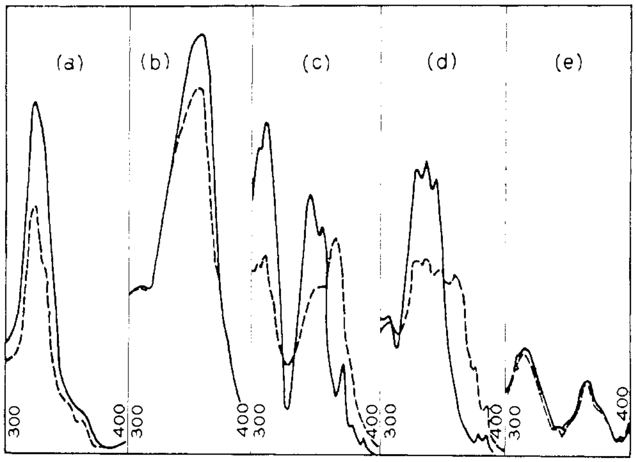

Figure 7.—Infrared spectra at low (——) and at room temperatures (– – –), for $Fe(S_2CNR_2)_3$ complexes with substituents NR_2 = (a) pyrrolidyl, (b) N,N-di-*n*-butyl, (c) N,N-di-*n*-propyl, (d) N,N-diethyl, and (e) N,N-diisopropyl.

Although unequivocal conclusions cannot be drawn from the infrared results at this stage, the temperature dependence of the magnetism is clearly in good accord with, and well explained by, the model and correlates well with the interpretation of the electronic spectra.

Experimental Section

The xanthate and dithiophosphate complexes were prepared by one of the methods described[1] for the dithiocarbamates: the sodium salt of the ligand was treated with a ferric salt in concentrated aqueous solution, and the resulting complex recrystallized from an organic solvent such as chloroform.

The magnetic measurements at various temperatures and pressures and density measurements on solid complexes were carried out as described previously.[2,15] The densities of solutions of complexes were measured at one temperature and atmospheric pressure, and their compressibilities and thermal expansion coefficients were assumed to be the same as that of the solvents used. No appreciable errors are introduced by this assumption.[15] The compressibility of chlorobenzene was obtained from ref 18, and references for the other solvents have been given elsewhere.[15]

Phase changes in solid complexes under pressure were investigated by compressing the samples in polythene tubes inserted into a steel cylinder. Reproducible discontinuities in the plot of volume against pressure were taken to be phase changes.

Infrared spectra were obtained at low and at room temperatures by mounting the samples in KBr disks on a copper block capable of being chilled with liquid air.

Acknowledgment.—We are indebted to Mr. E. S. Merritt for his assistance with the construction and maintenance of apparatus, to Dr. S. D. Hamann for access to a variable-pressure spectrophotometer, to Dr. J. M. James for access to a Unicam SP700 spectrophotometer, and to Dr. W. Zimmermann for the microanalytical figures.

(18) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 129 (1349).

Contribution from the Chemistry Department,
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Infrared Spectra of Divalent Metal Dithioacetylacetonates[1]

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The infrared spectra of iron(II), cobalt(II), nickel(II), palladium(II), and platinum(II) complexes of dithioacetylacetone have been recorded from 4000 to 300 cm^{-1}. Vibrational assignments were obtained by normal-coordinate analyses. Except for metal–sulfur vibrations, the spectra have been slightly affected by the nature of the coordinated metal. Metal–ligand bonding in dithioacetylacetonates and similar complexes was discussed on the basis of their molecular spectra.

Introduction

Although infrared spectra of several metal chelates of dithioacetylacetone have been reported,[2,3] normal-coordinate analyses have not previously been performed on these complexes. Where band assignments have been made, ordinary inspection methods were used. These assignments should be considered tentative since group frequencies are unreliable in the low-frequency region and the possibility of intramolecular vibrational coupling was ignored.

