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The Crystal Structure of *bis*-Ethylenethiourea-Cadmium Thiocyanate

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bis-Ethylenethiourea-cadmium thiocyanate crystallizes in the monoclinic system and is isostructural with the corresponding lead compound. The cell dimensions are:

$a = 15{\cdot}60 \pm 0{\cdot}04$, $b = 8{\cdot}17 \pm 0{\cdot}02$, $c = 11{\cdot}51 \pm 0{\cdot}01$ Å; $\beta = 95°\ 41'$;

the number of formula units per unit cell is 4 and the space group is C_{2h}^6–$C\ 2/c$. The structure has been solved by two-dimensional Patterson and Fourier syntheses, and refinement has been carried out with generalized projections of partial differences and back-shift corrections. The cadmium atom coordinates octahedrally with two sulphur atoms attached to ethylenethiourea molecules, and with two sulphur and two nitrogen atoms in four different NCS groups. The coordination polyhedra are therefore linked in chains by these NCS groups, which form bridges between cadmium atoms.

1. Introduction

The study of the structure of *bis*-ethylenethiourea-cadmium thiocyanate,

$$Cd\mathit{etu}_2(NCS)_2 \quad (\mathit{etu} = SC(NHCH_2)_2),$$

is part of an extensive series of research with the object of finding the nature of the coordination compounds formed by divalent cations and organic molecules containing sulphur. The thiocyanates of divalent metals form with thiourea ($tu = SC(NH_2)_2$) and ethylenethiourea two series of compounds:

$$Me^{II}tu_2(NCS)_2, \quad Me^{II} = Mn, Co, Ni, Cd$$

(Nardelli, Braibanti & Fava, 1957) and

$$Me^{II}etu_2(NCS)_2, \quad Me^{II} = Mn, Co, Ni, Cd, Pb$$

(Nardelli & Chierici, 1958). The thiourea compounds are all isostructural and triclinic and are characterized by a particularly small value of a translation identity period ($a \sim 3{\cdot}9$ Å). On the contrary, the ethylenethiourea compounds crystallize in two different systems: the compounds with Mn, Co, Ni are triclinic, whilst those with Cd and Pb are monoclinic. None of the ethylenethiourea derivatives has a translation period near 4 Å.

bis-Ethylenethiourea-cadmium thiocyanate and the isostructural lead compound have the following lattice parameters:

$Cd\mathit{etu}_2(NCS)_2$:

$a = 15{\cdot}60 \pm 0{\cdot}04$, $b = 8{\cdot}17 \pm 0{\cdot}02$, $c = 11{\cdot}51 \pm 0{\cdot}01$ Å, $\beta = 95°\ 41'$.

$Pb\mathit{etu}_2(NCS)_2$:

$a = 16{\cdot}25 \pm 0{\cdot}02$, $b = 7{\cdot}94 \pm 0{\cdot}01$, $c = 11{\cdot}95 \pm 0{\cdot}02$ Å, $\beta = 93°\ 8'$.

The unit cells contain $Z = 4$ formula units. The space groups consistent with the observed extinctions are C_{2h}^6–$C2/c$ and C_s^4–Cc.

2. Experimental

The usual habit of $Cd\mathit{etu}_2(NCS)_2$ crystals, obtained by slow recrystallization from alcoholic solution, was prismatic, showing the {100}, {110}, and {001} forms and being elongated along [001]. It was therefore easy to obtain a nearly cylindrical sample around [001] (cross-sectional dimension $\sim 0{\cdot}25$ mm.) by rubbing with a wet filter paper. This sample was used for taking integrated Weissenberg photographs (Wiebenga & Smits, 1950) of $hk0$ and $hk1$ reflexions. The same technique was used to obtain photographs of the $h0l$ and $h1l$ reflexions from a nearly spherical sample (mean diameter 0·30 mm.). All photographs were taken with the multiple-film method (Cu $K\alpha$-radiation, 120 hr. exposure time). The intensity determinations were carried out photometrically on 107 $h0l$, 173 $h1l$, 65 $hk0$, and 113 $hk1$ (out of a possible 113 $h0l$, 233 $h1l$, 91 $hk0$, and 157 $hk1$) reflexions. The corrections for polarization and Lorentz factors were made by means of a Cochran (1948) chart. Absorption corrections ($\mu = 177$ cm.$^{-1}$) were made assuming a cylindrical or spherical sample, but secondary extinction was not taken into account.

