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Infrared Spectra of Complexes of Metal Halides with Tetramethylurea and Tetramethylthiourea

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Infrared spectra have been obtained in potassium bromide disks for tetramethylurea complexes of $ZnBr_2$, ZnI_2, $CoBr_2$, and $PbBr_2$ and for tetramethylthiourea complexes of $ZnCl_2$, ZnI_2, $CoBr_2$, CoI_2, $CdBr_2$, CdI_2, $PdCl_2$, $PtCl_2$, and $PbBr_2$. All complexes are 2:1, ligand to metal halide, except those of $PbBr_2$ and $PtCl_2$, which are 1:1. The large shifts to high frequencies of the absorption maxima associated with the NCN antisymmetric stretching vibration in the spectra of all the complexes and the low frequencies of the C=O stretching vibration in the tetramethylurea complexes indicate appreciable $^{+}N{=}C{-}S^{-}$ and $^{+}N{=}C{-}O^{-}$ bond character.

Infrared absorption measurements have indicated that urea[2] forms nitrogen to metal bonds with Pt(II) and Pd(II) chlorides and oxygen to metal bonds with Cr(III), Fe(III), Zn, and Cu(II) chlorides, whereas in thiourea complexes[3] infrared spectra indicate only sulfur to metal bonding. Sulfur to metal bonds have also been revealed by the X-ray diffraction measurements of Nardelli and co-workers on solid complexes of metal halides with thiourea,[4] ethylenethiourea,[5] and tetramethylthiourea.[6]

Tetramethylurea and tetramethylthiourea are of particular interest because of steric effects. The nitrogen in the dimethylamino group is sterically less available for complex formation than the amino group. Infrared spectra indicate only oxygen to metal bonds in complexes of dimethylformamide[7] and dimethylacetamide[8]; platinum complexes of these amides have not been reported and attempts to prepare the palladium complexes of these amides have been unsuccessful. Also, the carbon–nitrogen–oxygen (or sulfur) skeleton in tetramethylurea and tetramethylthiourea cannot be coplanar without undue widening of the N–C–N angle; this departure from coplanarity is expected to decrease the over-all π-electron delocalization. The X-ray diffraction pattern for crystalline tetramethylthiourea has been interpreted[9] as indicating that each nitrogen atom is 0.75 Å. above the plane of the three attached carbon atoms. The dipole moment of tetramethylurea, 3.49 D., compared to the values 4.56 and 4.60 D. for urea and *sym*-dimethylurea,[10] indicates a smaller contribution of highly polar $^{+}N{=}C{-}O^{-}$ structures in tetramethylurea.

Tetramethylthiourea complexes with zinc, cobalt(II), cadmium, and mercury(II) chlorides have been reported.[6] X-Ray diffraction data indicate a tetrahedral configuration for the zinc and cobalt complexes; the conformations of the dimethylamino groups were not assigned. Infrared measurements have indicated oxygen to metal bonding in tetrachlorobis(tetramethylurea)tin(IV).[11]

The present investigation is concerned with the preparation of a number of complexes of metal halides with tetramethylurea and tetramethylthiourea and the investigation of the changes in the infrared spectra of these amides on complex formation.

Experimental Section

Preparation of Tetramethylurea Complexes.—The metal halides were dissolved in excess tetramethylurea (tmu) by heating and the complexes precipitated on addition of the solutions to petroleum ether; they were dried at 80° with phosphoric anhydride under vacuum.

Anal. Calcd. for $ZnBr_2(tmu)$: C, 26.25; H, 5.29. Found: C, 26.64; H, 5.47. Calcd. for $ZnI_2(tmu)_2$: C, 21.78; H, 4.39. Found: C, 22.06; H, 4.55. Calcd. for $CoBr_2(tmu)_2$: 26.63; H. 5.36. Found: C, 25.60; H, 5.49. Calcd. for $PbBr_2(tmu)$ C, 12.39; H, 2.48. Found: C, 11.26; H, 2.29.

