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Crystal structure of $\text{Cs}_2\text{LiCo}(\text{CN})_6$. BY ALEXANDER WOLBERG,* *Chemistry Department, Washington University, St. Louis, Missouri 63130, U.S.A.*

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$\text{Cs}_2\text{LiCo}(\text{CN})_6$ is cubic, with $a_0 = 10.54 \pm 0.01 \text{ \AA}$, space group $Fm\bar{3}m$ (O_h^5) and 4 molecules per unit cell. The Co–C and C–N bond lengths are 1.90 ± 0.02 and $1.16 \pm 0.02 \text{ \AA}$, respectively. The compound is isostructural with K_2NaAlF_6 .

The monoclinic salt $\text{K}_3\text{Co}(\text{CN})_6$ is widely used in paramagnetic studies as a diamagnetic host crystal. The purpose of this note is to report a successful attempt to prepare a cobaltihexacyanide salt, in which the site symmetry at the cobalt atom is O_h . The structure was determined by means of a single-crystal X-ray diffraction experiment.

Dicesium lithium cobaltihexacyanide, $\text{Cs}_2\text{LiCo}(\text{CN})_6$, was synthesized by mixing in a water solution the stoichiometric molar ratios of the individual alkali salts, which were prepared from the commercially available $\text{K}_3\text{Co}(\text{CN})_6$ by the method of Meyer & Chao (1937). A slow evaporation of a saturated solution of $\text{Cs}_2\text{LiCo}(\text{CN})_6$ produced pale yellow single crystals of sizes up to 0.5 cm on an edge.

Laue, rotation, and Weissenberg photographs taken with Mo $K\alpha$ and Cu $K\alpha$ radiation showed a face-centered cubic unit cell with $a_0 = 10.54 \pm 0.01 \text{ \AA}$ and with space group $Fm\bar{3}m$ (O_h^5), $F\bar{4}3m$ (T_d^2), or $F432$ (O^3), $Z = 4$ formulas per unit cell. The positions that can reasonably be occupied in an ordered structure by atoms with the multiplicities here present are the same in all three space groups (see Table 1); thus the space group $Fm\bar{3}m$ is indicated. This space group was chosen over the other two because the e.p.r. spectrum of $\text{Cr}(\text{CN})_6^{3-}$, doped into this crystal as 'host lattice', indicated that the site symmetry of the Co atom is $m\bar{3}m$. The structure is evidently of the K_2NaAlF_6 type (see final paragraph).

Table 1. Atomic positions and parameters

	Position	Coordinates (plus f.c.c.)	B_j
Co	4(a)	000	2.0 \AA^2
Li	4(b)	$\frac{1}{2} \frac{1}{2} \frac{1}{2}$	(2.0)*
Cs	8(c)	$\frac{1}{4} \frac{1}{4} \frac{1}{4}; \frac{3}{4} \frac{3}{4} \frac{3}{4}$	2.5
C	24(e)	$\pm x_c 00; \pm 0x_c 0; \pm 00x_c$. $x_c = 0.1800$	2.0
N	24(e)	$\pm x_N 00; \pm 0x_N 0; \pm 00x_N$. $x_N = 0.2900$	3.0

* The lithium contribution to the structure factors is so small that variations in the B_j have negligible effect; therefore this value must be considered with some caution.

The structural parameters x_c , x_N , and isotropic temperature factors B_j were refined by trial and error, with x_c varying from 0.1600 to 0.2000 and x_N from 0.2700 to 0.3100, both with intervals of 0.0025. The B_j 's were varied from 1.0 to 5.0 with intervals of 0.5. Atomic form factors were taken from *International Tables for X-Ray Crystallography* (1962); a dispersion correction of -2.0 electrons was applied to f_{Cs} .

The observed structure factors were obtained from an equatorial Weissenberg photograph, with Cu $K\alpha$ radiation, taken normally to the $[0\bar{1}1]$ axis of a crystal of $0.036 \times 0.026 \times 0.039 \text{ cm}^3$. Several differently timed exposures were taken on the same film, with small camera displacements in

between. Absorption, extinction, and Lorentz-polarization corrections were made. The absorption correction was derived from *International Tables for X-Ray Crystallography* (1962) for a spherical object with equivalent radius of 0.0205 cm. The extinction correction was assumed to obey $I_{\text{corr}} = I_{\text{obs}} / (1 - gI_{\text{obs}})$, where I_{obs} is the measured intensity after the correction for absorption. The best fit was obtained with $g = 4 \times 10^{-4}$ in inverse intensity units.

The odd reflections (to which Cs does not contribute) were used in refining all parameters except B_{Cs} for which the even reflections were used. The best parameters obtained are shown in Table 1, and the observed and calculated structure factors are compared in Table 2. The reliability index $R = \sum |F_o| - |F_c| / \sum |F_o|$ is 0.090. The uncertainty limits ($\pm 0.02 \text{ \AA}$ for the position parameters, and 0.5 \AA^2 for the B_j 's) are set by the increments used in varying the structural parameters, and are in good accord with what can be expected from a photographic intensity measurement.

