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The Crystal and Molecular Structure of Bis-biuret-Zinc Chloride

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Crystals of bis-biuret-zinc chloride, $Zn(C_2H_5N_3O_2)_2Cl_2$, are monoclinic, $P2_1/c$:

$$a = 8{\cdot}02,\ b = 7{\cdot}26,\ c = 11{\cdot}54\ \text{Å};\ \beta = 124{\cdot}7°,\ Z = 2\ .$$

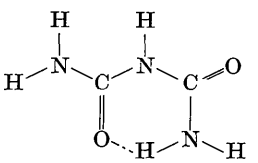
The structure, solved by means of three-dimensional Fourier methods, has been refined with anisotropic differential synthesis. The metal atom lies on a symmetry centre and coordinates octahedrally two chlorine atoms (Zn–Cl = 2·53 Å) and two pairs of oxygen atoms (Zn–O_1 = 2·05, Zn–O_2 = 2·03 Å), these last being at the corners of a slightly distorted square. The oxygen atoms belong to two biuret molecules which are in a *cis* configuration with nearly parallel C–O bonds. Steric hindrance between the oxygen atoms causes a slight departure from planarity in the biuret molecule, but each NH_2–CO–NH group itself preserves its planarity. The packing is determined chiefly by the hydrogen bonds NH · · · Cl = 3·24 Å. The probable distribution of the H's has been deduced indirectly and checked by an $F_o - F_c$ synthesis.

The structure of $Zn(C_2H_5N_3O_2)_2Cl_2$ is similar to that of $Cu(C_2H_5N_3O_2)_2Cl_2$ even though these two compounds are not isostructural. Their structures are quite different from that of $Cd(C_2H_5N_3O_2)_2Cl_2$ in which the biuret molecule is in a *trans* configuration and behaves as a monodentate ligand.

Introduction

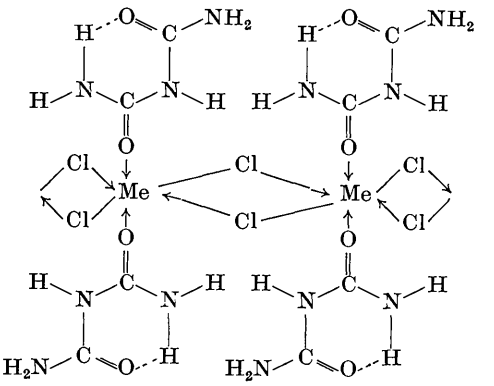
Some attention has been recently devoted to the structures of biuret metal complexes, these being the simplest compounds in which bonding interactions occur between metal ions and peptides.

The biuret molecule can have various structural configurations when acting as a ligand with metal atoms. The *trans* configuration



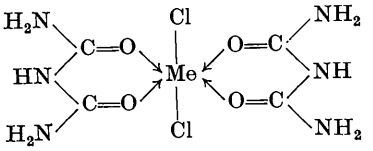
with a strong intermolecular NH · · · O hydrogen bond is present in biuret hydrate (Hughes, Yakel & Freeman, 1961) and it is also likely to occur in dioxane solution, as indicated by the relatively low dipole moment (3·27 D., Kumler, 1959).

The same configuration is preserved practically unchanged in crystals of bis-biuret-cadmium chloride and of bis-biuret-mercury(II) chloride (Cavalca, Nardelli & Fava, 1960); here biuret behaves as a monodentate ligand, and the donor atom is the oxygen atom not involved in hydrogen bonding. The coordination octahedra are linked in endless chains



with the metal and halide ions forming plane ribbons. This framework, which seems particularly preferred by the halo-complexes of cadmium, leaves open for further coordination at each metal atom two positions, which are *trans* with respect to the plane of the ribbon. In this case a chelation involving a *cis* form of biuret is obviously impossible.

A different situation occurs with Cu^{2+} and Zn^{2+} ions which seem to show a stronger tendency to give molecular rather than polymeric complexes, so that chelation is favoured and biuret can act as a bidentate ligand:



The chelation energy is sufficient to break the intermolecular hydrogen bond and to cause the rotation of half a molecule with respect to the other. This type of structure has been observed in bis-biuret-cupric chloride (Freeman, Smith & Taylor, 1959; Freeman & Smith, 1961) and bis-biuret-zinc chloride. The crystals of these compounds are not isostructural, but some similarities in their structures can be inferred from crystal data (Nardelli & Chierici, 1960).

A chelate complex is also present in potassium bis-biuret-cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961), but in this compound the complex is an ion, $[Cu(NHCONHCONH)_2]^{2-}$, and the coordination around copper involves the nitrogen atoms of the amide groups. Biuret now shows an ionized *cis* form with two nearly parallel C–N bonds, and most of the steric hindrance is removed by ionization of H^+'s.

In the present paper the results of the three-dimensional X-ray analysis of bis-biuret-zinc chloride are given.

Experimental

Crystal data

$Zn(C_2H_5N_3O_2)_2Cl_2$. $M=342{\cdot}5$, monoclinic prismatic, $a=8{\cdot}02\pm0{\cdot}01$, $b=7{\cdot}26\pm0{\cdot}01$, $c=11{\cdot}54\pm0{\cdot}01$ Å; $\beta=124{\cdot}7\pm0{\cdot}2°$.

$V=552$ Å^3, $Z=2$, $D_x=2{\cdot}06$, $D_m=2{\cdot}04$ g.cm.$^{-3}$ (flotation).

$\mu=77{\cdot}5$ cm.$^{-1}$ (Cu $K\alpha$).

$F(000)=344$.

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

Determination of structure factors

The intensity data were measured photometrically on multiple-film equi-inclination integrated and non-integrated Weissenberg photographs, taken with Ni-filtered Cu $K\alpha$ radiation.

The $h0l$, $h1l$, ..., $h6l$ layers were recorded by rotation around the b axis of a short prism showing nearly equal development of the {001} and {$\bar{1}$01} forms (the diamond-shaped cross-section had an edge of 0·024 cm.). To cross-correlate the b-axis data, the Weissenberg photograph of $\bar{n}, k, 2n$ reflexions was used; this was obtained by rotation around [201] of a fragment with nearly rectangular cross-section (0·038 cm. along and 0·022 cm. perpendicular to [010]).

Table 1. *Number of observed and possible independent reflexions with final R and R′ indices*

	Observed	Possible	R	R'
$h0l$	89	100	11·1%	11·4%
$h1l$	138	195	14·1	16·2
$h2l$	147	184	14·6	15·5
$h3l$	150	171	12·5	13·0
$h4l$	143	161	11·0	12·0
$h5l$	128	139	11·2	11·2
$h6l$	96	115	11·8	12·9
Overall	891	1065	12·5%	13·4%

The number of observed and possible independent reflexions is given in Table 1.

Discontinuous absorption effects were corrected graphically using Albrecht's (1939) method and the shape of the spots of non-equatorial layers was taken into account following Phillips (1956). The structure factors were derived by the usual formulae, the absolute scale being established first by Wilson's method, then by correlation with the calculated values.

Structure analysis and refinement

Since two molecules, $Zn(C_2H_5N_3O_2)_2Cl_2$, are contained in a unit cell, they must be on a symmetry centre. If the metal atom is located on the twofold (a): 0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$ positions, the signs of the highest $F_o(h0l)$ must be positive, as the influence of Zn is predominant. A $\varrho(X, Z)$ projection calculated with 50 $F_o(h0l)$ showed the location of the chlorine atom and indicated that the organic molecule is nearly perpendicular to the projection plane. Overlapping of the light atoms made any further work on this projection useless.

The next step was a three-dimensional Patterson calculation. Two sets of interactions between zinc and light-atoms due to a Patterson mirror parallel to (010) are present in Patterson space; chemical criteria were successfully applied to distinguish between these two sets.

