alogy with the reported $CH_3$ deformation frequencies in methyl halides.[19] The assignment of the lowest frequency band to a metal-to-nitrogen stretching vibration would leave unassigned one deformation vibration. (4) Finally, if this observed low frequency band were to be assigned to the metal-to-nitrogen stretching frequency, the value of the calculated force constant for cobalt(III) ammines would be about $6 \times 10^5$ dynes/cm. However, this value is much greater than would be expected for a stretching frequency involving only a single bond.

In connection with the $NH_3$ deformation frequencies explained above, we are reporting a nine-body calculation of the vibrations of the $[Hg(NH_3)_2]^{++}$ ion, in order to show a more exact treatment of the vibrational problem of a metal ammine complex. In this complex ion, the N–Hg–N atoms lie on a straight line[20] and, therefore, regardless of the relative positions of internal rotations of the two $NH_3$ groups with respect to each other, a $C_3$ axis of symmetry is always present. For this symmetry, the vibrational frequencies are independent of the relative positions of the two $NH_3$ groups.[20] If free rotation of the two $NH_3$ groups occurs the point group is $D'_{3h}$.

(19) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 314.

(20) M. Katayama, T. Shimanouchi, Y. Morino and S. Mizushima, J. Chem. Phys., 18, 506 (1950).

We have calculated the normal vibrations of the $[Hg(NH_3)_2]^{++}$ ion using the same force constants as those reported in our calculation of the infinite chain of $[Hg(NH_2)]^+$.[21] Table III lists the result

TABLE III

CALCULATED AND OBSERVED FREQUENCIES IN CM.$^{-1}$ OF $Hg(NH_3)_2^{++}$

| Symmetry of vibration for $D'_{3h}$ | Type of vibration | Calcd. value | Obsd. values | |
|---|---|---|---|---|
| $A_1$ | Hg–N stretching | 493 | $[Hg(NH_3)_2]Cl_2$ | $[Hg(NH_3)_2]Br_2$ |
| | $NH_3$ sym. def. | 1281 | I.R. inactive | I.R. inactive |
| $\bar{A}_2$ | Hg–N stretching | 533 | 513 | 499 |
| | $NH_3$ sym. def. | 1282 | 1268 | 1245 |
| $\bar{E}$ | $NH_3$ rocking | 788 | | |
| | $NH_3$ deg. def. | 1577 | I.R. inactive | I.R. inactive |
| $E$ | $NH_3$ rocking | 791 | 719 | 697 |
| | $NH_3$ deg. def. | 1577 | 1605 | 1595 |
| | N–Hg–N deformation | 159 | Outside the CsBr region | Outside the CsBr region |

of the calculation, together with the experimental values. The agreement between the theoretical and experimental values is satisfactory. In the lower frequency region, we have calculated the Hg–N stretching frequencies and also the N–Hg–N deformation frequencies.

(21) S. Mizushima, I. Nakagawa and D. M. Sweeny, ibid., 25, 1006 (1956).

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# Infrared Absorption Spectra of Inorganic Coördination Complexes. XIV. Infrared Studies of Some Metal Thiourea Complexes[1a]

By A. Yamaguchi, R. B. Penland, S. Mizushima,[1b] T. J. Lane,[1c] Columba Curran and J. V. Quagliano[1d]

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Infrared spectra of some metal thiourea complexes have been measured in the 2–35 $\mu$ region. The spectra reveal that thiourea forms sulfur-to-metal bonds in all complexes studied. The calculation of the normal vibrations of thiourea is reported. Based on the result of this calculation, the absorption bands observed in the metal thiourea complexes have been assigned.

## Introduction

Stable Werner type coördination complexes formed from metal salts with 2, 4 or 6 moles of thiourea are known. However, the inner structures of these complex salts have not been determined.

Crystal structure investigations of thiourea have established the coplanarity of the C, N and S atoms in the molecule.[2] Kumler[3] interpreted the dipole moment of thiourea as indicating a resonance hybrid with 20–30% contribution of highly polar structures and concluded that the structure of thiourea is not essentially different from that of simple thioamides.

(1) (a) Paper XIII in series, This Journal, 80, 525 (1958); (b) visiting Professor from Faculty of Science, Tokyo University; (c) Reverend Thomas J. Lane, C.S.C.; (d) to whom correspondence concerning this article should be addressed.

(2) R. G. Wyckoff and R. B. Corey, Z. Krist., 81, 386 (1932).

(3) W. D. Kumler and G. M. Fohler, This Journal, 64, 1944 (1942).

The present investigation was undertaken to assign the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule.

