A reinvestigation of the crystal structure of CoCl₂.2H₂O.* By B. MOROSIN and EDWARD J. GRAEBER,

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The crystal structure of $CoCl_2.2H_2O$ was first examined by the electron diffraction technique. Vainshtein (1949) deduced from the thirty-three listed reflections that the compound probably belonged to space group $C2/m$ and consisted of polymeric chains in which each chlorine ion was shared by two cobalt ions and the chlorine ions were arranged in a near square planar configuration about each cobalt ion. The remaining octahedral positions about the metal ion were filled with the water molecules.

Of particular interest to a current magnetic-resonance study were the unequal metal-ligand bond distances (2·53 and 2·54 Å). However, considering the sparse data, these could not be considered significantly different, and therefore a reinvestigation of the coordination about the cobalt(II) ion was considered desirable.

Experimental and structure determination

Single crystals of the dihydrate were grown from aqueous solutions at 70 °C and were sealed in glass capillaries to avoid conversion to the tetrahydrate. Precession and Weissenberg photographs were taken with molybdenum $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). The following cell dimensions were obtained by superimposing a sodium chloride ($a_0 = 5\cdot6394$ Å) pattern on the same films with the cobalt salt and are in agreement with those determined by Vainshttein:

$$a_0 = 7\cdot256, \quad b_0 = 8\cdot575, \quad c_0 = 3\cdot554 \text{ Å}; \quad \beta = 97° \ 33'.$$

Systematic absences for $h+k = 2n+1$ together with the final agreement between the calculated and observed structure factors confirm the probable space group $C2/m$. The average experimental density of $2\cdot50 \pm 0\cdot02$ g.cm⁻³ may be compared with the calculated density for two formulae per cell of $2\cdot513$ g.cm⁻³.

Three-dimensional data were collected by means of a General Electric single-crystal diffractometer employing Mo $K\alpha$ radiation. Each reflection was recorded through a 3° 2θ-scan using balanced metal filters (zirconium and yttrium plus aluminum). Intensities were recorded for 305 unique reflections of which 272 were considered to be observed. Graphical absorption corrections were applied since the needle of equidimensional rectangular cross section was mounted in an eccentric position with respect to the glass envelope. The Lorentz-polarization factor was applied to the intensity data, and structure factors were calculated by means of Thomas–Umeda (1957) scattering factors for cobalt, and the scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for hydrogen, chlorine, and oxygen. Calculations were carried out on a *CDC* 1604 computer.

The initial coordinates of Vainshtein (1949) were refined by several cycles of differential syntheses (Booth,

1946) individual isotropic temperature factors being used for chlorine, cobalt, and oxygen. The reliability index at this point was 0·09. A three-dimensional Fourier synthesis was calculated in order to differentiate hydrogen densities in the region of the oxygen. It was evident that anisotropic temperature factors were necessary for the chlorine and oxygen. These parameters were refined by several cycles of differential synthesis ($R = 0\cdot075$). The hydrogen was included in the position indicated by a final three-dimensional difference synthesis resulting in a final $R = 0\cdot073$. Table 1 lists the observed and calculated structure factors. Table 2 lists the final positional parameters with their estimated standard deviations (Cruickshank, 1949) and individual temperature factors.

