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Synthesis, Structure, and Properties of a new Ternary Metal Nirtide, Ca_3CrN_3

by

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Synthesis, Structure, and Properties of a New Ternary Metal Nitride, Ca_3CrN_3

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Abstract

We have synthesized a new ternary nitride, Ca_3CrN_3, from the binary nitrides at high temperature. The refined structure was solved in the Cmcm space group with lattice constants a=8.503(2), b=10.284(2), c=5.032(1), and R=3.9%, R_W=3.9%. This new structure type consists of sheets of $[CrN_3]^{6-}$ planar triangular units and calcium ions. Ca_3CrN_3 is insulating and paramagnetic with Cr^{3+} in the low spin state. This is the first unambiguous example of low spin Cr^{3+}. Larger than expected antiferromagnetic interactions produce a maximum in the magnetic susceptibility at 245K, eventhough the shortest Cr-Cr distance is 4.73Å.

Introduction

Although the chemistry of binary nitrides has been explored in detail, comparatively little work on ternary and quaternary nitrides has been reported. Preliminary work has shown that in addition to the facile formation and stability of ternary nitrides containing electropositive elements, these phases exhibit a variety of novel properties. Examples include the Ni d^9 configuration in CaNiN,[1] the layered structures of $MTaN_2$[2] (M=alkali metal), and the unique structure types found in $Ca_{21}Fe_3N_{17}$,[3] Li_3AlN_2,[4] and CaGaN[5]. These few results suggest that ternary nitrides will display an extensive assortment of new compounds and structure types. We therefore undertook a large scale investigation of alkaline earth and transition metal-containing nitrides.

Herein, we report a new compound and structure type, Ca_3CrN_3, discovered initially as an impurity phase in reactions of Ca_3N_2 in stainless steel containers.

Experimental Section

Starting Materials. Chromium nitride was prepared by heating Cr powder (-100mesh, 3N) in flowing nitrogen (prepurified by passing through finely divided copper at 150°C, and then activated alumina) at 800°C for 1 day. The product was ground and reheated several times, yielding a mixture of CrN and Cr_2N (approximately 50:50). Granules of calcium (2N) were reacted at 1000°C for 3 days in flowing nitrogen (prepurified as above) to yield pure Ca_3N_2. The binary products were identified by x-ray powder diffraction methods. Since both Ca_3N_2 and Ca_3CrN_3 are air sensitive, all manipulations were carried out in an argon filled glove box.

Synthesis of Ca_3CrN_3. The title compound was first discovered as a minority crystalline phase in a reaction of Ca_3N_2 and tin in a stainless steel tube. The bulk phase consisted of a grey powder, Ca_3SnN,[6] with a minority phase consisting of needle crystals distributed throughout. Microprobe analysis of the crystals indicated the presence of chromium (a component in the stainless steel) at a molar ratio Ca:Cr of 3:1.

The compound was then prepared as a majority phase by heating 0.2048g of the CrN/Cr_2N mixture (1.11 mmol of the hypothetical Cr_3N_2) and 0.6011g of Ca_3N_2 (4.06 mmol) in a sealed stainless steel tube under an argon atmosphere at 1350°C for 4 days, followed by cooling to 1050°C in 5h, and finally cooling to room temperature in 12h. There was no evidence of Ca_3N_2 remaining in the product mixture; however, the brittle nature of the once maleable tube indicated that the excess Ca_3N_2 was consumed by a reaction with the stainless steel. The product contained air-sensitive, burgandy-colored needle crystals up to 1mm in length, which were used for the structure determination. X-ray powder diffraction indicated a nearly pure Ca_3CrN_3 powder with a small unidentified impurity phase. The intensity of the strongest impurity diffraction peak was 6% as intense as the strongest peak of the majority phase.

