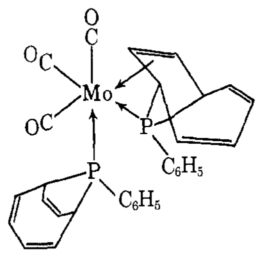

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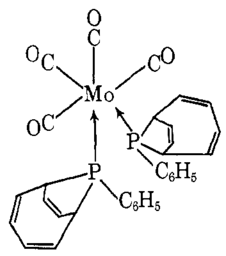

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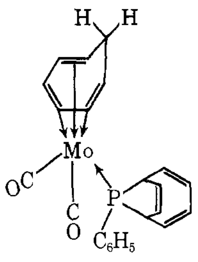

V

the complexes (triene)$Mo(CO)_3$ (triene = 1,3,5-cyclooctatriene or cyclooctatetraene) to react with carbon monoxide for a few minutes at atmospheric pressure to give the tetracarbonyls (triene)$Mo(CO)_4$, where only two of the three double bonds of the triene (those in relative 1,5 positions) remain complexed with the metal atom.

A minor product of the reaction between cycloheptatrienetricarbonylmolybdenum and $C_8H_8PC_6H_5$ is the red sublimable solid, $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$ (V), obtained in quantities too small for detailed study. Formation of this complex represents the first example of a reaction of cycloheptatrienetricarbonylmolybdenum with a ligand where the cycloheptatriene ligand is not removed. The relatively low yield of $C_7H_8Mo(CO)_2(C_8H_8PC_6H_5)$ indicates the low tendency for this type of reaction to occur.

This work provides a clear demonstration of the much lower tendency for carbon–carbon double bonds relative to a tricovalent phosphorus atom to bond to a transition metal. Certainly if the double bonds in 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II) possessed appreciable tendency to bond to a metal atom, chelate complexes of II involving both metal–phosphorus and metal–olefin bonds should be observed. The fact that only one derivative (*i.e.*, *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ (III)) with a metal–olefin bond could be prepared and that the metal–olefin bond in this derivative is readily cleaved by carbon monoxide to form *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$ (IV) demonstrates the lower tendency for metal atoms to bond to olefins than to tricovalent phosphorus atoms. Further work is in progress with vastly different types of unsaturated phosphines in attempts to explore the relative stabilities of metal–olefin and metal–phosphorus bonds in other types of systems.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67 and to Badische Anilin- und Sodafabrik for generous gifts of cyclooctatetraene.

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Metal Complexes of Thiocarbohydrazide

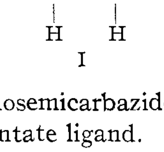
BY G. R. BURNS[1]

Received August 1, 1967

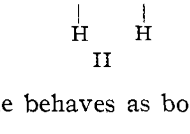
The ligand thiocarbohydrazide is shown to form a series of complexes with Zn(II), Cd(II), Hg(II), Fe(II), Co(II), Ni(II), Cu(II), and Pd(II). A comparison of their infrared and electronic absorption spectra with the spectra of thiosemicarbazide complexes of known structure suggests that bonding occurs through the thioketo group. Visible reflectance spectra and magnetic moments of the complexes of the first-row transition metal ions and the Mössbauer spectrum of the Fe(II) complex further suggest that they all have strongly distorted octahedral environments.

Introduction

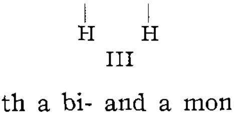
A number of ligands with dual sites available for coordination to metal ions have been studied. Of particular interest are thioamide and thiohydrazide derivatives which have both sulfur and nitrogen atoms as potential donors. Two ligands of this type are thiourea (I) and thiosemicarbazide (Htscaz) (II).



I



II



III

Thiourea acts as a monodentate ligand coordinating to metal ions using only the thioketo group,[2-4] whereas thiosemicarbazide behaves as both a bi- and a monodentate ligand.

X-Ray crystallographic measurements have shown that $Ni(Htscaz)_2SO_4 \cdot 3H_2O$[5] involves coordination by the thioketo group and the NH_2 group of the hydrazine

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(1) Department of Chemistry, The University, Reading, England.

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residue and that the red-brown complex, $Ni(tscaz)_2$,(6) is bonded through the thioenolic sulfur atom and the hydrazinic nitrogen (V, R = H). The thiosemicarbazide complexes of Zn(II),(7) Co(III), Cu(II), Pd(II), and Pt(II)(8-10) involve structures similar to that of the former Ni(II) complex, while crystallographic measurements have shown(11) that in Ag(Htscaz)Cl the ligand is monodentate, coordinating only through the sulfur atom (VIII, R = H).

Metal complexes of the next higher homolog in the series, thiocarbohydrazide (Htcaz) (III), have been prepared and studied in order to learn whether coordination to metal ions still occurs through the sulfur atom or whether advantage is taken of the available nitrogen donors to form a coordination sheath consisting of only nitrogen atoms.

The formation of colors and precipitates by thiocarbohydrazide with some metal ions in aqueous solution has been reported by Duval and Loc(12) and Buu-Hoï, Loc, and Xuong.(13)

Carbohydrazide (Hcaz), the oxygen analog of thiocarbohydrazide, was studied in acid solution and shown to form complexes with Zn(II), Cd(II), Cu(II), and Ni(II),(14) all of which were considered to be coordinated by two nitrogen atoms of each ligand molecule.

