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The Crystal Structures of Semicarbazide Complexes of Copper(II) and Zinc Chlorides

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Crystals of $Cu[OC(NH_2)NHNH_2]_2Cl_2$ and $Zn[OC(NH_2)NHNH_2]_2Cl_2$ belong to the same space group $P2_1/c$, but are not isostructural. The two structures were solved and refined by means of three-dimensional Fourier methods. Coordination in both compounds is octahedral, semicarbazide acting as a bidentate ligand through oxygen and hydrazinic nitrogen. The semicarbazide molecule is planar and there are no significant differences in the bond distances between metal-coordinated semicarbazide and semicarbazide hydrochloride. Packing and possible hydrogen bonding are discussed.

Introduction

The X-ray structural analysis of bis-semicarbazide-copper(II) chloride and bis-semicarbazide-zinc chloride was undertaken in this laboratory as part of a programme concerning the coordination by divalent metal atoms of organic molecules containing oxygen.

The present study shows that coordination in these two complexes does not lead to significant differences in the bond distances of the organic molecule in comparison with semicarbazide hydrochloride. A similar conclusion was noted previously for biuret in potassium bis-biuret-cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961) and in bis-biuret-zinc chloride (Nardelli, Fava & Giraldi, 1963).

Experimental

Crystals of bis-semicarbazide-copper(II) chloride and bis-semicarbazide-zinc chloride were obtained by slow evaporation of aqueous chloride solutions containing an excess of semicarbazide hydrochloride. When excess of metal chloride is employed, the monosemicarbazide complexes, $M[OC(NH_2)NHNH_2]Cl_2$ (M = Cu, Zn) are formed.

Crystal data

$Cu[OC(NH_2)NHNH_2]_2Cl_2$. $M=284{\cdot}6$. Blue thick plates, optically biaxial. Monoclinic. Rotation axis for photographs: [001].

$a=7{\cdot}56\pm0{\cdot}01$, $b=9{\cdot}26\pm0{\cdot}01$, $c=6{\cdot}88\pm0{\cdot}01$ Å; $\beta=102{\cdot}2\pm0{\cdot}2°$,

$V=471$ Å^3, $Z=2$, $D_x=2{\cdot}01$, $D_m=2{\cdot}16$ g.cm^{-3} (flotation),

$\mu=84{\cdot}1$ cm^{-1} (Cu $K\alpha$), $F(000)=286$.

Space group $P2_1/c$ (from systematic absences).

$Zn[OC(NH_2)NHNH_2]_2Cl_2$. $M=286{\cdot}4$. Colourless thin pseudo-hexagonal laminae, optically biaxial. Monoclinic. Rotation axes for photographs: [100] and [010].

$a=5{\cdot}13\pm0{\cdot}01$, $b=7{\cdot}13\pm0{\cdot}01$, $c=13{\cdot}26\pm0{\cdot}01$ Å; $\beta=109{\cdot}7\pm0{\cdot}1°$,

$V=457$ Å^3, $Z=2$, $D_x=2{\cdot}08$, $D_m=2{\cdot}10$ g.cm^{-3} (flotation),

$\mu=91{\cdot}6$ cm^{-1} (Cu $K\alpha$), $F(000)=288$.

Space group $P2_1/c$ (from systematic absences).

$Cu[OC(NH_2)NHNH_2]Cl_2$. $M=209{\cdot}5$. Blue, pleochroic, thick short prisms, optically biaxial. Orthorhombic.

Observed forms: {010}, {011}, {302}.

Rotation axis for photographs: [100].

$a=6{\cdot}9_0$, $b=10{\cdot}2_2$, $c=8{\cdot}2_6$ Å,

$V=582$ Å^3, $Z=4$, $D_x=2{\cdot}39$, $D_m=2{\cdot}39$ g.cm^{-3} (flotation).

Space groups $Pnma$ (D_{2h}^{16}), $Pn2_1a$ (C_{2v}^9) (from systematic absences).

$Zn[OC(NH_2)NHNH_2]Cl_2$. $M=211{\cdot}4$. Colourless tabular prisms, optically biaxial. Monoclinic. Rotation axes for photographs: [010], [100].

$a=12{\cdot}7_1$, $b=7{\cdot}4_7$, $c=14{\cdot}9_5$ Å, $\beta=110{\cdot}_3$,

$V=1331$ Å^3, $Z=8$, $D_x=2{\cdot}11$, $D_m=2{\cdot}10$ g.cm^{-3} (flotation).

Space group $P2_1/c$ (C_{2h}^5) (from systematic absences).

Crystal data were obtained by the standard methods using the axial reflexions in equatorial Weissenberg photographs. In the case of the first compound the *h0l* precession photograph too was used. No particular corrections were applied.

The standard deviations were estimated on the measured values by the usual formulae.

Determination of structure factors

For the copper compound the intensities of *hk*0, *hk*1, $\cdots$ *hk*5 reflexions were collected from integrated and non-integrated Weissenberg photographs (Cu $K\alpha$). 662 independent reflexions were observed out of the 831 possible reflexions. No absorption correction was made (cross-section nearly rectangular: 0·02 cm × 0·05 cm); the absolute scale for each layer was established

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

The transformation matrix from monoclinic x, y, z to orthogonal x', y', z' coordinates is:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

	x/a	y/b	z/c	x'(Å)	y'(Å)	z'(Å)	$\sigma(x')$	$\sigma(y')$	$\sigma(z')$ (×10³(Å))	$\lvert r(x)\rvert$	$\lvert r(y)\rvert$	$\lvert r(z)\rvert$
				$Cu[OC(NH_2)NHNH_2]_2Cl_2$								
Cu	0	0	0	0	0	0	—	—	—	—	—	—
Cl	0·2721	0·0710	0·3397	1·563	0·657	2·284	4	3	4	∞	∞	6
O	−0·1408	0·1678	0·0557	−1·145	1·554	0·375	10	8	11	4	∞	∞
N(1)	−0·3933	0·2220	0·1604	−3·204	2·055	1·078	16	11	17	19	∞	8
N(2)	−0·2811	−0·0050	0·2044	−2·420	−0·046	1·374	14	11	16	17	4	3
N(3)	−0·1278	−0·0981	0·1873	−1·237	−0·908	1·259	13	9	13	16	∞	9
C	−0·2643	0·1332	0·1378	−2·197	1·233	0·927	15	11	16	18	∞	8
				$Zn[OC(NH_2)NHNH_2]_2Cl_2$								
Zn	0	0	0	0	0	0	—	—	—	—	—	—
Cl	0·3554	0·1995	0·1464	1·169	1·423	1·827	4	4	4	8	∞	∞
O	−0·0980	−0·1591	0·1123	−1·005	−1·135	1·401	11	9	9	7	6	7
N(1)	−0·0491	−0·4497	0·1818	−1·065	−3·208	2·269	17	14	13	34	20	10
N(2)	0·2140	−0·3544	0·0838	0·723	−2·528	1·046	13	11	11	13	16	∞
N(3)	0·2860	−0·2142	0·0224	1·367	−1·528	0·280	12	11	11	12	16	∞
C	0·0163	−0·3133	0·1265	−0·482	−2·235	1·579	16	11	10	32	16	8

first by Wilson's method, then by comparison with the calculated values.

For the zinc compound the intensities of $h0l$, $h1l, \cdots h6l$ and $0kl$, $1kl, \cdots 4kl$ were collected from integrated and non-integrated Weissenberg photographs (Cu $K\alpha$). 892 (possible 987) independent reflexions were observed. Discontinuous absorption effects were corrected graphically by Albrecht's (1939) method. The cross-section of the sample used to take the first series of photographs was a parallelogram with sides 0·017 cm and 0·014 cm long. The sample used to collect the second series of data was pentagonal in section, its longest diagonal being 0·06 cm.

The intensities from different layers were put on the same scale by cross-correlation (Dickerson, 1959), the absolute scale being established first by Wilson's method.

For both compounds the correction for the shape of the spots of non-equatorial layers was made following Phillips (1956).

Structure analysis and refinement

The steps in solving and refining the structures of both compounds were:

(i) $P(U, V, W)$ Patterson synthesis,
(ii) Two cycles of three-dimensional Fourier synthesis,
(iii) Four cycles of three-dimensional $(F_o - F_c)$ synthesis,
(iv) One isotropic cycle of Booth's differential synthesis,
(v) Four anisotropic cycles of Booth's differential synthesis for the zinc complex, and seven anisotropic cycles for the copper complex.

The final coordinates with their e.s.d.'s (Cruickshank, 1949) and ratios (e.s.d.)/(shift) are listed in Table 1. The anisotropic thermal parameters, determined following Nardelli & Fava (1960), are reported in Table 2. In the case of the copper complex, they must be considered only as additional parameters for improving the agreement between the observed and calculated quantities, correlation of the different layers being neglected.

Table 2. *Thermal parameters* (Å²)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
	$Cu[OC(NH_2)NHNH_2]_2Cl_2$					
Cu	4·11	2·84	6·56	0·38	2·07	0·65
Cl	3·24	2·44	4·26	0·06	0·45	0·03
O	3·96	2·13	4·65	0·24	1·07	0·87
N(1)	3·89	3·51	5·76	0·84	1·59	−0·50
N(2)	2·01	2·67	5·75	0·17	2·36	0·10
N(3)	2·64	2·58	5·15	0·48	1·67	0·16
C	3·33	1·96	4·09	−0·45	1·49	0·05
	$Zn[OC(NH_2)NHNH_2]_2Cl_2$					
Zn	4·85	3·61	6·39	1·26	3·09	1·64
Cl	3·27	3·23	4·10	0·18	1·24	0·28
O	3·43	2·71	4·23	0·37	1·90	0·47
N(1)	4·39	2·99	4·38	−0·37	1·34	0·44
N(2)	3·02	2·24	4·22	0·61	1·09	0·84
N(3)	3·13	2·45	4·42	0·26	1·57	0·90
C	3·95	2·25	2·66	−0·39	0·80	−0·32

The final R(for observed reflexions only) and R' (including $F_o = \frac{1}{2}F_{\min.}$ for unobserved reflexions when $F_c \geq F_{\min.}$), with e.s.d.'s of the first derivatives of the electron density, are:

$Cu[OC(NH_2)NHNH_2]_2Cl_2$	$Zn[OC(NH_2)NHNH_2]_2Cl_2$
$R = 13{\cdot}2\%$	$R = 15{\cdot}2\%$
$R' = 17{\cdot}3\%$	$R' = 15{\cdot}8\%$
$\sigma(A_h) = 0{\cdot}9$ e.Å^{-4}	$\sigma(A_h) = 1{\cdot}1$ e.Å^{-4}
$\sigma(A_k) = 0{\cdot}9$	$\sigma(A_k) = 1{\cdot}1$
$\sigma(A_l) = 0{\cdot}7$	$\sigma(A_l) = 0{\cdot}8$

The observed and calculated values of the electron density and the second derivatives at the atomic peaks are compared in Table 3, in which the corresponding e.s.d.'s are quoted too.

The better general agreement observed for the copper complex is only apparent, being due to the scaling done for each layer separately. The two structures must be considered of about the same degree of refinement.

The F_c values reported in Table 4 are calculated with the final parameters of Tables 1 and 2, using the atomic scattering factors of Thomas & Umeda (1957) for Cu^{2+} and Zn^{2+}, of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Cl^-, O ,N and C.

Discussion

In both compounds each metal atom is surrounded by a *trans*-planar arrangement of two O and two N atoms lying at the corners of a distorted square. Semicarbazide acts as a bidentate ligand through O and hydrazinic N. The coordination is completed by two chlorine atoms which are on opposite sides of the square, so that the whole polyhedron can be described as an octahedron distorted to a bipyramid.

The molecular complexes are very similar, and yet the crystals are not isostructural. Figs. 1 and 2, which are diagrammatic projections of the structures on planes perpendicular to [100], show clearly the different packing of the molecular complexes.

