

A New Compound, Ca_3CoN_3 , with a Trigonal Planar $[\text{CoN}_3]^{6-}$ Anion

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A new compound, Ca_3CoN_3 , was prepared in a reaction of Ca_3N_2 and cobalt fine powder under a nitrogen stream at 1000°C . It has a monoclinic unit cell with $a = 6.308 \text{ \AA}$, $b = 5.137 \text{ \AA}$, $c = 5.933 \text{ \AA}$, and $\beta = 75.1^\circ$. It is not isostructural with other $A_3\text{MN}_3$ but has a closely related structure with a trigonal planar $[\text{MN}_3]^{6-}$ structural unit where A is an alkaline-earth metal and $M = \text{V}$, Cr , Fe . The Co^{3+} is assumed to be in a low spin d^6 state and to be coordinated by three nitrogen atoms accepting nitrogen's $2p$ electrons to their d^2s hybridized orbitals. Ca_3CoN_3 is nonmagnetic and semiconducting with a room temperature resistivity of $2.6 \times 10^2 \Omega \text{ cm}$ and with an activation energy of 0.02 eV . © 1995 Academic

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INTRODUCTION

Recently some kinds of double metal nitrides have been reported by combining the first row transition and alkaline-earth metals such as CaNiN (1), Ca_3VN_3 (2), Ca_3CrN_3 (3), SrNiN (4), Sr_3FeN_3 , Ba_3FeN_3 (5) and so on. Transition metals are coordinated with nitrogen atoms forming sheets with alkaline-earth metals interleaved with or included in the sheets. The coordination around the transition metal is either linear or trigonal planar in these alkaline-earth transition metal nitrides. The coordination manner seems to depend on the kind of transition metal. Nickel atoms are linearly coordinated by two nitrogen atoms, forming $[\text{NiN}_{2/2}]^{2-}$ chains in CaNiN and SrNiN . The chain is linear in CaNiN and zigzag in both SrNiN and BaNiN (6). The interchain alkaline-earth metals are always tetrahedrally coordinated with four nitrogen atoms in the neighboring $[\text{NiN}_{2/2}]^{2-}$ chains even if the chain shape is different, as mentioned in previous papers (1, 4, 6). The linear $[\text{MN}_{2/2}]^{2-}$ anion was also observed in Ca_2ZnN_2 (7). Early transition metals are surrounded by three nitrogen atoms, forming trigonal planar $[\text{MN}_3]^{6-}$ anions in Ca_3MN_3 ($M = \text{V}$, Cr) and A_3FeN_3 ($A = \text{Sr}$, Ba). Alkaline-earth ions link these $[\text{MN}_3]^{6-}$ anions, forming a

plane. The trigonal planar $[\text{MN}_3]^{6-}$ was also observed in Ca_6FeN_5 (8). The presence of double metal nitride has not yet been reported for cobalt. Cobalt is between iron and nickel in the $3d$ transition metal series in the periodic table. It is an open question whether the double metal nitride with cobalt has a linear chain anion with C_{2v} symmetry or a trigonal planar anion with D_{3h} symmetry.

In this paper, the presence of double metal nitrides with cobalt was investigated. The preparation, crystal structure, electrical properties, and magnetic properties of the new compound, Ca_3CoN_3 , are described.

EXPERIMENTAL

Calcium nitride Ca_3N_2 was prepared by nitridation of calcium metal as described in a previous paper (4). It was mixed with cobalt metal powder in the desired molar ratios. A small excess of calcium metal nitride was added to compensate for its loss with sublimation and with oxide formation during the reaction. The mixture was compressed into pellets and placed in stainless steel boats covered with the same compositional powder mixture to prevent CaO formation. Both the starting mixture and the product are sensitive to very small amounts of O_2 and H_2O remaining in the N_2 gas. The mixture was heated to 473 K under vacuum, reacted at 1273 K for 3 to 12 hr under a N_2 atmosphere, and then cooled to room temperature in 1 hr. The products were identified by a powder X-ray diffraction method using a diffractometer with $\text{CuK}\alpha$ radiation monochromatized with pyrolytic graphite. The sample loaded on a silica glass plate was set into a specially designed holder filled with pure argon gas to avoid air exposure during the measurements. Aluminum foil (0.007 mm thick) was used as its window.

Electrical resistivity was measured on the sintered pellet by a four-probe method in the temperature range from 10 to 300 K . Sample dimensions were $5 \times 15 \times 0.5 \text{ mm}$. Silver electrodes worked in ohmic contact. A constant dc current of 0.1 to 10 mA was applied during the measurement. The sample holder was sealed in an argon-filled metal holder, and the measurements were performed through the lead wire.

