EPR OF ELECTRON IRRADIATED $K_4Os^{II}(CN)_6$ IN KC1 SINGLE CRYSTALS

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ABSTRACT

Electron irradiation of the diamagnetic ion in a KCl host lattice at 77°K produces three paramagnetic Annealling experiments reveal that these species decay among themselves and among four other species. EPR studies indicate that each species can be assigned to a pentacoordinated $Os^{I}(CN)_{5}$ complex, with Sd^{7} low spin configuration arising from the trapping of an electron in a d_z^2 orbital, associated with a charge compensating vacancy located at different The EPR spectra evidenciate strong quadrupolar The g values, the magnetic hyperfine interaction and a minimum value for the quadrupolar interaction with 189 Os nucleus are presented and discussed. Ligand hyperfine structure with four equivalent and one non-equivalent nitrogens is measured and the ligand f_s and f_p spin densities calculated and discussed.

The relative contribution of 5d and 6p electrons to the electric field gradient is discussed and compared with Mössbauer spectroscopy results.

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I. INTRODUCTION

In previous work we have investigated by EPR the effects of electron irradiation of the complexes $K_3\text{Co}(\text{CN})_6$, $K_3\text{Rh}(\text{CN})_6$ and $K_3\text{Ir}(\text{CN})_6$, of $3d^6$, $4d^6$ and $5d^6$ configurations diluted in KCl single crystals $^{(1)}$, $^{(2)}$, $^{(3)}$. By dilution in KCl we have simplified the study by EPR since the dipole interactions are negligible and the complex is favourably oriented in the KCl cubic lattice. In these works we have given particular attention to the $S=\frac{1}{2}$ paramagnetic species with configuration and formed by the capture of one electron at the Al antibonding orbital of these complexes.

It has also been shown that pentacoordinated species, such as $\left[\operatorname{Co}\left(\operatorname{CN}\right)_{5}\right]^{3-}$ and $\left[\operatorname{Ir}\left(\operatorname{CN}\right)_{5}\right]^{3-}$ and mixed ligand species such as $\left[\operatorname{Rh}\left(\operatorname{CN}\right)_{4}\operatorname{Cl}_{2}\right]^{4-}$ are formed by the electron irradiations. The peculiar features of the EPR spectrum observed with the Iridium complexes (4) lead us to a detailed study of the influence of large quadrupolar interactions in such kind of work. Thus, for such nuclei which possess large nuclear quadrupole moment Q the low symmetry complexes as $\left[\operatorname{Ir}\left(\operatorname{CN}\right)_{5}\right]^{3-}$ induces a large EFG which couples with Q giving rise to an interaction which can be of the same order of magnitude of the usual magnetic hyperfine interaction. For such cases the spin-Hamiltonian parameters have been calculated forms.

procedure instead of the frequently employed perturbation methods. 189 Os is a possible candidate for such studies since the ratio Q/γ_N of its nuclear quadrupole moment measured in barns to the nuclear magnetic moment measured in nuclear magnetons is 3.07. In this work we have investigated by EPR along the same lines of the previous works the complex $Os(CN)_6$ in a KC1 lattice irradiated with electrons.

II. EXPERIMENTAL

Osmium. 1890s is present in 16.1%, and possesses a nuclear spin 3/2. The EPR spectra will be composed by the superposition of the lines corresponding to the zero nuclear moment Osmium isotopes (82%) and the lines corresponding to 189 Os isotope. The lines corresponding to the 187 Os isotope (nuclear spin 1/2) are not expected to be observed due to its low natural abundance.

Single crystals of KCl with $K_4Os(CN)_6$, of about 3mm edge, were obtained by slow crystalization of a saturated aqueous KCl solution with 0.7%M of the Osmium complex. In order to avoid efflorescence effects we added about 10% of glycerin to this solution.

