

The Crystal Structure and Magnetic Susceptibility of CsCoCl_3

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The crystal structure of CsCoCl_3 has been determined from integrated Weissenberg and precession photographs by application of standard procedures of X-ray crystal structure analysis. The space group is $P6_3/mmc$. Isotropic least squares refinement of 119 scaled and weighted reflexions gave the final R value 0.05. Precise values of the lattice constants and their standard deviations were derived from a powder photograph.

$$a_H = 7.2019 (4) \text{ \AA}, c_H = 6.0315 (5) \text{ \AA}, c_H/a_H = 0.8375.$$

The structure is another example of the CsNiCl_3 structure. The main feature of this structure is the existence of "linear" poly-ions $(\text{CoCl}_3)_n^{n-}$ formed by the trigonally deformed CoCl_6 -octahedra sharing pairs of opposite faces perpendicular to the c_H -axis. The Co-Cl distance is 2.447(3) \AA , the Co-Co distance within the poly-ions is 3.0158(3) \AA .

The magnetic susceptibility of a polycrystalline sample has been measured in the temperature range 80-300°K. The effective magnetic moment is strongly dependent on the temperature. At 296.5°K $\mu_{\text{eff}} = 4.77 \mu_B$, at 81.5°K $\mu_{\text{eff}} = 3.35 \mu_B$. The latter value is far below the "spin only" value of a quartet term.

Seifert¹ has demonstrated the existence of CsCoCl_3 by differential thermal analysis. The system $\text{CsCl}-\text{CoCl}_2-\text{H}_2\text{O}$ has been investigated at 25°C by Benrath,² who isolated $\text{CsCoCl}_3 \cdot 2\text{H}_2\text{O}$. At higher temperatures, however, the anhydrous compound can be prepared from an aqueous system by the procedure described below. The single crystals of CsCoCl_3 form bright blue, hexagonal prisms, which show parallel extinction between crossed Nicols. The compound is converted into the red di-hydrate when left in moist air.

PREPARATION OF CsCoCl_3

A solution containing 5.0 g of CsCl and 34.0 g of CoCl_2 in 61.0 g of H_2O was evaporated at 80°C until a slight crystallisation took place. The solution was then left for an hour in the open vessel at 50°C. The rather concentrated, deep blue solution and the separated crystals were quickly transferred to a warm filter-crucible. The major part of the mother liquor was removed by suction. The filter-crucible was then filled with warm toluene and

the complete separation of the crystals from the liquids was accomplished by centrifugation. The crystals were finally dried at 80°C. Yield approximately 2 g.

The correct composition of the compound was proved by chemical analysis. Cl, calculated 35.71 %, found 35.51 % (gravimetrically); Co, calculated 19.77 %, found 19.85 % (complexometrically, according to Schwarzenbach³).

UNIT CELL AND SPACE GROUP

A crystal with clean faces, showing perfect optical extinction in polarised light, was selected for the structure analysis and mounted in a thin-walled glass capillary. The length of the crystal was 0.510 mm and the average diameter of the nearly regular hexagonal cross-section was 0.15 mm, ($\mu=113 \text{ cm}^{-1}$, $\lambda=0.7107 \text{ \AA}$).

Weissenberg photographs of the $hk0$, $hk1$ and $hk2$ layers, and a $h0l$ precession-photograph taken with Zr-filtered Mo-radiation revealed the Friedel symmetry $6/mmm$. Preliminary values for the lattice parameters were derived from these films: $a_H=7.22 \text{ \AA}$ and $c_H=6.01 \text{ \AA}$.

Precise lattice parameters at 20°C were determined from an X-ray powder photograph taken with $\text{FeK}\alpha$ -radiation (MnO_2 -filter). A 19 cm Bradley and Jay camera which had been calibrated with NaCl, $a_0=5.63999 \text{ \AA}$ (20°C), was employed. All the observed powder lines were indexed as shown in Table 1. The lattice parameters were corrected for absorption by extrapolation to $\theta=90^\circ$, according to Nelson and Riley:⁴

$$a_H = 7.2019 (0.0004) \text{ \AA} \text{ and } c_H = 6.0315 \text{ \AA} (0.0005); c_H/a_H = 0.8375.$$

The figures in parentheses indicate the precision in terms of the standard deviations.

