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Crystallographic Studies of the Biuret Reaction.
II. Structure of Bis-biuret-copper(II) Dichloride, $Cu(NH_2CONHCONH_2)_2Cl_2$

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Bis-biuret-copper(II) dichloride, $Cu(NH_2CONHCONH_2)_2Cl_2$, forms blue-green crystals when an aqueous alcoholic solution of copper(II) chloride and biuret is slowly cooled. The structure was solved by standard Fourier methods and refined by least-squares with anisotropic thermal parameters ($R = 0{\cdot}091$). Hydrogen atoms were located in a three-dimensional ($F_o - F_c$) synthesis. The biuret molecules act as bidentate chelates *via* their oxygen atoms. The four oxygen atoms in the centrosymmetrical $[Cu(NH_2CONHCONH_2)_2]^{2+}$ ion form a square about the copper atom, whose elongated coordination octahedron is completed by the two chloride ions (Cu–O = 1·94 Å, Cu–Cl = 2·96 Å). The structure analysis was complicated by a space group ambiguity affecting only the light atoms. This ambiguity could not be resolved on the basis of the crystallographic data alone but only by invoking criteria of molecular geometry to eliminate a non-centrosymmetrical alternative to the actual structure.

Introduction

The violet complex, $K_2[Cu(NHCONHCONH)_2].4H_2O$, is formed by the reaction of alkaline biuret with copper(II). In this complex the biuret molecules act as bidentate chelates, the deprotonated amide nitrogen atoms being the ligand atoms (Freeman, Smith & Taylor, 1961). Under neutral conditions a blue-green complex, $[Cu(NH_2CONHCONH_2)_2]Cl_2$, can be isolated. In a preliminary study (Freeman, Smith & Taylor, 1959) it was found that the biuret molecules in the blue-green complex are also bidentate chelates but are probably coordinated to the copper atom *via* their oxygen atoms. This has been confirmed by the present detailed refinement.

Data

Tiny pale blue-green prisms of the complex were formed when a warm solution of copper(II) chloride and biuret in 95% alcohol was gradually cooled. Crystals could also be grown by allowing an alcoholic solution of copper(II) chloride to diffuse slowly into a similar solution of biuret through the base of a sintered glass crucible (porosity 3). The crystals were unstable in air but were protected during the X-ray exposures by a thin film of collodion.

The space-group and unit-cell dimensions have been previously reported by Nardelli & Chierici (1960) with whose results (N&C) our measurements (F&S) are in essential agreement after interchanging *a* and *b*:

$C_4H_{10}O_4N_6Cl_2Cu$ F.W. 340.63

Orthorhombic	N&C	F&S
a	7·99 ± 0·01	6·776 ± 0·006 Å
b	6·76 ± 0·01	8·025 ± 0·012
c	10·69 ± 0·01	10·734 ± 0·012
U	578	583 ± 2 Å^3
D_m	1·95	– g.cm^{-3}
Z	2	2
D_x	1·96	1·938 ± 0·007 g.cm^{-3}
μ(Cu $K\alpha$)	–	70·7 cm^{-1}

Space group *Pnnm* (D_{2h}^{12}) or *Pnn*2 (C_{2v}^{10}) from systematic extinctions (*h*0*l* absent for $h+l$ odd, 0*k*0 absent for *k* odd).

Pnnm confirmed by structure analysis.

The values of *a*, *b* and *c* were fitted by least squares to the values of $4\sin^2\theta/\lambda^2$ of 20 α_1 and α_2 components of *hk*0 and *h*0*l* reflexions with $51° \le \theta \le 82°$. The observations were arbitrarily given weights proportional to $\sin^2\theta$. The spacings were measured on zero-layer Weissenberg photographs taken with Cu $K\alpha$ radiation [λ(Cu $K\alpha_1$) = 1·5405, λ(Cu $K\alpha_2$) = 1·5443 Å.] and calibrated with sodium chloride powder lines. The probable errors in the dimensions were taken as three times the standard deviations calculated from the least-squares matrix.

Three-dimensional Weissenberg data were recorded about the *a* and *b* axes with Cu $K\alpha$ radiation. The intensities were estimated visually and were corrected for absorption and for the usual Lorentz and polarization factors. The program for making the absorption corrections (Lovell, 1961) used the method of Busing & Levy (1957) as extended by Wells (1960). Standard atomic absorption coefficients (*International Tables for X-ray Crystallography*, 1962) were used.

The data were placed on a common scale by comparisons of the intensities F_1^2 and F_2^2 of 387 reflexions recorded about both axes. The agreement factor $\Sigma|F_1-F_2|/\Sigma\frac{1}{2}|F_1+F_2|$ between the two sets of data was 6·1%. Of 770 independent reflexions within the observable range of $\sin\theta/\lambda$, intensities were measured for

