

0.1 Å above the base is calculated. This is probably very approximate, owing to the oversimplification of the ring current as a single loop. Deviations from this simple model would have the greatest effect on atoms very close to the current loop such as the boron atoms. As one moves further away from the loop, such deviations are expected to be more negligible. Also, it is quite optimistic to hope that ring-current contributions are the only major factors when considering boron atoms in several different bonding environments.

(2) A crude assumption is to project the electron cloud bonding the apex to the base along the curved surface area of the cone and to use the ring which bisects this surface area. This approach is based on nearly equal sharing of the bond electrons. This places the ring current at 0.33 Å above the basal plane.

(3) Considering that the apical boron has about a net +0.35 charge, the ring current may well be closer to the base than the 0.33 Å derived in (2) above.

From the above considerations, it is not surprising to find that the best $\Delta\tau$ fit for all compounds places the ring height at about 0.2 Å above the base. Not only does this approach account for the chemical shift difference for the apical and basal boron-attached methyl hydrogens, but it also correlates the relative magnitude of $\Delta\tau$ for the boron-bonded hydrogens in the parent compound and for the 2,3-dimethyl derivative reasonably well (Table III). There is some indication that this approach may work for other structurally related systems. A per-B-ethyl derivative of CB_5H_9 (iso-electronic and presumed isostructural with $\text{C}_2\text{B}_4\text{H}_8$)

has been recently reported.¹³ A comparison of $\Delta\tau$ (apex, base) values for methylene and methyl hydrogens gives $\Delta\tau_{\text{CH}_2} \sim 1.2$ and $\Delta\tau_{\text{CH}_3} \sim 0.54$ ppm. Since $\Delta\tau$ values of the α hydrogens are nearly identical for both $\text{C}_2\text{B}_4\text{H}_8$ and CB_5H_9 alkyl derivatives (~ 1.2 ppm), it should be possible to correlate β hydrogens for the ethyl derivatives of the two systems if nearly identical ring-current contributions are operating. A calculated value for the β hydrogens for the B-ethyl derivative of $\text{C}_2\text{B}_4\text{H}_8$ based on a ring-current contribution gives 0.57 ppm for $\Delta\tau_{\text{CH}_3}$. This is in quite good agreement with the value (*vide supra*) found for the CB_5H_9 derivative.

Also, for B_6H_{10} a calculated $\Delta\tau$ of 4.8 ppm agrees quite well with the observed $\Delta\tau$ 5.0 ppm¹⁴ for the terminal hydrogens. The structural parameters of B_6H_{10} are taken from previous X-ray data.¹⁵ Since the most recent charge distribution estimates give the apex boron close to zero charge,¹⁶ the ring loop current is positioned so that it bisects the nearly conical surface between the apex and basal plane.

Acknowledgments.—The authors wish to express their gratitude to the Office of Naval Research for financial support of this research. They also thank Professors M. F. Hawthorne and A. Burg for generous use of a 32-Mc ^{11}B nmr spectrometer.

(13) M. A. Grassberger, E. G. Hoffmann, G. Schomburg, and R. Köster, *J. Am. Chem. Soc.*, **90**, 56 (1968).

(14) Observed value taken from a ^{11}B -decoupled proton spectrum: J. Spielman, unpublished results.

(15) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).

(16) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 110.

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The Crystal Structure of Dicalcium Nitride

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The structure of a nitride of the stoichiometry Ca_2N has been determined from single-crystal X-ray data. Dicalcium nitride is rhombohedral with unit-cell dimensions $a = 6.603$ Å, $\alpha = 31^\circ 59'$, $D_m = 2.17$ g cm $^{-3}$, $Z = 1$, $D_o = 2.18$ g cm $^{-3}$, the space group being $R\bar{3}m$. Full-matrix least-squares refinement has reached $R = 0.13$ for 71 visually estimated reflections. Ca_2N has a layer structure of the *anti*- CdCl_2 type. The layers are widely separated, their closest approach being a Ca-Ca distance of 4.35 Å, much larger than those in the metal. The nitrogen atoms lie at centers of symmetry, within the layers, and have distorted octahedral coordination. The electrical properties of Ca_2N are discussed in relationship to the structure and with reference to other M_2X compounds.