Distances and angles in the coordination polyhedra are as follows:

	$Cu[OC(NH_2)NHNH_2]_2Cl_2$	$Zn[OC(NH_2)NHNH_2]_2Cl_2$
M–Cl	2·845 ± 0·005 Å	2·594 ± 0·004 Å
M–O	1·97 ± 0·01	2·06 ± 0·01
M–N(3)	1·99 ± 0·01	2·07 ± 0·01
O–M–N(3)	83·0 ± 0·4°	79·9 ± 0·4°
Cl–M–O	89·1 ± 0·3	92·5 ± 0·3
Cl–M–N(3)	86·5 ± 0·4	90·8 ± 0·3

The standard deviations are calculated from the formulae of Darlow & Cochran (1961) for bond lengths and of Darlow (1960) for angles.

Distances in the coordination polyhedra agree well with those found in other copper(II) and zinc compounds with similar coordination.

The M–O and M–N(3) distances are equal in each compound, but significantly shorter in the copper complex $[t_o=(l_1-l_2)/(\sigma_1^2+\sigma_2^2)^{\frac{1}{2}}=6\cdot3>3\cdot3$ for M–O; $t_o=4\cdot2>3\cdot3$ for M–N(3); significance test of Cruickshank & Robertson, 1953].

The ratio M–Cl/M–O = 1·44 for the copper complex is much larger than the same ratio (1·26) for the zinc complex, as a consequence of the Jahn–Teller effect in Cu^{2+}.

The comparison of distances and angles in semicarbazide coordinated by Cu^{2+} and Zn^{2+} with those found in semicarbazide hydrochloride (Nardelli, Fava & Gir-

Table 3. *Atomic peak heights* (e. Å^{-3}), *curvatures* (e. Å^{-5}) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
			$Cu[OC(NH_2)NHNH_2]_2Cl_2$					
Cu	obs.	45·8	381	511	261	−7	52	14
	calc.	46·6	387	512	266	−7	52	15
Cl	obs.	28·4	252	323	169	−15	7	−1
	calc.	28·7	254	323	173	−15	9	0
O	obs.	11·6	100	119	65	−3	11	3
	calc.	11·7	102	119	68	−3	12	3
N(1)	obs.	7·5	66	79	40	2	5	−3
	calc.	7·6	65	79	42	1	4	−2
N(2)	obs.	9·1	73	83	42	7	9	−10
	calc.	9·1	71	82	42	7	8	−11
N(3)	obs.	9·1	78	102	54	−3	10	0
	calc.	9·3	79	102	55	−3	10	0
C	obs.	8·1	68	82	42	−5	5	0
	calc.	8·2	69	83	44	−5	5	0
	e.s.d.	0·3	5	4	3	3	2	2
			$Zn[OC(NH_2)NHNH_2]_2Cl_2$					
Zn	obs.	53·5	530	549	466	35	218	61
	calc.	55·4	523	544	461	30	207	56
Cl	obs.	31·9	317	321	298	5	102	3
	calc.	32·7	316	316	296	4	100	4
O	obs.	12·8	114	119	112	−1	46	10
	calc.	13·1	114	120	112	−2	45	11
N(1)	obs.	9·2	75	81	75	0	28	4
	calc.	9·4	74	80	73	0	26	5
N(2)	obs.	11·0	98	107	89	11	28	2
	calc.	11·2	98	107	88	11	27	1
N(3)	obs.	10·9	106	103	92	7	37	5
	calc.	11·0	106	102	91	7	36	4
C	obs.	10·0	81	106	98	3	24	2
	calc.	10·0	79	106	96	3	23	2
	e.s.d.	0·4	5	5	4	3	3	2

Table 4(*a*). *Observed and calculated structure factors for* $Cu[OC(NH_2)NHNH_2]_2Cl_2$