The crystals were mounted and irradiated at 77° K in a cold finger variable temperature cryostat with 2 MeV electrons during 35 seconds and a current of 5 microamperes. The system of variable temperature uses a Elcint MCL-3 Temperature Controller. This system has a stability of 0.5° K in the range 77° - 300° K. After the irradiation the samples were kept at liquid nitrogen temperature or annealed at any desired temperature.

The EPR spectra have been obtained with a Varian 4500 X-band and Q-band spectrometer. For X-band examination the crystals were mounted in the cryostat in such a variation.

could be rotated around one of the KCl principal axes. When any of the other two axes of the crystal is parallel to the applied magnetic field one obtains, in one scanning, the three principal features of the spectrum. This gives an immediate check on the symmetry of the species under study.

For Q-band examination the crystals have been mounted and irradiated in the Q-band cavity at liquid mitrogen temperature. This has been possible with a surprisingly simple arrangement that consists of just imerging the lower metallic part of the Q-band cavity in a liquid nitrogen deward. Of course, with such a system we cannot vary the temperature, but we can perform angular variation measurements and check the coherence of the species assignments.

III - RESULTS

a) The paramagnetic species.

The spectra observed with the samples irradiated and recorded at 77°K (without any annealing) reveal the of three paramagnetic species A, B and C. The annealing the irradiated samples between 77°K and room indicates that the three species shown in fig.1 themselves and into at least four other species D, following the sequence $A \rightarrow B \rightarrow C \rightarrow D$, E, F, G. The EPR spectra of those species are almost identical except for the which are slightly different in the perpendicular Angular variation studies show that species C, D, E, F, G have axial symmetry. Species A have $g_X \neq g_y$ and the principal axes of the g-tensor coincident with the KC1 principal Species B also have $g_x \neq g_v$ but in this case the x and y principal axes of the g-tensor form an angle of 45° with the KC1 principal axes. The perpendicular part of the anather

the observed species ($g = g_X$ or $g = g_y$) consists of two sets of lines: a triplet and a quartet of triplets (figure 2). The first set of lines is attributed to the interaction (3.3G) of the unpaired electron with a ^{14}N which has a nuclear spin I=1. The nature of this more intense set of lines and the absence of further hyperfine,

Osmium complexes and that one cyanide of the complex is not equivalent to the others. This cyanide is an axial cyanide since it defines the principal symmetry axis of the complex.

The second set of lines, of less intensity, quartet of triplets and characterizes the hyperfine of ¹⁸⁹Os further split by the same superhyperfine interaction of the first set of lines. The relative intensity of the two sets of lines agrees well with the osmium isotopic composition. Spectra corresponding to 187 Os, nuclear spin 1/2, have not been observed due to its low natural abundance. The central lines of the quartet referred to above are superimposed and do not coincide with the first set of lines. This spectrum symmetrical, the distance from the central lines to the 1ow field lines is about one third of the distance to the high field component of the quartet.

This kind of EPR spectrum is very similar to the $[Ir(CN)_5]^{3-}$ spectrum, which presents a strong quadrupolar effect. The relevant difference, however, arises from the fact that in the present case the perpendicular spectrum is very assymmetric (figure 2). This spectrum has been interpreted by numerical diagonalization of a spin Hamiltonian which includes a quadrupolar term, using the MAGNSPEC program, similarly to the procedure of ref. 4:

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Unfortunately, in this case the satellite lines which appear in the SQI EPR spectra, are of negligible intensity and could not be measured. This is due to the fact that this SOI satellite lines are usually about 0,01 as intense as the central lines of the quartet and the natural abundance of 1890s is not high enough to distinguish them from the noise. 1_{ow} intensity of the satellite lines leads to the impossibility of measuring exactly the value of the quadrupolar interaction Table II shows the measured Spin Hamiltonian parameters for the seven observed species. The value of P that appears in this Table is the minimum value necessary for the fitting of the central lines (4). The observed assymmetry the perpendicular spectrum can be proved to be caused by the large value of A, as is shown in figure 3.

