vs. time data covering 4 half-lives were in general used and the fit to the equation was in general within the uncertainty of the absorbance measurements.

Registry No. $[Pt(NH_3)_4ClN_3]Cl_2$, 54566-84-6; $[Pt(C_2H_8N_2)_2ClN_3]Cl_2$, 54566-85-7; *trans*-$Pt(NH_3)_4Cl_2{}^{2+}$, 16986-23-5; *trans*-$Pt(en)_2Cl_2{}^{2+}$, 29646-65-9; $N_3{}^-$, 14343-69-2.

References and Notes

(1) (a) NSF undergraduate research participant. (b) Abstracted in part from the Ph.D. thesis of W.L.D.
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Infrared Spectra and Normal-Coordinate Analysis of 1,2-Dithiolate Complexes with Nickel

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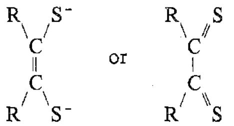
The infrared spectra of ten 1,2-dithiolate complexes of the type $[Ni(S_2C_2R_2)_2]^x$, where R is H, C_6H_5, CF_3, or CN and x is 0, 1−, or 2−, have been obtained. Nickel isotope substitution has been carried out to assign the Ni–S stretching modes. Normal-coordinate analyses have been made on all ten complexes to calculate the force constants as well as to give theoretical band assignments. The effects of changing the charge of the complex (x) and the substituent (R) on the stretching force constants have been discussed in terms of the Hückel MO theory.

Introduction

Metal complexes of 1,2-dithiolates or dithienes have been of great interest to inorganic chemists mainly because of their redox properties.[1,2] The oxidation state of the metal in dithienes is difficult to determine empirically. For example, the formal oxidation state of the metal in $Ni(S_2C_2R_2)_2$ may be +4 or 0 depending upon whether the ligand is regarded as a dinegative ion or a neutral species



The situation is more complicated if we consider a series of complexes such as $Ni(S_2C_2R_2)_2$, $[Ni(S_2C_2R_2)_2]^-$, and $[Ni(S_2C_2R_2)_2]^{2-}$ which have different net charges but almost identical geometrical structures.[3] Thus, the study of electron distribution in metal dithienes has been of particular interest to physical inorganic chemists. In fact, EPR spectra,[4] electronic spectra,[5] and X-ray photoelectron spectra[6] have been studied, and semiempirical MO calculations[7] have been made on metal dithienes.

As for vibrational spectra, Schrauzer and Mayweg[7] assigned the high-frequency infrared spectra and noted that the C=C stretching band gives the largest shift to a higher frequency as the negative charge of the complex increases. Adams and Cornell[8] assigned the metal–sulfur stretching bands of dithiene complexes (R = H, CF_3) and noted a slight decrease in frequency as the negative charge of the complex increases. Lakshmi et al.[9] reported the results of normal-coordinate analysis on the 1:1 metal–ligand model of the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ ion. This was followed by Siiman and Fresco,[10] who carried out normal-coordinate analyses on neutral dithiene complexes with nickel, palladium, and platinum. However, these previous investigations led to conflicting assignments. Furthermore, no systematic studies have been made on the effects of changing the charge of the complex (x) and the substituent (R) on the infrared spectra of the $[Ni(S_2C_2R_2)_2]^x$ type complexes. In this paper, we have prepared ten dithiene complexes where R is H, C_6H_5, CF_3, or CN and n is 0, 1−, or 2− and assigned their infrared spectra based on nickel isotope shifts[11] and normal-coordinate analysis. The effects of changing R and x have been expressed in terms of force constants. An attempt has been made to interpret the changes in force constants by combining the Hückel MO theory with Gordy's equation.

Table I. Analytical Data

	% Ni		
	Calcd	Found	Ref
$Ni(S_2C_2H_2)_2$	24.56	24.45	11
$N(C_2H_5)_4[Ni(S_2C_2H_2)_2]$	15.89	15.98	11
$Ni(S_2C_2(CF_3)_2)_2$	11.48	11.35	12
$N(C_2H_5)_4[Ni(S_2C_2(CF_3)_2)_2]$	9.15	9.28	12
$[N(C_2H_5)_4]_2[Ni(S_2C_2(CF_3)_2)_2]$	7.60	7.75	12
$Ni(S_2C_2(C_6H_5)_2)_2$	10.80	10.65	13
$N(C_2H_5)_4[Ni(S_2C_2(C_6H_5)_2)_2]$	8.71	8.62	12
$(N_2H_5)_2[Ni(S_2C_2(C_6H_5)_2)_2]$	9.63	9.42	13
$N(C_2H_5)_4[Ni(S_2C_2(CN)_2)_2]$	13.67	13.54	12
$[N(C_2H_5)_4]_2[Ni(S_2C_2(CN)_2)_2]$	10.49	10.32	14

Experimental Section

All the complexes were prepared by the literature method.[12-15] The references for preparation are given in Table I. It also gives the results of nickel analysis obtained by complexometric titration. The purity of these compounds was checked by comparing their physical properties (melting point, spectra, etc.) with published data. The complexes containing nickel isotopes were prepared on a milligram scale using ^{58}Ni (99.98% pure) and ^{62}Ni (99.02% pure) purchased from Oak Ridge National Laboratory. The purity of these isotopic compounds was checked by comparing their infrared spectra with published data.