The refinement was carried out by means of a $\varrho(X, Y, Z)$ synthesis, then by means of eight cycles of Booth's differential synthesis, four of them calculated with isotropic and four with anisotropic thermal parameters. In the first three cycles of differential synthesis, the scattering factor of N was also used for the oxygen atoms. Nitrogen and oxygen atoms were only differentiated on the basis of interatomic distances when these were not appreciably affected by the shifts of the atomic coordinates.

Table 2. *Anisotropic refinement parameters*

(B_{ij} in Å^2)

	Initial parameters	Parameter shifts				Final parameters
	I	II	III	IV	V	
Zn						
x/a	0	0	0	0	0	0
y/b	0	0	0	0	0	0
z/c	0	0	0	0	0	0
B11	2.23	0.63	0.40	0.25	0.17	3.68
B22	2.23	-0.14	0.03	0.02	0.02	2.16
B33	2.23	0.61	0.37	0.23	0.15	3.59
B23	-	0.02	0.02	0.01	0.01	0.06
B13	1.27	0.68	0.42	0.26	0.17	2.80
B12	-	0	0.01	0	0	0.01
Cl						
x/a	0.3268	0	0.0001	0.0002	0	0.3271
y/b	-0.0540	0	0.0002	0	0	-0.0538
z/c	0.2389	0	0.0001	0.0001	0	0.2391
B11	2.23	0.28	0.25	0.19	0.12	3.07
B22	2.23	-0.26	0.05	0.06	0.08	2.16
B33	2.23	0.26	0.22	0.16	0.10	2.97
B23	-	0.06	0.04	0.03	0.02	0.15
B13	1.27	0.40	0.28	0.19	0.12	2.26
B12	-	0.08	0.05	0.04	0.03	0.20
O_1						
x/a	0.1509	0	-0.0007	-0.0002	-0.0001	0.1499
y/b	0.5594	0.0001	0.0006	0.0001	0	0.5602
z/c	0.4095	0.0001	-0.0006	-0.0001	-0.0001	0.4088
B11	2.23	0.24	0.24	0.19	0.15	3.05
B22	2.23	-0.19	0.06	0.10	0.10	2.30
B33	2.23	0.23	0.20	0.16	0.12	2.94
B23	-	-0.15	-0.03	-0.01	0.01	-0.18
B13	1.27	0.45	0.32	0.21	0.16	2.41
B12	-	-0.13	-0.06	-0.04	0.01	-0.22
O_2						
x/a	0.0791	0.0005	-0.0003	-0.0003	-0.0001	0.0789
y/b	0.2334	0.0002	-0.0002	0.0002	0	0.2336
z/c	0.5037	0	0.0004	0.0001	0	0.5042
B11	2.23	0.51	0.49	0.27	0.17	3.67
B22	2.23	0.02	0.09	0.01	0	2.35
B33	2.23	0.81	0.42	0.19	0.10	3.75
B23	-	0.12	0.10	0.04	0.02	0.28
B13	1.27	0.81	0.45	0.22	0.13	2.88
B12	-	0.24	0.02	-0.01	-0.01	0.24
N_1						
x/a	0.2375	-0.0006	-0.0001	0	0	0.2368
y/b	0.2660	0.0003	0.0002	0.0001	0.0001	0.2667
z/c	0.3902	-0.0003	-0.0003	0	0	0.3896
B11	2.23	0.42	0.23	0.17	0.12	3.17
B22	2.23	-0.27	0.08	0.12	0.12	2.28
B33	2.23	0.23	0.18	0.17	0.13	2.94
B23	-	0	-0.02	-0.02	-0.03	-0.07
B13	1.27	0.48	0.31	0.23	0.16	2.45
B12	-	-0.06	-0.07	-0.07	-0.05	-0.25

	Initial parameters	Parameter shifts				Final parameters
	I	II	III	IV	V	
N_2						
x/a	0.3267	0	0.0004	0.0002	0.0002	0.3275
y/b	0.5133	0	-0.0009	-0.0002	-0.0001	0.5121
z/c	0.3190	0	-0.0003	-0.0001	0.0001	0.3187
B11	2.23	0.74	0.21	0.11	0.06	3.35
B22	2.23	0.19	0.21	0.14	0.09	2.86
B33	2.23	0.71	0.32	0.21	0.14	3.61
B23	-	-0.04	-0.01	-0.01	-0.01	-0.07
B13	1.27	0.71	0.32	0.18	0.12	2.60
B12	-	-0.13	-0.11	-0.08	-0.05	-0.37
N_3						
x/a	0.1752	0.0001	0.0003	0.0003	0.0002	0.1761
y/b	-0.0146	0.0005	-0.0006	0.0001	-0.0001	-0.0147
z/c	0.4441	-0.0001	0.0006	0.0002	0	0.4448
B11	2.23	0.72	0.31	0.20	0.16	3.62
B22	2.23	-0.16	-0.02	0.03	0.05	2.13
B33	2.23	0.42	0.07	0.05	0.05	2.82
B23	-	-0.04	0.10	0.07	0.04	0.17
B13	1.27	0.48	0.17	0.11	0.09	2.12
B12	-	0.03	0.05	0.03	0.01	0.12
C_1						
x/a	0.2314	0.0001	0.0003	0.0002	0	0.2320
y/b	0.4502	-0.0002	0.0006	0.0003	0.0002	0.4511
z/c	0.3745	0.0001	0.0003	0.0001	0	0.3750
B11	2.23	0.05	0.08	-	0.27	2.63
B22	2.23	-0.50	-0.02	-	0.04	1.75
B33	2.23	-0.09	0.02	-	0.25	2.41
B23	-	-0.09	-0.07	-	-0.05	-0.21
B13	1.27	0.22	0.13	-	0.54	2.16
B12	-	0.06	0.01	-	0.02	0.09
C_2						
x/a	0.1606	-0.0004	0.0003	-0.0001	-0.0001	0.1603
y/b	0.1653	-0.0006	0.0005	0.0003	0	0.1655
z/c	0.4495	0	-0.0002	-0.0001	-0.0001	0.4491
B11	2.23	-0.04	-0.03	-	0.02	2.18
B22	2.23	-0.48	-0.05	-	0.13	1.83
B33	2.23	-0.21	-0.09	-	0.04	1.97
B23	-	0	-0.02	-	-0.04	-0.06
B13	1.27	0.16	0.09	-	0.07	1.59
B12	-	-0.07	-0.02	-	0	-0.09

The anisotropic thermal parameters were determined and refined following the method of Nardelli & Fava (1960) using the second derivatives of electron density from the differential synthesis. An IBM 650 program gave the ΔB_{ij} shifts in only a few minutes for each atom, independently of the space group and number of reflexions. The progress of the anisotropic refinement is shown in Table 2 in which the shifts of coordinates and thermal parameters are reported. It appears that a faster convergence could be achieved by multiplying the shifts by a factor greater than unity. The refinement was considered to be complete when the shifts of fractional coordinates were less than 0·0002, corresponding to a sixth of the standard deviation.

The final orthogonal coordinates with their standard deviations (Cruickshank, 1949) are listed in Table 3.

