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CESARE OLIVA

Some E.P.R. experimental observations on phase transition

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica fisica. — *Some E.P.R. experimental observations on phase transition.* Nota di CESARE OLIVA (*), presentata (**) dal Socio L. MALATESTA.

RIASSUNTO. — In questo lavoro viene studiato lo spettro E.P.R. di esafluorofosfato di bisacetoneitriletris(dimetilpirazolil)-borato-nitrosilmolibdeno $[\text{Mo}^{\text{V}}(\text{tpzb})_3(\text{NO})(\text{NCMe})_2]\text{PF}_6$ [tpzb = tris(dimetilpirazolil)borato] in soluzione congelata di acetonitrile.

Tale spettro è composto da una sola riga simmetrica di forma lorentziana. Vengono quindi confrontati diversi modelli qualitativi per giustificare questa inattesa forma di riga e la sua variazione con la temperatura e la concentrazione del campione. Si ipotizza infine che in soluzione congelata si formino alte concentrazioni magnetiche locali dove gli effetti di restringimento della linea (dovuti a scambio spin-spin) potrebbero prevalere sugli effetti opposti dovuti a interazioni dipolari.

INTRODUCTION

EPR spectra observed from frozen solutions like those obtained from radicals trapped in polycrystalline or amorphous solids would be interpreted as the superposition of the spectra for all orientations [1]. It is well known that this yields spectra composed of asymmetric non-lorentzian lines. However the preparation of samples by freezing the solution typically produces solute segregation effects [2] which yield "magnetically concentrated" specimens, with "local" concentration of 1 to 10 mol l⁻¹. Furthermore, the freezing speed may have a great influence on the "local" concentration and on the related intermolecular magnetic interactions [3] affecting the EPR pattern. The spectrum for slowly frozen samples can show more markedly the intermolecular dipolar and/or exchange interactions brought about by solvent-solute segregation. In particular, if the freezing process is able to bring unpaired spins of neighbouring molecules into sufficiently close proximity, electron exchange interaction becomes strong enough to narrow the resonance signal and a single EPR line is detected. This is what has been observed in literature in the case of divalent copper complexes with nitrogen-containing ligands [4], in the case of spin-probe studies of glass-forming organic liquids [5] and in other cases [6, 7]. Higher concentrations of paramagnetic species, however, can also re-

(*) Dipartimento di Chimica Fisica ed Elettrochimica dell'Università e centro C.N.R. per lo Studio delle Relazioni tra Struttura e Reattività Chimica, via Golgi 19, 20133 Milano.

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sult in electron spin dipole broadening of the lines in the EPR spectrum [7]. For example this broadening effect has been observed in the spectra of Mn^{2+} and Gd^{2+} in a number of frozen aqueous solutions [8], and in EPR spectrum of an aqueous solution of the copper II 4,4', 4'', 4'''-tetrasulphophthalocyanine chelate [9] at 77 K.

EXPERIMENTAL RESULTS

A single lorentzian-shaped EPR line in frozen solution has been also found in this work from bis acetonitrile tris(dimethylpyrazolyl)boratonitrosylmolybdenum hexafluorophosphate in acetonitrile [10] whose EPR spectra in liquid solution have already been studied [11]. If the temperature is lowered, a phase transition of the solution occurs at about $-60/-70$ °C but the EPR spectrum detected at temperatures lower than the freezing point is still composed of one symmetric approximately lorentzian line (see fig. 1). Experimental spectra have been digitized by hand and then processed by the fitting programme

