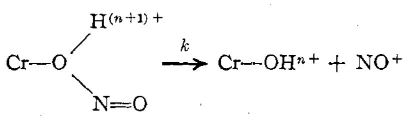
and $Cr(OH_2)_5ONO^{2+}$ involving $[H^+]^2$ argue against this mechanism. In fact, unless the nitritio N atom of Cr–ONO may act as a protonation site or the remote oxygen may be doubly protonated, these observations also conflict with a slow intracomplex proton-transfer mechanism. The standard specifiic acid catalyzed scheme already applied to $Cr(NH_3)_5ONO^{2+}$ and $Cr(OH_2)_5ONO^{2+}$ then seems to offer the simplest viewpoint for any rationalization of the data of Table III.

A general feature of this table is the rough grouping of $\Delta H^{\ddagger}$ values in accord with the charge of the substrate. Thus, for the 1+ complexes, $\Delta H^{\ddagger}$ lies in the range 20.3–24.3 kcal mol^{-1}, and for the 2+ complexes, $\Delta H^{\ddagger}$ is in the lower range 19.7–20.1 kcal mol^{-1}. While this distinction is not sharp in view of the experimental errors, it is what would be expected on the basis of a rate-determining reaction step (eq 6) where increased



$$\text{Cr—O}(H^{(n+1)+})(\text{N=O}) \xrightarrow{k} \text{Cr—OH}^{n+} + \text{NO}^+ \qquad (6)$$

positive charge on $Cr–OHNO^{n+}$ would be expected to facilitate the loss of positively charged NO^+. This conclusion, of course, assumes that the charge dependence of $\Delta H^{\ddagger}$ for the protonation preequilibrium is negligible (since under the assumed mechanism k_H of Table III becomes equal to k/K_a, where K_a is the acidity constant of $Cr–OHNO^{n+}$). While there is no direct evidence for this supposition, it would not be expected that $\Delta H^{\ddagger}$ for a rate-determining proton-attack mechanism would decrease with increase in substrate charge. Thus, data for the acid-catalyzed hydrolyses of $Cr(en)_2(ONO)X^{n+}$ complexes appear in no way inconsistent with the character and interpretation given by Matts and Moore[3,28] for $Cr(NH_3)_5ONO^{2+}$ and $Cr(OH_2)_5ONO^{2+}$ hydrolyses.

Aquation Reactions.—For the *trans*-$Cr(en)_2(ONO)X^{n+}$ systems where aquation (acid-independent) rate constants for NO_2^- loss could be determined (see Figure 6) or estimated, the relatively low rate of NO_2^- release found is consistent, assuming a dissociative mechanism, with the well-known affinity of Cr(III) for oxygen donors, resulting in a strong Cr–ONO bond. The stereoretentivity of these substitutions is consistent with observations on similar $Cr(en)_2XY^{n+}$ complexes. It is in our qualitative observations on *cis*-$Cr(en)_2(ONO)X^{n+}$, however, that a most remarkable feature of the Cr–ONO system, the cis-labilizing power of the nitrito ligand, is revealed. This is best considered for *cis*-$Cr(en)_2(ONO)Cl^+$. Chloride loss from this cation at 25° is far more rapid than that from *cis*-$Cr(en)_2(NCS)Cl^+$,[5c] *cis*-$Cr(en)_2Cl_2^+$,[5a] and *cis*-$Cr(en)_2(OH)Cl^+$.[29] Likewise (see Figure 6), nitrite loss from *cis*-$Cr(en)_2(ONO)_2^+$ is much faster than from *cis*-$Cr(en)_2(OH)ONO^+$, despite the labilization of many complexes by the presence of a hydroxo ligand. The source of this labilizing ability is not obvious; it could arise from a peculiar steric effect with the coordinated bent nitrito ligand or from unusual solvation properties of the Cr–ONO moiety, as well as from a more conventional π-donor electronic effect. This last possibility may perhaps be ignored since aquation of the X ligand of $Cr(en)_2(ONO)X^{n+}$ ($X^- = Cl^-, ONO^-$) seems to be completely stereoretentive.

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[29] D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 558 (1963).

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The Infrared Spectra of Metal Dithienes

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The infrared spectra of bis(1,2-dimethylethylene-1,2-dithiolato)nickel, -palladium, and -platinum, bis(ethylene-1,2-dithiolato)nickel, and bis(1,2-diphenylethylene-1,2-dithiolato)nickel have been recorded from 1600 to 300 cm^{-1}. Band assignments for in-plane infrared-active vibrations were obtained from normal-coordinate analyses. The nature and possible origin of infrared spectral anomalies are discussed. Bonding in chelate rings was interpreted on the basis of bond stretching force constants.