Normal-coordinate analyses[4-6] have been carried out for a number of acetylacetonates whose molecular structures are similar to the dithioacetylacetone metal chelates. These calculations were performed for a 1:1 metal–ligand model in which the methyl groups were considered as point masses. More recently, they were extended[7] by considering the total symmetry of the complex, either as 1:2 or 1:3 metal–ligand structures. Reasonably good agreement with the simple 1:1 model exists for band assignments in the region of intermediate frequency and for metal–oxygen vibrations in the low-frequency region. However, calculated force constants were found to be approximately 20% greater for the 1:1 chelate model in the lower frequency region.

As part of our investigation of the spectra of chelates of sulfur analogs of β-diketones, the infrared spectra of iron(II), cobalt(II), nickel(II), palladium(II), and

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(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968.

(2) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966).

(3) A. Ouchi, M. Hyodo, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **40**, 2819 (1967).

(4) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(5) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

(6) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(7) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).

platinum(II) dithioacetylacetonates have been recorded in the region 4000–300 cm^{-1}. To contrast the properties of the acetylacetonates with the dithioacetylacetonates and further examine the nature of metal–sulfur bonding, a normal-coordinate treatment has been completed. Since the observed bands can now be reasonably assigned and good agreement exists between calculated and observed frequencies, the simple chelate model used for the calculations appears satisfactory. The results of the calculations are reported here.

Experimental Section

Preparation of Compounds.—The Fe(II), Co(II), Ni(II), and Pd(II) complexes of dithioacetylacetone were prepared by passing dry hydrogen chloride gas for 1 hr through 300 ml of a 5% ethanolic solution of acetylacetone cooled to −78°. The hydrogen chloride was replaced by hydrogen sulfide gas and the bubbling continued for 0.5 hr. Upon addition of 0.1 mol of metal chloride dissolved in 400 ml of 1:1 water–ethanol solution, the chelate immediately precipitated. The products were recrystallized three times from acetone.

The Pt(II) and Pd(II) complexes of dithioacetylacetone were prepared by the addition of 30 ml of 2-mercapto-2-penten-4-one[8] to 5 g of K_2PtCl_4 or K_2PdCl_4 dissolved in 250 ml of 1:1 water–acetone heated close to the boiling point. The chelates precipitated from the almost boiling and vigorously stirred solution. Products were recrystallized three times from acetone.

Bis(dithioacetylacetonato)nickel(II) appeared as dark red crystals, mp >268° dec. *Anal.* Calcd for $C_{10}H_{14}S_4Ni$: C, 37.39; H, 4.39; S, 39.93. Found: C, 37.17; H, 4.45; S, 39.99. ^{1}H nmr spectrum ($CDCl_3$): $\delta(CH_3)$, 2.34 ppm; δ(CH), 7.13 ppm; intensity 6:1 (TMS = 0).

Bis(dithioacetylacetonato)cobalt(II) appeared as dark red-violet crystals, mp >250° dec. *Anal.* Calcd for $C_{10}H_{14}S_4Co$: C, 37.37; H, 4.39; S, 39.91. Found: C, 36.29; H, 4.41; S, 39.44.

Bis(dithioacetylacetonato)iron(II) appeared as black crystals, mp >260° dec. *Anal.* Calcd for $C_{10}H_{14}S_4Fe$: S, 40.29. Found: S, 41.33.

Bis(dithioacetylacetonato)palladium(II) appeared as bright red crystals, mp >260° dec. *Anal.* Calcd for $C_{10}H_{14}S_4Pd$: S, 34.77. Found: S, 34.41. ^{1}H nmr spectrum ($CDCl_3$): $\delta(CH_3)$, 2.52 ppm; δ(CH), 7.18 ppm; intensity 6:1 (TMS = 0).

Bis(dithioacetylacetonato)platinum(II) appeared as purple crystals, mp >260° dec. *Anal.* Calcd for $C_{10}H_{14}S_4Pt$: S, 28.03. Found: S, 27.63.

Spectral Measurements.—The spectra were recorded with a Perkin-Elmer 521 infrared spectrophotometer over the range 4000–300 cm^{-1}. Potassium bromide and cesium bromide pellets and Nujol mulls were prepared for all compounds. Calibration of frequency readings was performed with polystyrene film and water vapor.