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

h	k	l	$10F_o$	$10F_c$
1	0	0	376	522
2	0	0	437	-444
3	0	0	474	445
4	0	0	479	394
5	0	0	59	-48
6	0	0	40-	-22
7	0	0	356	379
8	0	0	271	208
9	0	0	102	-67
0	2	0	634	801
1	2	0	534	509
2	2	0	87	-45
3	2	0	498	505
4	2	0	582	605
5	2	0	37-	-18
6	2	0	102	64
7	2	0	241	215
8	2	0	119	92
9	2	0	25-	-4
0	4	0	196	224
1	4	0	103	144
2	4	0	354	420
3	4	0	370	441
4	4	0	202	235
5	4	0	248	239
6	4	0	151	127
7	4	0	66	54
8	4	0	41	24
0	6	0	129	130
1	6	0	264	323
2	6	0	286	342
3	6	0	119	116
4	6	0	72	93
5	6	0	170	175
6	6	0	213	181
7	6	0	56	50
8	6	0	33	10
0	8	0	63	73
1	8	0	160	163
2	8	0	228	233
3	8	0	141	137
4	8	0	79	71
5	8	0	147	136
6	8	0	117	103
0	10	0	123	112
1	10	0	123	118
2	10	0	132	128
3	10	0	85	82
4	10	0	54	49
5	10	0	65	55
1	1	0	79	114
2	1	0	103	-67
3	1	0	190	224
4	1	0	132	-137
5	1	0	116	-97
6	1	0	72	71
7	1	0	41-	-8
8	1	0	37-	-1
9	1	0	27-	-3
1	3	0	648	-619
2	3	0	79	72
3	3	0	63	76
4	3	0	92	-110
5	3	0	95	-79
6	3	0	146	133
7	3	0	132	104
8	3	0	149	-103
9	3	0	46	-31
1	5	0	339	-413
2	5	0	88	-94
3	5	0	223	240
4	5	0	116	-117
5	5	0	116	-115
6	5	0	182	150
7	5	0	65	49
8	5	0	116	-85
1	7	0	39-	46
2	7	0	153	148
3	7	0	92	73
4	7	0	44	-44
5	7	0	107	-86
6	7	0	72	-63
7	7	0	27-	-7
1	9	0	164	169
2	9	0	40-	-18
3	9	0	116	-117
4	9	0	43	50
5	9	0	65	54
6	9	0	87	-70
1	11	0	80	73
2	11	0	74	-72
3	11	0	116	-101
0	1	1	542	581
1	1	1	593	627
1	1	1	594	566
2	1	1	548	650
2	1	1	335	359
3	1	1	333	381
3	1	1	15-	25
4	1	1	20-	35
4	1	1	155	180
5	1	1	80	85
5	1	1	350	379
6	1	1	183	181
6	1	1	216	249
7	1	1	120	96
7	1	1	81	121
8	1	1	47	39
8	1	1	52	105
9	1	1	72	58
9	1	1	18-	83
0	3	1	46	59
1	3	1	110	152
1	3	1	527	453
2	3	1	415	369
2	3	1	650	535
3	3	1	379	314
3	3	1	583	521
4	3	1	379	330
4	3	1	189	282
5	3	1	175	195
5	3	1	195	202
6	3	1	144	129
6	3	1	132	160
7	3	1	72	70
7	3	1	25-	21
8	3	1	19-	16
8	3	1	34	50
9	3	1	15-	91
0	5	1	605	480
1	5	1	535	464
1	5	1	36	45
2	5	1	21-	-15
2	5	1	506	391
3	5	1	81	100
3	5	1	527	446
4	5	1	199	268
4	5	1	136	150
5	5	1	177	204
5	5	1	25-	26
6	5	1	46	26
6	5	1	128	145
7	5	1	86	80
7	5	1	152	168
8	5	1	102	116
8	5	1	18-	-7
0	7	1	463	386
1	7	1	563	460
1	7	1	26	-28
2	7	1	50	-36
2	7	1	92	74
3	7	1	69	-74
3	7	1	575	479
4	7	1	256	343
4	7	1	110	133
5	7	1	136	152
5	7	1	78	-111
6	7	1	74	-69
6	7	1	175	176
7	7	1	69	75
7	7	1	163	173
0	9	1	167	188
1	9	1	195	235
1	9	1	74	-71
2	9	1	25-	17
2	9	1	120	124
3	9	1	87	85
3	9	1	204	254
4	9	1	153	185
4	9	1	112	114
5	9	1	96	105
5	9	1	19-	13
6	9	1	78	77
0	11	1	69	79
1	11	1	87	104
1	11	1	94	115
2	11	1	100	131
2	11	1	42	55
3	11	1	52	58
3	11	1	22	24
0	2	1	466	-438
1	2	1	530	594
1	2	1	303	-263
2	2	1	375	350
2	2	1	409	376
3	2	1	316	-308
3	2	1	16-	-23
4	2	1	152	-197
4	2	1	232	-292
5	2	1	127	108
5	2	1	22-	-7
6	2	1	26-	24
6	2	1	210	203
7	2	1	136	-114
7	2	1	34	-17
8	2	1	36	31
8	2	1	50	-89
9	2	1	80	80
9	2	1	17-	52
0	4	1	67	-76
1	4	1	69	76
1	4	1	36	56
2	4	1	84	81
2	4	1	566	416
3	4	1	413	-352
3	4	1	72	84
4	4	1	125	-161
4	4	1	263	-370
5	4	1	183	196
5	4	1	42	-48
6	4	1	64	42
6	4	1	94	99
7	4	1	80	-70
7	4	1	39	-26
8	4	1	17-	6
8	4	1	21-	-21
0	6	1	130	-148
1	6	1	72	57
1	6	1	30	-32
2	6	1	23-	-5
2	6	1	34	40
3	6	1	25-	2
3	6	1	24-	-25
4	6	1	26-	15
4	6	1	42	51
5	6	1	26-	-6
5	6	1	26-	15
6	6	1	24-	-2
6	6	1	50	39
7	6	1	58	-51
7	6	1	21-	-10
8	6	1	28	-31
0	8	1	36	28
1	8	1	90	-85
1	8	1	98	-95
2	8	1	36	38
2	8	1	130	-142
3	8	1	102	99
3	8	1	46	45
4	8	1	30	23
4	8	1	86	91
5	8	1	58	-48
5	8	1	63	74
6	8	1	72	-59
6	8	1	19-	-7
7	8	1	13-	0
0	10	1	80	80
1	10	1	67	-72
1	10	1	72	73
2	10	1	108	-126
2	10	1	67	-65
3	10	1	52	45
3	10	1	20-	-13
4	10	1	50	33
4	10	1	74	89
5	10	1	44	-48
0	0	2	74	-23
1	0	2	948	1429
1	0	2	379	-465
2	0	2	613	507
2	0	2	584	774
3	0	2	126	-113
3	0	2	403	397
4	0	2	161	174
4	0	2	16-	-10
5	0	2	335	337
5	0	2	286	229
6	0	2	23-	21
6	0	2	440	533
7	0	2	136	-110
7	0	2	109	197
8	0	2	185	130
8	0	2	21-	-118
9	0	2	16-	70
0	2	2	64	73
1	2	2	424	462
1	2	2	74	94
2	2	2	477	493
2	2	2	604	617
3	2	2	47	-22
3	2	2	592	648
4	2	2	238	234
4	2	2	47	5
5	2	2	345	343
5	2	2	249	222
6	2	2	56	24
6	2	2	351	339
7	2	2	27	-21
7	2	2	41	47
8	2	2	80	65
8	2	2	20-	16
9	2	2	15-	92
0	4	2	205	222
1	4	2	201	202
1	4	2	525	482
2	4	2	143	146
2	4	2	450	508
3	4	2	223	236
3	4	2	141	141
4	4	2	130	134
4	4	2	232	222
5	4	2	109	93
5	4	2	187	204
6	4	2	170	133
6	4	2	68	76
7	4	2	92	65
7	4	2	58	62
8	4	2	39	33
8	4	2	18-	99
0	6	2	363	381
1	6	2	138	129
1	6	2	429	434
2	6	2	199	203
2	6	2	108	101
3	6	2	181	183
3	6	2	23	36
4	6	2	29	22
4	6	2	164	159
5	6	2	22-	-11
5	6	2	190	187
6	6	2	119	96
6	6	2	80	79
7	6	2	152	121
7	6	2	64	59
8	6	2	99	128
0	8	2	160	148
1	8	2	24	34
1	8	2	238	217
2	8	2	115	103
2	8	2	135	136
3	8	2	185	185
3	8	2	101	103
4	8	2	108	92
4	8	2	194	185
5	8	2	33	24
5	8	2	130	138
6	8	2	91	68
6	8	2	16-	19
7	8	2	50	38
0	10	2	50	49
1	10	2	56	55
1	10	2	92	95
2	10	2	109	103
2	10	2	101	87
3	10	2	124	120
3	10	2	82	72
4	10	2	82	68
4	10	2	112	113
5	10	2	115	104
0	1	2	149	-138
1	1	2	226	247
1	1	2	121	-115
2	1	2	97	113
2	1	2	287	-331
3	1	2	33	11
3	1	2	14-	34
4	1	2	135	116
4	1	2	185	128
5	1	2	127	-109
5	1	2	119	-59
6	1	2	101	-84
6	1	2	97	98
7	1	2	21-	11
7	1	2	23-	33
8	1	2	16-	17
8	1	2	59	-32
9	1	2	16-	-21
0	3	2	506	487
1	3	2	169	179
1	3	2	339	-328
2	3	2	203	-224
2	3	2	223	-234
3	3	2	119	21
3	3	2	89	105
4	3	2	82	82
4	3	2	58	-17
5	3	2	67	-68
5	3	2	97	-114
6	3	2	170	-147
6	3	2	45	-10
7	3	2	59	41
7	3	2	121	172
8	3	2	99	75
8	3	2	19-	16
9	3	2	13-	-75
0	5	2	287	280
1	5	2	85	67
1	5	2	27	-6
2	5	2	305	-329
2	5	2	205	-192
3	5	2	124	-100
3	5	2	170	152
4	5	2	183	185
4	5	2	89	90
5	5	2	64	-44
5	5	2	219	-237
6	5	2	119	-95
6	5	2	45	-39
7	5	2	62	53
7	5	2	108	126
8	5	2	16-	27
0	7	2	42	-51
1	7	2	42	-53
1	7	2	130	-112
2	7	2	47	-31
2	7	2	24	-24
3	7	2	39	39
3	7	2	97	87
4	7	2	47	38
4	7	2	91	71
5	7	2	20-	3
5	7	2	22-	28
6	7	2	56	-32
6	7	2	19-	-25
7	7	2	15-	-28
0	9	2	164	-156
1	9	2	64	-58
1	9	2	47	56
2	9	2	97	96
2	9	2	135	128
3	9	2	23	-24
3	9	2	58	-68
4	9	2	101	-102
4	9	2	68	-57
5	9	2	21	23
5	9	2	67	78
6	9	2	32	28
0	11	2	82	-78
1	11	2	16	-29
1	11	2	74	73
2	11	2	62	60
2	11	2	68	73
3	11	2	56	-68
0	1	3	363	393
1	1	3	145	181
1	1	3	351	337
2	1	3	103	111
2	1	3	85	105
3	1	3	271	285
3	1	3	217	289
4	1	3	235	227
4	1	3	417	468
5	1	3	28	20
5	1	3	233	222
6	1	3	38	37
6	1	3	80	67
7	1	3	108	95
7	1	3	31-	126
8	1	3	48	33
8	1	3	28-	121
9	1	3	22-	26
0	3	3	305	323
1	3	3	21-	10
1	3	3	378	406
2	3	3	305	307
2	3	3	197	217
3	3	3	242	242
4	3	3	158	143
4	3	3	257	268
5	3	3	106	99
5	3	3	178	213
6	3	3	75	64
6	3	3	31-	12
7	3	3	81	58
7	3	3	30-	80
8	3	3	26-	153
9	3	3	18-	73
0	5	3	69	67
1	5	3	295	311
1	5	3	335	325
2	5	3	304	337
2	5	3	258	264
3	5	3	67	65
3	5	3	28	-33
4	5	3	26	-25
4	5	3	69	74
5	5	3	69	66
5	5	3	195	235
6	5	3	116	93
6	5	3	233	201
7	5	3	16-	-2
7	5	3	27-	47
8	5	3	22-	96
0	7	3	30-	-26
1	7	3	197	194
1	7	3	148	148
2	7	3	328	345
2	7	3	360	356
3	7	3	30-	0
3	7	3	42	38
4	7	3	103	-97
4	7	3	92	-92
5	7	3	164	143
5	7	3	211	243
6	7	3	116	90
6	7	3	216	181
7	7	3	20-	-5
0	9	3	94	-78
1	9	3	73	61
1	9	3	158	145
2	9	3	144	135
2	9	3	257	248
3	9	3	28	35
3	9	3	98	91
4	9	3	31	29
4	9	3	56	61
5	9	3	95	97
0	11	3	15-	84
0	2	3	266	-248
1	2	3	285	-298
1	2	3	122	133
2	2	3	254	279
2	2	3	181	-183
2	2	3	244	283
3	2	3	207	-235
3	2	3	95	-78
4	2	3	154	163
4	2	3	154	-127
5	2	3	309	292
5	2	3	55	41
6	2	3	30-	-21
6	2	3	25-	9
7	2	3	64	-126
7	2	3	27-	33
8	2	3	94	-70
8	2	3	27-	23
9	2	3	20-	10
0	4	3	27-	23
1	4	3	176	-175
1	4	3	269	238
2	4	3	26-	19
2	4	3	23-	-14
3	4	3	140	140
3	4	3	297	-315
4	4	3	137	-136
4	4	3	45	37
5	4	3	112	-100
5	4	3	111	135
6	4	3	102	87
6	4	3	78	-64
7	4	3	37	28
7	4	3	29-	-17
8	4	3	24-	61
0	6	3	28-	-6
1	6	3	99	-100
1	6	3	94	84
2	6	3	23	-10
2	6	3	55	-42
3	6	3	38	-25
3	6	3	38	16
4	6	3	30-	-12
4	6	3	31-	-3
5	6	3	23	-18
5	6	3	31-	-14
6	6	3	22-	9
6	6	3	29-	-27
7	6	3	24-	-26
0	8	3	53	-35
1	8	3	40	40
1	8	3	102	-96
2	8	3	59	-53
2	8	3	71	60
3	8	3	32	-30
3	8	3	59	40
4	8	3	24-	3
4	8	3	29-	-4
5	8	3	28	14
5	8	3	26-	-25
6	8	3	22-	-12
0	10	3	26-	8
1	10	3	67	69
1	10	3	53	-51
2	10	3	34	-38
2	10	3	23-	16
3	10	3	128	-111
3	10	3	83	63
4	10	3	67	-77
0	0	4	52	-21
1	0	4	51	-29
2	0	4	362	425
2	0	4	267	234
3	0	4	178	194
3	0	4	130	-60
4	0	4	99	-95
4	0	4	301	227
5	0	4	29-	2
5	0	4	288	354
6	0	4	196	172
6	0	4	29-	110
7	0	4	44	45
7	0	4	29-	-56
8	0	4	26-	145
9	0	4	18-	118
0	2	4	164	174
1	2	4	43	-37
1	2	4	403	395
2	2	4	141	160
2	2	4	378	348
3	2	4	203	212
3	2	4	38	51
4	2	4	37	-26
4	2	4	171	218
5	2	4	72	56
5	2	4	275	261
6	2	4	146	129
6	2	4	29-	-14
7	2	4	29	28
7	2	4	29-	62
8	2	4	25-	147
9	2	4	16-	70
0	4	4	225	225
1	4	4	130	135
1	4	4	211	195
2	4	4	74	75
2	4	4	27	19
3	4	4	95	106
3	4	4	218	212
4	4	4	139	142
4	4	4	249	270
5	4	4	25	31
5	4	4	48	75
6	4	4	22-	3
6	4	4	68	78
7	4	4	27-	140
8	4	4	21-	112
0	6	4	237	247
1	6	4	227	237
1	6	4	44	-40
2	6	4	60	57
2	6	4	27	-25
3	6	4	80	84
3	6	4	172	168
4	6	4	106	113
4	6	4	178	171
5	6	4	17	16
5	6	4	74	90
6	6	4	43	-43
6	6	4	82	108
7	6	4	77	162
0	8	4	139	139
1	8	4	106	106
1	8	4	59	60
2	8	4	26-	-14
2	8	4	82	86
3	8	4	17	18
3	8	4	176	167
4	8	4	93	98
4	8	4	108	101
5	8	4	22-	-9
6	8	4	60	48
0	10	4	68	80
1	10	4	21	27
1	10	4	80	73
2	10	4	69	60
3	10	4	106	107
0	1	4	141	-156
1	1	4	99	-104
1	1	4	149	-135
2	1	4	116	111
2	1	4	40	42
3	1	4	27	13
3	1	4	130	146
4	1	4	43	13
4	1	4	23-	-9
5	1	4	72	66
5	1	4	106	103
6	1	4	27	-25
6	1	4	29-	15
7	1	4	37	-37
7	1	4	29-	-93
8	1	4	26-	-29
9	1	4	18-	-2
0	3	4	272	-282
1	3	4	127	127
1	3	4	123	-130
2	3	4	76	74
2	3	4	207	202
3	3	4	80	-101
3	3	4	23-	7
4	3	4	22	-16
4	3	4	72	-60
5	3	4	91	90
5	3	4	28-	38
6	3	4	19	10
6	3	4	29-	99
7	3	4	76	-79
7	3	4	28-	-56
8	3	4	23-	-103
0	5	4	85	-77
1	5	4	116	114
1	5	4	98	-80
2	5	4	68	65
2	5	4	154	131
3	5	4	159	-177
3	5	4	44	44
4	5	4	68	-69
4	5	4	218	-215
5	5	4	104	97
5	5	4	21	-23
6	5	4	19-	3

Table 4(*a*) (*cont.*)