The material used for susceptibility measurements was prepared by heating a pressed pellet of an intimate mixture of 0.3103g of CrN/Cr_2N (1.69 mmol of Cr_3N_2) and 0.5070g of Ca_3N_2 (3.43 mmol) powders in a sealed molybdenum crucible under argon at the heating schedule mentioned above. The only impurity observable in the product by powder x-ray diffraction was Cr metal. The most intense Cr peak was only 6% as intense as the strongest Ca_3CrN_3 peak. Since the lower symmetry of Ca_3CrN_3 splits the x-ray lines into many components, the impurity level of Cr was estimated to be less than 3 wt%. A larger percentage of Cr from the reaction mixture should have remained in the product; most of it must alloyed with the molybdenum crucible, as it is not observed in the product.

Magnetic Susceptibility. The magnetic susceptibility of the sample was measured by the Faraday technique in a previously calibrated system.[7] The susceptibility of a sample sealed in a thin-walled quartz tube was determined to be field independent at room temperature, showing that no ferromagnetic impurities were present. Figure 1 shows the results of a temperature dependent study between 30K and 750K at a magnetic field strength of 14.2 kG.

Fig. 1 (Magnetic Susceptibility Data)

The contribution of the <3 wt% Cr impurity to the observed peak in the susceptibility is negligible, since its gram susceptibility is approximately 3×10^{-6} emu/g and weakly temperature dependent, increasing by only 10% from 0K to 800K.[8]

Electrical Properties. The resistance of a pellet of

Ca_3CrN_3 was measured in a small press inside the glove box. The two pistons were electrically insulated from each other, allowing a two point measurement of the resistance. The resistance determined on a pellet 4.5mm in diameter and approximately 3mm thick was 45 kohm.

Structure Determination. Unit cell symmetry and approximate lattice constants were obtained from Weissenberg photographs of a crystal mounted along the needle axis. A 0.03 x 0.04 x 0.13 mm^3 crystal, sealed in a glass capillary under argon, was used in the structure determination. Data were collected on a Syntex $P2_1$ diffractometer using Mo K-α radiation and a graphite monochrometer. The choice of space groups was reduced to Cmcm, $Cmc2_1$, and C2cm by systematic absences, and the structure was solved using direct methods in the Cmcm space group. Refinement in either noncentrosymmetric space group resulted in no significant change in the structure or R factors. An empirical absorption correction (the psi scan method) was performed, and two octants of data were collected and merged to improve the data set. The largest peak in the final difference fourier map was 0.86 electrons. Final R=3.9% and R_w=3.9% were obtained after refinement. The structure determination and refinement were performed using Nicolet SHELXTL Plus software running on a Microvax computer. Table I summarizes data collection parameters. Atomic positions are listed in Table II.

Table I (Data Collection)

Table II (Atomic Positions)

After solving the structure, the powder patterns taken on a Scintag XDS2000 diffractometer could be indexed. The observed patterns matched that calculated by Lazy Pulverix[9] based on the single crystal data.

Results and Discussion

The structure of Ca_3CrN_3 (Fig. 2) consists of triangular $[CrN_3]^{6-}$ units with C_{2v} point symmetry separated by calcium atoms (the C_{2v} axis is parallel to the b-axis). A view down the a-axis clearly shows the sheet structure of the planar groups and the intervening Ca atoms. In each sheet the triangular units are pointing in the same direction.

Fig. 2 (View down a-axis)

Neighboring sheets are displaced by 1/2 in z and the orientation of the triangles is reversed.

Fig. 3 (View down c-axis)

A list of relevant bond distances and angles can be found in Table III.

Table III (Bond Distances and Angles)

Although the triangular planar coordination of a transition metal by nitrogen has been observed in molecular solids,[10,11] this is the first example of such coordination in the solid state. The coordination geometry around the nitrogens is a distorted octahedron, consisting of four "equatorial" Ca's, one "axial" Ca, and one "axial" Cr. The bond lengths about the unique N (N1c in Fig. 2) are 2x2.522Å, 2x2.419Å, and 2.388Å to Ca and 1.864Å to Cr. The two equivalent nitrogens (N1a and N1b in