Table 1. *Calculated and observed structure factors*

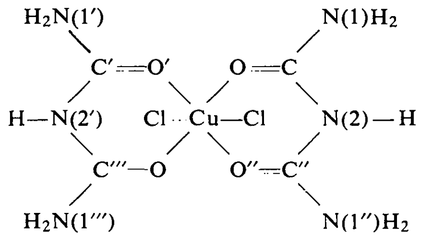
0 0		
2	97.03	89.93
4	56.17	64.26
6	69.90	77.09
8	83.27	85.04
10	51.13	54.64
12	9.94	11.01
0 1		
1	41.45	34.10
3	25.15	23.80
5	-3.72	10.69
7	44.49	47.41
9	13.15	14.86
11	8.08	8.19
13	6.70	7.83
0 2		
0	-55.74	44.43
2	-15.06	15.06
4	19.10	19.31
6	6.60	6.24
8	-11.37	11.25
10	-4.34	5.09
12	5.73	6.40
0 3		
1	59.44	48.52
3	60.32	63.58
5	66.06	64.42
7	16.43	16.21
9	32.89	25.47
11	23.51	24.64
13	15.17	14.58
0 4		
0	11.79	9.97
2	77.49	74.63
4	49.70	50.67
6	34.73	31.39
8	25.35	24.88
10	23.37	29.21
12	25.09	28.49
0 5		
1	2.74	1.83x
3	24.83	23.01
5	37.96	34.13
7	-2.82	3.62
9	3.65	6.12
11	9.69	10.93
0 6		
0	7.82	8.58
2	4.26	3.97
4	5.63	6.56
6	4.75	5.44
8	5.18	4.69
10	.68	3.18x
0 7		
1	35.39	28.97
3	9.88	9.82
5	-1.57	2.30
7	27.85	24.76
9	17.31	17.52
0 8		
0	44.90	34.21
2	19.71	17.33
4	19.40	19.11
6	21.04	21.58
8	21.93	21.94
0 9		
	-1.06	2.50
3	6.04	7.19
5	2.61	2.50
7	4.99	.52x
0 10		
0	-3.11	2.50
2	-.94	1.51x
1 0		
1	78.96	78.96
3	-4.68	6.20
5	8.90	7.31
7	34.81	36.20
9	29.55	29.01
11	4.24	5.01
13	4.05	4.57
1 1		
0	61.25	52.06
1	-13.75	17.96
2	46.44	46.02
3	81.37	70.18
4	17.53	15.30
5	35.35	40.45
6	33.25	30.04
7	15.55	16.33
8	30.96	29.72
9	-7.66	6.44
10	14.58	15.30
11	17.03	18.56
12	9.48	10.33
13	13.61	15.86
1 2		
0	28.56	36.08
1	48.09	43.31
2	-18.81	25.27
3	61.12	59.41
4	41.69	45.54
5	52.11	51.90
6	-1.13	2.30x
7	30.45	27.50
8	-8.51	10.89
9	20.72	20.15
10	11.70	12.91
11	19.47	21.70
12	1.04	2.94x
13	15.98	15.97
1 3		
0	27.25	29.57
1	-47.17	45.58
2	36.66	38.98
3	-23.84	21.26
4	48.03	51.34
5	-45.58	50.19
6	23.24	22.01
7	-17.42	17.13
8	14.56	12.40
9	-18.35	18.16
10	18.47	19.99
11	-7.71	10.13
12	14.19	15.30
13	-11.40	10.09
1 4		
0	-3.95	3.70
1	5.86	4.09
2	4.91	5.48
3	30.01	27.14
4	9.94	10.69
5	17.43	15.90
6	8.49	9.30
7	6.07	5.96
8	-1.32	2.15
9	5.80	5.92
10	-.20	3.02x
11	12.61	13.55
12	3.38	3.66
1 5		
0	19.72	16.97
1	40.28	33.50
2	27.34	24.12
3	17.22	17.96
4	39.48	35.88
5	31.65	26.15
6	22.47	20.19
7	18.70	18.48
8	10.68	12.16
9	20.73	20.39
10	13.55	14.74
11	5.99	7.07
12	13.20	9.74
1 6		
0	-3.82	3.38
1	30.11	28.53
2	-1.44	1.99
3	25.80	25.23
4	-36.58	31.67
5	22.52	20.15
6	-10.68	10.65
7	21.25	21.86
8	5.93	6.83
9	15.31	15.18
10	-7.33	7.79
11	10.63	9.18
1 7		
0	23.10	18.40
1	-7.78	7.99
2	11.69	11.40
3	-20.67	18.76
4	-2.25	3.81
5	-9.92	9.97
6	8.37	9.62
7	-10.65	12.28
8	14.08	14.46
9	-2.94	2.86
10	5.93	5.05
1 8		
0	3.08	4.21
1	14.17	13.59
2	10.04	9.58
3	3.19	3.74
4	19.86	18.24
5	5.28	6.52
6	10.33	11.01
7	9.50	10.57
8	2.74	3.46
1 9		
0	10.39	11.37
1	2.22	3.38
2	12.23	13.47
3	10.86	11.44
4	11.03	11.96
5	3.89	4.17
6	10.78	10.77
1 10		
0	-.54	1.31x
1	7.38	8.03
2	-7.14	6.83
3	8.52	7.39
2 0		
0	-69.53	82.85
2	16.19	20.78
4	-4.12	11.29
6	7.65	9.50
8	-1.63	6.20
10	-8.88	10.69
12	8.44	9.58
2 1		
0	-110.67	89.81
1	61.64	66.08
2	-32.25	34.77
3	33.35	33.98
4	6.48	6.95
5	50.38	51.90
6	-17.96	17.41
7	21.93	20.07
8	-36.50	31.79
9	28.37	24.36
10	-15.65	16.57
11	14.63	15.38
12	1.84	2.62
13	11.74	10.25
2 2		
0	91.32	85.95
1	-3.16	5.09
2	71.89	71.81
3	30.31	36.84
4	50.40	49.99
5	28.85	29.05
6	42.90	43.83
7	-10.52	10.41
8	41.83	36.56
9	4.58	5.32
10	30.26	28.77
11	10.02	10.65
12	17.40	17.01
13	5.55	5.21
2 3		
0	7.40	6.76
1	8.56	9.70
2	28.76	30.48
3	30.61	27.82
4	18.39	18.20
5	9.64	11.96
6	9.89	10.65
7	19.19	17.68
8	8.47	8.46
9	2.32	4.49
10	11.28	12.08
11	10.07	10.57