Experimental Section

Preparations.—The colors and precipitates reported by Loc and his co-workers were formed only in the presence of hydrazinedithiocarbazic acid, the precursor of thiocarbohydrazide, which suggests that they are salts of this acid and not derivatives of thiocarbohydrazide.

(a) **Thiocarbohydrazide.**—Carbon disulfide (15 ml) was added dropwise, with stirring, over a period of 1 hr to a warm (~50°) solution of hydrazine hydrate (50 ml) and water (150 ml). The mixture was then refluxed at 90° for 1 hr further and cooled; the colorless crystals which separated out were recrystallized from water.

Anal. Calcd for CH_6N_4S: C, 11.3; H, 5.7; N, 52.8; S, 30.2. Found: C, 11.6; H, 6.0; N, 51.7; S, 30.5.

(b) **Bis(thiocarbohydrazide)zinc(II) Chloride.**—A warm solution of zinc chloride in dimethylformamide–water (5:1) was added to a warm solution of thiocarbohydrazide in dimethylformamide in an approximately 1:2 mole ratio. Colorless crystals separated out from the solution on standing for 1 hr. These were filtered and washed with 0.1 *M* hydrochloric acid and then dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_2H_{12}N_8S_2ZnCl_2$: C, 6.9; H, 3.5; Zn, 18.8; Cl, 20.3. Found: C, 7.2; H, 3.7; Zn, 18.9; Cl, 20.6.

(c) **Bis(thiocarbohydrazide)cadmium(II) Chloride.**—Colorless crystals were obtained by a similar method to that given above.

Anal. Calcd for $C_2H_{12}N_8S_2CdCl_2$: C, 6.1; H, 3.1; N, 28.3; Cd, 28.4; Cl, 17.9. Found: C, 6.4; H, 3.4; N, 28.0; Cd, 28.4; Cl, 17.8.

(d) **Bis(thiocarbohydrazide)mercury(II) Chloride.**—Solutions of mercuric chloride and thiocarbohydrazide in dimethylformamide were mixed in an approximately 1:2 mole ratio. A dense white precipitate separated immediately. After standing for 30 min the compound was filtered, washed with a little 0.1 *M* hydrochloric acid, and then dried *in vacuo* over P_2O_5. It is important not to heat the mixed solutions as a black decomposition product is formed.

Anal. Calcd for $C_2H_{12}N_8S_2HgCl_2$: C, 5.0; H, 2.5; N, 23.1. Found: C, 5.2; H, 2.7; N, 22.3.

(e) **Bis(isothiocyanate)bis(thiocarbohydrazide)iron(II).**—A solution of potassium thiocyanate (2.0 g) in water (10 ml) was added slowly with stirring to a hot solution (~70°) of $FeSO_4 \cdot 7H_2O$ (2.8 g) and thiocarbohydrazide (2.0 g) in water (100 ml). The pale green crystals which separated were filtered, washed with hot water, and then dried *in vacuo* over P_2O_5 for 2 hr.

Anal. Calcd for $C_4H_{12}N_{10}S_4Fe$: C, 12.5; H, 3.2; Fe, 14.5. Found: C, 12.5; H, 3.3; Fe, 14.9.

(f) **Dichlorobis(thiocarbohydrazide)cobalt(II).**—Two isomers of this compound were isolated. A violet compound was prepared by adding a hot solution of $CoCl_2 \cdot 6H_2O$ (2.4 g), dissolved in the minimum volume of water, to a hot solution of thiocarbohydrazide (2.0 g) in water (20 ml) containing 1 ml of 2 *M* hydrochloric acid. Violet crystals separated out immediately, and after decanting the solution, these were washed with several portions of ethanol and then collected and dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_2H_{12}N_8S_2CoCl_2$: C, 7.0; H, 3.5; Co, 17.2. Found: C, 7.1; H, 3.7; Co, 16.7.

A brown isomer was prepared using the same reagents as above but in the absence of 2 *M* hydrochloric acid. The crystals which separated out were similarly treated.

Anal. Calcd for $C_2H_{12}N_8S_2CoCl_2$: C, 7.0; H, 3.5; Co, 17.2; Cl, 20.7. Found: C, 6.9; H, 3.7; Co, 17.2; Cl, 20.8.

(g) **Tris(thiocarbohydrazide)nickel(II) Chloride.**—Thiocarbohydrazide (3.5 g) was added to a solution of $NiCl_2 \cdot 6H_2O$ (2.4 g) in water (50 ml). A few drops of 2 *M* hydrochloric acid were added and the mixture was shaken for 1 hr. The resulting blue solution was filtered and allowed to stand in a desiccator over concentrated sulfuric acid. Blue crystals of the tris hydrate were formed over a period of approximately 10 days. The anhydrous complex was obtained by heating the hydrate at 110° for 24 hr.

Anal. Calcd for $C_3H_{18}N_{12}S_3NiCl_2$: C, 8.0; H, 4.1; N, 37.5; Ni, 13.1; Cl, 15.8. Found: C, 8.0; H, 4.3; N, 37.2; Ni, 12.8; Cl, 16.0.

(h) **Tris(thiocarbohydrazide)copper(II) Chloride.**—A solution of $CuCl_2 \cdot 2H_2O$ (1.7 g) in 2 *M* hydrochloric acid (5 ml) was added to thiocarbohydrazide (3.5 g) in 2 *M* hydrochloric acid (25 ml). The green precipitate which separated immediately was filtered, washed thoroughly with hot 0.1 *M* hydrochloric acid, and then dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_3H_{18}N_{12}S_3CuCl_2$: C, 8.0; H, 4.0; Cu, 14.0; Cl, 15.7. Found: C, 8.0; H, 3.9; Cu, 14.0; Cl, 15.5.