Table 3. *Atomic coordinates and their e.s.d.'s referred to orthogonal axes*

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

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

	x' (Å)	y' (Å)	z' (Å)	$\sigma(x')$	$\sigma(y')$ 10^3 (Å)	$\sigma(z')$
Zn	0	0	0	—	—	—
Cl	2·155	−0·391	1·264	2	3	4
O_1	0·988	4·067	4·032	6	9	9
O_2	0·520	1·696	5·458	7	11	11
N_1	1·560	1·936	3·413	8	8	12
N_2	2·158	3·718	2·181	8	11	13
N_3	1·160	−0·107	4·328	9	10	13
C_1	1·529	3·275	3·267	9	9	13
C_2	1·056	1·201	4·450	8	9	13

Table 4. *Observed and calculated structure factors*

A minus sign after an F_o means 'less than'

l	10|F_o|	10F_c
	0 0 1	
2	638	521
4	715	611
6	66	−37
8	334	327
10	32	36
12	97	87
	1 0 1	
0	645	796
2	1790	1927
4	580	537
6	185	182
8	127	130
10	51	60
	$\bar{1}$ 0 1	
2	307	382
4	88	−72
6	592	535
8	122	116
10	271	291
12	28	−24
	2 0 1	
0	439	−456
2	823	835
4	621	533
6	417	399
8	32−	−25
10	108	127
	$\bar{2}$ 0 1	
2	319	394
4	145	177
6	678	595
8	387	349
10	164	168
12	221	240
	3 0 1	
0	372	410
2	419	−390
4	204	405
6	139	153
8	126	157
	$\bar{3}$ 0 1	
2	197	−189
4	856	1034
6	286	237
8	577	562
10	190	186
12	294	314
14	15−	−27
	4 0 1	
0	67	78
2	51	58
4	112	−91
6	51	65
	$\bar{4}$ 0 1	
2	491	582
4	341	362
6	626	602
8	247	221
10	477	458
12	156	−136
14	140	134
	5 0 1	
0	66	79
2	232	233
4	108	−91
6	20−	18
	$\bar{5}$ 0 1	
2	486	526
4	151	155
6	484	469
8	257	217
10	64	−63
12	49	34
14	76	80
	6 0 1	
0	337	350
2	32−	3
4	122	135
	$\bar{6}$ 0 1	
2	33−	−34
4	496	476
6	77	−59
8	121	82
10	212	−207
12	364	323
14	22−	35
	7 0 1	
0	52	56
2	86	94
	$\bar{7}$ 0 1	
2	194	184
4	34−	29
6	34−	−9
8	198	−187
10	467	402
12	47	63
14	238	219
	8 0 1	
0	22−	−8
	$\bar{8}$ 0 1	
2	154	146
4	170	−153
6	57	47
8	252	210
10	313	283
12	169	135
14	16−	18
	$\bar{9}$ 0 1	
2	116	−110
4	90	101
6	92	82
8	433	388
10	26−	9
12	196	161
	$\bar{10}$ 0 1	
6	218	234
8	51	49
10	150	128
	0 1 1	
1	737	666
2	342	267
3	240	−140
4	55	44
5	400	316
6	42	−14
7	159	158
8	36−	−34
9	286	300
10	56	56
11	28−	76
12	17−	−26
	1 1 1	
0	237	−269
1	243	249
2	350	−333
3	692	726
4	173	128
5	334	−273
6	79	−58
7	289	258
8	36−	20
9	34−	1
10	28−	−33
11	155	170
	$\bar{1}$ 1 1	
1	345	561
2	305	407
3	63	23
4	203	−147
5	736	728
6	143	99
7	273	241
8	34−	54
9	342	356
10	36−	24
11	32−	37
12	26−	−58
	2 1 1	
0	332	−392
1	480	572
2	265	−243
3	323	299
4	237	−204
5	351	297
6	36−	12
7	94	−85
8	34−	−16
9	54	54
10	18−	−5
	$\bar{2}$ 1 1	
1	74	52
2	136	−160
3	648	1121
4	268	259
5	158	160
6	178	123
7	706	733
8	176	147
9	74	−58
10	111	−122
11	209	192
12	30−	2
13	22−	−34
	3 1 1	
0	24−	−13
1	358	386
2	101	−99
3	152	156
4	199	−186
5	337	335
6	55	−58
7	33−	19
8	28	−31
9	17−	23
	$\bar{3}$ 1 1	
1	407	527
2	114	114
3	304	425
4	318	335
5	588	632
6	257	198
7	133	114
8	96	−91
9	244	198
10	36−	12
11	36−	36
12	32−	40
13	103	108
	4 1 1	
0	58	53
1	71	72
2	34−	−34
3	323	332
4	37−	13
5	36−	15
6	99	−100
7	187	201
	$\bar{4}$ 1 1	
1	444	526
2	332	356
3	127	133
4	99	93
5	458	511
6	48	36
7	81	−49
8	94	−58
9	415	369
10	198	170
11	36−	29
12	139	125
13	149	139
14	21−	58
	5 1 1	
0	155	−155
1	238	241
2	59	52
3	48	54
4	34−	23
5	101	109
6	21−	7
	$\bar{5}$ 1 1	
1	32−	38
2	50	38
3	409	467
4	30−	41
5	105	−84
6	106	−102
7	608	599
8	294	253
9	36−	−33
10	146	126
11	372	337
12	149	119
13	133	117
14	23−	−58
	6 1 1	
0	37−	−54
1	122	126
2	34−	−14
3	30−	4
4	24−	12
	$\bar{6}$ 1 1	
1	125	122
2	63	−54
3	173	171
4	34−	−32
5	390	366
6	153	135
7	225	183
8	183	149
9	327	253
10	111	75
11	290	238
12	106	−83
13	299	296
14	23−	3
	7 1 1	
0	66	66
1	30−	−19
2	25−	−43
3	16−	90
	$\bar{7}$ 1 1	
1	255	231
2	36−	16
3	99	99
4	37−	−1
5	395	366
6	176	144
7	37−	−16
8	59	−58
9	483	439
10	81	−59
11	146	169
12	81	−76
13	161	144
14	21−	20
	8 1 1	
0	23−	1
	$\bar{8}$ 1 1	
1	63	68
2	31−	−12
3	272	236
4	68	62
5	70	−63
6	108	−97
7	410	372
8	85	−63
9	87	84
10	153	−127
11	289	252
12	28−	43
13	87	−88
14	56	−55
	$\bar{9}$ 1 1	
2	18−	−8
3	23−	32
4	51	−45
5	132	111
6	122	−94
7	178	159
8	96	−72
9	153	128
10	28−	4
11	26−	7
12	22−	−44
13	108	102
	$\bar{10}$ 1 1	