The observed density, determined by the pycnometer method, was $3.63 \text{ g}\cdot\text{cm}^{-3}$. The density calculated for 2 formula units per unit cell was $3.66 \text{ g}\cdot\text{cm}^{-3}$.

The reflexions hhl only, were systematically absent for $l=2n+1$; hence the space group must be either $P6_3mc$ or $P\bar{6}2c$ or $P6_3/mmc$. The latter, which is centrosymmetric, is considered the most probable. A comparison with a powder film of CsNiCl_3 , whose crystal structure is known,⁵ and a negative test for piezoelectricity, supported this assumption.

COLLECTION OF INTENSITY DATA

Intensity data for the reciprocal lattice planes $hk0-2$ were collected at 22°C by means of integrated Weissenberg exposures using Zr-filtered $\text{MoK}\alpha$ -radiation. Multiple-film technique with four films in each pack was employed. A long and a short exposure covering 80° of the appropriate reciprocal lattice plane was made with each film-pack. A film to film factor of about 2.9 was obtained by interleaved thin Ni-foils ($18 \text{ mg}\cdot\text{cm}^{-2}$). Integrated precession films with the $h0l$ reflexions were also made, mainly for scaling purposes. Since the precession geometry does not allow multiple-film work, a series of suitably timed precession photographs of the $h0l$ -plane was taken. Great care was taken to maintain the experimental conditions, including the photo-

Table 1. Observed and calculated $\sin^2\theta$ for CsCoCl₃.

<i>hkl</i>	<i>I</i>	$10^4 \sin^2\theta$		<i>hkl</i>	<i>I</i>	$10^4 \sin^2\theta$	
		obs.	calc.			obs.	calc.
101	s	499	499	402	s	4886	4883
110	vs	720	722	410	m	5056	5058
200	s	963	964	313	vw	5454	5449
002	s	1031	1030	322	w	5606	5606
201	vs	1219	1222	403	m	6180	6171
102	s	1271	1271	304	vw	6292	6287
211	m	1941	1944	330	m	6505	6503
202	s	1996	1994	323	w	6899	6894
300	vs	2165	2167	421	s	7003	7002
103	w	2561	2559	502			
212	s	2720	2716	224	vs	7030	7010
220	vs	2890	2890	205	w	7412	7402
203	s	3286	3282	511	vw	7725	7724
311	m	3393	3389	422	s	7783	7774
222	s	3924	3920	512	m	8496	8496
213	vw	4008	4004	600	s	8673	8670
004			4120	423	s	9063	9062
401	vs	4117	4111	414	m	9183	9178
321			4834	520	m	9393	9393
114	s	4837	4842				

FeK α , $\lambda_1=1.93597$ Å, $\lambda_2=1.93991$ Å. Temperature 20°C. *I*=estimated, relative intensity. s=strong, w=weak, v=very, m=medium.

graphic processing, as constant as possible. It was therefore satisfactory to find that the factors scaling the Weissenberg films to the first precession film were 2.83, 2.82, and 2.90 for *I*(*hk*0), *I*(*hk*1), and *I*(*hk*2), respectively.

The photographic density of all the spots on all films were determined with a Nonius densitometer No. II, and scaled to the first film in the respective film-packs. The arithmetic mean of all the observed photographic densities of the several symmetry related spots were taken to represent the integrated intensity of the appropriate *hkl*-reflexion. A total of 101 independent intensities, lying within a limiting value of $\sin\theta/\lambda$ approximately equal to 1, were derived from the Weissenberg films.