Fig. 2) have similar bond lengths, but the octahedral angles are considerably distorted from 90°, and the Cr-N bond lengths are compressed to 1.766Å. There are very few compounds with Cr-N bonds with which to compare distances. The Cr-N bond lengths in molecular solids range from a Cr-N formal triple bond (1.57Å)[12] to apparent single bonds in the range 2.04Å to 2.25Å[13-19]. In the solid state, Cr-N bond lengths average considerably larger (2.06Å to 2.93Å).[20-22] The Cr-N distances in the $[CrN_3]^{6-}$ unit indicate multiple metal to nitrogen bonding in comparison to the average Cr-N single bond distances in molecular solids. The closest Ca-Ca distance between the planar units (3.36Å) is slightly longer than in Ca_3N_2 (3.16Å)[23]. However, the closest Ca-N distances (2.38Å, 2.54Å) are similar to those in Ca_3N_2 (2.46Å)[23], Ca_3BiN (2.45Å)[6], and CaNiN (2.50Å)[1].

The Cr-Cr distances are much too long for any metal-metal bonding or significant direct exchange interactions. The shortest distance, 4.73Å, is between Cr in adjacent sheets (Cr1 or Cr2 to Cr3 in the unit cell below the one shown in Fig. 2). The next closest distances are 5.03Å (Cr1 to Cr2, across two sheets) and 5.06Å (Cr3 to Cr4 in Fig. 2).

These long Cr-Cr distances suggest a very small exchange interaction between paramagnetic Cr^{3+} ions. Consequently, we expected the susceptibility to follow a simple Curie-Weiss law, where the susceptibility is equal to $C/(T+\theta)$ and θ is expected to be less than 10K. We ignore the small temperature independent term expected in the susceptibility, since it is a sum of a small diamagnetic term (the core diamagnetism, between -0.2×10^{-6} and -0.33×10^{-6} emu/g[24], depending upon the poorly established value of the core diamagnetism for N in solids) and a small paramagnetic term (the van Vleck paramagnetism, which is unknown). The fact that the susceptibility does not follow the simple Curie-Weiss law (at least below approximately 400K) suggests that strong antiferromagnetic superexchange interactions must follow paths such as Cr-N···N-Cr or Cr-N-Ca-N-Cr. The lack of a sharp break in the susceptibility implies that three-dimensional long range order of the Cr spins does not occur above 30K. The broad peak in the susceptibility therefore suggests moderately strong antiferromagnetic interactions in only one or two dimensions.[25] Since the optimal exchange pathways are not obvious, it is not possible to be certain about the dimensionality of the exchange interactions. However, if the dominant exchange is between closest neighbor Cr atoms, then the exchange pathway forms a zig-zag chain parallel to the c-axis. The next closest Cr-Cr distances are only 0.3Å longer; consequently, our assignment of the optimal exchange path may not be correct.

In principle, the magnetic susceptibility can be used to determine the spin of the Cr. Since the Cr site symmetry is so low, none of the Cr d states are degenerate. Depending upon their relative splittings, the Cr^{3+} could be high spin (S=3/2) or low spin (S=1/2). If the exchange is Heisenberg-like and one-dimensional, the product of the molar susceptibility at the maximum and the temperature of the maximum is a function only of the spin.[25] The maximum molar susceptibility is 6.85×10^{-4} emu/mol and the temperature at the maximum is 240K. The product, 0.164 emu·K/mol, is close to that expected for S=1/2 (0.141 emu·K/mol), but much smaller than that expected for S=3/2 (0.648 emu·K/mol).[25] Since the experimental value is not exactly equal to the theoretical number for S=1/2, other exchange pathways may also be important.

At very high temperatures the effective moment per Cr theoretically must extrapolate to the free ion value. At the highest temperature of measurement we obtain $1.86\mu_B$, somewhat above the expected infinite temperature spin 1/2 value of $1.73\mu_B$ but considerably below the spin 3/2 value of $3.87\mu_B$. The source of the small discrepancy is not clear, but could be caused by a van Vleck susceptibility that is larger than the core diamagnetism or by a small thermal population of the excited spin 3/2 state. In any case, the spin state of Cr^{3+} in this compound is clearly low spin S=1/2.

The exchange energy, J, is also obtainable from the temperature of the maximum.[25] We obtain $J=185 \pm 5K$. It is surprising to us that such a large exchange can occur between paramagnetic centers almost 5Å apart. This is likely due to a large covalent contribution to the bonding and overlaps from one Cr to the next, although we did not expect the exchange to be so large, as previously discussed.