The infrared spectra were recorded on a Beckman IR 12 (4000–250 cm^{-1}) or a Perkin-Elmer Model 457 (4000–300 cm^{-1}) in KBr pellets or as Nujol mulls and on a Hitachi Perkin-Elmer FIS-3 far-infrared spectrophotometer (400–50 cm^{-1}) as Nujol mulls sandwiched between

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Table II. Structural Parameters[a]

	R			
	H	C_6H_5	CF_3	CN
Ni–S, Å	2.15	2.10	2.13	2.15
S–C, Å	1.71	1.71	1.70	1.72
C–R, Å	1.08	1.36	1.45	1.37
C≡N, Å				1.13
∠SMS, deg	88	91	91	91
∠SMS′, deg	92	89	89	89
∠MSC, deg	103	106.5	105.5	106.5
∠SCR, deg	119	120	120	118
∠CCN, deg				179

[a] Taken from ref 3.

polyethylene plates. To observe small shifts due to metal isotope substitution, far-infrared spectra were measured on an expanded scale with a scanning speed of 2 cm^{-1}/min. Reproducibility of the frequency reading was checked by multiple scans over the desired frequency range. Frequency reading was calibrated by recording the spectra of polystyrene, indene, and water vapor.

Normal-Coordinate Analysis

Figure 1 shows the 1:2 metal–ligand model of the nickel–dithiene complex used for our calculation. The substituent (R) was assumed to be a point mass. This model gives 33 normal vibrations which are classified into 6 A_g + 5 B_{1g} + 2 B_{2g} + 2 B_{3g} + 3 A_u + 3 B_{1u} + 6 B_{2u} + 6 B_{3u} under D_{2h} symmetry. In this paper, we have calculated only 12 in-plane infrared-active modes (B_{2u} and B_{3u}) by using Wilson's **GF** matrix method.[16] In the case of R = CN, the CN group was treated as a diatomic system, and 16 (8 B_{2u} + 8 B_{3u}) in-plane infrared-active modes have been calculated for the $[Ni(S_2C_2(CN)_2)_2]^x$ series.

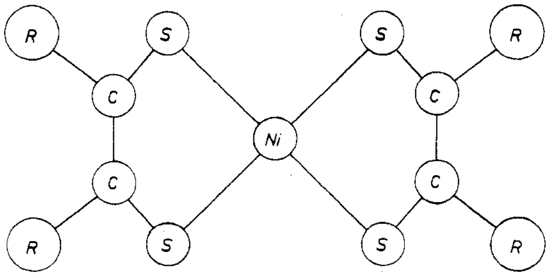


Figure 1. Structure of the $[Ni(S_2C_2R_2)_2]^x$ complex.

The **G** matrix elements were evaluated by using the structural parameters listed in Table II. It was assumed that these values do not change appreciably by changing the oxidation state of the complex. This assumption does not cause serious errors in our calculations since the vibrational frequency is much more sensitive to the change in force constants than those in bond distances and angles. The symmetry coordinates used are given elsewhere.[10,17]

The **F** matrix was expressed by using the Urey–Bradley force field consisting of 4 stretching (*K*), 6 bending (*H*), and 6 repulsive (*F*) force constants.[18] An initial set of force constants has been taken from those of $Ni(S_2C_2H_2)_2$,[10] $Ni(sacsac)_2$ (sacsac = dithioacetylacetone),[19] $Pd(S_2C_2O_2)_2$,[10] and $Pd(S_2CNH_2)_2$.[21] Table III lists the final sets of force constants obtained for ten compounds. As is seen in Table III, four bending and four repulsive constants which do not involve the R group were kept constant in all cases. Furthermore, only four stretching constants were adjusted for a series of complexes in which R is the same and *x* is different, since the changes in bending and repulsive force constants are much smaller than those in stretching force constants. As is shown in Tables IV–VII, the agreement between calculated and observed

Table III. Urey-Bradley Force Constants of $[Ni(S_2C_2R_2)_2]^x$ Complexes (mdyn/Å)[a]

		K(Ni–S)	*K*(C–S)	*K*(C–R)	*K*(C=C)	*H*(SCR)	*H*(CCR)	*F*(R· · ·S)	*F*(R· · ·C)
R = H	$x = 0$	1.46	3.34	4.19	4.46	0.17	0.16	0.45	0.60
	$x = 1-$	1.34	3.05	4.18	5.36	0.17	0.16	0.45	0.60
R = C_6H_5	$x = 0$	1.64	3.24	2.80	4.44	0.10	0.10	0.80	0.70
	$x = 1-$	1.39	2.93	3.42	5.30	0.10	0.10	0.80	0.70
	$x = 2-$	1.33	2.88	3.53	6.12	0.10	0.10	0.80	0.70
R = CF_3	$x = 0$	1.52	2.95	3.25	5.02	0.28	0.30	0.50	0.35
	$x = 1-$	1.40	2.84	3.11	5.68	0.28	0.30	0.50	0.35
	$x = 2-$	1.22	2.69	3.03	6.24	0.28	0.30	0.50	0.35
R = CN	$x = 1-$	1.53	3.20	3.48	4.99	0.26	0.30	0.60	0.70
	$x = 2-$	1.27	2.98	3.86	5.49	0.26	0.30	0.60	0.70

[a] The values of other force constants (mdyn/Å) were fixed for all the compounds studied: *H*(CCS) = 0.55; *H*(SNiS) = 0.08; *H*(SNiS′) = 0.08; *H*(NiSC) = 0.20; *F*(C· · ·S) = 0.80; *F*(S· · ·S) = 0.07; *F*(S· · ·S′) = 0.06; *F*(Ni· · ·C) = 0.0. For R = CN, δ(CCN) = 0.25 and *K*(CN) was taken as 16.9 and 16.7 mdyn/Å, respectively, for *x* = 1– and 2–.