Method of Calculation

Since vibrational coupling between ligands in acetylacetone chelates has been previously shown[4] to be small, a 1:1 metal–dithioacetylacetone model was adopted for this analysis. In Figure 1 the model for the cobalt(II) chelate is shown with the two methyl groups collapsed to point masses. The symmetry of the resultant nine-atom structure is C_{2v}. Of the 21 normal modes of vibration possible, 15 are infrared-active in-plane vibrations ($8\ A_1 + 7\ B_2$) and 6 are out-of-plane vibrations ($2\ A_2 + 4\ B_1$). Neither the latter vibrations nor the γ-carbon C–H stretching mode for which a "high-frequency separation" is applicable were treated in subsequent calculations. The symmetry coordinates for the in-plane vibrations are listed in Table I. Of the six redundant coordinates generated, four are readily removed while the other two were included in the calculation. In the final results these redundancies gave zero frequencies.

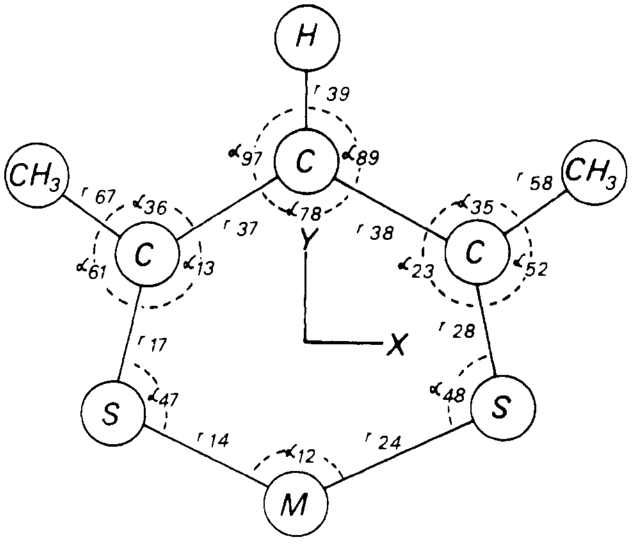

Figure 1.—Molecular model and internal coordinates.

TABLE I

SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS

Coordinates	Vibrational mode
A_1 Species	
$S_1 = (1/\sqrt{2})(\Delta r_{17} + \Delta r_{28})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{S})$
$S_3 = (1/\sqrt{2})(\Delta r_{37} + \Delta r_{38})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{C})$
$S_5 = (1/\sqrt{2})(\Delta r_{67} + \Delta r_{58})$	ν(C—R)
$S_7 = (1/\sqrt{2})(\Delta r_{14} + \Delta r_{24})$	ν(M—S)
$S_9 = \Delta r_{39}$	ν(C—H)
$S_{10}{}^a = (1/\sqrt{2})(\Delta\alpha_{36} - \Delta\alpha_{61} + \Delta\alpha_{35} - \Delta\alpha_{52})$	δ(C—R)
$S_{14} = (1/2)(\Delta\alpha_{13} + \Delta\alpha_{23} - \Delta\alpha_{47} - \Delta\alpha_{48})$	Ring def
$S_{17} = (1/\sqrt{12})(2\Delta\alpha_{12} + 2\Delta\alpha_{78} - \Delta\alpha_{13} - \Delta\alpha_{23} - \Delta\alpha_{47} - \Delta\alpha_{48})$	Ring def
$S_{18} = (1/\sqrt{2})(\Delta\alpha_{12} - \Delta\alpha_{78})$	Ring def
B_2 Species	
$S_2 = (1/\sqrt{2})(\Delta r_{17} - \Delta r_{28})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{S})$
$S_4 = (1/\sqrt{2})(\Delta r_{37} - \Delta r_{38})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{C})$
$S_6 = (1/\sqrt{2})(\Delta r_{67} - \Delta r_{58})$	ν(C—R)
$S_8 = (1/\sqrt{2})(\Delta r_{14} - \Delta r_{24})$	ν(M—S)
$S_{11}{}^a = (1/\sqrt{2})(\Delta\alpha_{36} - \Delta\alpha_{61} - \Delta\alpha_{35} + \Delta\alpha_{52})$	δ(C—R)
$S_{12}{}^a = \Delta\alpha_{97} - \Delta\alpha_{89}$	δ(C—H)
$S_{15} = (1/2)(\Delta\alpha_{13} - \Delta\alpha_{23} + \Delta\alpha_{47} - \Delta\alpha_{48})$	Ring def
$S_{16} = (1/2)(\Delta\alpha_{13} - \Delta\alpha_{23} - \Delta\alpha_{47} + \Delta\alpha_{48})$	Ring def

[a] Not normalized.