The Weissenberg-data were Lp-corrected by means of the factors listed in *International Tables*, Vol. II.⁶ The transmission factors calculated by Bond⁷ for a cylindrical specimen were used as an approximate correction for absorption.

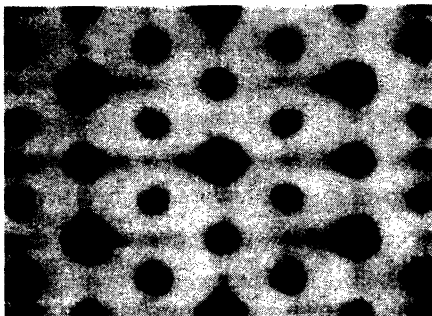


Fig. 1. Patterson projection of CsCoCl_3 on 001, calculated with the v. Eller Photosommateur.

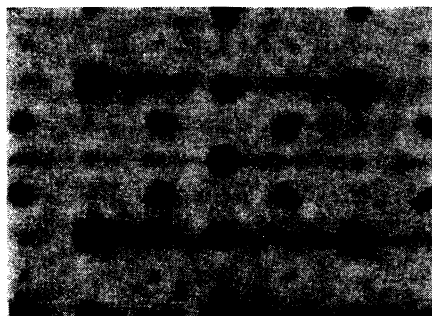


Fig. 2. Electron density projection of CsCoCl_3 on 001, calculated with the v. Eller Photosommateur.

DETERMINATION OF ATOMIC PARAMETERS

The $hk0$ -reflexions were first considered. A Patterson-projection $P(u,v)$, shown in Fig. 1, was prepared by means of the von Eller Photosommateur,⁸ (Nonius' model). The very well resolved projection implies the special positions a , d and h in space group $P6_3/mmc$:

- 2 Co in pos. a : 0,0,0 etc.
- 2 Cs in pos. d : $1/3, 2/3, 3/4$ etc.
- 6 Cl in pos. h : $x, \bar{x}, 1/4$ etc. $x \sim 0.157$

The signs of the structure factors were then estimated photographically with the special cassette⁸ provided with the Photosommateur, by putting $x=0.157$. Thus, the electron density projection $\rho(x,y)$, shown in Fig. 2, could be prepared without any lengthy calculation. The projection confirms the proposed model.

The $x(\text{Cl})$ -parameter was refined by difference maps prepared with the Photosommateur, the 220 reflexion being omitted.

The atomic scattering factors published by Cromer and Waber⁹ and by Cromer¹⁰ were used in the calculation of the structure factors. Only the real part of the corrections for anomalous dispersion was taken into account. An approximate overall temperature factor was determined graphically from a plot of $\log F_o/F_c$ versus $\sin^2\theta/\lambda^2$ for each difference projection.

The first pair of difference maps, having the $x(\text{Cl})$ -values 0.152 and 0.157, respectively, showed steep gradients at the proposed Cl-sites, indicating $0.152 < x < 0.157$. A second pair of maps further constricted the interval to $0.154 < x < 0.156$. A final, difference map, with $x(\text{Cl})=0.155$, did not show any distinct features at any of the atomic sites. The reliability-index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was now reduced to 0.065 from a starting value of 0.11.

At this stage of the analysis the IBM 7090 computer at NEUCC* in

* Northern Europe University Computing Center.

Lyngby came into work. A standard deviation was assigned to each independent reflexion by application of the theory of statistics of small samples to the sets of symmetry-equivalent reflexions, as suggested by Buerger.¹¹ The several films were rescaled to the first film in the respective film packs by means of the Scaling Algorithm written by Hamilton, Rollett and Sparks.¹² The program uses a maximum of 20 different weighing functions of the general form:

$$\sqrt{w} = 1/\sigma = A(I_{\text{obs}})^B$$

where A and B are constants, which were adjusted to make the formulas approximate the assigned standard deviations to within 5 %. The scaling program also corrects the Weissenberg-data for Lorentz and polarisation effects. A subprogram, necessary for the Lp-correction of the precession-data, was written by the author on the basis of the analysis given by Waser.¹³ The correction for absorption was made by means of Bonds transmission factors for a cylindrical specimen, as mentioned above.

