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The Crystal Structure of Bisthiourea Pyridinium Bromide

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The adduct of pyridinium bromide with two molecules of thiourea gives orthorhombic crystals, $a=14.756$ (2), $b=10.893$ (1), $c=8.363$ (1) Å and space group *Cmcm*. There are four formula units per cell. Full-matrix least-squares refinement on 893 observations gave an R value of 0.043. Anisotropic vibration was allowed for atoms other than hydrogen. For the hydrogen atoms of thiourea isotropic vibration parameters were refined; it was not possible to locate those on the pyridinium ion. The thiourea molecules lie on the mirror planes at $z=\frac{1}{4}$ and $\frac{3}{4}$ with the $N\cdots N$ vector along c in which direction $N-H\cdots S$ hydrogen bonds hold the molecules in columns. The pyridinium ions occupy spaces formed by eight sulphur atoms; each sulphur atom has four cation neighbours. Disorder of the pyridinium ions yields the $2/m$ symmetry required by the space group but parameter interaction precludes mathematical distinction between two types of disorder, $\frac{1}{2}$ nitrogen, $\frac{5}{8}$ carbon in each site or $\frac{1}{2}$ nitrogen, $\frac{1}{2}$ carbon in only two sites; however, the latter arrangement gives more chemically reasonable bond lengths. These two sites are at 3.642 (9) Å from the bromide ions. Each bromide ion has two such contacts, subtending an angle of 58.4°; on its other side are 4 hydrogen atoms each at 2.50 Å; they are bonded to nitrogen atoms of 4 thiourea molecules and the $N-H\cdots Br$ distance is 3.467 Å.

Introduction

Thiourea forms complexes with halides of nearly all metals from large univalent ones, *e.g.* caesium, to small transition metals, *e.g.* nickel. It also forms complexes with salts of the pyridinium and *N*-methylpyridinium ions, (Phillips, 1967), of stoichiometry pyrH^+X^- , bis-thiourea where X may be a halide, nitrate, or sulphate. Our original interest in these compounds was to study the interaction of thiourea with a non-spherical cation. Of the isomorphous series with X=Cl, Br or I we chose the bromide for a full structure analysis.

Experimental

Crystal data

Pyridinium bromide-bisthiourea, $\text{C}_7\text{H}_{13}\text{BrN}_5\text{S}_2$, $M=311.26$; orthorhombic, $a=14.756$ (2), $b=10.893$ (1), $c=8.363$ (1) Å, $U=1341$ Å³, $D_m=1.57$ g.cm⁻³, $Z=4$, $D_c=1.536$ g.cm⁻³. Systematic absences, hkl with $h+k$

odd, $h0l$ with l odd. $F(000)=628$. Zr-filtered Mo $K\alpha$ radiation. $\lambda(\text{Mo } K\alpha_1)=0.7093$ Å, $\mu(\text{Mo } K\alpha)=35.3$ cm⁻¹. Absorption correction applied. Space group *Cmcm*, established by structure analysis.

A crystal $0.5 \times 0.3 \times 0.3$ mm was mounted in Araldite on a rigid support* on the Picker diffractometer. Optimization of 23 reflexions centred on Mo $K\alpha_1$ radiation gave the orientation matrix and cell dimensions. Observations were collected for hkl and $hk\bar{l}$ to allow for possible significant differences caused by anomalous dispersion if the space group were non-centric. Shells of reciprocal space were measured from $2\theta=3^\circ$ to $2\theta=60^\circ$, when the crystal suddenly started to decompose rapidly. The $\theta-2\theta$ scan mode was used from 0.7° below 2θ for Mo $K\alpha_1$ to 0.8° above 2θ for Mo $K\alpha_2$ at $\frac{1}{2}^\circ$.min⁻¹. Backgrounds were measured for 20 sec at each end of the scan. Three reference reflexions 004,

* On a support designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

710 and 12,8,1 were measured after every 50 observations. Their variation is shown in Fig. 1; it corresponds to an initial fall followed by a rise, *i.e.* the rapid fall after 2100 reflexions had been measured is not shown. The occasional large fluctuation led us to choose an analytical method of compensation for scale variation of the measured reflexions. Altogether 2055 reflexions were measured, Lorentz and polarization factors were applied and the standard deviations in the observations calculated from the expression $\sigma^2(I) = [c + 0.25(t_c/t_b)^2(B_1 + B_2)]$ where c is the total integrated count obtained in time t_c , B_1 and B_2 are background counts each obtained in time t_b .