12	8.29	9.58
2 4		
0	25.85	22.37
1	-10.64	11.05
2	-1.98	3.78
3	-5.90	7.59
4	26.06	22.65
5	-.63	2.19x
6	10.31	9.70
7	-4.73	4.17
8	2.37	2.19
9	-6.40	6.40
10	8.88	9.70
11	-3.27	4.29
12	2.51	2.27
2 5		
0	7.76	9.38
1	33.06	29.53
2	-12.08	12.76
3	29.40	26.51
4	-14.96	13.31
5	12.02	11.25
6	-4.18	4.57
7	25.88	20.43
8	1.57	3.74x
9	16.76	16.17
10	-6.31	6.99
11	12.32	12.36
2 6		
0	31.96	29.88
1	20.79	19.39
2	30.24	29.25
3	-8.21	7.83
4	22.43	20.62
5	-12.37	11.84
6	22.76	22.57
7	15.55	15.70
8	18.80	20.43
9	9.42	9.54
10	15.03	13.99
2 7		
0	20.70	19.71
1	9.31	9.97
2	8.19	8.50
3	10.16	10.37
4	5.48	5.80
5	18.55	18.32
6	8.16	9.30
7	3.56	5.01
8	10.25	11.40
9	6.47	6.68
2 8		
0	-4.99	4.89
1	-9.26	8.78
2	6.22	6.04
3	4.01	5.05
4	-1.78	1.83
5	3.98	4.25
6	1.80	1.91
7	-4.24	4.45
8	2.21	2.07
2 9		
0	-13.13	14.19
1	16.24	17.64
2	-4.61	5.44
3	8.87	9.97
4	-.71	1.63x
5	10.96	11.84
6	-4.94	4.45
2 10		
0	11.67	10.53
1	4.89	4.65
2	11.59	11.29
3 0		
1	19.08	17.41
3	84.17	72.68
5	59.76	60.28
7	27.36	25.55
9	7.43	9.62
11	26.77	28.21
13	20.79	15.74
3 1		
0	36.92	38.47
1	-17.19	15.62
2	29.91	31.08
3	-8.90	8.98
4	46.86	50.31
5	4.76	5.48
6	23.19	22.69
7	-20.58	19.31
8	14.90	13.15
9	-2.67	3.81
10	18.24	18.84
11	-1.12	3.14x
12	12.49	12.24
13	-2.30	.99x
3 2		
0	-44.43	53.05
1	18.56	17.60
2	14.42	15.42
3	-4.36	7.91
4	8.64	8.94
5	-8.16	11.25
6	-1.65	2.54
7	7.94	7.23
8	-7.42	6.68
9	11.06	10.45
10	-3.14	5.21
11	1.66	2.94x
12	7.96	8.27
3 3		
0	25.61	20.78
1	11.25	12.20
2	29.97	31.19
3	18.59	17.72
4	14.95	13.87
5	26.79	26.31
6	23.91	21.78
7	.96	3.38x
8	17.66	20.62
9	7.85	9.30
10	8.23	9.26
11	8.12	9.14
12	8.19	7.83
3 4		
0	7.61	7.75
1	57.37	56.27
2	-.32	2.90
3	38.88	38.59
4	-2.70	2.98
5	45.58	44.78
6	-.96	2.50x
7	33.95	31.47
8	3.51	3.74
9	28.90	29.96
10	.70	2.23
11	14.34	13.75
3 5		
0	22.61	20.15
1	-4.31	4.49
2	16.31	14.66
3	-13.65	12.88
4	-6.81	6.48
5	-20.05	17.09
6	6.63	6.04
7	2.94	2.62
8	16.34	16.37
9	-5.57	5.21
10	6.56	6.68
11	-5.94	5.56
3 6		
0	22.97	20.03
1	.44	2.42x
2	.39	2.42x
3	-2.02	2.62
4	4.26	4.53
5	-1.16	3.18x
6	7.52	7.95
7	-1.50	3.74x
8	7.30	7.51
9	1.11	2.82
10	4.43	4.01
3 7		
0	11.52	11.56
1	9.48	10.21
2	20.22	19.55
3	8.72	10.21
4	35.36	30.32
5	3.40	3.62
6	19.48	19.31
7	10.00	10.25
8	6.83	6.80
9	4.26	3.30
3 8		
0	-5.33	5.56
1	12.05	12.48
2	-1.66	1.91
3	21.11	20.58
4	-2.43	2.58
5	14.92	15.30
6	-2.36	2.58
7	10.85	9.82
3 9		
0	6.50	7.71
1	-3.62	4.17
2	.18	1.67x
3	.76	1.55x
4	-.33	1.35x
5	4.18	3.06
4 0		
0	15.83	18.12
2	22.40	19.71
4	55.80	48.52
6	21.87	20.07
8	2.42	2.62
10	18.14	18.99
12	15.02	14.11
4 1		
0	60.06	55.71
1	12.33	9.42
2	31.07	31.11
3	38.10	36.72
4	22.44	21.78
5	21.43	19.87
6	18.40	17.68
7	13.36	12.52
8	26.92	23.68
9	7.11	7.83
10	21.42	20.62
11	14.00	14.07
12	5.90	5.40
4 2		
0	24.79	23.37
1	-17.10	17.48
2	20.39	19.99
3	-1.91	3.30
4	12.12	12.99
5	-11.66	11.56
6	14.44	14.27
7	-2.98	3.34
8	14.37	14.39
9	-11.04	11.21
10	9.53	10.09
11	-1.31	2.42x
12	5.20	3.81
4 3		
0	-21.33	18.92
1	34.89	28.41
2	-24.31	22.93
3	8.46	8.50
4	-4.20	4.53
5	17.92	15.02
6	-11.66	11.29
7	18.10	17.05
8	-16.26	18.08
9	17.93	18.56
10	-9.27	10.25
11	4.39	4.61
4 4		
0	28.15	25.59
1	17.94	16.17
2	26.33	23.56
3	7.08	7.07
4	3.79	4.01
5	2.61	2.54
6	17.70	17.13
7	10.58	10.93
8	22.09	22.61
9	10.74	10.57
10	5.63	6.20
11	4.06	3.50
4 5		
0	16.15	13.87
1	22.53	19.55
2	17.59	16.05
3	5.66	6.32
4	5.59	5.80
5	10.41	9.66
6	11.11	11.05
7	12.78	12.80
8	11.27	12.84
9	12.41	13.23