The structure was refined by means of the least squares program, ORFLS, written by Busing, Martin and Levy.¹⁴ The atomic form factors mentioned above were employed. Three series of calculations, each consisting of two cycles of isotropic refinement, were undertaken. The results are summarized in Table 2. The trial parameters in the first series of calculations, which involved all observed, independent reflexions, were those determined from the $hk0$ -reflexions. The four largest structure factors were some 20 % too low, presumably due to extinction. They were therefore omitted in the second series, which gave slightly reduced residuals, but no significant change in the parameters. Because approximately 1/4 of the reciprocal lattice points encompassed by a limiting value of $\sin\theta/\lambda=1$ did not give observable reflexions, a third series of calculations was undertaken. In this case, the intensities of the not observed reflexions were put equal to half the minimum observed intensity, and assigned a standard deviation of 50 %. Again, no significant change in the parameters ensued.

The calculated and observed structure factors are listed in Table 3.

Table 2. Final steps of refinement of the parameters of CsCoCl₃.

Number of reflexions	R'	R	$x(\text{Cl})$	$B(\text{Cs})$	$B(\text{Co})$	$B(\text{Cl})$
123	0.057	0.078	0.1545 (3)	1.42 (4)	1.39 (7)	1.33 (8)
119	0.050	0.068	0.1545 (3)	1.43 (4)	1.40 (7)	1.33 (8)
166	0.052	0.090	0.1545 (3)	1.44 (4)	1.39 (7)	1.34 (6)

$R' = \sqrt{\sum w(F_o - F_c)^2} / \sqrt{\sum w F_o^2}$; $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
Standard deviations are in parentheses.

Table 3. Observed and calculated structure factors for CsCoCl₃. Unobserved reflexions, designated with an asterisk, are assigned F_o -values corresponding to half the minimum observable intensity.