To minimize computing time only 1114 observations of the type hkl were used to solve the structure. Systematic absences were consistent with three space groups, $Cmcm$, Cmc , and Ama (or $C2cm$ in the same system of axes). A Patterson synthesis revealed Br-Br vectors corresponding to a Br ion at 0, y , 0.25 with $y = 0.08854$; location of one atom does not resolve the uncertainty in the space groups. One cycle of isotropic refinement gave an R value of 0.52, a Fourier synthesis revealed the non-hydrogen atoms. The thiourea molecule was lying with the S and C atoms at $z = 0.25$ and the two nitrogen atoms related by the mirror plane at $z = 0.25$. The pyridinium ion, however, was not lying in the only position of mm symmetry, *i.e.* with N and the γ -carbon atoms, at 0, y , $\frac{1}{2}$ but was arranged about the point of $2/m$ symmetry, 0, $\frac{1}{2}$, 0. This was consistent with a disordered pyridine in $Cmcm$, or as we thought more probable, a non-centrosymmetric space group. Full-matrix refinement (Vickery, 1970) in $Cmcm$ with all the pyridinium atoms taken as carbon, gave an R value of 0.19, with all shifts less than 0.2 of the corresponding standard deviations. A difference synthesis indicated anisotropic motion for the bromine, sulphur, and nitrogen atoms.

For full-matrix least-squares anisotropic refinement the program *NUCLS** was used. Scattering factors for Br⁻, S, C, and N were taken from Cromer (1965) with allowance for the real and imaginary parts of the anomalous dispersion of bromine. The scale was refined by the quadratic equation of Ibers (1969). All 2055 observations were included, the weighting scheme was adjusted to give approximately constant average values of $W\Delta F^2$ in various ranges of $|F_o|$ and $\sin \theta/\lambda$. The expression was $1/\sqrt{W} = \sigma_{\text{counting}} + 0.005|F_o| + 0.0002|F_o|^2$ where $|F_o|$ is on the measured scale. Parameters were the coordinates (not fixed by space group symmetry), anisotropic vibration for bromine, sulphur and nitrogen, and isotropic vibration for the carbon of thiourea and for the pyridinium ion with all atoms given the scattering factor of carbon. R was 0.063 and the anisotropic vibration parameters for the pyridinium ion reduced it to 0.055.

An absorption correction based on the Gaussian in-

tegration program of Ahmed, Hall, Pippy & Saunderson (1967), was now applied to the original observations. Before final refinement, consideration was given to the question of the uncertainty in the space group. This can be followed with the aid of Figs. 2 and 3 which show projections of the structure in $Cmcm$ and the designations of the atoms. The peaks in the Patterson synthesis were very sharp, giving no indication of the doubling required by lower symmetry space groups. An ordered structure with $C(2)$ or $C(2^{21})$ being a nitrogen atom is possible only in $Cmc2_1$. As $\Delta f''$ for bromine is 2.6 there should be some significant differences between the values of $|F_{hkl}|$ and $|F_{\bar{h}\bar{k}\bar{l}}|$ after correction for absorption, but none were found, indicating that this space group was most unlikely.

To fit the observed scaling of Fig. 1 a polynomial function was fitted by least squares with the IBM subroutine *POLY* for the 1130 computer; the corresponding smooth curve is shown. This was used to bring all $|F_{hkl}|$ and $|F_{\bar{h}\bar{k}\bar{l}}|$ to the same scale before average values were taken for use in further refinement. It is clear from Fig. 1 that the quadratic equation from the Ibers procedure does not fit the experimental points, tending to reduce too far the observations collected towards the end. This effect has been observed before (Bright, Milburn & Truter, 1971) and at first attributed to the standards being atypical in being planes of low θ and high intensity, *i.e.* those particularly subject to extinction. In the present work the standards were chosen from various ranges of θ with two of strong and one of medium intensity. However, the average value of $|F_o|$ falls during collection, which is done in shells of reciprocal space, *i.e.* the Ibers method reduces the apparent $|F_o|$ of the weaker reflexions for which $|F_o|$ tends to be larger than $|F_c|$. A possible explanation for this is that false values are produced for $|F_o|$ by thermal diffuse scattering.

