Acta Cryst. (1965). **18**, 618

The Crystal and Molecular Structure of Bisthiourea-cadmium Formate

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(*Received* 15 *May* 1964).

$Cd[SC(NH_2)_2]_2(HCOO)_2$ is an example of sulphur bridging in a coordination compound. The crystals are orthorhombic, $P2_12_12$, with $a = 8{\cdot}00_0$, $b \doteq 17{\cdot}87_8$, $c = 3{\cdot}93_3$ Å, $Z = 2$. The structure was determined and refined by Fourier three-dimensional methods, with photographic data collected around [100] and [001] (Cu $K\alpha$).

Each Cd coordinates octahedrally four S atoms, lying in a plane with Cd, and two oxygen atoms from two $HCOO^-$ groups, *trans* to the S plane. The octahedra are linked in chains running along [001], with a twofold axis along the chain, and two S atoms shared by two adjacent octahedra.

Packing and hydrogen bonding are discussed.

Introduction

Sulphur bridging in coordination compounds has been demonstrated by X-ray analysis in a few metal complexes: bisthiourea-nickel (II) thiocyanate (Nardelli, Braibanti & Fava, 1957), bisthiourea-lead (II) chloride (Nardelli & Fava, 1959), tristhiourea-copper (I) chloride (Knobler, Okaya & Pepinsky, 1959), monothiourea-lead (II) acetate (Nardelli, Fava & Branchi-1960), bis-*N*,*N*-di-n-propyldithiocarbamate-copper (II) (Peyronel & Pignedoli, 1962).

A further example of this behaviour is observed in bisthiourea-cadmium formate, for which crystal data and preliminary results of X-ray analysis have been published already (Nardelli, Fava & Boldrini, 1962). The present paper discusses the structure derived from a three-dimensional anisotropic refinement.

Experimental

$Cd[SC(NH_2)_2]_2(HCOO)_2$, $M = 354{\cdot}7$, orthorhombic.
$a = 8{\cdot}000 \pm 0{\cdot}009$, $b = 17{\cdot}878 \pm 0{\cdot}005$,
$c = 3{\cdot}933 \pm 0{\cdot}007$ Å.

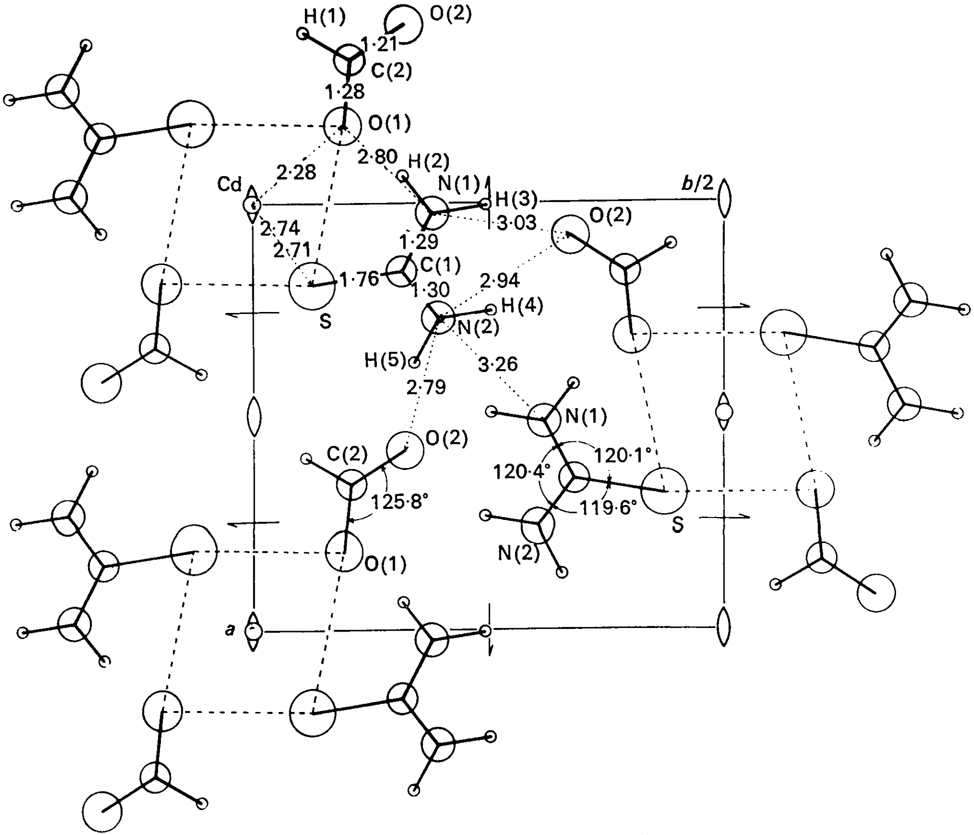

Fig. 1. Diagrammatic projection on (001).

Table 1. *Final atomic coordinates with their e.s.d.'s and ratios (e.s.d.)/(shift)*

	x/a	y/b	z/c	x(Å)	y(Å)	z(Å)	$\sigma(x)$	$\sigma(y)$ $\times 10^3$(Å)	$\sigma(z)$	$\|r(x)\|$	$\|r(y)\|$	$\|r(z)\|$
Cd	0	0	0·0970	0	0	0·382	—	—	3	—	—	26
S	0·1904	0·0622	0·6025	1·523	1·112	2·370	6	6	9	31	16	29
O(1)	−0·1815	0·0969	0·1677	−1·452	1·732	0·660	23	23	36	11	26	12
O(2)	−0·4148	0·1617	0·0896	−3·318	2·891	0·352	25	24	48	25	9	12
N(1)	0·0237	0·1902	0·5579	0·190	3·400	2·194	29	35	38	24	3	42
N(2)	0·2688	0·1968	0·8349	2·150	3·518	3·284	26	23	42	10	9	5
C(1)	0·1577	0·1583	0·6709	1·262	2·830	2·639	23	23	45	227	5	25
C(2)	−0·3349	0·1045	0·0780	−2·679	1·868	0·307	32	31	46	11	9	11

$U = 562\cdot5$ Å^3, $Z = 2$, $D_x = 2\cdot093$, $D_m = 2\cdot091$ g.cm^{-3} (flotation).
$\mu = 198\cdot3$ cm^{-1} (Cu $K\alpha$).
$F(000) = 348$.
Absent spectra: $h00$ and $0k0$ with h, k odd.
Space group: $P2_12_12$ (D_2^3).