By the other hand, due to the low intensity of species B, D, E, F and G, we could only measure their g-values.

In the parallel feature of the spectrum, which is common to all formed species, the superhyperfine mentioned above becomes rather complex (fig. 4a). The increasing number of lines is attributed to the interaction of the unpaired electron also with the nitrogens of the other ligands. This superhyperfine structure can be fairly well accounted for if we assume four equivalent cyanides and one nonequivalent (fig. 4b). Obviously these four equivalent cyanides must equatorial ones. The fitting of this spectrum has been with a small computer with a program which treats the spectrum only in first order, neglecting quadrupole interactions, assuming a Gaussian line shape. The assumed ligand Spin-Hamiltonian is the following:

$$\mathcal{H} = \frac{4}{121} \cdot \underline{S} \cdot \underline{A}^{eq} \cdot \underline{I}_{1} + \underline{S} \cdot \underline{A}^{ax} \cdot \underline{I}_{5}$$

The summation extends for the four equatorial nitrogens and I_5 is the nuclear spin of the axial nitrogen.

Table III shows the value of the ligand hyperfine parameters corrected for dipolar interactions and the ligand orbital spin densities \mathbf{f}_s and \mathbf{f}_p .

bue to the increasing in the number of the superhyperfine lines the parallel spectrum corresponding to the 189 Os complexes is hardly detectable in X-band. The parallel component of the 189 Os hyperfine tensor can only be measured in Q-band and its value is 170 Gauss.

b) The Annealing Experiments

The annealing studies have been done by heating the sample during 10 minutes at a given desired temperature and measuring the EPR spectra at 77° K.

Figure 5 shows the results of the annealing experiments. As can be seen from this figure the formed species transform among themselves in the following sequence: A + B + C + D, E, F, G.

At room temperature the samples become diamagnetic . After a new irradiation at 77° K all the kinetical process in entirely reproducible.

IV. DISCUSSION

On the nature of the formed species

The analisis of the superhyperfine structure strongly suggests that the formed species are essentially penta-coordinated Osmium complexes. The g-values characterizes an unpaired electron in an d_Z^2 antibonding orbital indicating that the Osmium (II) complex has been reduced to Osmium (I) by the irradiation, similarly to the reduction of the Fe, Ru, Co, Rh and Ir hexacyanides (1 - 6).

The assignment of the paramagnetic species as an Os (III) complex with d^5 configuration can be ruled out on the same basis as ennounced in ref. 3.

The results of the annealing experiments evidenciating that the formed species decay among themselves, the measured g-values and the identical superhyperfine structure of a11 species suggest that the charge compensating positive ion vacancy, created when the $\lceil Os(CN_6) \rceil^{4-}$ substitutes a $\lceil KC1_6 \rceil^{5-}$ group the KCl host lattice, is associated to the osmium pentacoordinated The movement of this vacancy with the could originate the differences among the seven observed species. In effect, if we include this vacancy in order to consider the symmetry properties of the paramagnetic species, it is easy to understand why species A has orthorrombic symmetry along X or Y-axis) and why species B has the X and Y principal components of the g-tensor making an angle of 45° with the KCl principal axes (vacancy in the equatorial plane, in the place of the nearest potassium atom). The other species, being axial, refer to osmium complexes associated with a vacancy along the symmetry axis or far enough to avoid disturbing the axial symmetry within the precision of our measurements.

