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ABSTRACT

Single crystals of KCl doped with $\text{Ni}(\text{CN})_4\text{K}_2$ 0.02M were irradiated with 2 MeV electrons. ESR studies of the samples with 70% of ^{13}C reveal the existence of four species assigned to be $(\text{Ni}(\text{CN})_4\text{Cl}_2)^{3-}$ and $(\text{Ni}(\text{CN})_4\text{Cl}_2)^{5-}$ in the isomeric states cis and trans. The form of the g and A tensors is discussed and it indicates that the great anisotropies observed in the cis species are due to the influence of the vacancy created by charge compensation.

1. INTRODUCTION

Danon and co-workers¹⁻⁶ produced paramagnetic d^7 species by electron irradiation of low spin d^6 complexes like $\text{M}(\text{CN})_6^{-2}$. In this paper we study the interesting case of paramagnetic species

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obtained by electron irradiation of low spin d^8 complexes. Earlier ESR studies¹⁻⁶ may be simplified³ introducing the complex ion in a cubic host lattice such as KCl. The advantages are obvious: diamagnetic dilution, stability by local charge compensation and a very easy orientation of the cubic crystal.

In this paper we study the coordination and the oxidation-reduction of $(\text{Ni}(\text{CN})_4)^{2-}$ in KCl. Diamagnetic $\text{Ni}(\text{CN})_4\text{K}_2$ shows square-planar symmetry. Assuming that no dissociation of the molecule is produced during the crystal growth or after irradiation we may expect the formation of two isomers: a trans-isomer if square-planar symmetry is preserved and a cis isomer if it is not. We found both types of isomers.

2. EXPERIMENTAL

The single crystals were grown by slow evaporation from saturated aqueous solution of KCl to which $\text{Ni}(\text{CN})_4\text{K}_2$ was added in molar proportion of 2 per cent. They were of about 5mm edge and the best ones were chosen by visual inspection.

Irradiation was performed at 77K. The irradiated samples were brought to room temperature and exposed to UV rays in order to eliminate the undesired signals from V_k centers. Each sample was irradiated during 20 seconds with 2MeV electrons at a current of $5\mu\text{A}$.

Spectra were obtained with a Varian 4500 X-band spectrometer at liquid nitrogen temperature. Q-band measurements were performed to obtain angular variation and to check on the coherence of the species assignment.

For examination in the spectrometer the crystals were

mounted on a cold-finger ESR cryostat in such a way that they could be rotated around one of the principal axis. In Fig. 1 we show a typical spectrum observed with 70% of ^{13}C .

3. ANGULAR DEPENDENCE OF g-FACTOR

For a paramagnetic complex ion in a cubic crystal the ESR spectrum is expected to present a complicated structure due to the fact that a number of non-equivalent positions in the host are possible. We shall now deduce the theoretical spectrum starting from an arbitrary position of the g-tensor associated to the complex ion and all possible non-equivalent positions generated from the host cubic symmetry.

For any paramagnetic complex ion the g-factor has an angular variation given by

$$g^2 = \vec{m} \cdot \vec{A} \cdot \vec{m} \quad (1)$$

where

$$A_{ij} = \sum_{k=1}^3 g_{ik} g_{jk} \quad (2)$$

and

$$g_{ik} = g_{ki} \quad (3)$$

for it is easy to show⁷ that the g-tensor for a Kramers' doublet is diagonal if there are two perpendicular C_2 axis coincident with the coordinate system of the complex ion. The matrix \vec{m} is the column matrix of the direction cosines of the magnetic field $\vec{H} = H_0 \vec{m}$ relative to the crystal cubic axis and \vec{m} is the row vector.

Since the host lattice has cubic symmetry there are twenty four different orientations for the g-tensor of a complex

ion. Having one of them, the others can be obtained from the relations:

$$\vec{g}_n = \Gamma_4(R_n) \vec{g} \Gamma_4(R_n) \quad n = 1, 2, \dots, 24 \quad (4)$$

Γ_4 is the fourth irreducible representation in Bethe notation and R_n is an element of the octahedral group O . From (1) and (4) it follows that

$$g_n^2 = \vec{m}_n \cdot \vec{A} \cdot \vec{m}_n \quad (5)$$

$$\vec{m}_n = \Gamma_4(R_n) \vec{m} \quad (6)$$

Without loss of generality the crystal axis of rotation can be taken in the z direction. Thus, the magnetic field is contained in the (xy) plane and m can be written as $\vec{m} = \cos\phi \hat{x} + \sin\phi \hat{y}$ where ϕ is the angle between the x axis direction and \vec{H} .