Intensities of $hk0, \cdots, hk3$ and $0kl, \cdots, 6kl$ reflexions were determined photometrically on multiple-film integrated and non-integrated equiinclination Weissenberg photographs (Cu $K\alpha$).

Correction for absorption: continuous around [001], discontinuous (Albrecht's (1939) method) around [100]. Shape of the spots was taken into account following Phillips (1956).

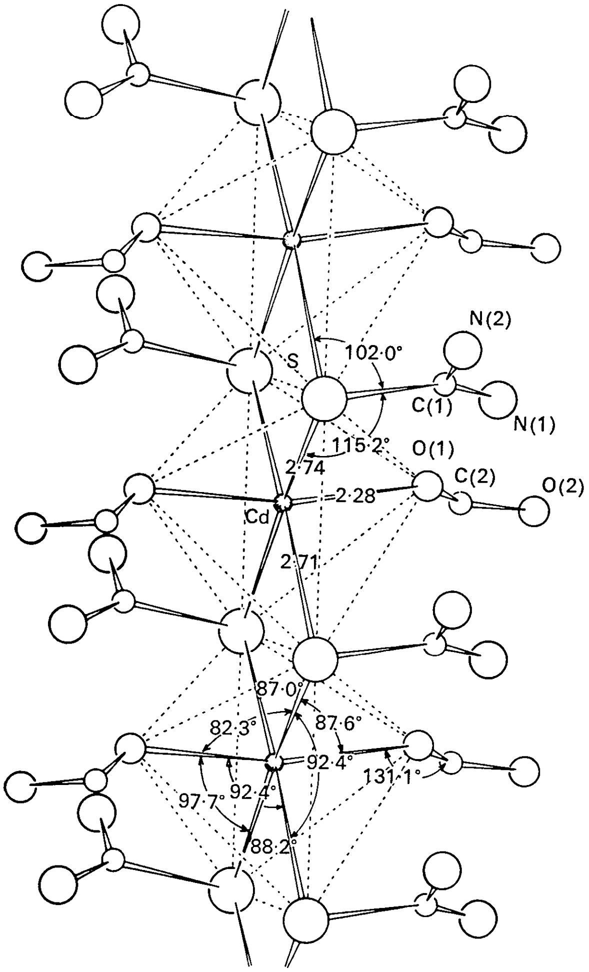

Fig. 2. Clinographic projection of a chain.

Refinement of the structure

The solution of the structure was obtained by means of Fourier methods from $hk0$ and $hk1$ data alone, as reported in the previous paper (Nardelli, Fava & Boldrini, 1962). The refinement, started with a three-dimensional Fourier synthesis, was followed by two isotropic cycles of $F_o - F_c$ synthesis and finished with four cycles of Booth's differential synthesis, the first with isotropic, the others with anisotropic thermal parameters. These were derived from the second derivatives following the method of Nardelli & Fava (1960).

The ratios (e.s.d.)/(shift) at the end of the refinement were as shown in Table 1. In the same Table the final coordinates with their e.s.d.'s (Cruickshank, 1949) are collected.

The final agreement indices (R, for observed reflexions only; R' including $F_o = \frac{1}{2}F_{min}$ when $F_c \geq F_{min}$ for unobserved reflexions; multiplicities not considered) and the e.s.d.'s of the electron-density and of its first and second derivatives, are:

$$R = 12\cdot8\% \qquad R' = 14\cdot1\%$$

$$\sigma(\varrho) = 0\cdot95 \text{ e.Å}^{-3}$$

$$\sigma(A_h) = 2\cdot7, \quad \sigma(A_k) = 2\cdot7, \quad \sigma(A_l) = 3\cdot4 \text{ e.Å}^{-4}$$

$$\sigma(A_{hh}) = 5\cdot4, \quad \sigma(A_{kk}) = 2\cdot1, \quad \sigma(A_{ll}) = 17\cdot3 \text{ e.Å}^{-5}$$

$$\sigma(A_{hk}) = 3\cdot1, \quad \sigma(A_{hl}) = 9\cdot1, \quad \sigma(A_{kl}) = 2\cdot0 \text{ e.Å}^{-5}.$$

The anisotropic thermal parameters at the end of the refinement are quoted in Table 2 and the observed and calculated structure factors are compared in Table 3.

