Electron Spin Resonance Studies of Irradiated Potassium Hexacyanocobaltate(III) in Various Host Lattices

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E.s.r. results for γ-irradiated $K_3Co(CN)_6$ in a wide range of alkali metal halide matrices are reported. The main paramagnetic species detected at 77 K were the pentacyanocobaltate(II) ion $[Co(CN_5)]^{3-}$, and the ' di-isocyanide ' $[Co(CN)_4(NC)_2]^{4-}$, but various halogen-substituted complexes were formed in low concentrations. On annealing, the ' di-isocyanide ' complexes were lost, probably by reaction with V_K centres, but the remainder were stable well above room temperature. The form of the g- and A-tensors are discussed, and it is suggested that the ' di-isocyanide ' complex probably contains two off-axis cyanide ions twisted through relatively small angles, rather than through 180° as previously postulated.

RECENT work on the irradiation of transition-metal complexes has shown that novel complexes can be produced. Danon and co-workers have studied the effects of high-energy electrons on pure $K_3Co(CN)_6$, and on $K_3Co(CN)_6$ doped in KCl, the product being formulated as the ' di-isocyanide ', $[Co(CN)_4(NC)_2]^{4-}$.[1,2] The analogous rhodium complex, $K_3Rh(CN)_6$, has also been electron-irradiated at low temperatures in a KCl host, the product being assigned to $[Rh(CN)_4(NC)_2]^{4-}$.[3] On annealing to 470 K chlorination occurred, giving $[Rh(CN)_4(Cl)_2]^{4-}$. Exposure of the d^6 complex, $K_4Fe(CN)_6$ to γ-rays resulted in an e.s.r. spectrum compatible with an Fe^I species with hyperfine structure from only one nitrogen atom.[4] McDowell *et al.*[5] have shown that loss of a cyanide ligand occurs when pure $K_3Co(CN)_6$ is X-irradiated at room temperature, producing the $Co(CN)_5^{3-}$ ion. This ion has also been studied in a variety of alkali-halide matrices by direct doping, the results being discussed in terms of $3d_{z^2}$–$4s$ orbital mixing.[6]

Our main aim has been to study the factors governing the formation of $Co(CN)_5^{3-}$ and the ' di-isocyanide ', and to probe the structure of the latter ion. Also we wished to investigate the replacement of cyanide by halide ions which is known to occur as a minor process.[6]

EXPERIMENTAL

Doped samples were obtained by crystallisation of the alkali-metal halide from aqueous solutions containing potassium hexacyanocobaltate(III) in concentrations varying from 0·005 to 5 mole %. AnalaR reagents were used without further purification. Finely powdered samples were exposed to ^{60}Co γ-rays from a Vickrad source at a dose rate of *ca.* 4 MRad h^{-1} for periods up to *ca.* 2 h.

E.s.r. spectra at the X-band were obtained on a Varian E3 spectrometer and those at the Q-band spectra on an instrument previously described.[7]

RESULTS AND DISCUSSION

Experimental results are summarised in the Table. There are two main cobalt(II) complexes formed by irradiation; one is clearly the $Co(CN)_5^{3-}$ ion from the similarity of the e.s.r. spectra to the spectra from powders doped directly with the ion.[6] There are two

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[1] J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Structure*, 1967, **1**, 127.

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subtly different types of e.s.r. spectra associated with this ion. These differences (Table) probably reflect the effect of charge-compensating vacancies in different locations relative to the complex ion. The other main complex formed is the cobalt(II) ' di-isocyanide ' species which, in most host lattices, exhibits resolvable hyperfine interaction with two equivalent ^{14}N nuclei. Again, two subtly different types of e.s.r. spectra are associated with this species; Type (1) [Figure 1(a)] having $g_x = g_y$ but $A_x \neq A_y$, and Type (II) [Figure 1(b)] having $g_x = g_y$ and $A_x = A_y$. (These differences were confirmed by analysis of the Q-band spectra.)

