Unstable Intermediates. Part XLVII.[1] Electron Spin Resonance Study of the Radical $(CN)_2^-$ in Irradiated Alkali Metal Cyanides and Potassium Chloride Crystals

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γ-Irradiation of sodium and potassium cyanide yields the radical $(CN)_2^-$, the cyanogen negative ion, which is analogous to the V_k-centres formed by irradiation of alkali halides. The electron spin resonance spectrum of the radical trapped in a single crystal of potassium chloride is reported and used to derive information about its shape and electronic structure.

γ-IRRADIATION of sodium cyanide yields an F-centre [2] analogous to F-centres in alkali halides. Other paramagnetic species are also formed, and one having two magnetically equivalent nitrogen atoms is the subject of this Paper. It is thought to be the radical $(CN)_2^-$, which is analogous to the V_k-centre in alkali halides.[3] This radical has also been detected in irradiated potassium cyanide, although the F-centre is formed only on irradiation of highly purified crystals.[4] It is also possible to trap this species in a potassium chloride lattice, and this has been used to obtain the e.s.r. spectrum of the radical oriented in single crystals.

This radical is of interest both in its formation in irradiated cyanides, which is further evidence for the close parallel between the ionic cyanides and the alkali halides, and also in its structure, which is related in some respects to the σ-radicals HCN^- [5] and HCO,[6-8] and to the H_2CN radical.[9] In these radicals there is usually a large amount of delocalisation of the unpaired electron, but the mechanism involved is poorly defined and further results are needed.

EXPERIMENTAL

Analytical grade potassium cyanide and reagent grade sodium cyanide were powdered in an oxygen-free dry-box and irradiated in sealed ampoules. Doped alkali halide crystals were obtained both by slow evaporation of aqueous solutions containing a tenfold excess of the halide, and also from the melt in evacuated crucibles by the Stockbarger technique. The presence of cyanide was confirmed by infrared spectroscopy.

γ-Irradiation was carried out in a Gamma-cell 220 and ultraviolet irradiation with a medium-pressure mercury lamp. Electron spin resonance spectra were recorded using X- and Q-band spectrometers. Single potassium chloride crystals were mounted on Perspex rods, which were so made that the crystals could be rotated about axes perpendicular to the 100 and 110 planes.

RESULTS

Powder Spectra.—The e.s.r. spectra of γ-irradiated powders of sodium and potassium cyanides and of potassium chloride doped with cyanide ions, when recorded at 77°K, were identical except for minor differences in resolution and g-values. These differences can be understood, at least partly, in terms of the phase changes which occur in sodium and potassium cyanides on cooling to 77°K, which reduces the symmetry of the lattice from cubic to orthorhombic.[10] The e.s.r. spectra at X- and Q-band frequencies of the doped potassium chloride sample are in Figure 1 (a) and (b). The interpretations beneath the spectra are supported by results from single-crystal spectra. These powder spectra are complicated by the fact that the g-tensor is not axially symmetric, in contrast with the hyperfine tensor. Another complication is the appearance of a non-principal feature displaced downfield from the principal ones.[11]

Attempts to observe this radical in other alkali halides failed, although infrared spectroscopy showed that cyanide ions had been incorporated. A similar effect has been noticed in the trapping of HCN^-, where only potassium chloride gave a well resolved spectrum.[5]

Irradiation at 77°K of potassium chloride crystals doped with cyanide, followed by measurement without warming, gave a spectrum characteristic of the Cl_2^- radical [Figure 1(c)]. The spectrum of $(CN)_2^-$ is very weak in comparison, but when the sample was warmed slightly and re-cooled to 77°K the Cl_2^- radical could no longer be observed and the signal assigned to the $(CN)_2^-$ radical was increased manyfold [Figure 1(d)]. The outer triplets in both spectra are attributed to the methyleneimino-radical (H_2CN). In contrast, irradiation of the pure alkali metal cyanides at 77°K yields the spectrum assigned to $(CN)_2^-$ directly, and warming of the samples has no noticeable effect.

Attempts to prepare this radical by ultraviolet irradiation at both room and liquid-nitrogen temperatures failed.