Table IV. Comparison of Observed and Calculated Frequencies of Bis(ethylene-1,2-dithiolato)nickel (cm^{-1})[a]

	$[Ni(S_2C_2H_2)_2]$		$[Ni(S_2C_2H_2)_2]^-$ [b]		
	Obsd	Calcd	Obsd	Calcd	Assignment[c]
B_{2u}	3018 m	3013.9	3010 sh	3011.6	ν(C–H)
	1350 s, 1358 sh	1353.0	1435 s	1433.6	ν(C=C)
	1110 m, 1098 s	1108.2	1105 m	1112.2	δ(C–H)
	798 m	812.9	790 sh	787.5	ν(C–S)
	428 (6.5) m	426.9 (7.3)	411.5 (8.0) m	411.8 (7.0)	ν(Ni–S)
	237 (2.5) m	230.0 (1.7)	233 (2.0) w	230.2 (1.7)	δ(SNiS)
B_{3u}	3030 m	3034.2	3040 m	3031.1	ν(C–H)
	1295 m, 1260 w	1259.0	1285 vw, 1273 m	1253.1	δ(C–H)
	878 s, 865 w	864.0	840 s	847.5	ν(C–S) + ring def
	735 s	733.6	705 sh, 694 m	724.4	Ring def
	398 (4.8) vw	400.8 (6.9)	385 sh[d]	384.6 (6.7)	ν(Ni–S)
	76 (0.0) w	76.1 (0.5)	76 (0.0) m	76.1 (0.5)	δ(SNiS′)
	760 s		720 s		π(C–H)
	307.5 (1.5) s		293.5 (1.0) s		π(ring)
	131.0 (1.8) m		134.0 (1.5) m		π(ring)

[a] Numbers in the parentheses indicate isotopic shifts, $\tilde{\nu}(^{58}Ni) - \tilde{\nu}(^{62}Ni)$. Intensity designation: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Bands due to the NEt_4^+ ion are not listed. [c] Key: ν, stretching; δ, in-plane bending; π, out-of-plane bending. [d] The isotope shift could not be observed.

Table V. Comparison of Observed and Calculated Frequencies of Bis(1,2-diphenylethylene-1,2-dithiolato)nickel (cm^{-1})[a]

	$[Ni(S_2C_2(C_6H_5)_2)_2]$		$[Ni(S_2C_2(C_6H_5)_2)_2]^-$ [b]		$[Ni(S_2C_2(C_6H_5)_2)_2]^{2-}$ [c]		
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Assignment
B_{2u}	1365 s	1364.8	1475 s	1459.9	1533 s	1537.9	ν(C=C)
	960 w	957.3	960 w	961.3	980 w	964.4	ν(C–S) + ν(C–Ph)
	475 (6.5) m	472.8 (5.7)	465 (5.3) w	456.4 (2.6)	450 w	455.5	ν(Ni–S) + ring def
	408 (1.0) vw	412.9 (1.8)	406 (1.4) vw	406.7 (4.3)	401 s	403.8	ν(Ni–S) + ring def
	202 (2.2) w	203.8 (2.6)		204.1 (2.6)	207 m	204.2	δ(SNiS)
	130 m	143.1	130 m	143.1	128 s	143.2	δ(SNiS)
B_{3u}	1175 m	1142.3	1172 s	1172.1	1180 m	1179.0	ν(C–Ph) + ν(C–S)
	880 s	892.8	870 m	873.1	870 m	870.0	ν(C–S)
	454 (5.0) w	453.5 (6.0)	428 (4.2) vw	423.1 (5.0)	418 sh	417.6	ν(Ni–S)
	342 sh	346.7 (0.4)	338 (0.0) sh	349.2 (0.3)	334 m[d]	349.7	δ(CCPh) + ring def
	220 (1.8) w	226.3 (1.6)	224 (2.2) w	227.7 (1.7)	222 w	227.7	Ring def
		40.9 (0.4)		40.5 (0.3)		40.8	δ(SNiS′)
	351 s		345 s		334 m[d]		π(C–Ph)
	286 (2.0) w		253 (2.5) w		248 m		π(ring)
	180 m				160 sh		π(ring)

[a] Bands due to the phenyl group and cation are not listed. [b] NEt_4^+ salt. [c] $N_2H_5^+$ salt. [d] Overlapped band.

Table VI. Comparison of Observed and Calculated Frequencies of Bis[1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato]nickel (cm^{-1})[a]

	$[Ni(S_2C_2(CF_3)_2)_2]$		$[Ni(S_2C_2(CF_3)_2)_2]^-$ [b]		$[Ni(S_2C_2(CF_3)_2)_2]^{2-}$ [b]		
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Assignment
B_{2u}	1425 m	1428.8	1485 s	1484.8	1534 s	1533.9	ν(C=C)
	932 m	942.5	918 m	927.4	905 s	911.3	ν(C–S) + ν(C–CF_3)
	465 m	453.3	449 m	440.6	422 w	424.2	ν(Ni–S)
	405 w	400.2		393.8	394 w	383.3	Ring def
	211 w	207.5	210 w	207.3	208 m	207.1	δ(SNiS)
	122 w	120.2	120 vw	120.1		119.9	δ(C–C–CF_3)
B_{3u}	1150 s	1146.2	1138 s	1133.6	1122 s	1122.9	ν(C–CF_3) + ν(C–S)
	860 s	849.7	847 m	841.1	836 m	830.6	ν(C–S)
	425 w	436	415 w	420.8	394 w	397.8	ν(Ni–S)
	325 m	317.6	325 m	315.8	329 m	314.1	δ(C–C–CF_3) + ring def
	225 w	225.9	222 w	223.3	220 vw	219.3	Ring def
		38.4		38.4		38.3	δ(SNiS′)
	373 s		364 s		351 s		π(C–CF_3)
	245 m		248 m		248 m		π(ring)

[a] Bands due to the CF_3 group and cation are not listed. [b] NEt_4^+ salt.