The relative values of $F_o^2(h0l)$ and $F_o^2(hk0)$ were put on an absolute scale by the Wilson (1942) method. A first scaling factor for $F_o^2(h1l)$ was obtained by comparison of the $h10$ reflexions with the same ones present in the $hk0$ photograph; $F_o^2(hk1)$ were likewise scaled using $h11$ reflexions. A first mean temperature coefficient was $\overline{B} = 2{\cdot}0$ Å^2. Scaling and mean temperature factors were improved by graphical comparison of F_o and F_c values for the reflexions of each photograph. Finally an isotropic temperature correction was determined for each kind of atom by a least-

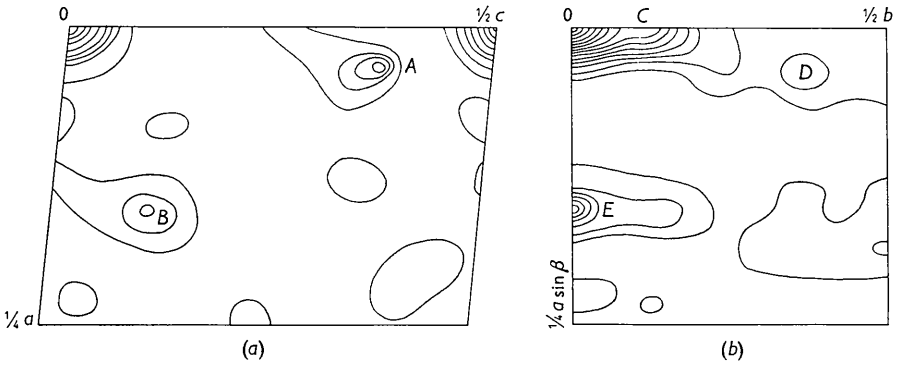

Fig. 1. Patterson projections: (*a*) $P(U, W)$, (*b*) $P(U, V)$. Contours at arbitrary intervals.

squares method (Cochran, 1951). The final values were 2·1 Å² for Cd and 2·8 Å² for all the other atoms.

3. *P(U,W)* and *P(U,V)* projections

The unit cell contains four molecules of $Cdetu_2(NCS)_2$, and so the cadmium atom must be located on one of the five special positions of the C_{2h}^6 space group or in the general position of the C_s^4 space group. Examination of the $P(U, W)$ Patterson projection (Fig. 1(*a*)) cannot distinguish between these possibilities as the Cd–Cd interactions occur only at the origin peak. On the other hand, in the $P(U,V)$ projection (Fig. 1(*b*)) the $C(U=0,\ W=0{\cdot}116)$ peak (due to the Cd–Cd interaction) shows that the Cd atom, having a degree of freedom in the y direction, must be in the $e(0, y, \frac{1}{4})$ position of the C_{2h}^6 space group or in the general position of the C_s^4 space group. In this latter case there is no crystallographic equivalence between atoms which are probably chemically equivalent. Considering this, the C_{2h}^6 space group was chosen as a starting point and this choice was later found to be correct.

The A, D and B, E peaks in the two Patterson projections were interpreted as due to the Cd–S_I and Cd–S_{II} interactions respectively. The other peaks involving lighter atoms were not taken into account.

The coordinates obtained from Patterson projections were:

	x/a	y/b	z/c
Cd	0	0·058	0·250
S_I	0·034	0·309	0·109
S_{II}	0·154	0·058	0·358

4. Fourier projections and refinements

The first $\varrho_0(X, Z)$ projection was obtained using the signs of the structure factors calculated by considering the heavier atoms only. As the peaks of the lighter atoms were unresolved, it was impossible to find the orientation of the organic molecule and of the NCS group. It therefore appeared convenient to consider the generalized projections $S_1(X, Z)$, $C_1(X, Z)$ and $\varrho_1(X, Z)=[S_1^2+C_1^2]^{\frac{1}{2}}$; the last was also combined with the $\varrho_0(X, Z)$ projection. From S_1 and C_1 projections y coordinates were obtained too.

From these projections it was possible to distinguish the light atoms of the organic molecule, which was found to be completed by the S_{II} sulphur atom. Carbon and nitrogen atoms of the NCS group were superimposed on two S_I atoms symmetrically placed with respect to the origin, and so at this stage they were ignored. Reliability indices were $R(h0l)=0{\cdot}214$, $R(h1l)=0{\cdot}213$.

A successive series of the same projections was calculated, subtracting out the cadmium and sulphur contributions, and this series was then used to locate the carbon and nitrogen atoms of the NCS group and to improve the coordinates of the other light atoms. The new R factors were $R(h0l)=0{\cdot}196$, $R(h1l)=0{\cdot}142$. Little further improvement of coordinates was obtained recalculating the projections either with all the light atoms contributions or with the sulphur contributions alone.

$\varrho_0(X, Y)$, $\varrho_1(X, Y)$ and $\{\varrho_0+\varrho_1\}(X, Y)$ were also calculated at this stage, but, owing to the extensive overlapping of the light atoms, they were used only to control the x and y coordinates of heavier atoms obtained from (X, Z)-projections. The final $\varrho_0(X, Y)$ projection (Fig. 3(*b*)) shows that all the light atoms lie on high electron-density regions.

