ELECTRON PARAMAGNETIC RESONANCE STUDY OF THE ION Ni^{2+} IN HEXAMETHYLAMINE NICKEL HALIDES IN A HIGH PULSED MAGNETIC FIELD

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Two complex salts of nickel hexamethylamine halides $[Ni(NH_2CH_3)_6]Br_2$ and $[Ni(NH_2CH_3)_6]Cl_2$, were examined by *X*-band EPR. Large values of the zero field splitting parameters for $S = 1$ spin levels were found in both at 77 K and room temperature. Further EPR experiments in the 30 to 80 GHz frequency range, carried out for the chloride in a wide temperature range from 2 K to 300 K, gave for the zero field splitting (ZFS) parameter $D = -2\,cm^{-1}$.

1. Introduction

Phase transitions exhibited by a group of metal hexammine halides of the general formula $[Me(NH_3)_6]X_2$, where X stands for Cl, Br, I, ClO_4, or BF_4 are associated with a structural change from cubic $Fm3m$ symmetry observed at room temperature to lower symmetry below the phase transition. Several properties are observed to undergo anomalous jumps and a systematic collection of T_c versus lattice constant data [1] enables us to draw the conclusion that, for a given anion, it is the metal complex radius that is responsible for the differences in transition temperature. For example, the phase transition temperature of chlorine nickel hexammine is 78 K, whereas for the larger $[Cd(NH_3)_6]^{2+}$ complex compound T_c is 175 K. The EPR linewidth anomaly observed in the nickel complexes has to be explained in terms of low symmetry crystal field splitting leading to an anisotropy of paramagnetic resonance. Though the magnitude of this splitting in diluted nickel complexes has been estimated to be a fraction of 1 cm^{-1} [2, 3], it has never been resolved in non-diluted nickel hexammine halides in the low symmetry phase. The specific nature of the

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NH_3 ligand viz., its symmetric-top shape is believed to be responsible for the perfect averaging of the crystal field distortions discussed in detail for the octahedral complex $[Ni(NH_3)_6]^{2+}$.

It was decided to study the consequences of replacing the ammonia molecules by less symmetric ligands, since lowering of the crystal field symmetry should reveal the fine EPR structure of the $[Ni(NH_2CH_3)_6]^{2+}$ complexes.

Two salts were studied: the chloride and bromide of the hexamethylamine complex.

2. Experimental

The compounds $[Ni(NH_2CH_3)_6]Cl_2$ and $[Ni(NH_2CH_3)_6]Br_2$ were prepared by standard methods, by reaction of saturated water solutions of nickel salt with a 25% water solution of methylamine.

The samples in the form of pale violet powders had to be kept under an inert atmosphere, as they are fairly unstable when exposed to moisture and air. *X*-band experiments were performed for both salts at room and liquid nitrogen temperatures where the broad signal derivative was recorded at 0.75 T. An almost symmetric line, of 0.20 T peak-to-peak linewidth, was found for both the bromide and chloride. At 77 K the position of the EPR signal shifted towards lower field values relative to the room temperature spectra. The position and shape of the EPR line was determined for the powder averaged anisotropy of the magnetic complexes. The energy of an $S = 1$ spin system in an axially symmetric complex is described by the spin Hamiltonian

$$\hat{\mathcal{H}} = g\mu_B(B_xS_x + B_yS_y + B_zS_z) + D(S_z^2 - \tfrac{2}{3}), \tag{1}$$

where the first term describes Zeeman splitting in the case of an isotropic g-factor and the second is the fine structure splitting term. D represents zero-field-splitting i.e. the energy gap between the singlet and spin doublet. The indices x, y and z refer to the crystal field: z is taken as the complex axis of the electric field gradient. For a given orientation of the magnetic field with respect to the crystal axes the energy of the $S = 1$ multiplet can be calculated from Eq. (1). For EPR at the frequency quantum $h\nu$ the resonance field values of the two allowed transitions $\Delta m_s = \pm 1$ are $B = B_0 \pm D$ for $B_z = B \neq 0$, $B_x = B_y = 0$ and also $B = \sqrt{(B_0 \pm D)B_0}$ in the situation when $B_x = B \neq 0$, $B_y = B_z = 0$. $B_0 = h\nu/g\mu_B$ and D are expressed in magnetic field units. From arguments of the random spatial distribution of complexes [4], the EPR absorption of a powder should exhibit extrema at the field values corresponding to the main orientations of the complexes. Thus, the EPR absorption detected at 0.75 T can be assigned a "perpendicular" orientation where $B_z = B_y = 0$ and $B = \sqrt{B_0(B_0 + D)}$. Zero field splitting, estimated from this formula, is 1.6 T i.e. very much more than the Zeeman splitting alone, $B_0 = 0.32$ T and g is assumed to be 2.18. The same values were obtained for the bromide and chloride salts. Further experiments were carried out in magnetic fields up to 10 T with EPR frequencies in the range from 30 to 80 GHz, with the intention of measuring the parameter D accurately. For temperatures down to 2 K the sign of D was established. Strong field measurements were performed