The low-temperature irradiation products of hexacyanocobaltate(III) ion varied with the size of the lattice. In large lattices only the ' di-isocyanide ' species was observed, in smaller lattices the ' di-isocyanide ' species and the pentacyanocobaltate(II) ion [Type (1)] were both found, and in small lattices only the pentacyanocobaltate(II) ion was formed. Annealing the low-temperature-irradiated samples to ambient temperatures resulted in loss of the ' di-isocyanide' complex but the pentacyanocobaltate(II) ion remained [Type (1)]. In those lattices for which only the ' di-isocyanide ' was detected at 77 K, low concentrations of the pentacyanide were always detected at room temperature, but we cannot argue that they were formed from the ' di-isocyanide ' since their spectra would have been hidden by that of the ' di-isocyanide ' at 77 K. It was found that irradiation of the samples for very short periods at room temperature (one minute or less) produced, in all cases, the same e.s.r. spectra as were observed after low-temperature irradiation with subsequent annealing to room temperature. Prolonged γ-irradiation of the chloride host lattices at room temperature gave some chloride substituted complexes in addition to the pentacyanocobaltate ion [Type (1)]. Annealing the samples, (i) which had been irradiated at low temperature and subsequently warmed to room temperature (ii) which

E.s.r. results for irradiation products of hexacyanocobaltate(III) in alkali metal halide host matrices

Host	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$A_{\parallel}^{N}$	$A_{\perp}^{N}$	$A_{\parallel}^{Cl}$	$A_{\perp}^{Cl}$	Assignment	Type	A_{iso}	$2B$
CsI	2·012	2·097	73	57	*a*	*a*			$Co(CN)_4(NC)_2^{4-}$	(I)	−28·3	104
	2·0049	2·159	89	23·4					$Co(CN)_5^{3-}$	(I)	−5·0	97·9
	2·0045	2·158	88	25					$Co(CN)_5^{3-}$	(II)	−6·6	98·3
CsCl	2·013	2·097	74	59	*a*	*a*			$Co(CN)_4(NC)_2^{4-}$	(I)	−27·9	105
	2·0045	2·158	89	24·4					$Co(CN)_5^{3-}$	(I)	−5·8	98·7
	2·0047	2·158	88	24					$Co(CN)_5^{3-}$	(II)	−5·6	92·4