Discussion

The crystal structure of $CoCl_2.2H_2O$ determined by this X-ray study is similar to that found by the electron
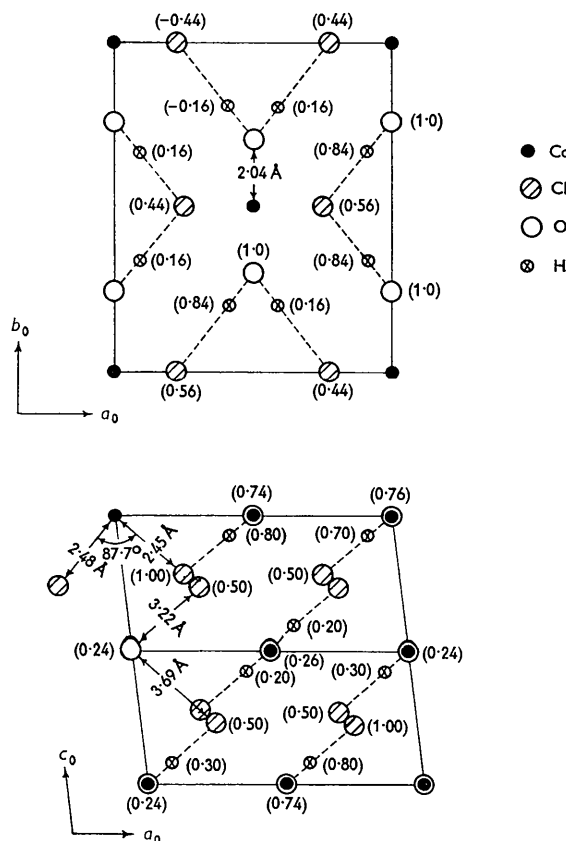

Fig. 1. (*a*) Projection along c_0. All heights of atoms are given (except zero). (*b*) Projection along b_0. Two cells are shown so as to include atoms and bonds which superimpose on each other. Two atoms on the cell edge have been left off to avoid ambiguity.

Table 1.