Introduction

Although the reactivity[1] and electronic structures[2] of metal dithienes have been extensively investigated, relatively little information about their infrared absorption spectra is available. Where band assignments have been made,[3] these were empirically deduced and only one or two bands were discussed in detail. Studies of the electronic spectra and structure of the molecular orbitals of metal dithienes[4] have indicated that these complexes possess novel delocalized systems.

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[1] G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

[2] G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

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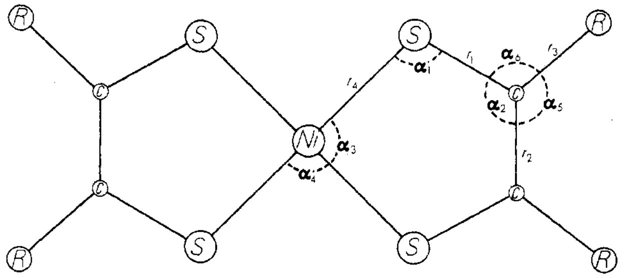

Figure 1.—Molecular model and internal coordinates for dithienes.

It is conceivable that a description of the bonding properties of metal dithienes in terms of bond stretching force constants between adjacent atoms in the chelate ring could contribute to an understanding of the properties of α-dithio diketonates.

Inspection of the infrared spectra of certain metal dithienes has revealed an abnormal feature among chelates with either methyl or hydrogen substituents. Several sharp transmission peaks occur between 1500 and 500 cm^{-1} in the infrared spectra of these complexes. As a consequence, it was not obvious whether molecular vibrations are responsible for the absorption near these transmission regions or if some unique explanation would be necessary to describe their origin.

On the basis of a normal-coordinate calculation similar to that performed for metal dithioacetylacetonates,[5] it has been possible to assign the in-plane infrared-active fundamentals in bis(1,2-dimethylethylene-1,2-dithiolato)nickel, -palladium, and -platinum, bis(ethylene-1,2-dithiolato)nickel, and bis(1,2-diphenylethylene-1,2-dithiolato)nickel.

Experimental Section

The chelates studied were prepared by previously described procedures.[3,6] All infrared spectra were recorded with a Perkin-Elmer 521 infrared spectrophotometer over the range 1600–300 cm^{-1}. Potassium bromide, cesium bromide, and silver chloride pellets and Nujol mulls were prepared for all compounds. Calibration of frequency readings was performed with polystyrene film and water vapor.

Bis(1,2-dimethylethylene-1,2-dithiolato)nickel appeared as purple crystals, mp 255°. *Anal.* Calcd for $C_8H_{12}S_4Ni$: C, 32.55; H, 4.09; parent mass, 294. Found: C, 32.66; H, 4.28; parent mass, 294.

Bis(1,2-dimethylethylene-1,2-dithiolato)palladium appeared as red crystals, mp >250° dec. *Anal.* Calcd for $C_8H_{12}S_4Pd$: C, 28.02; H, 3.52; parent mass, 342. Found: C, 28.08; H, 3.56; parent mass, 342.

Bis(1,2-dimethylethylene-1,2-dithiolato)platinum appeared as dark blue crystals, mp 315°. *Anal.* Calcd for $C_8H_{12}S_4Pt$: C, 22.26; H, 2.80; parent mass, 431. Found: C, 22.49; H, 2.87; parent mass, 431.

Bis(ethylene-1,2-dithiolato)nickel appeared as blue crystals, mp 160°. *Anal.* Calcd for $C_4H_4S_4Ni$: C, 20.09; H, 1.68; parent mass, 238. Found: C, 20.13; H, 1.82; parent mass, 238.

Bis(1,2-diphenylethylene-1,2-dithiolato)nickel appeared as purple crystals, mp 280°. *Anal.* Calcd for $C_{28}H_{20}S_4Ni$: C, 61.88; H, 3.70; parent mass, 542. Found: C, 61.87; H, 3.65; parent mass, 542.

Method of Calculation

The 1:2 metal–ligand model shown in Figure 1 was adopted for the normal-coordinate calculations. In bis(1,2-dimethylethylene-1,2-dithiolato)nickel, -palladium, and -platinum the methyl groups were treated as point masses equivalent to the sum of one carbon and three hydrogen masses. An X-ray investigation of the related compound[7] triphenylmethylphosphonium-bis(1,2-dicyanoethylene-1,2-dithiolato)nickel showed the anion possesses very nearly D_{2h} symmetry. Interatomic distances and angles that appear in Table I were transferred from the parameters[7] determined

TABLE I
GEOMETRIC PARAMETERS FOR 1,2-DIMETHYLETHYLENE-1,2-DITHIENES

	Ni	Pd	Pt
r_4, Å	2.15	2.26	2.32
α_1, deg	103	105	107
α_3, deg	92	87	85
α_4, deg	88	93	95

$r_1 = 1.71$ Å $\alpha_2 = 121°$
$r_2 = 1.36$ Å $\alpha_5 = 122°$
$r_3 = 1.43$ Å $\alpha_6 = 118°$