After scaling, averaging, and rejection of planes with $|F_o| < 3\sigma F_{\text{counting}}$ 893 observations were used in final least-squares refinement with anisotropic parameters

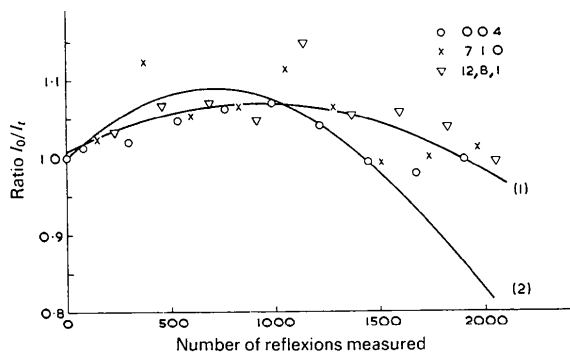


Fig. 1. Relation between the initial value of the intensity, I_o , for a standard reflexion and its value I_t when measured after t reflexions had been measured, compared with (1) the calculated polynomial curve and (2) the least-squares refinement by Ibers's (1969) method.

* *NUCLS*, the North Western University variant of the Busing-Lévy *ORFLS*.

for all atoms. R was reduced to 0.048. A difference synthesis showed the hydrogens on the thiourea molecule but not those of the pyridinium ion. Inclusion of the thiourea hydrogen atoms with scattering factor of Stewart, Davidson & Simpson (1965) and isotropic vibration parameters reduced R to 0.043. Two planes, (002) and (440), were omitted from the final cycles which were carried out to try to distinguish between the two possible disordered configurations on the pyridinium ion; (i) C(2) and C(2^{vii}) should each be $\frac{1}{2}$ carbon and $\frac{1}{2}$ nitrogen, or (ii) all atoms should be $\frac{1}{6}$ nitrogen and $\frac{5}{6}$ carbon. Suitable form factors were used for each of assumptions (i) and (ii); both refinements gave $R=0.043$ and $R' = \sum W(|F_o| - |F_c|)^2 / \sum W|F_o|^2 = 0.049$ with the maximum shift 0.2 of the corresponding standard deviation. Final parameters are shown in Tables 1 and 2 and observed and calculated structure factors [for model (i)] in Table 3. Only for C(2) and C(3) were the parameters more than 0.2 standard deviations different for models (i) and (ii). Bond lengths and angles were calculated for the two models; these are shown in Table 4 with their standard deviations derived from the variance-covariance matrix by the program ORFFE. The differences are statistically significant.

Table 1. Atomic coordinates with standard deviations in parentheses

Model (i)	x/a	y/b	z/c	U_{iso}
Br	0.0	0.08744 (5)	0.25	
S	0.23081 (8)	0.21760 (12)	0.25	
C(1)	0.31557 (25)	0.32279 (33)	0.256	
N	0.35056 (21)	0.36496 (27)	0.11419 (28)	
C(2)	0.0	0.38010 (71)	0.03904 (133)	
C(3)	0.07825 (36)	0.43964 (54)	0.02038 (116)	
H(1)	0.402 (2)	0.435 (3)	0.109 (5)	0.098 (9)
H(2)	0.338 (4)	0.344 (4)	0.025 (6)	0.130 (13)
Model (ii)				
C(2)	0.0	0.37943 (74)	0.03789 (137)	
C(3)	0.07740 (35)	0.43804 (52)	0.02126 (113)	

To choose between them the vibration parameters were examined; as shown in Table 2, the changes are small and in the directions to be expected, *i.e.* an increase as the ratio of N/C in the form factor curve increases. It appears that there are two minima in the least-squares function and this seemed possibly to be an example of parameter interaction (Geller, 1961) making the structure indeterminate. The correlation coef-