Table 2. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cd	2·51	2·20	2·74	0·00	0·00	0·07
S	2·37	1·65	3·23	−0·13	−0·06	0·31
O(1)	2·59	1·93	5·65	0·24	−0·42	−0·40
O(2)	3·34	2·18	7·64	−0·10	−0·78	0·36
N(1)	3·32	3·65	3·02	−0·44	−0·64	−0·18
N(2)	2·97	2·41	4·82	−0·79	0·92	−0·49
C(1)	2·03	2·10	4·75	−0·65	−1·02	−0·18
C(2)	3·19	2·54	5·37	−0·09	−0·63	−0·54

The scattering factors used throughout the calculations are those of Thomas & Umeda (1957) for Cd^{2+}, of Dawson (1960) for S and of Berghuis,

Table 3. *Observed and calculated structure factors*

A minus sign after an F_o means ,less than'.

h	k	l	$10F_o$	$10F_c$	α°
0	0	1	526	558	0
0	0	2	337	317	0
0	0	3	119	126	180
0	0	4	427	331	180
0	2	0	665	867	0
0	2	1	466	462	0
0	2	2	238	225	0
0	2	3	69	22	180
0	2	4	308	251	180
0	4	0	407	242	0
0	4	1	397	363	0
0	4	2	238	199	0
0	4	3	99	95	180
0	4	4	198	159	180
0	6	0	714	700	0
0	6	1	595	673	0
0	6	2	179	179	0
0	6	3	79	95	180
0	6	4	55-	114	180
0	8	0	109	31	0
0	8	1	724	851	0
0	8	2	79	60	0
0	8	3	89	97	180
0	8	4	51-	61	180
0	10	0	595	583	0
0	10	1	833	661	0
0	10	2	139	104	0
0	10	3	189	227	180
0	10	4	189	91	180
0	12	0	635	638	0
0	12	1	506	444	0
0	12	2	179	129	0
0	12	3	30	45	180
0	12	4	189	142	180
0	14	0	466	454	0
0	14	1	149	140	0
0	14	2	119	116	0
0	14	3	30-	8	180
0	16	0	466	438	0
0	16	1	60	23	0
0	16	2	208	172	0
0	16	3	26-	28	180
0	18	0	417	448	0
0	18	1	198	166	0
0	18	2	119	113	0
0	18	3	18-	25	0
0	20	0	318	368	0
0	20	1	208	220	0
0	20	2	50	40	0
0	22	0	69	55	0
0	22	1	208	202	0
2	0	0	248	227	0
2	0	1	456	597	0
2	0	2	268	300	0
2	0	3	99	114	180
2	0	4	43-	85	180
2	2	0	466	455	0
2	2	1	804	884	13
2	2	2	268	263	282
2	2	3	119	129	168
2	2	4	149	143	201
2	4	0	903	881	0
2	4	1	556	606	22
2	4	2	189	171	352
2	4	3	139	152	129
2	4	4	189	180	197
2	6	0	992	1129	0
2	6	1	407	427	8
2	6	2	288	287	335
2	6	3	139	144	129
2	6	4	228	207	186
2	8	0	863	807	0
2	8	1	377	378	355
2	8	2	179	171	317
2	8	3	50	46	188
2	8	4	278	223	173
2	10	0	516	523	0
2	10	1	198	127	311
2	10	2	288	261	31
2	10	3	69	66	276
2	10	4	298	165	171
2	12	0	466	484	0
2	12	1	456	418	347
2	12	2	268	180	53
2	12	3	109	117	232
2	12	4	179	126	178
2	14	0	308	295	0
2	14	1	476	446	358
2	14	2	89	91	41
2	14	3	119	117	225
2	16	0	238	230	0
2	16	1	318	316	359
2	16	2	69	69	28
2	16	3	69	75	170
2	18	0	189	193	0
2	18	1	318	326	1
2	18	2	36-	56	305
2	20	0	169	160	0
2	20	1	129	144	19
2	20	2	149	148	307
2	22	0	258	248	0
4	0	0	635	624	0
4	0	1	288	320	0
4	0	2	159	164	0
4	0	3	129	138	180
4	0	4	129	150	180
4	2	0	486	503	0
4	2	1	486	539	330
4	2	2	159	184	37
4	2	3	99	90	252
4	2	4	139	150	167
4	4	0	933	745	0
4	4	1	486	533	338
4	4	2	238	238	54
4	4	3	149	157	221
4	4	4	189	175	148
4	6	0	556	523	0
4	6	1	377	397	356
4	6	2	208	218	47
4	6	3	159	151	219
4	6	4	139	138	176
4	8	0	357	339	0
4	8	1	437	403	355
4	8	2	109	107	7
4	8	3	60	52	233
4	8	4	139	121	195
4	10	0	566	557	0
4	10	1	466	333	23
4	10	2	169	137	315
4	10	3	89	114	129
4	10	4	35-	116	190
4	12	0	268	268	0
4	12	1	337	292	29
4	12	2	308	207	304
4	12	3	109	150	107
4	14	0	347	353	0
4	14	1	298	271	355
4	14	2	198	167	303
4	14	3	60	66	135
4	16	0	308	390	0
4	16	1	189	208	8
4	16	2	89	79	0
4	16	3	15-	44	183
4	18	0	129	143	0
4	18	1	149	163	358
4	18	2	69	95	55
4	20	0	218	186	0
4	20	1	169	179	328
6	0	0	675	662	0
6	0	1	119	153	0
6	0	2	119	138	0
6	0	3	32-	9	180
6	0	4	159	165	180
6	2	0	585	581	0
6	2	1	318	347	13
6	2	2	119	145	320
6	2	3	89	103	130
6	2	4	129	149	196
6	4	0	397	307	0
6	4	1	278	321	27
6	4	2	139	154	331
6	4	3	79	83	130
6	6	0	218	183	0
6	6	1	198	209	9
6	6	2	149	148	297
6	6	3	50	66	111
6	8	0	288	267	0
6	8	1	437	431	355
6	8	2	69	49	354
6	8	3	79	88	177
6	10	0	308	297	0
6	10	1	496	373	352
6	10	2	129	140	37
6	10	3	99	108	216
6	12	0	268	293	0
6	12	1	228	206	345