TABLE II
SYMMETRY COORDINATES FOR BIS(1,2-DIMETHYLETHYLENE-1,2-DITHIOLATO)NICKEL IN D_{2h} SYMMETRY

Coordinate	Mode
B_{2u} Species	
$S_1 = \frac{1}{2}[(\Delta r_{6,10} + \Delta r_{9,13}) - (\Delta r_{7,11} + \Delta r_{8,12})]$	$\nu(\mathrm{C—CH_3})$
$S_2 = \frac{1}{2}[(\Delta r_{61} + \Delta r_{94}) - (\Delta r_{72} + \Delta r_{83})]$	$\nu(\mathrm{C}\overset{\cdots}{=}\mathrm{S})$
$S_3 = \frac{1}{2}[(\Delta r_{15} + \Delta r_{45}) - (\Delta r_{25} + \Delta r_{35})]$	$\nu(\mathrm{M—S})$
$S_4 = \frac{1}{\sqrt{2}}(\Delta r_{69} - \Delta r_{78})$	$\nu(\mathrm{C}\overset{\cdots}{=}\mathrm{C})$
$S_5 = \frac{1}{2}[(\Delta\alpha_{1,10} - \Delta\alpha_{10,9} + \Delta\alpha_{4,13} - \Delta\alpha_{13,6}) - (\Delta\alpha_{2,11} - \Delta\alpha_{11,8} + \Delta\alpha_{3,12} - \Delta\alpha_{12,7})]$	$\delta(\mathrm{RCS})$
$S_6 = \frac{1}{2\sqrt{2}}[(\Delta\alpha_{19} + \Delta\alpha_{46} - \Delta\alpha_{56} - \Delta\alpha_{59}) - (\Delta\alpha_{28} + \Delta\alpha_{37} - \Delta\alpha_{57} - \Delta\alpha_{58})]$	Ring def
$S_7 = \frac{1}{5\sqrt{2}}[(-\Delta\alpha_{19} - \Delta\alpha_{46} - \Delta\alpha_{56} - \Delta\alpha_{59} + 4\Delta\alpha_{14}) - (-\Delta\alpha_{28} - \Delta\alpha_{37} - \Delta\alpha_{57} - \Delta\alpha_{58} + 4\Delta\alpha_{23})]$	Ring def
B_{3u} Species	
$S_8 = \frac{1}{2}[(\Delta r_{6,10} - \Delta r_{9,13}) + (\Delta r_{7,11} - \Delta r_{8,12})]$	$\nu(\mathrm{C—CH_3})$
$S_9 = \frac{1}{2}[(\Delta r_{61} - \Delta r_{94}) + (\Delta r_{72} - \Delta r_{83})]$	$\nu(\mathrm{C}\overset{\cdots}{=}\mathrm{S})$
$S_{10} = \frac{1}{2}[(\Delta r_{15} - \Delta r_{45}) + (\Delta r_{25} - \Delta r_{35})]$	$\nu(\mathrm{M—S})$
$S_{11} = \frac{1}{2}[(\Delta\alpha_{1,10} - \Delta\alpha_{10,9} - \Delta\alpha_{4,13} + \Delta\alpha_{13,6}) + (\Delta\alpha_{2,11} - \Delta\alpha_{11,8} - \Delta\alpha_{3,12} + \Delta\alpha_{12,7})]$	$\delta(\mathrm{RCS})$
$S_{12} = \frac{1}{2\sqrt{2}}[(\Delta\alpha_{19} - \Delta\alpha_{46} + \Delta\alpha_{56} - \Delta\alpha_{59}) + (\Delta\alpha_{28} - \Delta\alpha_{37} + \Delta\alpha_{57} - \Delta\alpha_{58})]$	Ring def
$S_{13} = \frac{1}{2\sqrt{2}}[(\Delta\alpha_{19} - \Delta\alpha_{46} - \Delta\alpha_{56} + \Delta\alpha_{59}) + (\Delta\alpha_{28} - \Delta\alpha_{37} - \Delta\alpha_{57} + \Delta\alpha_{58})]$	Ring def
$S_{14} = \frac{1}{\sqrt{2}}(\Delta\alpha_{12} - \Delta\alpha_{34})$	$\delta(\mathrm{SMS})$

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[5] O. Siimann and J. Fresco, *Inorg. Chem.*, **8**, 1846 (1969).
[6] W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).
[7] C. J. Fritchie, *Acta Crystallogr.*, **20**, 107 (1966).

