The best procedure for purifying a cobalt salt is thus to start with cobalt nitrate, extract a solution 0.35 *M* in cobalt and 5 *M* in NH_4SCN with hexone at 1°, wash this once with 5 *M* NH_4SCN at 1° and evaporate the organic phase to dryness over H_2SO_4. With quantitative recovery of the organic phases, this procedure will yield more than 99.5% of the original cobalt with the nickel impurity reduced by a factor of 10^4. Recycling will give higher purifications.

The thiocyanate–hexone extraction has also been used in this Laboratory for the separation of carrier-free Ni^{57} tracer from proton-bombarded cobalt. Very high specific activity can be obtained if the cobalt target is first purified of nickel as described above.

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Infrared Absorption Spectra of Inorganic Coordination Complexes. VI. The Molecular Structure of 1,2-Dimethylmercaptoethane and its Metal Chelate Compounds[1]

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1,2-Dimethylmercaptoethane, $H_3CSCH_2CH_2SCH_3$, has several axes of internal rotation and, therefore, may exist in several molecular forms in the liquid state.[3] However, this molecule cannot exist in the extended form as a chelate ligand in coordination compounds. Therefore, marked differences in the absorption spectra are to be expected for the free organic compound and for the ligand in its metal complexes.

This study was carried out to investigate spectral differences between the free molecule and the molecule coördinated about a metal ion in order to contribute to the knowledge of the geometrical role of chelated ligands, having internal rotation axes, in metal complexes.

Experimental

Preparation of Compounds. 1,2-Dimethylmercaptoethane.—This compound was prepared according to the method of Morgan and Ledbury.[4] The product was a colorless liquid boiling at 181°, at atmospheric pressure.

Anal. Calcd. for $C_4H_{10}S_2$: S, 52.46; C, 39.29; H, 8.24. Found: S, 52.47; C, 39.11; H, 8.21.

Dichloro-(1,2-dimethylmercaptoethane)-platinum (II).—This compound was prepared according to the method of Tschugaeff.[5] The bright yellow product was recrystallized from hot water.

Anal. Calcd. for $Pt(C_4H_{10}S_2)Cl_2$: C, 12.39; H, 2.54; Cl, 18.25. Found: C, 12.43; H, 2.85; Cl, 18.05.

Dichloro-(1,2-dimethylmercaptoethane)-palladium (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The dark orange product was recrystallized from hot water.

Anal. Calcd. for $Pd(C_4H_{10}S_2)Cl_2$: C, 16.02; H, 3.36; Cl, 23.65. Found: C, 16.13; H, 3.53; Cl, 23.54.

Dichloro-(1,2-dimethylmercaptoethane)-copper (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The dark green product was recrystallized from hot alcohol as fine needles.

Anal. Calcd. for $Cu(C_4H_{10}S_2)Cl_2$: C, 18.71; H, 3.93; Cl, 27.63. Found: C, 18.76; H, 3.92; Cl, 27.68.

Dichloro-(1,2-dimethylmercaptoethane)-mercury (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The white crystalline powder was recrystallized from hot alcohol in the form of white needles.

Anal. Calcd. for $Hg(C_4H_{10}S_2)Cl_2$: C, 12.20; H, 2.56; Cl, 18.01. Found: C, 12.48; H, 2.76; Cl, 18.41.

Diiodo-(dimethylmercaptoethane)-cadmium (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The white product recrystallized from hot alcohol in the form of colorless prisms.

Anal. Calcd. for $Cd(C_4H_{10}S_2)I_2$: C, 9.85; H, 2.06; I, 51.96. Found: C, 10.15; H, 2.28; I, 52.39.

Bis-(1,2-dimethylmercaptoethane)-nickel(II) Thiocyanate.—This compound was prepared according to the directions of Tschugaeff.[6]

Anal. Calcd. for $[Ni(C_4H_{10}S_2)_2](SCN)_2$: C, 28.57; H, 4.80; N, 6.67. Found: C, 28.72; H, 4.94; N, 6.77.