6	12	2	89	88	68
6	12	3	79	80	236
6	14	0	228	248	0
6	14	1	119	123	343
6	14	2	99	112	51
6	16	0	228	247	0
6	16	1	79	94	348
6	16	2	89	109	345
6	18	0	198	244	0
8	0	0	89	70	0
8	0	1	288	284	0
8	0	2	50	36	0
8	0	3	19-	63	180
8	2	0	119	120	0
8	2	1	298	285	10
8	2	2	39-	60	1
8	2	3	18-	49	179
8	4	0	377	323	0
8	4	1	248	240	341
8	4	2	69	66	11
8	4	3	16-	66	219
8	6	0	437	387	0
8	6	1	119	132	5
8	6	2	99	78	17
8	8	0	347	329	0
8	8	1	99	81	27
8	8	2	89	97	349
8	10	0	327	292	0
8	10	1	79	77	338
8	10	2	99	82	344
8	12	0	159	148	0
8	12	1	149	127	1
8	14	0	129	116	0
10	0	0	298	225	0
10	0	1	19-	78	0
10	2	0	288	227	0
10	4	0	189	161	0
0	1	1	347	318	90
0	1	2	886	1081	90
0	1	3	248	241	90
0	1	4	288	230	90
0	3	1	456	479	90
0	3	2	456	444	90
0	3	3	280	300	90
0	3	4	218	140	90
0	5	1	99	72	90
0	5	2	258	284	90
0	5	3	347	353	90
0	5	4	198	175	90
0	7	1	546	597	90
0	7	2	318	307	90
0	7	3	476	525	90
0	7	4	54-	56	90
0	9	1	585	621	90
0	9	2	189	168	90
0	9	3	377	458	90
0	9	4	129	83	90
0	11	1	476	412	90
0	11	2	417	377	90
0	11	3	248	307	90
0	11	4	189	121	90
0	13	1	268	231	90
0	13	2	496	444	90
0	13	3	179	227	90
0	13	4	89	82	90
0	15	1	69	45	270
0	15	2	318	287	90
0	15	3	28-	59	90
0	17	1	60	72	90
0	17	2	367	359	90
0	17	3	60	70	90
0	19	1	139	132	90
0	19	2	308	311	90
0	21	1	139	151	90
0	21	2	50	120	90
2	1	0	437	461	180
2	1	1	466	555	84
2	1	2	288	329	107
2	1	3	407	464	98
2	1	4	139	126	78
2	3	0	446	298	180
2	3	1	357	387	67
2	3	2	318	323	108
2	3	3	387	435	101
2	3	4	149	124	60
2	5	0	28-	70	0
2	5	1	536	597	64
2	5	2	685	752	93
2	5	3	258	265	94
2	5	4	189	174	74
2	7	0	357	327	180
2	7	1	258	254	72
2	7	2	526	561	89
2	7	3	189	238	91
2	7	4	208	177	80
2	9	0	37-	50	180
2	9	1	178	150	145
2	9	2	466	480	81
2	9	3	129	167	83
2	9	4	198	142	93
2	11	0	327	326	0
2	11	1	238	192	119
2	11	2	446	417	90
2	11	3	149	199	78
2	11	4	218	148	113
2	13	0	99	115	0
2	13	1	337	312	116
2	13	2	238	204	92
2	13	3	238	294	89
2	13	4	22-	93	115
2	15	0	48-	43	0
2	15	1	337	330	98
2	15	2	228	221	83
2	15	3	228	254	91
2	17	0	48-	39	0
2	17	1	218	230	72
2	17	2	129	130	89
2	17	3	198	233	84
2	19	0	139	154	180
2	19	1	169	171	76
2	19	2	109	119	98
2	21	0	139	144	180
2	21	1	69	80	54
4	1	0	79	78	180
4	1	1	298	302	124
4	1	2	327	364	89
4	1	3	218	267	68
4	1	4	119	147	101
4	3	0	357	279	0
4	3	1	446	461	122
4	3	2	466	493	76
4	3	3	298	353	77
4	3	4	109	114	128
4	5	0	367	329	0
4	5	1	258	270	119
4	5	2	347	387	76
4	5	3	228	268	85
4	5	4	198	169	115
4	7	0	40-	47	0
4	7	1	387	388	110
4	7	2	308	333	102
4	7	3	248	270	84
4	7	4	109	99	109
4	9	0	44-	27	0
4	9	1	248	218	79
4	9	2	327	324	99
4	9	3	208	262	101
4	9	4	129	92	78
4	11	0	268	232	180
4	11	1	337	284	33
4	11	2	318	270	90
4	11	3	149	189	99
4	13	0	268	259	180
4	13	1	228	268	66
4	13	2	288	251	95
4	13	3	169	194	92
4	15	0	119	81	180
4	15	1	129	122	89
4	15	2	268	257	94
4	15	3	139	166	93
4	17	0	69	46	0
4	17	1	129	141	93
4	17	2	198	204	91
4	19	0	119	158	0
4	19	1	119	156	127
4	19	2	19-	118	81
4	21	0	20-	111	0
6	1	0	45-	22	180
6	1	1	169	214	54
6	1	2	397	465	98
6	1	3	89	155	95
6	1	4	79	110	86
6	3	0	179	119	180
6	3	1	228	248	64
6	3	2	238	278	98
6	3	3	169	222	101
6	3	4	89	125	67
6	5	0	218	174	180
6	5	1	179	190	60
6	5	2	198	224	95
6	5	3	159	188	102
6	7	0	119	91	180
6	7	1	159	177	66
6	7	2	119	137	100
6	7	3	189	251	88
6	9	0	49-	41	0
6	9	1	417	364	106
6	9	2	208	199	77
6	9	3	208	268	85
6	11	0	69	135	0
6	11	1	288	243	106
6	11	2	268	227	87
6	11	3	149	183	89
6	13	0	119	134	0
6	13	1	129	98	141
6	13	2	179	177	86
6	15	0	41-	39	0
6	15	1	99	104	122
6	15	2	189	208	88
6	17	0	99	75	180
6	17	1	50	60	44
8	1	0	89	61	180
8	1	1	169	181	80
8	1	2	39-	60	83
8	1	3	198	217	89
8	3	0	47-	35	0
8	3	1	288	218	98
8	3	2	169	173	89
8	3	3	182	178	95
8	5	0	46-	42	0
8	5	1	139	129	115
8	5	2	248	247	93