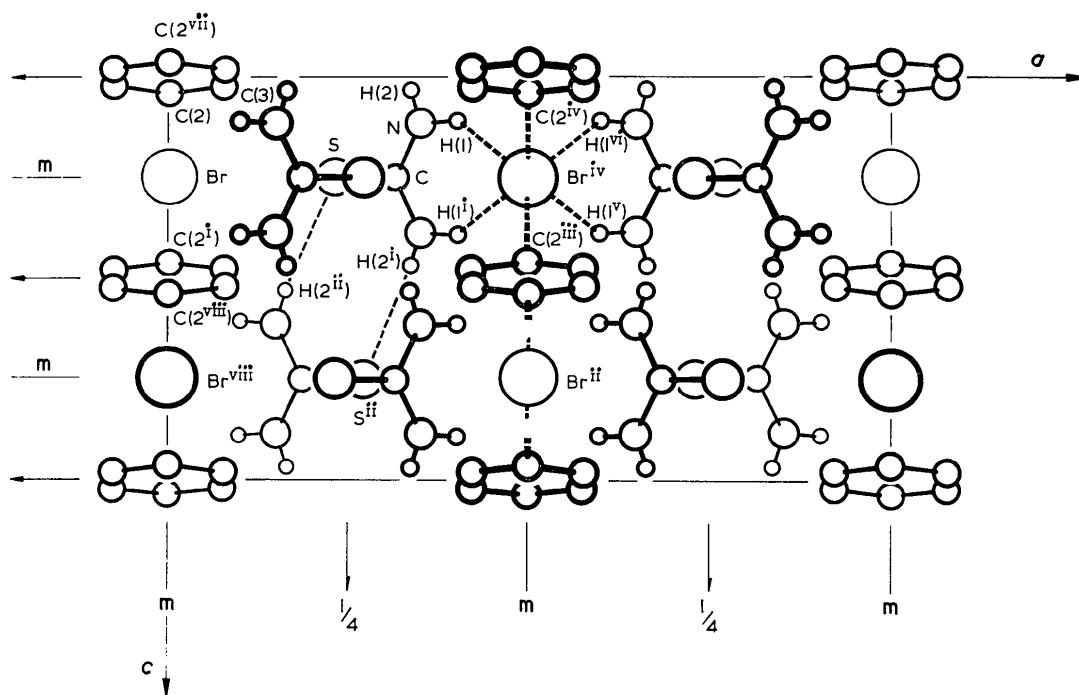


Fig. 2. The structure projected down the b axis. Pyridinium ions are centred on $x=0$ and $y=\frac{1}{2}$, or on $x=\frac{1}{2}$ and $y=1$. Hydrogen bonding with $S \cdots HN$ distances of 3.40 Å along the screw axes at $\frac{1}{4}$, $\frac{1}{4}$, z are indicated by broken lines. Broken lines from Br^{iv} show its four hydrogen neighbours and its two pyridinium ion neighbours.

Roman numeral superscripts refer to atoms related to those at x, y, z by the following:

i	$x,$	$y,$	$\frac{1}{2}-z$	vii	$x,$	$1-y,$	$-z$
ii	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$	viii	$x,$	$1-y,$	$\frac{1}{2}+z$
iii	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$	ix	$-x,$	$y,$	z
iv	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	z				
v	$1-x,$	$y,$	$\frac{1}{2}-z$				
vi	$1-x,$	$y,$	z				

Table 2. Anisotropic vibration parameters (in \AA^2) with their standard deviations in parentheses

Model (i)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.0318 (3)	0.0347 (3)	0.0526 (4)	0	0	0
S	0.0649 (8)	0.0790 (8)	0.0306 (5)	-0.0412 (6)	0	0
C(1)	0.0422 (19)	0.0441 (19)	0.0330 (17)	-0.0094 (15)	0	0
N	0.0681 (23)	0.0692 (16)	0.0359 (12)	-0.0303 (13)	0.0010 (11)	0.0011 (11)
C(2)[$\frac{1}{2}$ N]	0.2245 (97)	0.0896 (43)	0.1598 (75)	0	0	-0.0154 (47)
C(3)	0.1080 (46)	0.1387 (54)	0.2293 (82)	0.0403 (4)0	-0.0501 (59)	-0.0824 (66)
Model (ii)						
C(2)[$\frac{1}{6}$ N]	0.1909 (108)	0.0855 (50)	0.1529 (84)	0	0	-0.0144 (54)
C(3)[$\frac{1}{6}$ N]	0.1150 (46)	0.1476 (53)	0.2359 (83)	0.0469 (39)	-0.0552 (61)	-0.0882 (68)

ficients for the parameters of C(2) and C(3) are displayed in Table 4. These are lower than those, 0.61, 0.62 and 0.55 \AA , between the overall scale and the vibration parameters of bromine, but much larger than the rest of the coefficients, most of which are below 0.05. Changes in the form factors of one atom give changes in its vibration parameters and in the coordinates of the other atom.