h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$
$\bar{6}$	5	4	83	119	$\bar{1}$	9	4	77	70	6	1	5	19-	-9	0	5	5	136	126	$\bar{3}$	7	5	29	-30	$\bar{5}$	2	5	25-	-88	1	6	5	25-	5
$\bar{7}$	5	4	25-	-5	2	9	4	43	-42	$\bar{6}$	1	5	26-	183	1	5	5	26-	-3	$\bar{4}$	7	5	15-	12	6	2	5	40	-53	$\bar{1}$	6	5	76	-65
$\bar{8}$	5	4	17-	-38	$\bar{2}$	9	4	95	-101	$\bar{7}$	1	5	25-	145	$\bar{1}$	5	5	121	101	$\bar{4}$	7	5	234	194	$\bar{6}$	2	5	25-	-136	2	6	5	23	-38
0	7	4	51	-45	3	9	4	48	55	$\bar{8}$	1	5	20-	25	2	5	5	69	84	$\bar{5}$	7	5	164	125	$\bar{7}$	2	5	25-	24	2	6	5	27	-22
$\bar{1}$	7	4	19	3	$\bar{3}$	9	4	80	-70	0	3	5	143	147	$\bar{2}$	5	5	25	-28	$\bar{6}$	7	5	17-	-6	$\bar{8}$	2	5	20-	14	$\bar{3}$	6	5	24-	-7
$\bar{1}$	7	4	44	-34	$\bar{4}$	9	4	35	58	$\bar{1}$	3	5	124	144	$\bar{3}$	5	5	104	140	0	9	5	91	100	0	4	5	142	145	$\bar{3}$	6	5	25-	13
$\bar{2}$	7	4	28-	-3	$\bar{5}$	9	4	15-	5	$\bar{1}$	3	5	91	85	$\bar{4}$	5	5	161	135	1	9	5	27	-31	$\bar{1}$	4	5	20	40	$\bar{4}$	6	5	20-	2
$\bar{3}$	7	4	29-	13	0	1	5	140	151	2	3	5	25-	-6	$\bar{4}$	5	5	47	60	$\bar{1}$	9	5	140	140	1	4	5	30	-23	$\bar{5}$	6	5	25-	-22
3	7	4	25	-16	1	1	5	224	267	$\bar{2}$	3	5	203	180	4	5	5	262	214	$\bar{2}$	9	5	23	31	2	4	5	124	-146	$\bar{5}$	6	5	25-	-14
$\bar{3}$	7	4	29-	-7	$\bar{1}$	1	5	33	21	3	3	5	21	22	5	5	5	12	-14	$\bar{3}$	9	5	17-	42	$\bar{3}$	4	5	169	-140	$\bar{6}$	6	5	21-	-2
4	7	4	24-	-12	2	1	5	79	98	$\bar{3}$	3	5	271	231	$\bar{5}$	5	5	150	128	0	2	5	97	110	3	4	5	20	-33	$\bar{7}$	6	5	15-	38
$\bar{4}$	7	4	28-	-9	$\bar{2}$	1	5	173	182	4	3	5	76	84	6	5	5	24-	44	1	2	5	74	-79	$\bar{3}$	4	5	78	66	0	8	5	69	-73
5	7	4	17-	-6	3	1	5	45	-39	$\bar{4}$	3	5	164	134	$\bar{7}$	5	5	20-	74	$\bar{1}$	2	5	74	-78	4	4	5	64	77	1	8	5	22-	-15
$\bar{5}$	7	4	27-	-13	$\bar{3}$	1	5	241	246	5	3	5	52	65	0	7	5	104	107	2	2	5	142	-177	$\bar{4}$	4	5	67	60	$\bar{1}$	8	5	24-	3
$\bar{6}$	7	4	22-	-9	4	1	5	45	63	$\bar{5}$	3	5	26-	-12	1	7	5	33	-37	$\bar{2}$	2	5	111	-93	5	4	5	27	-38	2	8	5	29	38
$\bar{7}$	7	4	15-	11	$\bar{4}$	1	5	22-	35	6	3	5	16-	18	$\bar{1}$	7	5	192	171	3	2	5	47	47	$\bar{5}$	4	5	142	-123	$\bar{2}$	8	5	21	-17
0	9	4	68	67	5	1	5	74	86	$\bar{6}$	3	5	25-	84	2	7	5	38	42	$\bar{3}$	2	5	185	166	6	4	5	25-	-24	3	8	5	34	-38
1	9	4	74	-75	$\bar{5}$	1	5	25-	31	$\bar{7}$	3	5	24-	151	$\bar{2}$	7	5	25-	-4	4	2	5	107	122	$\bar{7}$	4	5	22-	62	$\bar{4}$	8	5	20-	10
										8	3	5	19-	33	3	7	5	131	159	4	2	5	181	162	0	6	5	40	42	5	8	5	16-	17

aldi, 1963), shows that the coordination makes no appreciable difference to the bond distances and angles (Table 5 and Fig. 3); the small difference observed for the C–N(2)–N(3) angle has only minor statistical significance.

However, the distortion from planarity observed in semicarbazide hydrochloride (N(3) is 0·44 Å out of the plane of the other heavy atoms), is not present in the coordinated molecule (Table 6): semicarbazide is quite planar in the zinc complex, and only small deviations from planarity (of minor statistical significance) are observed in the copper complex. This fact seems to confirm the hypothesis that the distortion observed in semicarbazide hydrochloride is due to the interactions with Cl^-'s involving the $-N(3)H_3^+$ group.

There are no variations in the intermolecular contacts O · · · N(3).

The planes of the semicarbazide molecules are slightly tilted with respect to the planes of coordination; the [MON(3)]–[ON(1)N(2)N(3)C] dihedral angles are

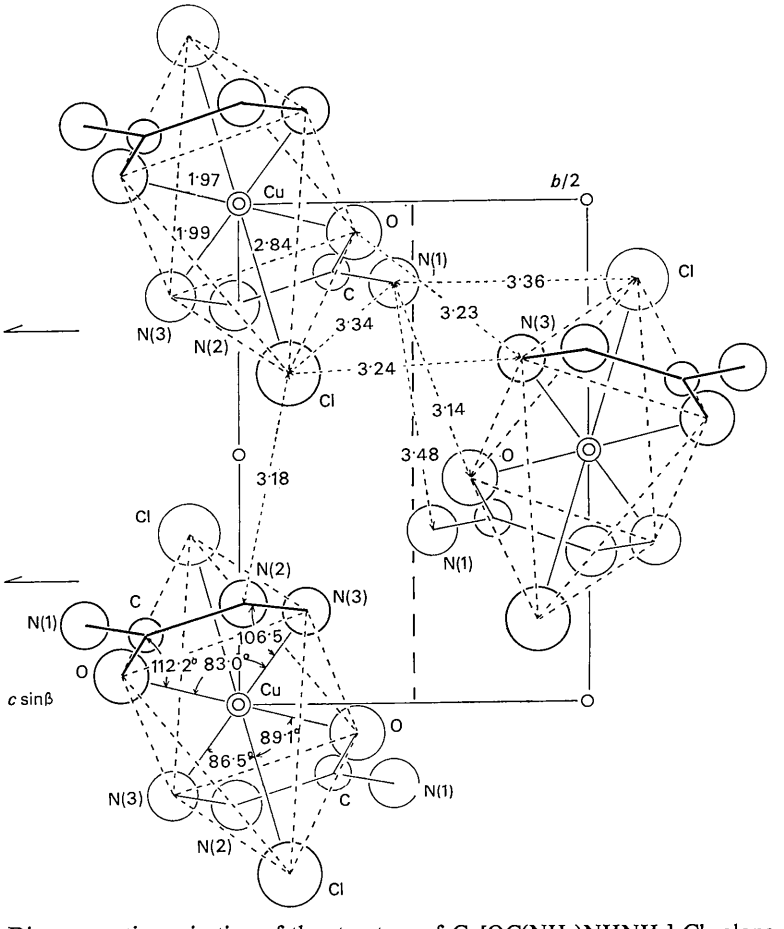

Fig. 1. Diagrammatic projection of the structure of $Cu[OC(NH_2)NHNH_2]_2Cl_2$ along [100].

Table 4(*b*). *Observed and calculated structure factors for* $Zn[OC(NH_2)NHNH_2]_2Cl_2$

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

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
1	0	0	894	778
2	0	0	301	293
3	0	0	712	572
4	0	0	96	48
5	0	0	104	83
6	0	0	88	69
0	2	0	157	-257
1	2	0	589	652
2	2	0	404	521
3	2	0	31	11
4	2	0	287	218
5	2	0	59	74
0	4	0	223	306
1	4	0	113	149
2	4	0	181	222
3	4	0	276	277
4	4	0	100	85
5	4	0	25	49
0	6	0	299	348
1	6	0	225	207
2	6	0	159	129
3	6	0	133	124
4	6	0	58	45
0	8	0	52	-45
1	8	0	116	83
2	8	0	65	42
0	0	2	575	590
1	0	2	159	-46
$\bar{1}$	0	2	866	987
2	0	2	595	568
$\bar{2}$	0	2	504	-457
3	0	2	303	205
$\bar{3}$	0	2	94	62
4	0	2	227	161
$\bar{4}$	0	2	392	251
5	0	2	148	124
$\bar{5}$	0	2	60	-49
$\bar{6}$	0	2	173	111
0	2	2	155	241
1	2	2	474	571
$\bar{1}$	2	2	63	-56
2	2	2	61	65
$\bar{2}$	2	2	469	680
3	2	2	227	211
$\bar{3}$	2	2	133	178
4	2	2	133	110
$\bar{4}$	2	2	18	-4
5	2	2	27	27
$\bar{5}$	2	2	165	182
$\bar{6}$	2	2	11-	4
0	4	2	186	249
1	4	2	145	185
$\bar{1}$	4	2	232	288
2	4	2	208	218
$\bar{2}$	4	2	127	162
3	4	2	83	71
$\bar{3}$	4	2	243	284
4	4	2	54	46
$\bar{4}$	4	2	188	193
5	4	2	30	48
$\bar{5}$	4	2	17-	8
0	6	2	180	177
1	6	2	146	122
$\bar{1}$	6	2	247	242
2	6	2	216	183
$\bar{2}$	6	2	92	76
3	6	2	98	92
$\bar{3}$	6	2	54	56
4	6	2	59	50
$\bar{4}$	6	2	89	79
0	8	2	158	120
1	8	2	170	124
$\bar{1}$	8	2	44	42
2	8	2	9-	-12
$\bar{2}$	8	2	243	157
$\bar{3}$	8	2	50	47
0	0	4	393	-333
1	0	4	209	161
$\bar{1}$	0	4	425	356
2	0	4	56	-34
$\bar{2}$	0	4	478	470
3	0	4	109	79
$\bar{3}$	0	4	54	-32
4	0	4	254	197
$\bar{4}$	0	4	396	337
5	0	4	94	-67
$\bar{5}$	0	4	269	186
$\bar{6}$	0	4	24-	13
0	2	4	561	679
1	2	4	174	200
$\bar{1}$	2	4	372	452
2	2	4	262	287
$\bar{2}$	2	4	316	374
3	2	4	124	125
$\bar{3}$	2	4	406	536
4	2	4	51	-48
$\bar{4}$	2	4	96	98
5	2	4	65	90
$\bar{5}$	2	4	110	103
$\bar{6}$	2	4	116	137

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
0	4	4	257	333
1	4	4	288	331
$\bar{1}$	4	4	243	287
2	4	4	88	95
$\bar{2}$	4	4	198	217
3	4	4	37	40
$\bar{3}$	4	4	152	158
4	4	4	50	52
$\bar{4}$	4	4	195	201
$\bar{5}$	4	4	52	67
0	6	4	34	-27
1	6	4	82	82
$\bar{1}$	6	4	91	88
2	6	4	92	90
$\bar{2}$	6	4	143	135
3	6	4	54	62
$\bar{3}$	6	4	28	23
$\bar{4}$	6	4	63	61
0	8	4	196	162
1	8	4	25	30
$\bar{1}$	8	4	108	99
$\bar{2}$	8	4	58	57
$\bar{3}$	8	4	105	118
0	0	6	553	543
1	0	6	181	151
$\bar{1}$	0	6	136	133
2	0	6	31	12
$\bar{2}$	0	6	657	605
3	0	6	362	302
$\bar{3}$	0	6	608	497
4	0	6	29-	14
$\bar{4}$	0	6	121	75
$\bar{5}$	0	6	247	181
$\bar{6}$	0	6	37	28
0	2	6	147	150
1	2	6	304	337
$\bar{1}$	2	6	534	554
2	2	6	259	318
$\bar{2}$	2	6	260	237
3	2	6	45	-33
$\bar{3}$	2	6	132	133
4	2	6	71	82
$\bar{4}$	2	6	231	237
$\bar{5}$	2	6	50	35
$\bar{6}$	2	6	78	81
0	4	6	286	366
1	4	6	165	180
$\bar{1}$	4	6	179	181
2	4	6	57	63
$\bar{2}$	4	6	120	108
3	4	6	104	112
$\bar{3}$	4	6	112	118
4	4	6	44	39
$\bar{4}$	4	6	103	104
$\bar{5}$	4	6	95	110
0	6	6	89	72
1	6	6	77	72
$\bar{1}$	6	6	90	68
2	6	6	29	39
$\bar{2}$	6	6	224	205
3	6	6	41	54
$\bar{3}$	6	6	178	163
$\bar{4}$	6	6	44	57
0	8	6	10	-5
1	8	6	26	28
$\bar{1}$	8	6	116	114
$\bar{2}$	8	6	40	44
0	0	8	476	384
1	0	8	42	-35
$\bar{1}$	0	8	447	433
2	0	8	274	239
$\bar{2}$	0	8	51	26
3	0	8	83	69
$\bar{3}$	0	8	546	448
4	0	8	75	-59
$\bar{4}$	0	8	300	226
$\bar{5}$	0	8	42	-28
$\bar{6}$	0	8	151	91
0	2	8	45	-50
1	2	8	213	225
$\bar{1}$	2	8	60	-48
2	2	8	48	-45
$\bar{2}$	2	8	285	315
3	2	8	16-	12
$\bar{3}$	2	8	20	-2
4	2	8	61	71
$\bar{4}$	2	8	71	68
$\bar{5}$	2	8	179	172
$\bar{6}$	2	8	31	30
0	4	8	131	143
1	4	8	20-	-10
$\bar{1}$	4	8	166	184
2	4	8	61	64
$\bar{2}$	4	8	20	24
3	4	8	45	61
$\bar{3}$	4	8	55	101
$\bar{4}$	4	8	124	121
$\bar{5}$	4	8	86	83
0	6	8	159	152
1	6	8	98	93