6	16−	−8
7	18−	−13
8	20−	−30
9	200	133
10	17−	7
	0 2 1	
1	332	272
2	233	−142
3	436	−363
4	478	413
5	88	64
6	53	−23
7	171	−153
8	163	154
9	116	109
10	37−	−8
11	29−	−20
	1 2 1	
0	114	130
1	70	−47
2	602	668
3	84	40
4	113	110
5	67	−53
6	141	140
7	80	−52
8	112	115
9	38−	−11
10	30−	23
	$\bar{1}$ 2 1	
1	258	−348
2	286	350
3	21−	−29
4	60	−15
5	313	−237
6	221	179
7	251	214
8	40−	−15
9	42	−42
10	215	235
11	36−	59
12	27−	−3
	2 2 1	
0	80	−31
1	25−	−6
2	481	486
3	208	171
4	220	178
5	135	−96
6	210	198
7	76	74
8	38−	−2
9	60	−74
	$\bar{2}$ 2 1	
1	288	−373
2	284	411
3	22−	−16
4	152	−104
5	122	96
6	322	267
7	180	138
8	311	288
9	41−	−23
10	125	137
11	49	−50
12	97	112
13	23−	23
	3 2 1	
0	432	524
1	302	315
2	61	−34
3	75	−61
4	353	348
5	109	107
6	58	66
7	36−	−38
8	74	87
	$\bar{3}$ 2 1	
1	121	131
2	203	−189
3	66	−71
4	537	634
5	413	417
6	360	311
7	257	−214
8	468	461
9	47	30
10	53	51
11	97	−96
12	133	137
13	52	60
	4 2 1	
0	94	100
1	37−	7
2	225	224
3	81	70
4	83	92
5	39−	24
6	99	111
7	26−	3
	$\bar{4}$ 2 1	
1	52	47
2	394	474
3	273	312
4	458	516
5	186	−177
6	589	589
7	77	−21
8	157	110
9	207	−177
10	291	264
11	108	108
12	78	−67
13	63	−81
14	125	188
	5 2 1	
0	133	136
1	156	−147
2	219	215
3	81	79
4	37−	28
5	31−	−31
6	59	97
	$\bar{5}$ 2 1	
1	63	49
2	522	611
3	36−	60
4	276	324
5	233	−233
6	400	368
7	71	−53
8	225	180
9	67	−10
10	123	99
11	41−	2
12	209	218
13	32−	−20
14	99	154
	6 2 1	
0	354	383
1	41−	3
2	38−	32
3	72	−84
4	92	112
	$\bar{6}$ 2 1	
1	112	100
2	102	115
3	241	−255
4	361	408
5	108	52
6	82	60
7	158	−141
8	352	310
9	183	152
10	170	150
11	115	−114
12	321	393
13	44	57
14	44	52
	7 2 1	
0	83	98
1	32−	−5
2	113	116
	$\bar{7}$ 2 1	
1	100	−97
2	175	170
3	42−	−22
4	112	113
5	77	−61
6	250	238
7	142	125
8	196	175
9	91	−78
10	435	472
11	86	92
12	46	77
13	42	−44
14	118	203
	8 2 1	
0	23−	3
	$\bar{8}$ 2 1	
1	96	−79
2	164	157
3	36−	54
4	38−	42
5	39−	−4
6	256	245
7	100	71
8	295	277
9	38−	−6
10	204	211
11	34−	46
12	111	139
13	24−	16
	$\bar{9}$ 2 1	
3	23−	−23
4	174	174
5	105	104
6	99	101
7	64	−57
8	244	244
9	100	114
10	30−	15
11	57	−75
12	131	198
	$\bar{10}$ 2 1	
8	18−	11
9	18−	−52
	0 3 1	
1	649	611
2	295	−192
3	273	214
4	264	−191
5	402	364
6	127	100
7	167	157
8	36−	6
9	143	151
10	90	97
11	39	49
	1 3 1	
0	533	654
1	377	404
2	221	−205
3	592	542
4	153	138
5	32−	34
6	207	−192
7	257	253
8	134	135
9	31−	37
10	23−	−22
	$\bar{1}$ 3 1	
1	332	497
2	16−	14
3	304	311
4	273	−247
5	556	457
6	253	227
7	144	132
8	41	−31
9	206	223
10	34−	−2
11	38	56
12	46	−53
	2 3 1	
0	64	25
1	380	405
2	436	423
3	311	284
4	80	−56
5	309	258
6	56	50
7	35−	39
8	31−	−42
9	74	93
	$\bar{2}$ 3 1	
1	222	259
2	298	−408
3	469	608
4	281	319
5	103	97
6	239	−194
7	467	439
8	77	90
9	71	67
10	218	−217
11	168	178
12	66	75
	3 3 1	
0	72	77
1	252	276
2	222	202
3	204	132
4	65	50
5	220	225
6	80	80
7	45	59
8	33	−44
	$\bar{3}$ 3 1	
1	280	331
2	23−	−19
3	167	203
4	25−	−25
5	404	417
6	119	−67
7	249	215
8	278	−245
9	236	226
10	36−	23
11	128	129
12	85	−80
13	85	104
	4 3 1	
0	209	214
1	78	80
2	96	−100
3	178	189
4	166	164
5	32−	15
6	42	−40
7	83	119
	$\bar{4}$ 3 1	
1	229	262
2	202	225
3	156	194
4	290	−304
5	392	425
6	52	−33
7	144	133
8	239	−234
9	336	324
10	36−	29
11	80	84
12	68	−68
13	98	106
	5 3 1	
0	143	−143
1	150	142
2	86	87
3	34−	41
4	30−	−28
5	24−	55
	$\bar{5}$ 3 1	
1	80	113
2	168	−178
3	325	382
4	83	52
5	92	91
6	297	−322
7	445	425
8	140	117
9	85	56
10	201	−190
11	224	199
12	104	110
13	69	80
	6 3 1	
0	72	−55
1	105	124
2	31−	11
3	26−	23
	$\bar{6}$ 3 1	
1	168	172
2	71	−67
3	149	162
4	72	−77
5	283	272
6	61	−22
7	177	140
8	88	−61
9	186	144
10	97	90
11	154	142
12	68	−68
13	118	135
	7 3 1	
0	92	92
1	115	52
	$\bar{7}$ 3 1	
1	136	156
2	85	80
3	91	93
4	146	−141
5	227	205
6	150	143
7	36−	−2
8	42	−43
9	262	242
10	131	121
11	73	85
12	60	−65
13	72	87
	$\bar{8}$ 3 1	
1	36	42
2	69	−67
3	144	126
4	122	118
5	33	−35
6	48	−37
7	235	215
8	203	184
9	58	61
10	115	−118
11	144	160
12	71	84
13	28	45
	$\bar{9}$ 3 1	
4	61	62
5	77	85
6	58	57
7	102	113
8	26−	−4
9	107	114
10	23−	20
11	90	101

