Low-frequency Single-crystal Vibrational Spectra of Bis(thiourea)dichlorocadmium and Tetrakis(thiourea)dichlorocadmium

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Raman spectra are reported for single crystals of the title compounds together with single-crystal i.r. reflectance data for the tetrakis-complex. The bis-complex is discussed on the basis of a factor-group analysis, but for the more complex unit cell of the tetrakis-complex a molecular model provides an adequate basis for assignment.

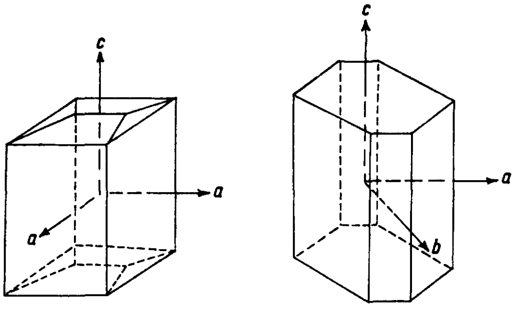
CO-ORDINATION complexes such as the title compounds yield complicated vibrational spectra, particularly in the low-frequency region. Assignment of such spectra is generally attempted on the basis of qualitative evidence, typically changes induced by variation of halogen and of metal atom. Although by no means proven, these assignments are commonly invoked by others interpreting the spectra of still more elaborate co-ordination compounds. In this paper we attempt to strengthen the assignment of the spectra of two thiourea complexes using single-crystal techniques. Two advantages stem from this approach. (i) Close-lying bands of different symmetry species are readily revealed in contrast to the rather broad composite bands commonly found in the spectra of polycrystalline samples. (ii) Knowledge of symmetry species considerably assists assignment, as shown below. Since all of the internal modes of thiourea are found above 400 cm^{-1} this study is restricted to lower frequencies.

EXPERIMENTAL

$CdCl_2(tu)_2$ (tu = thiourea) was prepared by mixing stoicheiometric amounts of $CdCl_2,2\frac{1}{2}H_2O$ and thiourea in aqueous ethanol. Crystals were grown by evaporation of the solution over several days. They showed well-developed 001 and 110 faces (Figure), although in some the 010 face was slightly developed; grinding and polishing was necessary to increase the size of this face. $CdCl_2(tu)_4$ was formed from stoicheiometric quantities of the reactants in absolute ethanol. Very slow evaporation of the solution over a period of weeks yielded crystals with well-developed 100 and 010 faces.

Crystals were oriented by *X*-ray diffraction techniques.

Raman spectra were obtained with a Coderg PH1 instrument using 632·8 and 488·0 nm excitation and a ' Cryocirc ' cold cell. I.r. spectra were obtained using Beckman–RIIC FS-620 and FS-720 interferometers.



(i) (ii)

Morphology of (i) $CdCl_2(tu)_4$, (ii) $CdCl_2(tu)_2$

RESULTS AND DISCUSSION

$CdCl_2(tu)_2$.—This complex crystallises in the orthorhombic system with the symmetry of space-group $Pm2_1n$ (C^7_{2v}), $z = 2$.[1] Considering the molecules as $CdCl_2(SC)_2$ the factor-group analysis in Table 1 results.

TABLE 1

Factor-group analysis of $CdCl_2(SC)_2$

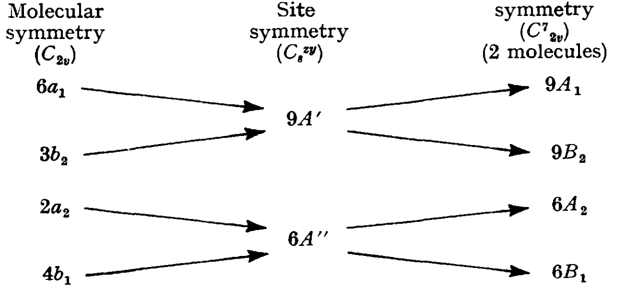
C^7_{2v}	N_T	A	T	R	N_i	Activity
A_1	12	1	1	1	9	z; xx,yy,zz
A_2	9	0	1	2	6	xy
B_1	9	1	0	2	6	x; xz
B_2	12	1	1	1	9	y; yz

A = Acoustic modes; T = translatory lattice modes; R = rotatory lattice modes; N_i = internal molecular modes excluding ν(C=S) but including torsions.