(i) **Bis(thiocarbohydrazide)palladium(II) Chloride.**—A solution of $PdCl_2$ (0.45 g) in 2 *M* hydrochloric acid was added to a solution of thiocarbohydrazide (0.55 g) in 2 *M* hydrochloric acid (20 ml). A yellow precipitate separated from the solution. This was filtered, washed with 0.1 *M* hydrochloric acid, and then dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_2H_{12}N_8S_2PdCl_2$: C, 6.2; H, 3.1; Pd, 27.3. Found: C, 6.5; H, 3.0; Pd, 27.0.

Spectroscopic Measurements.—Electronic spectra were obtained with a Unicam SP 700 recording spectrophotometer. Reflectance measurements were made using $MgCO_3$ as reference. Infrared spectra were obtained using a Perkin-Elmer Model 221 spectrophotometer.

Magnetic Measurements.—These were made by the Gouy method using $Ni(en)_3S_2O_3$(15) and $HgCo(NCS)_4$(16) as the calibrants.

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TABLE I

SYMMETRY COORDINATES FOR THIOCARBOHYDRAZIDE

Symmetry species	Symmetry coordinates	Description of mode
A_1	$S_1 = 1/\sqrt{2}(\delta r_1 + \delta r_1')$	CN str
	$S_2 = 1/\sqrt{2}(\delta r_2 + \delta r_2')$	NN str
	$S_3 = 1/\sqrt{2}(\delta r_3 + \delta r_3')$	NH str
	$S_4 = 1/2(\delta r_4 + \delta r_4' + \delta r_5 + \delta r_5')$	NH_2 str
	$S_5 = 1/2(\delta r_4 + \delta r_4' - \delta r_5 - \delta r_5')$	NH_2 str
	$S_6 = \delta R$	CS str
	$S_7 = 1/\sqrt{6}(2\delta\alpha_1 - \delta\alpha_2 - \delta\alpha_2')$	NCN bend
	$S_8 = 1/\sqrt{12}(2\delta\beta_1 + 2\delta\beta_1' - \delta\beta_2 - \delta\beta_2' - \delta\beta_3 - \delta\beta_3')$	CNN bend
	$S_9 = 1/2(\delta\beta_2 + \delta\beta_2' - \delta\beta_3 - \delta\beta_3')$	NH wag
	$S_{10} = 1/\sqrt{12}(2\delta\gamma_2 + 2\delta\gamma_2' - \delta\gamma_1 - \delta\gamma_1' - \delta\gamma_3 - \delta\gamma_3')$	NH_2 bend
	$S_{11} = 1/2(\delta\gamma_1 + \delta\gamma_1' - \delta\gamma_3 - \delta\gamma_3')$	NH_2 rock
B_1	$S_{12} = 1/\sqrt{2}(\delta r_1 - \delta r_1')$	CN str
	$S_{13} = 1/\sqrt{2}(\delta r_2 - \delta r_2')$	NN str
	$S_{14} = 1/\sqrt{2}(\delta r_3 - \delta r_3')$	NH str
	$S_{15} = 1/2(\delta r_4 - \delta r_4' + \delta r_5 - \delta r_5')$	NH_2 str
	$S_{16} = 1/2(\delta r_4 - \delta r_4' - \delta r_5 + \delta r_5')$	NH_2 str
	$S_{17} = 1/\sqrt{2}(\delta\alpha_2 - \delta\alpha_2')$	NCS bend
	$S_{18} = 1/\sqrt{2}(2\delta\beta_1 - 2\delta\beta_1' - \delta\beta_2 + \delta\beta_2' - \delta\beta_3 + \delta\beta_3')$	CNN bend
	$S_{19} = 1/2(\delta\beta_2 - \delta\beta_2' - \delta\beta_3 + \delta\beta_3')$	NH wag
	$S_{20} = 1/\sqrt{12}(2\delta\gamma_2 - 2\delta\gamma_2' - \delta\gamma_1 + \delta\gamma_1' - \delta\gamma_3 + \delta\gamma_3')$	NH_2 bend
	$S_{21} = 1/2(\delta\gamma_1 - \delta\gamma_1' - \delta\gamma_3 + \delta\gamma_3')$	NH_2 rock

TABLE II

FUNDAMENTAL FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTION FOR THIOCARBOHYDRAZIDE

Symmetry species	Cm^{-1} Obsd	Cm^{-1} Calcd	Potential energy distribution,[a] %
A_1	3300	3326	$S_3(100)$
	3270	3294	$S_5(100)$
	3205	3220	$S_4(100)$
	1622	1654	$S_{10}(100)$
	1530	1539	$S_9(85)$, $S_1(20)$, $S_2(6)$
	1287	1243	$S_1(53)$, $S_6(32)$, $S_7(16)$, $S_9(11)$
	1142	1154	$S_{11}(100)$
	1080	1063	$S_2(78)$, $S_6(10)$, $S_7(14)$
	930	865	$S_6(49)$, $S_8(24)$, $S_1(15)$
	469	464	$S_7(70)$, $S_6(9)$, $S_1(6)$
	326	337	$S_8(74)$, $S_1(8)$, $S_6(7)$, $S_2(6)$
B_1	3300	3324	$S_{14}(101)$
	3270	3294	$S_{16}(101)$
	3205	3220	$S_{15}(99)$
	1642	1658	$S_{20}(97)$
	1495	1497	$S_{12}(58)$, $S_{19}(50)$, $S_{13}(11)$
	1453	1448	$S_{19}(51)$, $S_{12}(38)$
	1142	1154	$S_{21}(101)$
	. . .	1049	$S_{13}(84)$, $S_{17}(11)$
	588	536	$S_{18}(75)$, $S_{17}(22)$
	. . .	178	$S_{17}(69)$, $S_{18}(22)$

[a] The PED among the diagonal force constants only is given and then only when the contribution is greater than 5%.