Tetramethylthiourea Complexes.—Cobalt halides were triturated with twice the molar quantities of tetramethylthiourea (tmtu) under a stream of dry nitrogen. The resulting mass was dissolved in a minimum of dry propanol and extracted with petroleum ether. The palladium and platinum complexes were prepared by adding a concentrated ethanol solution of 2 mmoles of tmtu to a water solution of 1 mmole of K_2PdCl_4 or K_2PtCl_4. As analysis indicated a 1:1 composition for the platinum complex, the preparation was repeated using a 1:1 ratio of components; the two analyses were almost identical. The solid complexes retained moisture to a much greater extent than most platinum and palladium complexes; they were dried with phosphoric anhydride under vacuum at 140° for 10 hr. $PbBr_2(tmtu)$ was prepared by mixing lead bromide with excess tmtu in a Wig-L-Bug for 30 sec. The mixture was then heated at 90° until the lead bromide completely dissolved in the melted tmtu (30 min.). The excess tmtu was removed by repeated washings with anhydrous ethyl ether. The other tmtu complexes were prepared by mixing ethanol solutions of the two components in a 2:1 ratio and separating the crystals after partial evaporation of the

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC document No. COO-38-382.

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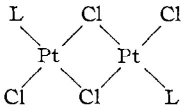
ethanol. The products were dried in a vacuum desiccator over phosphoric anhydride.

Anal. Calcd. for $CdBr_2(tmtu)_2$: C, 22.38; H, 4.51. Found: C, 22.53; H, 4.45. Calcd. for $CdI_2(tmtu)_2$: C, 19.04; H, 3.84. Found: C, 19.34; H, 3.98. Calcd. for $CoBr_2(tmtu)_2$: Co, 12.19. Found: Co, 13.07. Calcd. for $CoI_2(tmtu)_2$: C, 20.80; H, 4.19; Co, 10.21. Found: C, 20.03; H, 4.33; Co, 9.68. Calcd. for $ZnCl_2(tmtu)_2$: C, 29.97; H, 6.04. Found: C, 30.44; H, 6.12. Calcd. for $ZnI_2(tmtu)_2$: C, 20.58; H, 4.14. Found: C, 20.60; H, 4.06. Calcd. for $PbBr_2(tmtu)$: C, 12.03; H, 2.42; Pb, 41.50. Found: C, 12.48; H, 2.49; Pb, 41.71. Calcd. for $PdCl_2(tmtu)_2$: C, 27.19; H, 5.44. Found: C, 26.70; H, 5.53. Calcd. for $PtCl_2(tmtu)$: C, 15.07; H, 3.01. Found: C, 16.07; H, 3.26.

Infrared Spectra.—These were obtained in KBr disks using a Perkin-Elmer Model 421 spectrophotometer. Some of the spectra were checked in Nujol mulls.

Discussion of Results

With the exception of π complexes, 1:1 compounds of monodentate organic ligands with platinum halides are rare. $PtCl_2(tmtu)$ is expected to be a dimer of type I or II.



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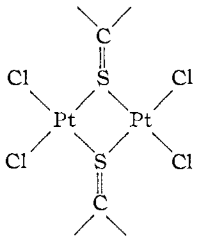

II

We are not aware of any previously reported coplanar square complexes of type II. Nardelli and co-workers[12] have reported X-ray diffraction data supporting sulfur bridges of this type in octahedral complexes of thiourea with cadmium and nickel isothiocyanates. The 1:1 complexes with lead bromide were not unexpected. A similar complex was obtained with dimethylformamide.[13] The 1:1 complex of thiourea with lead acetate contains three sulfur to lead bonds[14] and the 2:1 complex of thiourea with lead(II) chloride contains four sulfur to lead bonds (two per sulfur atom).[15] We are unaware of any crystal structure determination of complexes of lead bromide containing C=O—Pb bonds. It appears that these involve either (a) three-coordinate lead or (b) bromine bridges as in type I (but not a planar arrangement). The failure to isolate complexes of tetramethylurea with platinum and palladium chlorides is further evidence of the reluctance of these metals to interact with the $^{(CH_3)_2N}{>}C{=}O$ group.