It is convenient to decomposed the group O in terms of the left-cosets of the group $D_2 = (E, C_2^x) \times (E, C_2^z)$ resulting in

$$O = D_2, a_1 D_2, \dots, a_5 D_2 \quad 8$$

It follows that $C_2^z \vec{m} = -\vec{m}$ and the effect of C_2^x on \vec{m} is to turn ϕ into $-\phi$. Thus, applying C_2^z to \vec{m} we get that only twelve g_n -factors are different. Computing \vec{m}_n by means of e, a_1, \dots, a_5 which form the subgroup D_3 of O we obtain six g_n that are expressed analytically by:

$$g^2_{(ij)}(\phi) = A_{ii} \cos^2\phi + A_{ij} \sin 2\phi + A_{jj} \sin^2\phi \quad i \neq j \quad (7)$$

Equation (7) can be simplified by noticing that for $i < j$ we can define the new quantities $g^2_{1(ij)}$ and $g^2_{2(ij)}$ which satisfy:

$$g_{1(ij)}^2(\phi) = \frac{A_{ii} + A_{jj}}{2} + \frac{k_{ij}}{2} \text{sen } 2(\phi + \alpha_{ij}) \quad (8)$$

$$g_{2(ij)}^2(\phi) = \frac{A_{ii} + A_{jj}}{2} + \frac{k_{ij}}{2} \text{sen } 2(\phi - \alpha_{ij}) \quad (9)$$

where

$$k_{ij} = ((A_{ii} - A_{jj})^2 + 4 A_{ij}^2)^{1/2} \quad (10)$$

and the angle α_{ij} is such that

$$\text{tn } 2\alpha_{ij} = (A_{ii} - A_{jj})/2A_{ij} \quad (11)$$

We can expand the definitions given in (8) and (9) to account for $+\phi$ and $-\phi$:

$$g_{1(ij)}^2(\phi) = \frac{A_{ii} + A_{jj}}{2} \pm \frac{k_{ij}}{2} \text{sen } 2(\phi + \alpha_{ij}) \quad (12)$$

$$g_{2(ij)}^2(\phi) = \frac{A_{ii} + A_{jj}}{2} \pm \frac{k_{ij}}{2} \text{sen } 2(\phi - \alpha_{ij}) \quad (13)$$

From (12) and (13) it follows that the first two sums below

$$g_{1+(ij)}^2(\phi) + g_{1-(ij)}^2(\phi) = g_{2+(ij)}^2(\phi) + g_{2-(ij)}^2(\phi) = A_{ii} + A_{jj} \quad (14)$$

are independent of ϕ .

Equation (14) gives the possibility of fitting the observed angular variation of the ESR spectrum using a simple table of experimental $g^2(\phi_i)$ factors.

In Figure 2 we show the observed angular variation of g-factors. The lines joining experimental points were calculated subjected to condition (14).

The matrix A is easily computed from equations (11) and

(14). Even when more than one kind of complex ions is present, equation (11) can still be used, since for each ion i , from (11) we get:

$$k_{12}(i)\sin 2\alpha_{12}(i) - k_{13}(i)\sin 2\alpha_{13}(i) + k_{23}(i)\sin 2\alpha_{23}(i) = 0 \quad (15)$$

$$i = 1, 2, \dots$$

This relation determines the three parameters corresponding to each ion and the sign of α_{ij} so that the coordinate system of the g-tensor remains right-handed.

In Table I we show the obtained g-tensor values for the $\text{Ni}(\text{CN})_4\text{K}_2$ in KCl irradiated with electrons.

4. INTERPRETATION OF THE g-TENSORS

If the $\text{Ni}(\text{CN})_4\text{K}_2$ ion preserves the square-planar symmetry we can expect a $\text{Ni}(\text{CN})_4\text{Cl}_2$ trans isomer in a state of charge $\text{Ni}^+(3d^9)$ for reduction and as $\text{Ni}^{3+}(3d^7)$ for oxidation. The ordering is that given by the spectrochemical series rough approximation⁹. When Ni^{2+} captures an electron in the $\epsilon(b_1)$ orbital it is easy to calculate¹⁰ the resulting g-factors in second-order perturbation theory, obtaining:

$$\Delta g_{\parallel} = 8\lambda k_{\parallel}^2 / (E_{\zeta} - E_{\epsilon}) \quad (16)$$

$$\Delta g_{\perp} = 2\lambda k_{\perp}^2 / (E_{\eta, \xi} - E_{\epsilon}) \quad (17)$$

where λ is the spin-orbit coupling constant, k the orbital reduction factor, and E_{θ} , E_{ζ} , $E_{\eta, \xi}$ the orbital energies in Griffith nomenclature¹⁰.

For Ni^{3+} the unpaired electron is in a $\theta(a_1)$ orbital, and, being B the electrostatic parameter of Racah, the g -factor is given by¹⁰:

$$\Delta g_{\parallel} \approx 0 \quad (18)$$

$$\Delta g_{\perp} = 6\lambda k^2 / (E_{\eta, \xi} - E_{\theta} - 5B) \quad (19)$$

Using Equations (16) and (18) and values listed in Table I one finds that species I and II can be assigned to be $Ni(CN)_4Cl_2$ trans, in states of charge Ni^+ and Ni^{3+} respectively. The existence of a small distortion in g -values may be due to the influence of the vacancies created by charge compensation in the KCl lattice³.