H	K	L	OBS	CALC
2	0	0	17.0	18.8
4	0	0	48.4	78.1
6	0	0	7.6	7.6
8	0	0	30.1	29.2
1	1	0	49.6	52.8
3	1	0	27.8	28.3
5	1	0	36.5	37.1
7	1	0	7.1	7.7
9	1	0	20.9	18.9
0	2	0	63.5	71.9
2	2	0	26.9	-29.8
4	2	0	45.8	47.0
6	2	0	6.0	-5.0
8	2	0	23.9	21.8
1	3	0	37.8	41.1
3	3	0	21.8	21.2
5	3	0	31.2	30.4
7	3	0	5.5	5.7
9	3	0	19.6	16.7
0	4	0	84.9	92.4
2	4	0	13.3	13.8
4	4	0	59.2	58.5
6	4	0	6.1	6.3
8	4	0	26.6	24.6
1	5	0	34.9	35.9
3	5	0	22.5	22.5
5	5	0	29.3	29.1
7	5	0	8.4	7.4
0	6	0	41.1	42.0
2	6	0	8.2	-8.1
4	6	0	34.2	32.1
6	6	0	4.5	-2.2
8	6	0	17.6	15.8
1	7	0	20.0	19.5
3	7	0	11.7	11.2
5	7	0	18.6	18.2
7	7	0	4.0	3.6
0	8	0	41.8	41.0
2	8	0	6.7	5.6
4	8	0	27.0	31.3
6	8	0	4.6	4.0
1	9	0	19.7	19.3
3	9	0	13.6	13.1
5	9	0	17.7	16.7
0	10	0	22.0	21.4
2	10	0	< 3.7	-1.3
4	10	0	17.8	16.9
1	11	0	9.1	8.7
0	0	1	25.0	21.1
2	0	1	84.0	99.2
-2	0	1	88.2	103.8
4	0	1	8.4	8.1
-4	0	1	17.7	19.0
6	0	1	45.2	45.6
-6	0	1	43.1	41.2
8	0	1	< 3.6	1.9
-8	0	1	8.6	9.1
1	1	1	56.9	55.8
-1	1	1	23.5	21.1
3	1	1	28.7	29.0
-3	1	1	56.8	56.5
5	1	1	22.4	22.5
-5	1	1	7.3	7.7
7	1	1	19.7	18.9
-7	1	1	31.7	31.2
9	1	1	6.2	6.0
-9	1	1	< 3.8	1.3
0	2	1	27.7	-26.5
2	2	1	50.3	55.8
-2	2	1	52.3	51.9
4	2	1	11.6	-12.1
-4	2	1	6.1	-5.8
6	2	1	32.8	32.5
-6	2	1	28.2	27.8
8	2	1	5.9	-4.2
-8	2	1	< 3.5	3.4
1	3	1	43.6	42.3
-1	3	1	17.7	16.9
3	3	1	21.3	21.2
-3	3	1	43.8	46.4
5	3	1	17.5	17.7
-5	3	1	5.0	5.3
7	3	1	16.9	16.0
-7	3	1	28.2	27.4
-9	3	1	< 3.9	.7
0	4	1	16.8	15.4
2	4	1	62.4	69.9
-2	4	1	66.8	69.3
4	4	1	7.0	6.3
-4	4	1	13.3	13.5
6	4	1	37.4	37.7
-6	4	1	32.7	33.5
8	4	1	5.3	1.8
-8	4	1	7.6	7.9
1	5	1	37.5	38.6
-1	5	1	19.2	18.7
3	5	1	23.6	23.2
-3	5	1	39.0	40.1
5	5	1	18.7	18.9
-5	5	1	7.0	7.6
7	5	1	16.9	15.9
-7	5	1	26.1	25.0
0	6	1	7.2	-6.7
2	6	1	35.2	35.9
-2	6	1	33.6	34.5
4	6	1	6.7	-6.0
-4	6	1	< 3.0	-.6
6	6	1	23.7	23.3
-6	6	1	19.9	20.2
-8	6	1	< 3.9	3.1
1	7	1	22.3	21.8
-1	7	1	9.2	8.5
3	7	1	12.4	11.9
-3	7	1	24.7	25.4
5	7	1	11.1	10.8
-5	7	1	3.9	3.0
7	7	1	< 4.0	10.2
-7	7	1	18.4	17.4
0	8	1	7.3	6.4
2	8	1	36.3	35.5
-2	8	1	34.1	34.0
4	8	1	4.6	3.5
-4	8	1	8.0	7.0
6	8	1	23.6	22.2
-6	8	1	20.3	19.6
1	9	1	21.4	20.7
-1	9	1	11.7	11.3
3	9	1	14.0	13.4
-3	9	1	21.6	22.1
5	9	1	12.5	11.4
-5	9	1	5.9	5.7
0	10	1	< 3.7	-.7
2	10	1	19.7	18.8
-2	10	1	18.5	18.1
4	10	1	< 4.0	-1.3
-4	10	1	< 3.9	1.4
1	11	1	11.0	9.9
-1	11	1	5.0	4.1
0	0	2	69.0	68.9
2	0	2	12.4	12.4
-2	0	2	23.5	22.7
4	0	2	46.0	49.5
-4	0	2	46.2	44.7
6	0	2	3.3	2.4
-6	0	2	14.7	16.1
8	0	2	25.6	24.4
-8	0	2	15.3	16.9
1	1	2	12.9	11.3
-1	1	2	58.4	55.0
3	1	2	35.3	37.1
-3	1	2	5.1	4.8
5	1	2	11.1	11.5