The absorption maxima of chief interest in the spectra of tetramethylthiourea and its complexes are those associated with the N—C—N and C=S stretching vibrations. These are expected to shift to high and low frequencies, respectively, on the formation of sulfur to metal bonds. The frequency calculated by Mizushima, *et al.*,[3] for the N—C—N antisymmetric stretching vibration in thiourea-d_4 is 1451 cm.$^{-1}$ and the observed band ascribed in this vibration is at 1500 cm.$^{-1}$. We consider the absorption at 1504 cm.$^{-1}$ in the spectrum of solid tetramethylthiourea to be associated mainly with this vibration. The only other fundamental in this region, the CH_3 degenerate bending vibration, is almost always at a lower frequency than 1504 cm.$^{-1}$ and our experience with dimethylformamide, dimethylacetamide, and hexamethylphosphoramide is that the absorption associated with this bending vibration does not shift to high frequency on complex formation. In the spectra of the complexes, the strong absorption in the 1550 cm.$^{-1}$ region (Figure 1) is attributed to the N—C—N antisymmetric stretching vibration. The absorption at 1130 cm.$^{-1}$ (1126 cm.$^{-1}$ in the present investigation) in the spectrum of tetramethylurea has been assigned[16] to the C=S stretching vibration. The strong absorption at 1100 cm.$^{-1}$ in the spectra of tetramethylthiourea complexes (Figure 1), absent in the spectra of tetramethylurea complexes (Figure 2), is assigned to this vibration.

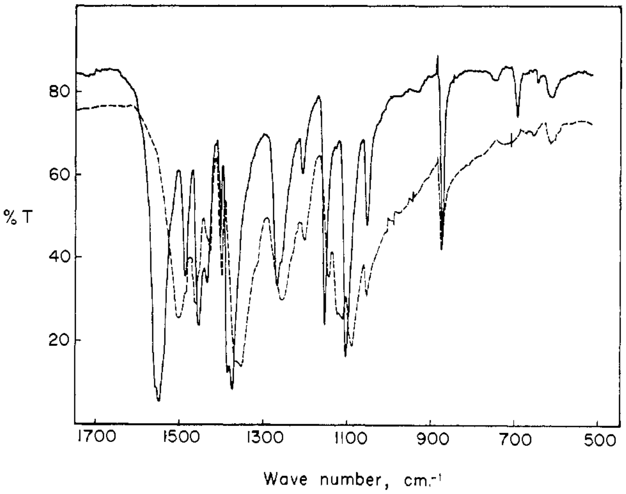

Figure 1.—Infrared spectra in KBr disks: --------, tetramethylthiourea; ———, diiodobis(tetramethylthiourea)cobalt(II).

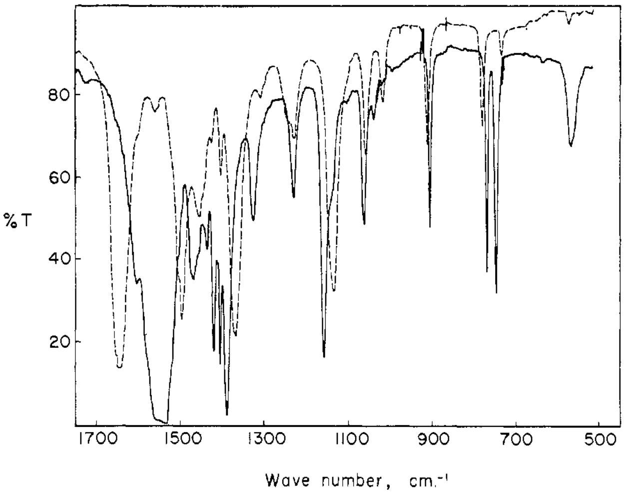

Figure 2.—Infrared spectra: --------, tetramethylurea, liquid film; ———, diiodobis(tetramethylurea)zinc in a KBr disk.

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TABLE I

SOME ABSORPTION MAXIMA (CM.$^{-1}$) IN THE SPECTRA OF TETRAMETHYLTHIOUREA COMPLEXES IN KBr DISKS

	NCN antisym. str.	C=S str.
Tetramethylthiourea	1504	1126
$ZnCl_2(tmtu)_2$	1544	1104
$ZnI_2(tmtu)_2$	1551	1105
$CdBr_2(tmtu)_2$	1550	1108
$CdI_2(tmtu)_2$	1545	1101
$CoBr_2(tmtu)_2$	1548	1104
$CoI_2(tmtu)_2$	1542	1098
$PdCl_2(tmtu)_2$	1549	1101
$PtCl_2(tmtu)$	1600	1102
$PbBr_2(tmtu)$	1553	1110 sh 1100

The frequencies observed in the 1550 and 1100 cm.$^{-1}$ regions are listed in Table I. There are no significant differences in the frequencies of the complexes with the exception of the high frequency (1600 cm.$^{-1}$) observed for $PtCl_2(tmtu)$. This compares with an average of around 1660 cm.$^{-1}$ for the C=N stretching frequency in aliphatic aldimines[17] and is indicative of a large double bond character for one or both nitrogen to CS bonds in this complex. It is suggestive of sulfur bridging (type II complex), which would increase the electron demand of the sulfur atom, but this is not supported by the C=S stretching frequency in the platinum complex, which is similar to the values for the other complexes.