Table 4 (*cont.*)

l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c	l	10|F_o|	10F_c
	0 4 1			3 4 1		8	237	216	9	60	77		3 5 1		12	118	126	5	59	20	2	101	107
1	368	293	0	281	315	9	82	93	10	43	53	0	41	32		6 5 1		6	175	184	3	63	62
2	467	375	1	219	215	10	48	45		0 5 1		1	230	243	0	79	-83	7	33-	-2	4	27-	42
3	346	-285	2	45	15	11	74	68	1	205	155	2	66	64	1	32	50	8	78	90		$\bar{4}$ 6 1	
4	361	305	3	232	-202	12	60	64	2	25-	-2	3	135	129	2	57	-52		$\bar{5}$ 6 1		1	69	-62
5	282	242	4	168	157	13	16-	17	3	122	86	4	71	-65		$\bar{6}$ 5 1		1	59	-75	2	110	119
6	232	203	5	48	51		6 4 1		4	216	-165	5	88	99	1	74	86	2	147	160	3	134	157
7	92	-90	6	102	115	0	97	109	5	232	188	6	47	41	2	114	-120	3	74	72	4	325	342
8	184	184	7	96	-113	1	56	60	6	82	-74	7	35	52		$\bar{3}$ 5 1		4	277	243	5	204	-191
9	148	160		$\bar{3}$ 4 1		2	21-	39	7	181	179	1	306	372	3	96	89	5	216	-183	6	217	191
10	83	97	1	223	258	3	47	-56	8	81	-83	2	117	124	4	135	-138	6	93	-80	7	38-	-8
	1 4 1		2	231	270				9	83	97	3	219	257	5	266	255	7	163	152	8	271	256
0	358	399	3	136	-172		$\bar{6}$ 4 1		10	81	107	4	301	318	6	63	31	8	39	45	9	116	-115
1	204	-173	4	386	415	1	134	147		1 5 1		5	231	215	7	274	250	9	31-	-62	10	106	94
2	677	648	5	315	310	2	28-	16	0	206	240	6	280	238	8	39-	27	10	19-	13	11	115	133
3	21-	-16	6	301	248	3	191	-201	1	220	211	7	108	95	9	179	167						
4	309	268	7	337	-325	4	184	170	2	274	-254	8	123	-130	10	108	91		2 6 1			5 6 1	
5	66	-49	8	222	197	5	212	221	3	120	93	9	60	51	11	174	181	0	203	218	0	139	174
6	167	159	9	94	86	6	165	153	4	174	157	10	37-	31	12	69	-85	1	111	-116	1	58	-70
7	41	14	10	168	177	7	128	-98	5	72	68	11	118	122		7 5 1		2	80	62	2	29-	42
8	110	113	11	67	-63	8	84	72	6	231	-220				0	140	156	3	91	77	3	69	107
9	55	53	12	137	157	9	240	227	7	96	87		4 5 1					4	202	178			
10	57	67		4 4 1		10	26-	40	8	34-	8	0	78	83		$\bar{7}$ 5 1		5	86	-77		$\bar{5}$ 6 1	
	$\bar{1}$ 4 1		0	199	198	11	119	-137	9	63	81	1	251	266	1	45	49	6	67	67	1	37-	-2
1	117	-138	1	27-	-10	12	142	160		$\bar{1}$ 5 1		2	89	-107	2	33-	-6	7	88	91	2	205	223
2	250	299	2	152	152	13	45	50	1	87	86	3	127	131	3	127	190		$\bar{2}$ 6 1		3	38-	22
3	245	238	3	28-	36		7 4 1		2	91	119	4	105	111	4	131	-125	1	144	-166	4	263	268
4	375	335	4	27-	6	0	20-	15	3	323	325	5	64	81	5	202	192	2	135	151	5	166	-160
5	140	-112	5	23-	-22	1	16-	-32	4	343	-321		$\bar{4}$ 5 1		6	165	166	3	31	-39	6	205	173
6	368	313	6	48	52		$\bar{7}$ 4 1		5	357	278	1	170	170	7	178	170	4	57	38	7	37-	20
7	281	259		$\bar{4}$ 4 1		1	48	-47	6	179	145	2	401	479	8	72	-72	5	35-	-10	8	209	188
8	156	202	1	38	-47	2	86	89	7	202	194	3	186	215	9	178	165	6	37-	25	9	33-	39
9	126	-135	2	262	281	3	70	68	8	72	64	4	37-	14	10	56	55	7	74	54	10	93	97
10	137	148	3	190	211	4	115	123	9	123	131	5	93	84	11	114	126	8	160	131	11	23-	18
11	19-	9	4	232	230	5	70	-46	10	77	87	6	78	59		$\bar{8}$ 5 1		9	86	-76		6 6 1	
	2 4 1		5	245	-237	6	67	64		2 5 1		7	126	109	3	127	125	10	91	117	0	96	133
0	120	123	6	214	184	7	160	143	0	129	-148	8	182	-188	4	104	118		3 6 1		1	20-	17
1	238	-212	7	111	98	8	41	42	1	142	121	9	222	190	5	95	108	0	98	92		$\bar{5}$ 6 1	
2	331	299	8	218	207	9	125	-137	2	148	137	10	113	104	6	86	-86	1	205	212	1	81	89
3	82	75	9	99	-91	10	186	197	3	189	174	11	130	133	7	123	123	2	152	161	2	191	211
4	345	298	10	236	231	11	59	59	4	153	-131	12	25-	12	8	90	92	3	127	-118	3	172	-189
5	243	-201	11	209	229	12	74	97	5	88	74		5 5 1		9	109	119	4	35-	22	4	81	74
6	156	153	12	21-	20		$\bar{8}$ 4 1		6	66	60	0	262	-286	10	120	-107	5	43	59	5	123	120
7	83	79	13	39	-39	2	86	100	7	34-	24	1	99	104		0 6 1		6	69	91	6	228	222
8	27	48		5 4 1		3	69	69	8	56	-67	2	41	36	1	252	217		$\bar{3}$ 6 1		7	82	-72
9	62	-64	0	114	117	4	22-	33		$\bar{2}$ 5 1		3	103	127	2	306	270	1	34-	48	8	84	60
	$\bar{2}$ 4 1		1	98	-103	5	23-	-53	1	281	353	4	23-	-28	3	164	-131	2	126	154	9	129	137
1	111	-119	2	133	139	6	57	71	2	254	-334		$\bar{5}$ 5 1		4	183	148	3	154	-163	10	145	166
2	308	412	3	134	130	7	23-	24	3	315	362	1	117	135	5	152	124	4	34-	20		$\bar{7}$ 6 1	
3	161	166	4	25	49	8	166	164	4	312	320	2	41-	-19	6	214	202	5	223	217	2	43	50
4	342	344	5	14-	-43	9	78	-89	5	296	278	3	100	89	7	123	-124	6	347	310	3	46	41
5	83	60		$\bar{5}$ 4 1		10	118	130	6	102	66	4	57	58	8	62	-58	7	264	-236	4	112	120
6	403	355	1	28	-43	11	18-	-30	7	203	171	5	133	130	9	105	109	8	147	128	5	31-	-17
7	51	40	2	179	184	12	64	88	8	280	274	6	293	-300		1 6 1		9	35-	10	6	84	75
8	248	224	3	47	78		$\bar{9}$ 4 1		9	64	77	7	290	244	0	171	202	10	168	196	7	93	104
9	117	-110	4	84	78	5	59	71	10	140	-156	8	203	195	1	107	-99	11	62	-78	8	144	165
10	107	112	5	139	-133	6	94	110	11	28-	22	9	249	231	2	180	159		4 6 1		9	97	-119
11	67	-76	6	224	213	7	128	-148				10	71	-71	3	84	64	0	104	113			
12	99	129	7	113	109	8	127	135				11	123	122	4	175	169	1	66	51			

Table 5. *Postulated hydrogen fractional coordinates and corresponding ϱ values in the final F_o-F_c synthesis*

	x/a	*y/b*	*z/c*	ϱ (e.Å^{-3})
H_1	0·333	0·652	0·303	0·6
H_2	0·397	0·419	0·290	1·0
H_3	0·118	−0·100	0·486	0·4
H_4	0·241	−0·071	0·397	0·7
H_5	0·307	0·193	0·351	0·5

The F_c values reported in Table 4 are calculated with the final parameters of Table 2, including the contributions of H's at the positions listed in Table 5 with an isotropic B value 3·0 Å^2. The H's were located by applying the criteria discussed in the next section. An F_o-F_c synthesis, calculated before the introduction of H's, gave at the positions assumed for these atoms the electron-density values reported in the last column of Table 5.

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

$$\sigma(\varrho)=0{\cdot}38 \text{ e.Å}^{-3}$$

$$\sigma(A_h)=0{\cdot}95, \quad \sigma(A_k)=0{\cdot}85, \quad \sigma(A_l)=0{\cdot}98 \text{ e.Å}^{-4}$$

$$\sigma(A_{hh})=4{\cdot}41, \quad \sigma(A_{kk})=3{\cdot}13, \quad \sigma(A_{ll})=4{\cdot}75 \text{ e.Å}^{-5}$$

$$\sigma(A_{hk})=2{\cdot}16, \quad \sigma(A_{hl})=3{\cdot}78, \quad \sigma(A_{kl})=2{\cdot}21 \text{ e.Å}^{-5}.$$

The observed and calculated values of electron density and second derivatives at the atomic peaks are compared in Table 6. They are influenced by the omission of reflexions with $k \geq 7$ ($k_{\max.}=9$ for Cu $K\alpha$ radiation) and by the possible errors in the scale factors for different layers. For these reasons the anisotropic thermal parameters B_{ij} listed in Table 2 must be considered simply as additional parameters introduced to reduce the residuals.

Table 6. *Comparison of peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *from differential synthesis*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Zn	obs.	68·0	763	535	777	−1	513	−2
	calc.	69·5	768	537	779	0	502	−4
Cl	obs.	36·6	412	288	420	5	265	2
	calc.	37·3	414	293	420	3	260	1
O_1	obs.	14·5	159	99	159	2	106	−4
	calc.	14·4	159	101	158	2	102	−4
O_2	obs.	13·1	136	78	127	3	87	−5
	calc.	13·0	139	78	128	4	87	−6
N_1	obs.	12·5	122	103	118	−3	75	0
	calc.	12·4	121	106	117	−2	72	−1
N_2	obs.	10·7	115	76	111	−3	69	3
	calc.	10·5	114	77	112	−1	67	2
N_3	obs.	10·6	107	84	109	−1	63	2
	calc.	10·8	110	85	109	−1	63	1
C_1	obs.	11·0	110	99	112	1	64	−2
	calc.	10·9	111	101	111	1	63	−1
C_2	obs.	11·7	129	95	114	10	72	−13
	calc.	11·9	127	98	113	9	69	−12

The scattering factors used throughout the calculations are those of Thomas & Umeda (1957) for Zn^{2+}, Berghuis *et al.* (1955) for Cl^-, O, N and C, and McWeeny (1951) for H.