10	7.24	6.80
4 6		
0	10.58	9.62
1	-6.42	6.12
2	10.26	9.93
3	-.09	3.18x
4	13.40	12.52
5	8.64	9.02
6	7.96	8.50
7	-5.58	5.88
8	6.40	6.24
9	-3.30	2.90
4 7		
0	-14.22	14.19
1	2.94	3.78
2	-6.18	6.08
3	18.71	18.36
4	-7.93	8.31
5	11.62	12.56
6	-5.82	7.07
7	5.07	5.09
8	-5.99	4.85
4 8		
0	6.34	8.03
1	10.22	11.56
2	7.20	8.86
3	2.70	2.50
4	16.06	17.64
5	1.57	1.99
6	7.16	6.80
4 9		
0	10.58	10.53
1	5.24	5.25
2	8.95	8.38
3	7.52	.72x
5 0		
1	4.75	4.93
3	3.00	3.46
5	6.67	6.00
7	-6.79	6.95
9	8.43	8.31
11	4.12	4.21
5 1		
0	1.43	1.03
1	7.58	7.07
2	21.48	19.95
3	-9.53	10.25
4	19.28	18.08
5	-15.64	14.90
6	12.88	11.52
7	6.22	6.76
8	5.76	6.80
9	4.01	4.29
10	6.90	6.99
11	-3.55	3.46
5 2		
0	14.71	14.70
1	32.09	31.19
2	-3.64	3.58
3	37.02	36.24
4	-3.77	3.78
5	35.76	34.10
6	2.04	2.66
7	24.05	26.23
8	3.27	3.97
9	15.47	15.78
10	1.68	1.79
11	14.35	9.82
5 3		
0	33.94	31.71
1	5.88	6.04
2	12.63	11.40
3	6.80	6.72
4	7.09	7.03
5	3.83	3.58
6	11.09	12.20
7	7.38	8.31
8	17.16	16.85
9	1.71	1.99
10	9.50	9.18
5 4		
0	2.82	3.06
1	1.58	1.83
2	2.23	1.95
3	-11.04	10.45
4	-2.93	2.66
5	-16.75	17.56
6	.07	2.98x
7	4.86	5.29
8	2.34	2.07
9	-1.35	2.03x
10	1.40	1.19x
5 5		
0	20.86	18.64
1	-2.37	2.42
2	14.02	13.27
3	-.84	3.62x
4	20.47	19.71
5	2.86	2.38
6	16.47	16.41
7	-5.12	5.05
8	10.05	10.41
9	.30	1.71x
5 6		
0	-8.39	7.59
1	20.72	19.91
2	6.48	6.72
3	25.71	24.20
4	12.20	11.92
5	22.20	20.82
6	4.37	5.13
7	15.81	14.58
8	-2.29	2.07
5 7		
0	-2.64	2.58
1	1.51	3.46x
2	2.45	3.46
3	4.74	5.17
4	-1.63	3.02x
5	5.89	5.76
6	-1.65	1.59
5 8		
0	5.74	6.12
1	-1.16	1.55x
2	-.19	1.47x
3	1.93	2.23
4	-2.76	.83x
6 0		
0	31.75	28.33
2	28.30	25.15
4	14.19	14.62
6	15.36	17.05
8	22.40	26.03
10	14.75	13.63
6 1		
0	-16.56	16.09
1	10.47	10.05
2	-14.43	13.71
3	9.91	9.18
4	-21.59	22.21
5	11.03	12.16
6	-10.15	10.37
7	5.91	6.76
8	-7.46	7.31
9	6.06	6.24
10	-11.48	7.67
6 2		
0	-2.92	4.17
1	16.33	15.62
2	1.90	2.94x
3	-4.15	5.05
4	9.54	10.61
5	3.15	3.42x
6	4.81	5.56
7	7.14	8.42
8	-1.89	2.58x
9	10.60	9.70
6 3		
0	17.92	19.67
1	18.08	19.23
2	15.91	15.97
3	13.42	13.47
4	2.49	3.18
5	8.40	9.42
6	9.74	10.29
7	14.01	14.50
8	13.44	13.79
9	10.18	8.70
6 4		
0	22.03	21.94
1	-5.77	5.60
2	13.91	14.42
3	-1.32	2.90x
4	10.50	10.69
5	.35	2.66x
6	11.72	12.20
7	-3.48	3.70
8	11.28	11.21
6 5		
0	-10.37	11.01
1	2.07	4.09x
2	-7.14	7.83
3	9.87	10.85
4	4.04	5.13
5	9.65	10.33
6	-4.41	4.09
7	3.61	4.25
6 6		
0	-.45	3.22x
1	.98	3.18x
2	3.91	4.01
3	9.05	7.87
4	4.57	4.21
5	2.60	2.38x
6	3.45	2.78
6 7		
0	8.44	8.86
1	11.46	10.37
2	6.58	6.36
3	4.26	3.78
4	10.25	1.31x
7 0		
1	18.37	19.59
3	12.34	13.91
5	6.56	7.75
7	16.33	16.25
7 1		
0	15.93	15.93
1	6.82	7.71
2	7.29	8.23
3	8.51	8.98
4	6.83	7.55
5	11.90	12.40
6	7.16	7.55
7	6.55	6.80
8	8.27	6.80
7 2		
0	8.33	9.14
1	.97	3.26x
2	2.13	3.22x
3	1.99	3.14x
4	-5.14	6.00
5	1.48	2.78x
6	.96	2.46x
7 3		
0	1.97	2.90x
1	-3.37	3.54
2	9.26	9.74
3	-13.49	13.87
4	8.51	9.38
5	-12.59	12.72
6	6.75	6.68
7	-3.51	3.54
7 4		
0	-.97	2.50x
1	12.66	13.71
2	2.43	2.90
3	15.07	15.93
4	8.41	8.19
5	17.41	16.53
6	3.86	3.85
7 5		
0	-.30	2.54x
1	5.71	6.24
2	5.73	6.44
3	14.61	14.07
4	5.26	5.60
5	11.80	9.74
7 6		
0	-1.16	1.95x
1	.08	1.91x
2	-2.43	1.63x
8 0		
0	-5.65	6.52
2	-6.81	7.75
4	-6.01	6.20
8 1		
0	2.94	3.18
1	11.03	11.25
2	2.08	2.46
3	4.92	5.32
4	6.78	6.28
5	4.26	3.97
8 2		
0	18.62	18.88
1	-.28	2.38x
2	15.63	15.90
3	.23	2.07x
4	10.12	9.38
8 3		
0	1.52	1.99
1	-2.91	2.98
2	-2.57	2.82
3	4.65	4.37
8 4		
0	-7.87	6.36
1	.66	1.31x