g Values and Hyperfine Interaction

For a C_{4v} low spin d^7 system with an unpaired electron in a d_2^2 orbital (2A_1 ground configuration) there will be a mixture via spin-orbit coupling with a 2E excited configuration. Formulae for the g-values and hyperfine interactions have been deduced in reference 4 without the use of perturbation theory, assuming a LCAO-MO scheme. These formulae are:

$$g_{11} = g_{0} \cos 2\theta + 2k'' \sin^{2}\theta$$

$$g_{\perp} = g_{0} \cos^{2}\theta + \sqrt{6} k' \sin 2\theta$$

$$A_{11} = \left[-k + \frac{4}{7} \alpha^{2} \cos^{2}\theta + \frac{12}{7} \alpha^{2} \sin^{2}\theta + -(\sqrt{6}/7)\alpha\beta\sin 2\theta \right] P$$

$$A_{\perp} = \left[-k - \frac{2}{7} \alpha^{2} \cos^{2}\theta - \frac{6}{7} \alpha^{2} \sin^{2}\theta - \frac{15}{14} \sqrt{6}\alpha\beta\sin^{2}\theta \right] P$$

where k' and k" are the orbital reduction factors and the angle θ is such that $\tan 2\theta = \frac{\sqrt{6} \ k' \ y}{1+y \ k''/2}$, where

$$y = \frac{\lambda}{E_2 - E_1}$$

k is the isotropic contact constant, $P = g_0 \beta g_N \beta_N < r^{-3} >$, λ is the spin orbit coupling constant and $(E_2 - E_1)$ is the energy difference between the 2A_1 and the 2E configurations .

To use the formulae above we must approximate the experimental data given in Table II to axial symmetry. This can be done by setting (species A) $g_{\perp}=2.1550$, $g_{\parallel}=g_{_{\rm Z}}$, $A_{\perp}=21 \times 10^{-4} {\rm cm}^{-1}$, $A_{\parallel}=A_{_{\rm Z}}$. Changing k" and ß from 1.0 to 0.80, the experimental values can be fitted with $|\alpha|^2=0.90\pm0.07$, k' = 0,33 \pm 0,02, $\theta=6.4^{\circ}\pm0.3$ and $y=0.32\pm0.03$. The positive combination of signs for the hyperfine interaction is the only possible combination which gives an acceptable value for $|\alpha|^2$. In the calculations we have used the value $< r^{-3} > = 8.8 \ a.\mu$. extrapolated from the value 9.24 $a.\mu$. for a 0s $5d^66s^2$ ion (7) assuming that the $< r^{-3} > variation$ from 0s $5d^66s^2$ to 0s $5d^7$ is equal to the $< r^{-3} > variation$ from 1r $5d^66s^2$ to 1r $5d^7(8)$.

The high $|\alpha|^2$ value indicates a low covalency involving the d_z^2 orbital in which the unpaired electron is located. It is important to note that similar result is obtained with the irradiated Ru cyanide with the 4d⁷ configuration⁽⁵⁾. Lower values of $|\alpha|^2$ are observed in Co and Ir cyanides $(|\alpha|^2 \equiv 0.5)$ for which much stronger covalency involves the d_z^2 unpaired electron orbital.

The value of the orbital reduction factor k' is found to be approximately the same (k' = 0.3) for the Ir and Os pentacyanides.

In order to understand these results one should note that in the Fe, Ru, Os series the oxidation state is formally I instead of II in the Co, Rh, Ir series. The low oxidation state of the metal tends to increase the π -character of the complex with increasing metal-to-ligand π -back bonding. Thus the π orbitals d_{xz} and d_{yz} will participate with increased covalency with the ligand orbital whereas the σ bonding d_z^2 orbital will have its participation in bonding reduced (high value of $|\alpha|^2$).

From reference 4, the orbital reduction factor k' can be approximated to $\alpha(\beta - \beta'S_e)$ assuming $\alpha > \alpha'$. The increased π -covalency increases the value of the overlap integral S_e in this relation and could explain the reduced value of k'.

The core polarization field per unpaired spin, χ , can be calculated from the Fermi contact term k (4). From our experimental data $\chi = +1$ 1.8 a. μ . A comparison of this large and positive χ value with the $\chi = -17.5 \pm 0.5$ a.u. value calculated in ref. 12 for divalent 5d ions suggests that there is a mixture of the 6s wave-function in the unpaired electron molecular orbital. Such a mixture has already been observed in other transition metal complexes with a tetaliar

Ligand Hyperfine Structure

The almost isotropic superhyperfine structure with the axial cyanide (very small f_p , Table III) is expected for a σ bonding with a strongly localized d_z^2 metal orbital. On the other hand, the f_s value is very close to the values found in the ${\rm Ir}^{II}({\rm CN})_5$ complex and in some covalent σ -bonding complexes $^{(9)}$. This result could suggest that a polarization mechanism is mainly responsible for the value of f_s in these complexes.