The $S_1(X, Z)$ and $C_1(X, Z)$ final projections are shown in Fig. 2(*a*), (*b*); Fig. 3(*a*) represent the corresponding $\varrho_1(X, Z)$ projection. As a further refinement isotropic thermal factors were calculated for each atomic kind and back-shift corrections for finite-series errors were applied. At the end of these refinements the R factors (for observed reflexions only) were:

$$R(h0l)=0{\cdot}165,\quad R(h1l)=0{\cdot}109\ ,$$
$$R(hk0)=0{\cdot}232,\quad R(hk1)=0{\cdot}151\ .$$

In Table 1 the observed structure factors are compared with those calculated.

5. Atomic coordinates and accuracy

The final coordinates are shown in Table 2. The x/a, y/b, z/c values are referred to monoclinic axes with

Table 1. *Observed and calculated structure factors*

h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c
2	0	0	176	174	$\bar{10}$	0	8	62	54	11	1	0	52	45	$\bar{7}$	1	8	95	95	2	4	0	34	60	6	6	1	21	-18
4			183	245	$\bar{12}$			89	78			1	27	-19			9	28	-33	4			52	71	8			32	-27
6			200	268	$\bar{14}$			66	65			2	113	-112			10	65	-62	6			-	-7	10			39	-41
8			145	118	$\bar{16}$			36	34			3	80	83			11	69	58	8			-	3	12			39	-46
10			66	32	2	0	10	63	-74			4	99	99			12	42	39	10			-	9	14			40	-62
12			92	45	4			43	-54			5	-	8			13	-	13	12			-	-16	16			25	-29
14			98	62	6			80	-74			6	30	-44			14	17	-21	14			-	-4	1	7	1	46	-52
16			23	19	8			97	-108			7	-	15	$\bar{9}$	1	1	-	-12	16			-	-5	3			-	-3
18			57	35	$\bar{10}$			52	-53			8	-	26			2	141	-150	18			-	6	5			40	-36
0	0	2	213	-222	$\bar{12}$			66	-57			9	-	-30			3	72	93	1	5	0	86	-70	7			35	-31
2			66	40	$\bar{14}$			82	-79			10	46	-40			4	106	101	3			61	-47	9			28	-35
4			172	-254	2	0	12	88	84			11	-	7			5	36	-35	5			36	-36	11			24	-26
6			176	-290	4			67	77	13	1	0	154	143			6	53	-54	7			-	-36	13			16	-22
8			118	-131	6			31	41			1	32	-25			7	-	-24	9			-	12	0	8	1	-	-2
10			156	-144	8			64	63			2	73	-72			8	36	48	11			-	10	2			22	-38
12			148	-140	$\bar{10}$			36	40			3	42	48			9	-	-28	13			-	-23	4			25	-46
14			63	-62	$\bar{12}$			-	12			4	-	24			10	50	-56	15			-	7	6			-	-4
16			32	-30	2	0	14	33	-39			5	-	10			11	44	51	17			-	2	8			-	-20
18			66	-46	4			35	-43			6	43	-42			12	66	66	0	6	0	81	-137	10			-	-23
0	0	4	-	-16	6			21	-28			7	-	12			13	-	-2	2			-	-39	12			-	-12
2			91	154	8			13	-19			8	56	49	$\bar{11}$	1	1	22	16	4			-	-28	1	9	1	-	7
4			83	62	1	1	0	116	190			9	31	-34			2	-	-8	6			59	-93	3			23	17
6			75	70			1	92	-82			10	36	-40			3	43	53	8			47	-63	5			26	31
8			51	55			2	146	-136	15	1	0	31	28			4	79	83	10			-	-17	7			16	19
10			113	109			3	52	-53			1	20	20			5	28	-30	12			43	-49	9			-	3
12			112	113			4	68	54			2	-	-29			6	107	-116	14			38	-43	0	10	1	17	46
14			62	56			5	34	-35			3	20	35			7	20	11	16			23	-23	2			14	18
16			105	98			6	102	-85			4	61	70			8	52	54	1	7	0	32	-52	4			17	29
18			63	58			7	118	101			5	-	-20			9	20	-34	3			-	-14	2	2	1	61	-56
0	0	6	170	-149			8	151	126			6	65	-60			10	-	-18	5			60	-61	4			67	-49
2			199	-210			9	-	11			7	20	14			11	-	18	7			66	-84	6			147	-147
4			111	-96			10	78	-68			8	33	37			12	22	31	9			65	-53	8			135	-154
6			54	-54			11	-	22	17	1	0	42	38			13	-	7	11			67	-55	$\bar{10}$			89	-75
8			76	-85			12	-	25			1	-	4	$\bar{13}$	1	1	62	-62	13			65	-83	$\bar{12}$			78	-63
10			31	-24			13	21	27			2	59	-54			2	116	-103	0	8	0	80	-103	$\bar{14}$			93	-74
12			23	-25			14	31	-36			3	32	35			3	56	63	2			65	-53	$\bar{16}$			35	-40
14			42	-30	3	1	0	99	115			4	52	48			4	50	50	4			66	-51	$\bar{18}$			-	-12
16			58	-59			1	92	-102			5	-	-21			5	-	2	6			57	-66	$\bar{1}$	3	1	143	-156
0	0	8	137	124			2	97	-100			6	31	-40			6	51	-66	8			48	-52	$\bar{3}$			145	-133
2			126	109			3	59	50	19	1	0	55	52			7	-	21	10			30	19	$\bar{5}$			125	-106
4			105	106			4	206	217			1	-	-11			8	62	70	12			36	-35	$\bar{7}$			158	-175
6			108	105			5	76	-77			2	43	-48			9	39	-49	1	9	0	48	-82	$\bar{9}$			121	-132
