

VIBRATIONAL SPECTRA OF COMPLEXES OF THIOUREA WITH ALKALI HALIDES*

Z. KSANDR, K. VOLKA and P. ADÁMEK

*Department of Analytical Chemistry and Department of Inorganic Chemistry,
Institute of Chemical Technology, Prague 6*

Received January 10th, 1972

The IR spectra of complexes of thiourea with KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr, CsI, TlCl, TlBr, and TlNO_3 , resp., were studied. The far-infrared and Raman spectra as well as the IR spectrum in polarized radiation were obtained for the complex with RbI. The results are discussed in terms of structure of the complexes.

Crystals of the complexes MX.4 TU of thiourea (TU) with ionic salts (MX) of monovalent cations belong to a low number of structural types¹⁻³; the corresponding space groups are $Bb\bar{a}m - V_h^{18}$ for MX = RbCl, CsCl, and TlCl, $P4/mna - D_{4h}^6$ for MX = KBr, RbBr, CsBr, KI, RbI, CsI and TlBr and $P4/mcc - D_{4h}^2$ for the complex with TlNO_3 . The position of molecules of thiourea in two model structural units of the complex MX.4 TU (with 8 units in one elementary cell) is represented by Fig. 1a, that of the thiourea molecules in the elementary cell of crystalline thiourea at room temperature (space group $Pbnm - V_h^{16}$, $Z = 4$)⁴ is given in Fig. 1b. The stability of the complexes formed is attributed exclusively to Coulomb interactions between the ions of the salt and thiourea dipoles^{2,3}.

In the present work the IR spectra were studied for the complete series of all complexes of thiourea with alkali halides, able to exist, *i.e.* complexes with KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr and CsI, isostructural complexes with TlCl and TlBr, and, in addition, the complex with TlNO_3 . The extension of the series by thallium complexes is interesting with respect to the complex $\text{TlNO}_3 \cdot 4 \text{ TU}$, the crystal structure of which is – among the complexes studied – of the highest symmetry. For the complex RbI.4 TU, the far-infrared and Raman spectra and the IR spectrum in polarized light were obtained in addition.

It is the purpose of this work to consider qualitatively the changes appearing in the vibrational spectrum of thiourea on its incorporation in the lattice of an alkali halide. Here we follow up the Stewart's study⁵ of infrared spectra of thiourea complexes formed during the pressing of thiourea into KBr, KI, and CsCl disks, respectively.

* Presented at the International Conference on Molecular Spectroscopy, Wrocław, Poland, September 15–19, 1972.

TABLE I

Vibrational Spectra of the Complex RbI.4 TU (cm^{-1})

Raman spectrum measured for powder samples, intensity in relative units (base 10); symmetry with respect to the factor group D_{4h}^6 given for the IR bands only.

Raman spectrum	Infrared spectrum		Symmetry of vibration
	Nujol	single crystal	
3 383(10)	(3 360 s) ^a	3 440	$A_{2u} + E_u$
3 326 (2)	(3 250 s)		
3 208 (1)			
3 193 (6.5)	(3 150 s)	(3 190)	$A_{2u} + E_u$
	(3 095 s)	(3 010)	A_{2u}
2 945(10)			
2 903 (6.5)		(2 920)	
2 873 (1)			
2 713 (2)			
	(2 670 s)	(2 680)	$A_{2u} + E_u$
(1 630) (0)	1 631 s	1 630	E_u
		1 615	E_u
		(1 610)	A_{2u}
(1 590) (0)	1 592 s	1 580	A_{2u}
		1 455	$A_{2u} + E_u$
		1 425	E_u
		1 380	E_u
	(1 300)		
	(1 150 s)		
1 094 (0.5)	1 083 s	1 080	E_u
	(980 m)		
	(890 w)		
	764 w	761	E_u
733 (5)	737 m	738	E_u
	730 m		
	723 m	725	E_u
	632 m	633	E_u
	616 m	618	E_u
	592 w	590	E_u
	500 s	500	E_u
483 (5)			
417 (0.5)			
176 (1)			
	157 s ^b		A_{2u}
	(147 m) ^b		
113 (10)	114 s ^b		E_u^c

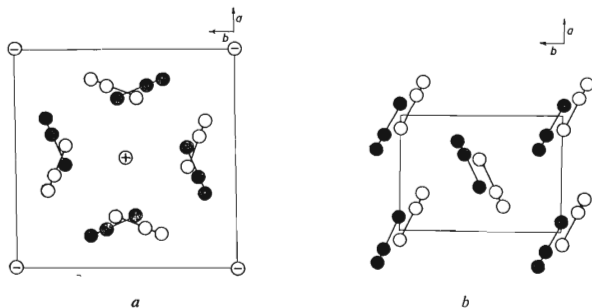


FIG. 1

Projection of the Model Unit of the Complex MX.4 TU (a) and of Thiourea (b) on the Plane ab

● Molecules lying in the symmetry planes $z = 0$, ○ molecules in the symmetry planes $1/2(a)$ and $1(b)$. Anions lie in $z = 0, 1/2$, cations in $z = 1/4, 3/4$.