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
$\bar{1}$	6	8	167	151
2	6	8	81	87
$\bar{2}$	6	8	153	133
$\bar{3}$	6	8	169	164
$\bar{4}$	6	8	77	74
0	0	10	63	46
1	0	10	231	181
$\bar{1}$	0	10	416	357
2	0	10	137	114
$\bar{2}$	0	10	140	110
3	0	10	90	-59
$\bar{3}$	0	10	37	-2
$\bar{4}$	0	10	423	319
$\bar{5}$	0	10	138	66
$\bar{6}$	0	10	19-	-1
0	2	10	213	210
1	2	10	32	42
$\bar{1}$	2	10	16-	15
2	2	10	19	4
$\bar{2}$	2	10	212	221
3	2	10	49	69
$\bar{3}$	2	10	294	309
$\bar{4}$	2	10	33	21
$\bar{5}$	2	10	147	129
$\bar{6}$	2	10	90	112
0	4	10	20-	32
1	4	10	20-	21
$\bar{1}$	4	10	163	178
2	4	10	20	31
$\bar{2}$	4	10	134	149
$\bar{3}$	4	10	77	88
$\bar{4}$	4	10	130	140
$\bar{5}$	4	10	70	76
0	6	10	59	48
1	6	10	73	73
$\bar{1}$	6	10	81	77
$\bar{2}$	6	10	50	40
$\bar{3}$	6	10	30	25
$\bar{4}$	6	10	68	61
0	0	12	76	53
1	0	12	104	84
$\bar{1}$	0	12	73	-51
2	0	12	76	-51
$\bar{2}$	0	12	127	96
$\bar{3}$	0	12	77	-64
$\bar{4}$	0	12	50	36
$\bar{5}$	0	12	294	174
0	2	12	103	92
1	2	12	31	40
$\bar{1}$	2	12	172	176
2	2	12	78	96
$\bar{2}$	2	12	50	62
$\bar{3}$	2	12	153	184
$\bar{4}$	2	12	103	112
$\bar{5}$	2	12	26	-11
0	4	12	52	56
1	4	12	29	36
$\bar{1}$	4	12	78	76
$\bar{2}$	4	12	126	134
$\bar{3}$	4	12	63	82
$\bar{4}$	4	12	44	53
0	6	12	17	13
$\bar{1}$	6	12	16-	2
$\bar{2}$	6	12	37	35
$\bar{3}$	6	12	18	7
0	0	14	106	76
1	0	14	96	-74
$\bar{1}$	0	14	63	32
$\bar{2}$	0	14	30-	0
$\bar{3}$	0	14	139	120
$\bar{4}$	0	14	41	36
$\bar{5}$	0	14	165	90
0	2	14	26	-20
1	2	14	56	66
$\bar{1}$	2	14	31	37
$\bar{2}$	2	14	71	86
$\bar{3}$	2	14	14-	11
$\bar{4}$	2	14	74	82
0	4	14	36	36
$\bar{1}$	4	14	25	30
$\bar{2}$	4	14	19	20
$\bar{3}$	4	14	45	56
$\bar{4}$	4	14	29	31
$\bar{1}$	0	16	196	148
$\bar{2}$	0	16	127	63
$\bar{3}$	0	16	78	58
$\bar{4}$	0	16	182	106
$\bar{1}$	2	16	31	-38
$\bar{2}$	2	16	44	44
$\bar{3}$	2	16	31	46
1	1	0	197	-178
2	1	0	192	183
3	1	0	488	-332
4	1	0	152	-114
5	1	0	146	130
6	1	0	37	-45
1	3	0	30	42
2	3	0	127	-203
3	3	0	25-	-7
4	3	0	94	-67

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
5	3	0	83	-103
1	5	0	31	-33
2	5	0	46	-41
3	5	0	20	-7
4	5	0	17-	4
5	5	0	31	-44
1	7	0	113	-95
2	7	0	28	6
3	7	0	93	-74
1	9	0	39	48
0	1	2	194	136
1	1	2	868	936
$\bar{1}$	1	2	217	330
2	1	2	28	-18
$\bar{2}$	1	2	223	294
3	1	2	275	-239
$\bar{3}$	1	2	111	-132
4	1	2	224	182
$\bar{4}$	1	2	141	140
5	1	2	21	-23
$\bar{5}$	1	2	25-	-9
$\bar{6}$	1	2	50	-65
0	3	2	231	281
1	3	2	153	-169
$\bar{1}$	3	2	37	50
2	3	2	43	48
$\bar{2}$	3	2	139	-127
3	3	2	83	74
$\bar{3}$	3	2	61	67
4	3	2	146	-121
$\bar{4}$	3	2	40	-38
5	3	2	21-	12
$\bar{5}$	3	2	26-	16
$\bar{6}$	3	2	12-	11
0	5	2	127	-140
1	5	2	71	-76
$\bar{1}$	5	2	87	-81
2	5	2	16	-10
$\bar{2}$	5	2	31	40
3	5	2	29	32
$\bar{3}$	5	2	56	44
4	5	2	16-	11
$\bar{4}$	5	2	18-	-8
$\bar{5}$	5	2	13-	3
0	7	2	16-	7
1	7	2	116	105
$\bar{1}$	7	2	116	108
2	7	2	12-	11
$\bar{2}$	7	2	138	93
3	7	2	49	-42
$\bar{3}$	7	2	8-	-14
$\bar{4}$	7	2	44	54
0	9	2	76	63
$\bar{1}$	9	2	26	29
0	1	4	486	418
1	1	4	226	226
$\bar{1}$	1	4	526	-610
2	1	4	347	-346
$\bar{2}$	1	4	63	35
3	1	4	149	133
$\bar{3}$	1	4	44	-43
4	1	4	45	43
$\bar{4}$	1	4	186	-212
5	1	4	73	-67
$\bar{5}$	1	4	133	118
$\bar{6}$	1	4	29	18
0	3	4	204	-226
1	3	4	208	-208
$\bar{1}$	3	4	179	185
2	3	4	88	71
$\bar{2}$	3	4	204	-213
3	3	4	104	-105
$\bar{3}$	3	4	115	-136
4	3	4	26-	-21
$\bar{4}$	3	4	77	79
5	3	4	22	29
$\bar{5}$	3	4	26-	-21
$\bar{6}$	3	4	15-	17
0	5	4	147	-160
1	5	4	111	-104
$\bar{1}$	5	4	124	-129
2	5	4	81	-73
$\bar{2}$	5	4	42	36
3	5	4	65	-68
$\bar{3}$	5	4	101	98
4	5	4	45	-47
$\bar{4}$	5	4	47	26
$\bar{5}$	5	4	13-	-14
0	7	4	15-	-4
1	7	4	26	-21
$\bar{1}$	7	4	126	-111
2	7	4	116	-94
$\bar{2}$	7	4	14-	5
3	7	4	5-	10
$\bar{3}$	7	4	8-	-15
$\bar{4}$	7	4	36	34
0	1	6	110	98
1	1	6	404	-405
$\bar{1}$	1	6	179	-174
2	1	6	28	-25

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
$\bar{2}$	1	6	356	-403
3	1	6	50	51
$\bar{3}$	1	6	200	198
4	1	6	54	-56
$\bar{4}$	1	6	103	-77
$\bar{5}$	1	6	78	-73
$\bar{6}$	1	6	136	129
0	3	6	140	-125
1	3	6	80	61
$\bar{1}$	3	6	110	112
2	3	6	49	-55
$\bar{2}$	3	6	192	214
3	3	6	30	-26
$\bar{3}$	3	6	111	-116
4	3	6	28	26
$\bar{4}$	3	6	63	64
$\bar{5}$	3	6	108	101
$\bar{6}$	3	6	16-	-19
0	5	6	67	67
1	5	6	62	72
$\bar{1}$	5	6	25	23
2	5	6	25	-20
$\bar{2}$	5	6	44	64
3	5	6	63	-76
$\bar{3}$	5	6	78	109
$\bar{4}$	5	6	55	49
$\bar{5}$	5	6	13-	-9
0	7	6	35	-26
1	7	6	161	-126
$\bar{1}$	7	6	54	-51
2	7	6	22	-23
$\bar{2}$	7	6	104	-89
$\bar{3}$	7	6	32	36
0	1	8	261	-238
1	1	8	51	-37
$\bar{1}$	1	8	159	164
2	1	8	44	50
$\bar{2}$	1	8	46	-19
3	1	8	77	-77
$\bar{3}$	1	8	23-	-8
4	1	8	56	56
$\bar{4}$	1	8	176	162
$\bar{5}$	1	8	134	-107
$\bar{6}$	1	8	17-	-8
0	3	8	20	19
1	3	8	74	-67
$\bar{1}$	3	8	103	-88
2	3	8	31	-27
$\bar{2}$	3	8	47	48
3	3	8	44	55
$\bar{3}$	3	8	27-	5
4	3	8	21	-33
$\bar{4}$	3	8	148	-109
$\bar{5}$	3	8	50	48
$\bar{6}$	3	8	14-	8
0	5	8	44	40
1	5	8	44	49
$\bar{1}$	5	8	71	-68
2	5	8	22	-27
$\bar{2}$	5	8	103	-104
$\bar{3}$	5	8	46	-57
$\bar{4}$	5	8	24	-23
$\bar{5}$	5	8	18	-18
0	7	8	87	-77
1	7	8	27	-31
$\bar{1}$	7	8	19	23
$\bar{2}$	7	8	25	-31
$\bar{3}$	7	8	32	-29
0	1	10	41	36
1	1	10	151	150
$\bar{1}$	1	10	80	-73
2	1	10	89	-86
$\bar{2}$	1	10	237	237
3	1	10	21	20
$\bar{3}$	1	10	37	35
$\bar{4}$	1	10	25-	4
$\bar{5}$	1	10	57	39
$\bar{6}$	1	10	90	-70
0	3	10	90	-94
1	3	10	111	-116
$\bar{1}$	3	10	28-	9
2	3	10	29	32
$\bar{2}$	3	10	74	-94
3	3	10	21	-38
$\bar{3}$	3	10	28-	5
$\bar{4}$	3	10	27-	-8
$\bar{5}$	3	10	43	-37
0	5	10	51	-46
1	5	10	67	-69
$\bar{1}$	5	10	92	-94
2	5	10	45	-65
$\bar{2}$	5	10	63	-110
$\bar{3}$	5	10	51	-57
$\bar{4}$	5	10	14-	-7
0	7	10	27	-20
$\bar{1}$	7	10	26	-21
$\bar{2}$	7	10	35	40
0	1	12	181	160
1	1	12	33	-30
$\bar{1}$	1	12	85	-84

