

## The Low-Symmetry Structure of Potassium Hexacyanochromate(III) at 4.2 K: A Neutron Diffraction Study

BY BRIAN N. FIGGIS, PHILIP A. REYNOLDS AND GEOFFREY A. WILLIAMS\*

*School of Chemistry, The University of Western Australia, Nedlands, Western Australia 6009, Australia*

(Received 1 July 1980; accepted 23 September 1980)

### Abstract

The structure of  $K_3[Cr(CN)_6]$  at 4.2 K has been determined by a single-crystal neutron diffraction study. The crystal was found to consist of four twins together with stacking disorder [triclinic,  $P\bar{1}$ ,  $a = 8.450$  (5),  $b = 10.576$  (8),  $c = 13.557$  (4) Å,  $\alpha = 90.0$  (1),  $\beta = 90.0$  (1),  $\gamma = 90.0$  (1)°]. Refinement of atom parameters with four extra population (twin and disorder) parameters gave  $R(F^2) = 0.053$  for 1575 reflections, and  $\chi(F^2) = 3.73$  at convergence. The  $P\bar{1}$  structure is related to the 295 K *Pcan* structure by symmetry-determined translations, but not rotations, of the constituent  $K^+$  and  $Cr(CN)_6^{3-}$  ions, together with some small additional distortions.

### Introduction

Chemical bonding and covalency effects in suitably paramagnetic chemically significant compounds can be studied using the technique of polarized neutron diffraction (Figgis, Mason, Smith & Williams, 1979). It is an attractive proposition to extend these studies to small molecules and ions which are expected to show a much greater degree of covalence than is found in substances already studied (Brown, Forsyth & Mason, 1980).

The compound  $K_3[Cr(CN)_6]$  contains the  $Cr(CN)_6^{3-}$  ion, and is well suited to the study of covalence by polarized neutron diffraction experiments. It is paramagnetic at 4.2 K ( $Cr^{III}$ ,  $S = \frac{3}{2}$ ), and shows high magnetization at reasonable applied magnetic field strengths (Figgis & Mitchell, 1978), which should allow considerable accuracy in the polarized neutron diffraction data. In addition, the Cr–CN bond is expected to be significantly covalent in nature. However, it is well known that both polytypism and phase transitions occur frequently in such complex cyanides, and these effects may vitiate the results of a polarized neutron diffraction experiment.

Kohn & Townes (1961) demonstrated the existence of *1M*, *2Or*, *3M* and *7M* polytypes in  $K_3[Co(CN)_6]$ , and Reynhardt & Boeyens (1972) also identified a *4Or* polytype. The nomenclature is that *1M* means a *single-layer monoclinic* polytype; *2Or* a *two-layer orthorhombic* polytype, etc. (Ramsdell, 1947). The structure of the *2Or* polytype of  $K_3[Cr(CN)_6]$  has been determined at room temperature by X-ray diffraction methods (Jagner, Ljungström & Vannerberg, 1974). Structural studies on  $M^{III}$  ( $M = \text{metal}$ ) hexacyanide polytypes show that, apart from the necessary changes in stacking sequence along the  $c$  crystal axis, the positional and thermal parameters are very similar in the *1M*, *2Or* and *4Or* polytypes (Reynhardt & Boeyens, 1972; Vannerberg, 1970, 1972; Figgis, Skelton & White, 1978).

Phase changes on change of temperature have been most clearly studied in  $Cs_2K[Fe(CN)_6]$  and related systems. They are characterized by small distortions from symmetric structures (Herren, Ludi & Fischer, 1979; and references therein). The symmetries can range from cubic to at least as low as monoclinic. The high residuals, typically  $R$  0.08–0.12, and some evidence of triclinic symmetry, raise doubts as to the completeness of the modelling.

As a precursor to a proposed polarized neutron diffraction experiment on  $K_3[Cr(CN)_6]$ , we have collected a neutron diffraction data set at 4.2 K. We will show that the structure is possibly too complex to warrant such an experiment at this stage.

### Experimental

Large transparent amber crystals of  $K_3[Cr(CN)_6]$  were grown by slow evaporation of solvent from an aqueous solution of  $K_3[Cr(CN)_6]$ . At 4.2 K the crystals were observed to be colourless. The measured density, 1.745 (5) Mg m<sup>-3</sup>, corresponds to that calculated from X-ray diffraction measurements on the *2Or* polytype, 1.747 (1) Mg m<sup>-3</sup> (Jagner, Ljungström & Vannerberg, 1974). Long-exposure Weissenberg X-ray photographs of small chips from the large crystals showed them to be the *2Or* polytype at room temperature.