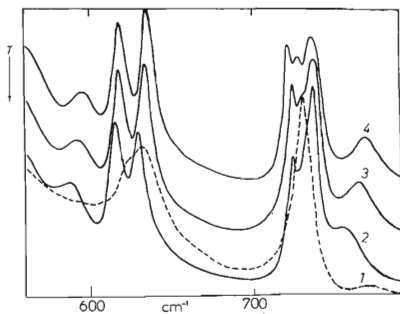


FIG. 2

Infrared Spectra of Nujol Mulls of Thiourea and Its Complexes with Alkali Iodides

1 Thiourea, 2–4 complexes: 2 CsI, 3 RbI, 4 KI.

Explanations to Table I:

^a Parentheses denote values for maxima of broad bands or inflexes, which could not be read off exactly; ^b Spectra of powder samples in polyethylene discs; bands found below 100 cm^{-1} : (99 s), (85 m), (68 w), 54 w, 44 w, 32 w, 25 w; ^c Assignment based on reflection measurements of thiourea⁷.

EXPERIMENTAL

Complexes of the composition MX.4 TU were prepared by the method described by Boeyens¹ from solutions in a mixture methanol-water. The alkali halide was added to the solution in a slight excess (3%). The composition of the complexes was checked by determining nitrogen and/or sulfur. Thiourea, alkali halides, and thallium salts were p.a. purity.

A bunch of parallel single crystals of RbI.4 TU, used for the measurements of IR spectra in polarized radiation, was prepared by a slow evaporation of a saturated solution in a mixture methanol-water. Discs of thiourea in KBr were prepared by using the usual technique, with the applied pressure of 10 t/cm².

Infrared spectra in the region 3600–400 cm⁻¹ (Nujol mulls) were measured on a spectrophotometer Perkin-Elmer 325. Measurements in polarized radiation on the same instrument with a built-in polarizer were carried out by using a lense beam condenser (1 : 4). Absorption spectra in the range 400–20 cm⁻¹ were obtained on a spectrophotometer FS-620 (RIIC-Beckman, London) on powder samples pressed in polyethylene discs; Raman spectra of powder samples were scanned on an instrument Coderg PH 1 with the excitation 632.8 nm (He-Ne laser).

RESULTS AND DISCUSSION

The reproduction of Stewart's experiments evidenced that the complex formation of thiourea with KBr in the solid state is conditioned by the presence of water; thus a characteristic splitting of absorption bands⁵ occurs in the presence of, *e.g.*, 0.05% water in KBr, whereas no splitting (with the pressures applied by Stewart) was observed after a perfect drying of KBr. This is in accordance with the experiments performed by Boeyens¹, who observed the complex formation only for pressures as high as 15.5 t and only after 24 h; neither in that case the moistening of the sample during the experiment can be excluded.

The spectra of Nujol mulls of thiourea do not exhibit changes indicating any formation of addition compounds, although the substance is known to form such compounds with a series of alkanes (for *n*-alkanes it is restricted⁶ to homologues C₁₄–C₁₉). No changes in the spectra of thiourea were observed for crystals isolated from a vigorously shaken mixture of its methanol solution with Nujol either.

The results of all the spectral measurements performed for the complex RbI.4 TU are given in Table I. The measurements in polarized IR radiation show that the internal vibrations of the E_u and A_u symmetry correspond, in terms of molecular symmetry C_s, to the symmetric and anti-symmetric vibrations, resp., with respect to the symmetry plane of the thiourea molecule (perpendicular to the plane of the molecular skeleton).

The IR spectra of thiourea and of its complexes are similar in their main features. They are all characteristic by a considerable complexity; the absorption bands are broad and overlapping particularly in the range of 1500–800 cm⁻¹ in Nujol mulls, but no essential simplification appears for measurements of crystalline samples either.

The best conditions for the consideration of the effect of the various ions on the spectrum of thiourea in complexes appear in the spectral range of 800–600 cm⁻¹. The comparison of the spectra of the complexes in that range is presented in Table II and Fig. 2. Changes observed in the remaining spectral parts are – for the various complexes – similar to those occurring for the RbI.4 TU complex; in the complexes with RbCl and CsCl, resp., two weak bands appear in addition at 3530–3515 cm⁻¹

TABLE II

Wavenumbers of Absorption Bands I–VII of Thiourea (TU) and Complexes MX.4 TU in the Range of 800–600 cm^{-1}

Distinct doublets or complex bands given in parantheses; bands I, III and VII are weak.