8			117	143			6	178	-169			3	-	19			10	47	-46	3			38	-46	$\bar{11}$			44	-33
10			29	32			7	114	102	$\bar{1}$	1	1	107	-90			11	-	11	5			35	-56	$\bar{13}$			122	-122
12			69	67			8	84	65			2	144	-178			12	17	32	7			24	-45	$\bar{15}$			36	-36
14			57	50			9	30	31			3	28	17	$\bar{15}$	1	1	-	-27	9			19	-22	$\bar{17}$			17	-15
0	0	10	63	-62			10	36	-34			4	127	113			2	58	-56	11			-	-14	2	4	1	119	-114
2			-	-18			11	-	5			5	75	-74			3	44	45	0	10	0	-	-25	4			68	-45
4			44	-59			12	39	42			6	84	-72			4	68	66	2			-	-22	6			82	-75
6			56	-60			13	38	-40			7	75	63			5	-	11	4			32	-33	8			78	-86
8			48	-57			14	49	-40			8	141	123			6	28	-32	6			-	-28	$\bar{10}$			-	-9
10			31	-34	5	1	0	139	150			9	-	-1			7	-	10	0	2	1	214	-254	$\bar{12}$			40	-32
12			71	-82			1	106	-126			10	137	-127			8	25	31	2			138	116	$\bar{14}$			66	-67
0	0	12	55	51			2	182	-235			11	78	71			9	28	-32	4			-	-22	$\bar{16}$			33	-44
2			38	48			3	67	70			12	67	61			10	36	-45	6			104	-114	$\bar{18}$			32	-33
4			59	72			4	133	140			13	27	-28			11	-	12	8			-	-24	$\bar{1}$	5	1	116	-132
6			23	39			5	-	17			14	25	-27	$\bar{17}$	1	1	-	-25	10			36	-36	$\bar{3}$			84	-83
8			-	8			6	-	-11	$\bar{3}$	1	1	53	-42			2	28	-31	12			101	-85	$\bar{5}$			78	-65
0	0	14	19	-24			7	59	63			2	178	-214			3	-	23	14			69	-62	$\bar{7}$			68	-78
2			44	-60			8	49	43			3	58	59			4	65	65	16			33	-39	$\bar{9}$			64	-69
4			33	-59			9	-	-12			4	188	181			5	-	-7	18			55	-49	$\bar{11}$			-	-10
2	0	2	94	-61			10	106	-98			5	96	-108			6	61	-63	1	3	1	83	-78	$\bar{13}$			69	-78
4			94	66			11	-	17			6	102	-90			7	27	31	3			38	-33	$\bar{15}$			37	-39
6			58	60			12	60	59			7	-	6			8	24	24	5			119	-129	2	6	1	59	-59
8			134	-126			13	28	-34			8	-	25			9	-	-17	7			73	-78	4			77	-77
$\bar{10}$			58	-39	7	1	0	148	155			9	54	52	$\bar{19}$	1	1	26	-37	9			62	-55	6			75	-89
$\bar{12}$			69	-49			1	67	-67			10	-	-13			2	32	-32	11			101	-88	8			74	-105
$\bar{14}$			133	-99			2	50	-52			11	49	50			3	-	5	13			124	-124	$\bar{10}$			51	-64
$\bar{16}$			97	-97			3	-	15			12	50	51			4	-	20	15			36	-39	$\bar{12}$			48	-63
$\bar{18}$			41	-44			4	35	27			13	-	-25			5	-	6	17			63	-61	$\bar{14}$			33	-51
2	0	4	203	172			5	32	38			14	53	-57			6	-	-28	0	4	1	219	-301	$\bar{1}$	7	1	33	-22
4			224	251			6	80	-84	$\bar{5}$	1	1	-	20	0	2	0	128	148	2			110	-78	$\bar{3}$			29	-31
6			62	63			7	71	79			2	76	-71	2			93	-142	4			180	-200	$\bar{5}$			22	-39
8			205	226			8	104	96			3	28	22	4			49	10	6			186	-211	$\bar{7}$			-	-24
$\bar{10}$			206	204			9	33	-33			4	93	84	6			113	92	8			113	-109	$\bar{9}$			-	-43
$\bar{12}$			107	94			10	67	-59			5	96	-100	8			99	95	10			81	-71	$\bar{11}$			-	-19
$\bar{14}$			113	78			11	-	-5			6	136	-139	10			93	80	12			90	-79	$\bar{13}$			-	-23
$\bar{16}$			112	94			12	19	28			7	48	39	12			102	96	14			53	-49	$\bar{15}$			-	16
$\bar{18}$			37	33			13	-	-21			8	144	142	14			92	96	16			-	-9	2	8	1	-	-2
2	0	6	166	-139	9	1	0	105	103			9	-	-13	16			28	41	18			40	-33	4			-	-15
4			228	-247			1	33	-29			10	68	-68	18			39	37	1	5	1	121	-141	6			-	18
6			112	-110			2	79	-73			11	53	55	1	3	0	88	97	3			89	-76	8			-	25
8			40	-34			3	79	78			12	31	28	3			43	39	5			130	-155	$\bar{10}$			-	-6
$\bar{10}$			134	-118			4	134	138			13	-	-3	5			77	65	7			85	-102	$\bar{12}$			-	-1
$\bar{12}$			41	-35			5	-	-19			14	37	-43	7			32	37	9			61	-53	$\bar{1}$	9	1	-	18
$\bar{14}$			-	-4			6	112	-116	$\bar{7}$	1	1	33	-24	9			29	30	11			59	-61	$\bar{3}$			-	0
$\bar{16}$			50	-30			7	57	62			2	112	-131	11			-	-13	13			55	-63	$\bar{5}$			-	2
$\bar{18}$			52	-38			8	53	50			3	66	71	13			36	32	15			20	-10	$\bar{7}$			-	20
2	0	8	43	48			9	-	-26			4	90	80	15			-	7	17			32	-27	$\bar{9}$			-	-1
4			59	55			10	34	-38			5	50	-59	17			-	20	0	6	1	58	-65	2	10	1	-	31
6			92	93			11	-	-8			6	89	-95	19			-	17	2			-	9	4			-	2
8			-	16			12	27	36			7	-	2	0	4	0	-	36	4			38	-37	6			-	17