TABLE III
OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) OF
BIS(1,2-DIMETHYLETHYLENE-1,2-DITHIOLATO)NICKEL, -PALLADIUM, AND -PLATINUM

	$Ni(C_2(CH_3)_2S_2)_2$		$Pd(C_2(CH_3)_2S_2)_2$		$Pt(C_2(CH_3)_2S_2)_2$		
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Predominant modes
				B_{2u}			
ν_1	1354	1320, 1399[a]	1374	1362	1354	1332, 1400[a]	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
ν_2	1030	1075	1041	1085	1037	1083	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
ν_3	578	565, 576[a]	581	570	569	560, 572[a]	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
ν_4	444	435	431	448	416	455	$\nu(\mathrm{M{-}S})$
ν_5	303	300	307	293	301	290	$\delta(\mathrm{C{-}CH_3})$
ν_6	205		187		170		Ring def
				B_{3u}			
ν_7	1245	1205	1226	1195	1224	1200	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
ν_8	901	905, 940[a]	915	936	904	916, 950[a]	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
ν_9	517	500	514	534	495	500	$\nu(\mathrm{M{-}S}) + \delta(\mathrm{C{-}CH_3})$
ν_{10}	417	400	412	385	410	402, 409[a]	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring def
ν_{11}	376	333	347	337	319	301	$\nu(\mathrm{M{-}S})$
ν_{12}	61		60		56		$\delta(\mathrm{SMS})$

[a] Second value is position of transmission peak.

TABLE IV
POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{iN}{}^2$ (PER CENT CONTRIBUTION) FOR $Ni(C_8H_{12}S_4)_2$

B_{2u}	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
S_1	0.183	1.000	0.500	0.030	0.003	0.001
S_2	0.102	0.748	1.000	0.051	0.000	0.000
S_3	0.000	0.004	0.154	1.000	0.119	0.007
S_4	1.000	0.020	0.176	0.049	0.091	0.004
S_5	0.127	0.026	0.065	0.060	1.000	0.033
S_6	0.045	0.010	0.015	0.025	0.004	1.000
S_7	0.001	0.001	0.043	0.012	0.026	0.297
Assignment	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{Ni{-}S})$	$\delta(\mathrm{C{-}CH_3})$	Ring def

B_{3u}	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
S_8	1.000	1.000	0.216	0.445	0.023	0.000
S_9	0.666	0.993	0.022	1.000	0.128	0.019
S_{10}	0.001	0.000	1.000	0.335	1.000	0.007
S_{11}	0.334	0.687	0.460	0.586	0.515	0.014
S_{12}	0.187	0.017	0.001	0.090	0.154	0.001
S_{13}	0.364	0.086	0.598	0.853	0.000	0.005
S_{14}	0.000	0.003	0.008	0.035	0.102	1.000
Assignment	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{Ni{-}S})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring def	$\nu(\mathrm{Ni{-}S})$	$\delta(\mathrm{SMS})$

for bis(1,2-dicyanoethylene-1,2-dithiolato)nickel anion. The 13-atom structure in D_{2h} point symmetry has 33 normal vibrations ($6\ A_g + 3\ A_u + 5\ B_{1g} + 2\ B_{2g} + 3\ B_{1u} + 6\ B_{2u} + 2\ B_{3g} + 6\ B_{3u}$). The latter are readily separable into 23 in-plane vibrations of the A_g, B_{1g}, B_{2u}, and B_{3u} classes and 10 out-of-plane vibrations. Four redundancies based on the dependent angle bending coordinate from angles about each of the four trigonal carbon atoms in the chelate ring were removed by a similarity transformation. Among the seven remaining redundancies two involve the sum of angles in the chelate rings.

$$S(A_g) = (\Delta\alpha_{19} + \Delta\alpha_{46} + \Delta\alpha_{56} + \Delta\alpha_{59} + \Delta\alpha_{14}) + (\Delta\alpha_{28} + \Delta\alpha_{37} + \Delta\alpha_{57} + \Delta\alpha_{58} + \Delta\alpha_{23})$$

$$S'(B_{3u}) = (\Delta\alpha_{19} + \Delta\alpha_{46} + \Delta\alpha_{56} + \Delta\alpha_{59} + \Delta\alpha_{14}) - (\Delta\alpha_{28} + \Delta\alpha_{37} + \Delta\alpha_{57} + \Delta\alpha_{58} + \Delta\alpha_{23})$$

Only the 12 in-plane infrared-active modes ($6\ B_{2u} + 6\ B_{3u}$) were considered in the calculations. Symmetry coordinates that were established for the B_{2u} and B_{3u} representations are listed in Table II. The kinetic energy or G matrix was formed according to previously described methods.[8] The potential constants were determined in a modified Urey–Bradley force field[9] in which bond stretching, angle bending, and nonbonded atom repulsive constants were included. The partitioned secular determinant $|GF - \lambda E| = 0$, seventh order in both B_{2u} and B_{3u} species, was solved for eigenvalues and eigenvectors by use of the McGill University IBM 360-75 computer. The single redundancies that remained in the B_{2u} and B_{3u} species produced zero frequencies in the eigenvalue problem.