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
2	1	12	18	-17
$\bar{2}$	1	12	91	-87
$\bar{3}$	1	12	131	120
$\bar{4}$	1	12	63	-72
$\bar{5}$	1	12	47	-32
0	3	12	81	-77
1	3	12	50	45
$\bar{1}$	3	12	22	25
$\bar{2}$	3	12	29	37
$\bar{3}$	3	12	57	-67
$\bar{4}$	3	12	28	30
0	5	12	18	-13
1	5	12	35	-37
$\bar{1}$	5	12	16-	11
$\bar{2}$	5	12	16-	4
$\bar{3}$	5	12	14-	13
0	1	14	35	-32
1	1	14	58	-53
$\bar{1}$	1	14	32	19
$\bar{2}$	1	14	178	-174
$\bar{3}$	1	14	45	-42
$\bar{4}$	1	14	67	50
$\bar{5}$	1	14	90	-70
0	3	14	19-	-3
$\bar{1}$	3	14	65	-62
$\bar{2}$	3	14	24	23
$\bar{3}$	3	14	25	-27
$\bar{4}$	3	14	60	-46
$\bar{2}$	5	14	9-	11
$\bar{1}$	1	16	20	5
$\bar{2}$	1	16	22	17
$\bar{3}$	1	16	62	-59
$\bar{4}$	1	16	40	48
0	1	1	437	533
1	1	1	233	271
$\bar{1}$	1	1	310	395
2	1	1	537	412
$\bar{2}$	1	1	168	235
3	1	1	228	200
$\bar{3}$	1	1	282	357
4	1	1	25-	3
$\bar{4}$	1	1	166	131
5	1	1	42	44
$\bar{5}$	1	1	31	25
$\bar{6}$	1	1	51	64
0	3	1	58	114
1	3	1	352	469
$\bar{1}$	3	1	288	411
2	3	1	46	-34
$\bar{2}$	3	1	516	639
3	3	1	50	49
$\bar{3}$	3	1	100	92
4	3	1	263	234
$\bar{4}$	3	1	217	230
5	3	1	31	31
$\bar{5}$	3	1	201	231
0	5	1	339	431
1	5	1	41	-42
$\bar{1}$	5	1	201	236
2	5	1	191	217
$\bar{2}$	5	1	92	-103
3	5	1	162	156
$\bar{3}$	5	1	218	234
4	5	1	28	-19
$\bar{4}$	5	1	50	54
5	5	1	46	80
$\bar{5}$	5	1	31	-33
0	7	1	35	22
1	7	1	297	299
$\bar{1}$	7	1	89	85
2	7	1	187	150
$\bar{2}$	7	1	371	233
3	7	1	82	71
$\bar{3}$	7	1	8-	5
$\bar{4}$	7	1	31	26
0	9	1	103	95
$\bar{1}$	9	1	74	68
0	1	3	500	512
1	1	3	680	674
$\bar{1}$	1	3	430	569
2	1	3	490	487
$\bar{2}$	1	3	269	303
3	1	3	170	172
$\bar{3}$	1	3	222	261
4	1	3	166	145
$\bar{4}$	1	3	250	282
5	1	3	71	71
$\bar{5}$	1	3	77	76
$\bar{6}$	1	3	31	34
0	3	3	460	611
1	3	3	132	145
$\bar{1}$	3	3	276	347
2	3	3	37	13
$\bar{2}$	3	3	483	560
3	3	3	196	208
$\bar{3}$	3	3	268	337
4	3	3	27-	-12
$\bar{4}$	3	3	43	-52
5	3	3	18-	2
$\bar{5}$	3	3	117	137

h	k	l	$\lvert 10F_o \rvert$	$10F_c$
$\bar{6}$	3	3	45	71
0	5	3	78	100
1	5	3	215	233
$\bar{1}$	5	3	369	432
2	5	3	226	238
$\bar{2}$	5	3	119	116
3	5	3	31	35
$\bar{3}$	5	3	47	55
4	5	3	157	145
$\bar{4}$	5	3	237	253
$\bar{5}$	5	3	13-	-17
0	7	3	165	121
1	7	3	123	103
$\bar{1}$	7	3	100	-78
2	7	3	105	63
$\bar{2}$	7	3	113	86
3	7	3	82	77
$\bar{3}$	7	3	143	122
$\bar{4}$	7	3	11-	-7
0	1	5	269	256
1	1	5	245	260
$\bar{1}$	1	5	90	124
2	1	5	30	33
$\bar{2}$	1	5	288	267
3	1	5	112	97
$\bar{3}$	1	5	230	204
4	1	5	103	92
$\bar{4}$	1	5	225	225
5	1	5	26	30
$\bar{5}$	1	5	203	184
$\bar{6}$	1	5	49	41
0	3	5	192	184
1	3	5	71	61
$\bar{1}$	3	5	333	403
2	3	5	335	340
$\bar{2}$	3	5	77	83
3	3	5	60	58
$\bar{3}$	3	5	159	182
4	3	5	24-	-16
$\bar{4}$	3	5	40	21
$\bar{5}$	3	5	67	-66
$\bar{6}$	3	5	76	97
0	5	5	185	199
1	5	5	262	243
$\bar{1}$	5	5	100	105
2	5	5	26	-25
$\bar{2}$	5	5	328	335
3	5	5	131	141
$\bar{3}$	5	5	109	101
4	5	5	82	91
$\bar{4}$	5	5	116	117
$\bar{5}$	5	5	121	150
0	7	5	115	87
1	7	5	40	40
$\bar{1}$	7	5	161	132
2	7	5	116	100
$\bar{2}$	7	5	12-	19
$\bar{3}$	7	5	127	129
$\bar{4}$	7	5	122	95
0	1	7	392	387
1	1	7	45	46
$\bar{1}$	1	7	349	366
2	1	7	25-	10
$\bar{2}$	1	7	285	300
3	1	7	47	50
$\bar{3}$	1	7	354	340
4	1	7	19	-12
$\bar{4}$	1	7	218	193
$\bar{5}$	1	7	180	152
$\bar{6}$	1	7	103	89
0	3	7	41	-34
1	3	7	384	365
$\bar{1}$	3	7	195	208
2	3	7	195	211
$\bar{2}$	3	7	291	316
3	3	7	27-	11
$\bar{3}$	3	7	85	80
4	3	7	87	93
$\bar{4}$	3	7	209	208
$\bar{5}$	3	7	103	93
$\bar{6}$	3	7	42	46
0	5	7	237	251
1	5	7	76	-76
$\bar{1}$	5	7	79	75
2	5	7	19	29
$\bar{2}$	5	7	37	42
3	5	7	80	108
$\bar{3}$	5	7	192	233
$\bar{4}$	5	7	40	34
$\bar{5}$	5	7	45	54
0	7	7	25	23
1	7	7	143	127
$\bar{1}$	7	7	143	132
2	7	7	22	22
$\bar{2}$	7	7	154	136
$\bar{3}$	7	7	7-	3
0	1	9	196	193
1	1	9	90	95
$\bar{1}$	1	9	325	349
2	1	9	122	128

Table 4(*b*) (*cont.*)