8	7	0	45-	29	180
8	7	1	69	94	59
8	7	2	268	270	87
8	9	0	41-	13	0
8	9	1	40	33	68
8	9	2	268	240	86
8	11	0	37-	64	180
8	11	1	69	52	127
8	11	2	19-	169	102
8	13	0	69	13	180
8	13	1	139	127	80
10	1	0	26-	39	0
10	1	1	19-	65	80
10	3	0	24-	39	0
1	1	0	734	1119	0
1	1	1	625	655	61
1	1	2	218	197	16
1	1	3	139	139	130
1	1	4	258	218	188
1	3	0	972	886	0
1	3	1	955	1027	23
1	3	2	268	257	324
1	3	3	218	201	116
1	3	4	218	209	192
1	5	0	833	811	0
1	5	1	397	426	9
1	5	2	377	353	319
1	5	3	159	155	126
1	5	4	179	169	205
1	7	0	446	404	0
1	7	1	556	578	8
1	7	2	208	179	297
1	7	3	60	91	141
1	7	4	109	135	189
1	9	0	595	545	0
1	9	1	695	689	343
1	9	2	149	142	342
1	9	3	119	146	209
1	9	4	179	130	157
1	11	0	575	550	0
1	11	1	446	372	345
1	11	2	347	295	62
1	11	3	109	158	229
1	11	4	159	124	172
1	13	0	417	406	0
1	13	1	377	332	354
1	13	2	278	224	71
1	13	3	79	86	249
1	13	4	198	139	162
1	15	0	496	500	0
1	15	1	278	259	355
1	15	2	198	175	15
1	15	3	60	71	229
1	17	0	367	358	0
1	17	1	189	181	352
1	17	2	129	121	330
1	17	3	30	35	147
1	19	0	248	247	0
1	19	1	169	155	9
1	19	2	149	151	285
1	21	0	238	240	0
1	21	1	208	222	35
3	1	0	327	307	0
3	1	1	675	787	356
3	1	2	228	219	2
3	1	3	129	131	173
3	1	4	79	87	162
3	3	0	506	494	0
3	3	1	595	619	355
3	3	2	139	133	75
3	3	3	89	92	229
3	3	4	129	135	169
3	5	0	992	975	0
3	5	1	367	375	334
3	5	2	179	166	15
3	5	3	159	169	212
3	5	4	179	186	176
3	7	0	724	759	0
3	7	1	318	323	2
3	7	2	198	192	10
3	7	3	50	50	179
3	7	4	248	210	177
3	9	0	754	796	0
3	9	1	278	241	30
3	9	2	179	197	12
3	9	3	69	28	35
3	9	4	288	204	184
3	11	0	595	571	0
3	11	1	298	241	348
3	11	2	238	246	321
3	11	3	32-	51	121
3	11	4	228	149	188
3	13	0	179	174	0
3	13	1	397	385	11
3	13	2	119	89	324
3	13	3	79	87	143
3	15	0	268	256	0
3	15	1	347	345	5
3	15	2	43-	17	8
3	15	3	79	101	173
3	17	0	189	180	0
3	17	1	318	345	350
3	17	2	40	37	331
3	17	3	16-	77	202
3	19	0	129	124	0
3	19	1	238	259	1
3	19	2	79	109	45
3	21	0	258	232	0
3	21	1	89	97	338
5	1	0	843	881	0
5	1	1	198	221	355
5	1	2	159	176	16
5	1	3	40	44	181
5	1	4	179	205	189
5	3	0	466	451	0
5	3	1	298	348	334
5	3	2	89	106	354
5	3	3	69	78	228
5	3	4	129	151	173
5	5	0	437	359	0
5	5	1	337	369	356
5	5	2	169	180	0
5	5	3	60	69	232
5	5	4	79	96	162
5	7	0	248	261	0
5	7	1	506	545	6
5	7	2	119	135	58
5	7	3	89	90	166
5	7	4	60	70	194
5	9	0	139	139	0
5	9	1	446	419	357
5	9	2	46-	26	47
5	9	3	89	115	177
5	11	0	318	330	0
5	11	1	367	314	12
5	11	2	159	119	309
5	11	3	69	84	178
5	13	0	387	418	0
5	13	1	258	245	355
5	13	2	129	119	324
5	13	3	22-	37	146
5	15	0	318	333	0
5	15	1	60	46	344
5	15	2	129	125	358
5	17	0	298	336	0
5	17	1	79	91	35
5	17	2	89	91	0
5	19	0	238	263	0
5	19	1	139	133	351
7	1	0	308	295	0
7	1	1	278	326	11
7	1	2	79	101	310
7	1	3	60	80	136
7	3	0	238	176	0
7	3	1	298	311	30
7	3	2	89	103	330
7	3	3	89	93	126
7	5	0	575	462	0
7	5	1	208	246	17
7	5	2	119	116	323
7	5	3	79	89	129
7	7	0	466	400	0
7	7	1	169	173	354
7	7	2	159	159	303
7	7	3	99	32	107
7	9	0	278	252	0
7	9	1	169	135	343
7	9	2	99	96	12
7	9	3	60	59	233
7	11	0	278	282	0
7	11	1	208	183	337
7	11	2	139	132	55
7	13	0	198	211	0
7	13	1	208	210	355
7	13	2	119	108	67
7	15	0	139	130	0
7	15	1	208	194	354
9	1	0	159	159	0
9	1	1	189	188	355
9	1	2	27-	71	3
9	3	0	258	236	0
9	3	1	198	191	332
9	3	2	69	78	60
9	5	0	198	178	0
9	5	1	139	146	333
9	5	2	109	107	64
9	7	0	218	206	0
9	7	1	159	152	1
9	9	0	278	227	0
9	9	1	129	116	9
1	0	1	129	150	90
1	0	2	585	713	90
1	0	3	198	208	90
1	0	4	218	180	90
1	2	0	218	166	180
1	2	1	685	757	42
1	2	2	556	581	90
1	2	3	367	383	103
1	2	4	208	164	68
1	4	0	23-	2	180
1	4	1	615	626	52
1	4	2	566	569	107
1	4	3	387	406	106
1	4	4	218	189	68
1	6	0	665	655	180
1	6	1	258	242	84
1	6	2	397	406	94
1	6	3	337	337	86
1	6	4	198	160	61
1	8	0	218	194	180
1	8	1	437	461	91
1	8	2	318	296	81