In a preliminary communication,¹ we reported the crystal structure of a novel subnitride, Ca_2N , first prepared by Ahmad and Tomlinson.² The analogous compounds of strontium, Sr_2N , and barium, Ba_2N , had been known previously.³

(1) E. T. Keve and A. C. Skapski, *Chem. Commun.*, 829 (1966).

(2) I. Ahmad, Ph.D. Thesis, London, 1963; I. Ahmad and J. W. Tomlinson, to be submitted for publication.

(3) S. M. Arya and E. A. Prokofyeva, *J. Gen. Chem. USSR*, **25**, 813 (1955).

The more usual nitride of calcium is Ca_3N_2 , four forms of which have been reported. Below 350°, black β - Ca_3N_2 is formed, which is pseudo-hexagonal.⁴ α - Ca_3N_2 is prepared at temperatures up to 1050°. It has a bcc lattice with $a = 11.40$ Å and has an *anti*- Mn_2O_3 structure.⁵ Yellow γ - Ca_3N_2 is formed above 1050°.^{4,6} A

(4) Y. Laurent, J. David, and J. Lang, *Compt. Rend.*, **259**, 1132 (1964).

(5) M. von Stackelberg and R. Paulus, *Z. Physik. Chem.*, **B22**, 305 (1933).

(6) Y. Laurent, J. Lang, and M. Th. Le Bihan, *Acta Cryst.*, **B24**, 494 (1968).

high-pressure form is produced at 1800° and 90 kbars pressure (Bradley, *et al.*,^{7a} called this the γ phase). Ca_{11}N_8 ^{7b} and Ca_3N_4 ⁸ are also known.

The unusual appearance, stoichiometry, and electrical properties⁹ of Ca_2N prompted us to determine its crystal structure in the hope that we would be able to interpret these properties in structural terms.

Experimental Section

Crystals of dicalcium nitride were supplied by Professor J. W. Tomlinson. They quickly decomposed in air, and had to be sealed under argon in Lindemann tubes. The preparation of Ca_2N is described elsewhere.³

The material was opaque and greenish black with a lustrous sheen. The individual crystals were blocks of ill-defined habit, although some prominent triangular faces could be observed. The one chosen for structural work, easily the best of many examined though still of poor quality, was a lump of about 0.3 mm in diameter.

Crystal Data.— Ca_2N is rhombohedral with $a = 6.603 \text{ \AA}$, $\alpha = 31^\circ 59'$, $V = 71.7 \text{ \AA}^3$, $D_m = 2.17 \pm 0.01 \text{ g cm}^{-3}$ (using a density gradient column), and $D_e = 2.18 \text{ g cm}^{-3}$ for $Z = 1$; the space group is $R\bar{3}m$. The equivalent hexagonal cell has $a = 3.638 \pm 0.003$ and $c = 18.78 \pm 0.009 \text{ \AA}$. In the initial stages of structure solution, a monoclinic cell was assumed: $a = 6.299$, $b = 3.638$, $c = 7.535 \text{ \AA}$, $\beta = 123^\circ 51'$, $Z = 2$, space group $C2/m$; see Figure 1.

The crystal was rotated about the monoclinic a axis and equi-inclination Weissenberg photographs of layers $0kl-5kl$ were taken with $\text{Cu K}\alpha$ radiation using the multiple-film technique. Some 121 reflections, independent in the monoclinic system, were estimated visually against a calibrated intensity scale. The systematic absences were hkl with $h + k \neq 2n$. These are consistent with $C2/m$, $C2$, and Cm . All the reflections present are indexable in the rhombohedral system, in which case there are no systematic absences. This is consistent with space groups $R32$, $R3m$, and $R\bar{3}m$. The last was assumed and shown to be correct by the successful refinement of the structure.

All calculations were carried out on the Imperial College IBM-7090 computer, using the X-RAY 63 system of crystallographic programs. Full-matrix least-squares refinements were continued until successive changes in parameters were less than 5% of their standard deviations. Atomic scattering factors used were for $\text{Ca}^{1.5+}$ and N^{3-} obtained from values tabulated for other ionization states.¹⁰ No absorption correction could be applied as the crystal was accidentally lost before being measured ($\mu = 301 \text{ cm}^{-1}$).

The accurate unit-cell dimensions were obtained by indexing the X-ray powder data given by Ahmad² (11.46-cm Philips camera and $\text{Cu K}\alpha$ radiation, $\lambda 1.5418 \text{ \AA}$) and subsequent least-squares refinement. The indexed powder pattern is given in Table I.