Calculated and observed frequencies with vibrational assignments for the nickel, palladium, and platinum chelates of 1,2-dimethylethylene-1,2-dithiolate appear in Table III. Since the average error for 30 frequencies was 3.48%, the agreement between calculated and observed values was considered satisfactory.

Assignment of vibrational modes was based on the evaluation of the potential energy distribution[10] for each normal coordinate. The per cent contribution of each symmetry coordinate to the normal modes is shown in Table IV for the nickel chelate. As a

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[8] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

[9] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[10] Y. Morino and K. Kuchitsu, *ibid.*, **20**, 1809 (1952).

further aid in making assignments the Jacobian matrix elements[11] were computed and support the assignments based on the potential energy distribution. A least-squares refinement routine[12] was employed to obtain optimum values for the force constants $K_1(M{-}S)$, $K_2(C\overset{\cdots}{-}S)$, $K_3(C{-}CH_3)$, $K_4(C\overset{\cdots}{-}C)$, $H_4(SCC)$, $H_5(SCCH_3)$, $F_4(C\overset{\cdots}{-}S)$, and $F_5(H_3C\overset{\cdots}{-}S)$. These appear in Table V. The other force constants were obtained from the dithioacetylacetonates.[5]

TABLE V

FORCE CONSTANTS[a] (MDYN/Å) FOR METAL DITHIENES

	Substituent				
	H	CH_3	C_6H_6	CH_3	CH_3
	Metal				
	Ni	Ni	Ni	Pd	Pt
$K_1(M{-}S)$	1.40	1.65	1.65	1.90	2.10
$K_2(C\overset{\cdots}{-}S)$	3.65	3.40	2.70	3.60	3.35
$K_3(C{-}R)$	4.70	3.40	3.60	3.40	3.50
$K_4(C\overset{\cdots}{-}C)$	4.70	4.40	4.80	4.50	4.40
$H_4(SCC)$	0.40	0.25	0.30	0.24	0.22
$H_5(SCR)$	0.10	0.28	0.10	0.33	0.28
$H_6(CCR)^b$	0.16	0.30	0.12	0.27	0.30
$F_4(C\cdots S)$	0.75	0.45	0.38	0.45	0.40
$F_5(R\cdots S)$	0.23	0.50	0.70	0.45	0.40
$F_6(C\cdots R)$	0.55	0.35	0.45	0.35	0.40

$H_1(SMS)^b = 0.04$ $F_1(S\cdots S)^b = 0.05$
$H_2(SMS)^b = 0.04$ $F_2(S\cdots S)^b = 0.05$
$H_3(MSC)^b = 0.05$ $F_3(M\cdots C)^b = 0.06$

[a] Stretching and bending repulsive force constant errors are 0.5 and 0.2 mdyn/Å, respectively. [b] Force constants constrained.

Normal-coordinate analyses were performed for metal dithienes with substituents other than methyl groups. After appropriate changes in mass and bond distances were made, the normal-coordinate calculations were repeated for the nickel chelates with hydrogen and benzene substituents. Interatomic distances and angles for $Ni(C_2S_2(C_6H_5)_2)_2$ were obtained from reported X-ray data.[13] After a carbon–hydrogen distance of 1.08 Å was taken, the geometric parameters of $Ni(C_2S_2H_2)_2$ were assumed identical with the ones adopted for $Ni(C_2S_2(CH_3)_2)_2$. The molecular parameters obtained from a single-crystal X-ray study[14] of $Ni(C_2S_2H_2)_2$ are very similar to those adopted for $Ni(C_2S_2(CH_3)_2)_2$. A high-frequency separation[8] of the carbon–hydrogen stretching frequencies was performed for bis(ethylene-1,2-dithiolato)nickel prior to solving the partitioned secular determinant for eigenvalues and eigenvectors. In bis(1,2-diphenylethylene-1,2-dithiolato)nickel vibrations of the phenyl group, which was assumed to be a point mass equivalent to six carbon and five hydrogen masses, were not treated in the normal-coordinate analysis. Observed and calculated frequencies for $Ni(S_2C_2H_2)_2$ and $Ni(S_2C_2(C_6H_5)_2)_2$ are reported in Tables VI and VII. The force constants that were employed appear in Table V. Assignment of the corresponding normal frequencies was derived from the potential energy distributions.