The G and F matrices are similar to those described for bis(acetylacetonato)copper(II).[9] The G matrix was evaluated by using the molecular parameters of bis(dithioacetylacetonato)cobalt(II).[10] The metal–ligand and adjusted ligand parameters used in the calculations for the chelates appear in Table II.

The eighth-order A_1 and B_2 secular equations of the

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[8] R. Mayer, G. Hiller, M. Nitzschke, and J. Jentzsch, *Angew. Chem. Intern. Ed. Engl.*, **2**, 370 (1963).

[9] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 277.

[10] R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

Table II

Molecular Parameters of Dithioacetylacetonates

	Fe(DTAA)$_2$	Co-(DTAA)$_2$	Ni(DTAA)$_2$	Pd-(DTAA)$_2$	Pt(DTAA)$_2$
$\alpha_{47} = \alpha_{48}$	118.4°	117.0°	116.4°	119.8°	121.3°
α_{12}	94.1°	97.0°	98.2°	91.4°	88.4°
$r_{14} = r_{24}$	2.21 Å	2.16 Å	2.14 Å	2.26 Å	2.32 Å

$r_{17} = r_{28} = 1.70$ Å

$r_{37} = r_{38} = 1.38$ Å

$r_{67} = r_{58} = 1.55$ Å

$r_{39} = 1.08$ Å

$\alpha_{13} = \alpha_{23} = 132.0°$

$\alpha_{78} = 125.0°$

$\alpha_{97} = \alpha_{89} = 117.5°$

$\alpha_{61} = \alpha_{52} = \alpha_{35} = \alpha_{36} = 114.0°$

Table III

Dithioacetylacetonate Force Constants (10^5dyn/cm)

	Fe-(DTAA)$_2$	Co-(DTAA)$_2$	Ni-(DTAA)$_2$	Pd-(DTAA)$_2$	Pt-(DTAA)$_2$
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	3.40	3.35	3.30	3.30	3.30
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	4.40	4.40	4.40	4.40	4.40
$K(\mathrm{C—CH_3})$	3.30	3.30	3.40	3.20	3.30
$K(\mathrm{M—S})$	1.45	1.55	1.65	1.85	1.95
$H(\mathrm{CCS})$	0 31	0.30	0.30	0.28	0.30
$H(\mathrm{H_3CCS})$	0.31	0.33	0.45	0.35	0.32
$F(\mathrm{C\cdots S})$	0.37	0.45	0.40	0.45	0.42
$F(\mathrm{S\cdots CH_3})$	0.35	0.42	0.45	0.50	0.36

M(DTAA)$_2$					
$K(\mathrm{C—H})$	4.70	$H(\mathrm{H_3CCC})$	0.25	$F(\mathrm{C\cdots CH_3})$	0.40
		$H(\mathrm{MSC})$	0.04	$F(\mathrm{C\cdots M})$	0.05
		$H(\mathrm{SMS})$	0.04	$F(\mathrm{S\cdots S})$	0.12
		$H(\mathrm{CCC})$	0.35	$F(\mathrm{C\cdots C})$	0.40
		$H(\mathrm{CCH})$	0.20	$F(\mathrm{C\cdots H})$	0.55

