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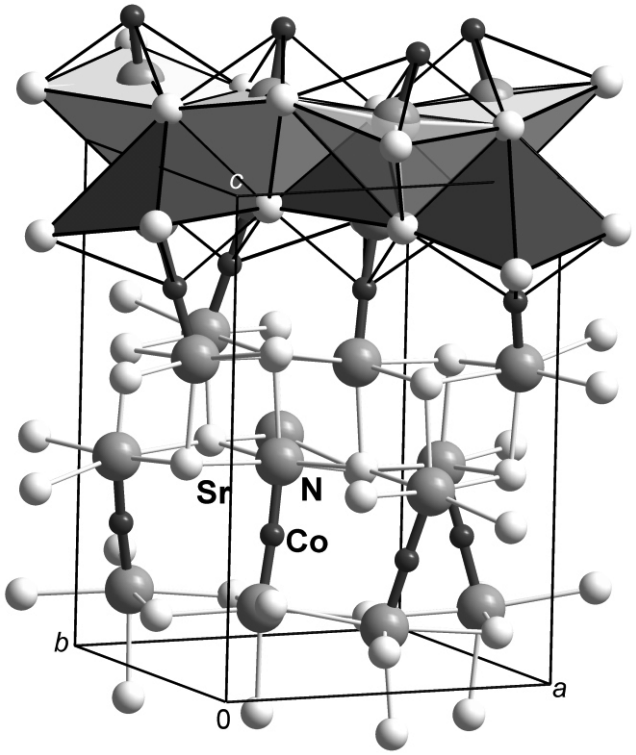
Crystal structure of pentastrontium bis(dinitridocobaltate(I)), $Sr_5[CoN_2]_2$, $Co_2N_4Sr_5$

Dedicated to Professor Hans-Jörg Deiseroth on the occasion of his 70th birthday

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Abstract

$Co_2N_4Sr_5$, tetragonal, *P*4/*ncc* (no. 130), a = 8.6730(5) Å, c = 12.443(1) Å, V = 936.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0293, $wR_{ref}(F^2)$ = 0.0684, T = 295 K.

Table 1. Data collection and handling.

Crystal:	grey prisms, size 0.13×0.19×0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	316.66 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 with Saturn724+ CCD, profile data from φ-scans
$2\theta_{max}$:	67°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10039, 902
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 816
$N(param)_{refined}$:	27
Programs:	SHELX, DIAMOND [10, 11]

Source of material

Strontium nitride, Sr_2N (prepared at 923 K from strontium metal, Alfa, 99.95%, and nitrogen, Praxair, 99.999%, additionally purified by molecular sieves) and Co powder (Chempur, 99.9%) were mixed in 5:4 molar ratio, intimately ground, pelletized and annealed at 1273 K for 50 h in a Ta crucible with a protective inlet made of Co foil to prevent side reactions with the crucible. After cooling down to room temperature at 10 K/h a dark grey powder was obtained, mainly consisting of the title compound according to powder diffraction data. Small prismatic single crystals were isolated for structure determination. All manipulations were carried out in an argon-filled glovebox due to high air- and moisture-sensitivity of both starting materials and final products.

Discussion

The title compound was first obtained by Bendyna [1] and assigned to the family of $AE_5[CoN_2]_2$ nitridocobaltates based on its X-ray powder pattern, isotypic to $Ca_4Ba[CuN_2]_2$ [2]. However, no structural characterization was conducted so far. Besides $AE_5[CoN_2]_2$, represented by $Ca_5[CoN_2]_2$ [3] and $Ca_4Ba[CoN_2]_2$ [4] phases, only a few nitridocobaltates are known up to now. In all these compounds Co atoms are twofold coordinated by N atoms, resulting in isolated $[Co^IN_2]^{5-}$ species [3–6] or extended $[Co^IN_{2/2}]_\infty^{2-}$ chains [7–8], respectively. The N atoms in the crystal structure of $Sr_5[CoN_2]_2$ form double layers of edge-sharing N-centered Sr_5 tetragonal pyramids running parallel (001). These layers are linked *via* common Co atoms, thereby completing the distorted octahedral environment of N. The resulting nearly linear $[Co^IN_2]^{5-}$ dumbbells (N–Co···N = 176.7(2)°) are tilted by 17.89(1)° with respect to [001]. Sr–N bond distances range from 2.563(3) Å to 2.818(4) Å. These values are in good agreement with literature data on Sr-containing nitrides [6, 8, 9]. The Co–N bond distance of 1.808(3) Å is in the typical range expected for nitridocobaltates [3–8].

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	16*g*	0.5501(4)	0.1406(4)	0.1118(3)	0.014(1)	0.010(1)	0.009(1)	–0.001(1)	–0.002(1)	0.000(1)
Sr(1)	4*c*	¼	¼	0.15352(6)	0.0107(2)	U_{11}	0.0151(3)	0	0	0
Sr(2)	16*g*	0.07635(4)	0.63269(4)	0.09827(3)	0.0090(2)	0.0078(2)	0.0088(2)	–0.0008(1)	0.0006(1)	0.0001(1)
Co(1)	8*f*	0.40890(6)	–*x*	¼	0.0096(2)	U_{11}	0.0076(3)	0.0017(2)	0.0000(2)	U_{13}

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