TABLE VI

OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) OF BIS(ETHYLENE-1,2-DITHIOLATO)NICKEL

	Obsd		
Calcd	Absorption	Transmission	Predominant modes
		B_{2u} Species	
1353	1340	1363	$\nu(C\overset{\cdots}{-}C)$
1076	1104, 1092	1108	$\delta(C{-}H)$
796	790		$\nu(C\overset{\cdots}{-}S)$
414	420		$\nu(Ni{-}S)$
258	. . .		Ring def
		B_{3u} Species	
1297	1288, 1253		$\delta(C{-}H)$
921	874	878	$\delta(C{-}H) + \nu(C\overset{\cdots}{-}S)$
656	714	765	$\nu(C\overset{\cdots}{-}S)$ + ring def
408	420		$\nu(Ni{-}S)$
91	. . .		$\delta(SNiS)$

TABLE VII

OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) OF BIS(1,2-DIPHENYLETHYLENE-1,2-DITHIOLATO)NICKEL

Calcd	Obsd	Predominant modes
		B_{2u} Species
1355	1358	$\nu(C\overset{\cdots}{-}C)$
896	878	$\nu(C\overset{\cdots}{-}S) + \nu(C{-}C_6H_5)$
473	465, 449	$\nu(Ni{-}S)$
369	403	$\nu(C{-}C_6H_5) + \nu(C\overset{\cdots}{-}S) + \nu(Ni{-}S)$
199		Ring def
118		$\delta(C_6H_5CS)$
		B_{3u} Species
1120	1135	$\nu(C{-}C_6H_5) + \nu(C\overset{\cdots}{-}S)$
746	745	$\nu(C\overset{\cdots}{-}S)$
464	465, 449	$\nu(Ni{-}S)$
307	300	$\delta(C_6H_5CS)$
230		$\nu(C{-}C_6H_5)$ + ring def
40		$\delta(SNiS)$

Results and Discussion

The infrared spectra of the Ni, Pd, and Pt chelates of 2,3-butanedithione are shown in Figure 2. The spectra are similar and contain at least three regions in which an anomalous dispersion curve is observed. Transmission peaks which appear near 1400, 950, and 580 cm^{-1} are followed by absorption maxima near 1330, 910, and 560 cm^{-1}. This phenomenon is less intense in the Pd complex than in the Ni and Pt chelates. The Pt chelate spectrum exhibits an additional dispersion curve in the region, 410–402 cm^{-1}. The absorption band near 402 cm^{-1} in the spectrum of the Pt complex is more intense than the corresponding bands near 400 and 385 cm^{-1} in the Ni and Pd dithienes.

The dispersion curves were observed for both pressed KBr, CsBr, and AgCl pellets and Nujol mulls containing finely powdered samples of the metal dithienes. The amount of sample grinding did not appear to affect the absorption spectra; however, higher concentrations of complex produced spectra with the dispersion effect enhanced. A large difference in the refractive index of the complex and the matrix material can produce a high degree of light scattering[15] from the

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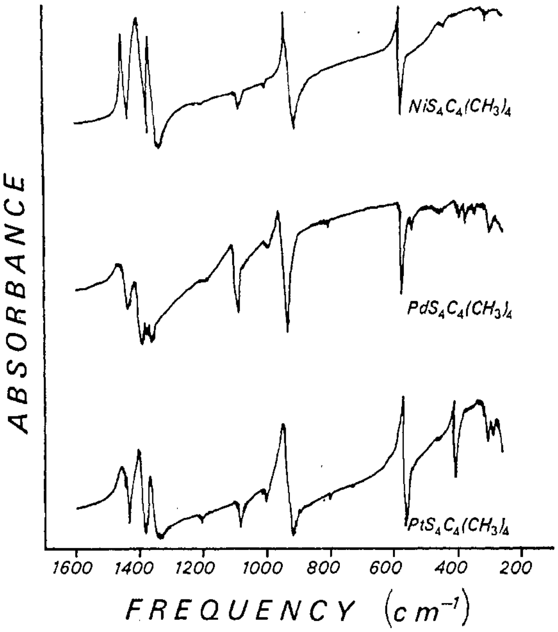

Figure 2.—Infrared spectra of metal dithienes in potassium bromide matrix.

sample. Since the solution spectra of these insoluble compounds could not be recorded, the Christiansen effect[15] was not excluded as an explanation for the anomalies.[15a]

Dimethylethylene-1,2-dithienes.—The frequencies and force constants in Tables III and V of bond stretching vibrations in the nickel, palladium, and platinum dimethylethylene-1,2-dithienes may be compared. The fundamental ν_1 is assigned to a relatively pure carbon-to-carbon stretching vibration and occurs near 1350 cm^{-1}. The corresponding force constant, $K(\text{C}\overset{\cdots}{-}\text{C})$, decreases in the order Pd > Ni ~ Pt. It is of interest to note that this stretching frequency has been employed to correlate trends in electron-transfer ability of metal dithienes.[2] Since the polarographic half-wave potential that was investigated[2] appears to depend on bonding properties in the entire chelate ring, metal–sulfur and carbon–sulfur stretching force constants as well as carbon–carbon constants could be of more value.

