

Barium Cobalt Trioxide

BY HIDEKI TAGUCHI, YASUO TAKEDA,* FUMIKAZU KANAMARU, MASAHIKO SHIMADA AND MITSUE KOIZUMI

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

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Abstract. BaCoO₃, hexagonal, *P6₃/mmc*, *a* = 5.645 (3), *c* = 4.752 (3) Å, *Z* = 2, *D_m* = 6.1, *D_x* = 6.18 g cm⁻³. The structure is characteristic with linear chains of face-sharing CoO₆ octahedra. BaCoO₃ can be regarded as a polyacid salt built up from chains of [CoO₃²⁻]_{*n*} groups held together by Ba²⁺ ions.

Introduction. The crystal used for structure determination was prepared at a high pressure (Shimada, Takeda, Taguchi, Kanamaru & Koizumi, 1975), and was about 0.1 × 0.1 × 0.3 mm. The Laue symmetry was found to be *6/mmm*. The systematic absences determined from precession and Weissenberg photographs were *hhl* for *l* = 2*n* + 1. Although three space groups (*P62c*, *P6₃mc* and *P6₃/mmc*) were possible, it was decided initially to refine the structure in the centrosymmetric *P6₃/mmc*.

All reflexions up to $\sin \theta/\lambda = 1.0$ were measured with Zr-filtered Mo *K*α radiation on a Rigaku automatic four-circle diffractometer, with a scintillation counter and a θ - 2θ scan technique. The intensities of symmetrically related reflexions were averaged to give 226 independent reflexion data. No absorption or extinction corrections were applied.

The three-dimensional Patterson map, which was calculated with *RSSFR-5* in the *UNICS* program system (Sakurai, 1967), indicated that the approximate positional parameters were 2(*a*) (0,0,0) for Co, 2(*d*) ($\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$) for Ba, and 6(*h*) (*x*, 2*x*, $\frac{1}{4}$) with *x* = $\frac{1}{8}$ for O in space group *P6₃/mmc*. A block-diagonal least-squares refinement was carried out with the program *HBL5-V* (Ashida, 1973). In the refinement procedure, neutral atomic form factors were taken from *International Tables for X-ray Crystallography* (1962). Weights were assigned according to the function $w = (\sigma^2 + a|F_o| +$

$b|F_o|^2)^{-1}$, where *a* = 0.0743 and *b* = 0.0060. Refinement was continued until the maximum shift of each parameter was less than one twentieth of its e.s.d. The final conventional *R* value was 0.060, while $R_w = \{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$ was 0.106. The final positional parameters are listed in Table 1.† In the absence of any stereochemical evidence to the contrary, *P6₃/mmc* is assumed to be correct.

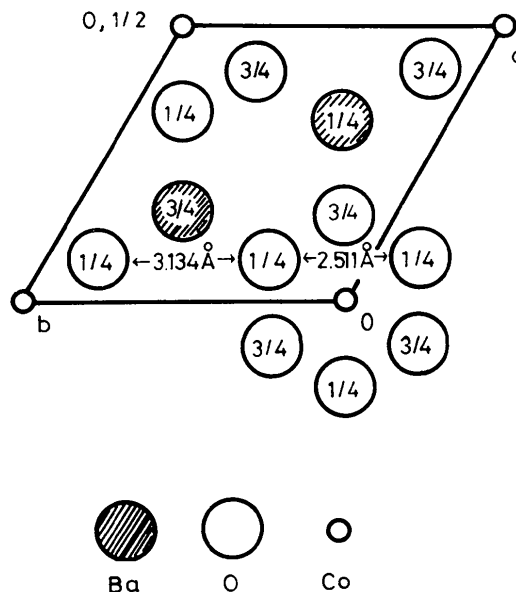
Discussion. BaCoO₃ powder was first synthesized by Gushee, Katz & Ward (1957). On the basis of powder work, they reported that BaCoO₃ was isostructural with BaNiO₃. The crystal structure of BaNiO₃ is described in terms of hexagonally close-packed BaO₃ layers and Ni ions located in the oxygen octahedra; these share a pair of opposite faces to form (NiO₃)_{*n*} columns parallel to *c*.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32396 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Present address: Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan.