form $|GF - E\lambda| = 0$ were solved for eigenvalues and eigenvectors by use of the McGill University IBM 360-75 computer. The sets of force constants which correspond to the observed frequencies are listed in Table III. A best-least-squares fit was obtained for the stretching force constants $K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, K $(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, $K(\mathrm{C—CH_3})$, and $K(\mathrm{M—S})$, two bending force constants $H(\mathrm{C—C—S})$ and $H(\mathrm{S—C—CH_3})$, and two repulsive force constants $F(\mathrm{C\cdots S})$ and $F(\mathrm{S\cdots CH_3})$. Except for the S···S repulsive force constant, the remaining force constants are essentially the same as those for acetylacetonates. A comparison of the observed frequencies and those calculated for the five chelates is shown in Table IV. Since the average error is 2.8% for 50 frequencies with a maximum deviation of ±1.8%, the agreement is considered good. The band assignments in Table IV were obtained from the normalized eigenvectors shown in Table V for Co(DTAA)$_2$ and subsequent calculation of the potential energy distribution in each eigenvalue. The results for Co(DTAA)$_2$ are typical and appear in Table VI. Further confirmation of the validity of these assignments may be obtained from evaluation of the Jacobian matrix elements relating small changes in frequency to similar changes in force constant. Small changes in force constant which result in comparatively large changes in frequency indicate that the force constant examined predominates the mode describing that frequency.

Values of Jacobian matrix elements for stretching force constants in the Co(II) chelate are shown in Table VII. The calculations support the assignments made on the basis of the potential energy distribution.

Table IV

Calculated and Observed Frequencies (cm^{-1}) of Metal Dithioacetylacetonates

	Fe(DTAA)$_2$		Co(DTAA)$_2$		Ni(DTAA)$_2$		Pd(DTAA)$_2$		Pt(DTAA)$_2$		
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Assignment
					A$_1$ Species						
λ_1	1300	1290	1300	1290	1307	1292	1299	1301	1296	1300	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
λ_2	1141	1151	1143	1156	1161	1158	1132	1150	1141	1156	$\nu(\mathrm{C—CH_3})$
λ_3	690	696	698	702	694	705	695	705	692	706	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
λ_4	540	552	548	558	565	559	563	560	548	557	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{M—S})$
λ_5	371	345, 365	377	371	388	371, 390	381	366	374	371	$\nu(\mathrm{M—S})$
λ_6	276	...	281	...	293	...	281	...	269	...	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{M—S})$
λ_7	163	...	160	...	160	...	148	...	137	...	Ring def
					B$_2$ Species						
λ_8	1473	1460	1475	1485	1479	1488	1474	1479	1474	1467	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \delta(\mathrm{C—H})$
λ_9	1331	1332	1331	1311	1336	1313	1331	1321	1329	1315	$\delta(\mathrm{C—H}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
λ_{10}	1044	1083	1042	1076	1050	1070	1029	1076	1041	1088	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
λ_{11}	747	738	752	749	760	750	753	751	747	751	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S}) + \nu(\mathrm{C—CH_3})$
λ_{12}	465	433	479	470	513	470	499	460	476	463	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{M—S})$
λ_{13}	310	...	317	...	323	...	309	...	307	...	Ring def
λ_{14}	285	...	292	...	297	...	283	...	264	...	$\nu(\mathrm{M—S})$

Results and Discussion

The infrared spectra of dithioacetylacetone chelates of several divalent metals [M(DTAA)$_2$] are shown in Figure 2. Differences in these spectra are slight except in the metal-sensitive region. Vibrational mode assignments based on potential energy distribution calculations for the in-plane vibrations are identical for corresponding frequencies in the five metal chelates. This suggests that the charge distribution in the sulfur and carbon-containing backbone of the chelate ring has changed little with different metals. The out-of-plane vibrations also vary slightly with change in chelated metal ion and can be readily assigned by reference to the out-of-plane vibrations in acetylacetonate chelates [M(AA)$_n$] with which they are almost identical as shown in Table VIII.

More significant differences exist among the metal–ligand vibrations. The metal–sulfur stretching force constants increase in the order Fe(II) < Co(II) < Ni(II) < Pd(II) < Pt(II) as may be noted in Table III.

