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ELECTRON PARAMAGNETIC RESONANCE IN COMPOUNDS OF DIVALENT SILVER

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Of the compounds of divalent silver ($4d^9$; $S = 1/2$), crystalline powders of several complex compounds ($^{1-3}$), as well as liquid and frozen solutions of salts (^{3,4}), have so far been studied by the EPR method. These studies made it possible in a number of cases to determine the principal values of the g-tensor of the Ag(II) ion and to find the constants of the hyperfine structure of the EPR line caused by the nuclear spins of the isotopes Ag^{107} and Ag^{109}. A number of questions, however, remained unresolved. In particular, no direct experimental evidence was obtained for the presence of a strong covalent bond of divalent silver with ligands, proposed by Bowers for $[Ag(Py)_4]S_2O_8$ (^{1}). Nor was the presence of strong exchange interactions between $4d$ electrons, which might be expected by analogy with compounds of divalent copper, established.

In crystalline powder $Ag(C_5H_5N)_4S_2O_8$, at a frequency $\nu = 450$ MHz and at 77°K, a single peak is observed with $g = 2.15$ and $\delta H = 26$ oersted. The line shape is close to Lorentzian; the ratio of the fourth moment to the second is 1.47. Upon heating to room temperature the line shape does not change appreciably, while the width increases to 40 oersted. These data indicate the undoubted presence of exchange interactions between $4d$ electrons in the Ag(II) compound studied. This conclusion is confirmed by the complete absence of any dependence of the paramagnetic absorption coefficient on the strength of the constant magnetic field, in the frequency range from 10 to 300 MHz. The absence of an effect in parallel fields is characteristic of substances with strong exchange, for which the spin-lattice relaxation time $T_1 \approx T_2$. For our compound, at 77°K, $T_2 = 3.5 \cdot 10^{-9}$ sec, and at 295°K, $T_2 = 1.6 \cdot 10^{-9}$ sec; T_1 for the same temperatures should be only slightly longer than the corresponding values of T_2. The dependence of T_2 on temperature is apparently connected with a change in the parameters of the crystal lattice of the substance (^{5}). At a frequency of 9320 MHz in $Ag(C_5H_5N)_4S_2O_8$, a broad asymmetric line is observed (see Fig. 1a). From analysis of the shape of this line, the values $g_\parallel = 2.17 \pm 0.01$ and $g_\perp = 2.08 \pm 0.01$, identical for 77°K and 295°K, were estimated. It should be noted that even moderately reliable results can be obtained only in finely dispersed powders. Exchange narrowing at a frequency of 9320 MHz is masked by broadening of the lines due to anisotropy of the g-factor. Investigation of dilute aqueous solutions of $Ag(C_5H_5N)_4S_2O_8$ proved possible only upon cooling them to 77°K. In the frozen aqueous solution, a considerable fraction of the complex silver ions enters persulfate crystals, but a certain proportion of these ions remains in a state isolated from one another. As a result, at a frequency of 9320 MHz a complex spectrum is observed, consisting of a broad asymmetric curve with $g_{\|} = 2.16 \pm 0.01$ and $g_{\perp} = 2.06 \pm 0.01$ (the crystalline part of the persulfate). Superposed on this curve are peaks of the hyperfine structure (supercooled persulfate solution).

The h.f.s. peaks are readily observed only on the line corresponding to $g_{\perp}$; as for the hyperfine components of the line corresponding to $g_{\|}$, their low intensity does not permit them to be detected. As can be seen from Fig. 1b, the hyperfine structure consists of 11 clearly resolved components, the components equidistant from the edges of the spectrum having approximately the same intensity.

Since the nuclei of the isotopes Ag^{107} and Ag^{109} have spin $I = 1/2$ and magnetic moments not very different from one another (0.1135 and 0.1305 n.m., respectively), the spectrum can be explained only by assuming a strong covalent bond of the Ag(II) ion with 4 pyridine molecules, each of which contains 1 nitrogen atom with $I = 1$. The distance between neighboring peaks at the edges of the spectrum, equal to 24 oersted, characterizes the h.f.s. constant due to the spins of the N^{14} nuclei.