KI	2·016	2·094	68·5	$\begin{pmatrix}67{\cdot}5\\57{\cdot}5\end{pmatrix}$	3·6	2·0			$Co(CN)_4(NC)_2^{4-}$	(II)	−31·6	103
	2·0048	2·157	90	$\begin{pmatrix}30\\25\end{pmatrix}$					$Co(CN)_5^{3-}$	(I)	−6·2	150
	b	2·158	90	26					$Co(CN)_5^{3-}$	(II)	−7·1	101
KBr	2·012	2·093	65·5	$\begin{pmatrix}67{\cdot}5\\62{\cdot}5\end{pmatrix}$	3·5	2·0			$Co(CN)_4(NC)_2^{4-}$	(II)	−34·2	102·3
	2·0047	2·154	84·6	$\begin{pmatrix}28\\30\end{pmatrix}$					$Co(CN)_5^{3-}$	(I)	−8·6	100
	2·0036	2·158	92	25					$Co(CN)_5^{3-}$	(II)	−5·9	101·8
KCl	2·012	2·107	70	58·8	3·7	2·5			$Co(CN)_4(NC)_2^{4-}$	(I)	−30·5	103·6
	2·013	2·106	71	62·5	3·7	*a*			$Co(CN)_4(NC)_2^{4-}$	(I)	−33·0	107·1
	ca. 2·01	2·101	6	70	*a*	*a*			$Co(CN)_4(NC)_2^{4-}$	(I)		
	2·0065	2·157	91·3	33					$Co(CN)_5^{3-}$	(II)	−12·3	107·5
	2·019	2·287	135	63			13	5	$Co(CN)_4Cl_2^{4-}$			
	b	2·153	85	34	*a*	2·1	*a*	4·3	$Co(CN)_4(NC)Cl^{4-}$			
KF	2·013	2·093	70	$\begin{pmatrix}70\\62{\cdot}5\end{pmatrix}$	3·5	*a*			$Co(CN)_4(NC)_2^{4-}$	(II)	−34	106·9
	b	2·158	90	25					$Co(CN)_5^{3-}$	(I)	−6·0	99·9
	b	2·158	90	26					$Co(CN)_5^{3-}$	(II)	−7·1	101
NaI	2·014	2·090	70	65·5	3·5	2·5			$Co(CN)_4(NC)_2^{4-}$	(I)	−33	105·7
	2·0045	2·154	91	22					$Co(CN)_5^{3-}$	(I)	−2·7	97·4
	2·0045	2·153	91	26					$Co(CN)_5^{3-}$	(II)	−6·1	100·9
NaBr	*b*	2·091	*b*	67					$Co(CN)_4(NC)_2^{4-}$	(I)		
	2·0049	2·154	91·5	23·8					$Co(CN)_5^{3-}$	(I)	−4·1	99·5
	2·0045	2·155	91·5	26					$Co(CN)_5^{3-}$	(II)	−6·3	101·8
NaCl	2·013	2·084	64·5	70·1					$Co(CN)_4(NC)_2^{4-}$	(I)	−37·0	104
	2·014	2·086	62·3	70·6					$Co(CN)_4(NC)_2^{4-}$	(I)	−38·3	103
	2·014	2·084	60·5	74·3					$Co(CN)_4(NC)_2^{4-}$	(I)	−41·1	104
	ca. 2·00	2·152	90	30					$Co(CN)_5^{3-}$	(II)	−9·3	103
	ca. 2·00	2·126	85	40			17	9·3	$Co(CN)_5Cl^{4-}$		−16·4	104·9
	b	*ca.* 2·3	*b*	52			*b*	6·5	$Co(CN)_4Cl^{3-}$			
	b	*b*	*b*	*b*			*b*	7·5	$Co(CN)_4Cl_2^{4-}$			
	b	*b*	*b*	*b*			*b*	12·0	$Co(CN)_4Cl_2^{4-}$			
LiBr	*ca.* 2·00	2·150	90	25					$Co(CN)_5^{3-}$	(I)	−5·0	98·6
LiCl	*ca.* 2·00	2·149	92·5	37·5					$Co(CN)_5^{3-}$	(I)	−15·2	111·7
	2·0044	2·148	92·6	30·6					$Co(CN)_5^{3-}$	(II)	−8·9	105·4