ν(C–S) modes occur well above the range of our study and must be subtracted but we must add the low-energy torsional modes of thiourea (about the Cd–S bonds) which are excluded by the above approximation. Molecular symmetry is C_{2v}, with the molecules occupying sites of C_s symmetry: correlation of molecular and unit-cell labels is shown in Table 2, and approximate descriptions of molecular modes in Table 3.

TABLE 2

Correlation table for $CdCl_2(SC)_2$



The crystals showed pronounced dependence of spectrum upon orientation as evidenced by the intensities listed in Table 4. The observed Raman lines lie in three groups: (a) 170—250 cm^{-1}, (b) 125—150 cm^{-1}, (c) <110 cm^{-1}. Since stretching modes must come higher in frequency than their associated bending modes ν(Cd–Cl) will be in the highest group, a conclusion strengthened by much qualitative evidence on halogeno-complexes. Similarly ν(Cd–S) will be higher than δ(SCdS) and almost certainly above δ- and π-(CdSC) modes. However, due to the small energy separations between bands there must be substantial mixing of internal co-ordinates; our descriptions, Table 3, must therefore be regarded as a guide only.

TABLE 3

Approximate mode descriptions for molecular $CdCl_2(SC)_2$, C_{2v}

a_1	ν_1	ν(S–C)	b_1	ν_9	ν(S–C)
	ν_2	ν(Cd–S)		ν_{10}	ν(Cd–S)
	ν_3	ν(Cd–Cl)		ν_{11}	δ(CdSC)
	ν_4	δ(CdSC)		ν_{12}	$\rho_w(CdCl_2)$
	ν_5	δ(ClCdCl)			
	ν_6	δ(SCdS)	b	ν_{13}	ν(Cd–Cl)
				ν_{14}	π(CdSC)
a_2	ν_7	π(CdSC)		ν_{15}	$\rho_r(CdCl_2)$
	ν_8	$CdCl_2$–CdS_2 torsion			

Torsions of thiourea about S–C bond, $a_2 + b_2$.

TABLE 4

Raman frequencies (cm^{-1}), peak heights (arbitrary units), and assignments for single-crystal $CdCl_2(tu)_2$ at ambient temperature

	Factor-group assignment C^7_{2v}	$z(xx)y$	$z(yx)y$	$z(xz)y$	$z(yz)y$	Molecular assignment C_{2v}
28	B_2	4			2	Lattice modes
38	A_1					
44	B_1			9		
58	B_2	3		4	170	
69	A_2		74	4		ν_8
72	A_1	18				ν_6
75	B_2				6	
78	B_1			31		ν_{12}
84	$A_1 + B_2$	12			47	ν_5
91	A_2		12			Ligand torsions? $\nu_{16\ 17}$
93	B_1			4		
101	B_2				14	ν_{15}
106	A_2	0	12			ν_7
125	B_2				6	ν_{14}
137	B_1			15		ν_{11}
148	A_1	21			0	ν_4
172	B_2		0	0	42	ν_{13}
182	(B_2) [a]					
206	A_1	6	0		0	$\nu_2 + \nu_3$
224	A_1	86	2	7	8	
234	A_2		1			ν_{10}
244	B_1			3		

[a] From i.r. spectrum, symmetry assumed.

The highest band observed is of B_1 symmetry; it must, therefore, originate (Table 2) in a molecular mode of either a_2 or b_1 symmetry. Therefore (Table 3) it is to be associated with ν_7 (a_2), ν_{10}, or ν_{11} (b_1); we regard ν_{10}, ν(Cd–S), as the most probable description. If the region 170—250 cm^{-1} is associated with ν(Cd–S) and ν(Cd–Cl) modes we would expect to find $3A_1 + 1A_2 +$

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[1] M. Nardelli, L. Cavalca, and A. Braibanti, *Gazzetta*, 1957, **87**, 137.