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TABLE 1
X-Ray Powder Diffraction Data of $\text{Ca}_3\text{CoN}_3^a$

$h k l$	d_{calc}	d_{obs}	I/I_0	$h k l$	d_{calc}	d_{obs}	I/I_0
1 0 0	6.096	6.037	6	0 0 6	2.011	2.017	20
0 0 1	5.734	5.683	18	2 2 1	1.960	1.951	8
1 0 1	4.844	4.833	12	3 0 2	1.904	1.900	14
1 1 0	3.928	4.026	15	0 1 3	1.792	1.802	14
1 1 1	3.524	3.453	15	3 1 2	1.786	1.782	10
2 0 0	3.048	3.093	16	2 1 -2	1.751	1.757	15
1 1 -1	3.016	3.025	7	0 3 0	1.712	1.711	5
0 0 2	2.867	2.851	8	3 2 0	1.593	1.583	7
		2.789	5	1 3 -1	1.556	1.559	6
2 1 0	2.621	2.697	100	2 0 4	1.448	1.447	5
0 2 0	2.568	2.547	54	3 1 -2	1.428	1.426	10
1 1 2	2.523	2.488	21	2 1 -3	1.401	1.405	9
2 0 2	2.422	2.422	11	1 3 -2	1.388	1.384	6
0 2 1	3.344	2.348	3	4 2 1	1.344	1.344	4
3 0 1	2.092			2 3 -2	1.267	1.261	6
3 0 0	2.032	2.040	6				

^a Monoclinic unit cell parameters: $a = 6.308$ (17) Å, $b = 5.137$ (9) Å, $c = 5.933$ (22) Å, and $\beta = 75.1$ (2)°.

Magnetic susceptibility was measured using a Faraday balance in the temperature range from 70 to 300 K in a field of 1 kOe. The susceptibility was also measured as a function of an applied field up to 14 kOe at room temperature. Powder samples were sealed in an evacuated silica glass capsule and loaded into the silica glass holder. Diamagnetic contributions of both the silica glass capsule and holder were corrected.

RESULTS AND DISCUSSION

The reaction of Ca_3N_2 with Ni and Co metals did not show the presence of a CaNiN -type solid solution. Cobalt nitride seems not to form an isostructural compound with CaNiN . The product without Ni was a mixture of an unknown compound with Co metal when the molar ratio of Ca/Co was 1. The relative amount of the unknown compound increased with an increasing Ca/Co ratio in the starting mixture. The simplest powder X-ray diffraction pattern without Co metal was obtained at a Ca/Co ratio of 3. The powder X-ray diffraction pattern could be indexed with a monoclinic cell with $a = 6.308$ Å, $b = 5.137$ Å, $c = 5.933$ Å, and $\beta = 75.1^\circ$, as depicted in Table 1. There seems to be no systematic extinction. Possible space groups are Pm , $P2$, or $P2/m$. The diffraction pattern could also be indexed with an orthorhombic cell having $a = 5.48$ Å, $b = 4.79$ Å, and $c = 12.06$ Å.

Several kinds of alkaline-earth transition metal nitrides A_3MN_3 have been reported, as mentioned above. They have trigonal planar $[\text{MN}_3]^{6-}$ anions which are isostructural to a carbonate ion belonging to D_{3h} . The anions are linked together with alkaline-earth ions, forming a sheet.

The manner of $[\text{MN}_3]^{6-}$ anion packing in a sheet is classified into two groups based on the size of the alkaline-earth ions. The present product, Ca_3CoN_3 , was not exactly isostructural with the previously found A_3MN_3 . However, some of the characteristic diffraction lines to A_3MN_3 were observed in the diffraction pattern and can be indexed with a monoclinic cell. The monoclinic lattice size can be related to those of other A_3MN_3 compounds as described elsewhere (9). Ca_3CoN_3 may also have a structure derived from the hcp packing of $[\text{CoN}_3]^{6-}$. Nitrogen content was estimated to be $\text{Ca}_3\text{CoN}_{2.89}$, with a Perkin-Elmer 240C by a modified Dumas method (10) where the sample was burned in the presence of CuO in order to take out its nitrogen as N_2 .

Electrically, polycrystalline Ca_3CoN_3 was semiconductive. The resistivity was $\rho = 2.55 \times 10^2 \Omega \text{ cm}$ at room temperature and its activation energy was 0.02 eV. The electrical resistivity at room temperature is much smaller than the reported values of $1.6 \times 10^7 \Omega \text{ cm}$ for Ca_3CrN_3 (3) and $2.4 \times 10^4 \Omega \text{ cm}$ for Ca_3VN_3 (2). The semiconductivity contrasts with the metallic nature of CaNiN , which has infinite linear $[\text{NiN}_{2/2}]^{2-}$ chains (1). The Co—Co distances were expected to be 6.308 and 5.933 Å within and across the Ca_3CoN_3 layer, respectively. These distances are much longer than the distance for metal—metal direct bonding in Co metal (2.5 Å). $[\text{CoN}_3]^{6-}$ units are linked together with Ca^{2+} cations. Ca_3CoN_3 is an insulator because $[\text{CoN}_3]^{6-}$ ions are separated from each other by Ca^{2+} cations.