Previous studies of some metal–urea complexes[4] have shown 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). It is of interest to compare the manner in which urea and thiourea molecules coördinate with metal atoms.

## Experimental

**Preparation of Compounds.**—Dichlorobis-(thiourea)-platinum(II), $[Pt(SC(NH_2)_2)_2Cl_2]$, prepared by the method of Kurnakow,[5] was dried in vacuo over phosphorus pentoxide.

(4) R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, ibid., 79, 1575 (1957).

(5) N. Kurnakow, J. prakt. Chem., [2] 50, 485 (1894).

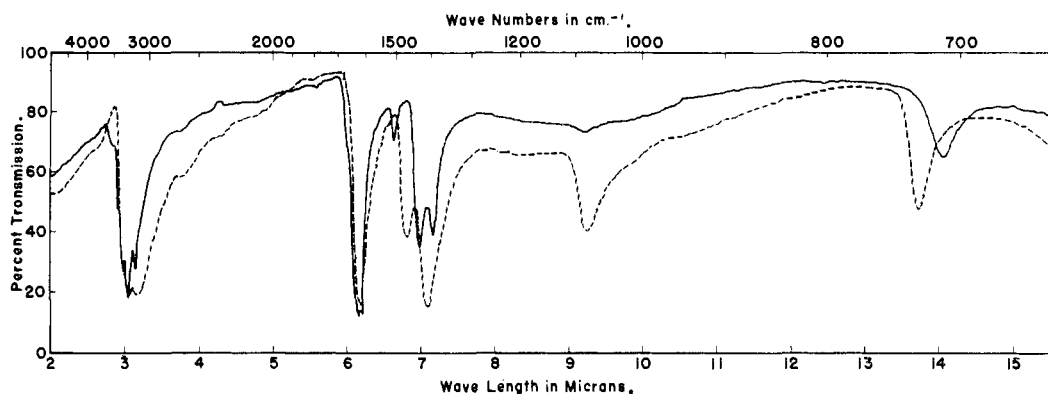Fig. 1.—Thiourea, ----------, dichlorobis-(thiourea)-platinum (II), [Pt{SC(NH₂)₂}Cl₂], ———.

*Anal.* Calcd. for Pt(C₂H₈N₄S₂)Cl₂: C, 5.74; H, 1.93. Found: C, 5.47; H, 2.18.

Tetrakis-(thiourea)-platinum(II) chloride, [Pt{SC-(NH₂)₂}₄]Cl₂, prepared by the method of Kurnakow,[5] was recrystallized from hot water as yellow needles and dried at 80°.

*Anal.* Calcd. for Pt(C₄H₁₆N₈S₄)Cl₂: C, 8.42; H, 2.83. Found: C, 8.63; H, 2.65.

Tetrakis-(thiourea)-palladium(II) chloride, [Pd{SC-(NH₂)₂}₄]Cl₂, prepared by the method of Kurnakow,[5] was recrystallized from hot water as bright red needles and dried at 80°.

*Anal.* Calcd. for Pd(C₄H₁₆N₈S₄)Cl₂: C, 9.96; H, 3.34. Found: C, 10.14; H, 3.37.

Dichlorobis-(thiourea)-zinc(II), [Zn{SC(NH₂)₂}₂Cl₂], prepared by the method of Maly,[6] was dried *in vacuo* over phosphorus pentoxide.

*Anal.* Calcd. for Zn(C₂H₈N₄S₂)Cl₂: C, 8.32; H, 2.90. Found: C, 8.50; H, 2.89.

Dithiocyanatobis-(thiourea)-nickel(II), [Ni{SC(NH₂)₂}₂-(SCN)₂], prepared by the method of Rosenheim and Meyer,[7] was dried *in vacuo* over P₂O₅.

*Anal.* Calcd. for Ni(C₄H₈N₆S₄): C, 14.69; H, 2.46. Found: C, 14.82; H, 2.61.

**Absorption Measurements.**—The infrared spectra were obtained by means of a Perkin–Elmer infrared spectrophotometer model 21 with sodium chloride and cesium bromide prisms over their regions of greatest resolution. The spectra of the solid complexes were obtained by the potassium bromide disk technique[8] and checked in Nujol mulls.

## Results

The spectra of thiourea and dichlorobis-(thiourea)-platinum(II) are illustrated in Fig. 1, and the experimental results obtained for the thiourea metal complexes are shown in Table I.