TABLE V

NORMALIZED L MATRIX ELEMENTS FOR Co(DTAA)$_2$

A_1	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7
S_1	0.255	−0.059	−0.196	0.084	0.014	−0.016	−0.004
S_3	−0.300	−0.141	−0.037	0.050	0.043	0.018	0.003
S_5	−0.044	0.362	0.056	0.111	0.031	−0.001	0.000
S_7	−0.011	0.013	0.026	−0.106	0.153	−0.100	−0.019
S_{10}	0.598	0.067	−0.031	−0.126	0.204	0.214	−0.007
S_{14}	−0.098	0.339	−0.179	−0.140	0.005	−0.034	0.121
S_{17}	0.291	−0.205	0.126	0.103	0.035	−0.015	0.146
S_{18}	−0.216	0.168	−0.190	−0.028	−0.043	0.029	0.059

B_2	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}	λ_{13}	λ_{14}
S_2	0.052	0.188	−0.191	0.190	−0.041	0.043	0.003
S_4	−0.388	−0.243	0.011	0.060	0.010	0.014	0.012
S_6	0.119	−0.008	0.340	0.134	−0.034	−0.009	−0.022
S_8	0.003	−0.006	0.022	−0.033	0.158	0.078	−0.122
S_{11}	0.077	0.321	−0.166	0.367	0.342	−0.149	0.034
S_{12}	1.479	−1.274	−0.380	0.152	0.013	0.207	−0.010
S_{15}	0.092	−0.026	0.117	−0.091	−0.016	−0.027	0.052
S_{16}	0.211	0.048	0.246	0.011	0.132	0.159	0.112

TABLE VI

POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{iN}^2\lambda N$ (PER CENT CONTRIBUTION) FOR Co(DTAA)$_2$

A_1	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7
S_1	0.482	0.028	1.000	0.603	0.021	0.042	0.004
S_3	1.000	0.239	0.054	0.322	0.282	0.084	0.004
S_5	0.014	1.000	0.078	1.000	0.093	0.000	0.000
S_7	0.000	0.001	0.008	0.406	1.000	0.718	0.034
S_{10}	0.345	0.005	0.003	0.175	0.539	1.000	0.002
S_{14}	0.015	0.193	0.175	0.353	0.001	0.041	0.699
S_{17}	0.129	0.069	0.085	0.187	0.026	0.008	1.000
S_{18}	0.070	0.046	0.189	0.014	0.037	0.028	0.159
Assignment	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	$\nu(\mathrm{C—CH_3})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{C—CH_3})$ + $\nu(\mathrm{M—S})$	$\nu(\mathrm{M—S})$	$\delta(\mathrm{C—CH_3})$ + $\nu(\mathrm{M—S})$	Ring def

B_2	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}	λ_{13}	λ_{14}
S_2	0.013	0.307	0.330	1.000	0.110	0.353	0.002
S_4	1.000	0.685	0.001	0.134	0.009	0.048	0.034
S_6	0.067	0.000	1.000	0.475	0.071	0.013	0.081
S_8	0.000	0.000	0.002	0.012	0.645	0.453	1.000
S_{11}	0.004	0.116	0.033	0.485	1.000	0.432	0.025
S_{12}	0.772	1.000	0.094	0.045	0.001	0.580	0.001
S_{15}	0.009	0.001	0.026	0.049	0.003	0.027	0.099
S_{16}	0.046	0.004	0.116	0.001	0.241	1.000	0.457
Assignment	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ + $\delta(\mathrm{C—H})$	$\delta(\mathrm{C—H})$ + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	$\nu(\mathrm{C—CH_3})$ + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ + $\nu(\mathrm{C—CH_3})$	$\delta(\mathrm{C—CH_3})$ + $\nu(\mathrm{M—S})$	Ring def	$\nu(\mathrm{M—S})$

TABLE VII

JACOBIAN MATRIX ELEMENTS, $(1/\lambda)(\partial\lambda/\partial K)$, FOR Co(DTAA)$_2$

A_1	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	0.065	0.005	0.134	0.040	0.002	0.005	0.001
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	0.090	0.026	0.005	0.014	0.023	0.007	0.001
$K(\mathrm{C—CH_3})$	0.002	0.171	0.011	0.070	0.012	0.000	0.000
$K(\mathrm{M—S})$	0.000	0.000	0.002	0.063	0.281	0.217	0.023