$h k l$	$ F_o $	F_c	$h k l$	$ F_o $	F_c	$h k l$	$ F_o $	F_c
1 0 0	27.8	23.3	9 5 0	*5.6	-2.4	10 0 2	14.7	19.0
2 0 0	42.5	-39.6	6 6 0	25.4	26.9	11 0 2	14.7	15.7
3 0 0	85.0	91.6	7 6 0	*5.6	1.6	1 1 2	25.4	-18.8
4 0 0	29.2	-23.7	8 6 0	*5.6	-3.4	2 1 2	73.5	71.5
5 0 0	13.5	-10.6	7 7 0	15.6	15.8	3 1 2	53.4	50.2
6 0 0	86.6	89.3	1 0 1	64.1	62.0	4 1 2	14.3	-16.0
7 0 0	24.1	18.8	2 0 1	113.8	-138.4	5 1 2	46.2	43.4
8 0 0	*4.8	-8.1	3 0 1	20.3	-17.9	6 1 2	23.3	21.6
9 0 0	23.6	22.2	4 0 1	88.1	91.5	7 1 2	10.7	-14.0
10 0 0	*5.1	-6.2	5 0 1	24.3	-21.7	8 1 2	28.2	25.6
11 0 0	*4.8	-5.9	6 0 1	*3.6	1.0	9 1 2	*5.1	12.7
12 0 0	14.9	16.1	7 0 1	27.4	28.2	2 2 2	83.8	-78.3
1 1 0	103.0	111.8	8 0 1	36.4	-36.7	3 2 2	36.4	31.4
2 1 0	*2.1	-0.9	9 0 1	15.9	-13.2	4 2 2	63.3	58.8
3 1 0	12.1	11.3	10 0 1	17.3	19.0	5 2 2	13.6	-9.5
4 1 0	70.2	71.4	1 1 1	0.0	0.0	6 2 2	40.6	38.3
5 1 0	*3.0	-3.9	2 1 1	46.3	42.7	7 2 2	31.5	30.5
6 1 0	12.6	10.3	3 1 1	47.7	-47.7	8 2 2	20.3	-20.3
7 1 0	40.3	40.9	4 1 1	13.4	12.2	9 2 2	*5.2	2.4
8 1 0	*4.5	-7.1	5 1 1	29.3	30.6	10 2 2	11.4	11.2
9 1 0	*4.9	2.1	6 1 1	32.1	-31.8	3 3 2	14.4	-18.4
10 1 0	19.8	19.8	7 1 1	*4.2	5.8	4 3 2	46.6	44.3
11 1 0	*5.6	-3.5	8 1 1	13.9	14.3	5 3 2	28.0	27.1
12 1 0	*5.6	1.3	9 1 1	14.2	-18.1	6 3 2	7.9	-9.3
13 1 0	15.2	9.7	2 2 1	0.0	0.0	7 3 2	21.0	21.5
2 2 0	132.7	156.8	3 2 1	46.7	45.3	8 3 2	*5.1	7.7
3 2 0	22.5	22.5	4 2 1	68.1	-70.0	9 3 2	*5.5	-9.0
4 2 0	18.8	-17.5	5 2 1	16.3	-17.5	10 3 2	14.0	11.7
5 2 0	48.7	46.5	6 2 1	43.1	43.8	4 4 2	37.9	-38.1
6 2 0	11.1	-12.6	7 2 1	*4.5	-7.2	5 4 2	13.3	9.4
7 2 0	*4.4	-10.3	8 2 1	*4.9	1.4	6 4 2	27.0	24.8
8 2 0	39.7	38.8	9 2 1	13.7	13.5	7 4 2	*5.1	-4.1
9 2 0	10.6	10.8	3 3 1	0.0	0.0	8 4 2	15.0	15.6
10 2 0	*5.5	-1.6	4 3 1	19.1	19.4	9 4 2	14.6	13.4
11 2 0	16.1	9.5	5 3 1	27.1	-28.6	5 5 2	14.1	-13.7
3 3 0	66.2	66.9	6 3 1	11.2	11.1	6 5 2	22.6	21.6
4 3 0	8.4	-9.9	7 3 1	14.0	18.1	7 5 2	13.4	13.3
5 3 0	*4.0	0.8	8 3 1	16.7	-15.8	8 5 2	*5.5	-4.0
6 3 0	34.2	33.6	4 4 1	0.0	0.0	6 6 2	*5.2	-13.6
7 3 0	*4.7	-4.4	5 4 1	24.3	24.1	7 6 2	*4.4	3.1
8 3 0	*5.1	6.2	6 4 1	30.1	-29.6	1 0 3	45.7	-48.6
9 3 0	18.4	20.7	7 4 1	*5.0	-10.6	2 0 3	96.5	103.1
10 3 0	*5.6	-3.6	8 4 1	18.6	16.1	3 0 3	14.6	13.9
4 4 0	70.5	71.3				4 0 3	76.4	-76.3
5 4 0	14.0	14.2	0 0 2	102.4	-123.7	5 0 3	17.5	18.4
6 4 0	*4.7	-7.0	1 0 2	65.6	66.0	6 0 3	*4.9	-0.8
7 4 0	20.2	19.6	2 0 2	103.2	108.8			
8 4 0	*5.4	-4.5	3 0 2	18.6	-15.3	0 0 4	119.4	140.3
9 4 0	*5.6	-4.9	4 0 2	79.7	77.3	1 0 4	17.5	11.2
10 4 0	12.9	13.6	5 0 2	57.6	55.2	2 0 4	24.3	-22.6
5 5 0	33.0	34.1	6 0 2	48.7	-47.3	3 0 4	60.0	61.4
6 5 0	*5.0	-7.3	7 0 2	15.8	10.2	4 0 4	14.5	-18.3
7 5 0	*5.4	-1.7	8 0 2	33.0	29.4	5 0 4	*7.4	-9.0
8 5 0	14.2	13.9	9 0 2	*4.9	-4.0	6 0 4	72.4	67.3

Table 3. Continued.