It is remarkable that in Os (CN), the hyperfine tensor values with the equatorial cyanides are almost identical to the values found for the ${\rm Ir}^{\rm II}({\rm CN})_5$ complex and for the $Mo(CN)_5NO^{3-}$, where the bonding with the equatorial is of π character (10). As has been suggested in ref. 3, in order to have a non-null overlap between the d_z^2 metal orbital and the ligand P orbitals, the metal must lie out of equatorial plane. This kind of structure is characteristic of square pyramidal penta-coordinated complexes (11) and indicates that our penta-coordination assignent is correct. The transference of unpaired electron density to the equatorial ligands via spin-orbit mixing of the ²E excited configuration can be estimated from the calculated value of θ and is 0.001 for a β ' value of 0.3. This low value rules out this contribution for a 5d complex even with a expected high of the spin-orbit coupling constant.

Electric Field Gradient at Os Nucleus

As referred in section III, in this work we could only measure a minimum absolute value for the quadrupolar interaction $|P_z| > 38 \times 10^{-4} \text{cm}^2$. This corresponds to a minimum value of 65 x 10^{17} V/cm² for the electric field gradient

The contribution to the electric field gradient of the unpaired electron at the d_z^2 orbital, neglecting spin-orbit contributions, can be written as follows:

$$q_{va1} = -\frac{4}{7} < r^{-3} >_{5d} (1 - R) |\alpha|^2$$

Neglecting the Sternheimer factor (1 - R) and using $\langle r^{-3} \rangle = 8.8$ a.u., with $|\alpha|^2 = 0.9$ we calculate $q_{val} = -43 \times 10^{17}$ V/cm².

Other contributions to the electric field gradient have to be considered in order to account for the measured value. These contributions can arise from population in the 6 $\rm p_z$ orbital which will add with negative sign to the $\rm d_z 2~EFG$ contribution. In order to account for the observed EFG the contribution of the 6 $\rm p_z$ orbital must be of the same order of magnitude as that arising from the $\rm d_z 2~electron$.

This seems to be reasonable in view of recent results obtained from Mössbauer quadrupole investigations with Ir(I) and Au(I) complexes, which indicate a dominant role of 6 p electrons as compared to the 5d contribution to the electric field gradient (13), (14).

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TABLE I: NON-RADIOACTIVE NATURAL ISOTOPIC COMPOSITION OF OSMIUM.

Isotope	Natural Abundance	μ _n	I
¹⁸⁴ 0s	1.59	0	0
¹⁸⁶ 0s	0.018	0	0
187 _{0s}	1.64	0.12	1/2
¹⁸⁸ 0s	13.3	0	0
¹⁸⁹ 0s	16.1	0.65	3/2
¹⁹⁰ 0s	26.4	0	0
192 _{0s}	41.0	0	0

TABLE II: MEASURED SPIN HAMILTONIAN PARAMETERS FOR THE OBSERVED SPECIES. A and P in 10^{-4} cm⁻¹.