$1B_1 + 3B_2$ modes since ν(Cd–S) spans the representation $A_1 + A_2 + B_1 + B_2$ and ν(Cd–Cl) $2A_1 + 2B_2$. A sole A_2 mode is, in fact, observed at 234 cm^{-1}; its proximity to the sole B_1 strengthens our supposition that both are associated with ν(Cd–S) motions. Certainly, from symmetry considerations, they are not due to ν(Cd–Cl); unless δ(CdSC) is higher than ν(Cd–Cl) (an improbable event) the above argument and assignment is valid. Two of the expected three A_1 modes are found and must clearly be described as ν(Cd–S) + ν(Cd–Cl), $\nu_{2,3,13}$. Correlation interaction yields a B_2 mode at 172 cm^{-1}, the separation of *ca.* 30 cm^{-1} from the A_1 components being reasonable for metal–halogen motion. In addition there is an intense band at 182 cm^{-1} in the i.r. spectrum,[2] not found in the Raman experiments; this must be of A_1 or B_2 symmetry the latter being the more probable. The association of the 172 cm^{-1} line with a Cd–Cl mode is supported by its non-appearance in Raman spectra of polycrystalline samples of $CdBr_2(tu)_2$ and $CdI_2(tu)_2$, Table 5.

TABLE 5

Raman spectra (cm^{-1}) of powder samples of $CdX_2(tu)_2$

X = Cl	Br	I	
243w	234w	232wm	ν(Cd–S)
224s	214s	215wm	
205w	160s	136vs	ν(Cd–X)
173wm			
147wm	144m		δ(CdSC)
138wm			
106vw	108w	100wm	
	94wm		
	87m	81ms	
73s	71w	64w	
58s	58s	54vs	
	53vs	37vs	
	38m	28wm	
		23ms	

Factor-group analysis [3] predicts 6 B_1 internal modes for two molecules $CdCl_2(SC)_2$. One of these is ν(S=C) and is above the frequency range discussed but there is a torsional mode which will be of low frequency and probably also of low intensity which must be added, keeping the total at six. There are no translational modes in B_1 and the two rotatory modes allowed cannot be high in frequency. Coupling between the two molecules in the unit cell requires B_1 modes to be accompanied by an A_2 component and *vice-versa*. There are A_2/B_1 pairs at 234/244 and 91/93 cm^{-1}; it is permissible to assume that the A_2 modes at 105 and 69 cm^{-1} and the B_1 modes at 137 and 78 cm^{-1} have vanishingly weak B_1 and A_2 components respectively. Thus in the region above 60 cm^{-1}, the region in which external modes are unlikely for this molecular crystal, it appears that all six of the internal mode pairs have been located.

Why should some of the components be missing? In this crystal an a_2 molecular mode yields $A_2 + B_1$ factor-group components. Thus, if we assume that a_2 molecular modes are responsible for the A_2 unit-cell modes with missing B_1 components we find that these must be assigned as ν_7 and ν_8 respectively. Similarly the lone B_1 modes at 137 and 78 cm^{-1} may be labelled ν_{11} and ν_{12} respectively. In any case, its position as the second highest B_1 mode observed makes the 137 cm^{-1} line a strong candidate for ν_{11}. The A_2/B_1 pair *ca.* 92 cm^{-1} could be one of torsional modes, or ν_{12}.

Similar arguments lead to the assignments shown for the A_1, B_2 unit-cell modes.

A partial assignment of the Raman spectra of the powders $CdBr_2(tu)_2$ and $CdI_2(tu)_2$ follows by comparison with the crystal assignment. The highest feature, assigned as ν_{10}(νCd–S) is roughly constant in frequency. The most striking change evident when looking at the three powder spectra together is that the most intense band moves steadily to lower frequency with change to heavier halogen. Bands *ca.* 140 cm^{-1} are also present throughout [due to δ(CdSC)] but in the iodide the intense ν(Cd–I) band overlays them.