h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$	h k l	$\lvert 10F_o \rvert$	$10F_c$
$\bar{2}$ 1 9	169	154	2 3 11	16	−11	1 2 1	225	−250	$\bar{2}$ 2 3	247	295	4 2 5	16−	−26	2 4 7	135	−147	$\bar{4}$ 6 9	34	40
3 1 9	34	45	$\bar{2}$ 3 11	28−	2	$\bar{1}$ 2 1	262	355	3 2 3	41	−10	$\bar{4}$ 2 5	83	−98	$\bar{2}$ 4 7	116	128	0 2 11	89	81
$\bar{3}$ 1 9	122	108	$\bar{3}$ 3 11	196	227	2 2 1	51	−50	$\bar{3}$ 2 3	70	−74	$\bar{5}$ 2 5	16−	−8	3 4 7	18−	5	1 2 11	16	−9
$\bar{4}$ 1 9	143	117	$\bar{4}$ 3 11	70	78	$\bar{2}$ 2 1	92	96	4 2 3	17−	7	6 2 5	40	39	$\bar{3}$ 4 7	152	−162	$\bar{1}$ 2 11	50	−56
$\bar{5}$ 1 9	52	34	$\bar{5}$ 3 11	51	40	3 2 1	241	−220	$\bar{4}$ 2 3	94	−105	0 4 5	242	−277	$\bar{4}$ 4 7	143	−152	2 2 11	72	−73
$\bar{6}$ 1 9	62	54	0 5 11	17	14	$\bar{3}$ 2 1	47	−53	5 2 3	90	−109	1 4 5	17−	−20	$\bar{5}$ 4 7	61	77	$\bar{2}$ 2 11	17−	−1
0 3 9	162	164	1 5 11	111	123	4 2 1	43	−14	$\bar{5}$ 2 3	16−	−3	$\bar{1}$ 4 5	208	266	0 6 7	44	−38	$\bar{3}$ 2 11	60	−63
1 3 9	216	208	$\bar{1}$ 5 11	96	100	$\bar{4}$ 2 1	24	29	6 2 3	26	−37	2 4 5	17	3	1 6 7	130	−116	$\bar{4}$ 2 11	120	−125
$\bar{1}$ 3 9	70	−70	$\bar{2}$ 5 11	126	144	5 2 1	30	−30	0 4 3	55	86	$\bar{2}$ 4 5	54	66	$\bar{1}$ 6 7	79	67	$\bar{5}$ 2 11	13−	−1
2 3 9	27−	−7	$\bar{3}$ 5 11	18	−26	$\bar{5}$ 2 1	64	−75	1 4 3	292	−351	3 4 5	159	−154	2 6 7	27	24	0 4 11	116	−112
$\bar{2}$ 3 9	267	289	$\bar{4}$ 5 11	91	107	6 2 1	9−	11	$\bar{1}$ 4 3	235	281	$\bar{3}$ 4 5	193	−211	$\bar{2}$ 6 7	148	−124	1 4 11	18	−11
3 3 9	61	71	0 1 13	71	62	0 4 1	98	138	2 4 3	79	85	4 4 5	16−	22	$\bar{3}$ 6 7	37	38	$\bar{1}$ 4 11	50	54
$\bar{3}$ 3 9	225	245	1 1 13	32	35	1 4 1	47	−67	$\bar{2}$ 4 3	106	−130	$\bar{4}$ 4 5	94	113	$\bar{4}$ 6 7	41	36	2 4 11	70	73
4 3 9	104	100	$\bar{1}$ 1 13	39	42	$\bar{1}$ 4 1	262	−349	3 4 3	54	−46	5 4 5	17−	−8	0 8 7	61	−53	$\bar{2}$ 4 11	63	−71
$\bar{5}$ 3 9	186	188	2 1 13	22	18	2 4 1	103	−126	$\bar{3}$ 4 3	189	214	0 6 5	218	206	$\bar{1}$ 8 7	81	−81	$\bar{3}$ 4 11	28	−33
6 3 9	41	56	$\bar{2}$ 1 13	131	126	$\bar{2}$ 4 1	32	−45	4 4 3	134	−108	1 6 5	73	−54	$\bar{2}$ 8 7	6−	3	$\bar{4}$ 4 11	58	78
0 5 9	40	30	$\bar{3}$ 1 13	134	140	3 4 1	195	195	$\bar{4}$ 4 3	170	168	$\bar{1}$ 6 5	103	−82	0 2 9	52	−48	$\bar{5}$ 4 11	19	−30
1 5 9	18	−14	$\bar{4}$ 1 13	102	86	$\bar{3}$ 4 1	41	46	5 4 3	36	59	2 6 5	82	−84	1 2 9	30	28	0 6 11	17	8
$\bar{1}$ 5 9	231	239	$\bar{5}$ 1 13	136	101	4 4 1	37	−44	$\bar{5}$ 4 3	25	24	$\bar{2}$ 6 5	23−	−9	$\bar{1}$ 2 9	51	65	$\bar{1}$ 6 11	139	−136
2 5 9	107	119	0 3 13	25	26	$\bar{4}$ 4 1	58	−64	0 6 3	65	−45	3 6 5	61	68	2 2 9	109	−110	$\bar{2}$ 6 11	22	−22
$\bar{2}$ 5 9	22	−21	1 3 13	30	31	5 4 1	14−	−14	1 6 3	116	114	$\bar{3}$ 6 5	131	124	$\bar{2}$ 2 9	46	61	$\bar{3}$ 6 11	17−	10
$\bar{3}$ 5 9	55	64	$\bar{1}$ 3 13	149	147	$\bar{5}$ 4 1	82	104	$\bar{1}$ 6 3	140	−138	$\bar{4}$ 6 5	92	−81	3 2 9	77	−88	0 2 13	31	32
4 5 9	127	155	$\bar{2}$ 3 13	37	38	0 6 1	195	−199	2 6 3	260	−229	0 8 5	115	−96	$\bar{3}$ 2 9	50	−55	1 2 13	47	52
$\bar{5}$ 5 9	18	−21	$\bar{3}$ 3 13	19	23	1 6 1	25	3	$\bar{2}$ 6 3	148	127	1 8 5	26	20	$\bar{4}$ 2 9	103	111	$\bar{1}$ 2 13	25	23
0 7 9	103	94	$\bar{4}$ 3 13	94	97	$\bar{1}$ 6 1	30	−5	3 6 3	87	−88	$\bar{1}$ 8 5	14−	−2	$\bar{5}$ 2 9	32	30	$\bar{2}$ 2 13	73	−73
1 7 9	41	72	$\bar{5}$ 3 13	11−	−4	2 6 1	20	11	$\bar{3}$ 6 3	37	−32	$\bar{2}$ 8 5	22	−16	6 2 9	43	−52	$\bar{3}$ 2 13	13	15
$\bar{1}$ 7 9	25	24	0 5 13	77	86	$\bar{2}$ 6 1	121	−123	4 6 3	25	32	$\bar{3}$ 8 5	51	−51	0 4 9	89	98	$\bar{4}$ 2 13	40	−34
$\bar{2}$ 7 9	156	148	$\bar{1}$ 5 13	13−	3	3 6 1	205	−200	$\bar{4}$ 6 3	25	24	0 2 7	82	−80	1 4 9	61	−61	$\bar{5}$ 2 13	32	−35
$\bar{3}$ 7 9	40	59	$\bar{2}$ 5 13	63	76	$\bar{3}$ 6 1	50	−35	0 8 3	13−	−9	1 2 7	132	−129	$\bar{1}$ 4 9	29	−21	0 4 13	96	−97
0 1 11	25−	13	$\bar{3}$ 5 13	63	78	4 6 1	21−	13	1 8 3	102	−66	$\bar{1}$ 2 7	59	−54	2 4 9	64	72	1 4 13	15	14
1 1 11	82	73	0 1 15	34	21	$\bar{4}$ 6 1	102	87	$\bar{1}$ 8 3	65	62	2 2 7	31	17	$\bar{2}$ 4 9	50	−43	$\bar{1}$ 4 13	67	−71
$\bar{1}$ 1 11	94	93	$\bar{1}$ 1 15	37	32	0 8 1	46	26	2 8 3	80	66	$\bar{2}$ 2 7	237	−246	3 4 9	41	54	$\bar{2}$ 4 13	49	55
2 1 11	43	42	$\bar{2}$ 1 15	20	17	1 8 1	103	−85	$\bar{2}$ 8 3	10−	−19	3 2 7	75	−80	$\bar{3}$ 4 9	96	113	$\bar{3}$ 4 13	51	−70
$\bar{2}$ 1 11	145	141	$\bar{3}$ 1 15	73	68	$\bar{1}$ 8 1	17−	23	$\bar{3}$ 8 3	40	21	$\bar{3}$ 2 7	125	135	$\bar{4}$ 4 9	67	−74	$\bar{4}$ 4 13	13−	5
3 1 11	31	28	$\bar{4}$ 1 15	58	56	2 8 1	89	−61	0 2 5	237	190	4 2 7	12−	−17	$\bar{5}$ 4 9	15−	8	0 2 15	44	−43
$\bar{3}$ 1 11	42	40	0 3 15	31	35	$\bar{2}$ 8 1	123	63	1 2 5	93	92	$\bar{4}$ 2 7	172	182	0 6 9	123	−108	$\bar{1}$ 2 15	25	28
$\bar{4}$ 1 11	101	93	$\bar{1}$ 3 15	21	25	$\bar{3}$ 8 1	5	12	$\bar{1}$ 2 5	360	−401	$\bar{5}$ 2 7	30	−18	1 6 9	27	27	$\bar{2}$ 2 15	12−	−1
$\bar{5}$ 1 11	132	92	$\bar{2}$ 3 15	82	89	0 2 3	98	−133	2 2 5	88	77	$\bar{6}$ 2 7	49	50	$\bar{1}$ 6 9	27	−25	$\bar{3}$ 2 15	11−	−12
0 3 11	137	132	$\bar{3}$ 3 15	17−	−5	1 2 3	259	299	$\bar{2}$ 2 5	143	−140	0 4 7	90	−110	2 6 9	31	−46	$\bar{4}$ 2 15	51	50
1 3 11	56	−51	$\bar{4}$ 3 15	7−	9	$\bar{1}$ 2 3	153	−187	3 2 5	151	145	1 4 7	20−	7	$\bar{2}$ 6 9	41	35	$\bar{1}$ 4 15	34	−45
$\bar{1}$ 3 11	44	42	0 2 1	264	−392	2 2 3	75	−71	$\bar{3}$ 2 5	172	167	$\bar{1}$ 4 7	182	−192	$\bar{3}$ 6 9	68	−59	$\bar{2}$ 4 15	10−	5

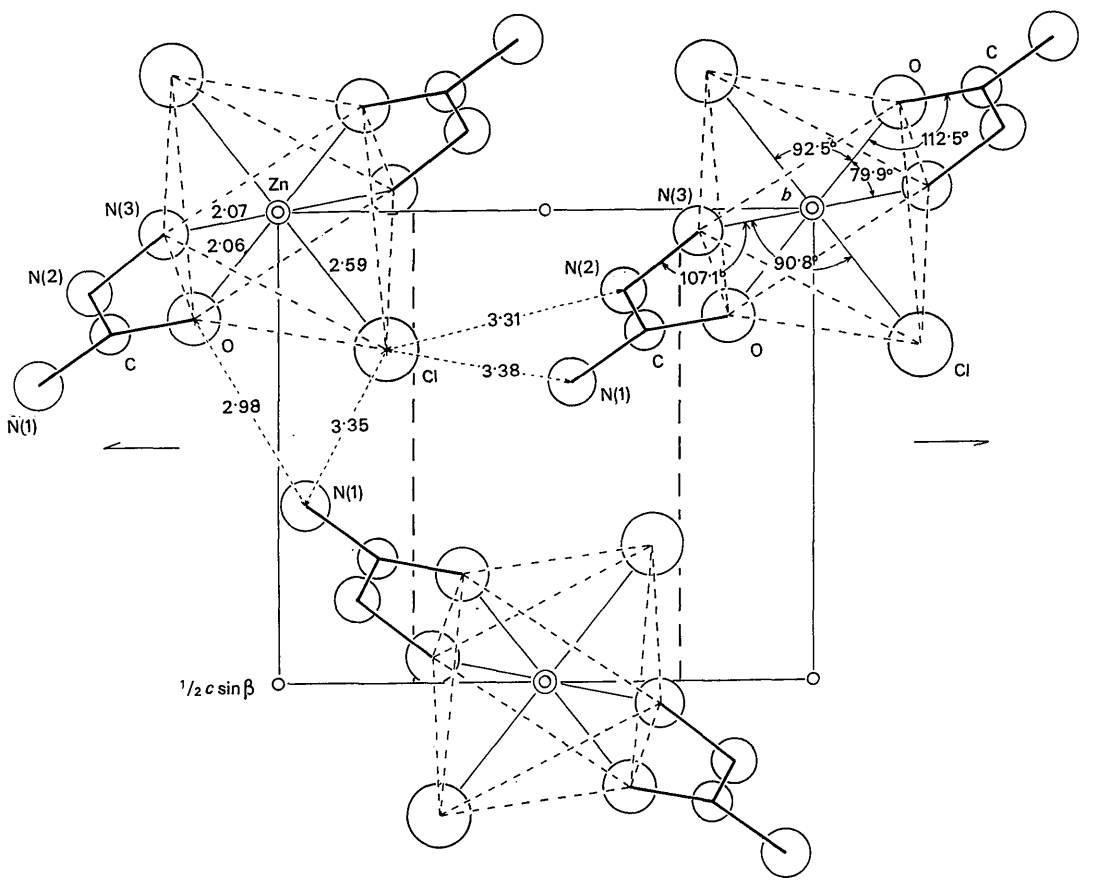

Fig. 2. Diagrammatic projection of the structure of $Zn[OC(NH_2)NHNH_2]_2Cl_2$ along [100].

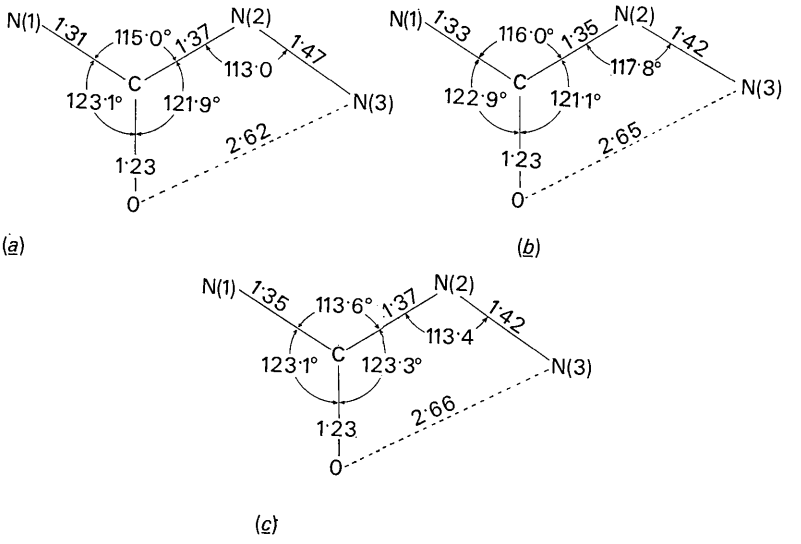

Fig. 3. Bond lengths and angles for semicarbazide in different compounds. (*a*) $Cu[OC(NH_2)NHNH_2]_2Cl_2$ (*b*) $Zn[OC(NH_2)NHNH_2]_2Cl_2$ (*c*) $OC(NH_2)NHNH_3Cl$.