\* Present address: Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria 3085, Australia.

There was noticeable, although weak, streaking along  $[00l]$  through  $h$ -odd reflections. This indicated some stacking disorder (Vannerberg, 1970). In addition to the systematic absences of the  $Pcan$  space group, the non-crystallographic absences  $hkl$  with  $h/2 + l = 2n + 1$ , and the visually estimated intensities, showed that our  $2Or$  crystals correspond well in structure to that determined by Jagner, Ljungström & Vannerberg (1974).

A crystal of dimensions  $2.8 \times 1.8 \times 4.0$  mm was mounted with  $[110]$  approximately parallel to the diffractometer rotation axis. Neutron diffraction intensity data were obtained at 4.2 K and  $\lambda = 1.176$  Å on the D15 normal-beam diffractometer with motorized lifting counter at the Institut Laue-Langevin, Grenoble. Cell parameters, together with their estimated standard deviations, were derived by a least-squares analysis of the setting angles determined for 21 angularly well separated reflections. Refinement of cell angles showed that they were within  $0.1^\circ$  of  $90^\circ$ . The  $1M$  polytype can have Bragg reflections (referred to the orthorhombic cell) at  $hkl$  and  $(h+1)k(l+\frac{1}{2})$  where  $h = 2n$  (Vannerberg, 1970). A search was made at a number of  $(h+1)k(l+\frac{1}{2})$  positions where a calculation predicted significant intensities from any possible  $1M$  polytype present. No intensity was found at any of these positions, placing an upper limit of 2% on the fraction of  $1M$  polytype present in the crystal. Both in this crystal, and in a second large crystal also studied, at high  $\sin \theta/\lambda$  values some peaks had unusual profiles, and some high-intensity peaks had unusually high backgrounds. These features probably reflect the stacking disorder already detected in the X-ray photographs.

Intensity measurements were made in the range  $0.04 < \sin \theta/\lambda \leq 0.78$  Å<sup>-1</sup>. Because of a restriction on the lifting angle of the counter, some high  $\sin \theta/\lambda$  data with  $h$  very different from  $k$  are missing from the full sphere of data. Intensities were measured *via* an  $\omega$ - $\theta$  scan, which was found to be appropriate for the mosaic spread of the crystal. No significant variation in the intensity of a standard reflection was observed throughout the data collection. Integrated intensities were obtained using a profile-analysis program, *COLL5* (Lehmann & Wilson, 1977), and geometrical corrections were applied. An absorption correction was not considered necessary since  $\mu = 0.0041$  mm<sup>-1</sup> at  $\lambda = 1.176$  Å (*International Tables for X-ray Crystallography*, 1968). After the averaging of Friedel pairs, 1579 observations remained.

The systematic absences expected for space group  $Pcan$  (in the  $h0l$ ,  $hk0$  and  $0kl$  reflections) had relatively large intensities in the measured data. Moreover, the non-crystallographic absences of  $hkl$  with  $h/2 + l = 2n + 1$ , observed in the room-temperature  $2Or$  polytype, were no longer absent. The only absences at 4.2 K may be  $h0l$  with  $h/2 + l = 2n + 1$ , where we observed

significant, but very weak, intensities. These weak intensities may be due to multiple-scattering effects obscuring real absences.

For  $h$ -even reflections, the symmetry of the intensities was orthorhombic within the counting errors. However, for the  $h$ -odd data there was a slight, but significant, lowering of the symmetry to at least monoclinic ( $F_{hkl}^2 \neq F_{h\bar{k}l}^2$ ). Because of the mechanical restriction on the lifting ( $\nu$ ) angle of the diffractometer, and the particular choice of crystal orientation, it was not possible to determine whether the symmetry is monoclinic or triclinic, *i.e.* whether  $F_{hkl}^2$  equalled  $F_{h\bar{k}l}^2$  or  $F_{\bar{h}kl}^2$ . The quality of the data may be judged from the index  $\sum \sigma(F^2)/\sum |F^2|$ , which is 0.0185.