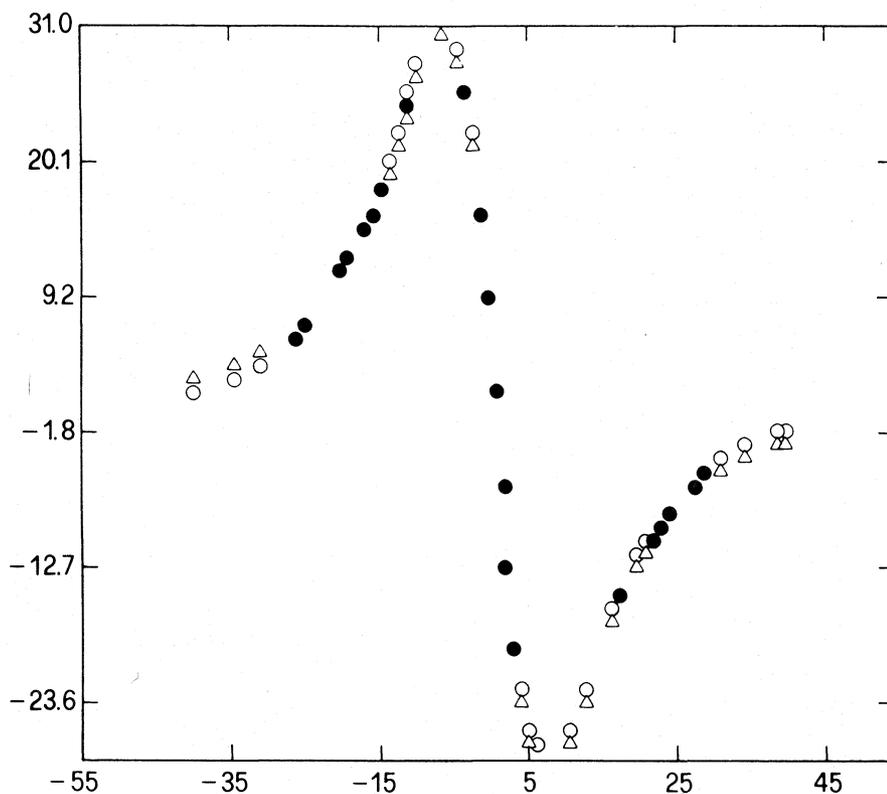


Fig. 1. - Experimental spectrum obtained with a sample 0.27 mol l^{-1} at -80 °C (frozen solution) and its best Lorentzian shaped fitting. Experimental points (\circ), calculated points (Δ) and experimental and calculated coincident points (\bullet) are shown.

EPR 80 [12]. Line-width values when the phase transition normally occurs with sample 0.27 mol l^{-1} are reported in fig. 2 *a*. At temperatures higher than or equal to $-60 \text{ }^{\circ}\text{C}$ the reported line-width is just the one due to the isotope ^{96}Mo (with $I = 0$) but a sextet due to the isotopes $^{95,97}\text{Mo}$ (with $I = 5/2$) is also detected [10, 11]. If the temperature is lowered very slowly it is also possible to obtain the solution in the underfreezing unstable situation. The line-width of the singlet due to ^{96}Mo in this case is reported in fig. 2 *b*. On the other hand it is also possible to obtain the overmelting situation starting from temperatures as low as $-130 \text{ }^{\circ}\text{C}$ and raising it very slowly. The line-width of the singlet obtained in this case is reported in fig. 2 *c*, and no spectrum composed by six lines is observable in this case.

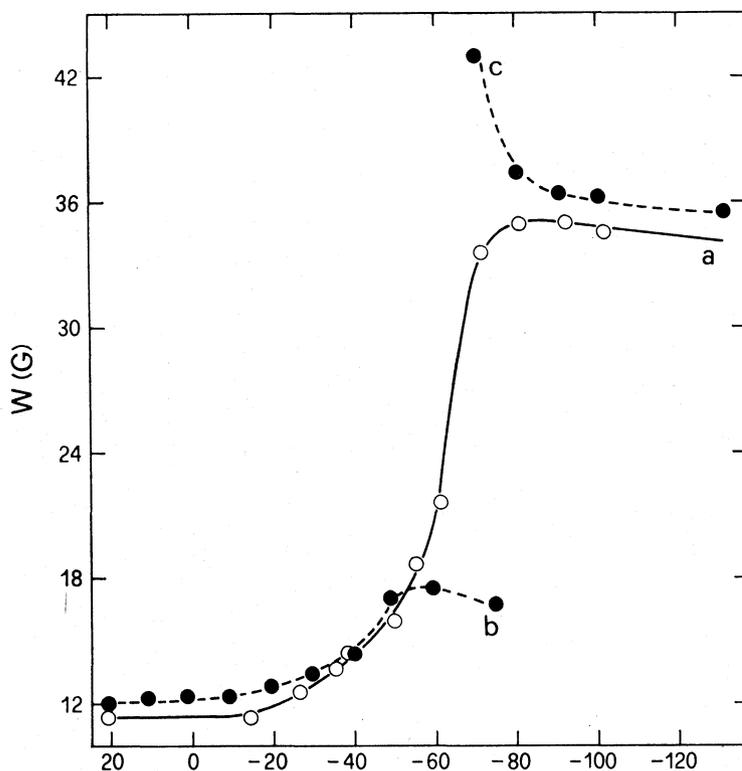


Fig. 2. - Experimental line-widths vs. temperature obtained with a sample 0.27 mol l^{-1} : *a*) when the phase transition normally occur; *b*) ^{96}Mo singlet line-width when the temperature is lowered very slowly. Underfreezing situation is also represented; *c*) line-width of the singlet which is the only spectrum obtained by raising very slowly the temperature starting from $-130 \text{ }^{\circ}\text{C}$.