Species III and IV can be interpreted as $Ni(CN)_4Cl_2$ cis isomer in states of charge Ni^+ and Ni^{3+} . However, the presence of one unpaired electron in the θ orbital implies an axially symmetric g -tensor because we assumed that η and ξ functions are degenerate. As can be seen in Table I the g -tensor for species III is not axially symmetric. This apparent discrepancy can be understood if the degeneracy of the η and ξ orbitals is raised and it can be raised by the contribution of the following terms: second-order terms appearing by the mixture with $(1/\sqrt{2})(4p_x + 4p_y)$ orbitals and/or static distortion induced by vacancies. These terms give rise in the expansion of V_{cis} to a term with the symmetry C_{ξ}^{T2g} . In order to calculate the contribution of this term we use the results obtained by Griffith¹¹, where R_1 and R_2 are arbitrary constants.

These matrices show that the term C_{ξ}^{T2g} can release the

$C_{\zeta}^{T_{2g}}$	θ	ζ
θ	0	R_1
ζ	R_1	0

$C_{\zeta}^{T_{2g}}$	η	ζ
η	0	R_2
ζ	R_2	0

(20)

degeneracy of the orbitals $\phi_1 = (1/\sqrt{2})(\eta+\xi)$ and $\phi_2 = (1/\sqrt{2})(\eta-\xi)$ and also produces a mixture of the θ and ζ orbitals.

Being

$$|\Psi_+\rangle = \cos\gamma |\theta\rangle + \sin\gamma |\zeta\rangle$$

(21)

$$|\Psi_-\rangle = -\sin\gamma |\theta\rangle + \cos\gamma |\zeta\rangle$$

for one electron in Ψ_+ orbital in second-order perturbation theory we obtain

$$g_{001} = g_0 + 8\lambda k_{\parallel}^2 \sin^2\gamma / (E_{\epsilon} - E_{\Psi_+})$$

$$g_{110} = g_0 + 2\lambda k_{\perp}^2 (\sqrt{3} \cos\gamma - \sin\gamma)^2 / (E_{\phi_1} - E_{\Psi_+})$$

$$g_{1\bar{1}0} = g_0 + 2\lambda k_{\perp}^2 (\sqrt{3} \cos\gamma + \sin\gamma)^2 / (E_{\phi_2} - E_{\Psi_+})$$

(22)

where

$$\tan 2\gamma = -2R_1 / (E_{\zeta} - E_{\theta})$$

(23)

For small and positive values of γ equation (22) and (23) show that the order $g_{001} < g_{110} < g_{1\bar{1}0}$ is obtained, in agreement with the g-values for species III given in Table I.

We shall now proceed to estimate the value of γ .

Considering only the first term in the expansion of $C_{\zeta}^{T_{2g}}$ of V in tesseral harmonics¹¹, we have

$$R_1 = \langle \theta | f(r) Z_{22}^S | \zeta \rangle = - 2A\sqrt{5/7} \quad (24)$$

$$R_2 = \langle \eta | f(r) Z_{22}^S | \xi \rangle = A\sqrt{15/7} \quad (25)$$

Thus, using (23), (24) and (25) one obtains:

$$R_2 = (\sqrt{3/4})(E_\zeta - E_\theta) \tan 2\gamma.$$

From (22) and the experimental ratio $\{(g_{110} - g_0)/(g_{1\bar{1}0} - g_0)\} = 0.57$, after some algebra one finds:

$$\frac{(\sqrt{3} - \tan \gamma)^2}{(\sqrt{3} + \tan \gamma)^2} \frac{4 + (\Delta_1/\Delta_2) \tan 2\gamma (2 \tan \gamma - \sqrt{3})}{4 + (\Delta_1/\Delta_2) \tan 2\gamma (2 \tan \gamma + \sqrt{3})} = 0.57$$

where $\Delta_1 = E_\zeta - E_\theta$ and $\Delta_2 = E_{\xi, \eta} - E_\theta$.

Assuming that $1 < (\Delta_1/\Delta_2) < 2$, we obtain $89 < \gamma < 5.59$. This relation shows that the mixture between θ and ζ is a small one and that the great anisotropy in g-values in species III is due to the addition of both effects, the mixture and the raise of degeneracy.

As species IV must be a cis Ni^{3+} ($3d^7$) with the unpaired electron in the $e(b_1)$ orbital, and assuming that η and ξ are degenerate, we have according to reference 11:

$$\Delta g_{zz} \approx 8\lambda k_z^2 / (\Delta_1 - \Delta_3) \quad , \quad \Delta g_{\perp} \approx 2\lambda k_{\perp}^2 / (\Delta_2 - \Delta_3 + 15B) \quad (26)$$

Using (26) we obtain $\Delta g_{\parallel} > \Delta g_{\perp}$ as observed experimentally. However, it is not possible to justify the observed anisotropy in (xy) plane for this species as previously by a term C_{ζ}^{T2g} that would raise the degeneracy between η and ξ , because the calculated principal directions of g-tensor in (xy) plane would necessarily be 110 and $1\bar{1}0$, which do not coincide with those observed experimentally.