### Refinement

Initial structure refinement used the least-squares program *CRYLSQ* (Stewart, 1976) in the full-matrix mode. At all times, refinement was based upon  $F_o^2$  values, the function minimized being  $\sum w(F_o^2 - F_c^2)^2$  where  $w = 1/\sigma^2(F_o^2)$  is the weight assigned to the  $F_o^2$  values.

A refinement in the space group  $Pcan$ , using unit weights and isotropic thermal parameters, and with starting coordinates taken from Jagner, Ljungström & Vannerberg (1974), reached an  $R(F) = \sum |F_o| - |F_c|/\sum |F_o|$  of 0.35. Examination of the  $F_o^2$  and  $F_c^2$  values showed fair agreement at low  $\sin \theta/\lambda$ , suggesting that the actual structure is not far from this minimum. Upon removal of all symmetry elements, except the centre of inversion, further refinement with isotropic thermal parameters gave an  $R(F)$  of 0.23. This minimum was at coordinates, in this  $P\bar{1}$  symmetry, closely consistent with  $P2_1/c$  symmetry. An examination of Fourier difference maps showed only structure very near atoms already in the model. Further refinement with anisotropic thermal parameters produced no real improvement [ $R(F) = 0.20$ ]. If the crystal was disordered, with a number of close possible atomic positions, anisotropic refinement would be expected to produce a larger effect than that observed. We were therefore forced to consider twinning effects.

If we assume that an initial  $Pcan$  structure has gone through a phase transition at some temperature between 4.2 K and room temperature, then a four-twin  $P\bar{1}$  model will include all symmetries (except obviously  $P1$ ). We attempted to fit  $F_o^2(hkl)$  to the expression  $c_1 F_o^2(hkl) + c_2 F_o^2(h\bar{k}l) + c_3 F_o^2(hkl) + c_4 F_o^2(h\bar{k}l)$ , in which  $c_1$  to  $c_4$  are refineable twin population parameters. This assumes that all four twins have identical cells, and contribute to every reflection. Since we also have evidence of stacking disorder, the scale factors of  $h$ -odd and  $h$ -even data were refined separately (the ratio is  $c_3$ ). In the  $Pcan$  structure, the amount by which the  $h$ -even scale factor exceeds that for  $h$ -odd is a

measure of the fraction of *ab* planes over which a stacking fault in the *c* axial direction occurs (Vannenberg, 1970). An isotropic-extinction parameter, which is assumed to be identical for all four twins, was also refined. This gave a  $6 + (4 \times 32) = 134$  parameter model, with isotropic thermal parameters for all atoms, and noting the condition  $c_1 + c_2 + c_3 + c_4 = 1$ . Included in the 1579 reflections are four very intense ones which may be highly affected by extinction effects. We removed these so as to reduce any bias in the final values of the other parameters. Such bias may arise through our gross assumption of uniform, isotropic, extinction. Least-squares refinement of this scattering model in two blocks was performed by use of a locally modified *ORFLS* program (Busing, Martin & Levy, 1962).

Refinement converged with  $R(F^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2 = 0.053$ ,  $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.064$ ,  $R(F) = 0.041$ , and  $\chi(F^2) = [\sum w(F_o^2 - F_c^2)^2 / (n - v)]^{1/2} = 3.73$ , where  $n = 1575$  and  $v = 134$  are numbers of observations and variables respectively. At convergence, the mean parameter shift-to-error ratio was 0.2:1. The atomic thermal parameters,  $10^4 U$ , refined to mean values of  $49 \pm 15$  for C,  $64 \pm 13$  for N,  $39 \pm 5$  for K, and  $16 \pm 12 \text{ \AA}^2$  for Cr. The errors quoted reflect the dispersion in the refined values, and are larger than the individual least-squares e.s.d.'s. The four twin populations refined to values  $c_1 = 0.20$  (1),  $c_2 = 0.20$  (1),  $c_3 = 0.32$  (1), and  $c_4 = 0.29$  (1). The disorder parameter  $c_5 = 1.179$  (6). The extinction parameter,  $r^*/\lambda$ , refined to  $1.8$  (1)  $\times 10^3$ , reflecting a small but significant extinction effect (Zachariassen, 1967). The neutron scattering lengths were taken from *International Tables for X-ray Crystallography* (1974).†

### Discussion

The final atomic positional and isotropic thermal parameters are listed together with their e.s.d.'s in Table 1. Tables 2 and 3 list the bond distances and bond angles in the two independent  $\text{Cr}(\text{CN})_6^{3-}$  anions.