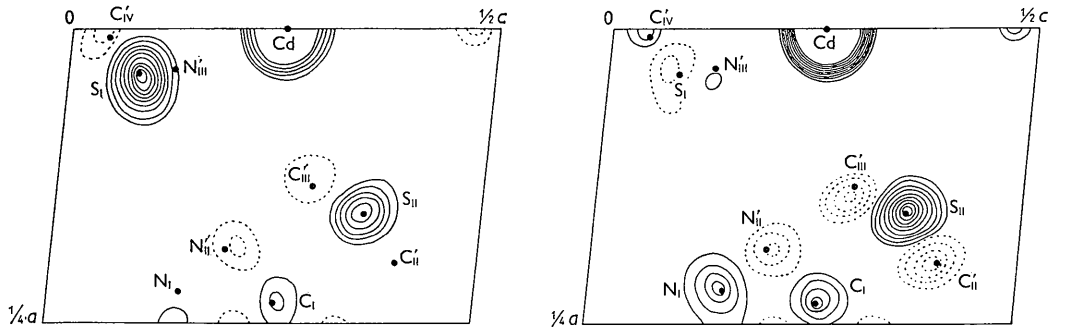

Fig. 2. (*a*) $S_1(X, Z)$, (*b*) $C_1(X, Z)$. Contour interval 2 e.Å^{-2} in light atoms, and arbitrary in others, starting from 3 e.Å^{-2}. Negative contours broken and zero contour omitted. The symbols primed indicate the atoms related to those in x, y, z by $\bar{1}$ or 2_1.