Another possibility to explain the observed anisotropy is to invoke the role of vacancies. From electrostatic point of view, if the vacancy for charge compensation is near the Ni^{3+} , it would minimize the crystal energy. Then, it is possible to assume that it is located as a second neighbour of the potassium. The observed g-values and principal directions are consistent with the vacancy located in the plane of η or ξ orbitals, given thus maximum splitting between them.

5. TRANSFERRED HYPERFINE STRUCTURE

Table I shows in brackets the calculated orbital densities f_{2s} and f_{2p} for ^{13}C and ^{35}Cl . Those values have not been corrected for 1s not for point dipole contributions¹² due to the absence of structure data for our species.

Since the anisotropic terms are small, we restrict the analysis to isotropic contribution, which can be described by the Hamiltonian term with the usual notations:

$$H = \sum_j A_s(j) \vec{S} \cdot \vec{I}_j \quad (27)$$

where

$$A_s(j) = (f_s/2s) A_{2s}(j) ,$$

$$A_{2s}(j) = (8\pi/3) g_n \beta_n g\beta |\psi_j(0)|_{2s}^2 \quad (28)$$

and j runs for different ligands.

In order to obtain approximated relationships between the splitting for different ions we use the group O_h . Since θ and ϵ are the two components of the representation E_g , using the generator C_4^x we obtain¹⁰:

$$|E_{g\theta} \rangle = (1/\sqrt{3})(|E_{g\epsilon} \rangle - 2C_4^x |E_{g\epsilon} \rangle) \quad (29)$$

which is valid for metal functions and for the MO of the same symmetry also. Hence, we can write for the MO of $|E_{g\epsilon} \rangle$ symmetry

$$|\epsilon \rangle = N\{d_{x^2-y^2} - (\lambda/2)(S_1 - S_2 + S_3 - S_4)\} \quad (30)$$

where we use d-nomenclature for metal orbitals; 1,2,3,4 label the ligands in (xy) plane and 5,6 the ligands on z axis.

Applying (30) in (29) we have

$$|\theta \rangle = N\{d_z^2 - (\lambda/\sqrt{12})(2S_5 - S_1 - S_2 - S_3 - S_4)\} \quad (31)$$

Then, it is easy to obtain the orbital densities listed in Table II using (30) and (31).

As we expect a weaker coupling with Cl ligands than that with ^{13}C , transferred hyperfine structures of species I, III and IV are very simple to interpret with the aid of Table II and Figure 4(a) and (b) which shows the array of ligands. The unpaired electron of species I is in an θ orbital, which implies a structure coming from the four equivalent ^{13}C . Species III with the electron in a ϵ orbital should present a spectrum of two axial equivalent ^{13}C and two equatorial with an approximate ratio of 4:1. Species IV should have only two equatorial and equivalent ^{13}C because the unpaired electron is in an ϵ orbital. The angular variation of the line width in the latter species must be due to the non-resolved structure of the chlorides.

It should be noted that we expect similar f_S values for Li^+ and Ni^{3+} because a contraction of the radial functions of Ni^{3+} can be compensated by a greater polarization of the ligands.

Then, from Table II, we expect for equatorial ^{13}C contribution to transferred hyperfine structure in species II, one third of that observed for species I and IV, i.e. 10^{-3} cm^{-1} . This value is ten times greater than the experimental error and then, detectable. The lack of observed ^{13}C structure in species II suggests that calculations must be carried out taking into account the mixture between θ and $4s$ orbitals. This argument is similar to that used in the analysis of isotropic contribution to hyperfine structure of D_{4h} complex ions¹³.

Let us calculate the minimum of the energy for the function $\Psi = c_1 d_1 + c_2 d_2 + c_3 \phi$ where d stands for metal functions and ϕ is a linear combination of the ligands' functions. In our case $d_1 = \theta$, $d_2 = 4s$ and $\phi = (1/2)(S_1^{\text{CN}} + S_3^{\text{CN}} + S_4^{\text{CN}})$.