Each of the four twin population parameters deviates slightly from  $\frac{1}{4}$ , the value expected in the absence of any biasing caused by thermal gradients, crystal-defect structure, etc. The value of  $c_5$  implies that 15% of the *bc* planes are stacked incorrectly. This value is sufficiently small that, given the small differences in the *1M* and *2Or* polytype structures apart from the stacking difference, we may expect only a small effect

Table 1. *Final atomic positional coordinates* ( $\times 10^4$ ) *and thermal parameters* ( $\text{\AA}^2 \times 10^4$ )

Isotropic thermal parameters are defined by

$$T = \exp[-8\pi^2 U (\sin^2 \theta) / \lambda^2].$$

	x	y	z	U
Cr(1)	1205 (9)	150 (7)	2424 (4)	5 (7)
Cr(2)	3728 (11)	4806 (7)	7440 (5)	28 (8)
K(1)	6294 (9)	188 (7)	2377 (4)	42 (8)
K(2)	3769 (9)	-7873 (6)	4980 (4)	40 (9)
K(3)	8743 (8)	-7736 (6)	4981 (4)	38 (10)
K(4)	-1247 (10)	4805 (7)	7397 (4)	35 (8)
K(5)	1244 (9)	2900 (7)	9991 (4)	47 (9)
K(6)	-3757 (8)	2687 (5)	-35 (4)	34 (9)
C(1)	1206 (5)	-1613 (4)	1791 (2)	45 (5)
C(2)	2979 (4)	-410 (4)	3412 (2)	32 (5)
C(3)	-490 (4)	-365 (4)	3448 (3)	43 (5)
C(4)	1247 (5)	1928 (4)	3111 (2)	66 (4)
C(5)	2955 (4)	777 (4)	1463 (2)	31 (5)
C(6)	-477 (4)	793 (4)	1452 (2)	30 (5)
C(7)	3784 (5)	6607 (4)	6830 (2)	51 (5)
C(8)	2012 (4)	5349 (5)	8413 (3)	64 (5)
C(9)	5478 (4)	5330 (5)	8450 (3)	60 (5)
C(10)	3727 (4)	3070 (3)	8092 (2)	31 (4)
C(11)	2028 (4)	4187 (5)	6466 (3)	69 (5)
C(12)	5488 (4)	4215 (4)	6449 (3)	67 (5)
N(1)	1232 (5)	-2622 (3)	1459 (2)	66 (3)
N(2)	3991 (3)	-686 (3)	3937 (2)	68 (4)
N(3)	-1448 (3)	-615 (2)	4028 (2)	48 (4)
N(4)	1315 (3)	2864 (3)	3539 (2)	68 (4)
N(5)	3997 (3)	1179 (4)	953 (2)	47 (4)
N(6)	-1462 (4)	1195 (4)	952 (2)	70 (4)
N(7)	3801 (4)	7605 (3)	6461 (2)	56 (4)
N(8)	1004 (3)	5643 (4)	8971 (2)	48 (4)
N(9)	6431 (4)	5588 (4)	9042 (2)	85 (4)
N(10)	3754 (4)	2122 (3)	8533 (2)	76 (4)
N(11)	1050 (4)	3769 (4)	5993 (2)	78 (4)
N(12)	6441 (3)	3829 (3)	5908 (2)	58 (4)

Table 2. *Bond distances* ( $\text{\AA}$ ) *in the*  $\text{Cr}(\text{CN})_6^{3-}$  *anions*

Cr(1)—C(1)	2.053 (1)	Cr(2)—C(7)	2.077 (1)
Cr(1)—C(2)	2.096 (1)	Cr(2)—C(8)	2.043 (1)
Cr(1)—C(3)	2.068 (1)	Cr(2)—C(9)	2.090 (1)
Cr(1)—C(4)	2.099 (1)	Cr(2)—C(10)	2.038 (1)
Cr(1)—C(5)	2.079 (1)	Cr(2)—C(11)	2.058 (1)
Cr(1)—C(6)	2.054 (1)	Cr(2)—C(12)	2.099 (1)
C(1)—N(1)	1.158 (1)	C(7)—N(7)	1.168 (1)
C(2)—N(2)	1.150 (1)	C(8)—N(8)	1.181 (1)
C(3)—N(3)	1.159 (1)	C(9)—N(9)	1.169 (1)
C(4)—N(4)	1.149 (1)	C(10)—N(10)	1.168 (1)
C(5)—N(5)	1.198 (1)	C(11)—N(11)	1.136 (1)
C(6)—N(6)	1.155 (1)	C(12)—N(12)	1.163 (1)

