[Contribution from the Department of Chemistry, University of Notre Dame]

Infrared Absorption Spectra of Inorganic Coördination Complexes. XXII. Infrared Studies of Methylthiourea and its Metal Complexes[1a,b]

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Infrared spectra of some metal methylthiourea complexes have been measured in the region from 2 to 15 μ. From the result it is concluded that for Zn(II) and Cd(II) complexes the coördination takes place through sulfur, whereas for Pt(II), Pd(II) and Cu(I) complexes it probably takes place through nitrogen.

Introduction

A study of infrared absorption spectra (2–35 μ region) was reported for some metal thiourea complexes.[1a] Also, considerable information on the infrared spectra of formamide, acetamide, N-methylformamide, N-methylacetamide and N,N′-dimethyloxamide[2] is available. The present infrared absorption study of methylthiourea and its metal complexes was undertaken to increase our knowledge of structure by substituting an alkyl group for a hydrogen atom.

Experimental

Preparation of Compounds.—Methylthiourea was prepared according to the method of Moore and Crossley.[3] The ligand was recrystallized three successive times from ethanol–water mixture and dried *in vacuo* over phosphorus pentoxide.

Tetrakis-(methylthiourea)-copper(I) chloride was prepared according to the method of Palmer[4] for a similar complex of thiourea.

Anal. Calcd. for $Cu(C_8H_{24}N_8S_4)Cl$: Cu, 13.83; C, 20.91; H, 5.26. Found: Cu, 13.88; C, 21.41; H, 5.21.

The complexes tetrakis-(methylthiourea)-platinum(II) chloride, and tetrakis-(methylthiourea)-palladium(II) chloride were prepared according to the method of Kurnakow[5] for similar complexes with thiourea.

Anal. Calcd. for $Pt(C_8H_{24}N_8S_4)Cl_2$: N, 17.88; C, 15.33; H, 3.86. Found: N, 17.74; C, 15.51; H, 3.94.

Anal. Calcd. for $Pd(C_8H_{24}N_8S_4)Cl_2$: N, 22.29; C, 19.11; H, 4.81. Found: N, 21.00; C, 18.11; H, 4.68.

The complex dichlorobis-(methylthiourea)-cadmium(II) was prepared according to the method of Rosenheim and Meyer[6] for a similar complex of thiourea.

Anal. Calcd. for $Cd(C_4H_{12}N_4S_2)Cl_2$: C, 13.21; N, 15.41; H, 3.33. Found: C, 12.92; N, 15.09; H, 3.28.

The complex dichlorobis-(methylthiourea)-zinc(II) was prepared according to the method of Maly[7] for a similar complex of thiourea.

Anal. Calcd. for $Zn(C_4H_{12}N_4S_2)Cl_2$: C, 15.17; N, 17.70; H, 3.82. Found: C, 15.97; N, 17.65; H, 3.83.

Absorption Measurements.—The infrared spectra of methylthiourea and its metal complexes were determined using a Perkin–Elmer infrared spectrophotometer Model 21 with sodium chloride and calcium fluoride prisms over their regions of greatest resolution. The spectra of the solid complexes were obtained by the potassium bromide disk technique. All studies were confined to the region from 2 to 15 μ.

Results

The experimental results obtained for methylthiourea and some of its metal complexes are presented in Table I.

Table I[a]

Absorption Maxima in Cm.$^{-1}$ of MeTu and its Metal Complexes

Methylthiourea	Complex Pt(II)	Pd(II)	Cu(I)	Zn(II)	Cd(II)
3300sh	3360sh	3360sh	3300sh	....	....
....	3280sh	3280sh	....	....	....
3240s	3180s	3190s	3230s	3270s	3250s
3150s	3040s	3050s	3160s	3180s	3100s
2940sh	2920sh	2920sh	2950sh	3050sh	2930sh
....	1660sh	1660sh	....	....	....
....	1635sh	1632sh	....	....	....
1634s	1625s	1620s	1620s	1634s	1629s
1550s	1575s	1565s	1568s	1578s	1575s
....	1545sh	1545sh	1555s	1510m	1528w
1490m	1474s	1480s	1475m	1495m	1490m
1455m	1455m	1448m	1455m	1155m	1464m
1408m	1404w	1405w	1405w	1408m	1416m
1296s	1282s	1285m	1292m	1303s	1303s
1257m	1238w	1240m	....	....	....
1148m	1148w	1148m	1145m	1160m	1167m
1124s	1125m	1122m	1117m	1120s	1142m
972m	965–975w	965–980w	970w	975w	988w
774m	762m	767m	765s	765s	775s
718s	710s	704s	738–728s	702s	717s