B_2	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}	λ_{13}	λ_{14}
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	0.002	0.034	0.057	0.108	0.012	0.031	0.000
$K(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	0.118	0.057	0.000	0.011	0.001	0.003	0.003
$K(\mathrm{C—CH_3})$	0.011	0.000	0.181	0.054	0.008	0.001	0.010
$K(\mathrm{M—S})$	0.000	0.000	0.001	0.003	0.185	0.103	0.297

An increase in coordinate bond strength from Fe(II) through Pt(II) is expected since the trends for metal–oxygen force constants and heats of formation of metal–oxygen bonds in acetylacetonates were shown to be identical.[5]

A comparison of frequencies and force constants for stretching modes of dithioacetylacetonates and acetylacetonates shows sulfur is less effective than oxygen in transmitting electronic effects to the chelate backbone. The comparison further shows systematic trends exist among the carbon–carbon bonds, carbon–donor atom bonds, and metal–ligand bonds. The C$\overset{\cdots}{-}$C stretching mode which appears between 1544 and 1601 cm^{-1} in the cobalt(II), nickel(II), palladium(II), and platinum(II) acetylacetonates[5,6] is located in the 1270–1301-cm^{-1} range of the dithioacetylacetonates. A concomitant decrease in C$\overset{\cdots}{-}$C force constants from 5.35 to 4.40 mdyn/Å also exists. Force constants for the C$\overset{\cdots}{-}$O stretching mode have a spread from 6.50 to 7.70 mdyn/Å while the C$\overset{\cdots}{-}$S stretching force constant ranges from 3.30 to 3.35 mdyn/Å in the same chelates. Metal–ligand vibrations conform to the same pattern since metal–oxygen force constants vary from 2.05 to 2.65 mdyn/Å while metal–sulfur force constants are found between 1.65 and 1.95 mdyn/Å in the Ni(II), Pd(II), and Pt(II) chelates. The reduction in stretching force constants accompanying sulfur-for-oxygen replacement has a counterpart in oxalato and dithiooxalato complexes.[11,12] In these cases K(C—C) de-

TABLE VIII

OUT-OF-PLANE VIBRATIONS (CM^{-1}) OF ACETYLACETONATES[a] AND DITHIOACETYLACETONATES

Chelate	Degenerate def	Sym def	$\rho_r(\mathrm{CH_3})$[b]	π(C–H)[c]
Fe(DTAA)$_2$	1430	1360	1005	838, 849
Co(DTAA)$_2$	1425	1346	1009	828
Ni(DTAA)$_2$	1430	1352	1014	831
Pd(DTAA)$_2$	1430	1343	1017	830
Pt(DTAA)$_2$	1430	1342	1011	833
Fe(AA)$_3$	1390	1365	1002	800, 770
Co(AA)$_3$	1390	1372	1022	780, 771, 764
Co(AA)$_2$	1398	1366	1020	767
Ni(AA)$_2$	1398	1367	1020	764
Pd(AA)$_2$	1395	1358	1022	781
Pt(AA)$_2$	1425	1375	1027	779

[a] See ref 4–6. [b] Methyl rock. [c] C–H out-of-plane bend.