with spectrometers of two types. In one, a nitrogen-cooled pulse solenoid served as a source of external magnetic fields up to 25 T of a pulse duration of several msec. The spectra were recorded by means of an oscillograph with thermal memory. The spectrometer was used in order to obtain a general picture of the spectrum with 2% accuracy as well as for the measurement of the lines in fields upwards of 3 T. In the other spectrometer, an electromagnet, with a field maximally attaining 3 T at an instability of 10^{-4}, was applied for more accurate determinations of the resonance fields of the lines in the low-field region, as well as for line shape recording. In either case a reflecting microwave cavity, located in a cryostat, were used. To avoid decomposition of the samples, the cavity was filled with helium gas. The low-field measurements were carried out at the boiling temperatures of liquid nitrogen, hydrogen and helium. The lowest temperature, lying at about 2 K, was attained by liquid helium pumping and was controlled through monitoring the helium vapour pressure. The EPR absorption signals were recorded.

Oscillograms of EPR spectra, taken with a pulsed magnetic field at the sample temperature 4.2 K, are shown in Fig. 1, for two frequencies of observation. As seen in Fig. 1a, at low frequency (36.4 GHz) the spectrum consists of three lines, the central line being

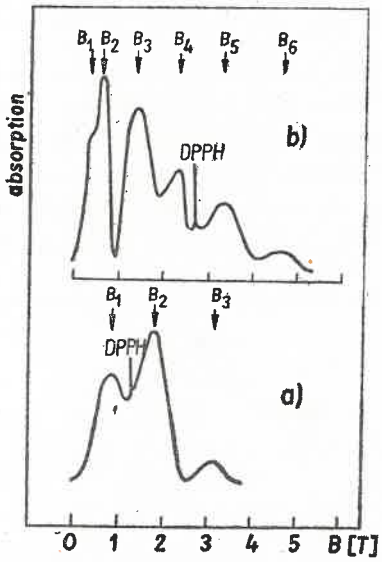

Fig. 1. EPR spectrum of $[Ni(NH_2CH_3)_6]Cl_2$ powder at 4.2 K from measurements in pulsed magnetic fields. The lines are labelled B_i as in Table I. The narrow line denoted DPPH corresponds to the signal from the diphenylpicrylhydrazyl standard: a) high frequency quantum 36.4 GHz, b) high frequency quantum 75.6 GHz

the most intense. At high frequency (75.6 GHz) and in fields up to 5 T, we succeeded in observing six absorption lines (Fig. 1b). Upwards of 5 T the lines were absent. The lowest-field line is poorly resolved against the background of the neighbouring strong line, whereas the other lines are distinct. The narrow lines for 1.3 T in Fig. 1a and 2.7 T in Fig. 1b correspond to the signal of the diphenyl-picryl-hydrazyl (DPPH) radical which

TABLE I

Absorption band maxima in the EPR spectrum of $[Ni(NH_2CH_3)_6]Cl_2$, for various frequencies. The notation B_i is that of Fig. 1. The calculated values are for $D = -2\,cm^{-1}$ and $g = 2.2$

ν[GHz]	B_i[T]							Remarks
	$i =$	1	2	3	4	5	6	
31	exp.	12.2	17.2					Static field
	calc.	9.4	17.8	30.5				
36.4 ($1.22\,cm^{-1}$)	exp.	8.5	18.0	31.5				Pulsed field
	calc.	7.7	20.0	32.3				
70	exp.	4.0	6.3	10.2	21.0			Pulsed field
	calc.	4.0	6.2	11.3	22.3	32.4	43.8	
75.6 ($2.52\,cm^{-1}$)	exp.		6.7	13.8	23.5	33.5	47.0	Pulsed field
	calc.	5.5	7.9	12.4	24.2	34.2	45.7	

was employed as a standard. With decreasing frequency in the 30–35 GHz range, the outside lines shifted towards the central line, which underwent a slight displacement towards lower fields. In the high-frequency interval 75 GHz, a decrease in frequency caused all lines to shift downwards. The resonance field strengths B_i, corresponding to the absorption maxima of the 4.2 K spectrum and various frequencies, are given in Table I, where the lines are labelled as in Fig. 1. Fig. 2 gives in idea of the absorption line-widths. As seen