[a] Abbreviations: MeTu, methylthiourea; s. strong; m, medium; w, weak; sh, shoulder.

Discussion

The normal vibration calculations and assignment of the bands observed in the infrared spectra of thiourea have been reported previously.[1a] When one of the hydrogens of thiourea is replaced by a methyl group, as in methylthiourea, two structures, the "*cis*" and "*trans*" forms, as shown in Fig. 1, are conceivable. The spectra of these forms can be explained by comparison with either a *cis*-thioamide and thiourea or a *trans*-thioamide and thiourea. However, in the case of methylurea[8] only "*trans*" amide frequencies (amide I, II and III) appeared in the spectra. It seems, therefore, reasonable to assign the bands of the methylthiourea spectra on the assumption that the compound exists in the *trans* form.

Methylthiourea complexes give two different kind of infrared spectra, zinc and cadmium complexes belonging to the first group and platinum, palladium and copper(I) complexes belonging to the second group. The fact that the molecules of the first group coördinate through sulfur and those of the second group through nitrogen might have been expected from previous studies of metal-urea

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[1] (a) Refer to Paper XIV, This Journal, **80**, 527 (1958); (b) presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1957; (c) to whom correspondence concerning this article should be addressed; (d) visiting Professor from Faculty of Science, Tokyo University.

[2] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956); **29**, 611 (1958).

[3] M. Horning, "Organic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 617.

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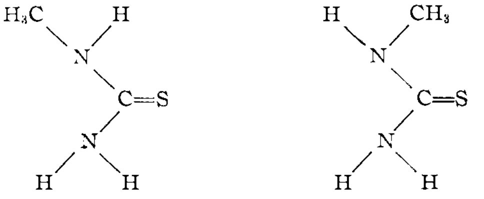
[7] R. Maly, *Ber.*, **9**, 172 (1876).

[8] Unpublished results from this Laboratory.



(*cis*) (*trans*)

Fig. 1.—Two possible configurations of methylthiourea.

complexes,[9] whose spectra showed that urea forms nitrogen-to-metal bonds with Pt(II) and Pd(II), and oxygen-to-metal bonds with Cr(III), Fe(III), Zn(II) and Cu(II).

The bands observed in the frequency region higher than 3000 cm.$^{-1}$ undoubtedly can be assigned to the N–H stretching frequencies. In zinc and cadmium complexes the frequencies are almost the same as those of the ligand. However, in platinum and palladium complexes, there is considerable decrease of the frequencies on coördination. The relation is the same as that of the urea complexes reported previously.[9] The band observed at 2940 cm.$^{-1}$ of methylthiourea can be identified with the C–H stretching frequency.

The strong band observed at 1634 cm.$^{-1}$ in the methylthiourea spectrum corresponds to the bands at 1610 and 1625 cm.$^{-1}$ for thiourea which were assigned to the NH_2 bending frequencies.[1a] This band of methylthiourea remains almost constant in frequency on coördination.

The strong band at 1550 cm.$^{-1}$ of methylthiourea can be explained as the amide II band or N–H deformation plus C–N antisymmetric stretching.[2,10] On coördination the frequency is increased by 25–28 cm.$^{-1}$ in the first group and only by about 10 cm.$^{-1}$ in the second group. This is understandable, since the C–N antisymmetric stretching frequency probably will be raised by the increment of the double bond nature of the C–N bond on coördination in the first group.