[a] Lines too broad to resolve. [b] Obscured by other features.

had been irradiated for short periods at room temperature, and (iii) which had been irradiated for prolonged periods at room temperature, at 430 K, produced identical e.s.r. spectra; in general, that of the pentacyanocobaltate(II) ion [Type (II)].

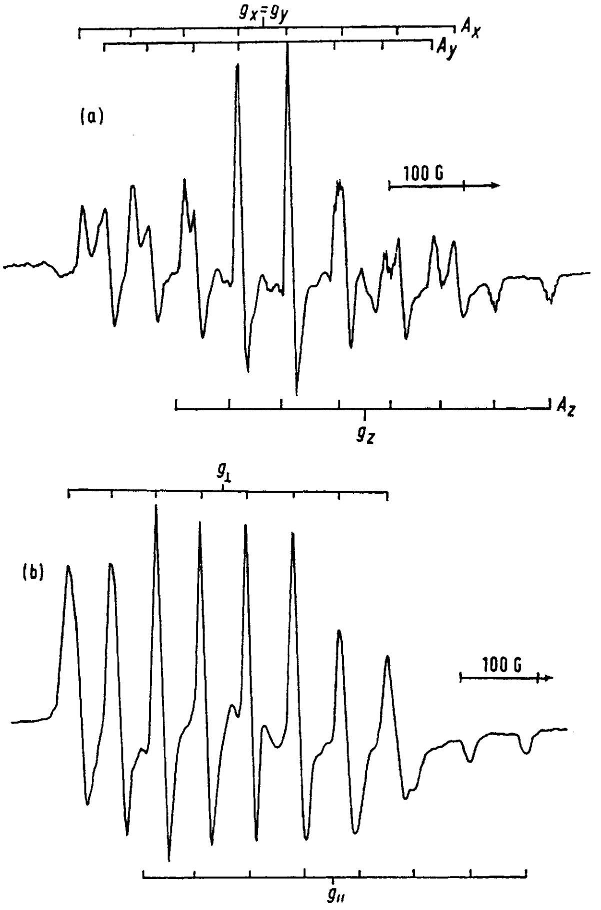


FIGURE 1 (a) X-Band e.s.r. spectrum of the 'di-isocyanide' species [Type (I)] in a host lattice of CsCl; (b) X-band e.s.r. spectrum of the 'di-isocyanide' species [Type (II)] in a host lattice of KI

Particular exceptions to these general trends occurred with the KCl and NaCl host lattices and to a lesser extent with the LiCl host. Low-temperature irradiation of the KCl host produced two types of 'di-isocyanide' spectra, one of which was lost on annealing to room temperature, being replaced by a third variant. In the NaCl host, low-temperature irradiation gave one 'di-isocyanide' complex together with the pentacyanocobaltate(II) ion [Type (II)]. On annealing, the 'di-isocyanide' spectrum disappeared and was replaced by two other 'di-isocyanide' e.s.r. spectra, the pentacyanocobaltate(II) ion [Type (II)] e.s.r. spectrum being retained.

The e.s.r. spectrum of the doped KCl crystals, after annealing for several hours at 430 K, exhibited five low-intensity septets on the low-field side of the pentacyanocobaltate(II) ion spectrum [Figure 2(a)] and two septets on the high-field side. The species responsible for this e.s.r. spectrum is thought to be $Co(CN)_4(Cl)_2{}^{4-}$, the two chloride ligands being *trans* to each other (Table). The annealing process also had a subtle effect on the pentacyanocobaltate(II) ion spectrum in that some superhyperfine lines were observed in the perpendicular region. Further experiments indicated that this species is probably $Co(CN)_4(NC)(Cl)^{4-}$ with a chloride ligand *trans* to an 'isocyanide' ligand. In contrast, the e.s.r. spectrum of the NaCl host, annealed for several hours at 430 K, showed three quartets to low field of the $Co(CN)_5(Cl)^{4-}$ ion e.s.r. spectrum, together with two overlapping septets, both apparently arising from the interaction of a cobalt(II) nucleus with two equivalent chlorine ligands, one having a coupling of 12 G, and the other 7·5 G. We tentatively assign the quartets to a $Co(CN)_4(Cl)^{3-}$ species