The running index is *l*. Unobservably weak reflexions are denoted by ×. Reflexions 493 and 674, which apparently lay beyond the edges of the films, were omitted from the refinement.

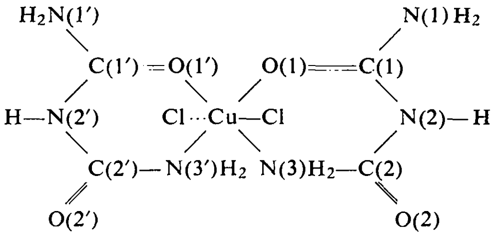
710. The standard deviations of the structure amplitudes were estimated by plotting the r.m.s. differences between the two values of doubly observed reflexions, averaged over ranges of $|F_{obs}|$*. For 60 unobservably weak reflexions, F_{unobs} was taken as $\frac{1}{2}F_{min}$ with standard deviation $12^{-\frac{1}{2}}F_{min}$ (Ibers, 1956), where F^2_{min} was the lowest observation in the same region of reciprocal space.

Structure analysis and refinement

The general features of the structure were immediately deduced from two-dimensional Patterson syntheses followed by electron-density projections using phases determined by the copper and chlorine atoms. It was apparent that the copper atom of $[CuBiuret_2]Cl_2$ is located at the origin. The biuret molecules act as bidentate chelates and lie perpendicular to the plane (001). The four ligand atoms of the two biuret molecules form an approximate square about the copper. The two chlorine atoms lie on or near the perpendicular to this square and through the copper atom (*i.e.* at or near $z=0$). Peak heights and bond-lengths in zero-layer and generalized projections were consistent with a model (I) of point symmetry $2/m$ in which the biuret molecules are chelated *via* their two amide *oxygen* atoms.



(I)



(II)

Owing to the high degree of symmetry of this trial structure, refinement was carried out in the centrosymmetric space-group *Pnnm*, although an unsymmetrical oxygen–nitrogen chelated structure (II) belonging to *Pnn*2 was investigated in parallel (see p. 158). In order to prejudice the refinement as little as possible in favour of either structure, the initial structure factors were calculated with a single average scattering factor for all the oxygen and nitrogen atoms. In the resultant three-dimensional Fourier synthesis in space-group *Pnnm*, both the peak heights and bond lengths turned out to be those expected for a biuret molecule chelated *via* its two oxygen atoms:

l(Cu–Cl) $=3{\cdot}01$ Å
l(Cu–O) $=1{\cdot}92$
l(O=C) $=1{\cdot}23$
l(C–NH_2) $=1{\cdot}36$
l(C–NH–) $=1{\cdot}33$

The reliability index for all reflexions was $R=0{\cdot}152$. A full-matrix least-squares refinement with isotropic thermal parameters converged after four cycles ($R=0{\cdot}138$). Three full-matrix least-squares cycles with anisotropic thermal parameters completed the refinement.

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* The e.s.d.'s could be adequately represented by the functions – (i) $\sigma(F)=a|F_{obs}|$ for $|F_{min}|\le|F_{obs}|\le 5$, and (ii) $\sigma(F)=a|F_{obs}|+b(|F_{obs}|-5)^2+c(|F_{obs}|-5)^3$ for $|F_{obs}|>5$, where $a=5\times10^{-2}$, $b=1{\cdot}25\times10^{-4}$, $c=2\times10^{-7}$.

Table 2

Final fractional coordinates, standard deviations (Å) and magnitudes of shifts in final least-squares cycle
Shifts refer to last two digits in σ.

Atom	x	$\sigma(x)$(shift)	y	$\sigma(y)$(shift)	z	$\sigma(z)$(shift)
Cu	0	—	0	—	0	—
Cl	0·3006	0·0014 (00) Å	−0·2626	0·0013 (01) Å	0	—
O	0·1254	0·0028 (00)	0·1326	0·0023 (00)	0·1281	0·0029 (00) Å
N(1)	0·2198	0·0050 (06)	0·3736	0·0030 (05)	0·2128	0·0043 (05)
C	0·1774	0·0035 (00)	0·2817	0·0034 (02)	0·1142	0·0037 (06)
N(2)	0·1943	0·0046 (00)	0·3569	0·0043 (05)	0	—

Final anisotropic temperature parameters $T_f=\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)\}$
with standard deviations (in parentheses) and final shifts.
S.D.'s and shifts refer to last two digits in b_{ij}.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	0·0182 (04)0	0·0094 (3)0	0·0029 (1)0	−0·0038 (1)0	0	0
Cl	0·0151 (04)0	0·0104 (3)0	0·0058 (3)0	−0·0006 (3)0	0	0
O	0·0176 (07)0	0·0083 (9)0	0·0042 (5)0	−0·0016 (7)0	−0·0017 (6)0	−0·0002 (4)1
N(1)	0·0285 (12)0	0·0114 (5)0	0·0059 (4)0	−0·0044 (6)1	−0·0030 (5)0	−0·0019 (3)1
C	0·0129 (07)0	0·0088 (5)0	0·0038 (3)0	−0·0000 (4)0	−0·0009 (3)0	−0·0001 (3)1
N(2)	0·0159 (10)0	0·0095 (6)0	0·0037 (4)0	−0·0017 (6)0	0	0

The final refinement criteria were: $R=0{\cdot}091$, weighted reliability index $R'=0{\cdot}141$, and $\Sigma w\Delta^2=2{\cdot}59$.

The least-squares calculations were made with the program ORXLS (Busing & Levy, 1959). The function minimized was $\Sigma w(\|F_{\rm obs}\|-\|F_{\rm calc}\|)^2$, and the observations were given weights w equal to $1/\sigma^2(F)$. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen, oxygen, chlorine and Cu^+. The scattering factor for Cu^+ was corrected for anomalous dispersion by subtracting 2·1 electrons over the whole $\sin\theta$ range (Dauben & Templeton, 1955). The calculated and observed structure factors are listed in Table 1 and the atomic parameters in Table 2.

As a final confirmation of the structure, a three-dimensional difference Fourier synthesis was calculated. Five intense low-angle reflexions for which $|F_o| \ll |F_c|$ – 020, 031, 110, 113 and 210 – were omitted. The standard deviation $\sigma(\varrho)$ of the electron-density $\varrho(xyz)$ (Cruickshank & Robertson, 1953) was 0·28 $e.Å^{-3}$. The difference map contained only three positive peaks with maxima equal to $3\sigma(\varrho)$: 0·88, 0·85 and 0·82 $e.Å^{-3}$. From their positions, these peaks clearly corresponded to the three crystallographically independent hydrogen atoms in the asymmetric unit, two being bonded to the amide nitrogen and one to the central imide nitrogen. Their locations and environments are listed in Table 3. The fourth highest peak had a height of $2{\cdot}5\sigma(\varrho)$ and lay between the copper and chlorine atoms, close to the origin; coupled with a negative peak at the origin it was ascribed to uncorrected anisotropy in the scattering curve of the copper atom. All other peaks were smaller than $2\sigma(\varrho)$.