The most important change of spectrum on coördination is observed in the complexes of the second group for the band at 1490 cm.$^{-1}$ of the ligand, which arises from a vibration consisting of NH_2 rocking, C–N symmetric stretching and C=S stretching motions. The intensity of the band becomes much stronger and the frequency is lowered by 10–16 cm.$^{-1}$, as seen in Fig. 2. In contrast to this there is observed no appreciable change of frequency and intensity in the first group, as in the case of the thiourea complexes.

The methyl group attached to the nitrogen atom will exert three deformation vibrations, the degenerate, symmetric and rocking. By comparison with the spectra of molecules containing CH_3 groups,[2,10] it is possible to identify the three frequencies at 1455, 1408, and the paired values 1148 and 1124 cm.$^{-1}$ with the degenerate, symmetric and rocking frequencies, the last being split into two peaks. Formation of the complexes does not change the frequency values of these deformation vibrations.

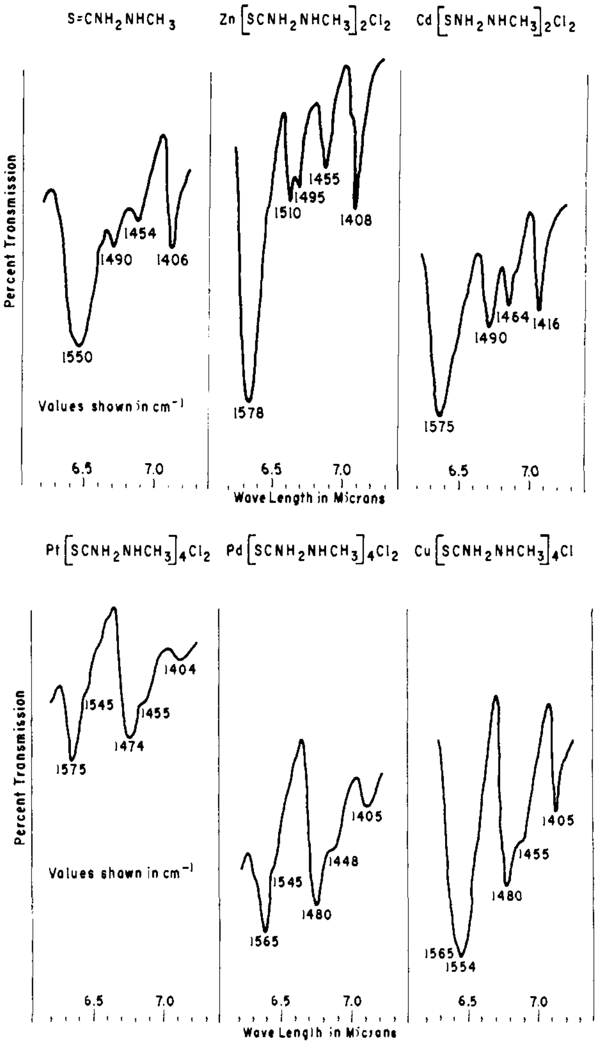


Fig. 2.—Infrared spectra of methylthiourea and its coördination complexes in the region from 6.2 to 7.2 μ.

As a result of comparison with the spectra of several amides[2,10] the band at 1296 cm.$^{-1}$ in the methylthiourea spectra is explained as the amide III band and assigned to C–N antisymmetric stretching and N–H deformation motions. In the first group of complexes this frequency is raised by 5–8 cm.$^{-1}$ and in the second group it is decreased by 10–13 cm.$^{-1}$. This behavior is almost the same as that observed for the amide II band.

The band at 972 cm.$^{-1}$ for methylthiourea can be considered to correspond to the band at 1083 cm.$^{-1}$ in the spectra of thiourea, which has been assigned to a motion consisting of symmetric C–N stretching, NH_2 rocking and C=S stretching. The corresponding bands of the complexes have been found in the region 965–990 cm.$^{-1}$ and are considerably decreased in intensity. This is due to the fact that the contribution of the C=S stretching motion in the first group of complexes becomes very small on complexing and in consequence the C–N symmetric stretching motion becomes the main contributor to the 972 cm.$^{-1}$ band. Since the C–N symmetric stretching motion will appear as a very weak absorption band, the 972 cm.$^{-1}$

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(9) R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **79**, 1575 (1957).