on the derived parameters for an ideal *2Or* structure. The mean Cr—C bond length is 2.071 (22)  $\text{\AA}$ , with a C—N bond length of 1.163 (16)  $\text{\AA}$ . The e.s.d.'s quoted are those associated with averaging the 12 independent bond lengths. These errors are some *twenty times* larger than the least-squares-derived e.s.d.'s in the individual lengths. It is evident from this, and from the angles in Table 3, which again differ from ideal values by up to

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35724 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond angles ( $^{\circ}$ ) in the  $\text{Cr}(\text{CN})_6^{3-}$  anions

Cr(1)–C(1)–N(1)	177.87 (4)	Cr(2)–C(7)–N(7)	178.02 (5)
Cr(1)–C(2)–N(2)	177.41 (10)	Cr(2)–C(8)–N(8)	178.75 (16)
Cr(1)–C(3)–N(3)	177.91 (3)	Cr(2)–C(9)–N(9)	177.23 (5)
Cr(1)–C(4)–N(4)	175.55 (2)	Cr(2)–C(10)–N(10)	174.77 (2)
Cr(1)–C(5)–N(5)	176.24 (2)	Cr(2)–C(11)–N(11)	173.76 (3)
Cr(1)–C(6)–N(6)	175.88 (3)	Cr(2)–C(12)–N(12)	176.77 (9)
Cr(1)–C(1)–C(2)	90.59 (2)	Cr(2)–C(7)–C(8)	90.89 (3)
Cr(1)–C(1)–C(3)	92.39 (3)	Cr(2)–C(7)–C(9)	90.09 (2)
Cr(1)–C(1)–C(4)	178.09 (2)	Cr(2)–C(7)–C(10)	177.42 (8)
Cr(1)–C(1)–C(5)	91.57 (2)	Cr(2)–C(7)–C(11)	92.99 (3)
Cr(1)–C(1)–C(6)	91.88 (3)	Cr(2)–C(7)–C(12)	90.12 (3)
Cr(1)–C(2)–C(3)	89.54 (4)	Cr(2)–C(8)–C(9)	90.27 (4)
Cr(1)–C(2)–C(4)	87.56 (2)	Cr(2)–C(8)–C(10)	88.45 (2)
Cr(1)–C(2)–C(5)	88.96 (4)	Cr(2)–C(8)–C(11)	90.47 (4)
Cr(1)–C(2)–C(6)	176.92 (24)	Cr(2)–C(8)–C(12)	178.99 (39)
Cr(1)–C(3)–C(4)	87.12 (2)	Cr(2)–C(9)–C(10)	87.42 (2)
Cr(1)–C(3)–C(5)	175.78 (12)	Cr(2)–C(9)–C(11)	176.82 (15)
Cr(1)–C(3)–C(6)	92.21 (4)	Cr(2)–C(9)–C(12)	89.83 (4)
Cr(1)–C(4)–C(5)	88.87 (2)	Cr(2)–C(10)–C(11)	89.51 (2)
Cr(1)–C(4)–C(6)	89.99 (3)	Cr(2)–C(10)–C(12)	90.55 (2)
Cr(1)–C(5)–C(6)	89.12 (4)	Cr(2)–C(11)–C(12)	89.38 (4)

$3^{\circ}$  (100 standard deviations), that the  $\text{Cr}(\text{CN})_6^{3-}$  anions are significantly distorted from ideal octahedral. This distortion has not been clearly observed before in hexacyanide complexes due to less accurate structure determinations with higher values of least-squares-derived e.s.d.'s. These resulted from less data, and less adequate modelling (reflected in higher residuals). Our spread in values ( $3^{\circ}$ ,  $0.05 \text{ \AA}$ ) is, however, consistent with the previous work.