A band near 560 cm^{-1} arises predominantly from a $\nu(\text{C}\overset{\cdots}{-}\text{S})$ mode. Bands near 1200, 1080, and 910 cm^{-1} are assigned to the $\text{C}\overset{\cdots}{-}\text{S}$ stretching mode coupled to a C—CH_3 stretching vibration. Values for the carbon–carbon stretching force constants are the same for the chelate rings of dithioacetylacetonates[5] and dithienes. In addition, the value 3.40 mdyn/Å for $K(\text{C—CH}_3)$ in these dithienes agrees closely with the corresponding constant, 3.30 mdyn/Å, of dithioacetylacetonates.[5] However, the carbon–sulfur constants are higher in the metal dithienes and decrease in the order Pd > Ni > Pt. Metal–sulfur force constants $K(\text{Ni–S})$ = 1.65 mdyn/Å and $K(\text{Pd–S})$ = 1.90 mdyn/Å are virtually identical with the same constants in dithioacetylacetonates[5] but $K(\text{Pt–S})$ = 2.10 mdyn/Å is higher in the dithiene complex.

Nickel Dithienes.—The infrared spectra of nickel dithienes with hydrogen, methyl, and phenyl substituents are compared in Figure 3. The spectrum of bis(ethylene-1,2-dithiolato)nickel exhibits the same dispersion effect as its methyl-substituted counterpart but the spectrum of bis(1,2-diphenylethylene-1,2-dithiolato)nickel appears normal. Conductivity data[16] obtained from current measurements on pressed pellets subject to an applied voltage indicated the sequences Pd > Ni > Pt and H > C_6H_5 > CH_3, for decreasing conductivity of metal dithienes. The measured conductivity does not correlate with the predominance of dispersion anomalies or with the chelate ring bond stretching force constants.

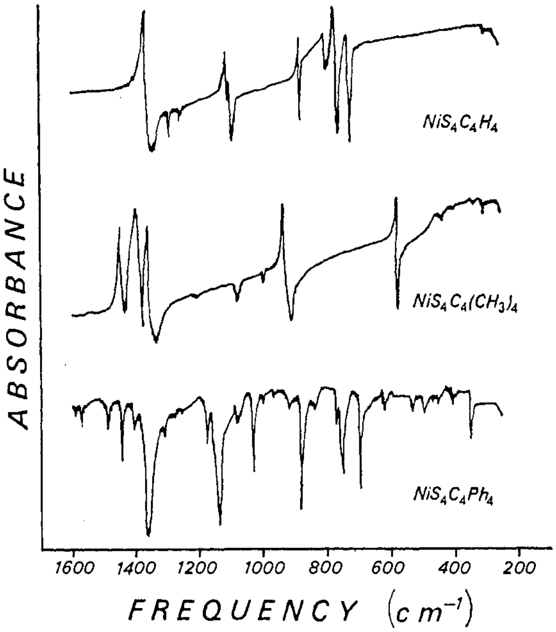

Figure 3.—Infrared spectra of nickel dithienes in potassium bromide matrix.

It is of interest to note that assignments for normal vibrations in $\text{Ni}(\text{C}_2\text{S}_2\text{H}_2)_2$ and $\text{Ni}(\text{C}_2\text{S}_2(\text{C}_6\text{H}_5)_2)_2$ change significantly and qualitative inspection of the infrared spectrum of $\text{Ni}(\text{C}_2\text{S}_2(\text{CH}_3)_2)_2$ probably would not be sifficient to assign bands in the former chelates.

Vibrations of the $\text{B}_{2\text{u}}$ Species.—As in the case of dimethylethylene-1,2-dithienes the highest band recorded was assigned as $\nu(\text{C}\overset{\cdots}{-}\text{C})$ in $\text{Ni}(\text{C}_2\text{S}_2\text{H}_2)_2$ at 1340 cm^{-1} and in $\text{Ni}(\text{C}_2\text{S}_2(\text{C}_6\text{H}_5)_2)_2$ at 1358 cm^{-1}. In the proton-substituted complex a new band appears close to 1104 cm^{-1} and is assigned to an in-plane carbon-hydrogen bending mode. An absorption peak near 878 cm^{-1} in $\text{Ni}(\text{C}_2\text{S}_2(\text{C}_6\text{H}_5)_2)_2$ originates from the coupled mode $\nu(\text{C}\overset{\cdots}{-}\text{S}) + \nu(\text{C—C}_6\text{H}_5)$. The increased mass of the phenyl group may have contributed to the shift of the 1075-cm^{-1} band $[\nu(\text{C—CH}_3) + \nu(\text{C}\overset{\cdots}{-}\text{S})]$ in $\text{NiC}_4\text{S}_4(\text{CH}_3)_4$ to 878 cm^{-1} in $\text{NiC}_4\text{S}_4(\text{C}_6\text{H}_5)_4$. The carbon–sulfur stretching frequency near 790 cm^{-1}

(15a) NOTE ADDED IN PROOF.—The Christiansen effect has been confirmed by the absence of anomalies in the infrared spectra of the dithienes pressed in thallous chloride matrices.