Line-width measurements have been repeated with frozen samples (at the concentration values of 0.27 mol l^{-1} and of 0.019 mol l^{-1}). In every case a low reproducibility of the line-width trend with temperature has been observed. Sets of twelve spectra at $-100 \text{ }^{\circ}\text{C}$ have also been detected with samples 0.27 mol l^{-1} and 0.019 mol l^{-1} . The mean values of line-width in these two cases

are of $37.47 + - .04$ G and of $45.2 + - .1$ G respectively. The maximum value of the difference between the line-width of two such spectra are of .5 G and 1.5 G respectively. In every case the spectral areas have been measured but no regular or reproducible trend with temperature has been observed, at variance with the case reported in reference [5]. Furthermore, differences between areas measured at different temperatures are of the same order of magnitude as differences between different measurements accomplished at the same temperature (-100 °C), and so they cannot be attributed to the different temperatures at which the spectra have been detected.

DISCUSSION

The irreproducibility of the trend with temperature of the line-width can perhaps be attributed to the different non-controllable delays spent by the system to attain the desired temperature in each experiment. In fact the freezing speed greatly influences the observed effects [3] together with the thermal properties of the tube containing the sample and with the thermal properties of conduction of latent heat of fusion into the liquid [2].

The only other case, to our knowledge, of an EPR spectrum of a Molybdenum compound in frozen solution which is composed by just one symmetric line is the one of $P Mo^V Mo_{11} O_{40}^{4-}$ between 77 K and 298 K reported in reference [13], where a model has been proposed in which the unpaired electron undergoes a rapid "hopping" delocalization, but this model was unable to account for all experimental data therein reported. On the other hand the fact that in our case the line-width decreases with the sample concentration between 0.019 mol l^{-1} and 0.27 mol l^{-1} leads also to the exclusion of a model such as the one proposed for $Cu (H_2O)_6^{2+}$ for which [14] isotropic thermal exchange between three equivalent Jahn-Teller distorted states are sufficiently rapid above 50 K to give a single EPR line. The present case appears more similar to the one found in literature for EPR spectra in liquid solutions of the radical di-t-butyl nitroxide (DTBN) in dimethylformamide [15]. In that case a line narrowing proportional to sample concentrations (when lower than 1 mol l^{-1}), due to spin-spin exchange was observed, and a dipolar broadening at higher concentrations. This could be also our case in which the paramagnetic particles may be located near one another in the frozen solution forming stochastic (random) clusters-couples, triples, etc., depending also on the concentration of the sample. The contribution $(T_2^{-1})^*$ to line-width not directly due to spin exchange, but caused by the magnetic dipole, anisotropic Zeeman, anisotropic hyperfine and isotropic hyperfine interactions, can be expressed through the relation:

$$(1) \quad (T_2^{-1})^* = (T_2^{-1})_{ss} + (T_2^{-1})_z^a + (T_2^{-1})_{hf}^a + (T_2^{-1})_{hf}^i$$

where the first term at right (due to magnetic dipole interaction) is increasing

with the concentration but in the present case it has a negligible effect with respect to the spin exchange contribution at concentration between 0.019 and 0.27 mol l⁻¹.

The general expression for the terms at right in the eq. (1) are reported elsewhere [4]; here we outline that all of them are dependent on an effective time of correlation specific of each contribution, which, in general, depends on the Brownian rotation time of the complex τ_c and on the frequency of the spin exchange ω_e . It has been also reported that such a correlation time is not greater than τ_c for dipole interaction, anisotropic Zeeman and anisotropic hyperfine interactions.

Furthermore the experimental spectrum in the present case is composed of just one lorentzian-shaped line, and so we must hypothesize that the two last contributions in the eq. (1) must be neglected. Otherwise two different lines with the same g value but different widths would be detected due to the magnetically different Mo isotopes. Since anisotropy of the g factor is not observed experimentally in this work, the following condition must also be satisfied:

$$(2) \quad \tau_c^{-1} g \gg (g_{\parallel} - g_{\perp}) \beta H_0 / \hbar .$$

Substituting into the eq. (2) the values of the magnetic parameters reported elsewhere [10] for the compound here investigated we obtain:

$$(3) \quad \tau_c \ll 4 \cdot 10^{-10} \text{ s} .$$

A similar result has been also reported in literature [4] for a concentrated liquid solution of divalent copper complexes with nitrogen-containing ligands.