Defining

$$\epsilon_i = \langle d_i | h | d_i \rangle$$

$$\epsilon_\phi = \langle \phi | h | \phi \rangle$$

$$S_i = \langle d_i | \phi \rangle$$

$$\beta_i = \langle d_i | h | \phi \rangle$$

where h is an appropriated Hamiltonian for a single electron, and taking into account that

$$\langle d_1 | h | d_2 \rangle = \langle d_1 | d_2 \rangle = 0,$$

we obtain the eigenvalues from the roots of the cubic form:

$$z = (\epsilon - \epsilon_1)(\epsilon - \epsilon_2)(\epsilon - \epsilon_\phi) - (\beta_1 - S_1\epsilon)^2(\epsilon - \epsilon_2) - (\beta_2 - S_2\epsilon)^2(\epsilon - \epsilon_1)$$

Thus, the unpaired electron is in the Ψ_n orbital with energy ϵ^n where $\epsilon_1 < \epsilon^n < (\epsilon_1 + \epsilon_2)/2$. The corresponding coefficient c_3 is given by

$$c_3 = \{1 - ((\beta_2 - S_2 \epsilon^n)/(\beta_1 - S_1 \epsilon^n))^2 (\epsilon^n - \epsilon_1)/(\epsilon_2 - \epsilon^n)\} (\beta_1 - S_1 \epsilon^n) c_1 / (\epsilon^n - \epsilon_\phi).$$

Calling f the factor in curly brackets, the fact that no ^{13}C transferred hyperfine structure is observed, is consistent with $|f| < 1/3$. This result requires the condition $\epsilon_{4S} - \epsilon_\theta \ll \epsilon_\theta - \epsilon_\phi$. Thus, it is possible to explain the absence of ^{13}C hyperfine structure in species II by a large mixture of the 4S orbital to the θ orbital which increases its non-bonding character in the equatorial plane.

6. DISCUSSION

Using equations (17), (19), (22) and (26) respectively for species I, II, III and IV we can calculate expressions for g_a and g_b . From these expressions and the measured values of g_a and g_b it is possible to calculate the difference $\Delta E = |E_\eta - E_\xi|$. The comparison between the values of ΔE for the four observed species can suggest some mechanism on the origin of the molecular distortion of the complex ion.

Assuming equal orbital reduction factors for both g_a and g_b , taking $\lambda(\text{Ni}^{3+})/\lambda(\text{Ni}^+) = 1.2^{14}$, we found by these calculations:

$$\Delta E_I < \epsilon_0^{(*)}, \quad \Delta E_{II} = 2\epsilon_0, \quad \Delta E_{III} \approx 30\epsilon_0, \quad \Delta E_{IV} \approx 21\epsilon_0 \quad (32)$$

(*) Since species I was found to be axially symmetric, the E_T difference is reported in the limit of the experimental error

$$|g_a - g_b| < 10^{-4} \text{ in equation } \Delta E_I \approx 2k^2 \lambda |g_a - g_b| / \Delta g_a \Delta g_b.$$

where

$$\epsilon_0 = k^2 \lambda(\text{Ni}^+)/4$$

The fact that similar values are obtained for ΔE_{III} and ΔE_{IV} suggests that the observed anisotropies are due to similar deformation of the molecule which could arise by the presence of the vacancy needed for charge compensation.

The calculated ΔE_{I} and ΔE_{II} values for the trans isomer are in agreement with experimental fact that these species are more stable^{15,16} than the cis ones and consequently less deformable.

We have also performed measurements of the ESR spectrum of electron irradiated $(\text{Ni}(\text{CN})_4)^{2-}$ ion in NaCl¹⁵. It is interesting to observe that in this host only a trans $\text{Ni}(\text{CN})_4\text{Cl}_2$ species is formed. Similar results were reported by Jain et al.¹⁶ but with the difference that authors invoke a two vacancy mechanism for the Ni^{3+} species in NaCl.

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SPECIES	g TENSOR ORIENTATIONS.			$g_c = g''$	g_a	g_{\perp}	g_b	TRANSFERRED HYPERFINE STRUCTURE $\times 10^4 \text{ cm}^{-1}$	
	a	b	c					^{13}C	
I	100	010	001	2.134		2.043		CI (35)	4 equivalent $A_{\text{iso}} = 35(3\%)$ $A_p = 0(0)$
II	100	010	001	2.008	2.173		2.175	2 equivalent $A_{\text{iso}} = 17(1\%)$ $A_p = 8(20\%)$	not resolved
III	110	$\bar{1}\bar{1}0$	001	2.010	2.132		2.231	not resolved	2 equivalent(1) 2 equivalent(2) $A_{\text{iso}}^1 = 14(2\%)$ $A_{\text{iso}}^2 = 7(1\%)$ $A_p^1 = A_p^2 = 0$
IV	100	010	001	2.268			2.103	not resolved (line width varies with the angle)	2 equivalent $A_{\text{iso}} = 21(2\%)$ $A_p = 1 \pm 2(-0)$

TABLE I. ESR data for $\text{Ni}(\text{CN})_4\text{K}_2$ 2% molar in KCl irradiated at liquid-nitrogen temperature.