Table VII. Comparison of Observed and Calculated Frequencies of Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel (cm^{-1})[a]

	$[Ni(S_2C_2(CN)_2)_2]^-$			$[Ni(S_2C_2(CN)_2)_2]^{2-}$			
	Obsd			Obsd			
	NEt_4^+ salt	Na^+ salt	Calcd	NEt_4^+ salt	Na^+ salt	Calcd	Assignment
B_{2u}	2194 sh	2190 s[b]	2200.0	2195 s	2205 s[b]	2197.8	ν(C≡N)
	1435 sh	1435 m	1435.5	1485 s	1485 s	1486.0	ν(C=C)
	1060 s	1050 w	1015.8	1055 m	1060 m	1013.4	ν(C–S) + ν(C–C)
	535 m	530 m	534.0 (0.3)	535 m	525 m	531.2 (0.1)	Ring def + ν(C–S)
	468 (3.8) m	468 m	453.5 (1.9)	457 (3.0) w	455 m	443.8 (1.0)	ν(Ni–S) + δ(CCN)
	396 (5.8) m	396 m	415.2 (4.0)	365 sh[c]	365 sh	393.9 (5.7)	ν(Ni–S) + δ(CCN)
	224 (2.2) m		216.1 (2.2)	219 (2.2) m		216.3 (2.3)	δ(SNiS) + ring def
	107 s		106.7	107 s		106.5	δ(CCN) + ring def
B_{3u}	2210 s	2190 s[b]	2203.4	2205 sh	2205 s[b]	2201.5	ν(C≡N)
	1160 s	1160 s	1194.1	1170 s	1160 s	1206.6	ν(C–C) + ν(C–S)
	885 w	880 w	914.6	865 s	865 m	897.9	ν(C–S)
	505 s	505 s	495.5 (0.8)	505 s	505 s[b]	486.2 (0.2)	Ring def + δ(CCN)
			444.8 (2.9)			433.7 (1.8)	Ring def + ν(Ni–S)
	365 (3.9) s	368 m	356.2 (3.5)	357 (4.0) s	358 m	342.5 (4.5)	ν(Ni–S) + ring def
	180 (1.2) m		182.0 (0.5)	177 (1.2) m		181.4 (0.6)	δ(CCN)
			42.3 (0.3)			42.3 (0.3)	δ(SNiS′)
	1105 w	1105 m		1105 m	1110 m		π(C–CN)
	525 m	525 sh		498 sh	500 sh[b]		π(C–CN)
	282 (2.0) m	281 m		274 (2.2) m	274 m		π(ring)
	134 sh			134 sh			π(ring)

[a] Cation bands are not listed. [b] Overlapped band. [c] The isotopic shift could not be determined.

frequencies is satisfactory in view of the approximations used.

Results and Discussion

Negatively charged complexes exhibit many bands due to cations such as the tetraethylammonium and hydrazonium ions. These cation bands have been identified by comparing the spectra of neutral complexes with those of anionic complexes containing different cations. The spectra were also compared with published data.[8,10] The bands due to internal modes of the R group have also been identified by using similar methods.

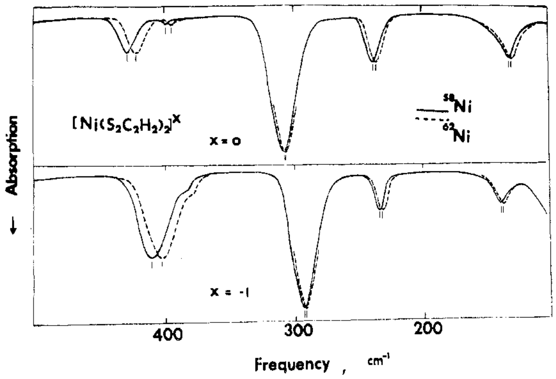


Figure 2. Low-frequency infrared spectra of $[Ni(S_2C_2H_2)_2]^x$.

In the low-frequency region, the metal–ligand stretching bands have been assigned based on metal isotope data. Other bending modes have been assigned from normal-coordinate calculations.

The $[Ni(S_2C_2H_2)_2]^x$ Series. Previously, Adams and Cornell[8] obtained the infrared spectra of $Ni(S_2C_2H_2)_2$ and $(NEt_4)_2[Ni(S_2C_2H_2)_2]$. Siiman and Fresco[10] measured the spectrum and carried out normal-coordinate analysis of the former. Figure 2 shows the infrared spectra of the $[Ni(S_2C_2H_2)_2]^x$ series below 500 cm^{-1}, and Table IV compares the observed and calculated frequencies. The last column of the table gives the band assignments based on potential energy distribution. It is noted that our assignments are markedly different from those of previous investigators.[8,10]

In general, our assignments above 500 cm^{-1} are similar to those of Siiman and Fresco[10] but different from those of Adams and Cornell.[8] Our calculated frequencies are much closer to the observed frequencies than those of Siiman and Fresco. Marked differences in assignments occur below 500 cm^{-1} where the Ni–S stretching bands are expected to appear. Originally, Adams and Cornell[8] assigned two bands at 422 and 311 cm^{-1} of the neutral complex and at 419 and 295 cm^{-1} of the mononegative complex to the Ni–S stretching modes. However, the former bands near 420 cm^{-1} give large shifts (6.5 to 8.0 cm^{-1}) whereas the latter bands near 300 cm^{-1} give only small shifts (1.5 to 1.0 cm^{-1}) by the ^{58}Ni–^{62}Ni substitution. Furthermore, our calculations indicate that two Ni–S stretching frequencies cannot be separated by more than 100 cm^{-1} unless an unreasonably large repulsive $F(S\cdots S)$ value is used. We have, therefore, assigned the latter bands to a bending mode.

Siiman and Fresco[10] on the other hand assumed that two Ni–S stretching bands of the neutral complex are accidentally overlapped at 420 cm^{-1}. Although their calculation predicted a separation of only 6 cm^{-1} for two Ni–S stretching modes, we could not find a reasonable set of force constanats which gives such a small separation. Using a very concentrated Nujol mull, we were able to observe a weak band at 398.0 cm^{-1} which shifts by 4.8 cm^{-1} upon the Ni isotope substitution. Therefore, two bands at 428 and 398 cm^{-1} have been assigned to the Ni–S stretching modes of the neutral complex. As is seen in Table IV, our calculations support these assignments. In the mononegative ion, the lower frequency Ni–S stretching band was observed at 385 cm^{-1}. It was not possible, however, to measure its isotope shift because of the poor band shape. Other bending modes have been assigned as are shown in Table IV.