The magnetic susceptibility was measured as a function of an applied field. The ferromagnetic impurity contribution was subtracted using the von Bernus method (11). The amount of Co impurity was estimated to be up to 1 wt%. The corrected susceptibility was $5.3 \times 10^{-5} \text{ emu/g}$ at 300 K. It was almost temperature independent. Assuming the alkaline-earth element to be divalent, the trigonal planar ion is formally $[\text{CoN}_3]^{6-}$. The trigonal coordination can be attained in a d^2s electron configuration around Co^{3+} . The temperature-independent magnetism is evidence that the Co^{3+} has six 3d electrons in a low-spin state. The relatively large susceptibility on the order of 10^{-6} emu/g may indicate that the ferromagnetic impurity contribution has not yet been completely removed.

Assuming the alkaline-earth element to be a divalent cation, the trigonal planar anion is formally written as $[\text{MN}_3]^{6-}$. The transition metals are coordinated with three nitrogen atoms in D_{3h} symmetry. Co^{3+} with d^6 is in a low-spin state. These electrons are accommodated in the nonbonding d_{z^2} , d_{xz} , and d_{yz} orbitals if the direction perpendicular to the plane is taken as the z direction. Two empty d orbitals, $d_{x^2-y^2}$ and d_{xy} , hybridize with a 4s orbital to form a trigonal planar coordination around the transition metal. Each d^2s hybridized orbital accepts two electrons from the ligand nitride ion, as illustrated in Fig. 1, forming

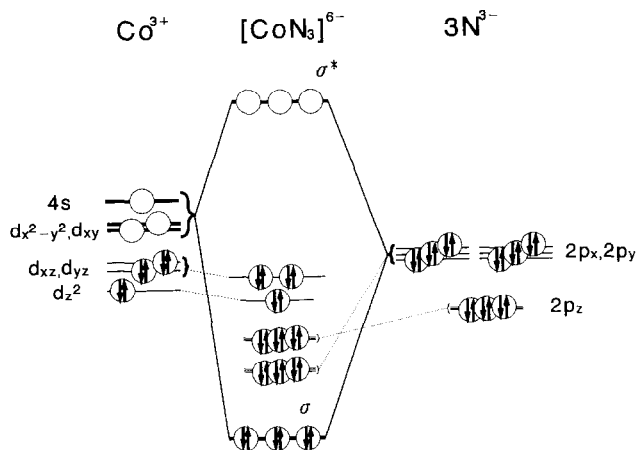


FIG. 1. Schematic representation of energy levels for the trigonal planar $[\text{CoN}_3]^{6-}$ anion.

a covalent bond. Early 3d transition metals up to cobalt can have trigonal planar coordination because the three nonbonding orbitals can accommodate 3d electrons of trivalent ions up to six.

Simple nitride of Fe, Co, Ni, and so on easily decompose, releasing their nitrogen above 500°C. It has been difficult to obtain their nitrogen-rich nitrides, due to the low decomposition temperature. However, the transition metal nitrides containing alkaline-earth metal were prepared in a temperature range between 800 and 1000°C. They have a strong covalent bond between the transition metal and the nitrogen as well as an ionic bond between the alkaline-earth metal and the nitrogen.

In conclusion, a new double metal nitride, Ca_3CoN_3 , was prepared in a reaction between Ca_3N_2 and Co metal under a nitrogen atmosphere. It has a monoclinic cell with lattice parameters of $a = 6.308 \text{ \AA}$, $b = 5.137 \text{ \AA}$, $c = 5.933 \text{ \AA}$, and $\beta = 75.1^\circ$. It was not isostructural with but was expected to have a structure closely related to that of the

other known Ca_3MN_3 ($M = \text{V}, \text{Cr}$). The structure was expected to be composed of trigonal planar $[\text{CoN}_3]^{6-}$ anions with D_{3h} symmetry linked by Ca^{2+} cations, forming Ca_3CoN_3 sheets stacked along the c direction. The compound was a semiconductor with an activation energy of 0.02 eV, and was nonmagnetic, with a low-spin d^6 configuration. Nitrogen atoms are assumed to be covalently bonded with the cobalt, donating their 2p electrons to the hybridized d^2s cobalt orbitals.

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