The distortion from the 'ideal' initial *Pcan* structure is not random. We can define three planes ( $p'_1, p'_2, p'_3$ ) through each of the independent  $\text{Cr}(\text{CN})_6^{3-}$  units (*A* and *B*) by least-squares methods, each of which is defined by Cr and eight almost coplanar C and N atoms. We define  $p_1^A = p'_1{}^A + p'_2{}^A$ ,  $p_2^A = p'_1{}^A - p'_2{}^A$ , and  $p_3^A = p'_3{}^A$ , as these are more conveniently related to the crystal axes *a, b, c*. For each of the  $\text{Cr}(\text{CN})_6^{3-}$  anions, *A* and *B*, the three planes are, within  $1^{\circ}$ , orthogonal. Moreover, the normals to the planes  $p_1^A$  and  $p_1^B$  are both, within  $1^{\circ}$ , collinear with the crystal *a* axis. In addition,  $p_2^B$  and  $p_3^B$  can be generated from  $p_2^A$  and  $p_3^A$  by a twofold rotation about the *b* axis, again within  $1^{\circ}$  (together with some translation). The planes  $p_2^A, p_3^A, p_2^B, p_3^B$  make an angle of  $25.3(6)^{\circ}$  with the *b* axis (or  $90-25.3^{\circ}$ ). We can compare this with  $25.5(5)^{\circ}$  from Jagner *et al.*'s (1974) results.

We conclude that on lowering the temperature, the distortion does not involve any significant rotation of the  $\text{Cr}(\text{CN})_6^{3-}$  anions.

We make a similar analysis for translations of the  $\text{Cr}(\text{CN})_6^{3-}$  anion centroids and the  $\text{K}^+$  ions from symmetry-fixed positions in *Pcan* (more accurately, pseudosymmetry in the *x* coordinate). These changes are shown in Table 4, and they are large and significant. They appear to correspond to a translation with no component in the *x* direction and which retains the symmetry  $\pm(x, y, z)$  and  $\pm(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z)$ . While this explains the major part of the change from *Pcan*,

Table 4. Translations from 'ideal' (*Pcan*) pseudosymmetry positions of the ions at 4.2 K

Atoms or ions related by the approximate symmetry  $\pm(x, y, z)$ ,  $\pm(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z)$  are grouped in pairs.

Ion	$10^4 x$	$10^4 y$	$10^4 z$
$[\text{Cr}(1)(\text{CN})_6^{3-}]$	1 (2)	-196 (28)	42 (11)
$[\text{Cr}(2)(\text{CN})_6^{3-}]$	3 (7)	221 (33)	36 (14)
$[\text{K}(1)^+]$	-44 (9)	-188 (7)	123 (4)
$[\text{K}(4)^+]$	-3 (10)	195 (7)	103 (4)
$[\text{K}(2)^+]$	-19 (9)	373 (6)	20 (4)
$[\text{K}(5)^+]$	6 (9)	-400 (7)	9 (4)
$[\text{K}(3)^+]$	7 (8)	236 (6)	19 (4)
$[\text{K}(6)^+]$	7 (8)	-187 (5)	35 (4)

this simple set of four independent translations ( $0, \Delta Y, \Delta Z$ ) is not a complete explanation. There are significant departures (5–10 standard deviations), with  $\langle U^2 \rangle^{1/2} \sim 0.03 \text{ \AA}$ , of individual atoms from such an idealized  $P\bar{1}$  structure. The spread in thermal parameters is also larger than expected. While this may also occur in a fully ordered  $P\bar{1}$  structure, we should note we have 15% stacking faults which may become important at this level of detail in the analysis. It is not unreasonable to suppose that, since the translational change is small, the phase change from *Pcan* to  $P\bar{1}$  associated with the lowering of temperature may involve the freezing out of a softened zone-centre translational mode in *Pcan*, whose eigenvector is approximately given by Table 4. This is followed by a small amount of apparently random change in coordinates. Magnetization-density measurements by polarized neutron diffraction yield magnetic structure factors rather slowly ( $\sim 20$  min per reflection). This, combined with the twelve independent Cr–CN bonds, and the complication of twinning would make such an experiment long, susceptible to systematic error, and, at this stage, unattractive.

We thank the Science Research Council (UK) and the Australian Research Grants Committee for support. GAW thanks the Australian Institute of Nuclear Science and Engineering for a Research Fellowship. We thank Mr Andrew Smith for help with the experiment.

## References

- BROWN, P. J., FORSYTH, J. B. & MASON, R. (1980). *Philos. Trans. R. Soc. London*. In the press.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- FIGGIS, B. N., MASON, R., SMITH, A. R. P. & WILLIAMS, G. A. (1979). *J. Am. Chem. Soc.* **101**, 3673–3675.
- FIGGIS, B. N. & MITCHELL, L. S. (1978). Unpublished results.