Table 1. *Positional parameters*

	Position	<i>x</i>	<i>y</i>	<i>z</i>
Ba	2(<i>d</i>)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
Co	2(<i>a</i>)	0	0	0
O	6(<i>h</i>)	0.1482 (10)	-0.1482 (10)	0.25

Fig. 1. A representation of the crystal structure of BaCoO₃, viewed along *c*.

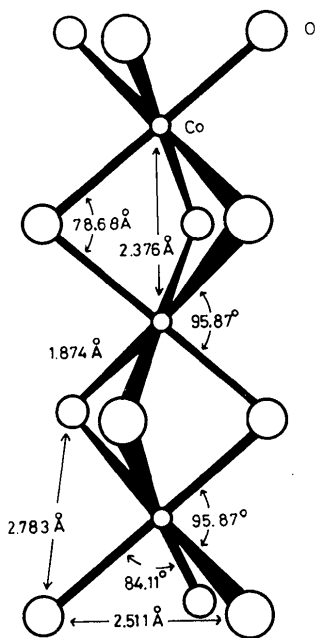


Fig. 2. A perspective view of the anionic chain in BaCoO₃.

However, BaNiO₃ does not have an ideal hexagonally close-packed arrangement of Ba and O ions, but all the O ions are remarkably close to Ni ions and form a trigonally distorted octahedron; the Ni⁴⁺-O distance is much shorter than that expected from the ideal ionic model (Takeda, Kanamaru, Shimada & Koizumi, 1976).

Figs. 1 and 2 show the Co environment and the hexagonal close packing of the Ba and O ions in BaCoO₃.

The structure was found to be isostructural with BaNiO₃, and the positional parameters are almost the same as those of BaNiO₃. Within the BaO₃ layers, the O-O distance is 2.511 Å, while the O-O distance between the layers is 2.783 Å. The Ba-O distance within the layer is 2.828 Å. Although these lengths must be equal for ideal hexagonal close packing of Ba and O, the O-O distance within the layer is much shorter than that between layers. These three oxygens forming short O-O distances make a triangular plane sharing the faces of the CoO₆ octahedra columns. The Co⁴⁺ ions in the columns face each other at a very short distance of 2.38 Å (2.41 Å in BaNiO₃); this will produce a large electrostatic repulsion between the metal ions. As the O atoms of face-sharing triangles mutually approach, as mentioned above, the O ions are considered to screen the Coulomb interaction between Co⁴⁺ ions and weaken the repulsion. The Ba²⁺ ions play a role in adjusting the spacing between these chains.

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Bis(3,5-dimethyl-1,2-dithiolium) Tetrachlorocobaltate(II)

BY GRAHAM A. HEATH, PETER MURRAY-RUST AND JUDITH MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

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Abstract. C₁₀H₁₄Cl₄CoS₄, *M_r* = 463.2, monoclinic, *C2/c*, *a* = 17.67 (2), *b* = 7.70 (1), *c* = 15.78 (2) Å, β = 122.22 (1)° from diffractometer measurements (Mo *K*α radiation); *V* = 1817.9 Å³, *Z* = 4, *F*(000) = 924, μ = 17.70 cm⁻¹. The compound is isostructural with the corresponding tetrachloroferrate(II) [Freeman, Milburn, Nockolds, Mason, Robertson & Rusholme, *Acta Cryst.* (1974), **B30**, 886-910].

Introduction. Blue-green crystals of the title compound (Heath, Martin & Stewart, 1969*a,b*)* suitable for X-ray examination were obtained from ethanolic HCl. Systematic absences (from Weissenberg and precession photographs) *hkl*, *h + k* odd and *h0l*, *l* odd indicated space groups *Cc* or *C2/c*. The latter was assumed since

* Hereafter HMS.