Diamagnetic corrections were made from Pascal's constants as listed by Figgis and Lewis.[17]

Results and Discussion

Infrared Spectra.—The infrared spectra of the metal thiocarbohydrazide complexes were interpreted by first carrying out a normal coordinate analysis of the free ligand.

The thiocarbohydrazide molecule was treated as though it has C_{2v} symmetry thus enabling the problem to be reduced to one of solving for the 21 in-plane normal coordinates.

A Urey–Bradley force field was employed, the individual constants being transferred from studies of the normal coordinates of various thioamides[18] and hydrazine.[19] The *G* matrix was set up by assuming the following bond lengths: *r*(CS), 1.71 Å; *r*(CN), 1.33 Å; *r*(NN), 1.43 Å; *r*(NH), 1.00 Å. All valence angles were assumed to be 120°.

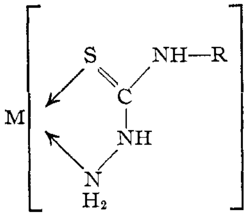
A summary of the results of this analysis based on the symmetry coordinates shown in Table I is given in Table II in the form of a potential energy distribution of each normal mode among these symmetry coordinates.

By using the above assignments and by observing the changes in the infrared spectrum of thiosemicarbazide when metal complexes of known structure are formed it was possible to interpret the analogous changes in the infrared spectrum of thiocarbohydrazide on complex formation.

Lists of certain bands observed in the infrared spectra of thiocarbohydrazide and the metal complexes are given in Table III. Similar bands observed in the infrared spectra of thiosemicarbazide, $Ni(Htscaz)_3Cl_2$, $Ni(tscaz)_2$, and Ag(Htscaz)Cl are included in Table IV.

A qualitative interpretation of the infrared spectrum of thiosemicarbazide has been published[20] and is in reasonable agreement with our assignments.

The similarity among the infrared spectra of $Zn(Htcaz)_2Cl_2$, $Cd(Htcaz)_2Cl_2$, $Hg(Htcaz)_2Cl_2$, and both isomers of $[Co(Htcaz)_2Cl_2]$ and $Ni(Htcaz)_3Cl_2$ would suggest that they have similar structures. Of the possible structures illustrated below, X-ray crystallographic studies have shown the existence of IV,[5,7] V,[6] and VIII[11] (R = H).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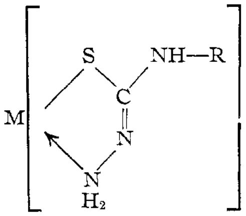
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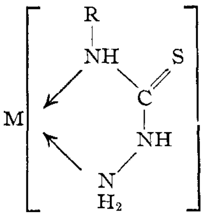
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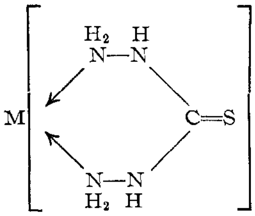
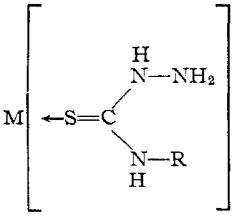

VII


VIII

In the infrared spectrum of $Ni(Htscaz)_3Cl_2$, which is considered to have structure IV (R = H),[8,21] bands

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Table III

Infrared Absorption Bands of Metal Thiocarbohydrazide Complexes[a] (cm^{-1})

Assignment[b]	Htcaz	Zn(II)	Cd(II)	Hg(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Pd(II)
νNH	3300 m		3300 m		3320 m				3312 m
		3280 sh	3280 s	3275 s		3285 s		3250 s	
νNH_2	3270 s				3280 s		3250 s		3140 s
		3200 s	3200 s	3140 sh		3238 s		3150 s	
		3255 s	3235 s	3180 s	3215 s	3255 s	3155 s	3210 s	3075 s
νNH_2	3205 s								
		3096 s	3110 s	3090 s	3165 s	3190 s	3100 s	3110 sh	2975
αNH_2	1642 s	1644 s	1640 s	1642 s	1631 sh	1643 s	1625 s	1644 s	1645 s
αNH_2	1622 s	1619 s	1613 s	1615 s	1624 s	1615 s	1608 s	1623 s	1620 s
		1564 m	1564 m	1564 sh			1549 m		1565 m
βNH + νCN	1530 s				1537 m	1568 s		1573 s	
		1550 sh	1553 m	1555 m			1532 m		1550 m
νCN + βNH	1495 m	1501 m	1501 s	1501 m	1497 m	1504 s	1495 m	1510 s	
					1300 m				1316 m
νCN + νCS	1287 s	1325 m	1322 m	1311 m		1311 m	1312 m	1343 m	
					1275 sh				1295 w
		1160 s	1150 s	1140 s	1152 s	1156 s	1164 s	1205 s	1186 s
βNH_2	1142 s								
		1130 m	1118 m	1093 s	1112 w	1113 m	1128 sh	1144 m	1156 s
									1113 m
									960 s
νCS + αCNN + νCN	930 s	983 s	977 s	971 s	935 s	974 s	951 s	1010 s	
									913 s

[a] Spectra were measured as Nujol and hexachlorobutadiene mulls. [b] ν, α, and β denote stretching, bending, and rocking or wagging modes, respectively. Relative band intensities are denoted by s, m, w, and sh, meaning strong, medium, weak, and shoulder, respectively.