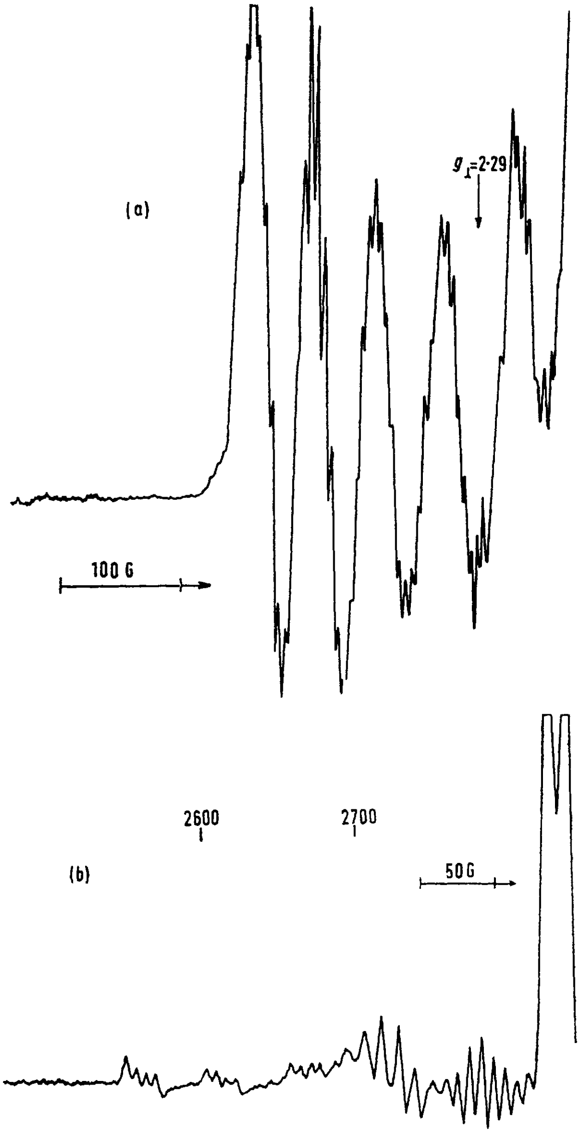


FIGURE 2 (a) Perpendicular features of the $[Co(CN)_4Cl_2]^{4-}$ species showing superhyperfine interaction with two equivalent chlorine nuclei, observed at X-band in a KCl host lattice; (b) the low-field perpendicular lines of the chlorinated species in the X-band e.s.r. spectrum of the NaCl host since, by comparison with other cobalt complexes, the $Co(CN)_5(Cl)^{4-}$ ion is expected to have a lower $g_\perp$ value. We assign the two sets of septets to *trans*-dichloro-species of cobalt in slightly different environments.

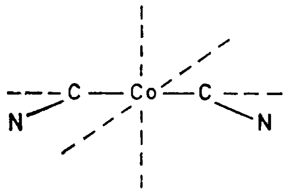
Nature of the ' Di-isocyanide ' Complex.—In our earlier study of the corresponding iron complex [4] we discussed the appearance of three lines from a single interacting nitrogen in terms of three effects, (i) loss of one *trans*-cyanide and consequent increased interaction with the other, (ii) complete inversion of one cyanide to give an ' isocyanide ' linkage, and (iii) hydrogen-atom addition to one cyanide. In the present case (i) is meaningless, and anyway no ^{14}N hyperfine coupling is detected for the remaining *trans*-cyanide for the $Co(CN)_5^{3-}$ ion. Hydrogen-atom addition is also unreasonable, which leaves (ii) as a possibility. This structural change is favoured strongly by Danon and his co-workers,[1,2] since the ' isocyanide ' bonds are unstable in the pure solid but are stabilised by charge compensating vacancies in cubic lattices, one for Fe^{II} and two for Co^{III}. However, the magnitude of the ^{14}N hyperfine tensors are extremely small for an ' isocyanide ' bonded along the z-axis. This can be compared with coupling in the region of 15 G from ^{14}N in d^9 phthalocyanine complexes,[8] and d^7 nitrosyls.[9] Thus there is no compelling reason for postulating an inversion of 180° and, by analogy with the known behaviour of diatomic ligands in the presence of one or two electrons formally in the d_{z^2} orbital, we postulate a relatively minor twist, possibly in the region of 10—40°. This may be envisaged as a form of Jahn–Teller distortion, the twisting of both *trans*-ligands effectively trapping the extra electron in the d_{z^2} orbital.

The constancy of the magnetic parameters for the ' di-isocyanide ' complex (we continue with this nomenclature for convenience only) suggests that the extent of twist is dictated by intramolecular electronic and steric requirements and not by the host lattice. However, the non-appearance of this species in the smaller host lattices does suggest that any steric resistance to such twisting inhibits the formation of the complex.