Table 3 (*cont.*)

h	k	l	$\lvert 10F_o \rvert$	$10F_c$	α°
1	8	3	347	409	92
1	8	4	99	87	79
1	10	0	238	220	90
1	10	1	615	471	115
1	10	2	407	395	84
1	10	3	248	300	81
1	10	4	268	139	115
1	12	0	347	343	0
1	12	1	318	268	126
1	12	2	427	322	83
1	12	3	198	248	75
1	12	4	149	115	127
1	14	0	318	305	0
1	14	1	208	187	92
1	14	2	367	326	85
1	14	3	179	219	99
1	16	0	119	105	180
1	16	1	198	173	115
1	16	2	347	327	89
1	16	3	129	148	77
1	18	0	179	168	180
1	18	1	119	99	71
1	18	2	208	215	102
1	18	3	79	127	87
1	20	0	119	135	180
1	20	1	159	187	40
1	20	2	198	184	92
1	22	0	79	81	180
1	22	1	149	166	63
3	0	1	427	488	90
3	0	2	139	183	90
3	0	3	382	462	90
3	0	4	169	166	90
3	2	0	318	286	0
3	2	1	476	505	79
3	2	2	268	294	83
3	2	3	397	472	90
3	2	4	79	93	118
3	4	0	129	74	180
3	4	1	476	486	135
3	4	2	476	493	82
3	4	3	258	297	78
3	4	4	89	105	100
3	6	0	208	167	0
3	6	1	298	311	92
3	6	2	526	561	95
3	6	3	139	159	92
3	6	4	189	175	100
3	8	0	119	101	0
3	8	1	198	205	65
3	8	2	546	567	86
3	8	3	149	194	91
3	8	4	179	147	91
3	10	0	189	146	180
3	10	1	48–	23	124
3	10	2	516	491	93
3	10	3	129	165	93
3	10	4	298	168	79
3	12	0	169	137	180
3	12	1	288	247	69
3	12	2	357	264	102
3	12	3	179	226	95
3	12	4	13–	108	77
3	14	0	99	56	180
3	14	1	298	302	81
3	14	2	159	152	75
3	14	3	208	250	90
3	16	0	48–	14	0
3	16	1	228	242	93
3	16	2	159	150	100
3	16	3	198	231	93
3	18	0	44–	31	0
3	18	1	238	248	102
3	18	2	89	104	88
3	20	0	60	90	0
3	20	1	109	110	107
5	0	1	198	232	90
5	0	2	556	685	90
5	0	3	89	115	90
5	0	4	109	157	90
5	2	0	18–	40	180
5	2	1	189	187	121
5	2	2	377	424	93
5	2	3	149	188	67
5	2	4	99	127	96
5	4	0	42–	41	0
5	4	1	208	232	121
5	4	2	258	292	83
5	4	3	198	251	96
5	4	4	89	118	94
5	6	0	32–	8	180
5	6	1	298	313	89
5	6	2	208	251	85
5	6	3	278	330	85
5	6	4	79	99	102
5	8	0	228	221	0
5	8	1	327	337	82
5	8	2	79	86	107
5	8	3	268	337	91
5	10	0	99	59	180
5	10	1	417	320	89
5	10	2	189	186	90
5	10	3	189	245	97
5	12	0	248	222	180
5	12	1	228	201	87
5	12	2	347	264	93
5	12	3	149	186	87
5	14	0	48–	31	0
5	14	1	79	67	81
5	14	2	278	273	94
5	14	3	89	107	93
5	16	0	43–	33	180
5	16	1	39–	29	42
5	16	2	238	269	88
5	18	0	35–	15	0
5	18	1	50	61	78
7	0	1	149	167	90
7	0	2	179	195	90
7	0	3	179	226	90
7	2	0	119	87	180
7	2	1	258	291	56
7	2	2	149	189	108
7	2	3	179	227	104
7	4	0	119	51	180
7	4	1	189	221	60
7	4	2	189	222	90
7	4	3	119	170	100
7	6	0	218	150	180
7	6	1	139	140	53
7	6	2	308	320	100
7	6	3	109	143	95
7	8	0	238	149	180
7	8	1	169	134	114
7	8	2	248	256	87
7	8	3	99	123	88
7	10	0	79	122	0
7	10	1	159	114	134
7	10	2	189	181	78
7	12	0	149	185	0
7	12	1	149	141	106
7	12	2	268	199	90
7	14	0	50	77	0
7	14	1	179	165	116
7	14	2	129	123	79
7	16	0	26–	6	0
7	16	1	60	124	95
9	0	1	169	160	90
9	0	2	139	136	90
9	2	0	40–	3	180
9	2	1	149	126	127
9	2	2	119	131	78
9	4	0	208	168	0
9	4	1	169	144	134
9	4	2	139	164	79
9	6	0	60	68	0
9	6	1	149	137	108
9	6	2	19–	148	88
9	8	0	33–	8	180
9	8	1	79	74	95
9	10	0	50	38	180

Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O, N, C.