Table IV

Infrared Absorption Bands of Metal Thiosemicarbazide Complexes[a] (cm^{-1})

Assignment[b]	Htscaz	Ni-(Htscaz)$_3$Cl$_2$	Ni-(tscaz)$_2$	Ag-(Htscaz)Cl
νNH	3360 m	3360 m		3340 m
			3438 s	3310 m
νNH_2	3245 s	3260 s		
			3175 s	3250 s
			3270 s	
νNH_2	3170 s	3150 s		3155 s
			3112 s	
			1643 s	
αNH_2	1643 s	1621 s		1635 s
			1630 s	
			1616 s	
αNH_2	1620 s	1600 s		1612
			1590 s	
		1548 sh		
βNH + νCN	1530 s			1540 m
		1532 m		
νCN + βNH	1480 m		1521 s	1480 m
		1325 m	1320 m	1292 m
νCN + νCS	1282 s			
		1285 sh	1284 sh	1275 w
		1205 s	1227 s	
βNH_2	1160 s			1149 s
		1117 m	1136 m	
				806 s
νCS + νCN	798 s	798 s	678 s	782 s

[a] See footnote *a*, Table III. [b] See footnote *b*, Table III.

which have been assigned as νNH_2 and βNH_2 in the free ligand are split, giving one band with a lower and one with a higher frequency. Similar splitting is observed in the spectra of the metal thiocarbohydrazides mentioned above, from which it can be concluded that structures IV and VI are possible but that structure VII in which both of the NH_2 groups are coordinated is unlikely.

Bands at 1530 and 1495 cm^{-1} in thiocarbohydrazide are assigned as coupled modes consisting principally of βNH and νCN. The band of higher frequency, which is predominantly βNH, is split and raised in the complexes while the band at 1495 cm^{-1} is raised only slightly. These shifts can be explained by structure IV, whereas structure VI, involving a coordinated NH group, would require a lowering of one of the split βNH bands.

Of the analogous bands in thiosemicarbazide, at 1530 and 1480 cm^{-1}, that of higher frequency is absent in the infrared spectrum of Ni(tscaz)$_2$ while the low-frequency band is raised to 1521 cm^{-1} with increased intensity, due to the large increase in the C–N bond order. Both changes substantiate the assignments made for these bands.

The C=S stretching vibration contributes to two bands in thiocarbohydrazide. However, both contain contributions from other vibrations, in particular νCN. These bands, at 1287 and 930 cm^{-1}, are raised in the metal complexes implying that for structure IV the increase in the C–N bond order nullifies any lowering of νCS on coordination. The raising of these bands to higher frequencies could also be explained by structure VI. The evidence against this interpretation is that the comparable bands in thiosemicarbazide undergo a negligible shift in Ni(Htscaz)$_3$Cl$_2$. Only for the thioenolic structure, as in Ni(tscaz)$_2$, is any significant shift observed, the band at 798 cm^{-1} being lowered by ~100 cm^{-1}.

These results suggest that the thiocarbohydrazide complexes of Zn(II), Cd(II), Hg(II), Co(II), and Ni(II) have structure IV (R = NH_2) in which changes in the

TABLE V

ELECTRONIC ABSORPTION SPECTRA

Compound	ν_{max}, cm^{-1}
[Fe(Htcaz)$_2$(NCS)$_2$]	8,800 13,600 ($^5T_{2g} \longrightarrow {}^5E_g$); ~15,400; 18,600; 21,300; 23,200
[Co(Htcaz)$_2$Cl$_2$] (violet)	8,300 ($^4T_{1g} \longrightarrow {}^4T_{2g}$); ~15,000 ($\longrightarrow {}^4A_{2g}$); 17,800 20,300 ($\longrightarrow {}^4T_{1g}$(P))
[Co(Htcaz)$_2$Cl$_2$] (brown)	8,300 ($^4T_{1g} \longrightarrow {}^4T_{2g}$); ~15,000 ($\longrightarrow {}^4A_{2g}$); 17,900 ~23,000 ($\longrightarrow {}^4T_{1g}$(P))
Ni(Htcaz)$_3$Cl$_2$	9,500 10,500 ($^3A_{2g} \longrightarrow {}^3T_{2g}$); ~12,500 ($\longrightarrow {}^1E_g$); 16,300 ($\longrightarrow {}^3T_{1g}$(F)); 26,100 ($\longrightarrow {}^3T_{1g}$(P))
Ni(Htcaz)$_3$Cl$_2$^{a}	9,500 10,500 ($^3A_{2g} \longrightarrow {}^3T_{2g}$); 16,500 ($\longrightarrow {}^3T_{1g}$(F)); ~26,200 ($\longrightarrow {}^3T_{1g}$(P))
Ni(Htscaz)$_3$Cl$_2$^{a}	9,600 10,500 ($^3A_{2g} \longrightarrow {}^3T_{2g}$); 16,450 ($\longrightarrow {}^3T_{1g}$(F)); ~26,700 ($\longrightarrow {}^3T_{1g}$(P))
Ni(Hcaz)$_3$Cl$_2$^{a}	9,600 10,200 ($^3A_{2g} \longrightarrow {}^3T_{2g}$); ~12,500 ($\longrightarrow {}^1E_g$); 16,100 ($\longrightarrow {}^3T_{1g}$(F)); ~27,400 ($\longrightarrow {}^3T_{1g}$(P))
Cu(Htcaz)$_3$Cl$_2$	13,700; 17,200
Pd(Htcaz)$_2$Cl$_2$	23,000; 26,700

[a] These spectra were measured in aqueous solution, the remainder all being reflectance spectra.