The calculations were done with the IBM 650 programs of Brown, Lingafelter, Stewart & Jensen (1959) for structure factors and Fourier syntheses and those of Shiono (1957, 1959) for differential synthesis.

Discussion

In bis-biuret-zinc chloride each metal atom is surrounded by a planar arrangement of four oxygen atoms lying at the corners of a slightly distorted square. 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 a distorted octahedron or a tetragonal bipyramid (Fig. 1). The distortion is obviously due to the different size of the ligands.

The distances and angles in the coordination polyhedron are (when the coordinates are not indicated the atom is at x, y, z):

$Zn(0, \frac{1}{2}, \frac{1}{2})$–$Cl(x, \frac{1}{2}-y, \frac{1}{2}+z)$	2·529 ± 0·003 Å
$Zn(0, \frac{1}{2}, \frac{1}{2})$–$O_1$	2·046 ± 0·008
$Zn(0, \frac{1}{2}, \frac{1}{2})$–$O_2$	2·027 ± 0·011
O_1–$Cl(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·221 ± 0·009
O_2–$Cl(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·250 ± 0·011
O_1–$Cl(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	3·285 ± 0·007
O_2–$Cl(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	3·232 ± 0·009
O_1–$O_2(\bar{x}, 1-y, 1-z)$	2·952 ± 0·013
O_1–O_2	2·806 ± 0·014

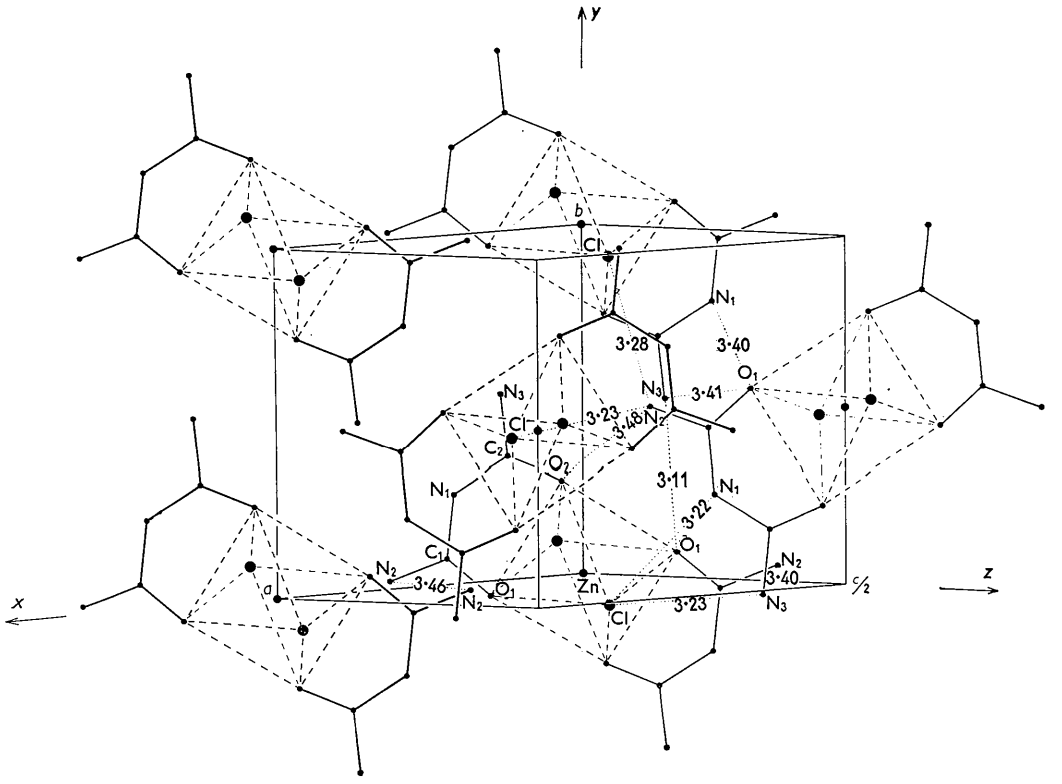


Fig. 1. Clinographic projection of the structure.

O_1–Zn($0, \frac{1}{2}, \frac{1}{2}$)–$O_2$	87·1 ±0·3°
O_1–Zn($0, \frac{1}{2}, \frac{1}{2}$)–Cl($x, \frac{1}{2}-y, \frac{1}{2}+z$)	88·9 ±0·2
O_2–Zn($0, \frac{1}{2}, \frac{1}{2}$)–Cl($x, \frac{1}{2}-y, \frac{1}{2}+z$)	90·3 ±0·3

The standard deviations are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles; the effects of errors in cell parameters were calculated following Darlow & Cochran (1961), and are negligible.

The Zn–O_1 and Zn–O_2 distances are not significantly different [$t_o=(l_1-l_2)(\sigma_1^2+\sigma_2^2)^{-\frac{1}{2}}=1\cdot397<1\cdot960$: significance test of Cruickshank & Robertson, 1953]. Their average value,

$$(\sum_i l_i\sigma_i^{-2}/\sum_i \sigma_i^{-2}) \pm (\sum_i \sigma_i^{-2})^{-\frac{1}{2}} = 2\cdot039 \pm 0\cdot006 \text{ Å},$$

is equal to the sum of the covalent radii: $r_0=0\cdot66$ Å (Pauling, 1960); $r_{Zn}=1\cdot38$ Å (octahedral, Merritt *et al.*, 1954). The distance Zn–Cl is in good agreement with the sum of Pauling's ionic radii, 2·55 Å. Both types of contact, O–O and O–Cl, are consistent with the sums of van der Waals radii: 2·80 and 3·20 Å respectively.

The organic molecule is in a *cis* form with both C–O bonds nearly parallel. This configuration is quite different from that of biuret in biuret hydrate and in bis-biuret-cadmium chloride. The bond distances and angles are:

C_1–O_1	1·227 ± 0·013 Å
C_2–O_2	1·244 ± 0·015
C_1–N_1	1·347 ± 0·012
C_2–N_1	1·367 ± 0·015
C_1–N_2	1·331 ± 0·017
C_2–N_3	1·318 ± 0·014
O_1–C_1–N_1	125·7 ± 1·0°
O_2–C_2–N_1	124·0 ± 1·0
C_1–N_1–C_2	127·6 ± 0·9
O_1–C_1–N_2	120·2 ± 1·0
O_2–C_2–N_3	120·2 ± 1·0
N_1–C_1–N_2	114·1 ± 1·0
N_1–C_2–N_3	115·7 ± 1·0

Table 7. *Comparison of bond lengths and angles for biuret molecule in different compounds*

	$C_2H_5N_3O_2.xH_2O$(1)		$Zn(C_2H_5N_3O_2)_2Cl_2$(2)		$Cd(C_2H_5N_3O_2)_2Cl_2$(3)		$K_2[Cu(C_2H_3N_3O_2)_2].4H_2O$(4)	
	t_o	Averaged length or angle	t_o	Averaged length or angle	t_o	Averaged length or angle	t_o	Averaged length or angle
C–O	0·28	1·25 ± 0·02 Å	0·86	1·23 ± 0·01 Å	0·42	1·25 ± 0·04 Å	1·32	1·26 ± 0·01 Å
C–NH	0·24	1·40 ± 0·02	1·04	1·36 ± 0·01	0·18	1·35 ± 0·03	1·27	1·40 ± 0·01
C–NH_2 (or NH^-)	0·86	1·35 ± 0·02	0·59	1·32 ± 0·01	0	1·35 ± 0·03	0·24	1·34 ± 0·01
O–C–NH	*3·25*	*121 ± 1°*	1·21	125 ± 1°	0·51	120 ± 2°	0·35	116 ± 1°
O–C–NH_2 (or NH^-)	1·66	123 ± 1	0	120 ± 1	0·18	121 ± 2	0·42	127 ± 1
HN–C–NH_2 (or NH^-)	1·68	116 ± 1	1·14	115 ± 1	0·29	119 ± 2	0·04	118 ± 1

(1) Hughes, Yakel & Freeman, 1961. (2) Present paper.
(3) Cavalca, Nardelli & Fava, 1960. (4) Freeman, Smith & Taylor, 1961.