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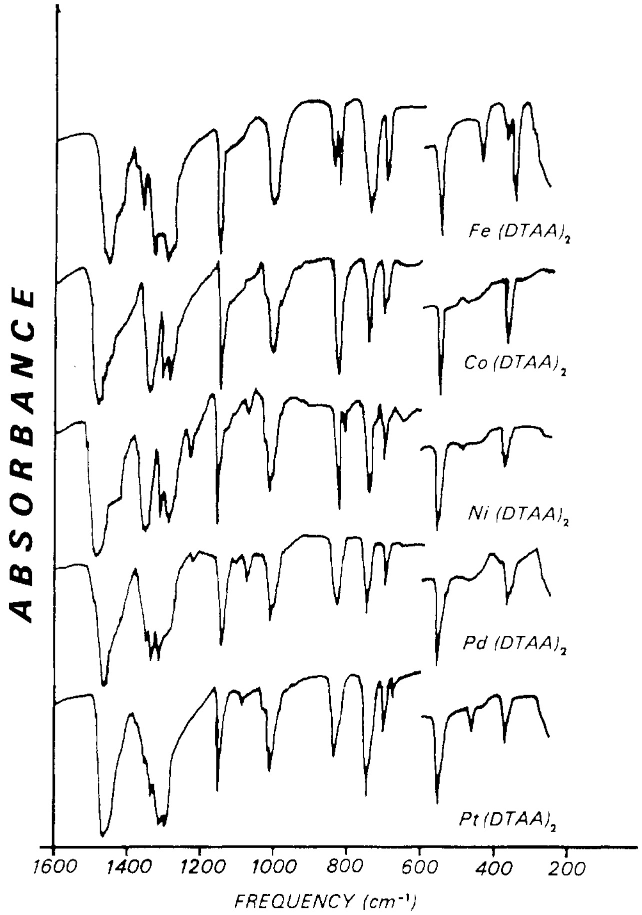

Figure 2.—Infrared spectra of dithioacetylacetonates.

creases from 3.50 to 2.60 mdyn/Å, K(C—O) has a value of 5.00 mdyn/Å while K(C—S) is 3.30 mdyn/Å, and K(Pt—O) equals 2.70 mdyn/Å, whereas K(Pt—S) is 2.30 mdyn/Å. The simultaneous decreases observed for the carbon–carbon, metal–ligand, and carbon–donor atom bonds indicate that a weakened ring system exists in the dithioacetylacetonates. In the case of the six-membered chelates, the presence of large sulfur atoms requires an expansion of the carbon bond angles from 120°. However, in all cases it would be necessary also to invoke fundamental electronic differences to differentiate between sulfur and oxygen.

Infrared studies of thiocyanato complexes have shown the C—S stretching frequency is much higher in M—N═C═S (ν ~820 cm^{-1}) than in M—S—C≡N (ν ~700 cm^{-1}).[13,14] Results of vibrational studies on thiourea and its metal complexes indicate the C—S bands close to 700 cm^{-1} in the spectra of the complexes correspond to the 730-cm^{-1} band in the free ligand.[15] The band assigned to the C—S stretching vibration in dithioacetylacetonates occurs near 705 cm^{-1}. Decrease of the C—S frequency upon coordination with metals can be associated with a reduction in the C—S bond order. The similarity in C—S frequency upon coordination further suggests that the C—S bond order in dithioacetylacetonates is similar to that in thiocyanato (M—S–) and thiourea complexes.

The stretching modes associated with the sulfur atom in metal dithioacetylacetonates, M(DTAA)$_2$, dithiooxalates, M(S$_2$O$_2$C$_2$)$_2^{2-}$, and dithiocarbamates, M(S$_2$CNH$_2$)$_2$ have been listed in Table IX. Comparison of these chelates reveals that a regular decrease in the C—S stretching frequency is accompanied by an increase in the M—S band. This suggests that the metal–sulfur bonds in dithiooxalates are strongest and decrease in strength from dithiocarbamates to dithioacetylacetonates. Similarly, C—S bonds in dithioacetylacetonates are the strongest and decrease in strength from dithiocarbamates to dithiooxalates.

Table IX

Comparison of Dithioacetylacetonate, Dithiooxalate, and Dithiocarbamate Frequencies (cm^{-1}) and Force Constants (mdyn/Å)

Vibration	Metal	M(DTAA)$_2$	M(S$_2$O$_2$C$_2$)$_2^{2-}$ [a]	M(S$_2$CNH$_2$)$_2$ [b]
ν(C–S)	Ni(II)	705	570	630
	Pd(II)	705	568	625
	Pt(II)	706	573	622
ν(M–S)	Ni(II)	371, 390	435, 420	385
	Pd(II)	366	430, 420	387
	Pt(II)	371	436, 422	375
Force constant				
K(C–S)	Pt(II)	3.30	3.30	3.00
K(M–S)	Pt(II)	1.95	2.30	2.10

[a] Reference 12. [b] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).

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