Single-crystal Spectra.—Since the powder spectra of this radical in the pure cyanides and in potassium chloride doped with cyanide are so similar, only doped single crystals of potassium chloride were used as these were easier to grow and handle. Furthermore, these crystals suffer no change of phase on cooling, which nevertheless resulted in a marked narrowing of the lines. With the pure cyanides the spectra at room temperature were complicated by other species such as F-centres.[2]

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[1] Part XLVI, W. M. Fox, J. A. McRae, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1967, 1773.

[2] T. A. Claxton, D. J. Greenslade, K. D. J. Root, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 2050.

[3] T. G. Castner and W. Kanzig, *J. Phys. and Chem. Solids*, 1957, **3**, 178.

[4] K. D. J. Root, unpublished results.

[5] K. D. J. Root, M. C. R. Symons, and B. C. Weatherley, *Mol. Phys.*, 1966, **11**, 161.

[6] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1661.

[7] J. A. Brivati, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 237.

[8] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1966, **44**, 4626.

[9] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1938.

[10] A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 1962, p. 733.

[11] R. Neiman and D. Kivelson, *J. Chem. Phys.*, 1961, **35**, 156.

On rotation about a C_4-axis, two distinct sets of quintets were observed at most orientations (Figure 2). Each quintet has an identical set 90° out of phase, and the two different sets of quintets are themselves out of phase by 45°. In Figures 2 and 3, dotted lines indicate experimental observations and broken lines join extrapolated points where the lines were obscured by other overlapping lines. To facilitate interpretation, the spectra were recorded and calibrated every $2\frac{1}{2}$°. Rotation about the other two C_4-axes gave identical spectra.

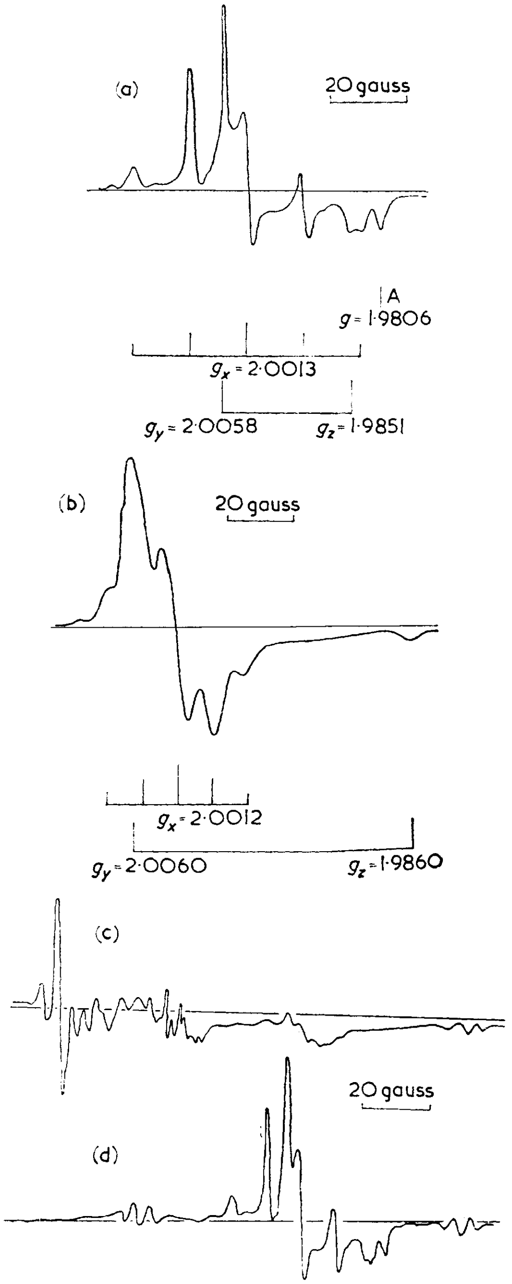

FIGURE 1 Electron spin resonance spectra of γ-irradiated polycrystalline potassium chloride doped with CN^-, recorded at 77°K