C=S bond order are negligible by comparison with the changes in the C—N bond order.

Large shifts to higher frequencies are observed in the infrared spectrum of Cu(Htcaz)$_3$Cl$_2$, for all bands due partly to νCN. Among the first-row transition metals, Cu(II) displays the strongest Arhland, Chatt, and Davies B-type character,[22] so that, of the thiocarbohydrazide complexes of these metals (providing they all have structure IV), Cu(Htcaz)$_3$Cl$_2$ should have the strongest metal to sulfur bond. According to the above explanation this would result in a high C–N bond order, which is observed and which therefore favors the assignment of structure IV (R = NH$_2$) for Cu(Htcaz)$_3$Cl$_2$.

In Pd(Htcaz)$_2$Cl$_2$, the stretching vibrations assigned to the free NH$_2$ group in the other complexes appear to be absent. The bands at 1142 and 930 cm^{-1} in the free ligand are split into three bands and two bands, respectively. The splitting of the latter band is similar to the splitting observed for the 798-cm^{-1} band of thiosemicarbazide in Ag(Htcaz)Cl. The Ag(I) complex was shown to contain sulfur atoms in two different environments, coordinated to two and three silver atoms, respectively. The sulfur atoms in Pd(Htcaz)$_2$Cl$_2$ may likewise be involved in two different environments. However, this would not explain the changes in νNH$_2$ and βNH$_2$, and it is necessary to invoke either structure VI in which Pd(II) is coordinated by four nitrogen donors or a polymeric structure similar to IV but with the free NH$_2$ groups linking the monomer units.

The small shifts observed for the ligand absorption bands in the infrared spectrum of [Fe(Htcaz)$_2$(NCS)$_2$] suggest that thiocarbohydrazide is only weakly coordinated through the thioketo group and the hydrazinic nitrogen atom. The remaining octahedral lattice sites are presumably filled by the thiocyanate groups for which two bands are observed, at 2088 and 474 cm^{-1}. The first is assigned as the C≡N stretching frequency while the latter is assigned as the NCS deformation mode. It has been shown[23] that in N-thiocyanato complexes the deformation mode is similar to that for potassium thiocyanate, occurring at approximately 470 cm^{-1}, while in S-thiocyanato complexes it is lowered and split. The C≡N stretching frequency is less characteristic; however, Mitchell and Williams[24] have observed that the frequency is usually lower for N-thiocyanato than for S-thiocyanato groups. Hence the observed bands suggest the presence of N-thiocyanato groups in [Fe(Htcaz)(NCS)$_2$].

Electronic Spectra and Magnetic Moments.—The absorption bands observed in the visible and near-infrared spectra of the metal thiocarbohydrazides Ni(Htscaz)$_3$Cl$_2$ and Ni(Hcaz)$_3$Cl$_2$ are given in Table V. Assignments have been made for the Fe(II), Co(II), and Ni(II) complexes assuming octahedral symmetry about the metal atom.

The double peak for [Fe(Htcaz)$_2$(NCS)$_2$] at 13,600 and 8800 cm^{-1} (see Figure 2) is comparable to that at 10,400 and 8500 cm^{-1} in the spectrum of Fe(H$_2$O)$_6$$^{2+}$, where the splitting was attributed to a Jahn–Teller distortion.[25] Confirmation of a distorted octahedral environment is obtained from the value for the room-temperature magnetic moment, given in Table VI.

TABLE VI

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Compound	$10^6\chi^m$, cgsu	$10^6\chi^{dia}$, cgsu	μ_{eff}, BM	T, °K
[Fe(Htcaz)$_2$(NCS)$_2$]	10,240	−197	5.00	293
[Co(Htcaz)$_2$Cl$_2$] (violet)	9,070	−181	4.65	290
[Co(Htcaz)$_2$Cl$_2$] (brown)	8,850	−181	4.62	292
Ni(Htcaz)$_3$Cl$_2$·3H$_2$O	3,787	−281	3.10	293
Cu(Htcaz)$_3$Cl$_2$	1,650	−241	2.11	291

The value for high-spin Fe(II) compounds in an octahedral field should be ~5.5 BM,[26] but this is lowered by a distortion of the cubic field.

The Mössbauer spectrum of [Fe(Htcaz)$_2$(NCS)$_2$] was measured at room temperature. The quadrupole split-

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ting parameter, ΔE_q, was found to have a value of 2.98 mm sec^{-1}, and the isomer shift, δ, a value of $+1.00$ mm sec^{-1}, with respect to stainless steel. It has been shown[27] that for high-spin Fe(II) in an octahedral field ΔE_q should be zero, but that for fields of lower symmetry ΔE_q will be nonzero. The magnitude of ΔE_q is therefore a measure of the distortion from octahedral symmetry about the iron atom, so that the value for [Fe(Htcaz)$_2$(NCS)$_2$] confirms the anisotropy shown by the electronic spectrum and the magnetic moment.