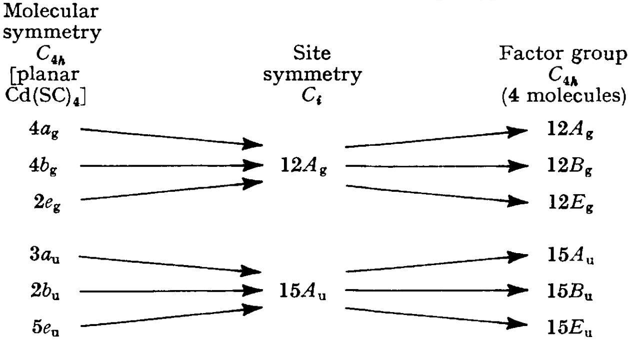
TABLE 6

Factor-group analysis of $CdCl_2(SC)_4$

C_{4h}^4	A_g	B_g	E_g	A_u	B_u	E_u
N_T	15	15	15	18	18	18
A				1		1
T				2	3	2
R	3	3	3			
N_i	12	12	12	15	15	15
Activity I.r.				z		x,y
Activity Raman	$xx + yy$; zz	$xx - yy$; xy	(xz,yz)			

TABLE 7

Correlation Table for $CdCl_2(SC)_4$



$CdCl_2(tu)_4$.—This compound is isostructural with the cobalt analogue for which the full three-dimensional structure has been determined.[4] It has the symmetry of the tetragonal group $P4_2/n$ (C_{4h}^4), $z = 4$. With four molecular units in the primitive cell, factor-group analysis predicts a very large number of optically active modes for this crystal, Table 6. The physical process which generates this multiplicity of modes is correlation interaction between the four symmetry-related molecules. Proceeding *via* the site symmetry, C_i, we see (Table 7) that, for example, each molecular a_g mode (assuming idealised C_{4h} symmetry, see below) will yield a vector

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[2] D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1967, 884.

[3] D. M. Adams and D. C. Newton, 'Tables for Factor Group and Point Group Analysis,' Beckman-RIIC Limited, Croydon, 1970.

[4] J. E. O'Connor and E. L. Amma, *Inorg. Chem.*, 1969, **8**, 2367.

$A_g + B_g + E_g$. Interaction of this type is clearly evidenced by the correlation splittings observed in such crystals as $Cr(CO)_3(\pi\text{-}C_6H_6)$[5] and K_2CrO_4.[6] However, these are crystals in which the bonds which are associated with the most strongly perturbed vibrations are oriented in such a way that physical interaction between molecular units is strong. In this thiourea complex the molecules are ' insulated ' from each other by the bulky ligands. If we consider the region below 400 cm^{-1} (because all of the ligand modes are higher than this), we might reasonably expect to interpret the crystal spectrum in terms of that due to a single molecule, plus lattice modes. We note in particular that the non-bonded Cl · · · Cl distances are so large that no correlation interaction can be physically significant. The numbers of bands found in each C_{4h} symmetry species is well below that required by factor-group analysis but close to what is required for one molecule plus lattice modes.

Molecular symmetry is only C_i if we include the ligands. The modes of the CdS_4Cl_2 kernel might reasonably be considered in terms of a point group with a C_4 axis and, since this is approximately parallel to the crystal *c* axis, the symmetry species can be correlated directly with those of the factor group (C_{4h}). Combining a C_4 axis with the known centre of symmetry requires C_{4h} to be used as the approximation to molecular symmetry, thus making a one-to-one correspondence between molecular and crystal symmetry species. Deviations from this model are to be expected for modes involving Cd–S–C bending and torsions of thiourea with respect to the rest of the molecule; a few weak bands might therefore appear in addition to those predicted by the molecular C_{4h} model (Table 8) due to lifting of degeneracies.

TABLE 8

Approximate normal modes for $CdCl_2(SC)_4$ with idealised C_{4h} symmetry

a_g	ν_1	ν(C–S)	a_u	ν_{11}	ν(Cd–Cl)
	ν_2	ν(Cd–S)		ν_{12}	δ(CdSC)
	ν_3	ν(Cd–Cl)		ν_{13}	δ(SCdCl)
	ν_4	δ(CdSC)			
			b_u	ν_{14}	δ(CdSC)
b_g	ν_5	ν(C–S)		ν_{15}	δ(SCdCl)
	ν_6	ν(Cd–S)			
	ν_7	δ(CdSC)	e_u	ν_{16}	ν(C–S)
	ν_8	δ(SCdS)		ν_{17}	ν(Cd–S)
				ν_{18}	δ(CdSC)
e_g	ν_9	δ(CdSC)		ν_{19}	δ(SCdS)
	ν_{10}	δ(SCdCl)		ν_{20}	δ(SCdCl)

Torsions of thiourea about C–S bonds, $a_g + b_g + e_u$.