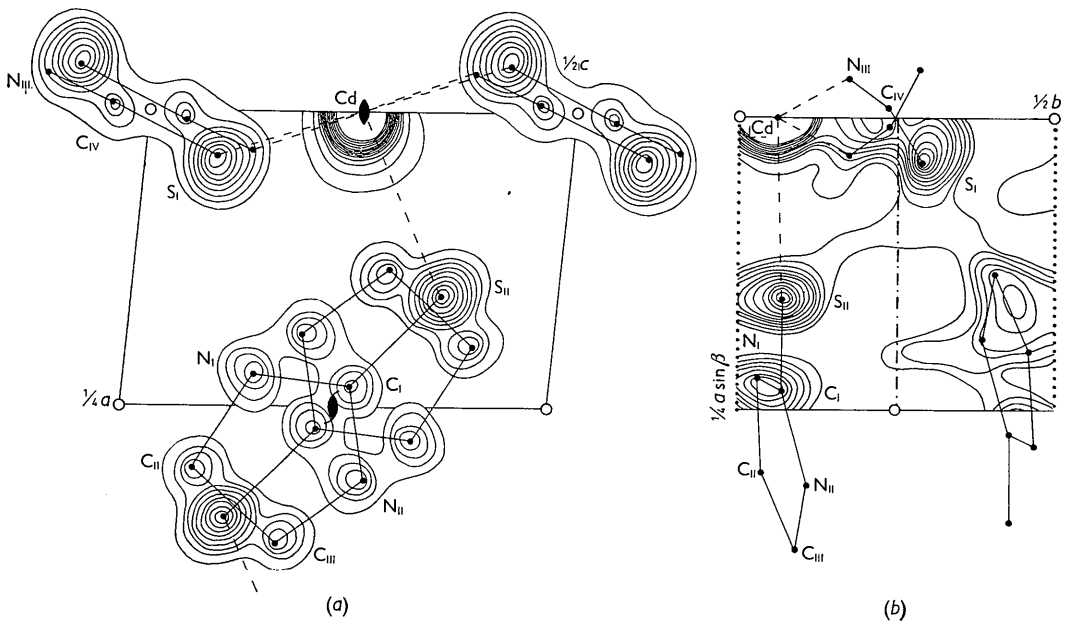

Fig. 3. (*a*) $\varrho_1(X, Z)$, (*b*) $\varrho_0(X, Y)$. Contour invervals as in Fig. 2.

the origin at the centre of symmetry. The x', y', z' coordinates are referred to orthogonal axes a', b, c, with a' being taken perpendicular to the b and c crystal axes, so that

$$x' = x \sin\beta,\ y' = y,\ z' = z + x\cos\beta\ .$$

The standard deviations of the atomic coordinates of the Cd and S atoms were estimated by Cruickshank's (1949) method from $\varrho_1(X, Z)$ for $\sigma(x)$ and $\sigma(z)$ and from $\varrho_0(X, Y)$ for $\sigma(y)$. For the light atoms $\sigma(x)$ and $\sigma(z)$ were found in the same way, and $\sigma(y)$ was obtained using the relation (Bryden, 1958)

$$\sigma(y_r) = \{b/2\pi A\}\{\Sigma(\Delta F)^2\}^{\frac{1}{2}}/(\varrho_1)_r\ ,$$

where A is the area of the cell projection, and $\sigma(\Delta F)^2$ is taken over all the $h1l$ observed reflexions.

The mean values of the standard deviations were: Cd–$\sigma(y) = 0{\cdot}006$ Å, S–$\sigma(x) = 0{\cdot}010$, $\sigma(y) = 0{\cdot}025$, $\sigma(z) = 0{\cdot}009$ Å, light atoms–$\sigma(x) = 0{\cdot}030$, $\sigma(y) = 0{\cdot}162$, $\sigma(z) = 0{\cdot}023$ Å.

The standard deviations of the electron densities $\sigma(\varrho)$ were 1·84 e.Å^{-2} for $h0l$ data, 1·16 e.Å^{-2} for $h1l$ data and 2·72 e.Å^{-2} for $hk0$ data.

Table 2. *Atomic coordinates*

	x/a	y/b	z/c	x' (Å)	y' (Å)	z' (Å)
Cd	0	0·0605	0·250	0	0·494	2·878
S_I	0·039	0·286	0·088	0·605	2·337	0·953
S_{II}	0·153	0·073	0·362	2·375	0·596	3·931
C_I	0·233	0·070	0·267	3·617	0·572	2·713
C_{II}	0·301	0·040	0·096	4·673	0·327	0·640
C_{III}	0·369	0·091	0·199	5·728	0·743	1·720
C_{IV}	−0·009	0·241	−0·032	−0·140	1·969	−0·353
N_I	0·222	0·033	0·155	3·446	0·270	1·441
N_{II}	0·314	0·103	0·296	4·874	0·842	2·922
N_{III}	−0·033	0·179	−0·123	−0·512	1·462	−1·365