(10) S. Mizushima and T. Shimanouchi, "Festschrift Arthur Stoll," Sandoz Ag., Basel, 1957, p. 305.

band is considerably decreased in intensity. In the case of the second group the contribution of the C=S stretching and the NH_2 rocking motions to the 970 cm.$^{-1}$ band will be decreased, since this contribution is greater for the 1490 cm.$^{-1}$ band as is seen from the increased intensity of this band. Therefore, the intensity of the band at 970 cm.$^{-1}$ will also be decreased on complexing as in the case of the first group.

The band at 774 cm.$^{-1}$ of methylthiourea is considered to correspond to the band at 731 cm.$^{-1}$ of thiourea which arises from the motion consisting of C=S stretching and symmetric C–N stretching. This frequency corresponds to those of the bands observed in the spectra of the complexes in this region.

Finally the band observed at 718 cm.$^{-1}$ for methylthiourea may be explained as the out-of-plane NH_2 bending vibration. This band is shifted on deuteration, and no corresponding band was observed for symmetric dimethylthiourea. Bands of almost the same frequency are observed in the spectra of the complexes.

As explained above, the spectra of the metal complexes measured in this experiment can be divided into two groups. There is no doubt that the coördination of the first group takes place through sulfur. However, for the second group the spectral evidence for the coördination through nitrogen is not so conclusive as in the case of the urea complexes. This is due to the fact that the C=O stretching frequency in urea or methylurea lies well above the C–N stretching frequency, whereas the C=S frequency is not much different from the C–N frequency.

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The Effect of Coördination on Electron Withdrawal

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The electron withdrawing power of a group III metal is found to decrease when it is coördinated with diethyl ether. It is also confirmed that gallium has a greater electronegativity than aluminum.

Introduction

In trying to relate chemical shifts in proton magnetic resonance spectra, with the nature of the substituent attached to the proton, a relationship was developed between the separation of methyl and methylene protons of an ethyl group and the electron withdrawal power of the substituent attached to the ethyl group.[1] For the halogens this relationship could be expressed by: electronegativity = $0.695(\Delta CH_3 - \Delta CH_2) + 1.71$. By changing the constant to 2.1 good agreement was found with the metal alkyls and hydrogen itself.[2] Since there is a large magnetic anisotropy associated with the unshared pairs of electrons of the halogens, this will affect the shielding of protons adjacent to them. Therefore a different constant term is required when this additional shielding is absent. This equation predicts a reversal in the positions of the resonance lines due to the methyl group and the methylene group for a substituent of low electronegativity, and this has been shown for $AlCl(C_2H_5)_2$.[3] A similar type of equation, based on rather limited data, has been developed to relate spin coupling between the protons with the electronegativity of the substituent.[4]

It was thought that since electron withdrawal tendencies can be obtained for individual elements in their ethyl compounds by this method, it would also be useful in studying the change in electron withdrawal upon coördination of an element.

Experimental

The proton resonance spectra were obtained at 40 Mc. in a manner described previously.[5] Triethylgallium, originally prepared in this Laboratory[6] and stored in a sealed ampoule, was distilled before use. Triethylgallium etherate was prepared from triethylgallium and diethyl ether and excess ether was removed by pumping at $-40°$. Triethylaluminum was obtained from U. S. Industrial Chemicals Co., and the etherate was prepared in the same way as the gallium compound. Conventional vacuum techniques were employed throughout. Triethyloxonium fluoroborate was kindly supplied by A. M. Eastham of the National Research Council. Solutions in spectroscopic grade methylene chloride and acetonitrile were prepared in an inert atmosphere.

Results

The proton magnetic resonance spectra obtained from a series of compounds are shown in Table I.

In all cases except gallium triethyl and aluminum triethyl J/δ was small enough so that the values of J and δ were obtained by direct measurement of the separation of the lines in a multiplet and between the centers of the two multiplets, respectively. This approximation might cause a slight error for the ethyl groups attached to gallium in gallium triethyl etherate. However, a more refined method of calculation could not be

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(1) B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77**, 3977 (1955).

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(6) L. M. Dennis and W. Patnode, *ibid.*, **54**, 182 (1932).