Table 2. Calculated and observed values of $F(hkl)$

h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	1	1	89.7	82.3	4	0	0	608.5	560.5
5	1	1	58.7	61.4	6	0	0	112.5	-88.2
7	1	1	66.5	67.0	8	0	0	256.1	265.8
9	1	1	22.5	23.0	10	0	0	54.5	-51.4
11	1	1	35.9	37.4	12	0	0	151.0	135.8
1	3	3	73.6	67.3	0	2	2	510.0	413.1
3	3	3	53.8	54.4	2	2	2	416.6	-399.9
5	3	3	38.1	42.1	4	2	2	229.8	294.2
7	3	3	42.9	47.0	6	2	2	234.0	-202.1
					8	2	2	164.2	164.4
1	5	5	42.5	42.5	10	2	2	96.8	-104.8
3	5	5	35.7	34.4	12	2	2	82.1	89.7
5	5	5	31.3	28.8					
7	5	5	37.9	36.7	0	4	4	378.7	387.8
					2	4	4	176.2	-195.1
1	7	7	47.7	47.3	4	4	4	269.5	292.9
3	7	7	38.5	39.6	6	4	4	122.6	-109.4
5	7	7	37.2	36.3	8	4	4	170.7	165.6
7	7	7	32.8	34.3	10	4	4	59.6	-62.6
					12	4	4	79.0	90.1

The Co–C and C–N bond lengths of $1.90 \pm 0.02 \text{ \AA}$ and $1.16 \pm 0.02 \text{ \AA}$, respectively, are in good agreement with those reported in the literature for $\text{K}_3\text{Co}(\text{CN})_6$. Barkhatov & Zhdanov (1942) and Barkhatov (1942) using X-ray diffraction found them to be 1.9 \AA and 1.2 \AA , respectively, and Curry & Runciman (1959) using neutron diffraction reported that they were 1.89 \AA and 1.15 \AA , respectively. Curry & Runciman also found that the B_j 's are different for the different atoms. The larger temperature factor of nitrogen demonstrates the larger vibrational amplitude of nitrogen compared to carbon and cobalt. The trend should

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be $B_N > B_C > B_{Co}$, but because of the limited sensitivity of this experiment to temperature effects it seems that $B_C = B_{Co}$.

The prototype of this structure elpasolite, K_2NaAlF_6 , was originally studied by powder techniques (Menzer, 1932; Frondel, 1948; Steward & Rooksby, 1953). According to these workers the crystal belongs to the $Pa\bar{3}$ (T_h^9) space group. However, more recently Helmholz (1959) and Helmholz, Guzzo & Sanders (1961) assigned to this crystal the $Fm\bar{3}m$ (O_h^2) space group, after a single-crystal study. There are now available several more examples of members of this isostructural family, e.g. K_2NaGaF_6 (Helmholz, 1959), K_2NaCrF_6 and K_2NaFeF_6 (Knox & Mitchell, 1961), K_2NaTiF_6 (Bright & Wurm, 1958) and the current work on $Cs_2LiCo(CN)_6$, all having the $Fm\bar{3}m$ space group. In addition, the e.p.r. studies of FeF_6^{3-} and CrF_6^{3-} doped in K_2NaGaF_6 (Helmholz, 1959; Helmholz, Guzzo & Sanders, 1961) and $Cr(CN)_6^{3-}$ in $Cs_2LiCo(CN)_6$ (to be published) showed no evidence of any distortion of the octahedral complexes. Evidence of a reversible transition, which could be ascribed to misalignment of the complex axes with respect to those of the unit cell, were found in our e.p.r. work on $Cr(CN)_6^{3-}$ in $Cs_2LiCo(CN)_6$ at about 70°K. We feel that this work should be emphasized since it seems that the remarks of Helmholz, Guzzo & Sanders (1961) on the elpasolite structure have been overlooked.

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Crystallographic data for carbazole, indole and phenanthridine. BY P. T. CLARKE and J. M. SPINK, *National Physical Laboratory, Teddington, Middlesex, England*

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Carbazole, indole and phenanthridine are shown to be orthorhombic with four molecules in the unit cell. The first two have space groups $Pna2_1$ (or $Pnma$) and $Pna2_1$ (or $Pnma$), and the last one $P2_12_12_1$.

As part of a series of studies of the electro-optic properties of some heterocyclic molecules we have determined crystallographic constants (Table 1) for carbazole, indole and phenanthridine. The X-ray data were obtained from oscillation and Weissenberg photographs with Cu $K\alpha$ radiations. The densities were determined by flotation; the instrument produced by Crystal Structures Ltd was used to test for the piezoelectric effect. In the cases of indole and carbazole the non-centrosymmetric space group $Pna2_1$ is

preferred to the alternative centrosymmetric possibility $Pnma$ despite the lack of any detectable piezoelectric effect since the symmetry requirements imposed by $Pnma$ would lead to improbable packing arrangements. All cell dimensions are accurate to about 0.4%. No further crystallographic studies of these compounds are contemplated.

This work forms part of the programme of the Division of Molecular Science at the National Physical Laboratory.

Table 1. *Crystallographic data for carbazole, indole and phenanthridine*

	Carbazole	Indole	Phenanthridine
Empirical formula	$C_{12}H_9N$	C_8H_7N	$C_{13}H_9N$
Molecular weight	167.21	117.15	179.21
Solvent	Ethanol	Cyclohexane	Cyclohexane and ethanol
Habit	Thin plates	Thin plates	Flat needles
Piezoelectric effect	Nil	Nil	Nil
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Systematic absences	$0kl, k+l \neq 2n$ $h0l, h \neq 2n$	$0kl, k+l \neq 2n$ $h0l, h \neq 2n$	$h00, h \neq 2n$ $0k0, k \neq 2n$ $00l, l \neq 2n$
Space group	$Pna2_1$ (or $Pnma$)	$Pna2_1$ (or $Pnma$)	$P2_12_12_1$
Molecules per unit cell	4	4	4
Cell dimensions			
a (Å)	5.73	14.89	11.72
b (Å)	19.27	7.87	16.41
c (Å)	7.82	5.64	4.97
V (Å ³)	825.3	660.7	955.9
Density (observed)	1.285	1.188	1.19
Density (calculated)	1.30	1.19	1.24