To our knowledge this is the first unambiguous example of a doped silicates suggests that chromium occupies both octahedral and tetrahedral sites and that the tetrahedrally coordinated Cr^{3+} is low spin, but we could find no references to a concentrated chromium compound that contained such low spin species.

To summarize, the new phase, Ca_3CrN_3 has been prepared by reaction of the binary nitrides at high temperature. The compound represents a new structure type, consisting of triangular planar $[CrN_3]^{6-}$ units separated by calcium atoms. It is a paramagnetic insulator with low spin Cr^{3+}, and low-dimensional antiferromagnetic interactions.

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Supplementary Material

Tables of observed and calculated structure factors (2 pages); table of refined anisotropic thermal parameters (1 page) are available for Ca_3CrN_3. Ordering information is given on any current masthead page.

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Table I. Summary of Crystal and Diffraction Data for Ca_3CrN_3

space group	Cmcm (No.63)
Z	4
a, b, c (Å)	8.503(2), 10.284(2), 5.032(1)
V ($Å^3$)	440
crystal dimmensions (mm)	0.03 x 0.04 x 0.13
2θ max (deg), scan type	55, w-2θ
octants measured	±h,k,l
x-ray radiation	Mo k-α
monochrometer	graphite
measured reflections	577
observed reflections[a]	303
independent reflections	263
abs coefficient, μ (mm^{-1})	5.79
R^b, $R_w{}^c$ (%)	3.9, 3.9

[a] $F_o{}^2 > 3s(F_o{}^2)$

[b] $R = S(|F_o| - |F_c|)/S(|F_o|)$

[c] $R_w = [S(w(|F_o| - |F_c|)^2)/S(w|F_o|^2)]^{1/2}$, $w = s(F_o)^{-2}$

Table II. Positional Parameters for Ca_3CrN_3

Atom	Site	x	y	z
Ca	4c	0	0.1079(2)	0.25
Ca	8g	0.2843(2)	-0.1174(1)	0.25
Cr	4c	0.5	0.1945(2)	0.25
N	4c	0.5	0.3757(8)	0.25
N	8g	0.6918(8)	0.1286(6)	0.25

Table III. Important Distances (Å) and Angles (deg) in Ca_3CrN_3

Nonbonding Interactions	
Cr(1)····Cr(2)	5.032(1)
Cr(1)····Cr(3)	4.726(1)*
Cr(1)····Ca(1a)	3.234(2)
Cr(1)····Ca(1b)	3.234(2)
Cr(1)····Ca(3a)	3.213(1)*
Cr(4)····Ca(2a)	3.695(2)
Ca(1b)····Ca(3b)	3.355(3)
Ca(1b)····Ca(4b)	3.349(2)
Ca(2b)····Ca(2c)	3.368(3)
Ca(2b)····Ca(3a)	3.491(1)*
Ca(2a)····Ca(2c)	3.668(4)
Ca(2a)····Ca(3a)	3.757(2)
Ca(2a)····Ca(4b)	3.487(2)

Bonding Interactions	
Cr(1)-N(1b)	1.766(7)
Cr(1)-N(1a)	1.766(7)
Cr(1)-N(1c)	1.864(8)
Ca(1a)-N(1c)	2.522(1)
Ca(1b)-N(1c)	2.522(1)
Ca(2a)-N(1c)	2.419(2)
Ca(2a)-N(1b)	2.728(6)
Ca(2b)-N(1b)	2.629(7)
Ca(3b)-N(1c)	2.388(8)
Ca(4a)-N(2a)	2.538(6)

Bond Angles	
N(1a) - Cr(1) - N(1c)	112.6(2)
N(1b) - Cr(1) - N(1c)	112.6(2)
N(1b) - Cr(1) - N(1a)	134.9(4)

*Distance indicated is from an atom in the unit cell shown to an atom in an adjacent unit cell, respectively.