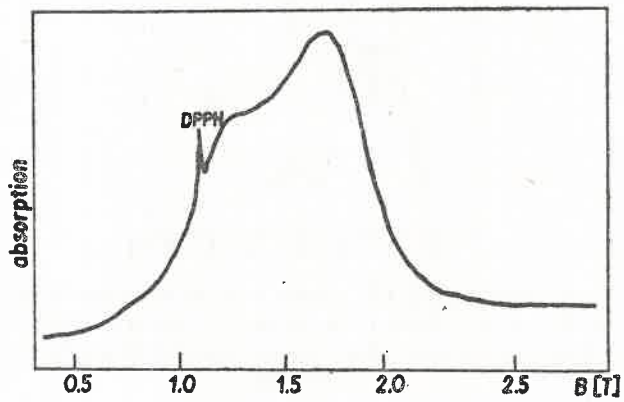

Fig. 2. EPR spectrum of $[Ni(NH_2CH_3)_6]Cl_2$ powder recorded at 31 GHz and 4.2 K in the field of an electromagnet. The narrow DPPH line is that of the standard

from Fig. 2, the width of the EPR lines for $[Ni(NH_2CH_3)_6]Cl_2$ is considerable. For example, the halfwidth of the line, shown in Fig. 2 with a resonance field of 1.72 T at its absorption maximum, amounts to about 0.45 T, measured on its high-field shoulder.

With temperature varying in the 4.2–293 K range the picture of the spectrum remains qualitatively the same; however, with increasing temperature, the intensity of the lines decreases in general so that only the strongest lines were accessible to observation at room temperature. As the temperature decreased from 4.2 K to 2 K at frequencies of about 75 GHz, the line with a maximum in a field of 4.7 T weakened markedly in comparison to the others.

Assessment on the basis of the EPR line profiles observed suggests that the energy of a 75 GHz quantum exceeds D, whereas that of a quantum of the frequency 35 GHz is less than D.

Were one to assume, as is done in Refs [4, 5], that the positions of the absorption line maxima observed for the powder lie close to the resonance field values for lines of permitted transitions for the extreme orientations $B \parallel z$ and $B \perp z$, the lines denoted as B_1 and B_3 in Fig. 1a for the frequency 36.4 GHz and as B_1 and B_6 in Fig. 1b for 75.6 GHz

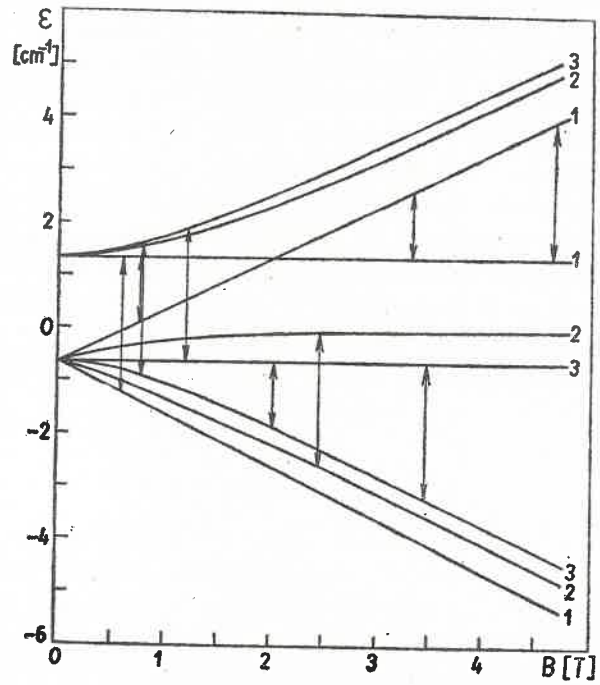

Fig. 3. Energies of the components of $S = 1$ vs the external magnetic field calculated with the Hamiltonian (1) for $g = 2.2$ and $D = -2\ \mathrm{cm}^{-1}$, at the various field orientations: *1* — $B \parallel z$; *2* — B at an angle of 54.7° to z; *3* — $B \perp z$. Arrows indicate the positions of the lines from transitions at the frequency 75.6 GHz (large) and 36.4 GHz (small)