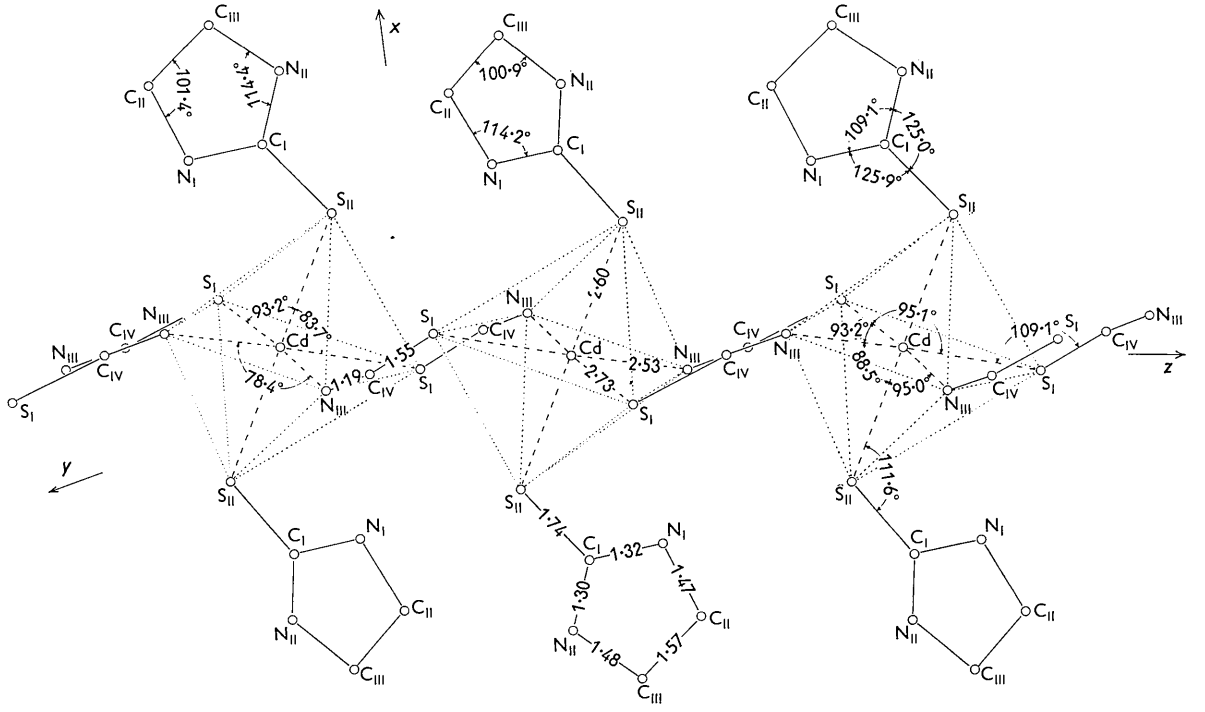

Fig. 4. Clinographic projection of a chain in Cd*etu*$_2$(NCS)$_2$.

6. Discussion of the structure

The coordination around each cadmium atom is octahedral, as it coordinates two S_{II} atoms of two ethylenethiourea molecules, two S_I and two N_{III} atoms of four different NCS groups. Each pair of equivalent atoms is related by the 2-fold axis running through the cadmium atom. The octahedra are linked in slightly zigzag chains by NCS groups forming bridges between the cadmium atoms. These chains lie along [001] (Fig. 4).

The bond distances and angles in the coordination polyhedron are listed below. (When the coordinates are not given the atom is in the x, y, z or—for the atomic symbol primed—$\bar{x}, \bar{y}, \bar{z}$ position.)

Cd–S_I	= 2·73 ± 0·02 Å
Cd–S_{II}	= 2·60 ± 0·01
Cd–N'_{III}	= 2·53 ± 0·13
S_I–Cd–$S_I(\bar{x}, y, \frac{1}{2}-z)$	= 95·1 ± 0·8°
S_I–Cd–N'_{III}	= 93·2 ± 2·6°
S_I–Cd–S_{II}	= 93·2 ± 0·5°
S_{II}–Cd–$S_I(\bar{x}, y, \frac{1}{2}-z)$	= 83·7 ± 0·5°
S_{II}–Cd–N'_{III}	= 95·0 ± 0·8°
S_{II}–Cd–$N_{III}(x, \bar{y}, \frac{1}{2}+z)$	= 88·5 ± 0·8°
N'_{III}–Cd–$N_{III}(x, \bar{y}, \frac{1}{2}+z)$	= 78·4 ± 5·9°

To evaluate the standard deviations of the distances and angles the relations given by Ahmed & Cruickshank (1953) were used. The distances and angles in the ethylenethiourea molecule are:

S_{II}–C_I	= 1·74 + 0·03 Å (1·708 Å)
C_I–N_I	= 1·32 ± 0·06 Å (1·322 Å)
C_I–N_{II}	= 1·30 ± 0·06 Å
N_I–C_{II}	= 1·47 ± 0·04 Å (1·471 Å)
N_{II}–C_{III}	= 1·48 ± 0·04 Å
C_{II}–C_{III}	= 1·57 ± 0·07 Å (1·536 Å)

N_I–C_I–S_{II}	= 125·9 ± 2·4°	(124·8°)
N_{II}–C_I–S_{II}	= 125·0 ± 2·3°	
N_I–C_I–N_{II}	= 109·1 ± 3·2°	(110·2°)
C_I–N_I–C_{II}	= 114·2 ± 3·3°	(112·6°)
C_I–N_{II}–C_{III}	= 114·4 ± 3·2°	
N_I–C_{II}–C_{III}	= 101·4 ± 2·9°	(102·4°)
N_{II}–C_{III}–C_{II}	= 100·9 ± 3·0°	