Species	A	В	C	D	E	F	G
g Values ^a	g _{XX} ,g _{yy} ,g _{ZZ} directions coincident with the KCl	the g _{xx} ,g _{yy} direction form an angle of 45° with the KC1	Axial symmetry	Axial symmetry	Axial symmetry	Axial symetry	Axial symmetry
	<pre>principle axes g_{xx} = 2.1579 g_{yy} = 2.1520</pre>	x,y axis g _{xx} = 2.1627 g _{yy} = 2.1565	g ₁ = 2.1532	g ₁ = 2.1581	g_= 2.1459	g ₁ = 2.1395	g ₁ = 2.1519
	$g_{zz} = 1.9753$	$g_{zz} = 1.9753$	$g_{ } = 1.9753$	$g_{ j } = 1.9753$	$g_{ } = 1.9753$	g = 1.9753	g _{ii} = 1.9753
189 _{0s hfs} a,b	A ₁ = 21.2	•	$A_{\perp} = 20.6$			•	
	A _{II} = 161	A ₁₁ = 161	A ₁₁ = 161	•) 	
	$P_{x} = P_{y} > +19$	$P_x = P_y > +19$					
	P _z >-38	P ₂ > - 38	(·		

- a. The experimental error in g,A_L and A_U is 0.5 x 10^{-4} , 0.5 x 10^{-4} cm⁻¹ and 1.0 x 10^{-4} cm⁻¹ respectively.
- b. The sign of A_{\perp} , A_{\parallel} and P_{z} have not been determined experimentaly and are discussed in the text.

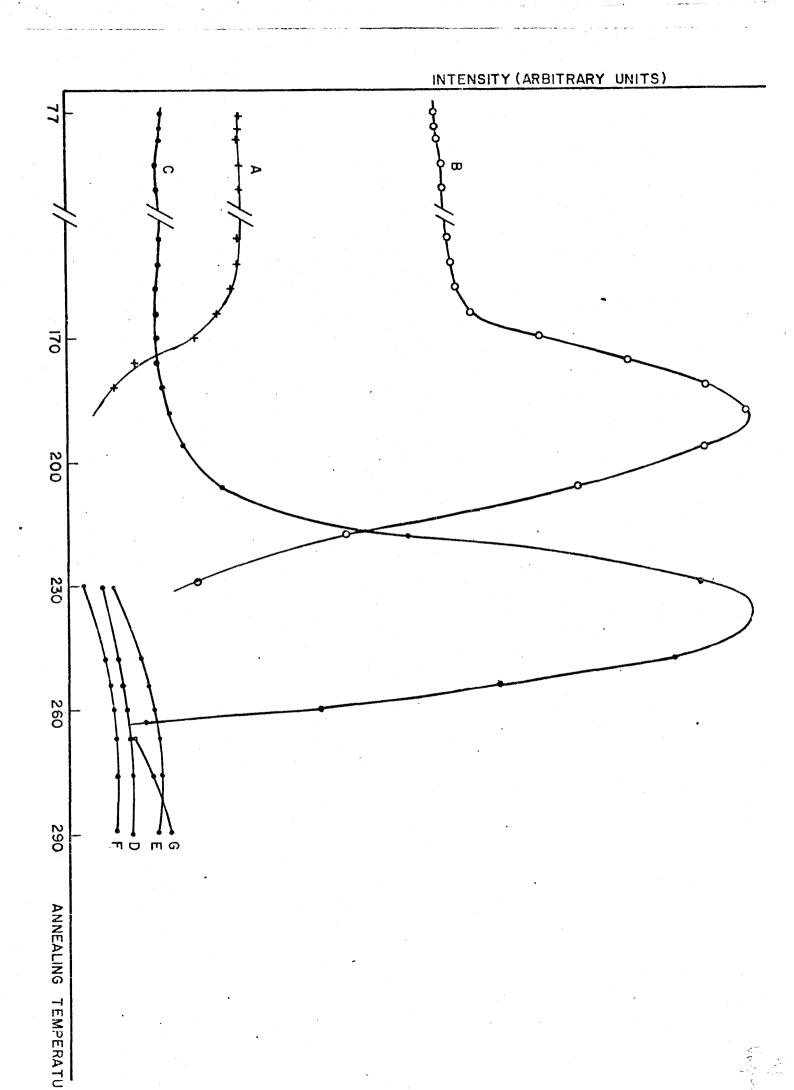
TABLE III: LIGAND HYPERFINE PARAMETERS $(10^{-4} cm^{-1})^a$ AND ORBITAL SPIN DENSITIES FOR THE OBSERVED SPECIES.