Table 3. *Locations of hydrogen atoms deduced from final* (F_o-F_c) *synthesis*

Atom	Attached to	x	y	z
H(1)	N(1)	0·200	0·336	0·297
H(2)	N(1)	0·269	0·477	0·199
H(3)	N(2)	0·250	0·477	0

Bond lengths and angles, including those involving the hydrogen atoms, are shown in Table 4. The structure is illustrated in Fig. 1. The twofold z axis and the mirror plane (001) both pass through the copper atom at the origin. Within one complex, the twofold axis relates the two chlorine atoms and the equivalent atoms of the two biuret molecules. The chlorine atoms and the imide nitrogen atoms N(2) and N(2′) lie on the mirror plane which also reflects O into O″, C into C″ and N(1) into N(1″), respectively.

Detailed description of structure

Within the accuracy of the determination, the bond lengths and angles of the biuret molecule in this complex are entirely consistent with those found in biuret hydrate (Hughes, Yakel & Freeman, 1961; Craven, Freeman & Sabine, 1966) and in its complexes with zinc (Nardelli, Fava & Giraldi, 1963), cadmium (Cavalca, Nardelli & Fava, 1960) and copper at high pH (Freeman, Smith & Taylor, 1961). From these structure analyses there are now available five sets of dimensions for biuret molecules (reviewed by Nardelli, Fava & Giraldi, 1963) and nine sets of dimensions for crystallographically distinct $-NH-CO-NH_2$ groups. There is a considerable spread among the precisions to which these have been refined. It is therefore impossible to confirm whether there are systematic trends in the bond-lengths. (One would, for instance, expect the $C=O$ to be the longer, the shorter the neighbouring $C-NH_2$ or $C-NH-$ is.)

The copper atom has coordination number 6 and a tetragonally distorted octahedral environment. The bonding to the four ligand oxygen atoms is covalent and the Cu–O bond-lengths (1·935 Å) are equal to the sum of the covalent radii [$r_O=0{\cdot}66$ Å, $r_{Cu}=1{\cdot}28$ Å (Pauling, 1960, pp. 224, 252)]. The Cu–Cl distances (2·96 Å) are too large for covalent binding ($r_{Cl}=0{\cdot}99$ Å). They are consistent with ionic bonding between Cl^- and Cu^{2+} ions [$r_{Cl^-}=1{\cdot}81$ Å, $r_{Cu^{2+}}=0{\cdot}81$ Å (Pauling, 1960, pp. 514, 515)], provided that allowance is made for

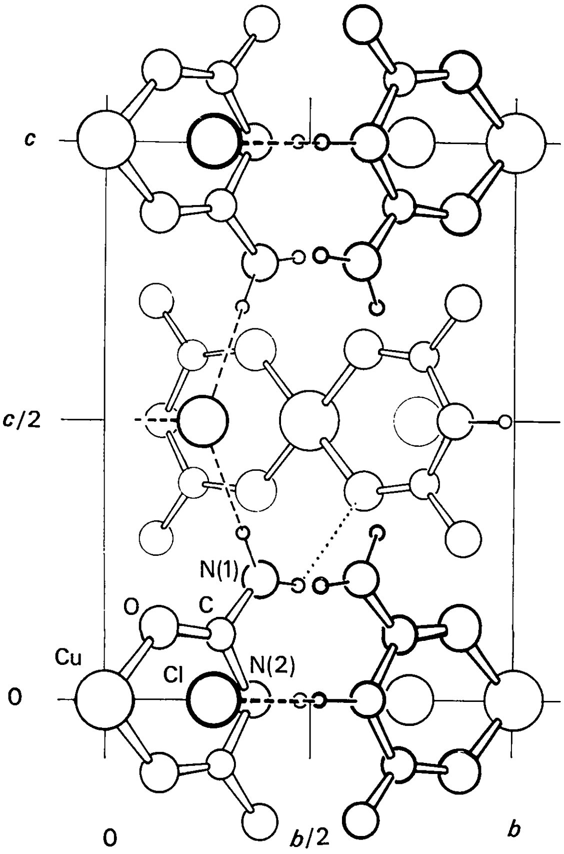

Fig. 1. Unit cell of $Cu(NH_2CONHCONH_2)_2Cl_2$, projected on (100). x axis into page. Not all hydrogen atoms are shown. Dashed lines indicate hydrogen bonds. Dotted line represents short contact which is *not* a hydrogen bond (see text).

(i) the Jahn–Teller increase of the effective radius of the Cu^{2+} ion in the direction perpendicular to the square of the four closest ligands*, and

(ii) the partial neutralization of the Cu^{2+} ion charge by complex formation, since this will also have the effect of increasing the ionic radius ($r_{Cu^{2+}} : r_{Cu^{+}} : r_{Cu^{0}} = 0{\cdot}81 : 0{\cdot}96 : 1{\cdot}28$ Å).

For comparison, the metal–chlorine distances in $Zn(biuret)_2Cl_2$ correspond to the sum of the ionic radii, and in $Cd(biuret)_2Cl_2$ more nearly to the sum of the covalent radii.

The $[Cu(biuret)_2]^{2+}$ ion is not planar. Table 5 lists the equations of the planes fitted to the 'coordination square' OO″O‴O′ (plane 1), the biuret molecule (plane 2) and the individual $-NH-CO-NH_2$ groups (plane 3). As a consequence of the space-group symmetry, planes 1 and 2 are perpendicular to {001}. The normals to these two planes make angles of 38° 36′ and 17° 9′, respectively, with the x axis. The complex is therefore folded along the lines O · · · O″ and O′ · · · O‴ in such a way that the biuret planes are at 21° 27′ to the coordination square.