Table 5. *Comparison of bondlengths and angles for semicarbazide molecule in metal complexes and in semicarbazide hydrochloride*

	$Cu[OC(NH_2)NHNH_2]_2Cl_2$ (I)	$Zn[OC(NH_2)NHNH_2]_2Cl_2$ (II)	(t_0)I–II	(I − II) averaged* (III)	$OC(NH_2)NHNH_3Cl$ (IV)	(t_0)III–IV
C–O	1·23 ± 0·02 Å	1·23 ± 0·02 Å	0·00	1·23 ± 0·01 Å	1·23 ± 0·02 Å	0·00
C–N(1)	1·31 ± 0·02	1·33 ± 0·02	0·71	1·32 ± 0·01	1·35 ± 0·02	1·34
C–N(2)	1·37 ± 0·02	1·35 ± 0·02	0·71	1·36 ± 0·01	1·37 ± 0·02	0·45
N(2)–N(3)	1·47 ± 0·02	1·42 ± 0·02	1·77	1·45 ± 0·01	1·42 ± 0·02	1·34
O · · · N(3)	2·62 ± 0·01	2·65 ± 0·02	1·34	2·63 ± 0·01	2·66 ± 0·02	1·34
O–C–N(1)	123·1 ± 1·2°	122·9 ± 1·5°	0·10	123·1 ± 0·9°	123·1 ± 1·5°	0·00
N(1)–C–N(2)	115·0 ± 1·4	116·0 ± 1·2	0·54	115·8 ± 0·9	113·6 ± 1·3	1·39
N(2)–C–O	121·9 ± 1·2	121·1 ± 1·1	0·49	121·6 ± 0·8	123·3 ± 1·4	1·05
C–N(2)–N(3)	113·0 ± 1·2	117·8 ± 1·0	3·07	115·9 ± 0·8	113·4 ± 1·2	1·74

* Averaging formula used: $(\Sigma l_i\sigma_i^{-2}/\Sigma\sigma_i^{-2}) \pm (\Sigma\sigma_i^{-2})^{-\frac{1}{2}}$

Table 6. *Analysis of the planarity in coordinated semicarbazide*

Equation of the plane referred to orthogonal axes: $m_1x' + m_2y' + m_3z' = d$

	$Cu[OC(NH_2)NHNH_2]_2Cl_2$					$Zn[OC(NH_2)NHNH_2]_2Cl_2$		
best plane through		ON(1)N(2)N(3)C		ON(1)N(2)C		ON(1)N(2)N(3)C		
m_1		0·3565		0·3687		0·4459		
m_2		0·2875		0·2630		0·3369		
m_3		0·8890		0·8916		0·8292		
d		0·3874		0·3255		0·3325		
	$\sigma_\perp$(Å)*	Δ(Å)	$\Delta/\sigma_\perp$	Δ(Å)	$\Delta/\sigma_\perp$	$\sigma_\perp$(Å)*	Δ(Å)	$\Delta/\sigma_\perp$
O	0·010	−0·016	−1·60	−0·005	−0·50	0·010	−0·001	−0·10
N(1)	0·016	0·020	1·25	−0·005	−0·31	0·014	−0·007	−0·50
N(2)	0·016	−0·042	−2·63	−0·005	−0·31	0·011	0·005	0·48
N(3)	0·012	0·030	2·50	(0·102)	(8·50)	0·010	−0·006	−0·60
C	0·016	0·008	0·50	0·015	0·94	0·012	0·009	0·71
$\Sigma(\Delta/\sigma_\perp)^2$			17·54		1·32			1·35
$\chi^2_{95\%}$			5·99		3·84			5·99

* $\sigma_\perp = \{m_1^2\sigma^2(x') + m_2^2\sigma^2(y') + m_3^2\sigma^2(z')\}^{\frac{1}{2}}$

164·5° and 168·0° for the copper and zinc complexes respectively.

The possible orientation of N–H bonds is indicated in the stereographic projections of Figs. 4 and 5, which represent the environments of N atoms in the copper and zinc complexes respectively. Of course, these environments are different, as the packing is different in the two compounds.

The following contacts can be considered as hydrogen bonds:

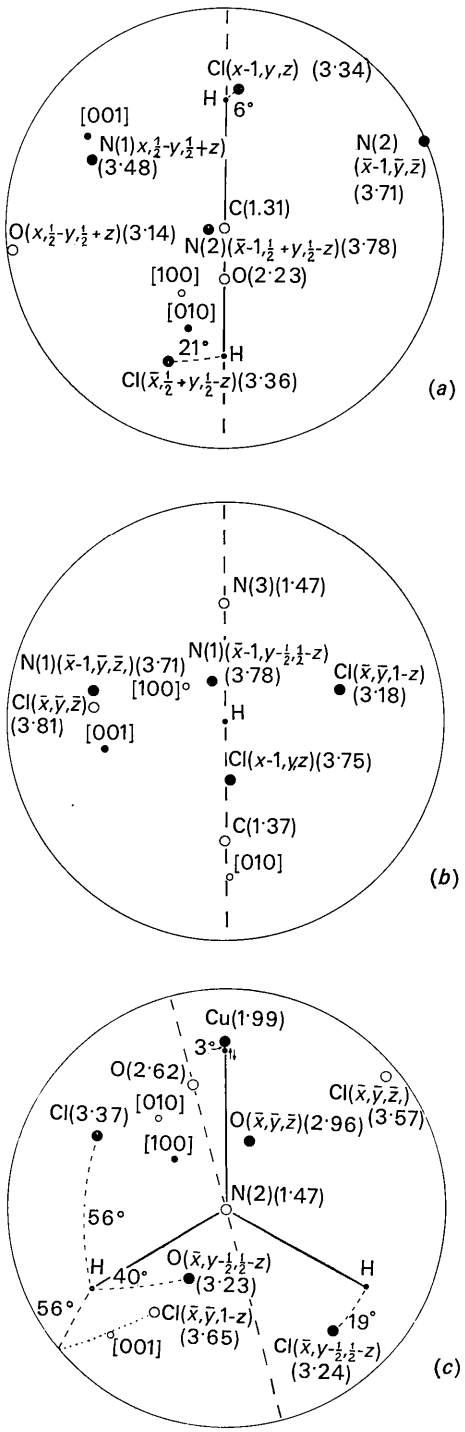

Fig. 4. $Cu[OC(NH_2)NHNH_2Cl_2$. Stereographic projection of the environment of (*a*) N(1), viewed down N(1)–C, (*b*) N(2), viewed down H–N(2), (*c*) N(3), viewed down N(3)–N(2).

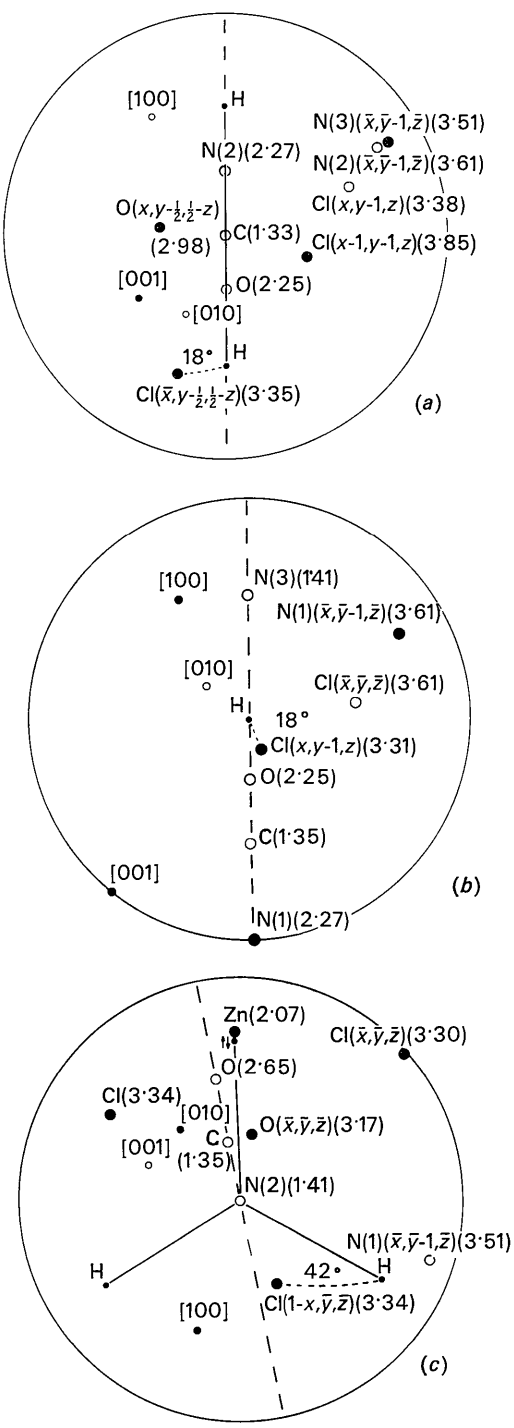

Fig. 5. $Zn[OC(NH_2)NHNH_2]_2Cl_2$. Stereographic projection of the environment of (*a*) N(1), viewed down N(1)–C, (*b*) N(2). viewed down H–N(2), (*c*) N(3), viewed down N(3)– N(2),

For $Cu[OC(NH_2)NHNH_2]_2Cl_2$

N(1)–Cl($x-1, y, z$)	3·34 ± 0·02 Å
N(1)–Cl($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	3·36 ± 0·01
N(3)–Cl($\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$)	3·24 ± 0·01

For $Zn[OC(NH_2)NHNH_2]_2Cl_2$

N(1)–Cl($\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$)	3·35 ± 0·02 Å
N(2)–Cl($x, y-1, z$)	3·31 ± 0·01

The other packing contacts shorter than 3·5 Å are:

$Cu[OC(NH_2)NHNH_2]_2Cl_2$

Cl–O	3·43 ± 0·01 Å
Cl–O($\bar{x}, \bar{y}, \bar{z}$)	3·48 ± 0·01
Cl–N(2)($\bar{x}, \bar{y}, 1-z$)	3·18 ± 0·02
Cl–N(3)	3·37 ± 0·01
O–N(1)($x, \frac{1}{2}-y, z-\frac{1}{2}$)	3·14 ± 0·02
O–N(3)($\bar{x}, \bar{y}, \bar{z}$)	2·96 ± 0·02
O–N(3)($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	3·23 ± 0·01
N(1)–N(1)($x, \frac{1}{2}-y, \frac{1}{2}+z$)	3·48 ± 0·03

$Zn[OC(NH_2)NHNH_2]_2Cl_2$

Cl–O	3·38 ± 0·01 Å
Cl–O($\bar{x}, \bar{y}, \bar{z}$)	3·25 ± 0·01
Cl–N(1)($x, 1+y, z$)	3·38 ± 0·02
Cl–N(3)	3·34 ± 0·01
Cl–N(3)($\bar{x}, \bar{y}, \bar{z}$)	3·30 ± 0·01
Cl–N(3)($1-x, \bar{y}, \bar{z}$)	3·34 ± 0·01
O–N(1)($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)	2·98 ± 0·02
O–N(3)($\bar{x}, \bar{y}, \bar{z}$)	3·17 ± 0·01

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The Crystal and Molecular Structure of *cis,cis*-1, 2, 3, 4-Tetraphenylbutadiene

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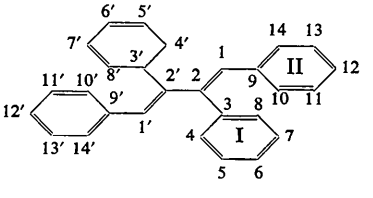
The crystal structure of *cis, cis*-1,2,3,4-tetraphenylbutadiene has been determined by application of the symbolic addition procedure. The space group is $P2_1/c$ with cell dimensions: $a=5{\cdot}87$, $b=21{\cdot}31$, $c=8{\cdot}13$ Å, and $\beta=97°\ 05'$. Since $Z=2$, the asymmetric unit is one-half the molecule. The butadiene chain is planar and the C–C distances show the typical effects of conjugation. One pair of phenyl rings forms an angle of 34° with the plane of the chain and the other pair of phenyl rings make an angle of 75°. The angle between the planes of the phenyl rings is 69°.

Introduction

Phenyl rings substituted on the same or adjacent atoms usually rotate about the connecting bonds so as to maximize the intramolecular distances between them. The present investigation on *cis, cis*-1,2,3,4-tetraphenylbutadiene,



was undertaken to determine the degree of rotation of the phenyl rings from the plane of the butadiene chain, especially the degree of rotation of the two rings at the extremes of the butadiene group where the effects of conjugation may tend to keep the rings coplanar with the chain. Since the diffraction data show that the molecule has a center of symmetry, the atoms have been numbered as shown above.

Experimental

Crystals of tetraphenylbutadiene are white needles elongated parallel to the *a* axis. Intensity data were obtained with copper radiation from multiple film, equi-inclination Weissenberg photographs with the crystal mounted on the *a* axis. All cell dimensions were determined from *hk*0 and *h*0*l* precession photographs. The space group was found to be $P2_1/c$ and the cell parameters are: