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Crystal Structure of Rubidium Cobalticyanide

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Abstract—The crystal structure of $Rb_3[Co(CN)_6]$ was determined by X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$, $a = 7.163(2)$, $b = 10.601(3)$, $c = 8.675(3)$ Å, $\beta = 107.83(2)°$, $V = 627.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.497$ g/cm^3, $R = 0.0844$, $wR = 0.2090$ for 769 measured reflections. The coordination polyhedron of the Co atom is the regular octahedron $[Co(CN)_6]$. The Rb(1) atoms are in the cavities of the octahedral structure; the Rb(2) atoms are in the cavities of the trigonal prisms, additional two atoms being more distant. All the cyano groups of the complex are in terminal positions.

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Cyanide complexes of cobalt have been investigated by many researchers. Numerous studies were devoted to the synthesis of various cobalti- and cobaltocyanides. The crystal structures were determined for $H_3[Co(CN)_6]$ [1–3], $K_3[Co(CN)_6]$ [4–9], $M_3[Co(CN)_6]_2 \cdot xH_2O$ (M^{2+} = Mn, Fe, Co, Ni, Zn, Cd, and Cu) [10], $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$ [11], $Ag_3[Co(CN)_6]$ [8], $Ag_2Tl[Co(CN)_6]$, $AgTl_2[Co(CN)_6]$, $Tl_3[Co(CN)_6]$ [12], $SrK[Co(CN)_6] \cdot 2.5H_2O$, and $CaK[Co(CN)_6] \cdot 2.5H_2O$ [13]. Cobalt cyanide complexes contain *s* and *d* elements in the outer sphere; however, although the cell parameters and crystal symmetries differ, the cobalticyanide ion has an octahedral structure in all complexes.

The goal of this study was to obtain rubidium cobalticyanide, $Rb_3[Co(CN)_6]$ (**I**), and determine its crystal structure.

EXPERIMENTAL

Synthesis of complex I. Rubidium carbonate was added at room temperature to cobalticyanic acid until carbon dioxide ceased to evolve ($H_3[Co(CN)_6]$was prepared by passing a solution of $K_3[Co(CN)_6]$ through a cation exchanger in the H^+ form). The resulting solution was left for slow crystallization. Light yellow crystals formed after several weeks were suitable for X-ray diffraction analysis. Elemental analysis for carbon and nitrogen was performed on an automated C, H, N analyzer.

For $C_6CoN_6Rb_3$		
anal. calcd. (%):	C, 15.29;	N, 17.83.
Found (%):	C, 15.12;	N, 17.54.

The IR spectrum of complex **I** was recorded on a Perkin-Elmer 1720 FTIR spectrometer (KBr pellets) in the 400–4000 cm^{-1} range. The IR spectrum shows an intense absorption band at 2132 cm^{-1} (ν(CN) stretching vibrations), which agrees with data for $K_3[Co(CN)_6]$ (**II**): this band appears at 2143, 2129, and 2126 cm^{-1} [14]. In the Berlin blue analog $Co_3^{II}[Co^{III}(CN)_6]_2 \cdot 12H_2O$, the corresponding vibration absorbs at 2170 cm^{-1} [15]. The lower ν(CN) values indicate the presence of terminal cyano groups, while the higher ν(CN) values indicate the presence of bound cyano groups.

X-ray diffraction analysis. An array of reflection intensities was collected at 173 K with a STOE IPDS diffractometer [16] (MoK_α radiation, $\lambda = 0.7103$ Å, graphite monochromator, φ scan mode, 0°–180°, scan step $\Delta\varphi = 1.0°$, frame exposure time 2 min, $3.8° < 2\theta < 50.3°$, detector distance 135 mm). The structure was solved by direct methods (SHELX-97) [17, 18]. The atomic positions were refined by the full-matrix least-squares method (on F^2) in the anisotropic approximation. Empirical correction for absorption was applied with DELrefABS in the PLATON program [19]; the transmission factors T_{min}/T_{max} are 0.083/0.537. The projection of structure **I** (figure) was displayed with the

Table 1. Crystallographic parameters and a summary of data collection for $Rb_3[Co(CN)_6]$

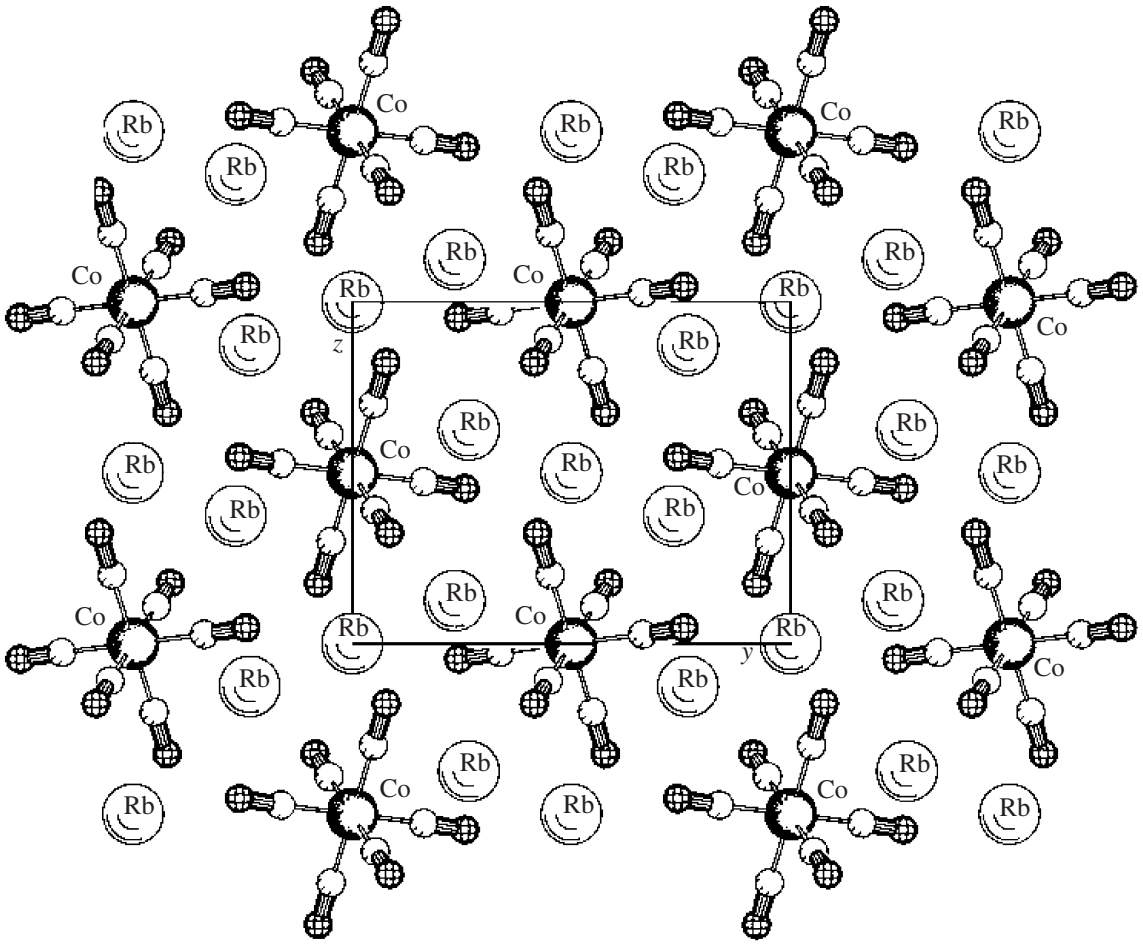
Parameter	Value
Crystal size	0.50 × 0.50 × 0.50 mm
M	471.46
Crystal system;	Monoclinic
Space group	$P2_1/c$
Cell parameters:	
a, Å	7.163(2)
b, Å	10.601(3)
c, Å	8.675(3)
β, deg	107.83(2)
V, Å^3	627.1(3)
Z	2
ρ_{calcd}, g/cm^3	2.497
μ, mm^{-1}	12.916
θ, deg	2.99–25.16
Number of measured reflections	2808
Number of independent reflections	1110
Number of reflections with $I > 2\sigma(I)$	769
R_{int}	0.2245
Number of parameters refined	71
R factors for all reflections	$R = 0.1108$, $wR = 0.2290$
R factors ($I > 2\sigma(I)$)	$R = 0.0844$, $wR = 0.2090$
S	0.991
$\Delta\rho_{min}/\Delta\rho_{max}$, *e* Å^{-3}	–1.744, 2.902

Table 2. Atomic coordinates and equivalent isotropic thermal parameters for $Rb_3[Co(CN)_6]$

Atom	*x*	*y*	*z*	U_{equiv}, Å^2
Rb(1)	0	0	0	0.0341(6)
Rb(2)	0.4998(2)	0.2339(11)	0.1257(16)	0.0383(5)
Co(1)	1.0	0	0.5	0.0217(7)
N(1)	0.7138(17)	–0.0849(9)	0.6762(13)	0.032(3)
N(2)	0.7082(17)	–0.0773(8)	0.1764(13)	0.0331(2)
N(3)	0.8090(19)	0.2573(7)	0.4542(16)	0.032(3)
C(1)	0.821(2)	–0.0528(10)	0.6098(15)	0.043(5)
C(2)	0.819(2)	–0.0481(9)	0.2987(15)	0.036(4)
C(3)	0.8840(2)	0.1628(12)	0.4736(16)	0.041(4)

Table 3. Selected bond lengths and angles in $Rb_3[Co(CN)_6]$

Bond	*d*, Å	Angle	ω, deg
Co(1)–C(1)	1.901(14)	C(1)Co(1)C(2)	90.4(6)
Co(1)–C(2)	1.898(13)	C(1)Co(1)C(3)	89.5(6)
Co(1)–C(3)	1.899(13)	C(2)Co(1)C(3)	89.0(5)
N(1)–C(1)	1.144(18)		
N(2)–C(2)	1.156(17)		
N(3)–C(3)	1.125(16)		



Projection of structure **I** along axis *x*.

ATOMS program [20]. Crystallographic data for structure **I** have been deposited with the Cambridge Crystallographic Data Collection (no. 676 311).

Crystallographic parameters of **I** and a summary of data collection are given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Selected bond lengths and angles are listed in Table 3.

RESULTS AND DISCUSSION

In crystal structure **I**, the Co(1) and Rb(1) atoms are in the centers of symmetry; the Rb(2) atom is in the general position. The cobalt atom is coordinated by six C atoms of six cyano groups forming a regular octahedron. The Co–C and C≡N distances agree with the literature data [21]. The terminal positions of all cyano groups are consistent with the IR spectroscopic data. The Rb(1) atoms are in the cavities of the octahedral structure; the Rb(2) atoms are in the cavities of the trigonal prisms, additional two atoms being somewhat more distant. The shortest Rb(2)–Co(1) distance is 4.734(3) Å. Structure **I** is similar to structure **II** (space group $P2_1/c$, a = 6.994, b = 10.367, c = 8.360 Å, β = 107.19°, Z = 2 [6, 7]); the higher value of the parameter a in structure **I** is due to the difference between the radii of the rubidium (1.49 Å) and potassium ions (1.33 Å).

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