The Solution and Refinement of the Structure

The position of the calcium atom was obtained from a Patterson map, and the nitrogen position was unmistakably shown on a Fourier synthesis phased on the calcium atom. Refinement in the space group $C2/m$ on 121 reflections using interlayer scales as parameters reached $R = 0.16$. All bond lengths and angles equivalent in the rhombohedral space group but not in the monoclinic refined to within one standard deviation of their mean. At this stage, the data were transformed

(7) (a) R. S. Bradley, D. C. Munro, and M. Whitefield, *J. Inorg. Nucl. Chem.*, **28**, 1803 (1966); (b) Y. Laurent, J. Lang, and M. Th. Le Bihan, *Acta Cryst.*, in press.

(8) Y. Okamoto and J. C. Goswami, *Inorg. Chem.*, **5**, 1281 (1966).

(9) J. W. Tomlinson, private communication.

(10) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

TABLE I
DICALCIUM NITRIDE X-RAY POWDER PATTERN

l	d_{obsd}^a	h	k	l	d_{calcd}^b	d_{exld}
		(hexagonal)				
vs	6.21	0	0	3	6.21	6.26
ms	3.13	0	0	6	3.12	3.13
s	2.99	1	0	2	2.98	2.99
vs	2.62	0	1	4	2.61	2.62
w	2.414	1	0	5	2.407	2.414
vw	2.080	0	0	9	2.082	2.087
w	2.034	0	1	7	2.038	2.043
ms	1.875	1	0	8	1.878	1.883
s	1.815	1	1	0	1.815	1.819
vw	1.743	1	1	3	1.743	1.746
vw	1.605	0	1	10	1.611	1.613
ms	1.567	2	0	1	1.567	1.570
w	1.549	0	2	2	1.551	1.553
ms	1.494	1	0	11	1.499	1.501
w	1.369	1	1	9	1.369	1.371
w	1.356	2	0	7	1.357	1.358
w	1.309	0	2	8	1.307	1.308
w	1.253	0	0	15	1.251	1.252
w	1.180	2	1	2	1.180	1.181
w	1.155	1	2	4	1.153	1.154
vw	1.089	1	2	7	1.088	1.089
vw	1.063	2	0	13	1.064	1.065
vw	1.051	3	0	0	1.050	1.050
vw	1.043	0	0	18	1.043	1.043
vw	1.033	3	0	3	1.035	1.036
vw	0.792	3	1	10	0.792	0.792

^a We are grateful to Professor J. W. Tomlinson and Dr. I. Ahmad for allowing us to quote these values. ^b The error term $\Delta \sin^2 \theta = D \sin^2 2\theta [(1/\sin \theta) + (1/\theta)]$ has been used in calculating these values.

to rhombohedral indices, the scaling being fixed on the basis of previous refinement. Equivalent reflections were averaged, leaving 71 independent ones. Isotropic refinement, with only one over-all scale parameter, reached $R = 0.13$. In both cases Hughes' weighting scheme¹¹ was used, where $w = 1$ for $F < F^*$ and $\sqrt{w} = F^*/F$ for $F \geq F^*$; $F^* = 11.0$ (absolute scale) was found to be optimum. The function being minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$; R has the usual meaning, $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. The eight unobserved reflections were not included in the refinement. Owing to the poor quality of the crystal and the lack of an absorption correction, any extinction errors were ignored.

A final difference Fourier ($F_o - F_c$) shows no unusual feature, the highest peak being about one-sixth of that of a nitrogen atom.

The final positional and thermal parameters are shown in Table II. The negative temperature factor of the calcium ion is explained by uncorrected absorp-

(11) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

tion errors. Table III shows a list of observed and calculated structure factors.