(a) X-Band spectrum after irradiation at room temperature; (b) Q-band spectrum after irradiation at room temperature; (c) X-band spectrum after irradiation at 77°K; (d) X-band spectrum after irradiation at 77°K, followed by warming to room temperature and re-cooling to 77°K

These results can be assigned to radicals oriented parallel to a face diagonal of the unit cell of the halide. If this is correct the spectrum should be simplified in a characteristic manner (see Figure 4) if the crystal is rotated about a C_2-axis. This is the case, and the sets of lines observed are shown in Figure 3. Figure 3(c) shows the quintet due to radicals rotated about a non-principal axis. There were two sets, but for simplicity only one is shown. It can be seen that these non-principal lines are displaced further downfield than the principal ones, and hence will give rise to extra features in the powder case, as in fact occurs. In Figure 1, for example, the line 'A' has the same g-value as the limiting point of the highest-field lines in Figure 3(c).

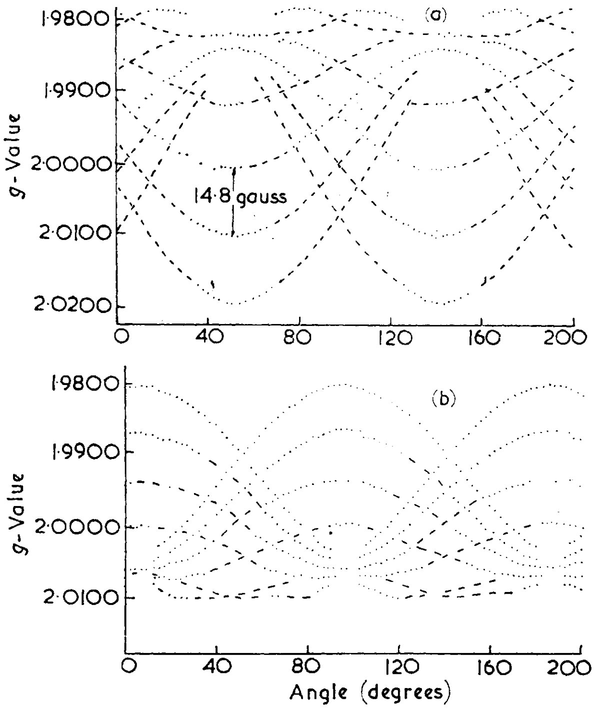

FIGURE 2 Results from the X-band spectrum of a single potassium chloride crystal doped with CN^- after γ-irradiation at room temperature

Variation of $A(^{14}N)$ and g for rotation about a C_4-axis for radicals in (a) the 100 plane (xz-plane of Figure 4), and (b) the 001 plane

Weak satellite lines, assigned to radicals containing ^{13}C, were detected for the central lines of the quintet, although for some orientations they were obscured by the much more intense central lines. The splitting between these satellite lines corresponds to the nitrogen hyperfine coupling, and for two directions the ^{13}C tensor could be measured directly. The third direction, which corresponded to that of the low g-value, has been estimated from non-principal values. The data were sufficient to warrant the tentative conclusion that the principal axes of the ^{13}C hyperfine tensor lie within about 15° of the other tensor axes, but the smallness of the anisotropic component makes it impossible to state the exact directions.

Comparison of the single-crystal spectra with the powder spectra makes the interpretation relatively easy, since two of the principal g-values and one of the principal nitrogen hyperfine coupling constants can be correlated. Hence the spectra in Figure 2 are assigned to radicals aligned parallel and perpendicular to the axis of rotation, respectively, and those in Figure 3 (a) and (b) to the radical being rotated perpendicular and parallel to the nitrogen tensor. The A- and g-tensors are in Table 1, and in Table 2 the ^{13}C and ^{14}N tensors have been separated into their isotropic and anisotropic parts. The nitrogen tensor has a sign ambiguity and both possible values are given.