That the shifts in the absorption maxima on complex formation are not primarily solid-state effects is evident from spectra obtained for methylene chloride solutions. The spectrum of tetramethylthiourea in this solvent has a strong broad absorption centering at 1497 cm.$^{-1}$. Solutions of the zinc bromide and zinc iodide complexes absorb strongly at 1555 cm.$^{-1}$ with a shoulder at 1540 cm.$^{-1}$, whereas the spectrum of the cadmium bromide complex has a maximum absorption at 1540 cm.$^{-1}$ and a shoulder at 1555 cm.$^{-1}$. The spectra of the solutions of all three of these complexes show split peaks in the C=S stretching region, at about 1105 and 1095 cm.$^{-1}$. The shifts observed on complex formation for the bands attributed to the N—C—N and C=S stretching vibrations, both in the solid state and in solution, indicate that despite the steric prevention of coplanarity for the carbon–nitrogen–sulfur skeleton there is appreciable $^{+}N{=}C{-}S^{-}$ character for tetramethylthiourea in the complexes.

In the spectra of tetramethylurea complexes the absorptions of particular interest are the N—C—N and C=O stretching vibrations. A normal vibration calculation for urea-d_4 by Mizushima, et al.,[18] has yielded a frequency of 1477 cm.$^{-1}$ for the N—C—N antisymmetric stretching vibration, compared to an observed value of 1490 cm.$^{-1}$, and a frequency of 1597 cm.$^{-1}$ for the C=O stretching vibration (mixed with the N—C—N symmetric stretching mode), compared to an observed value of 1610 cm.$^{-1}$. We have assigned the absorptions at 1499 and 1640 cm.$^{-1}$ in the spectrum of liquid tetramethylurea (Figure 2) to mainly the antisymmetric N—C—N and the C=O stretching vibrations, respectively.

TABLE II

SOME ABSORPTION MAXIMA (CM.$^{-1}$) IN THE SPECTRA OF TETRAMETHYLUREA COMPLEXES IN KBr DISKS

	C=O str.		NCN anti-sym. str.	C=O bend.	
Tetramethylurea (liquid)	1640		1499	781	
$ZnBr_2(tmu)_2$		1555–1535		769	749
$ZnI_2(tmu)_2$		1555–1535		768	749
$CoBr_2(tmu)_2$		1555–1535		766	749
$PbBr_2(tmu)$	1585		1525	765	748

On complex formation of tetramethylurea with lead(II) chloride the absorption associated with the carbonyl vibration is lowered to 1585 cm.$^{-1}$ and the antisymmetric N—C—N frequency is increased to 1525 cm.$^{-1}$ (Table II), indicating oxygen to lead bonding. Frequencies of 1569 and 1513 cm.$^{-1}$ in the spectrum of solid $SnCl_4(tmu)_2$ have been assigned to these vibrations[11] and Jose Philip in this laboratory has observed frequencies of 1571 and 1520 cm.$^{-1}$ in the spectrum of this complex. In the spectra of the bistetramethylurea complexes of zinc iodide (Figure 2) and zinc bromide and cobalt bromide (Table II), a broad absorption band occurs in this region with a maximum extending from 1555 to 1535 cm.$^{-1}$. This is attributed to a merging of the absorptions associated with the C=O and antisymmetric N—C—N vibrations. The greater frequency shifts for these vibrations than for those in the lead(II) chloride and tin(IV) chloride complexes suggest stronger oxygen to metal bonds in the zinc and cobalt complexes. Infrared spectra have indicated[13] that dimethylformamide also forms a weaker dative bond with lead(II) than with the first series transition metals in DMF–metal halide complexes.