-5	1	2	38.7	39.9
7	1	2	13.9	14.8
-7	1	2	< 3.1	1.1
-9	1	2	20.5	19.4
0	2	2	46.2	40.6
2	2	2	7.0	-7.1
-2	2	2	2.8	-.8
4	2	2	32.5	33.9
-4	2	2	26.4	27.2
6	2	2	7.0	-6.1
-6	2	2	6.4	7.3
8	2	2	19.3	18.3
-8	2	2	11.3	12.2
1	3	2	7.9	6.6
-1	3	2	48.4	45.2
3	3	2	29.0	30.4
-3	3	2	3.7	2.9
5	3	2	8.8	8.8
-5	3	2	33.7	35.2
7	3	2	12.3	12.7
-7	3	2	< 3.2	.5
0	4	2	53.7	52.0
2	4	2	9.9	9.8
-2	4	2	17.2	16.6
4	4	2	38.6	40.5
-4	4	2	32.8	35.1
6	4	2	< 3.3	2.2
-6	4	2	11.9	13.2
-8	4	2	13.7	14.3
1	5	2	11.6	11.0
-1	5	2	41.3	40.5
3	5	2	28.5	29.6
-3	5	2	5.3	5.6
5	5	2	10.3	10.5
-5	5	2	27.6	31.1
7	5	2	12.3	12.6
-7	5	2	< 3.4	1.9
0	6	2	28.0	27.9
2	6	2	3.7	-2.9
-2	6	2	< 2.8	2.3
4	6	2	23.3	24.2
-4	6	2	18.8	20.1
6	6	2	4.6	-3.4
-6	6	2	5.0	6.2
1	7	2	4.4	3.7
-1	7	2	26.3	26.0
3	7	2	18.1	18.5
-3	7	2	< 3.0	1.5
5	7	2	6.0	5.5
-5	7	2	21.5	21.9
-7	7	2	< 3.6	.6
0	8	2	28.5	28.1
2	8	2	< 3.2	5.5
-2	8	2	8.7	8.8
4	8	2	23.6	23.6
-4	8	2	19.6	19.9
-6	8	2	7.7	8.2
1	9	2	7.7	7.2
-1	9	2	22.5	22.3
3	9	2	17.6	17.0
-3	9	2	4.5	4.6
-5	9	2	18.0	17.9
0	10	2	15.0	14.9
2	10	2	< 3.6	.2
-2	10	2	< 3.6	2.7
0	0	3	17.6	16.4
2	0	3	34.3	35.8
-2	0	3	33.1	32.1
4	0	3	6.0	6.6
-4	0	3	18.0	19.1
6	0	3	23.2	24.3
-6	0	3	14.0	16.3
-8	0	3	12.1	12.8
1	1	3	42.9	38.3
-1	1	3	3.2	1.4
3	1	3	3.3	2.7
-3	1	3	38.5	38.0
5	1	3	20.6	22.5
-5	1	3	3.0	.8
-7	1	3	21.6	22.7
0	2	3	5.9	4.9
2	2	3	23.9	24.2
-2	2	3	21.6	20.7
4	2	3	< 2.9	-1.6
-4	2	3	10.2	10.8
6	2	3	16.6	17.6
-6	2	3	9.1	11.0
-8	2	3	9.0	9.8
1	3	3	34.5	32.9
-1	3	3	2.9	-.4
3	3	3	< 2.8	1.1
-3	3	3	33.9	33.4
5	3	3	18.3	19.7
-5	3	3	3.2	.2
-7	3	3	20.1	20.5
0	4	3	14.7	13.6
2	4	3	29.1	29.7
-2	4	3	27.2	26.3
4	4	3	5.4	5.7
-4	4	3	14.8	15.8
-6	4	3	11.8	13.7
1	5	3	32.8	30.5
-1	5	3	3.1	2.8
3	5	3	3.9	3.6
-3	5	3	30.3	29.9
5	5	3	17.2	18.4
-5	5	3	< 3.0	1.7
-7	5	3	17.7	18.1
0	6	3	4.5	4.3
2	6	3	17.1	17.6
-2	6	3	15.1	15.2
4	6	3	< 3.2	-.3
-4	6	3	7.7	8.5
-6	6	3	7.2	8.4
1	7	3	20.2	20.6
-1	7	3	< 3.0	-.2
3	7	3	< 3.2	.7
-3	7	3	20.1	21.1
-5	7	3	< 3.2	.4
0	8	3	8.6	8.3
2	8	3	17.4	17.7
-2	8	3	15.4	15.6
-4	8	3	9.3	9.7
0	0	4	17.9	17.6
2	0	4	10.1	11.1
-2	0	4	16.3	16.5
4	0	4	15.5	16.7
-4	0	4	9.8	11.4
-6	0	4	13.6	14.2
1	1	4	< 2.7	-.8
-1	1	4	29.6	27.7
3	1	4	21.6	22.7
-3	1	4	< 2.7	.5
-5	1	4	20.1	20.7
0	2	4	12.4	11.7
2	2	4	5.2	5.5
-2	2	4	11.5	11.4
-4	2	4	6.6	7.6
-6	2	4	10.7	11.4
1	3	4	3.2	-1.4
-1	3	4	27.1	24.5
3	3	4	19.5	20.2
-3	3	4	< 2.7	-.0
-5	3	4	17.8	18.7
0	4	4	16.1	14.9
2	4	4	9.3	9.5
-2	4	4	14.4	14.0
-4	4	4	8.7	9.8
1	5	4	< 2.9	.6
-1	5	4	23.8	22.1
-3	5	4	< 2.9	1.4
0	6	4	9.1	8.8
-2	6	4	8.6	8.5