The comparison between observed and calculated peak heights and curvatures is given in Table 4.

Table 4. *Atomic peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5})

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Cd	obs.	134·7	1398	1468	1301	0	0	27
	calc.	137·5	1421	1455	1354	0	0	9
S	obs.	39·1	427	441	392	−6	2	1
	calc.	40·1	428	444	396	−6	6	−1
O(1)	obs.	12·2	115	118	94	11	−20	−26
	calc.	12·9	112	115	99	11	−19	−25
O(2)	obs.	11·4	105	116	71	3	−7	12
	calc.	11·7	103	115	77	3	−6	10
N(1)	obs.	9·4	92	77	89	−6	−2	1
	calc.	10·3	91	79	89	−5	−1	3
N(2)	obs.	11·4	102	122	80	−10	7	−12
	calc.	11·2	102	123	83	−8	6	−11
C(1)	obs.	10·1	117	122	75	5	−6	−3
	calc.	10·4	114	124	78	7	−4	−2
C(2)	obs.	8·5	83	88	74	−4	−4	−3
	calc.	9·0	81	89	79	−4	−2	−2

Discussion

Each Cd coordinates octahedrally four S atoms lying in a plane containing Cd, and two oxygen atoms from two HCOO$^-$ groups, *trans* to the S plane (Figs. 1 and 2). There are two non-equivalent Cd–S distances; (when the coordinates are not indicated the atom is at *x*, *y*, *z*):

Cd–S	2·740 ± 0·008 Å
Cd–S $(x, y, z-1)$	2·709 ± 0·008 .

These distances cannot be considered significantly different:

$$t_0=(l_1-l_2)/(\sigma_1^2+\sigma_2^2)^{\frac{1}{2}}=2\cdot75\ .$$

The distance

$$\text{Cd}-\text{O}(1)\quad 2\cdot28\ \text{Å} \pm 0\cdot02\ \text{Å}$$

is in good agreement with those already found in other compounds, *e. g.* in bisacetamide-cadmium chloride, 2·23 Å (Cavalca, Nardelli & Coghi, 1957), in bisurea-cadmium chloride, 2·28 Å (Nardelli, Cavalca & Fava, 1957), in monomethylurea-cadmium chloride, 2·18 Å (Nardelli, Coghi & Azzoni, 1958), in bisbiuret-cadmium chloride, 2·34 Å (Cavalca, Nardelli & Fava, 1960).

The octahedra are linked in endless chains running along [001], with a twofold axis along the chain axis, and two S atoms shared by two adjacent octahedra. These octahedra are slightly distorted, as can be seen from the values of the angles on Cd:

S–Cd–S$(\bar{x}, \bar{y}, z)$	87·0 ± 0·2°
S–Cd–S$(x, y, z-1)$	92·4 ± 0·2
S$(x, y, z-1)$–Cd–S$(\bar{x}, \bar{y}, z-1)$	88·2 ± 0·2
S–Cd–O(1)	87·6 ± 0·8
O(1)–Cd–S$(\bar{x}, \bar{y}, z)$	82·3 ± 0·8
O(1)–Cd–S$(x, y, z-1)$	97·7 ± 0·8
O(1)–Cd–S$(\bar{x}, \bar{y}, z-1)$	92·4 ± 0·8

The thiourea molecule is planar, the least-squares equation of the plane being:

$$0\cdot4657\,x+0\cdot2054\,y-0\cdot8608\,z+1\cdot1019=0\ .$$

The e.s.d.'s are such that distances and angles are not significantly different from those found in uncoordinated thiourea:

	Bisthiourea-cadmium formate	Thiourea (Kunchur & Truter, 1958)
S–C(1)	1·76 ± 0·02 Å	1·71 ± 0·01 Å
C(1)–N(1)	1·29 ± 0·04	1·33 ± 0·01
C(1)–N(2)	1·30 ± 0·04	
S–C(1)–N(1)	120·1 ± 2·5°	122·2 ± 0·6°
S–C(1)–N(2)	119·6 ± 2·0	
N(1)–C(1)–N(2)	120·4 ± 2·6	115·6 ± 1·1 .