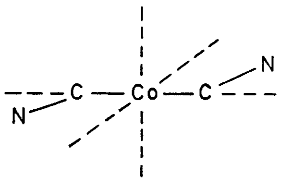
That the hyperfine coupling to nitrogen should increase on twisting is understandable since ^{14}N coupling *via* the σ-orbital of cyanide, which is all that can occur for the linear configuration, is extremely small. This is at first sight surprising, but is probably related to the fact that the spin density on nitrogen in the cyanide radical (which is $^2\Sigma$) is very small, and is apparently negative.[10] On twisting off this axis, interaction with ^{14}N becomes more direct, especially if the ligand shifts laterally at the same time, as might be expected. Since we have no idea of the degree of twist, further discussion is unwarranted. The appearance of a comparable isotropic ^{14}N hyperfine coupling for *trans* alkyl or aryl ' isocyanides ' [11,12] may also reflect slight tilting off the z-axis for these ligands. These are, of course, incapable of bonding *via* nitrogen to the metal ion.

This postulate helps to explain two other surprising observations. One is that $g_{\parallel}$ is in the region of 2·012 rather than being close to the free-spin value as is normally observed for d_{z^2} complexes. Delocalisation on to tilted cyanide ligands will permit orbital motion around their molecular axis, which would be expected to give a positive g_z-increment. This may then, indirectly, bring the filled $d_{xz,yz}$ levels into play.

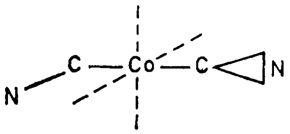
Also, the formation of two distinct types of ' di-isocyanide ', one having an axially symmetric cobalt A-tensor and the other not, becomes explicable. If the distortion takes the form of an in-plane *cis*- or *trans*-bend (I and II) then the d_{xz} and d_{yz} orbitals become different, but for a 90° distortion as in (III) they remain equivalent. We expect some small contribution to the total ^{59}Co A-tensor for spin-polarisation of the $d_{xz,yz}$ electrons, and this will be unequal for (I) and (II), but not for (III). Hence we tentatively suggest that the axially symmetric complex has structure (III) and the unsymmetrical complex has structure (I) or (II).



(I)



(II)



(III)

There is a significant difference between the A_{iso} term for the ' di-isocyanide ' complexes and the $Co(CN)_5^{3-}$ ions (Table). This arises in part because of the appreciable 4s-character, contributing to the orbital for the latter ion. Thus, if the difference of about 25 G in the values for $A_{iso}(^{59}Co)$ is taken as a measure of the loss of 4s-character for the six-co-ordinated complex (this phenomenon was discussed in depth in ref. 6), taking $A°$ (4s, Co) as *ca.* 1320 G,[13] we have a loss of *ca.* 2% 4s

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[8] (*a*) E. M. Roberts and W. S. Koski, *J. Amer. Chem. Soc.*, 1960, **82**, 3006; (*b*) E. M. Roberts and W. S. Koski, *ibid.*, 1961, **83**, 1865; (*c*) D. Kivelson and R. Nieman, *J. Chem. Phys.*, 1961, **33**, 149.

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[12] M. E. Kimball, D. W. Pratt, and W. C. Kaska, *Inorg. Chem.*, 1968, **7**, 2006.

[13] Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

spin density. The gain in $2B$ is *ca.* 3 ± 2%, so once allowance has been made for this, there is little further change.

This implies that delocalisation on to the single cyanide ligand in $Co(CN)_5^{3-}$ is comparable with, or slightly greater than, that on to the two twisted cyanide ions in the ' di-isocyanide '. This is in accord with the concept of a Jahn–Teller-type distortion.

Loss of CN^- *and Gain of Halide.*—In order to fix the envisaged distortion, any one of the six cyanide ions can be lost, provided there is sufficient room. This is probably provided by neighbouring cation vacancies which may or may not be near enough to participate. This may account for the low proportion of $Co(CN)_5^{3-}$ ions found when the ' di-isocyanide ' is also formed. Only in three lattices that are too small to permit the required twisting do we find the $Co(CN)_5^{3-}$ species predominating.

On annealing, the electron seems to be most easily lost by the ' di-isocyanide ' being presumably recaptured by V_K centres, whereas $Co(CN)_5^{3-}$ ions are, of course, stable in these environments. Addition of halide ions seems to be limited to intermediate-size lattices which support the ' di-isocyanide ' species only reluctantly.

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