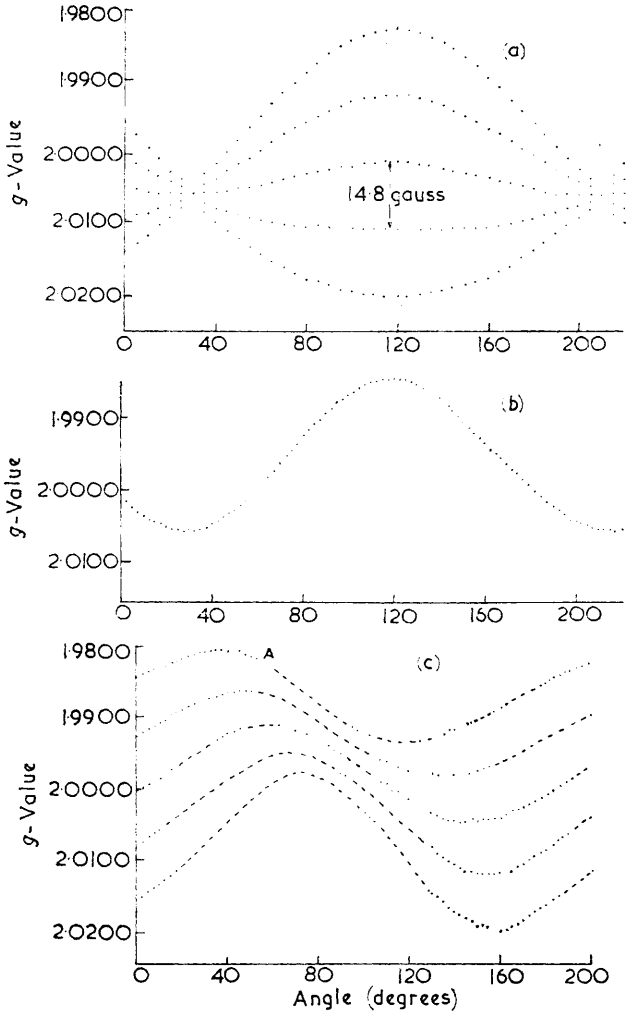

FIGURE 3 As for Figure 2, the results being displayed in three parts

Variation of $A(^{14}N)$ and g for rotation about a C_2-axis for (a) radicals along the axis of rotation (z of Figure 4), (b) radicals perpendicular to the axis of rotation (x of Figure 4), and (c) radicals in planes at 45° to the axis of rotation

TABLE 1

Principal values of the ^{14}N, ^{13}C, and g-tensors for the $(CN)_2^-$ radical

	^{14}N (gauss)	^{13}C (gauss)	g
x *	14·8	67·0	2·0013
y	2·5	56·0	2·0058
z	2·5	56 †	1·9851

* See Figure 4. † Based upon the assumption that the ^{13}C tensor has axial symmetry.

TABLE 2

Isotropic (A_{iso}) and anisotropic ($2B$) terms, and derived spin densities (a^2) for the $(CN)_2^-$ radical

Nuclei	$2B$ (gauss)	A_{iso} (gauss)	a^2_s *	a^2_p *
^{14}N † (i)	8·9	5·9	0·011	0·261
(ii)	10·9	3·9	0·007	0·320
^{13}C	7·3	59·7	0·054	0·113

* Estimated using the data and method given in P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1966. † The $2B(^{14}N)$ direction is parallel to the C_2-axis of the crystal.

DISCUSSION

Identification.—Our conclusion that the radical is the cyanogen negative ion is based on the following considerations. (*a*) The e.s.r. spectrum shows the presence of two equivalent nitrogen atoms, and also ^{13}C lines which are approximately twice as intense as would be expected for one carbon atom per molecule in natural abundance. (*b*) The species is observed in both irradiated alkali cyanides and potassium chloride doped with cyanide ions. The low-temperature irradiation experiments show that it can be obtained from the Cl_2^- radical. (*c*) The orientations in potassium chloride are very similar to those for the Cl_2^- radical,[3] as would be expected for bonding between two adjacent cyanides in chloride ion sites.