- FIGGIS, B. N., SKELTON, B. W. & WHITE, A. H. (1978). *Aust. J. Chem.* **31**, 1195–1199.
- HERREN, F., LUDI, A. & FISCHER, P. (1979). *Acta Cryst.* **B35**, 3129–3130.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 197–199. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 270–271. Birmingham: Kynoch Press.
- JAGNER, S., LJUNGSTRÖM, E. & VANNERBERG, N.-G. (1974). *Acta Chem. Scand. Ser. A*, **28**, 623–630.
- KOHN, J. A. & TOWNES, W. D. (1961). *Acta Cryst.* **14**, 617–622.
- LEHMANN, M. S. & WILSON, S. (1977). Internal Report, Institut Laue–Langevin, Grenoble.
- RAMSDALL, L. S. (1947). *Am. Mineral.* **32**, 64–82.
- REYNHARDT, E. C. & BOEYENS, J. C. A. (1972). *Acta Cryst.* **B28**, 524–529.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- VANNERBERG, N.-G. (1970). *Acta Chem. Scand.* **24**, 2335–2347.
- VANNERBERG, N.-G. (1972). *Acta Chem. Scand.* **26**, 2863–2876.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1981). **B37**, 508–513

## An X-ray Diffraction Study of Tricaesium Tetrachlorocobaltate(II) Chloride at 295 K

BY PHILIP A. REYNOLDS, BRIAN N. FIGGIS AND ALLAN H. WHITE

*School of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia*

(Received 1 July 1980; accepted 10 November 1980)

### Abstract

An X-ray diffraction data set consisting of 1772 unique reflections (27118 measured) has been collected on  $\text{Cs}_3\text{CoCl}_5$  at 295 K. The unit cell is tetragonal,  $I4/mcm$ , with  $a = 9.2315$  (15),  $c = 14.5535$  (24) Å,  $Z = 4$ . A free-atom form factor, harmonic model does not fit the data well. From the low-angle low-intensity data [ $R(F) = 0.022$ ,  $R_w(I) = 0.030$  for 54 unique reflections] charges of  $+1.27 \pm 0.10$  e on the cobalt and  $-0.82 \pm 0.12$  e on the tetrachlorocobaltate-anion Cl atoms are obtained. The cobalt possesses a  $3d$  population of  $7.1 \pm 0.1$  e and a much more diffuse charge of  $0.6 \pm 0.16$  e. Comparison with neutron diffraction, polarized neutron diffraction and spectroscopic results suggests that the highest-angle data may be substantially affected by anharmonicity. 'Anharmonicity' parameters are derived.

### Introduction

Tricaesium tetrachlorocobaltate(II) chloride has recently been the subject of neutron diffraction (Figgis, Mason, Smith & Williams, 1980) and polarized neutron diffraction (Figgis, Reynolds, Williams, Mason, Smith & Varghese, 1980) experiments at 4.2 K. The derived electronic spin density shows the effect of covalence in the crystal  $[\text{CoCl}_4]^{2-}$  anions. Complementary charge-

density studies by means of X-ray diffraction experiments are desirable. Previous photographic X-ray diffraction experiments (Powell & Wells, 1935; Figgis, Gerloch & Mason, 1964) were of limited extent in reciprocal space and neglected large absorption effects. Before collecting a low-temperature reflection data set we analysed the room-temperature data for any chemically significant information resolvable from the thermal motion. A room-temperature neutron diffraction study has been performed concurrently (Williams, Figgis & Moore, 1980).

### Experimental

The crystal used was an almost regular truncated tetragonal prism, prepared from solution (Figgis, Reynolds, Williams, Mason, Smith & Varghese, 1980). The unit cell of the tetragonal crystal was determined by a least-squares fit of ten reflections centred in the counter aperture of a Syntex  $P2_1$  four-circle X-ray diffractometer. A complete sphere of data, approximately to the limit in that of observable intensities, was collected. The crystal dimensions and experimental conditions are given in Table 1. After correction for the slight change in standard intensities, the intensities of Friedel-pair-related equivalent reflections were equal, within errors in counting and standardization. These Friedel-related intensities were accordingly averaged before an absorption correction was made. An