Apparatus and Procedure.—All spectra were obtained by means of Perkin–Elmer model 21 recording infrared spectrophotometer, employing a NaCl prism. The liquid and solid state spectra of 1,2-dimethylmercaptoethane were obtained from thin films of the compound contained in a low temperature cell similar to that described by Wagner and Horning.[7] The spectra of the solid complexes were obtained by means of the KBr disk technique[8] and checked by measurements in nujol mulls.

Experimental Results

The infrared frequencies of both the liquid and the solid states of 1,2-dimethylmercaptoethane are shown in Table I.

TABLE I[a]

INFRARED FREQUENCIES IN CM.$^{-1}$ OF 1,2-DIMETHYLMERCAPTOETHANE

Solid state	Liquid state	Solid state	Liquid state
2910 s	2925 s	. .	1010 m sh
2300 vw	2350 vw	964 vs	958 vs
2010 vw	1970 vw	. .	900 w
1430 vs	1430 vs	. .	840 m
1320 m	1323 m	735 vs	736 vs
. .	1270 s	728 vs sh	. .
1210 vs	1203 vs	678 vs	682 vs
1137 s	1136 s		

[a] Abbreviations: s = strong; m = medium; w = weak; v = very; sh = shoulder.

The infrared frequencies of metal complexes containing 1,2-dimethylmercaptoethane as a ligand are shown in Table II.

Discussion of Results

A comparison of the spectra of 1,2-dimethylmercaptoethane in the liquid state with the solid state shows that the former has more absorption peaks. The number of peaks observed in the spectrum of the ligand in the solid state are not so numerous as to be incapable of assignment upon the basis of a single molecular form. This form is probably the extended form.[3]

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[1] For paper IV in this series see THIS JOURNAL, **77**, 5508 (1955).

[2] (a) Abstracted from the Ph.D. thesis of Daniel M. Sweeny, Notre Dame, August, 1955. Supported in part under AEC Contract AT (11-1)-38, Radiation Project of the University of Notre Dame. (b) Visiting Professor from Faculty of Science, University of Tokyo.

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TABLE II[a]

INFRARED FREQUENCIES IN CM.$^{-1}$ OF METAL COÖRDINATION COMPOUNDS CONTAINING 1,2-DIMETHYLMERCAPTOETHANE AS A CHELATE GROUP

(DME)-$PtCl_2$	(DME)-$PdCl_2$	(DME)-$CuCl_2$[c]	(DME)-$HgCl_2$[d]	(DME)-CdI_2[e]	$(DME)_2$Ni-$(SCN)_2$[f]
2950 w	2930 w	2900 vw	2910 vw	.....	2900 w
....	.....	.....	.....	.....	2085 vs
1445 m	1440 s	1440 m	1422 m	1425 s	1425 s
1420 s	1415 s	1425 s	1405 m	1410 s	.....
1305 m	1320 s	1320 m	1330 vw	.....	1324 w
....	.....	.....	1280 vw	.....	.....
....	1258 s	1258 m	1264 vw	1260 s	1265 w
....	.....	1177 w	1180 vw	1182 w	1182 w
1130 w	1145 s	1146 w	1160 vw	1127 w	1125 w
1028 m	1036 s	1021 s	1034 s	1024 w	1025 vw
972 s	977 vs	.....	980 s	973 s	970 s
964 s	962 sh	970 s	966 s	962 s	955 sh
915 m	913 w	903 m	885 s	890 w	892 w
852 s	849 sh[b]	845 s	829 s	826 vw	849 m
....	838 m	840 s	.....	.....	.....

[a] DME = 1,2-dimethylmercaptoethane; all other abbreviations same as Table I. [b] In some cases we observed another peak quite close to one of the CH_2 rocking vibration bands which may be assigned to an overtone, combination tone, etc. [c] Other peak at 650 s. [d] Other peaks at 732 w; 705 w. [e] Other peak at 713 w. [f] Other peaks at 805 s; 658 w.