The $[Ni(S_2C_2(C_6H_5)_2)_2]^x$ Series. Siiman and Fresco[10] studied the infrared spectrum of the neutral complex. In general, their spectrum and assignments above 400 cm^{-1} are in good agreement with ours. We obtained the infrared spectra of three compounds (x = 0, 1–, and 2–) and carried out normal-coordinate analyses on all of them. Figure 3 illustrates the low-frequency infrared spectra and Table V lists the observed and calculated frequencies and band assignments.

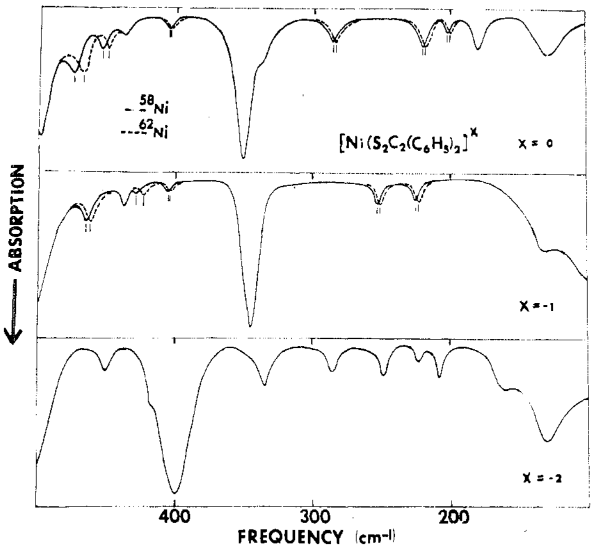


Figure 3. Low-frequency infrared spectra of $[Ni(S_2C_2(C_6H_5)_2)_2]^x$.

Due to the presence of the phenyl group, the spectra of these complexes are much more complicated than those discussed previously.

The complexes of this series exhibit several medium or weak bands in the 500–350-cm^{-1} region. Previously, Schrauzer and Mayweg[14] assigned two bands at 408 and 354 cm^{-1}, and Siiman and Fresco[10] assigned two bands at 465 and 449 cm^{-1} of the neutral complex to the Ni–S stretching modes. Our isotope study shows that two bands at 475 and 454 cm^{-1} of the neutral complex and two bands at 465 and 428 cm^{-1} of the mononegative complex show large shifts by the ^{58}Ni–^{62}Ni substitution. Therefore, these bands have been assigned as the Ni–S stretching modes. Table V shows that calculated frequencies and isotopic shifts are in good agreement with those observed. Although the calculated isotope shift of the 406-cm^{-1} band is smaller than that observed, it was not possible to improve our calculation since this vibration couples strongly with the 465-cm^{-1} mode. Although the metal isotope substitution was not carried out on the dinegative complex, two bands at 450 and 418 cm^{-1} have been assigned to the Ni–S stretching vibrations based on similarity of the spectra between this and mononegative complexes.

Other low-frequency bands have been assigned as are shown in Table V. The strong band at 351 cm^{-1} of the neutral complex was previously assigned to the Ni–S stretching mode. However, it gives no metal isotope shift. In this work, this band has been assigned as the out-of-plane bending mode of the S(C)C–R group where R is the phenyl group. It is interesting to note that the frequency of this mode is inversely proportional to the square root of the mass of the R group as expected.

R	CN	CF_3	C_6H_5
Mass$^{1/2}$	$26^{1/2}$	$69^{1/2}$	$77^{1/2}$
$\tilde{\nu}$, cm^{-1}	525–470	373–351	351–334

It was also noted that its frequency decreases as the negative charge of the complex ion increases. This result suggests that the C—S, C═C, and C—R bond orders are influenced by the charge of the complex.

The $[Ni(S_2C_2(CF_3)_2)_2]^x$ Series. Figure 4 shows the low-frequency infrared spectra of this series, and Table VI gives the observed and calculated frequencies and band assignments. In this case, the metal isotope data are lacking since it was not possible to prepare these compounds on a milligram scale. Previously, Adams and Cornell[8] assigned the Ni–S stretching bands at 465 and 373 cm^{-1} for x = 0, 447 and 364 cm^{-1} for x = 1–, and 424 and 351 cm^{-1} for x = 2–. We have assigned

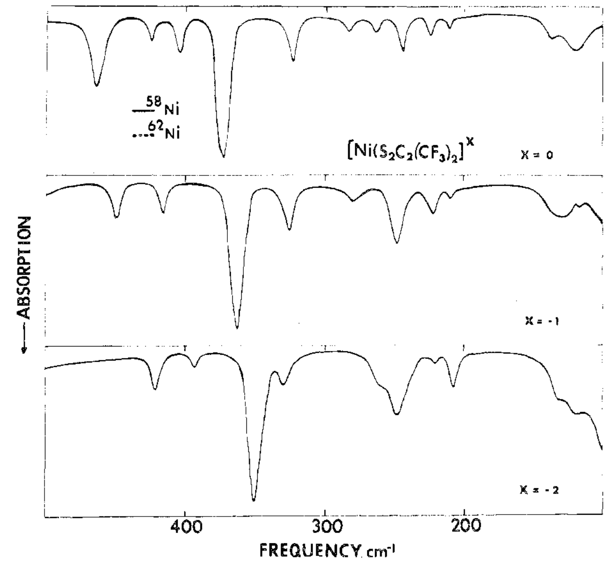


Figure 4. Low-frequency infrared spectra of $[Ni(S_2C_2(CF_3)_2)_2]^x$.