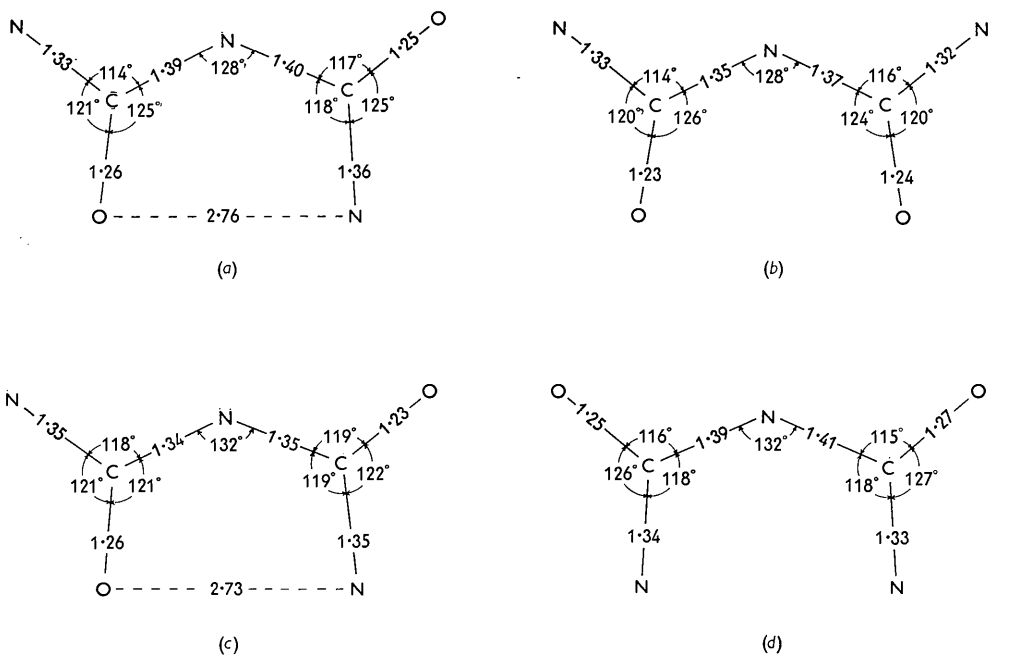


Fig. 2. Bond lengths and angles in the biuret molecule in different compounds:
(*a*) $C_2H_5N_3O_2.xH_2O$; (*b*) $Zn(C_2H_5N_3O_2)_2Cl_2$; (*c*) $Cd(C_2H_5N_3O_2)_2Cl_2$; (*d*) $K_2[Cu(C_2H_3N_3O_2)_2].4H_2O$.

Table 8. *Analysis of the planarity in the biuret molecule*

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

Best plane through	$O_1O_2N_1N_2N_3C_1C_2$		$O_1C_1N_1N_2$		$O_2C_2N_1N_3$	
m_1	0·8734		0·8493		0·8894	
m_2	0·0662		0·0765		0·0301	
m_3	0·4826		0·5224		0·4562	
d	3·1388		3·2563		3·0041	
	$\sigma_\perp$ (Å)*	Δ (Å)	$\Delta/\sigma_\perp$	Δ (Å)	$\Delta/\sigma_\perp$	Δ (Å)	$\Delta/\sigma_\perp$
O_1	0·007	−0·061	−8·71	0·000	0·00	—	—
O_2	0·008	0·062	7·75	—	—	−0·001	−0·12
N_1	0·009	−0·001	−0·11	0·000	0·00	−0·001	−0·11
N_2	0·010	0·045	4·50	0·000	0·00	—	—
N_3	0·010	−0·044	−4·40	—	—	−0·001	−0·10
C_1	0·010	−0·010	−1·00	0·000	0·00	—	—
C_2	0·009	0·011	1·22	—	—	0·001	0·11
$\Sigma(\Delta/\sigma_\perp)^2$			178·04		0·00		0·05
χ^2_{95}%			9·49		3·84		3·84

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

These values are all in good agreement with those found in amide groups (see, for example, Davies & Pasternak, 1956; Hahn, 1957; Tomiie, Koo & Nitta, 1958; *Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958).

There are no significant differences between the corresponding bond lengths and angles in the two NH_2–CO–NH parts of the biuret molecule, as indicated by the t_o values quoted in Table 7. This correspondence is also observed in biuret hydrate, in bis-biuret-cadmium chloride and in potassium bis-biuret-cuprate (II) tetrahydrate (Fig. 2); the t_o and averaged values for these compounds are also listed in Table 7. The comparison between these values shows that the coordination seems to make no appreciable difference to the bond distances as observed by Freeman, Smith & Taylor (1961) in biuret hydrate and potassium bis-biuret-cuprate(II) tetrahydrate. (There are possibly some minor differences in angles for the last compound.) This observation has also been made by Strandberg, Lindqvist & Rosenstein (1961) for the glycylglycine molecule in copper(II) mono-glycylglycine trihydrate.

The angles

$$C_1\text{–}O_1\text{–}Zn(0,\tfrac{1}{2},\tfrac{1}{2}) \qquad 127{\cdot}2\pm0{\cdot}7°$$
$$C_2\text{–}O_2\text{–}Zn(0,\tfrac{1}{2},\tfrac{1}{2}) \qquad 127{\cdot}9\pm0{\cdot}8$$

give a sum of 719·5° together with the others in the hexagonal chelate ring. This is not significantly different from that (720°) required for a planar system. Nevertheless, the N_1, C_1 and C_2 atoms lie −0·052, −0·138, −0·142 Å from the plane through $O_1O_2Zn(0,\frac{1}{2},\frac{1}{2})$; the equation of this plane is:

$$0{\cdot}8444x'+0{\cdot}1437y'+0{\cdot}5161z'=3{\cdot}4996\ .$$

The analysis of the planarity in the organic molecule, shown in Table 8, indicates that the deviations from the best least-squares plane (Schomaker, Waser, Marsh & Bergman, 1959) through all the atoms are statistically significant while each NH_2–CO–NH group is quite planar (considering of course the heavy atoms). Steric hindrance between the oxygen atoms causes a rotation of the two groups pivoted on the N_1 central nitrogen, the dihedral angle between the planes $O_1C_1N_1N_2$ and $O_2C_2N_1N_3$ being 174·8°.

The same kind of distortion has been found in biuret hydrate in which the dihedral angle between the two NH_2–CO–NH groups is 174·5° and in potassium bis-biuret-cuprate(II) tetrahydrate in which this angle is 175·0°. In bis-biuret-cadmium chloride the deviations from planarity ($\bar{\Delta}=0{\cdot}04$, $\Delta_{max.}=0{\cdot}06$ Å) are within the range of e.s.d.'s, but these are much larger than those of the previous compounds because of the presence of the heavy cadmium atom.

The observed distortion seems to indicate some independence of the amide groups in biuret and is in agreement with the small double-bond character of C–NH bonds in the three configurations assumed by biuret, as can be seen by averaging the mean values of Table 7 and deducing the corresponding V.B. bond orders:

Bond	Mean length	Bond order*
C–O	$1{\cdot}24_6$ Å	1·45
C–NH_2 (or NH^-)	$1{\cdot}33_3$	1·41
C–NH	$1{\cdot}38_1$	1·22

* Bond order–distance curves were derived using the well known Pauling's relation: $r_x=r_1-(r_1-r_2)3x/(2x+1)$ with $r_1=1{\cdot}474$, $r_2=1{\cdot}265$ Å for C–N (Donohue, Lavine & Rollet, 1956) and $r_1=1{\cdot}43$, $r_2=1{\cdot}17$ Å for C–O (Abrahams, 1956).