<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c
0 0 5	0.0	0.0	4 0 5	53.8	56.9	3 0 6	*6.9	-9.8
1 0 5	27.6	33.8	0 0 6	45.2	-55.1	4 0 6	39.4	41.3
2 0 5	66.9	-72.1	1 0 6	29.3	30.0			
3 0 5	*6.9	-10.1	2 0 6	49.7	51.1			

DESCRIPTION OF THE STRUCTURE

The crystal structure of CsCoCl₃ is of the CsNiCl₃-type.⁵ Systematically it may be described as derived from a hexagonal (h) packing of layers of the composition CsCl₃ by introduction of a Co²⁺-ion in 1/4 of the octahedral holes. The principal feature of the structure is the existence of discrete poly-ions (CoCl₃)_n⁻, formed by face-sharing octahedra as shown in Fig. 3. The poly-ions are held together laterally by the 12-coordinated Cs⁺-ions. The interatomic distances calculated from the final parameters are listed in Table 4.

The coordination polyhedron of Co²⁺ is a trigonally deformed octahedron with a Co—Cl distance approximately 0.1 Å less than the sum of the ionic radii (Pauling).¹⁵ The examples collected in Table 5, however, show that this is normal for Cl-bridged Co(II)-compounds. The Co—Co distance within the poly-ions is remarkably short. A regular octahedral coordination, however, would demand an even shorter Co—Co distance, *viz.* 2.825 Å.

Two Cl—Cl distances are observed within the poly-ion. The Cl(2)—Cl(3) distance, the "out of plane" type, equals two van der Waals' radii.¹⁵ The Cl(1)—Cl(3) distance, the "in plane" or "shared" type, is considerably shorter. This is quite common in compounds with face-sharing octahedra, and is quoted as evidence for the essentially ionic character of the structure.

Two different Cs—Cl distances are observed. The shortest, the "in plane" type, is the same as that found in CsCl, *viz.* 3.57 Å.

The shortest distance between the poly-ions is 3.864 Å, (Cl(3)—Cl(4)).

THE MAGNETIC PROPERTIES

The magnetic susceptibility of powdered CsCoCl₃ was determined in the temperature range 80—300°K by means of the modified Sucksmith balance.¹⁹ Polycrystalline samples for the magnetic measurements were prepared by melting an equimolecular mixture of the component salts in an atmosphere

Table 4. Interatomic distances (Å) and bond angles (°). Standard deviations in parentheses.

Co —Cl(3)	2.447 (3)	Co—Co	3.0158 (3) = $\frac{1}{2}c_H$
Cs —Cl(3)	3.604 (3)	Co—Co	7.2019 (4) = a_H
Cs —Cl(2)	3.751 (2)	\angle Cl(1)—Co—Cl(2)	93.99 (4)
Cl(1)—Cl(3)	3.338 (4)	\angle Cl(1)—Co—Cl(3)	86.01 (4)
Cl(1)—Cl(2)	3.579 (3)	\angle Cl(1)—Cs—Cl(2)	58.19 (6)
Cl(3)—Cl(4)	3.864 (4)	\angle Cl(1)—Cs—Cl(3)	55.18 (5)

Table 5. Colour and Co—Cl distances in some hexacoordinated Co(II)-compounds. Standard deviations are in parentheses. py=pyridine.

Compound	Colour	Co—Cl distances in Å
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ ¹⁶	pink-violet	2.450 (3), 2.478 (3).
$\alpha\text{-Copy}_2\text{Cl}_2$ ¹⁷	violet	2.49
$\text{Co}(\text{AlCl}_4)_2$ ¹⁸	bright blue	2.453 (9), 2.475 (13), 2.472 (12).
CsCoCl_3	bright blue	2.447 (3).

of dry HCl. The raw materials were CsCl Merck and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ *p.a.*, Merck. The latter was carefully dehydrated in an atmosphere of dry HCl and then purified by sublimation *in vacuo*. The correct composition of the product was controlled by chemical analysis. The X-ray powder diagram of the substance is identical with that of CsCoCl_3 .