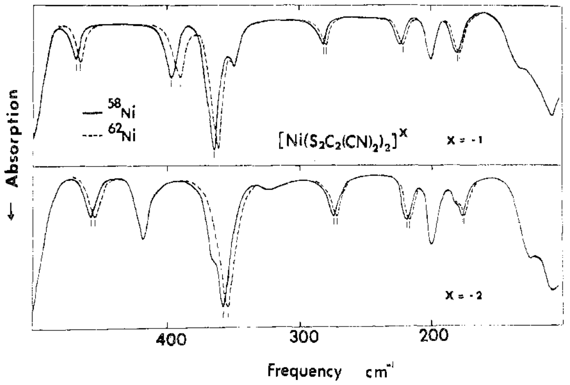


Figure 5. Low-frequency infrared spectra of $[Ni(S_2C_2(CN)_2)_2]^x$.

their higher frequency bands (465–424 cm^{-1}) to the Ni–S stretching modes. However, their lower frequency bands (373–351 cm^{-1}) have been assigned to the C–CF$_3$ out-of-plane bending mode because of the reason mentioned above. Weak bands at 425–394 cm^{-1} of these complexes have been assigned to the other Ni–S stretching bands.

The $[Ni(S_2C_2(CN)_2)_2]^x$ Series. Adams and Cornell[8] obtained the infrared spectra of the tetraethylammonium salts of this series (x = 1– and 2–), and suggested that several bands between 400 and 250 cm^{-1} are associated with Ni–S stretching modes. Lakshmi et al.[9] carried out normal-coordinate analysis on the 1:1 metal–ligand model of the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ ion and assigned two bands at 498 and 453 cm^{-1} to the Ni–S stretching modes. Figure 5 shows the infrared spectra of this series and Table VII gives the observed and calculated frequencies and band assignments. Three bands at 468, 396, and 365 cm^{-1} of the mononegative complex give relatively large shifts by the ^{58}Ni–^{62}Ni substitution. As is seen in Table VII, all these bands are due to the Ni–S stretching coupled with several deformation modes.

Two bands at 457 and 357 cm^{-1} of the dinegative complex give large shifts by the metal isotope substitution. In addition, there is a shoulder at 365 cm^{-1} which disappears upon metal isotope substitution. Thus, these three bands have been assigned to the Ni–S stretching coupled with deformation modes. Although our calculation predicted a ring deformation (coupled slightly with the Ni–S stretching mode) at ca. 440 cm^{-1}, this band was not observed possibly because it was too weak.

Effect of Changing Oxidation State. The most important change upon reduction of the complex is an increase in the C=C stretching frequency.[1] This frequency is a rough measure of the C=C bond strength since it couples very little with other modes. Other bands are shifted more or less to lower frequencies upon reduction. Our calculations show that the C—S and Ni—S stretching modes often couple with other modes. Therefore, changes in these bonds cannot be discussed in terms of frequencies.

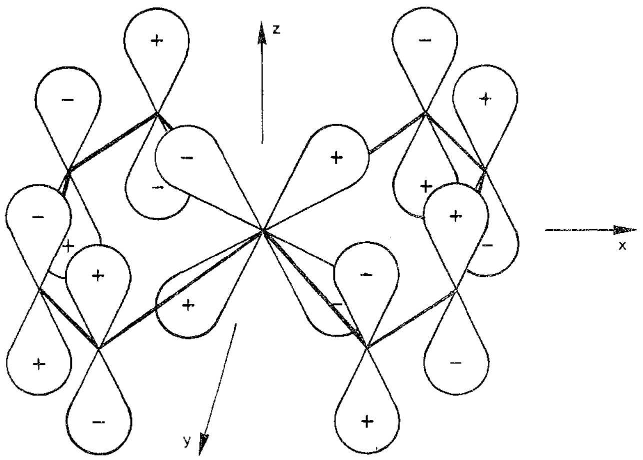
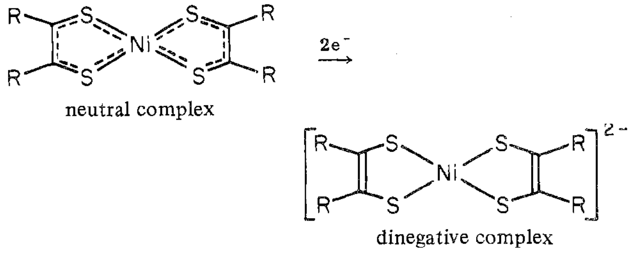


Figure 6. The B_{2g} orbital of the nickel–dithiene complex.

Table III shows that K(C=C) increases by ca. 20% whereas K(Ni—S) and K(C—S) decrease by ca. 10 and 5%, respectively, upon reduction of the neutral complex by one unit charge. In the Urey–Bradley force field, the stretching force constants of the pure double and single CC bonds are 7.4 (CH_2=CH_2) and 2.48 mdyn/Å (CH_3—CH_3), respectively.[22] The present K(C=C) values are 4.44–5.02, 4.99–5.68, and 5.49–6.24 mdyn/Å, respectively, for the neutral, mononegative, and dinegative complexes. The Urey–Bradley force constant for the pure C—S single bond is 2.43–2.60 mdyn/Å.[22] In this work, K(C—S) is 2.95–3.34, 2.84–3.20, and 2.69–2.98 mdyn/Å, respectively, for the neutral, mononegative, and dinegative complexes. It is seen that these values are always slightly larger than that of a pure C—S single bond and that its value decreases as the negative charge of the complex increases. The same trend is found for K(Ni—S) which is 1.64–1.46, 1.53–1.34, and 1.33–1.22 mdyn/Å, respectively, for the neutral, mononegative, and dinegative complexes. The Ni—S bond of the $[Ni(CS_3)_2]^{2-}$ ion is known to have partial double-bond character, and its K(Ni—S) value is estimated to be 1.41 mdyn/Å.[23] Based on these force constant data, the changes in electronic structure upon reduction may be roughly represented by



Force Constants and Hückel MO Theory. A more quantitative treatment may be made by using the MO theory. The fact that all stretching force constants are changed upon reduction definitely indicates that the added electrons enter an MO which is strongly delocalized. The MO's are formed by a linear combination of the ligand π and metal orbitals of proper symmetry. According to Schrauzer and Mayweg,[7] the lowest unoccupied MO of the neutral complex is the B_{2g} orbital which consists of the $3d_{xz}$ orbital of the metal and the π orbital of the ligand shown in Figure 6. In the mononegative complex, this orbital is bonding with respect to the C=C bond but antibonding with respect to the C—S and Ni—S bonds. The addition of one electron to this orbital is expected to strengthen the C=C bond and weaken the C—S and Ni—S bonds. This is in perfect agreement with the results of normal-coordinate analysis (Table III). The addition of the second electron enhances the same trend. However, the changes in force constants in this case are less than those in going from neutral to mononegative complexes. This result cannot be explained by the simple Hückel MO treatment since it does not consider the dependency of orbital energies upon the electron occupancy of each orbital. We have, therefore, used the average values when the changes in force constants were calculated for each step of two-electron reduction (R = C_6H_5, CF_3).