The distorted octahedral environment is also observed for the Co(II) and Ni(II) complexes.

The band assigned as the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition in each of the isomeric complexes, [Co(Htcaz)$_2$Cl$_2$] (see Figure 1), is split, although by different amounts. This has been explained[28] as a tetragonal or rhombic distortion of the cubic field. The different splitting for the brown and violet isomers suggests that they may be *trans* and *cis* geometrical isomers, as a larger splitting is expected for the *trans* isomer.

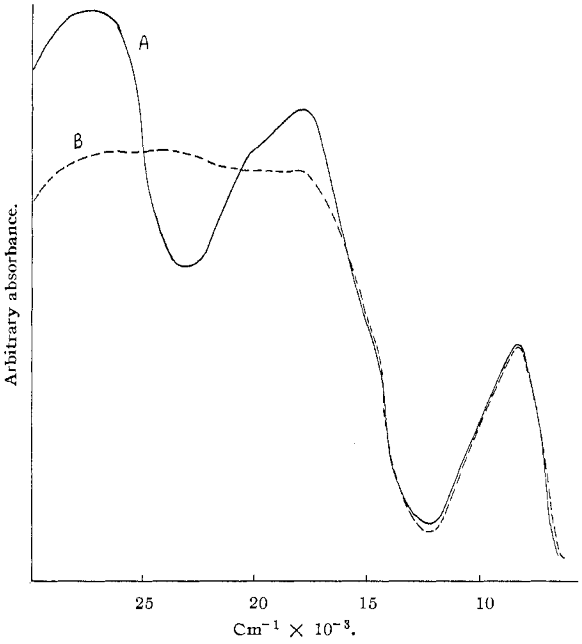

Figure 1.—Reflectance spectra of isomeric [Co(Htcaz)$_2$Cl$_2$]: A, violet isomer; B, brown isomer.

The splitting of the first spin-allowed band ($^3A_{2g} \rightarrow {}^3T_{2g}$) in the Ni(II) complexes (see Figure 3) indicates a tetragonal distortion similar to that observed in Ni(Htscaz)$_3$I$_2$[29] and *trans*-Ni(py)$_4$Cl$_2$.[30] A detailed study of *trans*-Ni(NH$_3$)$_4$(NCS)$_2$ and *trans*-Ni(NH$_3$)$_4$(NO$_2$)$_2$ showed that the tetragonal splitting of the octahedral levels was dependent on the relative positions of the axial and equatorial ligands in the spectrochemical series.[31]

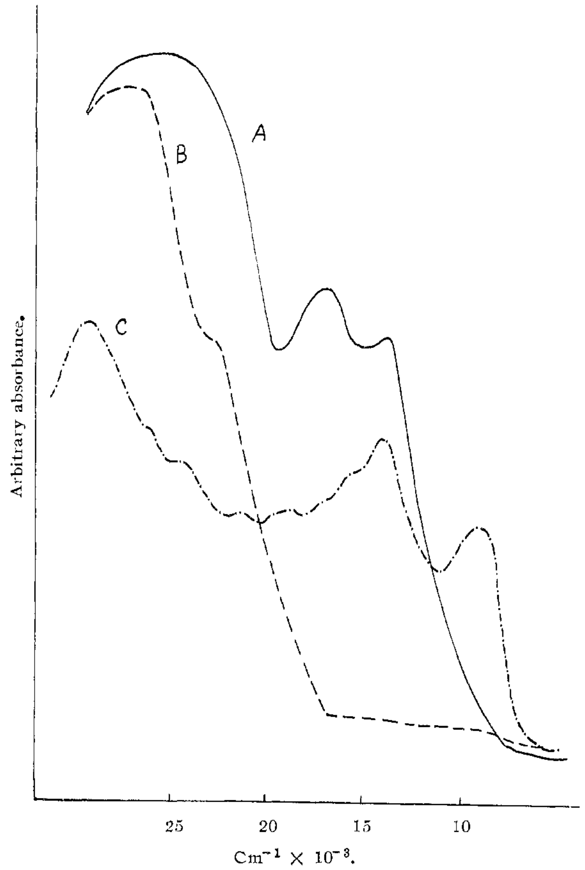

Figure 2.—Reflectance spectra of: A, Cu(Htcaz)$_3$Cl$_2$; B, Pd(Htcaz)$_2$Cl$_2$; C, [Fe(Htcaz)$_2$(NCS)$_2$].