The 'biuret-plane' mentioned above was fitted to the biuret molecule by least-squares, giving each atom an appropriate weight. All the atoms except the oxygens deviate from plane 2 by statistically significant amounts. The two individual $-NH-CO-NH_2$ groups are, however, planar, the angle between their normals being 6° 21′. The configuration may be visualized by starting from a coplanar condition and folding the molecule about a line through N(2) in the xy plane, or by rotating the amide

Table 4. *Interatomic distances and inter-vector angles*

Symmetry-related atoms are denoted as follows:

Superscript	Location	Superscript	Location
—	$x \quad y \quad z$	vii	$\frac{1}{2}-x \quad y-\frac{1}{2} \quad z-\frac{1}{2}$
′	$x \quad \bar{y} \quad \bar{z}$	viii	$\frac{1}{2}-x \quad y-\frac{1}{2} \quad \frac{1}{2}-z$
″	$x \quad y \quad \bar{z}$	ix	$\frac{1}{2}-x \quad y+\frac{1}{2} \quad \frac{1}{2}+z$
‴	$\bar{x} \quad \bar{y} \quad \bar{z}$	x	$\frac{1}{2}-x \quad y+\frac{1}{2} \quad \frac{1}{2}-z$
iv	$x \quad y-1 \quad z$	xi	$x+\frac{1}{2} \quad \frac{1}{2}-y \quad \frac{1}{2}-z$
v	$x \quad y+1 \quad z$	xii	$x-\frac{1}{2} \quad \frac{1}{2}-y \quad \frac{1}{2}-z$
vi	$1-x \quad \bar{y} \quad z$		

(*a*) Dimensions of the bis-biuret-copper(II) dichloride complex

Bond	Length l	$\sigma(l)$	Angle	θ
Cu—Cl	2·960 Å	$0{\cdot}001_4$ Å	O—Cu—O″	90·6°
Cu—O	1·935	0·003	O—Cu—Cl	94·8
C═O	1·256	0·005	Cu—O═C	124·2
C—N(1)	1·321	0·006	O═C—N(1)	119·8
C—N(2)	1·371	0·006	O═C—N(2)	123·3
N(1)-H(1)	0·97	—	N(1)-C—N(2)	116·9
N(1)-H(2)	0·91	—	C—N(2)-C″	126·8
N(2)-H(3)	1·01	—	C—N(1)-H(1)	123
			C—N(1)-H(2)	117
			H(1)-N(1)-H(2)	119
			C—N(2)-H(3)	116

(*b*) Hydrogen bonds and short non-bonded contacts

Vector	Distance
$N(1) \cdots Cl^{ix}$	3·28 Å
$Cl \cdots N(1^{vii})$	
$Cl \cdots N(1^{viii})$	
$H(1) \cdots Cl^{ix}$	2·31
$N(1) \cdots O^{x}$	2·89
$O \cdots N(1^{viii})$	
$H(2) \cdots O^{x}$	2·36
$N(2) \cdots Cl^{v}$	3·15
$Cl \cdots N(2^{iv})$	
$H(3) \cdots Cl^{v}$	2·14
$N(1) \cdots O^{xi}$	3·24
$O \cdots N(1^{xii})$	
$N(2) \cdots Cl^{vi}$	3·47
$Cl \cdots N(2^{vi})$	
$Cl \cdots Cl^{vi}$	4·97

Angle	θ
$C—N(1) \cdots Cl^{ix}$	124°
$N(1)–H(1) \cdots Cl^{ix}$	174
$H(1)–N(1) \cdots Cl^{ix}$	5
H(1)–N(1)—H(2)	119
$H(2)–N(1) \cdots Cl^{ix}$	119
$C—N(1) \cdots O^{x}$	163
$N(1)–H(2) \cdots O^{x}$	118
$H(2)–N(1) \cdots O^{x}$	46
$H(1)–N(1) \cdots O^{x}$	74
$Cl^{ix} \cdots N(1) \cdots O^{x}$	73
$C(1)–N(2) \cdots Cl^{v}$	117
$N(2)–H(3) \cdots Cl^{v}$	169
$H(3)–N(2) \cdots Cl^{v}$	7

Angle	θ
$Cu—Cl \cdots N(1^{vii})$	74°
$Cu—Cl \cdots N(1^{viii})$	
$N(1^{vii}) \cdots Cl \cdots N(1^{viii})$	141
$Cu—O \cdots N(1^{viii})$	101
$Cu—O \cdots H(1^{viii})$	86
$C═O \cdots N(1^{viii})$	131
$C═O \cdots H(1^{viii})$	137
$Cu═Cl \cdots N(2^{iv})$	121
$N(2^{iv}) \cdots Cl \cdots N(1^{vii})$	108
$N(2^{iv}) \cdots Cl \cdots N(1^{viii})$	

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* In an earlier paper (Freeman, Schoone & Sime, 1965) it was suggested that the Jahn–Teller distortion may be simulated by increasing the covalent radius of Cu in the direction perpendicular to the square of the four closest ligands. Even with the suggested empirical increment of 0·37 Å, the sum of the covalent radii is much smaller than the observed Cu–Cl distance. If the same increment is added to the radius of Cu^{2+}, an effective ionic radius of 1·18 Å is predicted for copper in the directions of the chloride ions, compared with the experimental value of $2{\cdot}96 - 1{\cdot}81 = 1{\cdot}15$ Å).

Table 5. *Planes of best fit*

		Cu & 4O's	Biuret	$-NHCONH_2$
Plane No:		1	2	3
Δ_i = Distances of atoms* from planes of best fit† (Å)				
Atom	$w_i^{-\frac{1}{2}}$	Δ_i	Δ_i	Δ_i
Cu	—	0*	−0·493	−0·427
O	0·0027	0*	0·005*	$0{\cdot}000_3$*
C	0·0035	−0·471	−0·011*	−0·002*
N(1)	0·0042	−0·707	0·046*	0·001*
N(2)	0·0044	−0·758	−0·080*	0·001*
N(1″)	0·0042	−0·707	0·046*	0·253
C″	0·0035	−0·471	−0·011*	0·134
O″	0·0027	0*	0·005*	0·152
Coefficients for planes $lX+mY+nZ+p=0$‡				
l		0·7815	0·9555	0·9555
m		−0·6240	−0·2948	−0·2899
n		0	0	−0·0553
p		0	−0·4933	−0·4271

* Only the atoms marked have been included in the calculation of each plane.

† $w_i=1/\sigma_i^2$ = weight of ith atom used in calculating planes of best fit, where $\sigma_i^2=\frac{1}{3}[\sigma^2(X_i)+\sigma^2(Y_i)+\sigma^2(Z_i)]$ is averaged variance of atomic position in $Å^2$.

‡ X, Y, Z are orthogonal coordinates in Å.

groups in opposite senses about their N(2)–C bonds. The sense of these deviations from planarity is such that the chelate rings –Cu–O–C–N(2)–C″–O″–Cu– are in flat 'boat' configurations.