The magnetic susceptibility was measured in the temperature interval 80—300°K. The results are listed in Table 6.

A plot of the effective magnetic moment $\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr.}} T} \mu_B$ versus the absolute temperature is shown in Fig. 4. In the upper half of the investigated temperature interval, the effective magnetic moment of CsCoCl_3 is pretty near that of Cs_3CoCl_5 (the straight line), where the Co^{2+} -ion is known to be tetrahedrally coordinated.²⁰ The rule about the relationship between

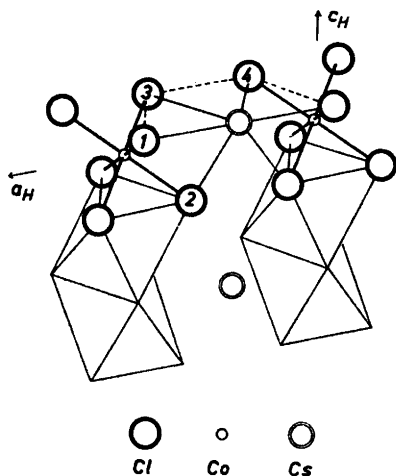


Fig. 3. Principal feature of the structure of CsCoCl_3 : $(\text{CoCl}_6)_n^{n-}$ poly-ions held together laterally by Cs^+ -ions.

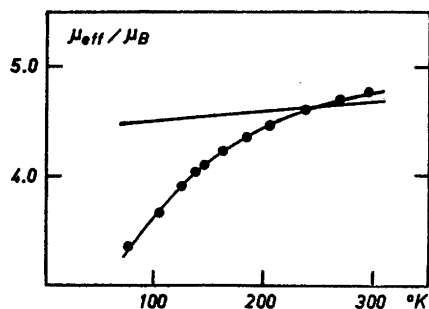


Fig. 4. Temperature dependence of the effective magnetic moment of CsCoCl_3 (full circles), and of Cs_3CoCl_5 (the straight line).

Table 6. Magnetic properties of CsCoCl₃. χ_g = gram-susceptibility. $\chi_M^{\text{corr.}}$ = molar susceptibility corrected for diamagnetism. $\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr.}} T} \mu_B$, (Bohr magnetons).

Temp. °K	$\chi_g \times 10^6$	$\chi_M^{\text{corr.}} \times 10^4$	μ_{eff}/μ_B
296.5	31.6	95.4	4.77
270.0	33.6	101.5	4.70
238.0	36.6	110.3	4.60
204.0	40.2	121.0	4.46
184.0	42.5	127.9	4.36
162.5	45.2	136.1	4.22
145.5	47.3	142.3	4.09
138.5	48.6	146.0	4.04
125.5	50.0	150.4	3.90
104.0	53.2	160.0	3.66
81.5	56.8	170.5	3.35

coordination and magnetic moment for Co(II)-compounds thus does not apply to CsCoCl₃. Furthermore, the effective magnetic moment of CsCoCl₃ decreases rapidly with decreasing temperature. At 80.5°K μ_{eff} is far below the "spin only" value of a quartet term, and a further reduction with decreasing temperature obviously will take place. How far it goes, cannot be predicted from the present data. No field strength dependence of the susceptibility is observed.

A further investigation of the magnetic properties of CsCoCl₃ at liquid helium temperatures is under way.

Acknowledgements. The author is indebted to the head of the department, professor Dr. phil. R. W. Asmussen, for discussions and advices. Thanks are also due to professor P. F. Andersen who kindly put the sample used for the magnetic measurement at my disposal, and to professor V. Frank, who performed the test for piezoelectricity. A grant from *Otto Mønstedts Fond* is gratefully acknowledged.

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Received February 23, 1968.