The apparent vibration parameters are large, as would be expected for a superposition of two (or six) orientations. An attempt was made to carry out a molecular vibration analysis using Cruickshank's (1956) equations for a rigid body. Reference axes were chosen with 3 as the normal to the plane, and 1 along the C(2) \cdots C(2^{vii}) direction. For T_{11} , T_{22} , and ω_{33} , values

of 0.098, 0.071 \AA^2 , and 0.068 radians² were obtained; the matrix for the terms T_{33} , ω_{11} , and ω_{22} had a determinant almost zero (0.047) so no reliable values for these could be obtained. A similar effect was reported for the ordered pyridinium ion in pyridinium hydrogen nitrate (Cerewitz, Robertson & Meyers, 1965). Allowance for rotation about the plane normal gives a 'correction' for libration of +0.045 \AA on the bond lengths to give the results in Table 5. We regard this 'correction' as an indication of the possible magnitude of error due to libration.

For the thiourea molecule with axes chosen as 1 along C-S and 3 normal to the plane, a molecular vibration analysis gave $T_{11}=0.034$, $T_{22}=0.031$, $T_{33}=0.040$ \AA^2 , $\omega_{22}=0.050$ and $\omega_{33}=0.002$ radians². With an estimated deviation of 0.005 (\AA^2 or radians²) the values of $T_{13}=-0.000$, $\omega_{11}=-0.008$, and $\omega_{13}=-0.001$ are not significantly different from zero. Application of librational corrections gave the values shown in Table 5.

Computations were carried out on (a) an IBM 1130 computer, (b) the CDC 6600 in the University of London Computing Centre. Setting angles for, and processing observations from the Picker diffractometer were carried out on (a). This computer was also used

Table 3. Observed and calculated structure amplitudes ($\times 10$)

Column headings are $|F_o|$ $|F_c|$. Planes omitted from the final cycles were (002) with $|F_o|=62$, $|F_c|=73$ and (440) with $|F_o|=10$ and $|F_c|=6$.

h	k	l	$ F_o $	$ F_c $
0	0	0	1000	1000
0	0	1	100	100
0	0	2	100	100
0	0	3	100	100
0	0	4	100	100
0	0	5	100	100
0	0	6	100	100
0	0	7	100	100
0	0	8	100	100
0	0	9	100	100
0	0	10	100	100
0	0	11	100	100
0	0	12	100	100
0	0	13	100	100
0	0	14	100	100
0	0	15	100	100
0	0	16	100	100
0	0	17	100	100
0	0	18	100	100
0	0	19	100	100
0	0	20	100	100
0	0	21	100	100
0	0	22	100	100
0	0	23	100	100
0	0	24	100	100
0	0	25	100	100
0	0	26	100	100
0	0	27	100	100
0	0	28	100	100
0	0	29	100	100
0	0	30	100	100
0	0	31	100	100
0	0	32	100	100
0	0	33	100	100
0	0	34	100	100
0	0	35	100	100
0	0	36	100	100
0	0	37	100	100
0	0	38	100	100
0	0	39	100	100
0	0	40	100	100
0	0	41	100	100
0	0	42	100	100
0	0	43	100	100
0	0	44	100	100
0	0	45	100	100
0	0	46	100	100
0	0	47	100	100
0	0	48	100	100
0	0	49	100	100
0	0	50	100	100
0	0	51	100	100
0	0	52	100	100
0	0	53	100	100
0	0	54	100	100
0	0	55	100	100
0	0	56	100	100
0	0	57	100	100
0	0	58	100	100
0	0	59	100	100
0	0	60	100	100
0	0	61	100	100
0	0	62	100	100
0	0	63	100	100
0	0	64	100	100
0	0	65	100	100
0	0	66	100	100
0	0	67	100	100
0	0	68	100	100
0	0	69	100	100
0	0	70	100	100
0	0	71	100	100
0	0	72	100	100
0	0	73	100	100
0	0	74	100	100
0	0	75	100	100
0	0	76	100	100
0	0	77	100	100
0	0	78	100	100
0	0	79	100	100
0	0	80	100	100
0	0	81	100	100
0	0	82	100	100
0	0	83	100	100
0	0	84	100	100
0	0	85	100	100
0	0	86	100	100
0	0	87	100	100
0	0	88	100	100
0	0	89	100	100
0	0	90	100	100
0	0	91	100	100
0	0	92	100	100
0	0	93	100	100
0	0	94	100	100
0	0	95	100	100
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0	0	98	100	100
0	0	99	100	100
0	0	100	100	100