TABLE II
DICALCIUM NITRIDE FINAL POSITIONAL PARAMETERS, ISOTROPIC TEMPERATURE FACTORS (B), AND STANDARD DEVIATIONS FROM REFINEMENT IN THE RHOMBOHEDRAL SYSTEM

	x	$B, \text{\AA}^2$
Two Ca in $\pm(x, x, x)$	0.2680 (3)	-0.59 (18)
One N at 0, 0, 0	0	0.30 (67)

TABLE III
DICALCIUM NITRIDE OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS^a

h	k		$ F_o $	F_c	h	k	l	$ F_o $	F_c	
0	0	1	L	1.59	-2.06	2	3	-1	16.44	17.45
0	0	2		19.98	-18.74	2	3	3	17.57	18.96
0	0	3		8.89	-7.96	2	3	4	14.55	-15.25
0	1	-3		14.20	-15.68	2	3	5	6.52	-6.01
0	1	-2	L	2.99	-0.11	2	3	6	12.91	17.99
0	1	-1		22.83	27.83	2	4	4	8.03	-6.22
0	1	1		19.60	-23.84	2	4	5	20.63	18.91
0	1	2		11.39	11.35	2	4	6	4.19	5.16
0	1	3		17.61	19.30	3	3	3	22.57	-17.98
0	1	4		9.45	-7.91	3	3	4	8.37	-6.56
0	2	-2		18.00	19.48	3	3	5	19.68	20.24
0	2	2		20.63	22.39	3	3	6	5.57	5.33
0	2	3		9.15	-8.23	3	4	4	27.32	23.51
0	2	4		12.47	-12.22	3	4	5	7.47	6.20
0	3	3		12.99	-12.43	3	4	6	14.50	-16.15
0	3	4		12.78	14.03	3	5	5	19.47	-16.66
1	1	-3	L	1.41	-0.52	3	5	6	3.63	1.83
1	1	-2		17.87	20.38	4	4	4	10.62	7.73
1	1	-1	L	2.47	0.47	4	4	5	20.89	-17.94
1	1	1		12.62	19.47	4	4	6	2.67	2.03
1	1	2		23.31	30.54	4	4	7	18.56	18.87
1	1	3		7.98	-8.82	4	5	5	5.48	2.41
1	1	4		12.39	-12.43	4	5	6	18.13	20.09
1	2	-2	L	2.41	-0.42	4	5	7	1.96	-2.64
1	2	-1		16.49	-16.83	4	6	7	13.34	-14.98
1	2	2		11.22	-10.31	5	5	5	26.29	21.95
1	2	3		14.16	-14.44	5	5	7	18.65	-15.12
1	2	4		14.98	15.27	5	5	6	2.27	-2.53
1	2	5		14.67	12.35	6	6	6	16.96	-15.52
1	3	-1		7.98	7.95	5	6	7	12.65	9.62
1	3	3		18.39	17.20	5	7	7	11.18	16.27
1	3	4		14.80	13.36	6	6	6	13.25	10.12
1	3	5		15.71	-13.45	6	6	7	20.80	16.75
2	2	-2		15.93	-15.60	6	6	8	11.27	-9.70
2	2	-1		6.91	7.96	6	7	7	9.93	-9.74
2	2	2		17.44	-17.12	6	7	8	10.18	-10.68
2	2	3		21.58	22.28	7	7	7	11.22	-10.73
2	2	4		12.99	14.89	7	7	8	17.70	15.46
2	2	5		13.08	-13.62	7	8	8	11.57	10.46
						8	8	8	8.20	-14.47

^a Rhombohedral indices are used. Unobserved reflections are marked by L, and in these cases $|F_o|$ corresponds to the minimum observable value. $F(000) = 47$.

Discussion

Figures 1 and 2 show that Ca_2N has a layer structure of the *anti*- CdCl_2 type. Each layer may be thought of as two sheets of calcium atoms with a sheet of nitrogen sandwiched between them.

The nitrogen atoms lie at centers of symmetry, on inversion triads. They have an octahedral environment, illustrated in Figure 3, with six equal N-Ca distances of 2.433 Å, but there is some angular distortion and the octahedra are slightly flattened in the direction of the triad axis. The N-Ca distance may be compared with that found in $\alpha\text{-Ca}_3\text{N}_2$ of 2.46 Å⁶ and an average distance of 2.434 Å in Ca_{11}N_8 .^{7b}

Within a layer, each calcium atom is in contact with three nitrogens at 2.433 Å (Figure 4). There are three nearest neighbor calcium atoms at 3.230 Å and six more at 3.638 Å. The nearest calciums in the next layer are 4.347 Å apart, which is the closest approach of atoms in adjacent layers. Thus the Ca-Ca distance between the layers is significantly longer than that found in the metal, *i.e.*, 3.947 Å in the α form and 3.877 Å in the γ form.¹² The layers, therefore, may be thought of as