should correspond to transitions with $B \parallel z$, whereas to $B \perp z$ should correspond the lines B_2 of Fig. 1a and B_2, B_3, B_5 of Fig. 1b. This hypothesis is supported by the fact that, for the powder, the line intensities are greater for the perpendicular than for the parallel orientation, due to the distribution statistics of the randomly oriented crystallites. The resonance field values experimentally measured for the lines cited above agree satisfactorily to within

an accuracy of about 10% with those calculated for the Hamiltonian (1) at $D = -2\,\mathrm{cm}^{-1}$ and $g = 2.1$–2.2. Fig. 3 shows the energies of the ground state $S = 1$ components versus the external field for the orientations $B \parallel z$ (curves *1*) and $B \perp z$ (curves *3*) and $D = -2\,\mathrm{cm}^{-1}$, with $g_{\parallel} = g_{\perp} = 2.2$. Arrows in Fig. 3 indicate the transitions possible for the two values, 75.6 GHz and 36.4 GHz, of the high frequency quanta used in the experiments. The calculated field strengths are given in Table I.

In addition to the lines of permitted transitions, the powder spectrum can exhibit lines of forbidden transitions for external field orientations intermediate between $B \parallel z$ and $B \perp z$. The curves *2* of Fig. 3 show the energy of the levels as a function of the external field for the intermediate orientation defined by the angle 54.7° between the directions of the field B and the z-axis. One notes from Fig. 3 that, for a frequency of about 75.6 GHz, the position of the line $B_4 = 2.35$ T in the spectrum is close to that of the "forbidden" transition at an intermediate orientation, and presumably the line B_4 originates in such a transition. For the low frequency (35 GHz), the "forbidden" transition lies between the fields for B_1 and B_2. In the spectrum, the line of the low frequency "forbidden" transition is not apparent because of its considerable line-width, but obviously affects the positions of the B_1 and B_2 maxima. This perhaps explains the divergence between the experimental and calculated positions of the lines B_1 and B_2. It is worth noting that with increasing frequency the position of the "forbidden" transitions should shift towards stronger fields i.e. from B_1 towards B_2. Consequently, at 31 GHz the resonance field of the "forbidden" transition has to lie near that of the line B_1 and to perturb its position more strongly, whereas at 36.4 GHz the line B_2 has to be the more strongly perturbed by the "forbidden" transition. Hence, the error in the calculated positions of B_1 and B_2 has to vary with frequency. This in fact is the case, as can be seen from Table I.

On comparison of the spectra for $T = 4.2$ K and $T = 2$ K the sign of D is seen to be negative.

3. *Discussion of the results*

A more accurate description of the spectrum requires the solution of a highly involved problem requiring, beside the above considered factors defining the EPR spectrum of $[Ni(NH_2CH_3)_6]Cl_2$ powder, considerations bearing on the contribution from the spin-spin interaction. Inasmuch as the spectral lines of this magnetically concentrated specimen are rather broad, the shape of the spectrum apparently reveals an influence of the dipole--dipole interaction of the Ni^{2+} ions. As to the exchange interaction, its role in the EPR spectrum of $[Ni(NH_2CH_3)_6]Cl_2$ remains to be clarified. At the lowest temperatures 2 K not only does the EPR spectrum not vanish — its vanishing would point to a transition of the compound into a magnetically ordered state — but moreover, the lines fail to exhibit a perceptible broadening (commonly apparent when short-range magnetic ordering sets in).

This shows that the exchange interaction energy is not considerable, though the evaluation of its magnitude is by no means easy. The value of the D-parameter found for the $[Ni(NH_2CH_3)_6]^{2+}$ complex is by one order of magnitude larger than that measured for

the hexammine nickel complex in the low symmetry phase. Both methylamine complex salts: the bromide and chloride were X-ray examined for a possible regular crystal structure; however, the diffraction pattern failed to correspond to any cubic group arrangement. It appears that both hexamethylamine compounds exist in the lower symmetry phase throughout the whole temperature range accompanied by a distortion of the $[Ni(NH_2CH_3)_6]^{2+}$ complex as seen by EPR. Compared to hexammine nickel compounds it can be referred to as a model structure for the low symmetry phase of ammonia complex salts.

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