Table 2. *Atomic coordinates and temperature factor coefficients with their standard deviations*

	x	σx	y	σy	z	σz
Co	0		0		0	
Cl	0·2373	0·0003	0		0·5582	0·0006
O	0		0·2378	0·0005	0	
H	0·0604	0·0060	0·3000	0·0740	0·1560	0·0550

	B or B_{11}	B_{22}	B_{33}	B_{13}
Co	1·700			
Cl	1·960	2·500	2·002	−0·102
O	2·900	2·025	3·290	−0·532
H	2·00			

diffraction study. The polymeric chains of cobalt and chlorine atoms in a near-square planar arrangement are parallel to the c_0 axis and are held together by hydrogen bonds. These bonds (3·219 Å compared with 3·690 Å for the other oxygen–chlorine separation) are formed between the oxygen atom of the water molecule completing the octahedral coordination about the cobalt and the chlorine atom of an adjacent polymeric chain (Fig. 1). The slightly unequal bond lengths between the cobalt and chlorine atoms are confirmed (Table 3), as are the slight distortions from the square planar arrangement of the chlorine and cobalt atoms. The bond lengths

Table 3. *Bond lengths and angles*

Bond length			
			σ
Co–Cl	2·450 Å	0·003 Å	
Co–Cl	2·478	0·003	
Co–O	2·040	0·006	
Cl–O	3·219	0·007	
Cl–O	3·690	0·007	
O–H	0·85	0·26	
Angle			
Cl–Co–Cl	87·68°	0·23°	
H–O–H	102·2		
O–H–Cl	164·2		
Co–O–Cl	134·29	0·52	
(along H-bond)			

compare favorably with those reported by Ibers (1962) for the 'blue' octahedral complex of $Co(AlCl_4)_2$ (2·45 and 2·47 Å for Co–Al); however, the bond angles (87·7, 90, 90) are not as distorted (84·2°; 86·7° and 89·7°). The environment of the cobalt ion in the dihydrate is compared with that of the dipyridine complex (Dunitz, 1957) in Fig. 2. Both structure determinations yield the slightly acute bond angle along the polymeric chains formed by the chlorines and cobalt ions. Ferguson (1960) has suggested that this rhombic distortion in the dipyridine complex has its origin in the Jahn–Teller effect* so that

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* It has been pointed out that distortions by this mechanism for cobalt(II) are possible (Griffith & Orgel, 1957; Orgel & Dunitz, 1957), and this may explain the small departures
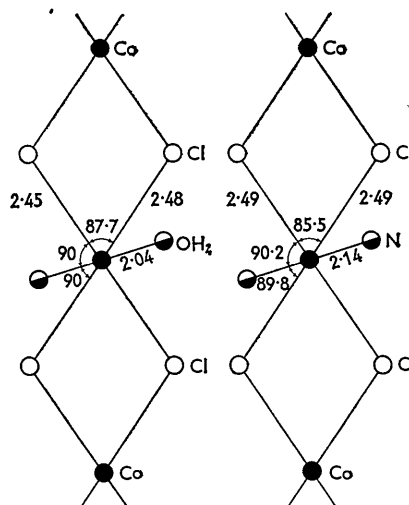

Fig. 2. Comparison of the polymeric chains in the crystal structures of the dihydrate and dipyridine complexes of cobalt chloride. In both complexes the polymeric chain parallels the c_0 axis; however, there is no direct comparison of the other crystallographic axes.

the doubly degenerate state for cobalt(II), ^4Eg, is split into two states, $^4B_{2g}$ and $^4B_{3g}$. The absorption spectra and nuclear magnetic resonance studies of the compound will be reported elsewhere.

The assistance of Mr. G. H. Conrad in collecting the intensity data is acknowledged.

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from regular tetrahedral symmetry found in $CoCl_4^{2-}$ ion of Cs_3CoCl_5 (Powell & Wells, 1935) and Cs_2CoCl_4 (Poraj-Koshitz, 1956).