The coordinates of the hydrogen atoms were calculated using trigonal sp^2 bonds for nitrogens and assuming a N–H distance of 1·04 Å. These coordinates are reasonable, taking into account the results of the last F_o-F_c synthesis (Table 5) and the orientation of the possible hydrogen bonds.

The angular criterion for hydrogen bonding (Donohue, 1952; Fuller, 1959) is fulfilled for the following contacts:

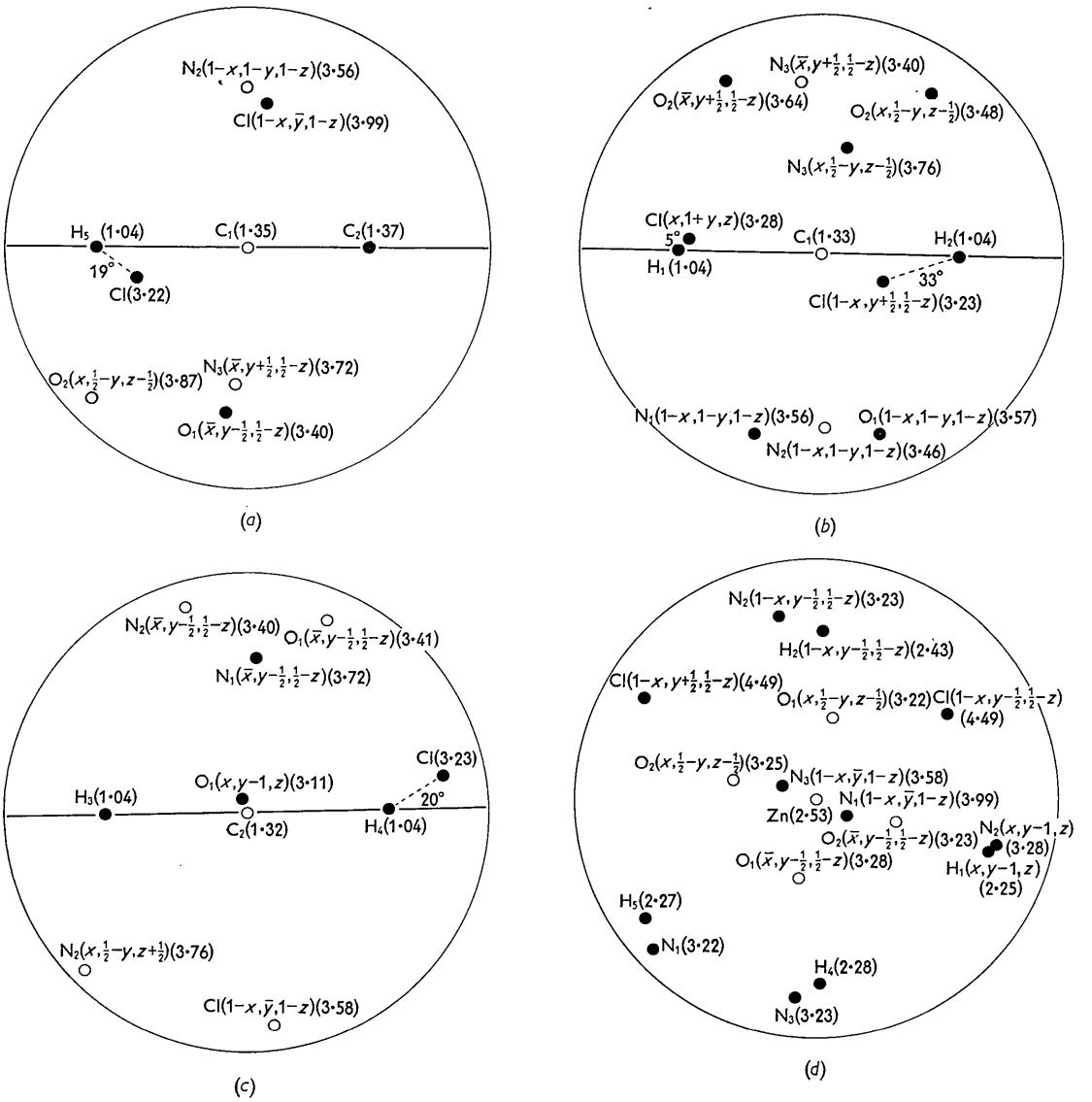


Fig. 3. Stereographic projections of the environment of:
(*a*) N_1, viewed down N_1–C_1; (*b*) N_2, down N_2–C_1; (*c*) N_3, down N_3–C_2; (*d*) Cl, down Cl–Zn.

N_1–Cl	$3{\cdot}223 \pm 0{\cdot}011$ Å
N_2–Cl(x, $1+y$, z)	$3{\cdot}282 \pm 0{\cdot}012$
N_3–Cl	$3{\cdot}234 \pm 0{\cdot}013$

as shown in the stereographic projections of Fig. 3. The distance N_2–Cl($1-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$) $= 3{\cdot}233 \pm 0{\cdot}011$ Å can hardly be considered as a hydrogen bond owing to the large value (33°) of the corresponding H–N–Cl angle.

All the other distances are consistent with the packing requirements, those shorter than 3·5 Å being as follows:

O_1–N_1($\bar{x}$, $y+\frac{1}{2}$, $\frac{1}{2}-z$)	$3{\cdot}398 \pm 0{\cdot}012$ Å
O_1–N_3($\bar{x}$, $y+\frac{1}{2}$, $\frac{1}{2}-z$)	$3{\cdot}408 \pm 0{\cdot}014$
O_2–N_2(x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	$3{\cdot}477 \pm 0{\cdot}015$
N_2–N_2($1-x$, $1-y$, $1-z$)	$3{\cdot}462 \pm 0{\cdot}014$
N_3–N_2($\bar{x}$, $y-\frac{1}{2}$, $\frac{1}{2}-z$)	$3{\cdot}404 \pm 0{\cdot}013$
N_3–O_1(x, $y-1$, z)	$3{\cdot}105 \pm 0{\cdot}014$

The calculations were performed on the IBM 650 computer of the Centro Calcoli e Servomeccanismi della Università di Bologna with financial support from Consiglio Nazionale delle Ricerche. The programmes for structure factors and Fourier calculations were obtained through the courtesy of Dr L. H. Jensen and those of differential synthesis through the courtesy of Prof. G. A. Jeffrey. It is a pleasure to thank all these people and Prof. L. Cavalca for his valuable interest.

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Neutron Diffraction Study of Magnesium Deuteride*

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A magnesium deuteride preparation of composition $Mg(D_{0\cdot9}H_{0\cdot1})_2$ is found to be tetragonal with $a=4\cdot5025$, $c=3\cdot0123$ Å. The atomic positions are:

2 Mg in (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, 4(D + H) in $\pm$ $(xx0)$ $(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ with $x=0\cdot306\pm0\cdot003$.

The bond lengths are Mg–6D = $1\cdot95\pm0\cdot02$ Å. The structure is of the rutile type.

Some years ago it was shown by X-ray diffraction (Ellinger *et al.*, 1955) that magnesium hydride is tetragonal with two molecules in a unit cell of dimensions $a=4\cdot5618\pm0\cdot0005$, $c=3\cdot0205\pm0\cdot0005$ Å.

The two magnesium atoms were found to be in positions $(0, 0, 0)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. It was suggested that the hydrogen atoms were located at the sites

$$\pm(x, x, 0)(\tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{1}{2})$$

with $x \approx 0\cdot306$, *i.e.* that MgH_2 has the rutile type of structure. However, the hydrogen atoms had no measurable effect on the diffraction intensities, and accordingly there was no experimental proof for the proposed hydrogen positions. A direct determination of the hydrogen sites by means of neutron diffraction was therefore undertaken, using the deuteride in preference to the hydride.

Magnesium deuteride was prepared by reaction of deuterium gas with magnesium metal (obtained by decomposition of MgH_2) for four days at 510 °C.

* Work done under the auspices of the U.S. Atomic Energy Commission.