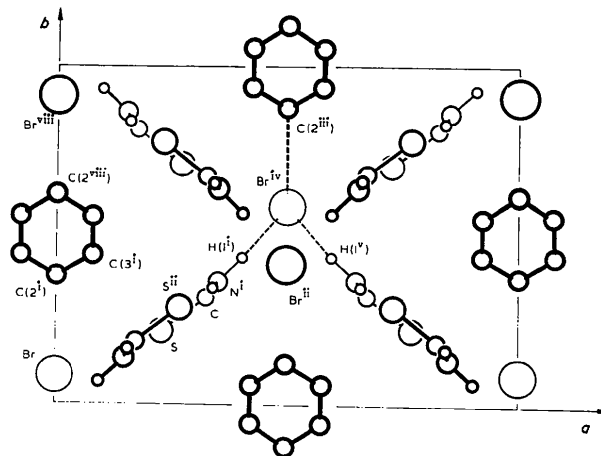


Fig. 3. The structure projected down the c axis with the consequence that mirror-related atoms eclipse one another, *i.e.* C(2ⁱⁱⁱ) is over C(2^{iv}), C(2ⁱ) is over C(2), etc.

for calculating intermolecular distances, mean planes through groups of atoms, the polynomial curve of Fig. 1, isotropic full-matrix least-squares, three-dimensional Fourier syntheses, and absorption correction. *NUCLS4* and *ORFFE* (the Busing-Levy programs with local modifications) were run on (b).

Table 4. *Correlation coefficients in the least-squares matrix*

Key		≤0.1	blank							
		0.1-0.2	A							
		0.2-0.3	B							
		0.3-0.4	C							
(a) Between parameters of C(2) and those of C(3)										
	C(3)	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	y	B	B		B	B		A		
	z		A	A	A	B	B	A	C	C
	U_{11}		C			B	A	B		
	U_{22}		B			C	B	B		A
	U_{33}		B				B	A		
	U_{23}			B					B	
(b) Between the coordinates of C(3) and its vibration parameters										
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}				
x	A			C	A					
y		A	A	B						
z										

Table 5. *Results for the thiourea molecule and pyridinium ion*

	Uncorrected	Corrected for libration
S-C	1.696 (4) Å	1.709 Å
C-N	1.330 (3)	1.335
N-H(1)	1.08 (3)	
N-H(2)	0.80 (5)	
S-C-N	121.3 (2)°	121.6°
N-C-N	117.4 (3)	116.8
H(1)-N-H(2)	109 (4)	

Equation of the plane through the molecule $-0.6727x + 0.7400y = -0.5352$

Deviation of the atoms (Å)	
S	-0.0014
C	0.0049
N	-0.0017
H(1)	0.0449
H(2)	-0.0376

Description of the structure and discussion

Thiourea molecules lie in mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ with the $N \cdots N$ axis parallel to the c axis of the crystal in which direction the molecules are held by $N-H(2) \cdots S$ hydrogen bonds, 3.40 Å, with an angle 170.5° at H(2). These can be seen in Fig. 2 and edge on in Fig. 3. Similar bonding holds the molecules along the b axis in uncomplexed thiourea and the dimensions in Table 5, agree with those obtained by X-ray (Truter, 1967), electron (Dvoryankin & Vainstein, 1960), and neutron diffraction (Elcombe & Taylor, 1968) for thiourea. In the present compound the largest rotational oscillation is about the inertial axis parallel to the $N \cdots N$ vector whereas in thiourea it is about the S-C bond. The explanation for this is probably that the $H(1) \cdots Br$ contacts are less rigid than the $H(2) \cdots S$ contacts.

It is not possible to quote accurate values for the dimensions of the pyridinium ion. The results in Table 5 show differences greater than the standard deviation between model (i) and model (ii) and there is a further uncertainty in the application of a librational correction of 0.045 Å. However, comparison with other pyridinium compounds shows that model (i), *i.e.* end-to-end disorder gives more chemically reasonable dimensions. Ordered unsubstituted pyridinium ions are found in some structures with strong $N-H \cdots X$ bonding. The most accurate determination is that of the nitrate (Cerevitz, Robertson & Meyers, 1965) in which all angles are close to 120° and the bond lengths not significantly different, C-N = 1.35 (2) and C-C = 1.38 (2) Å (corrected for libration). In the chloride (Rérat, 1962) the angle at nitrogen is 129° , C-N = 1.32 and C-C = 1.41 Å and in the reineckate (Takeuchi & Pepinsky, 1957) the angle at nitrogen is 134° and the lengths C-N 1.35 and C-C 1.39 Å. In three isomorphous disordered structures $pyH^+AsF_6^-$, PF_6^- , and SbF_6^- (Copeland, Conner & Meyers, 1965) the angle of 120° was imposed by the symmetry and the average C-C (or C-N) distances were 1.38, 1.38, and 1.40 Å. In the disordered tetrachloroantimonate the length was 1.37 Å (Porter & Jacobson, 1970).