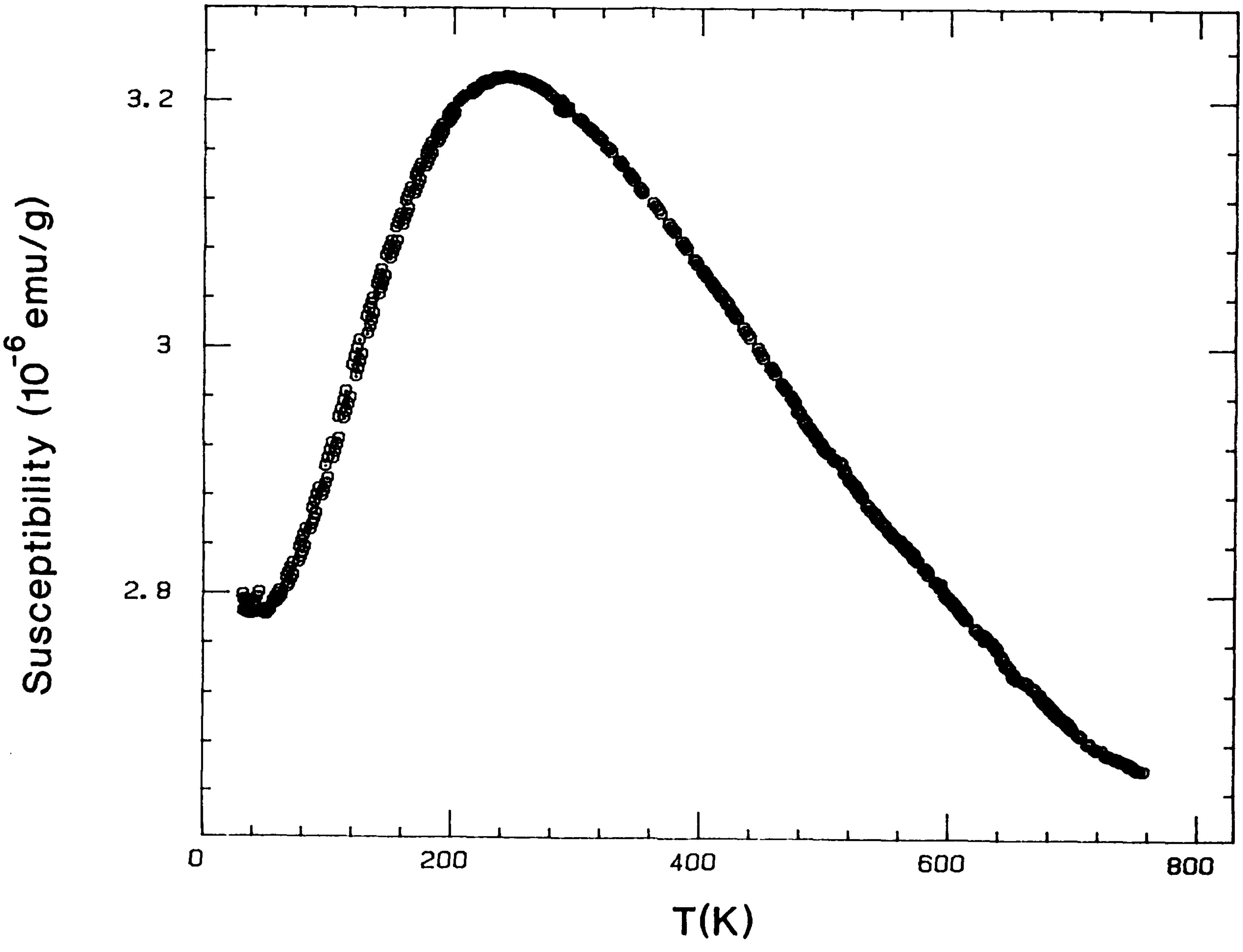
Figure Captions

Figure 1. Temperature dependence of the magnetic susceptibility of Ca_3CrN_3.

Figure 2. A view of Ca_3CrN_3 down the c-axis shows one unit cell, and indicates the labels used to identify the atoms in Table III.