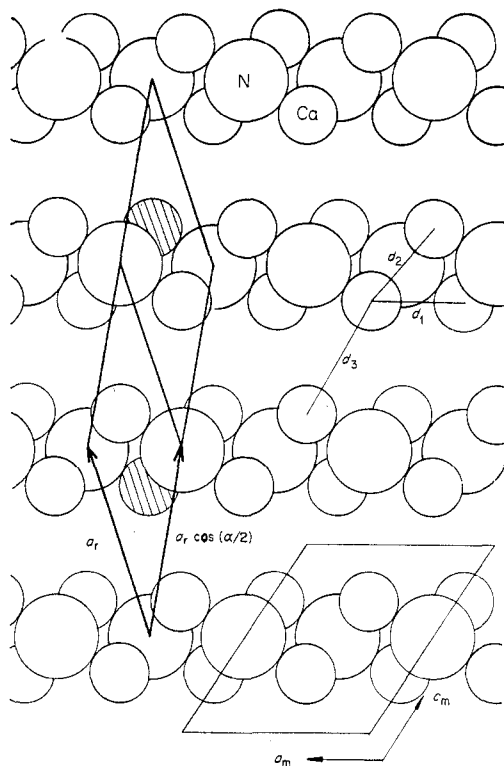


Figure 1.—The layer structure of Ca_2N . The rhombohedral [111] axis, which runs perpendicular to the layers, passes through the two hatched calcium atoms and the nitrogen atom at the origin of the rhombohedral cell outlined. The monoclinic cell referred to in the text is also shown; the projection corresponds to [010] of this cell. d_1 , d_2 , and d_3 are the shortest metal-metal distances parallel to the layer, across the layer, and between layers, respectively (see Table V).

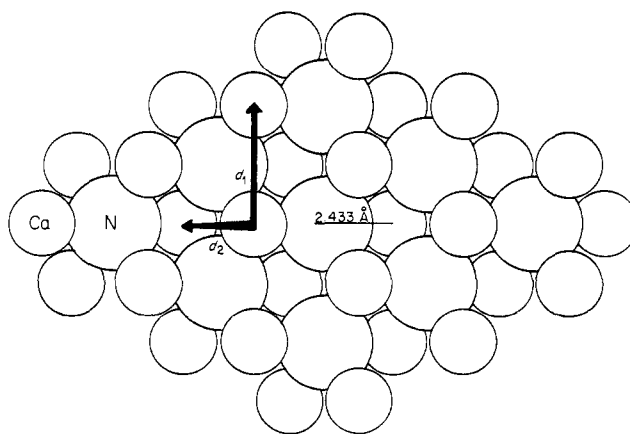


Figure 2.—A single layer in the Ca_2N structure, looking down the [111] rhombohedral axis.

being separated by large “gaps.” The final bond lengths and angles and their standard deviations are listed in Table IV.

An essentially ionic structure is proposed for Ca_2N . The difference of the electronegativities of the two elements would support this view. The similarity of the Ca-N distance to those found in the normal calcium nitrides also suggests ionic bonding. The fact that Ca-Ca distances are less than those in the metal does not, of course, necessarily imply that metal-metal bond-

(12) J. F. Smith, O. N. Carlson, and R. W. West, *Trans. Electrochem. Soc.*, **103**, 409 (1956).

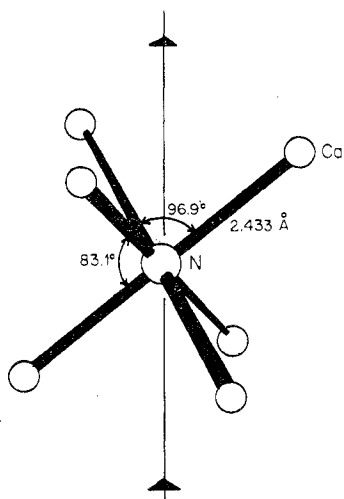


Figure 3.—The nitrogen coordination.

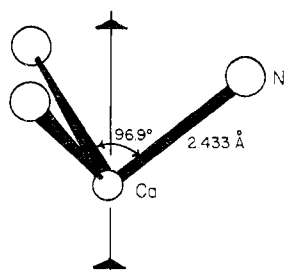


Figure 4.—The calcium coordination.