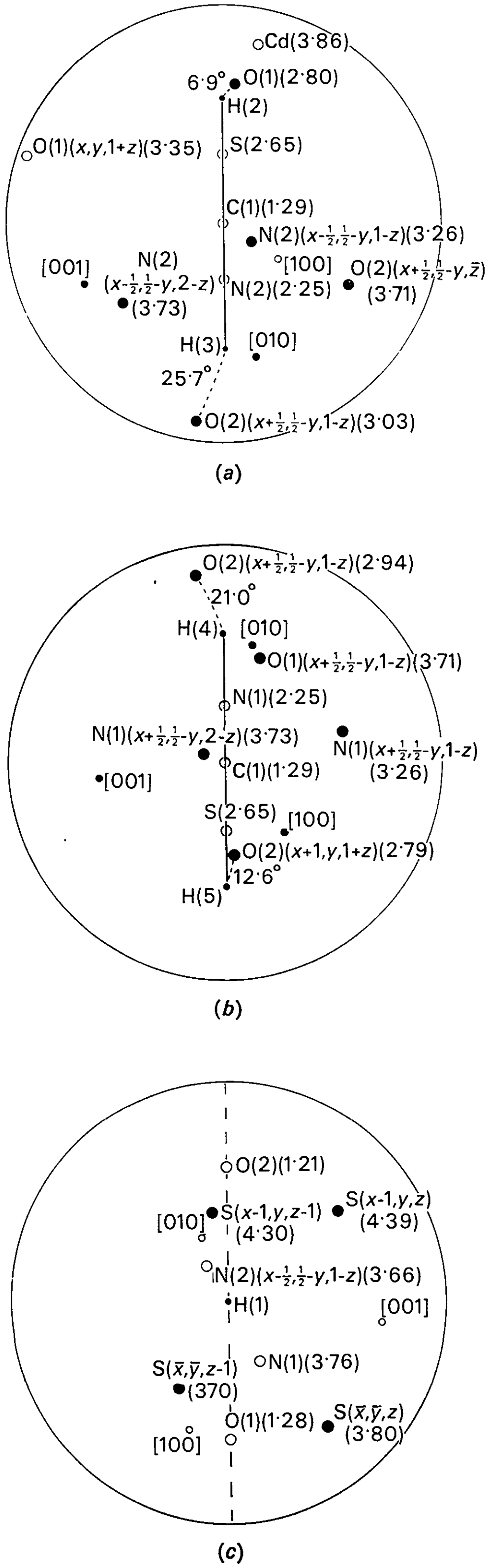

Fig. 3. Stereographic projection of the environment of (*a*) N(1) viewed down N(1)–C(1), (*b*) N(2) viewed down N(2)–C(1), (*c*) C(2) viewed down H(1)–C(2).

The same conclusion holds for the $HCOO^-$ group when compared with formic acid:

	Bisthiourea-cadmium formate	Formic acid (Kwei & Curl, 1960)
C(2)–O(1)	1·28 ± 0·04 Å	1·343 Å
C(2)–O(2)	1·21 ± 0·04	1·202
O(1)–C(2)–O(2)	125·8 ± 3·2°	124° 53′

Direct location of H atoms is impossible owing to the presence of the heavy cadmium atom. Nevertheless, a set of reasonable coordinates can be deduced assuming a trigonal distribution for the $-NH_2$ and $HCOO^-$ groups and the values $N-H=1·03$ and $C-H=1·07$ Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958). These coordinates are listed in Table 5.

Table 5. *Postulated hydrogen fractional coordinates*

	x/a	y/b	z/c
H(1)	−0·398	0·056	−0·014
H(2)	−0·064	0·159	0·428
H(3)	0·005	0·247	0·598
H(4)	0·250	0·253	0·876
H(5)	0·376	0·171	0·924

From the stereographic projections of Fig. 3 it can be shown that the angular criterion for hydrogen-bonding (Donohue, 1952; Fuller, 1959) is adequately fulfilled for the following contacts:

N(1) · · · · O(1)	2·80 ± 0·04 Å
N(2) · · · · O(2) ($x+1$, y, $1+z$)	2·79 ± 0·04 .

The weaker contacts:

N(2) · · · · O(2) ($x+\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$)	2·94 ± 0·03 Å
N(1) · · · · O(2) ($x+\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$)	3·03 ± 0·05

correspond to a greater bond distortion.

The coordination of O(2), shown in Fig. 4, is represented by a severely distorted tetrahedron.

The orientation of the plane of thiourea is determined mainly by the N(1)–H(2) · · · O(1) hydrogen

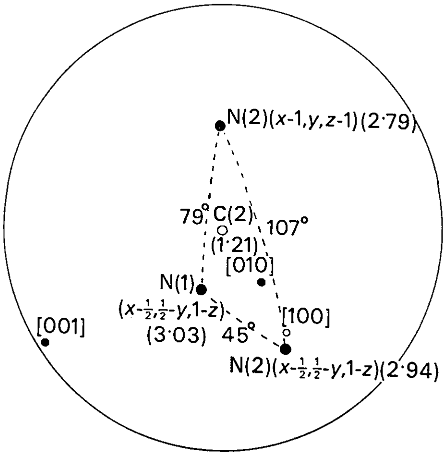

Fig. 4. Stereographic projection of the environment of O(2) viewed down O(2)–C(2).

bond. This interaction and the packing in the chain can account for the departure of the angles around S from the tetrahedral value:

Cd–S–Cd	92·4°
Cd–S–C(1)	115·2
Cd–S $(\bar{x}, \bar{y}, z-1)$–C(1) $(\bar{x}, \bar{y}, z-1)$	102·0 .

Packing of the chains is determined by N · · · O(2) contacts involving two different $HCOO^-$ groups in adjacent chains.

This work was made possible by financial support from the Consiglio Nazionale delle Ricerche.

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The Structure of the Crystalline Intermolecular Complex: Guanidinium Chloride–Disordered *N*,*N*-Dimethylacetamide (3:1)

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(*Received* 1 *June* 1964)

The crystalline complex guanidinium chloride–*N*,*N*-dimethylacetamide is monoclinic, space group $I2/a$, with lattice constants:

$$a=23{\cdot}47,\ b=14{\cdot}90,\ c=11{\cdot}95\ \text{Å};\ \beta=90{\cdot}95^\circ\ .$$

The crystal structure was solved by the heavy atom method and consists of a framework of guanidinium chloride with cylindrical cavities parallel to the c axis. The three guanidinium chloride molecules were refined by least-squares methods to an R value of 0·16. The disordered dimethylacetamide molecules lie in the cylindrical cavities (average diameter about 6 Å) that are continuous through the crystal.

Introduction

A program of study of the crystal structures of molecular complexes involving effective protein denaturants and model compounds has been undertaken in this laboratory in an effort to show specific interactions between protein denaturing agents and amino acid residue-like compounds. A number of these molecular complexes have been obtained; their significance has been discussed elsewhere (Bello & Haas, 1965).

Originally, it was expected that the complex of guanidinium chloride (GCl) with *N*,*N*-dimethylacetamide (DMA) would show interactions between the ions and the DMA, a proline residue analogue. After the crystal structure had been determined, however, it was apparent that no specific bonding could be attributed to the DMA molecules in the crystal.

Experimental

Crystals of the GCl–DMA complex were produced by saturating warm DMA (100 °C) with GCl and allowing the solution to cool slowly. Crystals used for the X-ray analysis were mounted in glass capillaries direct-