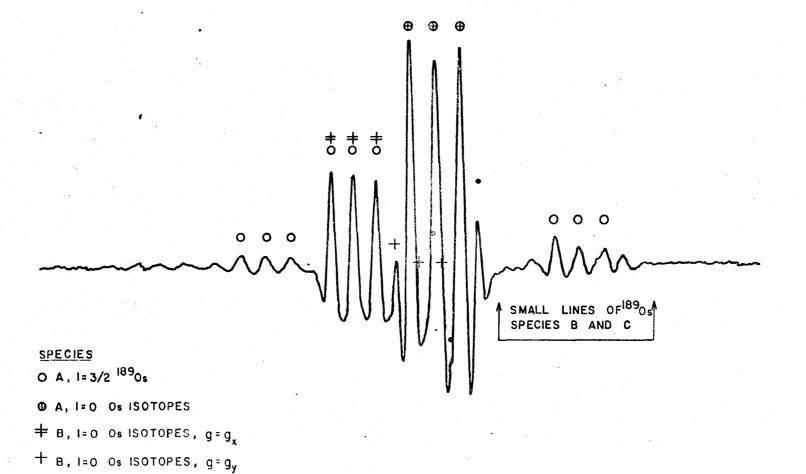
A _x	Ay	Az	fs	fp
$C^{14}N$ axial ^{b,c} + 3.4	+3.4	+3.3	0.007	≈ 0
C ¹⁴ N equat ^{b,c} - 0.1	-0.1	+2.8	0.002	0.060 ^d

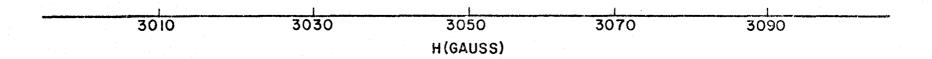
- a The estimated error in the measured ligand hyperfine parameters is $\pm 0.1 \times 10^{-4} \text{cm}^{-1}$.
- b In coordinate system with z slong C_4 axis.
- c For \boldsymbol{p}_z , assuming \boldsymbol{p}_x and \boldsymbol{p}_y have no spin density.
- d Positive sign combination for A_x , A_y and A_z leads to f_s and f_p values of 0.002 and 0.052, respectively.

CAPTION TO THE FIGURES

- Fig. 1: Second derivative X-band perpendicular spectrum of $0.78M \text{ K}_4\text{Os}(\text{CN})_6$ in KCl single crystals, taken with the magnetic field parallel to one of the crystalline main axes at 77^{O}K . The sample has been irradiated at 77^{O}K and kept at this temperature.
- Fig. 2: a) Spectrum taken at the same conditions as the spectrum shown in fig. 1. The sample has been annealed at 190° K during 10 minutes. Conventions are the same as fig.1. Species B has disapeared. b) Theoretical reconstitution of species A 189Os isotope using the MAGNSPEC program.
- Fig. 3: Perpendicular ($\theta = 90^{\circ}$) SQI EPR transitions (S=1/2, I=3/2) as a function of the parallel component of the hyperfine interaction, as given by the numerical diagonalization. The relative intensity of the central lines to the satellites is about 100:1. The other Spin-Hamiltonian parameters are given in table II assuming an axial g-tensor.
- Fig. 4: Ligand hyperfine interaction in the $g=g_z$ spectrum, identical for all the observed species. a) Recorded spectrum at $77^{\circ}K$; b) reconstitution made assuming interaction with four equivalent ^{14}N and one non-equivalent. The lines are assumed to be Gaussian with a linewidth of 2G.
- Fig. 5: Results of the annealing experiments. The samples have been heated during 10 minutes at a given annealing temperature and cooled down to 77°K in order to record the spectra.







• C, 1=0 Os ISOTOPES