TABLE IV
DICALCIUM NITRIDE INTERATOMIC DISTANCES AND ANGLES,
AND STANDARD DEVIATIONS

	No. of dist	Dist, Å
N-Ca	6	2.433 (7)
Ca-N	3	2.433 (7)
Ca-Ca	3	3.230 (8) (d_2)
	6	3.638 (3) (d_1)
	3	4.347 (8) (d_3)
Angle		Deg
Ca-N-Ca		96.9 (2) or 83.1 (2)
N-Ca-N		96.9 (2)

ing is present (see, for example, the alkali metal oxides M_2O where M^+-M^+ distances are shorter than in the corresponding metal). Ideally, there would be an excess of one electron per formula unit, which would be essentially free and would give rise to the lustrous graphitic appearance of the crystals. The fact that Ca_2N gives off ammonia and hydrogen in contact with water and not nitrogen indicates that the nitride is not an interstitial one.

Structural comparison may be made with Cs_2O ,¹³ which also has an *anti*- $CdCl_2$ type of structure, the main difference being that in Ca_2N the shortest metal-metal distance between layers is substantially greater than the corresponding one within the layer, whereas for Cs_2O (where there is no excess of electrons) they are of the same order.

(13) K.-R. Tsai, P. M. Harris, and E. N. Lassetre, *J. Phys. Chem.*, **60**, 338 (1956).

Further structural comparison may be made with other M_2X compounds probably containing excess electrons, such as Ag_2F ,^{14,15} Ti_2O ,¹⁶ and Ti_2S .¹⁷ The first two of these are layer structures, Ag_2F being of the *anti*- CdI_2 type. If one considers (Table V) the metal-metal distances within the layers (d_2 as defined in Figure 1) and those between layers (d_3), then Ca_2N and Ag_2F are two extremes; *i.e.*, in the latter compound d_3 is shorter than d_2 whereas in Ca_2N the opposite is true. In the case of Ti_2O the two distances are very similar. (A layer is still taken to mean an anion sheet between two metallic sheets.) This difference is illustrated schematically in Figure 5.

TABLE V
MINIMUM METAL-METAL CONTACTS (Å)

	Intralayer			In metal
	Parallel to layer (d_1)	Across layer (d_2)	Interlayer (d_3)	
Ca_2N	3.64	3.23	4.35	3.877 (γ form) 3.947 (α form)
$(Cs_2O)^a$	2.89 (in columns)	5.8 (between columns)		5.24
Ag_2F^b	2.996	3.87	2.814	2.889
Ti_2O^c	2.96	3.06	2.87	2.894
Ti_2S^d	3.00	...	2.79	2.894

^a K.-R. Tsai, P. M. Harris, and E. N. Lassetre, *J. Phys. Chem.*, **60**, 345 (1956). ^b See ref 15. ^c See ref 16. ^d See ref 17.

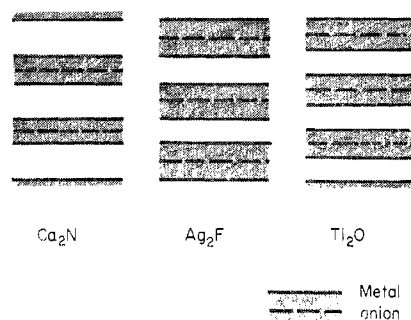


Figure 5.—A schematic representation of the layers in Ca_2N , Ag_2F , and Ti_2O .

The extent to which Ti_2S may be discussed in this context is limited, since it differs structurally from the compounds mentioned above, in that all atoms occur at two levels; *i.e.*, each layer in this case consists of a single sheet which includes both the anions and cations. The minimum metal-metal contacts between the layers (d_3) are however, shorter than those within the sheet (d_1).

Preliminary studies⁹ of the electrical properties of powder compacts of Ca_2N indicate that the conductivity is in the semiconductor range (about $0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature) and that the temperature coefficient is positive. These observations may be related to the structure by reference to a lower oxide of cesium, Cs_2O . This compound contains columns of O-Cs octa-

(14) H. Terrey and A. Diamond, *J. Chem. Soc.*, 2820 (1928).

(15) Gy. Argay and I. Náray-Szabó, *Acta Chim. Acad. Sci. Hung.*, **49**, 329 (1966).