For our preferred model, (i), the average after correction for libration is 1.39 Å while for model (ii) one bond length is 1.40 Å before correction and implausibly long after correction.

Each pyridinium ion is in a space formed by eight

Table 5 (cont.)

Dimensions in the pyridinium ion

	Model (i)		Model (ii)	
	Uncorrected	Corrected	Uncorrected	Corrected
C(2)-C(3)	1.334 (7) Å	1.379 Å	1.316 (7) Å	1.361 Å
C(3)-C(3 ^{vii})	1.358 (14)	1.403	1.396 (13)	1.441
C(2)-C(3)-C(3 ^{vii})	120.0 (5)°		119.7 (5)°	
C(3)-C(2)-C(3 ^{ix})	120.0 (9)		120.5 (9)	

Equation of the plane through the molecule $0.236y + 0.972z - 1.285 = 0$

thiourea molecules. The distances from C(3ⁱ) to S and to Sⁱⁱ are 3.82 and 4.00 Å respectively, and C(2) to S is 4.2 Å. In addition there are contacts to bromide ions at 3.64 Å from C(2). Round the bromide ion there are contacts at 2.50 Å from H(1) of four thiourea molecules, and the two contacts at 3.64 Å from pyridinium ions. These are indicated in Figs. 2 and 3 by the broken lines to Br^{iv} from H(1), H(1ⁱ), H(1^v), H(1^{vi}), C(2ⁱⁱⁱ), and C(2^{iv}); in Fig. 3 only the higher one, e.g. C(2ⁱⁱⁱ) is marked, because the mirror-related atoms are eclipsed. Angles subtended at bromine are C(2)···Br···C(2) 58.3°, H···Br···H 56.5, 71.0, and 96.8° and the H···Br···C(2) angles are 110.6 and 143.9°. Neither the length, 3.47 Å nor the geometry of the N-H(1)···Br system suggests strong hydrogen bonding, the angle subtended at hydrogen is 143.9°, while the angles subtended at Br do not correspond to interaction from regularly distributed lone pairs of electrons on the anion. The hydrogen atoms on the pyridinium ions could not be located but probable positions are at 1 Å from and completing a trigonal arrangement about the carbon atoms; this would give a hydrogen atom on C(2) at 2.50 Å from the bromide ion and the tilt of the pyridinium ion is such that the line through C(2ⁱ) and C(2^{viii}) makes an angle of 11.4° with that through Br and Br^{viii}.

In their extensive study of the ionic complexes of thiourea, Boeyens & Herbststein (1967) found a ratio of alkali metal or thallium to thiourea of 1:4 and showed that the structures were based on columns of thiourea molecules with cations surrounded by eight sulphur atoms and the anions (and sometimes water molecules) in the cavities formed by the NH₂ groups, and, in some cases, hydrogen bonded to these groups.

The columns are comparable with those in the present structure and we consider, by the criteria of N···S' distances less than 3.5 Å and C-N···S' angles of approximately 120°, that they are held by N-H···S' hydrogen bonds in the direction of the N···N vector of thiourea, which coincides in all cases with the *c* axis of the crystal. The evidence from published structures is presented in Table 6. Other authors do not empha-

size this point and Boeyens & Gafner's (1968) treatment is based on electrostatic interactions only. The difference between the present structure and those of the metal complexes is best described with reference to Fig. 3; here the overlapping thiourea molecules are parallel and each sulphur (at say $z = \frac{1}{4}$) has four cation neighbours, the two visible at $z = \frac{1}{2}$ and two underneath at $z = 0$. In the metal complexes the overlapping molecules make an angle of 60° with the two sulphur atoms close to one cation at $z = \frac{1}{2}$, an additional pair of thiourea molecules coordinate the other cation, with the result that there is a complete enclosure of the cation with no cation-anion contact.

