl	25.9	16.0	12.9	—	9.6	9.6	9.6	0.84	0.82
	Br	24.9	15.2	11.9	—	9.4	9.4	9.5	0.83	0.81
	NO_3	27.2	17.1	12.7	10.4	9.4	10.1	10.5	0.90	0.87

VI lists the values of the observed absorption maxima. All these complexes exhibit three bands due to spin-allowed d–d transitions of the octahedral Ni^{II} system.[17] The $Ni(adimen)_2X_2$ series exhibits the spin-forbidden $^3A_{2g}$–^1E_g transition as a weak band at ca. 12×10^3 cm^{-1}. In general, the $^3A_{2g}$–$^3T_{2g}$ transition of the O_h complex splits into two bands when the symmetry is lowered from O_h to D_{4h}. As is seen in Figure 4 and Table VI, this splitting has been observed for all the $Ni(ete)_2X_2$ complexes studied. Thus, the symmetry of these complexes can be taken as D_{4h} although their actual symmetry is D_{2h}. This result suggests that the spectroscopic characteristics (D_q and β) of the S donor (thioether) are very similar to those of the N donor (amine) as pointed out by Jörgensen.[18] In Table VI, he have computed the D_q and β values from the observed spectra. For the $^3A_{2g}$–$^3T_{2g}$ transition we took the baricenter of the two bands, considering the weights of individual transitions according to their degeneracies. The energy of $^3B_{2g}$ is in this case smaller than that of ^3E_g, due to the large D_q values of the ligands in the square-planar plane. These values have been compared with theoretical values calculated by assuming the rule of an average environment and by using literature values given for these individual donor atoms.[17] The values for NO_3 and I were estimated to fit the observed frequencies since they are not given in literature. Their values are NO_3: 10 Dq = 1000 cm^{-1}. β = 0.85; I: $10D_q$ = 650 cm^{-1}, β = 0 65. As is shown in Table VI, the theoretical D_q values are in good agreement with the experimental values for all the complexes studied.

The theoretical β values for the dth and ete complexes become too large with the β values given in literature (0.84).[17] It was noted that the deviation of the β value of the ete complexes is about one half of that of the dth complex. This result suggests that the literature value of the thioether group is too large. In Table VI we have calculated the theoretical β values by using 0.70 for the thioether group. With this new β value, good agreement between experimental and theoretical values is achieved, as is seen in Table VI.

(17) L. Sacconi, *Transition Metal Chem.*, *4*, 199 (1968).
(18) C.K. Jörgensen, *J. Inorg. Nucl. Chem.*, *24*, 1571 (1962).