The large shift in the tetramethylurea carbonyl frequency on complex formation with zinc and cobalt halides, around −90 cm.$^{-1}$, compares with average shifts of −30 and −50 cm.$^{-1}$ in the C=O stretching frequency of dimethylformamide[7] and dimethylacetamide,[8] respectively, on complex formation with a variety of metal halides. This indicates a large $^{+}N{=}C{-}O^{-}$ character in tetramethylurea complexes, suggesting conformations of the dimethylamino groups more favorable for π-electron delocalization than in liquid tetramethylurea. These complexes are partially dissociated in solution. The main, broad absorption in this region for $ZnBr_2(tmu)_2$ in methylene chloride solution has a maximum at 1565 cm.$^{-1}$, indicating a large negative shift for the carbonyl stretching frequency comparable to that observed for the solid complex.

Two strong absorption bands in the 750 cm.$^{-1}$ region of the spectra of tetramethylurea complexes (Figure 2 and Table II), absent in the spectra of tetramethyl-

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thiourea complexes, are assigned to C=O bending vibrations. These do not show the increase in frequency on complex formation that was observed for the N—C=O bending vibration in dimethylformamide.[13,19]

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Infrared and Proton Magnetic Resonance Spectra of Imidazole, α-Alanine, and L-Histidine Complexes in Deuterium Oxide Solution[1]

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The infrared spectra of imidazole and imidazolium ion in D_2O have been assigned on the basis of isotopic substitution results. Spectral changes attendant upon coordination of imidazole and α-alanine with divalent metal ions in D_2O have been observed. Formation constants for monodentate coordination of alanine at lower pD values have been evaluated. The results for imidazole and alanine are employed in interpreting the infrared spectrum of L-histidine in D_2O as a function of pD. The structures of metal–histidine complexes as a function of solution pD have been inferred from infrared data, which indicate the presence of monodentate, bidentate, and tridentate 1:1 histidine complexes at various levels of solution acidity. At pD >11 a histidine complex is formed involving coordination to the amino group and the deprotonated (anionic) imidazole moiety. The pD dependence of the infrared spectra provides information relating to the formation constants for complex formation; the magnitudes of certain frequency shifts provide information which relates to the enthalpy of formation of the coordinate bond. In particular, the shift in frequency of the antisymmetric carboxylate stretching mode upon coordination at the α-amino group is related to the strength of the metal–amino group interaction.

The interaction of metal ions with polypeptides and proteins is a subject of perennial interest. It is helpful in learning about such systems to understand first the interaction of metal ions with simple "model compounds" which are active components of the more complicated polypeptide chains. Histidine is one of the strongest metal coordinators among the amino acids and plays an important role in binding of metal ions by proteins. The imidazole group of histidine is of prime biological importance in that it is generally responsible for most of the buffering power of proteins in the physiological pH range and is a binding site for metal ions in insulin and serum albumin.[3,4]

Many investigations of metal interaction with aqueous histidine have been reported in the literature. Most of this work has been concerned with the determination of stability constants.[5-8] From a comparison of these stability constants with those of structurally related ligands, several authors have proposed possible structures for the aqueous histidine complexes.[9-12] In each instance, only indirect structural evidence obtained from stability constant measurements has been cited. Furthermore, with the exception of recent work on Co(II)–histidine complexes by McDonald and Phillips,[13] no investigation dealing with the structure of histidine complexes as a function of solution pH has been reported in the literature.

Infrared spectroscopy in aqueous medium furnishes interesting and useful information regarding the interaction of an amino acid or other similar ligand with metal ions. The ligand itself, in the absence of metal ion, may exhibit a spectrum which varies with the pH (or pD if the solvent is D_2O), *i.e.*, the spectra of acid and conjugate base forms of the ligand may differ significantly. Information regarding interaction of the ligand with metal ion can then be acquired by observation of the quantitative effect which the metal ion exerts on the pH (pD) dependence of the ligand spectrum. Infrared spectroscopy offers the singular advantage in this connection that the spectral changes seen are characteristic of protonated and deprotonated forms of specific functional groups, such as amino or carbonyl. Whereas in the more conventional titrimetric procedure for learning about formation constants, a single observable (the proton activity) is measured over the entire range of acidities, the infrared spectral method furnishes in the most fortunate cases separate data about the proton equilibria at each of the sites at which equilibrium with proton is established. The infrared method suffers from the disadvantage of requiring rather high concentrations of ligand and metal ion, however, and can therefore not be

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(2) Alfred P. Sloan Research Fellow; to whom correspondence and reprint requests should be addressed.

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