MX	I	II	III	IV	V	VI	VII
—	769	—	730	—	(631)	—	—
KI	768	(736)	(728)	722 ^a	634	617	(595)
RbI	764	737	730	723	632	616	(592)
CsI	757	737	—	724	629	615	587
KBr	770	739	734 ^b	724	634	620	—
RbBr	765	739	—	726	632	618	—
CsBr	—	740	—	727	630	617	—
TlBr	766	738	730	723	630	616	—
RbCl	—	734	727	—	(631)	(627)	—
CsCl	—	736	730	—	(629)	(625)	—
TlCl	—	741	—	726	630	618	—
TlNO ₃	761	—	726	—	628	—	—

^a A weak band observed also at 703 cm^{-1} by Stewart⁵; ^b Not observed by Stewart⁵.

and 1650 cm^{-1} , indicating the presence of water in the crystal lattice^{1,3}. The absorption band of thiourea at 730 cm^{-1} belongs to a high extent to the stretching vibration of the C=S bond (50 or 35% according to⁸ or^{9,10}, resp.), the band at 630 cm^{-1} was attributed to the out-of-plane vibrations of the thiourea skeleton⁸⁻¹⁰. The splitting of the two bands is characteristic of the corresponding space group of the crystal of the complex. For crystals of the D_{4h}^6 symmetry the separation of the components is 13–15 and 13–17 cm^{-1} , resp., whereas for the symmetry V_h^{18} the estimate of the separation is 7–8 cm^{-1} for the two bands (with the exception of the complex TlCl₄.4 TU (V_h^{18}) exhibiting the separation of 15 cm^{-1}). No splitting appears for the TlNO₃.4 TU complex (D_{4h}^6). Group analysis performed for simplified models (Fig. 1a, 1b) with the molecule of thiourea reduced to a two-particle system C=S shows (Table III) that the two C=S vibrations, symmetry B_{2u} and B_{3u} , active in the IR spectrum of thiourea, are transformed to a single degenerate vibration E_u , active in the infrared, when passing to the complex unit (point group C_{4h}). In the spectrum of thiourea, the corresponding wavenumbers are^{9,10} 731 and 730 cm^{-1} . In accordance with that simple model, a single absorption band is observed at 726 cm^{-1} for the TlNO₃.4 TU complex, where all the molecules of thiourea in the elementary cell of the crystal lie in equivalent positions, with the site symmetry C_s . In crystals of complexes of the D_{4h}^6 symmetry, a partial removal of degeneracy occurs; as a con-

sequence, two or three absorption bands appear at 730 cm^{-1} , corresponding to different dipole-dipole, resp. dipole-ion interactions of the three crystallographically non-equivalent molecules of thiourea. Degeneracy is totally removed in complexes of the V_h^{18} symmetry, where the thiourea molecules with the site symmetry C_s occurs in four crystallographically non-equivalent positions, which is manifested in the spectrum by a complex absorption band with unresolved maxima. The out-of-plane vibrations of the thiourea skeleton of the B_{2u} and B_{3u} symmetry appear^{9,10} at 618 and 633 cm^{-1} , resp. It can be shown that those vibrations, too, are transformed to a single degenerate vibration of the E_u symmetry in the complex unit. A single band at 628 cm^{-1} corresponds to that vibration in the $TiNO_{3,4}$ TU complex, whereas doublets appear in the other complexes (Table II). The comparison of the results of this simple model analysis with the group analysis of the complete vibrational problem of the elementary cell of the complex (Table III) indicates that the interactions between the structural units of the crystal lattice are not very strong. The position of the "split" band depends on the corresponding cation or anion bound. Boeyens² has shown that the value of the lattice energy of the alkali halide can serve as a criterion for the complex formation between the halide and thiourea. Interesting correlations occur between that lattice energy and the separations of the components of the split bands. The shifts of the four most intense bands of the complexes with respect to the wavenumbers 630 and 730 cm^{-1} of thiourea (values obtained as average values for the various symmetry species of ref.⁹) in dependence on the lattice (cohesive) energy of the halide bound are illustrated by Fig. 3.

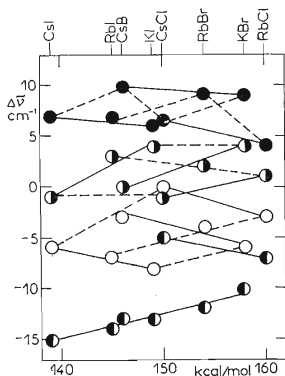


FIG. 3

Shifts of Some IR Bands of the Complexes in Dependence on the Lattice Energy² of the Corresponding Alkali Halides

The shifts $\Delta\bar{\nu}$ are related to the wavenumbers 730 (II, IV) and 630 cm^{-1} (V, VI); designation (Table III): ● II, ○ IV, ● V, ○ VI. Full lines link the data for identical anions, dashed lines those for identical cations.