Although the spectrum of the ligand in the liquid state contains all the peaks present in the spectrum of the solid state, there are, in addition, other peaks which indicate the presence of one or more molecular forms other than the extended form. It is important to realize, however, that some of the absorption peaks assigned to the extended form may overlap those of other molecular forms present in the liquid state. Taking this into account, the spectra observed for the various metal complexes investigated can be explained as arising from the vibrations of the ligand in some configuration other than the extended form. We do not observe in the spectra of these metal complexes any absorption peaks characteristic only of the extended form of the ligand. Therefore, it is reasonable to conclude that the ligand is not present in its extended form.

To facilitate the understanding of our interpretations of the spectra, assignments of the peaks observed in the region extending from 740 to 950 cm.$^{-1}$ are first presented. In a previous paper[9] it was shown that this part of the spectrum is the region characteristic of the CH_2 rocking frequencies associated with the molecular type $XH_2C–CH_2X$. If the ligand part of the metal complexes is present in the extended form, then the appearance of only one absorption peak at about 740 cm.$^{-1}$ is expected, but not the appearance of two absorption peaks, corresponding to the CH_2 rocking frequencies of the *gauche* form.[9] Since, in the solid state of 1,2-dimethylmercaptoethane, only one absorption peak at 735 cm.$^{-1}$ is observed in this region, it is quite reasonable to conclude that the extended form of the molecule is present. However, the spectrum of the ligand itself in the liquid state reveals the presence of two absorption peaks at 900 and 840 cm.$^{-1}$. Therefore, on the basis of the results of our previous communication[9] we can definitely conclude that in the liquid state of 1,2-dimethylmercaptoethane some molecules are in the *gauche* form, since the $H_2C–CH_2$ segment of the molecule is in the *gauche* configuration.

The presence of the *trans* CH_2 rocking vibration of the extended form of the free ligand is indicated by the peak at 736 cm.$^{-1}$ which is observed for both the liquid and solid states, in perfect agreement with expectations. The peak at 736 cm.$^{-1}$ disappears completely in the spectra of these metal chelate complexes and it can be concluded with certainty that the ligand in the complex is not present in the extended form. The presence of the two CH_2 rocking peaks at approximately 900 and 845 cm.$^{-1}$, shows that the form actually present should be a gauche form.

With regard to the frequency region just considered, all the experimental data are consistent with the conclusions that (1) the solid state of the 1,2-dimethylmercaptoethane consists of only the extended form of the molecule; (2) the liquid state consists of both extended and gauche forms of the molecule; (3) the chelated ligand is present only in the gauche form. This bears an important relation to the optical isomerism of a new type described in a previous communication.[10]

In other spectral regions not thus far discussed, changes in spectra were observed on transitions between the liquid state, solid state and metal complexes containing the ligand. Three definite differences in spectra were observed on transition from the solid to the liquid state, namely, the disappearance of an absorption peak at 728 cm.$^{-1}$, and the appearance of two absorption peaks at 1010 and 1272 cm.$^{-1}$. These latter peaks at 1010 and 1272 cm.$^{-1}$ undoubtedly can be assigned to the gauche form of the molecule. Their modes are probably C–C stretching and CH_2 wagging, respectively. The peak at 728 cm.$^{-1}$ can probably be assigned to one of the C–S stretching frequencies. The absence of this peak in the spectrum of the liquid state of 1,2-dimethylmercaptoethane may be attributed to its being overlapped by the peak at 736 cm.$^{-1}$ which is assigned to the *trans* CH_2 rocking vibration.

There are, however, many peaks present in the spectra which show no essential difference upon the transition from the solid state to the liquid state. The most intense of these absorption peaks appear at about 1430 and 960 cm.$^{-1}$. These peaks can be assigned, respectively, to the CH_3 degenerate deformation together with the CH_2 bending deformation, and the CH_3 rocking vibration.[11] It will be seen readily from Table II that the absorption spectrum of the copper(II) complex contains only those peaks which can be assigned to the gauche form. The other coördination compounds can be treated in an analogous manner, although some differences in spectra exist which do not essentially affect the above conclusions.

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