There are five hydrogen atoms in the biuret molecule. Three take part in two crystallographically independent types of hydrogen bond: N(1)–H(1) · · · Cl^{ix} (3·28 Å) and N(2)–H(3) · · · Cl^{v} (3·15 Å). The atoms H(1) and H(3) lie almost directly on the bond directions. The bond $N(2^{iv})$ · · · Cl makes an angle of 157° with the bisector of $N(1^{vii})$ · · · Cl · · · $N(1^{viii})$, so that the environment of the acceptor ion Cl^- is a flattened trigonal pyramid. The Cl^-–Cu vector passes through the base of this pyramid, making angles of 121° with $N(2^{iv})$ · · · Cl and 36° with the plane of $N(1^{vii})$, Cl^- and $N(^{viii})$; this confirms that the copper–chlorine interaction is not covalent.

A third contact of hydrogen-bond length, N(1) · · · O^{x} (2·89 Å), is not a hydrogen bond. The angle H(2)–N(1) · · · O^{x} is 46°, H(2) makes only a van der Waals contact (2·36 Å) with O^{x}, and the N(1) · · · O^{x} vector makes unsuitable angles with the other bonds at both N(1) and O^{x} (Table 4).

The bond lengths and the approximately planar trigonal distributions of bonds at all carbon and nitrogen atoms confirm the expected resonance of the –NH–CO–NH_2 groups. The state of hybridization of the ligand oxygen atom is less clear. The C=O bond-length corresponds to a bond-number 1·6, but the copper atom bonded to the oxygen lies 0·43 Å out of the plane of the amide group.

Indeed, the folding of the complex ion into three approximately planar but not coplanar sections is one of its least easily explained features. By contrast, in bis-biuret-zinc(II) dichloride the $[Zn(biuret)_2]^{2+}$ ion is almost planar (Nardelli, Fava & Giraldi, 1963). The hydrogen bonding in the zinc(II) complex is more efficient, in the sense that it involves all five hydrogen atoms. It is not clear why the copper(II) complex packs differently and hydrogen-bonds less efficiently in the crystal, but given this arrangement it seems that the complex must become non-planar in order to form any hydrogen bonds at all.

Investigation of alternative structure

The conclusion that the bis-biuret-copper(II) complex ion is a symmetrical oxygen–oxygen chelate is based on the successful refinement to the level where the hydrogen contributions are significant. The possibility that the biuret molecules are chelated symmetrically but through their amide nitrogen atoms can be dismissed: the four nitrogen atoms would then be quadrivalent and this would result in the loss of the resonance energy of the amide groups (Rabin, 1956). The exchange of the peripheral nitrogen atoms for the ligand oxygen atoms would also cause the loss of the amide nitrogen–chlorine hydrogen bonds, resulting in further destabilization. For these reasons we did not test this alternative structure, remembering that coordination through four *deprotonated* amide nitrogen atoms occurs in potassium bis-biureto cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961).

There exists the logical possibility that the complex may be a chemically symmetrical oxygen–oxygen chelate but that it crystallizes in the non-centrosymmetric space-group *Pnn*2 instead of *Pnnm*. In space group *Pnn*2, {001} is not a mirror plane, but atoms such as O(1) and O(1′) are still related by the twofold z axis. Chemically equivalent atoms such as O(1) and O(1″) in one biuret molecule are now crystallographically distinct. Refinement in *Pnnm* would give each atom of such a pair a position which would be the average of the two true positions, and would also force the chlorine and imide-nitrogen atoms to have $z=0$ (no longer required by symmetry). The resolution of the final difference map confirms, however, that the two halves of each biuret molecule are equivalent.

It is, finally, possible that biuret acts as a nitrogen–oxygen chelate and that the complex has structure (II) in space group *Pnn*2. This possibility was more difficult to eliminate, although preliminary parallel refinement of (I) and (II) by generalized Fourier and difference syntheses consistently favoured the symmetrical oxygen–oxygen chelate (I), using the reliability index R as a criterion (Freeman, Smith & Taylor, 1959). Immediately after the calculation of the first three-dimensional Fourier synthesis, structure (I) gained further support from a least-squares refinement in which the 'occupation-numbers' of all the atomic sites in the symmetrical structure converged to 1·03 ± 0·03. Despite these early indications, the full-matrix least-squares refinement of (I) was repeated in space-group *Pnn*2. The initial atomic coordinates were again taken from the three-dimensional Fourier synthesis, initial individual atomic thermal parameters were taken from the first refinement cycle of the symmetrical structure, and atomic scattering factors were allocated to correspond with structure (II). After four cycles of isotropic refinement, the non-symmetrical structure converged with the same reliability index as the symmetrical structure at the corresponding stage, $R=0\cdot138$ (and $\Sigma w\Delta^2=4\cdot37$).

In contrast with model (I), however, (II) now had some bonds with unacceptable lengths (*e.g.* C(1)–N(2), 1·23; C(2)–N(2), 1·50 Å). The thermal parameters for (II), while within the bounds of credibility, extended over a wider range ($B_i=1\cdot59$ to 4·24) than for model (I) ($B_i=1\cdot87$ to 3·34) without any apparent correlation with the structural features. Structure (II) was therefore rejected. It should be noted that this rejection was based on assumptions as to what were likely and unlikely molecular parameters. The crystallographic refinement criteria alone could not distinguish between (I) and (II).

Conclusion

Chemically, the most interesting result of this work is the support which it gives to the current picture of the interaction between copper(II) and peptide groups. At neutral *p*H, although copper(II) has a higher affinity for nitrogen than for oxygen, the metal is bound at the amide oxygen atom. It is only at higher *p*H's, when an amide hydrogen atom has been dissociated, that the nitrogen atom becomes a binding site. The same behaviour is found in the only other case where comparable structure analyses are available, namely the copper(II) complexes formed by glycylglycylglycine at low *p*H (Freeman, Robinson & Schoone, 1964) and at high *p*H (Freeman, Schoone & Sime, 1965).

The complex cation, having a peripheral positive charge, forms fewer hydrogen bonds with its environment than does the violet anionic complex. There is a shortage of hydrogen-bond donor atoms in the crystal, which is held together mainly by electrostatic attractions between the complexes and the chloride ions. It is not easy to trace cause and effect in this observation.

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