TABLE III

Results of Group Analysis of Vibrations of Thiourea (TU) and MX.4 TU Complex Crystals

T' External translatory modes, R' external rotatory modes, n_i' internal vibrations¹¹; system of axes chosen so that the plane determined by the *a* and *b* axes is parallel with the symmetry plane of thiourea molecules, i.e. the parameters of the Bravais cell are in the order *c* > *b* > *a*; factor groups: TU V_h^{16} , MCl.4 TU V_h^{18} , MX.4 TU D_{4h}^6 , Z = 4 and 8, respectively.

TU				MCl.4 TU M = Rb, Cs, Tl				MX.4 TU X = Br, I M = K, Rb, Cs, Tl				
	T'	R'	n _i '	T'	R'	n _i '	activity IR Ra	T'	R'	n _i '	activity IR Ra	
<i>A_g</i>	2	1	10	23	8	80	— +	<i>A_{1g}</i>	11	4	40	— +
<i>B_{1g}</i>	2	1	10	23	8	80	— +	<i>A_{2g}</i>	12	4	40	— —
								<i>B_{1g}</i>	10	4	40	— +
								<i>B_{2g}</i>	11	4	40	— +
<i>B_{2g}</i>	1	2	8	13	16	64	— +	<i>E_g</i>	14	16	64	— +
<i>B_{3g}</i>	1	2	8	13	16	64	— +					
<i>A_u</i>	1	2	8	13	16	64	— —	<i>A_{1u}</i>	6	8	32	— —
<i>B_{1u}</i>	0	2	8	12	16	64	E <i>c</i> —	<i>A_{2u}</i>	6	8	32	E <i>c</i> —
								<i>B_{1u}</i>	5	8	32	— —
								<i>B_{2u}</i>	6	8	32	— —
<i>B_{2u}</i>	1	1	10	22	8	80	E <i>b</i> —	<i>E_u</i>	23	8	80	E <i>a, b</i> —
<i>B_{3u}</i>	1	1	10	22	8	80	E <i>a</i> —					

Simplified model ^a											
TU						Complex unit					
<i>A_g</i>	2	1	1	—	+	<i>A_g</i>	5	1	1	—	+
<i>B_{1g}</i>	2	1	1	—	+	<i>B_g</i>	4	1	1	—	+
<i>B_{2g}</i>	1	1	0	—	+	<i>E_g</i>	6	2	0	—	+
<i>B_{3g}</i>	1	1	0	—	+	<i>A_u</i>	2	1	0	E <i>c</i> —	
<i>A_u</i>	1	1	0	—	—	<i>B_u</i>	2	1	0	— —	
<i>B_{1u}</i>	0	1	0	E <i>c</i> —		<i>E_u</i>	8	2	2	E <i>a, b</i> —	
<i>B_{2u}</i>	1	1	1	E <i>b</i> —							
<i>B_{3u}</i>	1	1	1	E <i>a</i> —							

^a Thiourea molecule is considered as a two-particle system, the complex is simplified to a single complex unit, point group C_{4h} , containing four thiourea molecules and four anions on $z = 1/2$, and two cations on $z = 1/4$ and $3/4$.

The rough similarity of the spectra of thiourea and the complexes is preserved also in the range $400-100\text{ cm}^{-1}$. Strong bands at 171 and 110 cm^{-1} in the thiourea spectrum belong to the rotatory motions of the molecule^{7,12}. In the spectrum of the RbI.4 TU complex, the position of the latter band remains practically constant; the band at 171 cm^{-1} is shifted 14 cm^{-1} to lower frequencies, which can be interpreted as a certain "loosening" of the thiourea molecule in the direction of the crystal axis c .

Below 100 cm^{-1} , weak bands appear in the spectrum of the complex, belonging to translatory oscillations. A band at 54 cm^{-1} is observed in the spectrum of the complex at room temperature; it appears, however, also in the spectrum of thiourea, if cooled down to the temperature of liquid nitrogen.

We wish to thank Dr H. Schulze and Dr. N. Weinstock, Anorganisch-chemisches Institut, Universität Göttingen, for scanning Raman spectra and Dr J. Petzelt and Mrs I. Mayerová, Institute of Physics, Czechoslovak Academy of Sciences, Prague, for measuring the far-infrared spectra. We are further indebted to Dr J. Moravec, Institute of Nuclear Research, Prague - Řež, for the loan of the beam condenser for the IR measurements, and Dr M. Závětová, Institute of Physics of Solids, Czechoslovak Academy of Sciences, Prague, for enabling us to perform some IR measurements on the instrument of the Institute.

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Translated by the author.