## Discussion

The calculation of in-plane normal vibrations of thiourea has been made for the C₂ᵥ model. A potential function of the Urey–Bradley type has been used

$$\bar{V} = \Sigma \frac{1}{2} K_i (\Delta r_i)^2 + \Sigma \frac{1}{2} H_{ij} r_i^0 r_j^0 (\Delta \alpha_{ij})^2$$
$$+ \Sigma \frac{1}{2} F_{ij} (\Delta q_{ij})^2 + \text{linear terms}$$

where $r_i$ and $r_j$ are bond lengths with equilibrium values $r_i^0$ and $r_j^0$; $\alpha_{ij}$ bond angles and $q_{ij}$ distances between non-bonded atoms. In addition $K$, $H$ and $F$ represent stretching, bending, and repulsive force constants, respectively.

(6) R. Maly, *Ber.*, **9**, 172 (1876).
(7) A. Rosenheim and V. J. Meyer, *Z. anorg. Chem.*, **49**, 13 (1906).
(8) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952); J. P. Faust and J. V. Quagliano, *ibid.*, **76**, 5346 (1954).

The values of the force constants used in this calculation are shown in Table II. Except for $K$(C–N), $K$(C=S), $H$(HNH), $H$(SCN) and $F$-(S. . . .N), the values of these constants are the same as those used in our calculation of the normal

TABLE I[a]

ABSORPTION MAXIMA IN CM.⁻¹ OF METAL THIOUREA CO-ORDINATION COMPOUNDS

| [Pt{SC(N-H₂)₂}₄]Cl₂ | [Pd{SC(N-H₂)₂}₄]Cl₂ | [Pt{SC(N-H₂)₂}₂Cl₂] | [Zn{SC(N-H₂)₂}₂Cl₂] | [Ni{SC(N-H₂)₂}₂(SCN)₂] |
|---|---|---|---|---|
| 3360s | ... | 3370s | 3360s | 3340s |
| 3290s | 3290s | 3280s | 3290s | 3250s |
| 3160s | 3120s | 3180s | 3160s | 3170s |
| ... | 3050s | ... | ... | 2080vs |
| 1647s | 1638s | 1628s | 1635s | 1642s |
| 1624s | 1625s | 1615s | 1615s | 1625sh |
| 1521w | 1520w | 1510w | 1498m | 1510m |
| 1500w | ... | ... | 1445s | 1442m |
| 1428sh | 1425sh | 1432s | 1408s | 1415m |
| 1406m | 1402m | ... | 1210vw | 1385m |
| 1386sh | 1380sh | 1398s | 1103w | 1105vw |
| 1180vw | 1180vw | ... | ... | 810m |
| 1090vw | 1090vw | 1035vw | 720sh | 718vw |
| 696m | 696m | 710m | 713m | 697m |
| 637w | 630w | ... | ... | 597w |
| 562w | 578w | 550w | 555w | 555w |
| 500w | ... | ... | 500w | 525w |
| 474w | 470w | 465w | 475w | ... |
| ... | 445w | ... | ... | ... |
| ... | 408w | ... | ... | ... |
| 303vw | 300vw | 318vw | ... | 300w |
| 276w | ... | ... | 280w | 276w |

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

vibrations of urea molecules.[9] Furthermore, the equilibrium bond lengths have been taken as C=S = 1.64 Å. and C–N = 1.35 Å. The N–H length has been assumed to be 1.00 Å. and all the bond angles as 120°. The calculated and the observed values of the normal frequencies are listed in Table III. The assignment of the observed frequencies agrees well with the calculated values but better agreement can be obtained if the values of the force constants are changed properly.

The potential energy distribution among symmetry coördinates also has been calculated and on

(9) A. Yamaguchi, T. Shimanouchi and S. Mizushima, to be published.

TABLE II

Force Constants (in $10^5$ Dynes/cm.) of Thiourea

| | | | | | |
|---|---|---|---|---|---|
| $K$(C—N) | 4.5 | $H$(SCN) | 0.24 | $F$(S$\cdots$N) | 1.06 |
| $K$(C=S) | 3.2 | $H$(CNH) | .21 | $F$(N$\cdots$N) | 0.60 |
| | | $H$(HNH) | .39 | $F$(C$\cdots$H) | 0.92 |
| | | $H$(NCN) | .57 | $F$(H$\cdots$H) | 0 |