(16) S. Andersson, S. Åsbrink, B. Holmberg, and A. Magnéli, *Bull. Nat. Inst. Sci. India*, **14**, 136 (1958).

(17) J. P. Owens, B. R. Conard, and H. F. Franzen, *Acta Cryst.*, **23**, 77 (1967).

hedra, but the Cs–Cs distances between columns are about 0.5 Å greater than in metallic cesium. Tsai, *et al.*,¹⁸ have shown that powdered Cs₃O has metallic conductivity. This implies that a single crystal of Cs₃O has near-metallic conductivity in all directions, and therefore suggests that the “free” electrons are situated in the space (continuous in three dimensions) between the columns as opposed to being localized to the columns themselves. The latter alternative would result in a unidirectional conductivity, contradicting the experimental observations.

If the analogy can be carried to Ca₂N, the excess electrons should be localized to the large gaps, which are continuous in two dimensions, between the layers. Such an arrangement would help to balance the electrostatic environment of the Ca²⁺ ions. The layers, all of which are identical, would be left essentially ionic in character. Comparison of intralayer bond lengths with those of other nitrides supports this view. The excess electrons in the “gaps” on either side of a layer would then be separated by a barrier in which electrons are highly localized. In the “gaps,” however, potential variation parallel to the layers would be minimal and metallic conductivity might be expected in this plane. On the other hand, the larger potential variation perpendicular to the layers could provide a barrier to conduction which would become less effective as the electrons become more energetic with an increase in temperature. Thus in the translayer direction a much lower value of conductivity may be expected, which however would increase with an increase in temperature, in the manner of a semiconductor.

This postulate would explain the experimental observation for a powder compact, since it is the poorer conductor which would dominate the conductivity of a powder composed of a mixture of two different conductors. The temperature coefficient of a mixture would, however, be a proportional average of the components. In the case of Ca₂N, therefore, at least one direction in a single crystal should have a positive temperature coefficient of conductivity.

The electrical conductivities^{8,9,19,20} of powders of the

(18) K.-R. Tsai, P. M. Harris, and E. N. Lassetre, *J. Phys. Chem.*, **60**, 345 (1956).

(19) F. K. McTaggart, *Australian J. Chem.*, **11**, 471 (1958).

(20) R. Hilsch, G. v. Minnigerode, and H. v. Wartenberg, *Naturwissenschaften*, **44**, 463 (1957).

M₂X materials discussed are listed in Table VI, together with the conductivity of the appropriate metal. The ratio of these two, listed in the last column, indicates that all of the materials have conductivities near those of the corresponding metal, except Ca₂N and Ba₂N which are about 10⁶ times poorer conductors than the metals. These results may be related to the ionic nature of the layers in Ca₂N and Ba₂N (presumably), the partially ionic–metallic¹⁵ character of Ag₂F, and the covalent–metallic¹⁷ character of Ti₂S, Ti₂Se, and Ti₂Te.

Investigation of the electrical properties of single crystals of these compounds only appears to have been pursued for Ag₂F. Conductivity parallel to the layers at room temperature is reported to be 4×10^4 ohm⁻¹ cm⁻¹.²⁰ It is interesting to note, however, that Ag₂F was recently shown to be a superconductor²¹ and it was found that supercurrents can flow both parallel to the layers and perpendicular to them.

TABLE VI

Compd	Conductivity of powder, ^a ohm ⁻¹ cm ⁻¹	Metal	Conductivity of metal, ohm ⁻¹ cm ⁻¹	Ratio
				$\sigma(M)/\sigma(M_2X)$
Ba ₂ N ⁸	1×10^{-2}	Ba	1.4×10^4	1.4×10^6
Ca ₂ N ⁹	2×10^{-1}	Ca	3×10^6	1.5×10^6
Ag ₂ F ²⁰	4×10^4	Ag	6.1×10^6	15
Ti ₂ S ¹⁹	3×10^3	Ti	2×10^4	6.7
Ti ₂ Se ¹⁹	5×10^3			4.0
Ti ₂ Te ¹⁹	5×10^3			4.0

^a Except for Ag₂F, see text.

The consideration of the crystal structure of Ca₂N, in the context of the electrical measurements performed on the powder, has led us to suggest that a single crystal of Ca₂N should have very anisotropic electrical properties. Parallel to the layers it ought to be a good conductor, whereas across them it should behave as a semiconductor. These predictions await experimental verification.

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