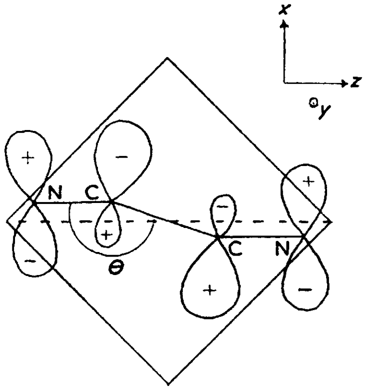

FIGURE 4 Orientation of the radical in a 100 plane of the crystal, showing the principal directions of the g and ^{14}N hyperfine tensors

The simplest species whose structure is in accord with these considerations is the cyanogen negative ion ($N^-C^-C^-N^-$). This radical also accords with the quantitative examination of the e.s.r. results discussed in the following section.

Shape of the Radical.—We consider that the radical will have the bent *trans*-configuration shown in Figure 4, for the following reasons. (*a*) The radical can be thought of as being derived by the addition of an electron to the stable molecule $(CN)_2$, and since the lowest vacant orbital has antibonding character, some bending is expected.[12] (*b*) Despite the large experimental error, we can put an upper limit of about 3 to the p/s ratio, derived from the ^{13}C hyperfine coupling tensor. This is far too small for a linear molecule. (*c*) The fact that the g-tensor is not axially symmetric, and does not deviate

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[12] A. D. Walsh, *J. Chem. Soc.*, 1953, 2266.

far from the free-spin value, would be difficult to understand in terms of a linear structure.

We cannot estimate the bond angle precisely, but in order to reconcile the similarities of the ^{13}C and ^{14}N tensor directions and the high *s*-character on carbon, we suggest that θ is about 150°.

Table 2 contains two possible sets of the nitrogen hyperfine tensors. These two sets together with the ^{13}C data can be used to derive approximate values for the total spin density, 88 and 98%, respectively. Hence we favour the second set. This assignment yields a *p*/*s* ratio on nitrogen of 45, compared with only 24 for the first set. This is close to the value 43 for the related radical H_2CN.[4]

Electronic Structure.—The orbital of the unpaired electron in Figure 4 can be thought of as being derived from the π_u-orbital of the linear molecule. However, for the bent molecule there can be considerable mixing with the other in-plane orbitals, and by analogy with such radicals as HCN^- [5] we expect considerable delocalisation into the σ-framework, and particularly into the C–C σ-bond. Indeed, since the addition of one further electron results in the formation of two separate cyanide ions, the C–C bond in $(CN)_2^-$ is probably weak. It is in this respect that the analogy with V_k-centres in alkali halides is useful.

The effect of having spin density in the C–C σ-bond and to a lesser extent in the C–N σ-bonds will be to reduce the magnitude of the principal values of the anisotropic part of the ^{13}C tensor, and to remove axial symmetry. Also the total *s*-character will be increased. Our data on the ^{13}C-tensor are not sufficient to enable us to distinguish these features, owing to the small anisotropic part of the ^{13}C tensor.

Mechanism of Formation of the Cyanogen Negative Ion.—On irradiation of potassium cyanide or sodium cyanide, electrons are released which can be trapped at vacancies to form *F*-centres, or at transition metal ions.[4] The most likely source of the electrons is the cyanide ion which can be ionised to form the cyanide radical. This can in turn attack a cyanide ion to form $(CN)_2^-$. This is further evidence that the cyanide ion can act as a trap for electron-deficient species,[5] and it is evidently more efficient than chloride ions. The stability of cyanide transition metal complexes of both high and low oxidation state is evidence of its ability to donate as well as accept electrons.

When cyanide ions are dispersed in alkali halide matrices, there is a high probability that a cyanide ion can have a nearest neighbour cyanide ion, since each anion has 12 nearest neighbour anions. We have been unable to detect any resonance spectrum that could be assigned to CN radicals or to radicals such as $(Cl-CN)^-$, which might be expected from radicals that do not have cyanide neighbours.

In alkali halides there appear to be two methods of forming the $(CN)_2^-$ ion. The first is identical with the method in pure ionic cyanides, the other is through a Cl_2^- ion intermediate. This intermediate is formed by ionisation of a halide ion, and if the irradiation is carried out at or below 77°K this can be trapped as the Cl_2^- ion. On warming the hole becomes mobile, but is ultimately trapped at sites containing pairs of cyanide ions.

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