Force Constants and Charge Distribution. Recently, Hinkel and Devlin[24] calculated the stretching force constants of tetracyanoethylene and its mononegative anion by combining Gordy's equation[25] with Hückel's MO theory. In the following, we have applied their method to nickel–dithiolato complexes.

Gordy's equation is written as

$$K_{AB} = aP_{AB}[(X_A X_B/d^2)]^{3/4} + b \qquad (1)$$

where K_{AB} is the force constant, P_{AB} is the bond order, X is the electronegativity, d is the internuclear distance, a and b are constants, and A and B are atoms. The bond order P_{AB} is defined in the Hückel MO calculations as[26]

$$P_{AB} = \sum_{i=1}^{N} n_i C_{iA} C_{iB} \qquad (2)$$

where n_i is the number of electrons occupying the ith MO, N is the total number of MO's, and C_{iA} and C_{iB} are the coefficients of the AO of the atoms A and B, respectively, in the ith MO. In this simplified treatment, the coefficients, C_{iA} and C_{iB}, do not depend upon the occupancy of other MO's. Then, the only change which results from one-electron reduction is the addition of a term such as $n_j C_{jA} C_{jB}$ where j refers to the MO to which an extra electron is added. Thus, the change in bond order ΔP_{AB} caused by one-electron reduction is given by

$$\Delta P_{AB} = C_{jA} C_{jB} \qquad (3)$$

Since Gordy's constants, a and b, are the same for the neutral and mononegative complexes, a combination of eq 1 and 3 gives the expression

$$\Delta K_{AB} = k\Delta P_{AB} = kC_{jA} C_{jB} \qquad (4)$$

where $k = a[(X_A X_B/d^2)]^{3/4}$. Equation 4 is simplified to

$$\Delta K_{AA} = kC_{jA}{}^2 \qquad (5)$$

if A is symmetry equivalent to B. In this case, C_{jA} can be calculated directly from ΔK_{AA} and k. Once C_{jA} is known, C_{jB} of the A–B bond can be calculated from eq 4. By using similar procedures, it is possible to calculate C_{ji} values of all the atoms in the molecule. It should be noted, however, that the final results may contain appreciable errors since errors are accumulated during this process.

Using eq 5, we first calculated $C_{jC}{}^2$ from ΔK_{CC} (Table III). k was taken to be 4.9 from the slope of a plot of K(CC) vs. bond order in the ethane, ethylene, and acetylene series.[22] Using Gordy's equation, k was estimated to be 4.7. Then, C_{jS} was calculated from eq 4 with known values of C_{jS}, ΔK_{CS}, and k. k was estimated to be 2.9 from Gordy's equation.[25] Although no literature values are available for k, it is not unreasonable to use 2.9 since K(C–S) for a single C–S bond is about 2.6 mdyn/Å.[22] After calculating C_{jC} and C_{jS}, we calculated C_{jNi} by using the normalization condition

$$\sum_X C_{jX}{}^2 = 1 \qquad (6)$$

The reason for using eq 6 rather than eq 4 is that Gordy's equation may not be adequate for transition metal–ligand bonds. Table VIII summarizes the final results.

Table VIII. Changes in Force Constants and Charge Densities upon Reduction of Nickel-Dithiene Complexes

R	ΔK-(C=C)	P_{CC}	$C_{jC}{}^2$	ΔK-(C–S)	P_{CS}	$C_{jS}{}^2$	Electron density: Ligand	Electron density: Metal ($C_{jNi}{}^2$)	σ[c]
H	0.90	0.18	0.18	0.29	0.10	0.05	0.94 (0.82)[a]	0.06 (0.18)[a]	0.0
C_6H_5	0.84	0.17	0.17	0.18	0.06	0.02	0.77	0.23	0.06
CF_3	0.62	0.13	0.13	0.13	0.04	0.01	0.57	0.43	0.42
CN	0.50	0.10	0.10	0.22	0.08	0.06	0.62 (0.58)[b]	0.38 (0.42)[b]	0.52

[a] Reference 7. [b] Reference 4. [c] Hammett constant (see ref 27).

As is shown in Table VIII, the electron density is always larger on the ligand than on the metal. In the case of R = H, 94% of the extra electron due to one-electron reduction resides on the ligand orbital. This is comparable to the value of 82% which was obtained by Schrauzer and Mayweg[7] from the analysis of electronic spectra. In the case of R = CN, Maki et al.[4] from their ESR study estimated that 42% of the electron is on the metal orbital. This is in very good agreement with our value (38%).

As stated previously, the orbital accepting an electron upon reduction of the complex is an antibonding combination of a ligand π and the d_{xz} orbital of the metal. In the case of R = H, the ligand π orbital lies energetically much higher than the d_{xz} orbital. As a result, the antibonding orbital has little d_{xz} character. If one replaces H by a better electron acceptor, the π orbital is stabilized and becomes closer to the d_{xz} orbital. Stabilization of the π orbital is also manifested by the linear relationship between the redox potential of the complex and the Hammett constant (σ)[27] of the R group, which was found by Olson et al.[28] They suggested that the larger the Hammett constant, the more electrons tend to shift from the ligand to the metal. In terms of the MO theory, this indicates that the contribution of the d_{xz} orbital to the antibonding MO orbital increases as the Hammett constant becomes larger. This is clearly demonstrated by the results shown in Table VIII where the density of the extra electron on the Ni atom increases in the order of R = H < C_6H_5 < CF_3 < CN.