B_g *Species*.—One B_g mode ν(Cd–S), ν_6, is expected well above the others followed by ν_7, δ(CdSC) and ν_8, δ(SCdS); Raman lines at 209, 147, and 87 cm^{-1} are accordingly assigned to them (Table 9). The lines at 60 and 52 cm^{-1} are associated with rotatory modes which must certainly be combined with torsional modes of thiourea. A very weak line at 107 cm^{-1} is in a region which appears to be characteristic of δ(CdSC) modes and is presumed to be evidence of the symmetry approximations discussed above.

TABLE 9

Raman frequencies (cm^{-1}), intensities (arbitrary units) and assignments for single-crystal $CdCl_2(tu)_4$ at ambient temperature

Frequency and assignment	C_{4h}^4	$x(zz)y$	$x(yx)y$	$x(zx)y$	$x(yz)y$	Mode description
41	E_g			13	15	Molecular rotatory modes mixed with thiourea torsional modes
42	A_g	94				
49	E_g			12	14	
52	B_g		5			
60	B_g		36			
62	E_g			4	4	
69	A_g	4				
72	E_g			38	39	
78	A_g	16				
87	B_g		56			ν_8
91	A_g	4				δ
107	B_g		2			δ
109	A_g	100				ν_4
112	E_g			8	9	ν_{10}
129	A_g	4				δ
137	E_g			9	10	ν_9
147	B_g		6			ν_7
153	A_g	5				ν_3
208	A_g	10				ν_2
209	B_g		1			ν_{10}

δ = Modes not predicted on idealised C_{4h} molecular symmetry, due to δ(CdSC) motions.

E_g *Species*.—The two highest E_g modes are of the δ(CdSC) type and are, therefore, associated with the 137 and 112 cm^{-1} lines. There is a clear gap between 112 cm^{-1} and a series of low-lying E_g lines beginning at 72 cm^{-1} and due to torsions and rotatory lattice modes.

A_g *Species*.—From their frequency the 208 and 153 cm^{-1} lines can be assigned to ν_2, ν(Cd–S) and ν_3, ν(Cd–Cl). ν_3 Can hardly be lower than this as even this frequency represents the motion of a largely ionic-bonded chlorine. In addition this symmetry species shows weak bands (129 and 91 cm^{-1}) of a frequency compatible with δ(CdSC) motion but which are not expected on the idealised C_{4h} model.

TABLE 10

I.r. frequencies (cm^{-1}) for $CdCl_2(tu)_4$

Mull	Single-crystal reflectance		Assignment
	A_u	E_u	
	34w		Translatory lattice modes
		42w	
	66w		
		67m	
	90m		ν_{13}
97w			
		99s	ν_{19}
112m			ν_{18} and other δ(CdSC) modes (see text)
124m			
149s		146s	
164ms	162sh		ν_{12}
		167w	
183vs	180s		ν_{11}
205w,sh			ν_{17}

A_u *Species*.—The three internal modes can be assigned

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[5] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1969, 2077; D. M. Adams and A. Squire, *ibid.*, 1970, 814.

[6] D. M. Adams, M. A. Hooper, and M. H. Lloyd, *J. Chem. Soc.* (*A*), 1971, 946.

as shown in Table 10 with a fair degree of confidence. The intense antisymmetric Cl–Cd–Cl mode at 180 cm^{-1} is above the corresponding symmetric stretch, ν_3, and the other modes lie in regions consistent with the Raman assignment.

E_u *Species*.—In this species, apart from ν_{17}, ν(Cd–S) we expect a group of δ(CdSC) modes (including splitting due to departure from C_{4h}), ν_{19}, δ(SCdS) and several lattice modes. Assignments are shown in Table 10.

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