LIGAND	θ	ϵ
axial (2 equiv.)	f_s	0
equatorial(4 equiv.)	$f_s/4$	$3f_s/4$

TABLE II. Orbital densities. $f_s = N^2 \lambda^2 / 3$

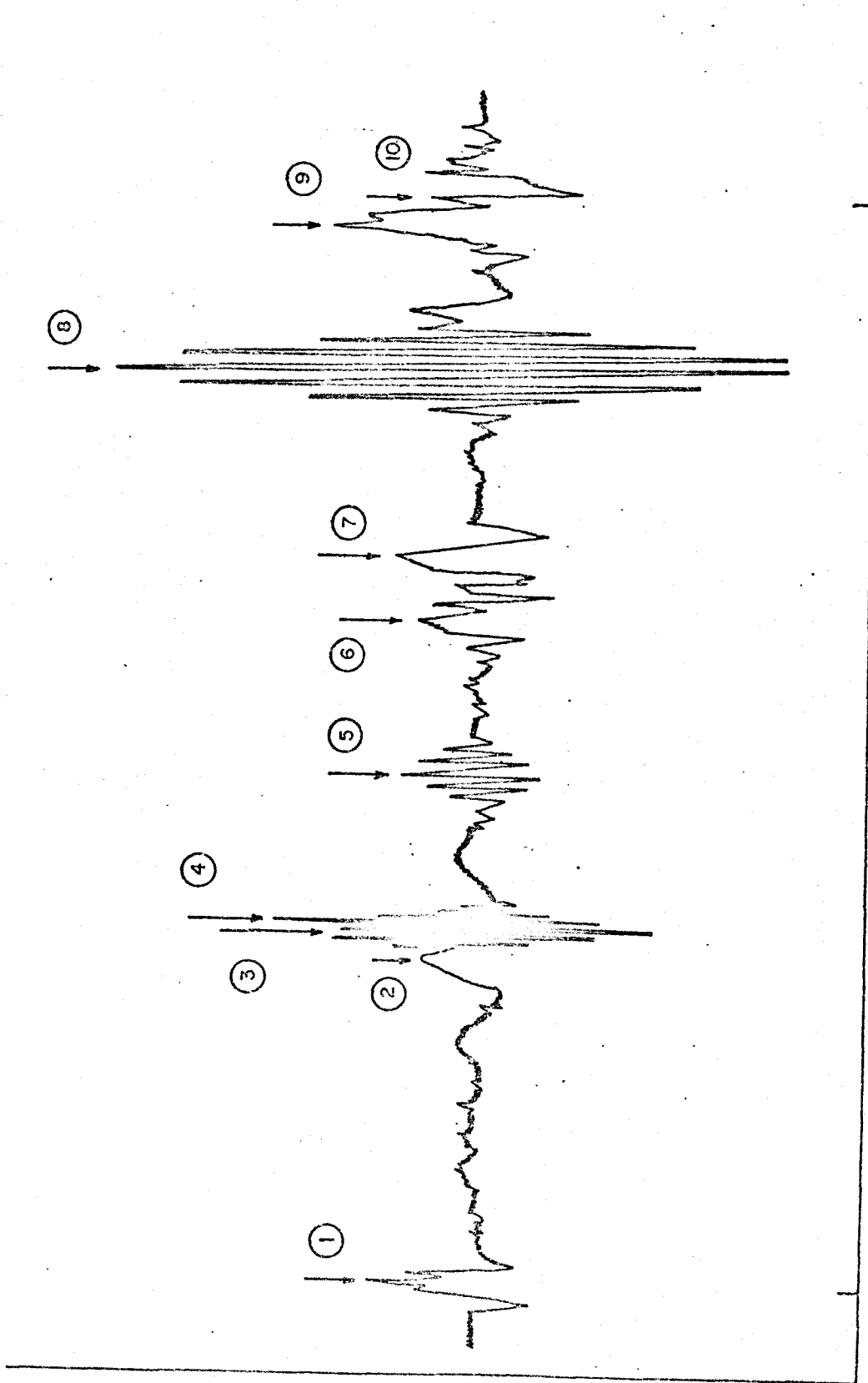


FIG-1

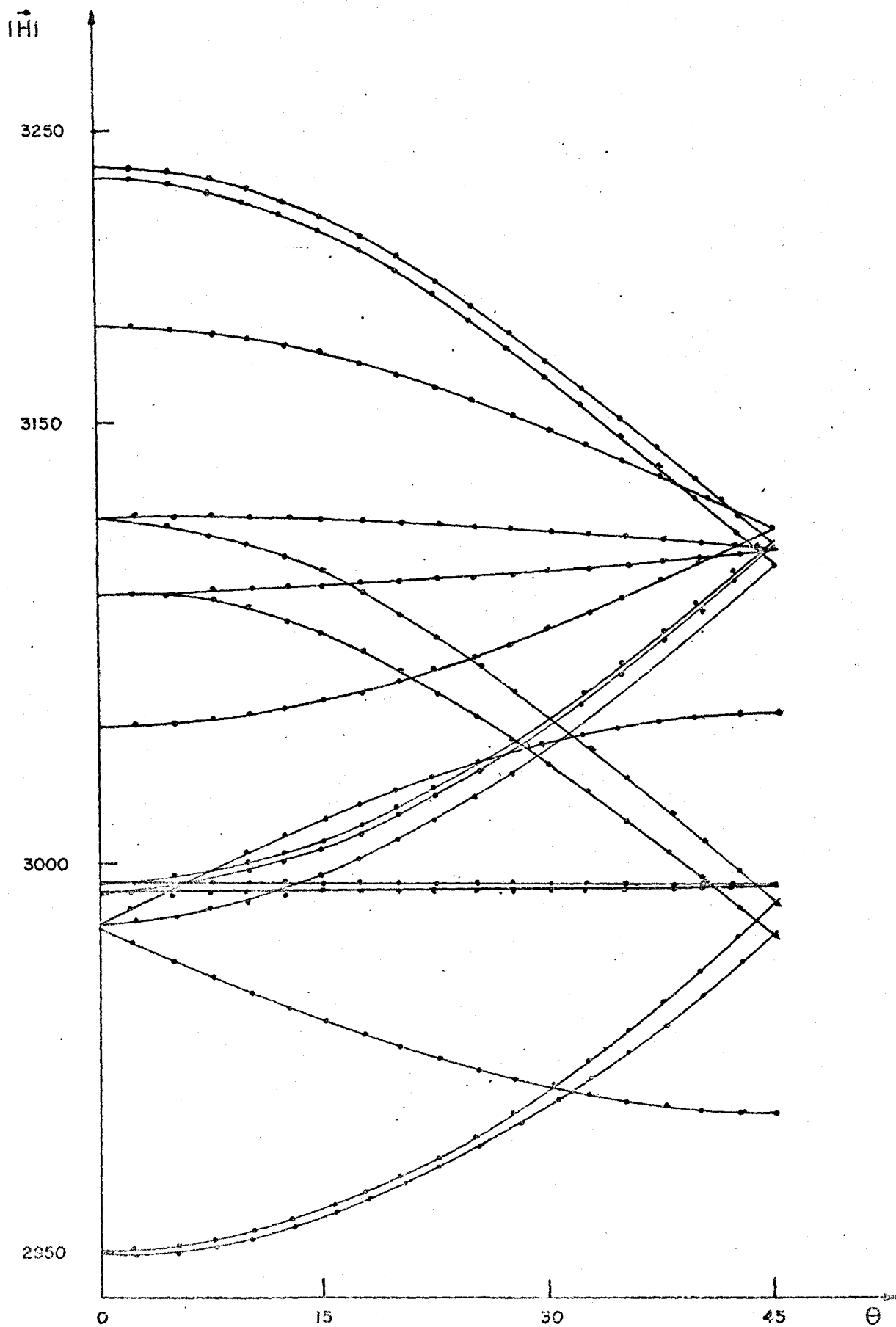


FIG-2

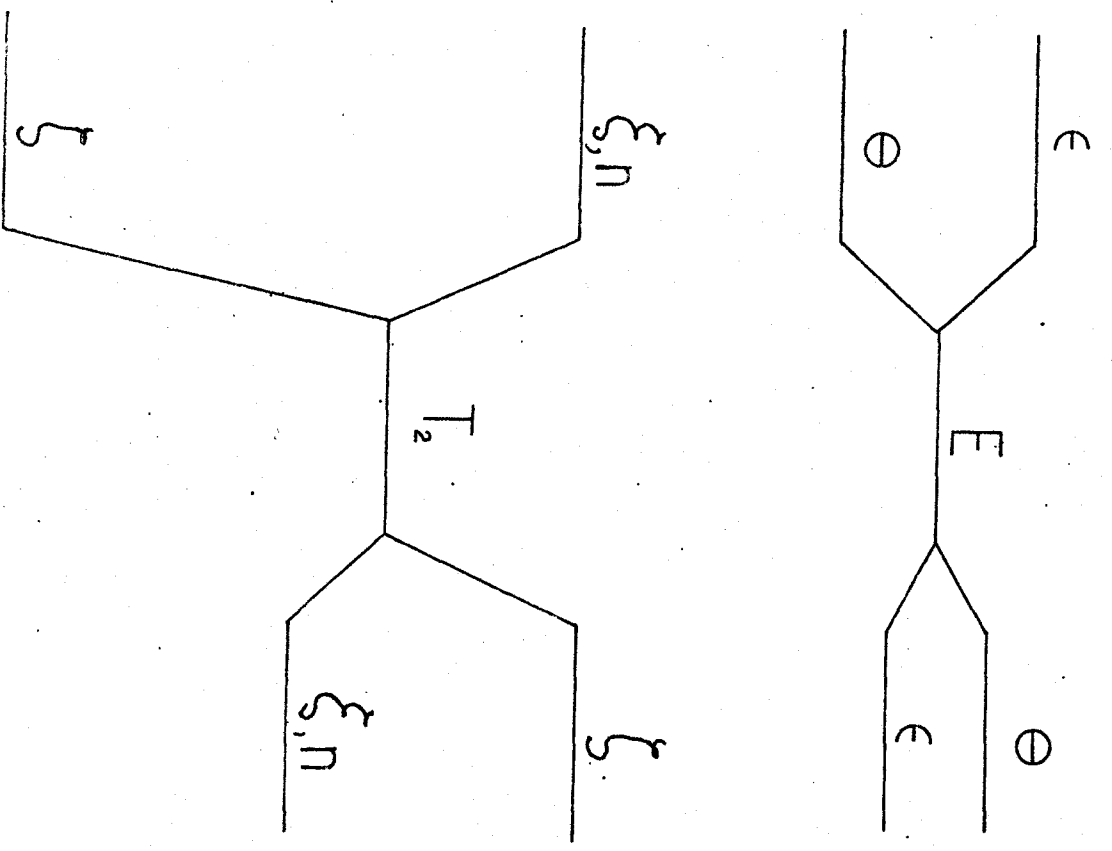


FIG. 3

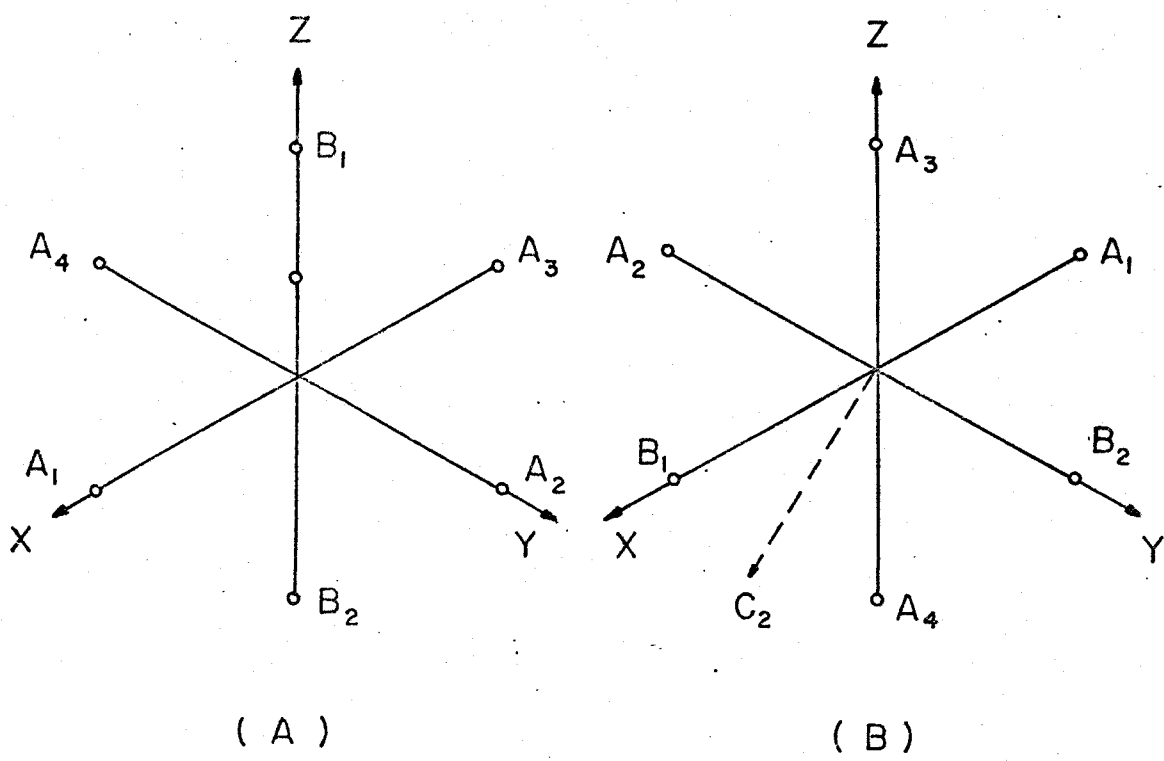


FIG- 4

FIGURE CAPTIONS

Figure 1 - ESR spectrum of single crystals of KCl with 0.02M of $\text{Ni}(\text{CN})_4$, irradiated at 77K, recorded at 77K, Q band. Numbers 1 to 10 run for $g_c(\text{IV})$, $\{(g_a^2(\text{III}) + g_b^2(\text{III}))/2\}^{1/2}$, $g_b(\text{II})$, $g_a(\text{II})$, $g_c(\text{I})$, $g_b(\text{IV})$, $g_a(\text{IV})$, $g_\perp(\text{I})$, $g_c(\text{III})$ and $g_c(\text{II})$ respectively.

Figure 2 - Experimental angular variation of g-factors of single crystals of KCl with 0.02M of $\text{Ni}(\text{CN})_4$, irradiated at 77K, recorded at 77K, X band.

Figure 3 - Energy levels for different isomers. Left: trans. Right: Cis.

Figure 4 - Trans (a) and cis (b) array of ligands. A_i stands for each CN in position i. B_i stands for each Cl in position i.

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