The values in brackets are those found by Wheatley (1953) in ethylenethiourea crystals. The figures obtained are satisfactory even though the coordinates of the light atoms are subject to relatively rather high errors. There are no significant departures of the ethylenethiourea atoms from the plane (calculated by the least-squares method)

$$0{\cdot}277x' - 1{\cdot}520y' + 0{\cdot}318z' = 1 .$$

This plane is roughly perpendicular to [010], and so large errors in the y coordinates have little effect on the distances and angles. The distances in the NCS group are:

$$S_I\text{–}C_{IV} = 1{\cdot}55 \pm 0{\cdot}05 \text{ Å}$$
$$C_{IV}\text{–}N_{III} = 1{\cdot}19 \pm 0{\cdot}10 \text{ Å} .$$

Owing to the errors in bond lengths, bond orders cannot be deduced and also the angle S_I–C_{IV}–N_{III} = 165 ± 9° is not worth discussing. A departure from linearity of this group has been already found in $Hg(SCN)_4^{2-}$ (163° 12′) by Scouloudi (1953) and by Lindqvist (1957*a*, *b*) in AgSCN and $NH_4Ag(SCN)_2$.

However, Lindqvist does not consider the deviation from linearity of SCN group he found to be significant, being smaller than that calculated from the standard deviations of atomic positions. In Ni*tu*$_2$(NCS)$_2$ the NCS group was found to be linear, as it was in $NH_4[Cr(SCN)_4(NH_3)_2]\frac{2}{3}H_2O$ (Saito, Takeuchi & Pepinsky, 1955), in $Ni(NH_3)_3(NCS)_2$ and in $Ni(NH_3)_4(NCS)_2$ (Paraj-Kojic, Antzishkina, Dickareva & Jukhnov, 1957).

The angle Cd–S_I–C_{IV} = 109·1 ± 4·4° suggests that the bonds on the S_I atoms are tetrahedral. The rather high error in the Cd–N'_{III}–C'_{IV} = 143 ± 12° angle, makes any interpretation uncertain.

It is particularly interesting to compare the structure of Cd*etu*$_2$(NCS)$_2$ with that of Ni*tu*$_2$(NCS)$_2$ which is isostructural with Cd*tu*$_2$(NCS)$_2$. The substitution of thiourea for ethylenethiourea does not limit its consequences to an alteration of the crystal structure due only to steric-hindrance, but the observed modifications are more chemical in nature. In Cd*tu*$_2$(NCS)$_2$ the coordination around the cadmium atom is also octahedral but in this case the bridges between the coordination polyhedra are constituted by sulphur atoms of thiourea which are forming two coordinative bonds.

The bond angle Cd–S_{II}–C_I = 111·6 ± 1·1° in Cd*etu*$_2$(NCS)$_2$ suggests tetrahedral bonds to the S_{II} atom, as has been found in Ni*tu*$_2$(NCS)$_2$. The coordination of the NCS groups in Cd*etu*$_2$(NCS)$_2$, which occurs through the ends of the molecule, follows what has been found by Lindqvist (1957*a*, *b*). Lindqvist observes that, while with the elements of the first long row of the Periodic Table the metal atom coordinates the nitrogen-ends of the NCS groups and in the second and third long rows the coordination is through the sulphur-ends, the cadmium atom can coordinate the nitrogen or the sulphur atoms as well. The isostructurality found between Cd*etu*$_2$(NCS)$_2$ and Pb*etu*$_2$(NCS)$_2$ shows that lead represents an exception to the previous generalization. The packing distances shorter than 4 Å are:

N_I – S_I		= 3·55 ± 0·10 Å
N_I – N'_{III}		= 3·41 ± 0·12
N_I – S_{II}	$(x, \bar{y}, z-\frac{1}{2})$	= 3·54 ± 0·05
C_{II} – S_{II}	$(x, \bar{y}, z-\frac{1}{2})$	= 3·49 ± 0·05
N_{II} – C_{II}	$(x, \bar{y}, z+\frac{1}{2})$	= 3·67 ± 0·08
C_I – C_{II}	$(x, \bar{y}, z+\frac{1}{2})$	= 3·94 ± 0·06
S_{II} – C_{II}	$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	= 3·90 ± 0·16
C_I – N_I	$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	= 3·94 ± 0·22
S_I – N_{II}	$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	= 3·63 ± 0·12
N_{III} $(\bar{x}, 1-y, \bar{z})$ – C_{III}	$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	= 3·07 ± 0·14
N_{III} $(\bar{x}, 1-y, \bar{z})$ – N_{II}	$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	= 3·05 ± 0·14

The shortest distances observed involve the nitrogen atoms of the NCS groups and of the ethylenethiourea molecules. This indicates that the packing of the chains is based on the formation of hydrogen bonds.

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