Finally the observed line widths in the region of the exchange narrowing (that is at least between 0.019 mol l⁻¹ and 0.27 mol l⁻¹ in our case) can be expressed through the equation [7]:

$$(4) \quad \Delta H = \Delta H_0 + A/C$$

where the parameters ΔH_0 and A are generally independent of the concentration C and of the temperature. The observed variations in the line widths must be then just attributed to variations of the local concentration of the paramagnetic molecules eventually produced by the variation of the temperature, but not directly to this variation. In particular it is possible to evaluate the parameters ΔH_0 and A by the experimental values of ΔH obtained as the mean values of the line widths of twelve spectra detected at -100 °C with the sample 0.019 mol l⁻¹ and with the sample 0.27 mol l⁻¹. In this way we obtain: $\Delta H_0 \cong 37.$; $A \cong 0.16$.

The observed behaviour of the line-width in frozen solution (with sample 0.27 mol l⁻¹) (see the right side of fig. 2) can also be described through a "Cuspid Catastrophe" model [16] in which the two controlling factors are the sample temperature and the dilution in the liquid solution cells contained in the sol-

vent frozen bulk (see fig. 3). When we start our measurements from the lowest possible temperature, more different concentration values are possible in the cells, due to the freezing speed of the sample and to the other above-mentioned factors. On the right side of the fig. 2 two different situations of this kind are shown. When temperature is raised (starting from its lowest value) some more frozen solvent molecules melt and the liquid cells become less concentrat-

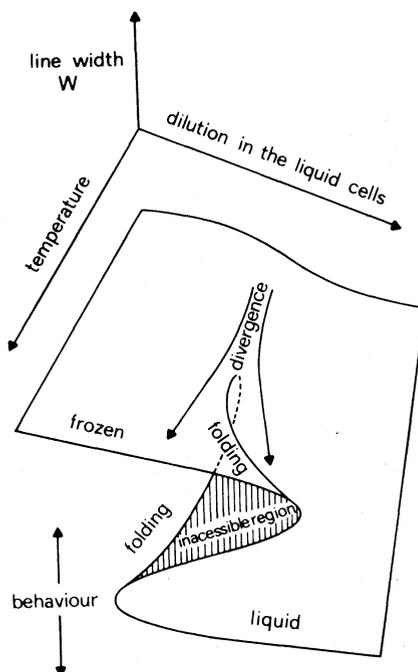


Fig. 3. — The « Cusp Catastrophe model » applied to the observed phase transition behaviour.

ed. In the situation reported in fig. 2 *a* (less concentrated cells at starting lowest temperature), a further dilution (via temperature raising) yields a loss in the spin-exchange narrowing effect and a little line broadening is observed. When the phase transition temperature is attained, the dipolar broadening effect also disappears and the rotational diffusion narrowing effect in the liquid solution is observed. The line broadening due to the loss of the spin-exchange narrowing effect is more dramatic with more concentrated cells (fig. 2 *c*). In this case the overmelted situation can also be observed; in fact a static and no more a collisional spin-exchange mechanism would better account for the experimental observations. This hypothesis could be also suggested by the following further result. We prepared two identical samples 0.38 mol l^{-1} concentrated and just with one of them we detected at room temperature an EPR pattern composed of one broad lorentzian line-whose line-width was of $43.8 \pm .1 \text{ G}$, at variance with the regular spectrum [11] shown by the other sample (singlet line-width of $13.22 \pm .04 \text{ G}$). Two months later the former sample showed

two EPR lines corresponding to the two principal g values of the powder compound (fig. 4), though it was again in liquid (or gel) limpid solution; however this pattern disappeared when the sample was shaken. This fact could be interpreted on the ground that at high concentration values dimerization or cluster formation have a high probability of occurring (also at room temperature) and that many phenomena of different kind contribute to the observed EPR patterns.

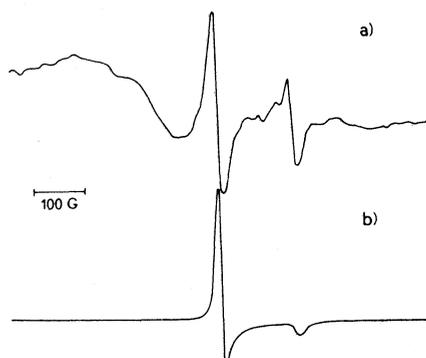


Fig. 4. — Observed EPR spectra at room temperature (a) with a sample in acetonitrile 0.38 mol l^{-1} concentrated, two months after its preparation, and (b) with a powder sample.

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