From the data given in Table VIII, it is also possible to calculate the change in the Ni–S bond order, ΔP_{NiS}, upon reduction. However, ΔP_{NiS} is expected to be relatively small since both coefficients, C_{iS} and C_{iNi}, are small. It is, therefore, not surprising that relatively small changes in K(Ni–S) were observed for each series (Table III). If one plots ΔP_{NiS} vs. ΔK(Ni–S) for complexes containing different R groups, a straight line passing through the origin is obtained. The slope (ca. 2.0) gives the k value of eq 4 for the Ni–S bond.

R	H	C_6H_5	CF_3	CN
ΔK(Ni–S)	0.12	0.16	0.15	0.26
ΔP_{NiS}	0.057	0.072	0.078	0.13
ΔK(Ni–S)/ΔP_{NiS}	2.1	2.2	1.9	2.0

Thus far, we have discussed the effect of one-electron reduction on the C=C, C—S, and Ni—S bond orders and calculated the charge distribution of this extra electron on the metal and the ligand. It is rather difficult, however, to estimate these quantities on an absolute scale. Table III shows that the value of K(Ni–S) ranges from 1.64 to 1.22 mdyn/Å depending upon the charge (x) and the substituent (R). It is reasonable to conclude from these data that the strength of the Ni–S bond is reduced from that of a partial double bond to that of an almost single bond upon reduction in each series of R. However, a detailed discussion about the relationship between the Ni–S bond strength and the real oxidation state (charge) of the metal or the electronic effect of the substituent

(R) cannot be made until more quantitative information becomes available from other sources such as electronic and ESR spectra and rigorous MO calculations.

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Registry No. $Ni(S_2C_2H_2)_2$, 19042-52-5; $N(C_2H_5)_4[Ni(S_2C_2H_2)_2]$, 15528-35-5; $Ni(S_2C_2(CF_3)_2)_2$, 18820-78-5; $N(C_2H_5)_4[Ni(S_2C_2(CF_3)_2)_2]$, 15225-60-2; $[N(C_2H_5)_4]_2[Ni(S_2C_2(CF_3)_2)_2]$, 15613-49-7; $Ni(S_2C_2(C_6H_5)_2)_2$, 28984-20-5; $N(C_2H_5)_4[Ni(S_2C_2(C_6H_5)_2)_2]$, 38930-10-8; $(N_2H_5)_2[Ni(S_2C_2(C_6H_5)_2)_2]$, 38883-74-8; $N(C_2H_5)_4[Ni(S_2C_2(CN)_2)_2]$, 15077-50-6; $[N(C_2H_5)_4]_2[Ni(S_2C_2(CN)_2)_2]$, 15665-90-4.

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Infrared Spectra of Metal Complexes of Octaethylchlorine Analogs of Chlorophyll and Heme d

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The infrared spectra of *trans*-octaethylchlorine (OEC) and its divalent metal complexes of the types M(OEC) (M = Zn, Cu, Ni) and $Mg(OEC)(py)_2$ and ferric complexes Fe(OEC)X ($X^- = F^-, Cl^-, Br^-, I^-$) have been measured from 4000 to 100 cm^{-1}. The M–N(OEC) and Mg–N(py) stretching bands have been assigned based on metal isotope substitution. The similarity of the spectra of OEC complexes and of chlorophylls has been discussed.

Introduction

It has been generally recognized that knowledge of the coordination behavior of the magnesium ion in chlorophyll is important in the understanding of the photosynthetic process. Unfortunately, X-ray analysis has not been carried out because of the difficulty in preparing sufficiently large single crystals of chlorophyll.[1] Thus far, infrared and NMR spectroscopy has provided valuable information about the structural chemistry of chlorophyll.[2,3] For example, Katz and his coworkers have provided spectral evidence to show that the chlorophylls are aggregated in nonpolar solvents and in the solid state.[3] It is of special interest that they have made an empirical assignment of two magnesium–nitrogen stretching vibrations in addition to a peak characteristic of aggregation.[5] Their assignment, however, seems to require more reliable evidence. To this end, we have performed a systematic study on the infrared spectra of *trans*-octaethylchlorine (OEC) complexes.

In this paper, we report definitive assignments of metal–nitrogen stretching frequencies of the divalent metal chlorines based on metal isotope experiments. The infrared spectra of the halide complexes of ferric octaethylchlorine have also been reported and the iron–nitrogen stretching frequencies assigned based on a comparison with the spectra of ferric octaethylporphyrin for which isotope experiments were performed.[6] The iron complex of chlorine (heme d) is also found in some hemoprotein enzymes (cytochrome *cd*) such as "ferrocytochrome:nitrite oxidoreductase", the structure and function of which has not been fully understood as yet.[7] The molecular structure of OEC metal complexes is closely related to chlorophyll except for the fifth isocyclic ring (Figure 1).

Experimental Section

Preparation of Compounds. *trans*-Octaethylchlorine ($OECH_2$) was stereoselectively prepared according to the method of Whitlock et al.[8] The spectral data (visible and NMR) were in good agreement with those reported.[8-12]

$Mg(OEC)(py)_2$. A pyridine solution of $OECH_2$ (100 mg) and anhydrous magnesium perchlorate (200 mg) was sealed in a glass tube and subsequently heated on an oil bath at 100° for 24 hr. The solution was deaerated in a glass tube by a repeated freeze–thaw process under vacuum before sealing. The resulting solution of Mg(OEC) was concentrated to a small volume under vacuum and then poured into 300 ml of ether containing a small amount of pyridine. The ether solution was successively washed several times with equal volumes

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