TABLE III

Observed and Calculated Frequencies in Cm.$^{-1}$ of Thiourea and Thiourea-$d$ (Except for N-H Stretching Frequencies)[a]

| Molecule | Type of vibration | Calcd. | Obsd. |
|---|---|---|---|
| | $NH_2$ bending | 1619 | 1610 |
| | $NH_2$ rocking, N–C–N stretching and C=S stretching | 1450 | 1417 |
| | N–C–N stretching and $NH_2$ rocking and C=S stretching | 1059 | 1083 |
| $A_1$ | C=S stretching and N–C–N stretching | 757 | 730 |
| | NCN deformation | 498 | 488 |
| $SC(NH_2)_2$ | | | |
| | $NH_2$ bending | 1623 | 1625 |
| | N–C–N stretching | 1473 | 1470 |
| $B_1$ | $NH_2$ rocking | 1153 | 1114 |
| | NCS deformation | 462 | 415 |
| | N–C–N and C=S stretching | 1371 | 1380 |
| | $ND_2$ bending | 1204 | 1190 |
| $A_1$ | $ND_2$ rocking and N–C–N stretching | 882 | 910 |
| | C=S and $ND_2$ rocking | 704 | 668 |
| | NCN deformation | 440 | .. |
| $SC(ND_2)_2$ | | | |
| | N–C–N stretching | 1451 | 1500 |
| $B_1$ | $ND_2$ bending | 1188 | 1143 |
| | $ND_2$ rocking | 893 | 826 |
| | NCS deformation | 426 | .. |

[a] The assignment to the $A_1$ and $B_1$ symmetry types of thiourea has been confirmed by the measurement of infrared dichroism.

the basis of this result the types of vibration have been determined as shown in Table III.

The high frequency N–H absorption bands in the spectrum of thiourea were not shifted to lower frequencies on the formation of the metal–thiourea complexes. This indicates that nitrogen-to-metal bonds are not present[10] and that therefore the bonding in these complexes must be between the sulfur and metal atoms.

The formation of S → M bonds is expected to increase the contribution of the highly polar structure

$$H_2N^+ \diagdown C\text{---}S^- \diagup H_2N$$
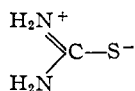
to the thiourea molecule, resulting in a greater double bond character for the nitrogen-to-carbon bond and a greater single bond character for the carbon-to-sulfur bond.

(10) G. F. Svatos, C. Curran and J. V. Quagliano, This Journal, 77, 6159 (1955).

The assignment of the absorption bands observed for the metal thiourea complexes follows.

(1) The bands observed in the 3 $\mu$ region are undoubtedly assigned to the N–H stretching vibrations. These bands are sharper in the spectra of the metal complexes than in thiourea; this suggests that hydrogen bonding is not present in these coördination compounds.

(2) The bands observed at about 1600 cm.$^{-1}$ correspond to the bands of thiourea of almost the same frequency and can be assigned to the $NH_2$ bending vibrations.

(3) The bands observed at about 1500 cm.$^{-1}$ correspond to the 1470 cm.$^{-1}$ band of thiourea assigned to the N–C–N stretching vibration of the $B_1$ type. The frequency increase observed for the complexes can be explained as resulting from the greater double bond character of the carbon-to-nitrogen bond on complex formation.

(4) The bands at about 1400 cm.$^{-1}$ correspond to the 1417 cm.$^{-1}$ band ($A_1$) of thiourea assigned to the $NH_2$ rocking vibration and N–C–N and C=S stretching vibrations. The nature of the vibrations is changed slightly on coördination through the sulfur atoms.

(5) A conspicuous difference in the spectrum of thiourea and the spectra of its metal complexes appears in the region at about 1100 cm.$^{-1}$. A strong absorption of thiourea at 1083 cm.$^{-1}$ is extremely weakened or disappears on complex formation. This observation can be explained by the considerable change in the nature of the N–C bond as well as of the C=S bond on coördination of thiourea through the sulfur atom; in these complexes the N–C–N stretching frequency is increased and the C=S stretching frequency is decreased. Therefore, in coördination complexes, the contribution of the C=S vibration to the 1100 cm.$^{-1}$ band is decreased and the intensity of this band is reduced. The symmetric N–C–N stretching vibration ($A_1$) cannot contribute much to the intensity, as has been shown for the spectrum of urea.[9]

(6) The bands observed at about 700 cm.$^{-1}$ in the spectra of the complexes correspond to the 730 cm.$^{-1}$ band of thiourea. The lowering of frequency can be attributed to the reduced double bond character of the C=S bond.

The absorption bands in the spectra of the metal–thiourea complexes which have been assigned to the particular vibrations noted above all indicate the presence of sulfur-to-metal bonds in these metal complexes.

The spectral investigations of urea and thiourea metal complexes were undertaken preliminary to the determination of infrared absorption spectra of amino acids containing carbonyl, thiocarbonyl and sulfhydryl groups.

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