Figure 3. A view of the structure down the a-axis. The Ca atoms are open circles, Cr atoms are dotted circles, and N atoms are partially hatched circles.

Fig 1



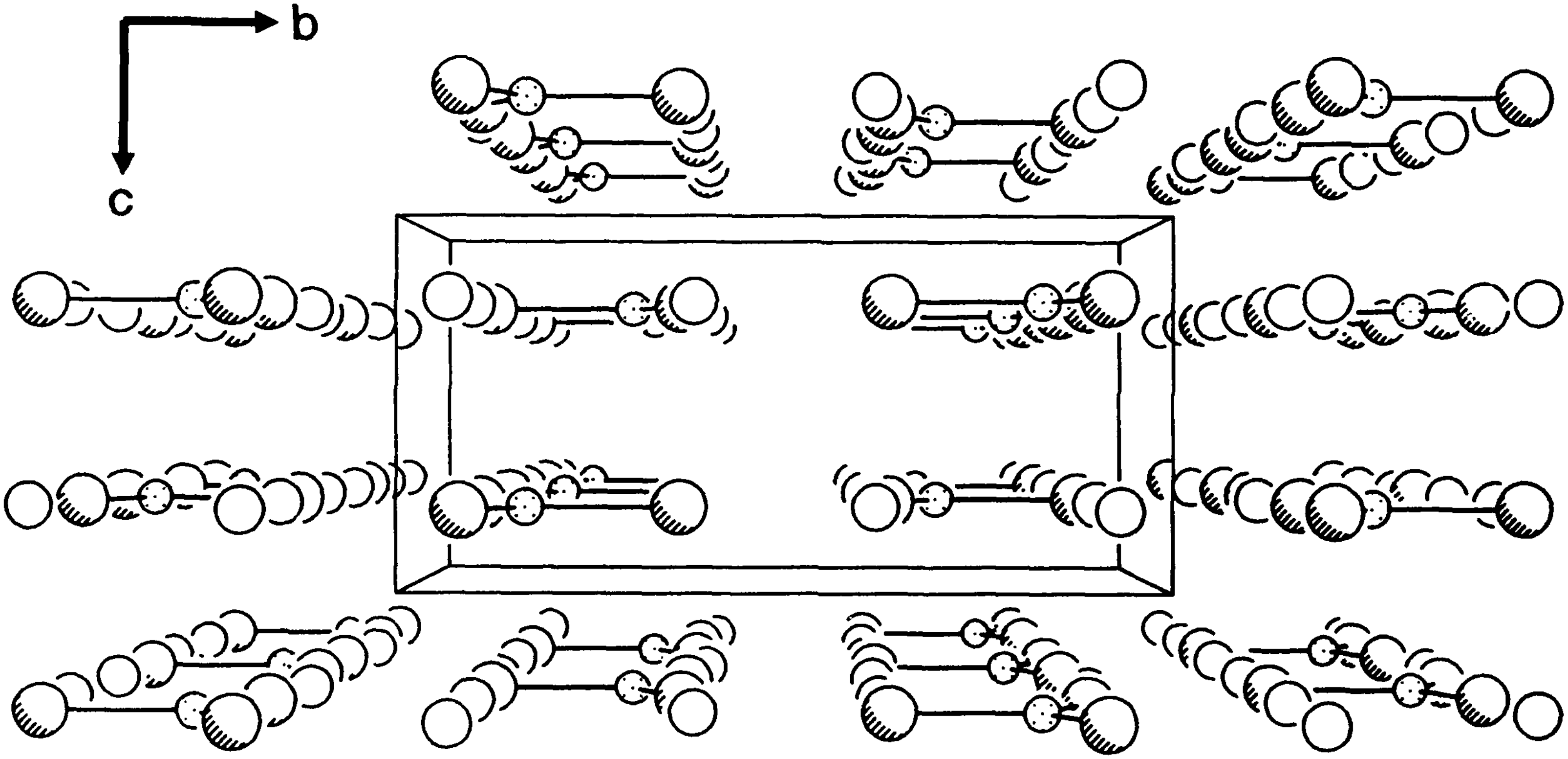
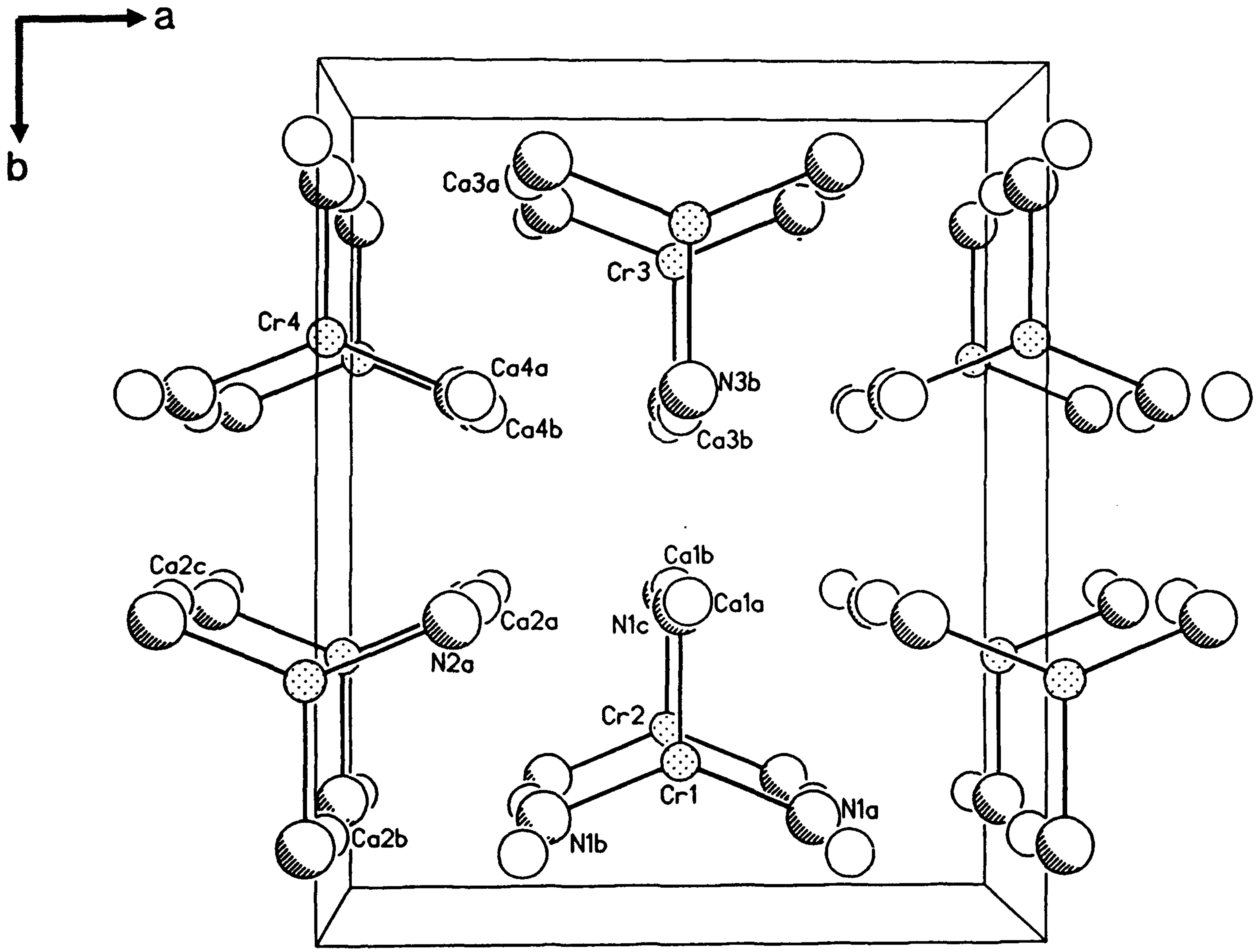

b
c

Fig 3


a
b
Ca3a
Cr3
Cr4
Ca4a
Ca4b
N3b
Ca3b
Ca1b
Ca2c
Ca1a
N1c
Ca2a
N2a
Cr2
Cr1
N1a
N1b
Ca2b