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Table 6. *Hydrogen bonding in some MX(thiourea)₄ compounds*

MX	Reference	<i>c</i> (Å)	N-H···S (Å)	C-N···S (°)	Space group
TiH ₂ PO ₄	<i>a</i>	8.27	3.41, 3.44	123, 120	<i>Cccm</i>
CsF	<i>b</i>	8.51	3.46, 3.50	122, 123	<i>Ibam</i>
TiC ₆ H ₅ COO	<i>c</i>	8.15	3.49, 3.40	119, 117	<i>Cmcm</i>
CsCl	<i>d</i>	8.51	3.40, 3.54	128, 120	<i>Bbcm</i>
			3.42, 3.47	126, 119	
TiClO ₃	<i>e</i>	8.201	3.32, 3.32	125, 125	<i>B2/m</i>
			(3.54, 3.62)	(113, 112)	
TiNO ₃	<i>f</i>	8.2	3.36	120	<i>P4/mcc</i>
C ₅ NH ₆ Br	present	8.363	3.395	122.5	<i>Cmcm</i>

(a) Verhoef & Boeyens (1968)

(b) Boeyens (1968a)

(c) Verhoef & Boeyens (1969)

(d) Boeyens (1968b)

(e) Mitchell & Boeyens (1970)

(f) Boeyens & Herbststein (1967)

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The Crystal Structure of K_2PtCl_4 and K_2PdCl_4 : with Estimates of the Factors Affecting Accuracy

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The structures of K_2PtCl_4 and K_2PdCl_4 have been determined with improved accuracy. The Pt-Cl distance is 2.308 (2) Å, or 2.316 Å after correction for thermal motion; the corresponding values for Pd-Cl are 2.313 (2) Å and 2.318 Å. In both compounds the K-Cl distances are 2.40 Å and the closest Cl-Cl distances 3.27 Å. After correcting for absorption and some minor causes of variation, and after allowing for statistical counting errors, there remained a variation of about 2% between the measured amplitudes of symmetry-related reflexions. This variation is approximately equal to the conventional *R*-value, and has no obvious explanation. Corrections for absorption and for anomalous dispersion have little effect on the calculated positions of the atoms, but have large effects on the e.s.d.'s and on the thermal parameters; they are therefore essential if corrections for thermal vibration are to be calculated.

Introduction

This work was undertaken to determine accurate interatomic distances in K_2PtCl_4 and K_2PdCl_4 as part of studies of the effects of substitution in square planar complexes of Pt(II) and Pd(II). The structures of K_2PtCl_4 and K_2PdCl_4 are known (Dickinson, 1922; Theilacker, 1937), but accurate coordinates have not previously been determined. The experimental results for K_2PtCl_4 were used to make estimates of various sources of error, including errors due to absorption, under the conditions normally used for data-collection, in order to decide how the accuracy can best be improved.

PART I: K_2PtCl_4

Experimental

Crystal data: K_2PtCl_4 , $M=415.3$; tetragonal, $a=b=7.025$ (3), $c=4.144$ (2) Å, $V=204.5$ Å³; space group $P4/mmm$ (D_{4h}^1 , No. 123), $Z=1$, $D_c=3.350$, $F(000)=184$; Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), $\mu=220$ cm⁻¹; Zr filter; Picker automatic four-circle diffractometer.

Unit cell

Measurements were made of the diffractometer setting angles χ , φ , ω , 2θ for 16 reflexions. The crystal was in a random orientation and the following cell dimensions, assuming triclinic symmetry, were obtained by a least-squares analysis:

$$a = 7.0275 (26) \quad b = 7.0218 (24) \quad c = 4.1444 (13) \text{ \AA} \\ \alpha = 89.973 (24) \quad \beta = 90.048 (27) \quad \gamma = 89.996 (27)^\circ$$

The tetragonal unit-cell dimensions given in the crystal data above and used in the subsequent crystal structure analysis were derived from these values by taking the mean of *a* and *b*.

Intensity measurements

2434 observations were made of reflexions in the ranges $\sin \theta/\lambda \leq 0.904$ for $\bar{h}kl$ and $h\bar{k}l$ and $\sin \theta/\lambda \leq 0.897$ for hkl and hkl . The measurements of intensity were made using a θ - 2θ continuous scan from 0.6° below α_1 to 0.7° above α_2 at a rate of $0.5^\circ 2\theta/\text{min}$; the background was measured for 20 sec at each end of the scan range. 400 and 040 were used as standard reflexions, the intensity of each being remeasured after every 40 reflexions (*i.e.* every 5 hours). The moving average of these standard reflexions was used to calculate a local

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