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in $NiC_4S_4H_4$ is considerably higher than the corresponding frequency near 565 cm^{-1} in $NiC_4S_4(CH_3)_4$. Since the $K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ values 3.65, 3.40, and 2.70 mdyn/Å for H-, CH_3-, and C_6H_5-substituted nickel dithienes decrease sharply, dithiene substituents could profoundly influence the stability of the carbon–sulfur bonds. It seems that carbon–sulfur bonds are strongest for $NiC_4S_4H_4$ and decrease in strength from $NiC_4S_4(CH_3)_4$ to $NiC_4S_4(C_6H_5)_4$.

The nickel–sulfur asymmetric stretching vibration appears near 420, 435, and 465 and 449 cm^{-1} in the H, CH_3, and C_6H_5 complexes, respectively. The corresponding force constants, K(Ni–S), are 1.40, 1.65, and 1.65 mdyn/Å. This order is the reverse of the trend noted for the carbon–sulfur stretching force constants in these compounds.

Vibrations of the B_{3u} Species.—In $NiC_4S_4H_4$ the asymmetric carbon–hydrogen bending mode occurs near 1288 cm^{-1} while a mixed vibration, $\delta(\mathrm{C—H}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, has its normal frequency close to 874 cm^{-1}. In dimethylethylene-1,2-dithienes the vibrations in the same frequency range are $\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ at 1205 and 905 cm^{-1} and in $NiC_4S_4(C_6H_5)_4$ the corresponding modes, $\nu(\mathrm{C—C_6H_5}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, near 1135 and 745 cm^{-1} are shifted to lower frequencies. In addition, $NiC_4S_4H_4$ has a normal mode near 714 cm^{-1} which is assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring deformation. Nickel–sulfur asymmetric stretching vibrations occur near 420, 500, and 465 and 449 cm^{-1} in the H, CH_3, and C_6H_5 chelates, respectively. In $NiC_4S_4(CH_3)_4$ ν(Ni—S) is mixed with the asymmetric in-plane methyl bending vibration; however, a pure Ni—S stretching mode does occur near 333 cm^{-1}. The phenyl group in-plane bending vibration appears near 300 cm^{-1} in $NiC_4S_4(C_6H_5)_4$ and the 400-cm^{-1} band in $NiC_4S_4H_4$ was assigned as $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + ring deformation.

The out-of-plane vibrations in the metal dithienes were not included in normal-coordinate calculations but can be identified by reference to the position of these vibrations[5,17] in chelates of similar structure and composition. The frequencies and assignments for out-of-plane modes are shown in Table VIII.

TABLE VIII

OUT-OF-PLANE FREQUENCIES (CM^{-1}) OF $M(C_2S_2(CH_3)_2)_2$ AND $Ni(C_2S_2H_2)_2$ AND BENZENE RING VIBRATIONS IN $Ni(C_2S_2(C_6H_5)_2)_2$

Vibration	$Ni(C_2S_2(CH_3)_2)_2$	$Pd(C_2S_2(CH_3)_2)_2$	$Pt(C_2S_2(CH_3)_2)_2$	$Ni(C_2S_2H_2)_2$
CH_3 degen def	1427	1431	1430	. . .
CH_3 sym def	1375	1389, 1375	1379	. . .
CH_3 rock	994	995	998	. . .
C–H out-of-plane bend	. . .	. . .	. . .	754
Phenyl group	1592, 1573, 1409, 1442, 1400, 1309, 1278, 1255, 1175, 1108, 1074, 1025, 998, 983, 962, 910, 900, 836, 762, 691, 650, 613, 526, 493, 350			

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Hindered-Ligand Systems. V. Stability Constants for Some Metal Complexes of *cis,cis*-1,3,5-Triaminocyclohexane[1]

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The acid dissociation constants for the trihydrochloride of *cis,cis*-triaminocyclohexane (*cis,cis*-tach) have been determined in 0.1 M KCl at 25.0°. The equilibria which exist between the ligand and the Ni(II), Cu(II), or Zn(II) ions were investigated under identical conditions. A comparison of the formation constants of the 1:1 complexes of *cis,cis*-tach and those of other tridentate amines is presented and discussed. The spectra (electronic and esr) of the new bis complex $Cu(cis,cis\text{-tach})_2^{2+}$ are presented.

Stability constants of some metal complexes containing *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) were first reported by Brauner and Schwarzenbach.[2] Among several unusual results associated with this study was the conclusion that measurable quantities of a dicoordinated, singly protonated complex existed. It was suggested that the ligand was probably constrained to the boat conformation because of steric and electrostatic repulsion between the positively charged metal ion and the ammonium groups. Another unusual result occurred when they observed no complex formation with Ni(II).

Subsequent studies[3] have, however, shown that the method of synthesis employed by Brauner and Schwar-

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