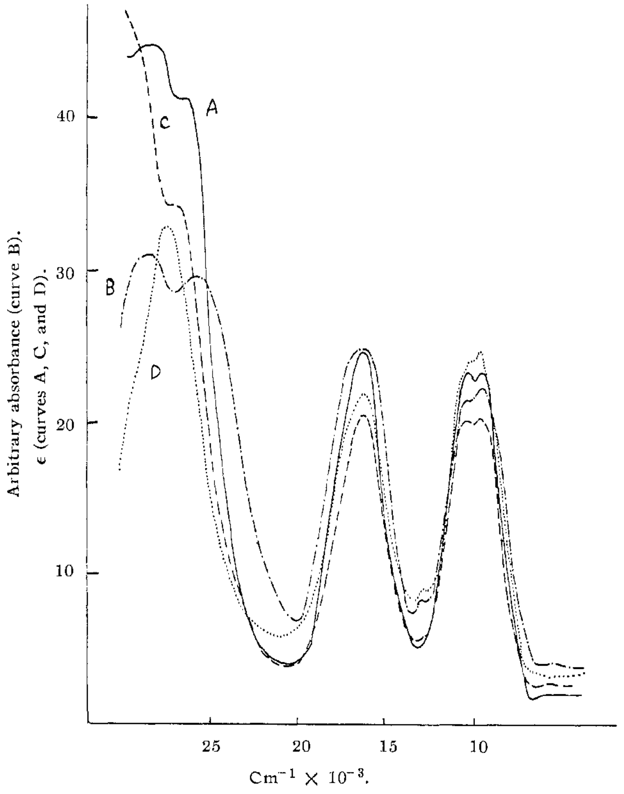

Figure 3.—Electronic absorption spectra of: A, Ni(Htcaz)$_3$Cl$_2$ in H$_2$O; B, Ni(Htcaz)$_3$Cl$_2$ (solid reflectance); C, Ni(Htscaz)$_3$Cl$_2$ in H$_2$O; D, Ni(Hcaz)$_3$Cl$_2$ in H$_2$O.

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The large splittings observed for $Ni(Htcaz)_3Cl_2$, $Ni(Htscaz)_3Cl_2$, and $Ni(Hcaz)_3Cl_2$ of 1000, 900, and 600 cm^{-1}, respectively, suggest the environments 3N,3S and 3N,3O, as an environment consisting only of nitrogen atoms would be expected to show negligible splitting.

The molar conductance of 10^{-3} *M* $Ni(Htcaz)_3Cl_2$ was measured at 25° in aqueous solution and the value of 220 ohm^{-1} is in agreement with it being a 1:2 electrolyte.

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Complexes of Sulfoxides. II. Metal–Oxygen Stretching Vibrations in Complexes of Dimethyl Sulfoxide and Dimethyl Sulfoxide-d_6 and the Point Group of the Cation

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Consideration of the ways of placing dimethyl sulfoxide (DMSO) ligands around a central metal atom leads to the conclusion that the point group of an $[M(DMSO)_6]^{n+}$ cation must be D_{3d} or S_6. The infrared spectra of several complexes with the formula $[M(DMSO)_6]^{n+}(ClO_4)_n$ have been studied with special emphasis on the region 600–200 cm^{-1}. A band assigned to the metal–oxygen stretching vibration appears in the region 444–415 cm^{-1} for all the M(II) complexes studied; for Cr(III) it appears at 529 cm^{-1}. The frequency order found is Cr(III) > Ni(II) > Co(II) > Zn(II) > Fe(II) > Mn(II), in agreement with other studies. Behavior of the C–S–O angle deformation vibrations as bonding strength is increased leads to the conclusion that S_6 is the actual point group of the cation.

Introduction

The use of dimethyl sulfoxide (DMSO) as a ligand in the formation of transition metal complexes was first reported by Cotton and co-workers.[1,2] Following a thorough vibrational analysis of the free ligand,[3] they were able to determine whether bonding in the complex was through the sulfur or the oxygen in DMSO by noting whether ν_{SO}, the S–O stretching frequency, increased or decreased on complexation. It is tempting to extend this method and use the magnitude of the shift in ν_{SO} as a measure of the strength of the coordinate bond, but this approach is open to question, mainly because the vibration labeled ν_{SO} is far from being a pure stretch. The analysis of Horrocks and Cotton[3] indicates that about half of the potential energy of this vibration is associated with methyl rocking motions. The composition of the normal coordinate will change on complexation, effectively masking any trend involving metal–ligand bond strength. Currier and Weber[4] have, in fact, examined the quasi-octahedral complexes of manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) with DMSO, diphenyl sulfoxide, phenyl methyl sulfoxide, di-*n*-propyl sulfoxide, and di-*n*-butyl sulfoxide and have found that little significance could be attached to $\Delta\nu_{SO}$.

A more reliable source of information concerning the strength of the coordinate bond is the set of vibrations which involve this bond directly, *i.e.*, those which (in the first approximation) involve the motion of the DMSO molecule as a whole and thus have no counterpart in the spectrum of the free ligand. If the DMSO molecule is regarded as a single particle, then an octahedral DMSO complex $[M(DMSO)_6]^{n+}$ may be considered as belonging to point group O_h with a vibrational representation $\Gamma_{vib} = A_{1g}$ (Raman) + E_g (Raman) + F_{2g} (Raman) + $2F_{1u}$ (ir) + F_{2u} (inactive).[5]

With due regard for degeneracies, this Γ_{vib} accounts for 15 vibrational degrees of freedom. Internal vibrations of the ligands account for $6 \times 24 = 144$ degrees of freedom. However, the $[M(DMSO)_6]^{n+}$ complex has 61 atoms, giving it $3(61) - 6 = 177$ vibrational degrees of freedom; we have accounted for 159 and are still missing 18. These are the rotations of the free ligands, which are transmuted into rocking, wagging, and twisting modes on complexation. Twelve of these may be incorporated into a model of O_h symmetry by making it 13-atomic, rather than 7-atomic, as, for example, chromium hexacarbonyl.[6] The vibrational representation then becomes $2A_{1g} + 2E_g + F_{1g} + 2F_{2g} + 4F_{1u} + 2F_{2u}$, with F_{1u} the only infrared-active species. The normal modes belonging to this repre-

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