Assuming all pyridine molecules to be equivalent, one would expect the appearance of $(2I_{\mathrm{Ag}} + 1)(2I_{\mathrm{N}} + 1) = 18$ hyperfine components. However, if the mean hyperfine-structure constant A for the $Ag^{107,109}$ nuclei is close in magnitude to twice the value of the hyperfine-structure constant A' for the N^{14} nuclei, then instead of 18 peaks we should have 11, which is in fact observed experimentally. However, the impossibility of verifying this conclusion from the intensities of the components makes it not entirely reliable. Attempts to obtain a solid solution of $Ag(Py)_4S_2O_8$ by dilution with the isomorphous salt $Cd(Py)_4S_2O_8$ in ratios of 1:1, 1:10, and 1:500 were unsuccessful. In the mixed salts obtained, at 77°K and frequency $\nu = 9320$ MHz, the hyperfine structure is not resolved. At a frequency of $\nu = 450$ MHz at 77°K, the single absorption line undergoes only slight broadening compared with the undiluted salt. Meanwhile, in the presence of appreciable exchange, even slight dilution should lead to strong broadening of the line and, subsequently, to the appearance of hyperfine structure. Therefore it must be assumed that we did not succeed in obtaining a homogeneous solid solution of $Cd(Py)_4S_2O_8$ and $Ag(Py)_4S_2O_8$.

Fig. 1. E.p.r. lines at $\nu = 9320$ MHz: *a*—in polycrystalline powder $Ag(Py)_4S_2O_8$; *b*—in frozen aqueous solution $[Ag(Py)_4]S_2O_8$; *c*—aqueous solution of $Ag(ClO_4)_2$; *d*—supercooled solution of $Ag(ClO_4)_2 \cdot xH_2O$ in hydrochloric acid.

From the same considerations it follows that the indicated solid solution was not obtained by the authors of work (^{2}) either. At a frequency of 9320 MHz, at room temperature, in liquid solutions of $Ag(NO_3)_2$ and $Ag(ClO_4)_2$ in the corresponding acids, a single absorption line is observed with g-factors 2.165 and

2.160, respectively (see Fig. 1c). The line width δH for a solution of $Ag(NO_3)_2$ in $10\,M$ nitric acid at 295°K is 62 oersted; for a solution of $Ag(ClO_4)_2$ in $5\,M$ hydrochloric acid, 65 oersted. In supercooled dilute solutions of $Ag(NO_3)_2 \cdot xH_2O$ in $10\,M$ nitric acid and in $5\,M$ hydrochloric acid, at a frequency of 450 MHz at 77°K, a hyperfine structure is observed in the form of a well-resolved doublet with a constant of 37 oersted and with $g = 2.17$. The strong-field condition is satisfied even at a frequency of 270 MHz. At a frequency of 9320 MHz an anisotropic spectrum arises (see Fig. 1d), described by the spin-Ha

Hamiltonian:

$$H = g_{\|}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y),$$

where $S = 1/2$, $I = 1/2$, $A_{\text{av}} = 45$ Oe, $B_{\text{av}} = 30$ Oe, $g_{\perp} = 2.069$, $g_{\|} = 2.341$ for $Ag(NO_3)_2 \cdot xH_2O$; for $Ag(ClO_4)_2 \cdot xH_2O$ the constants have the following values: $A_{\text{av}} = 47$ Oe, $B_{\text{av}} = 29$ Oe, $g_{\perp} = 2.071$, and $g_{\|} = 2.337$.

In liquid solutions, at a not very high viscosity, a line with an averaged g-factor equal to $g_{\text{av}} = \frac{1}{3}(g_{\|} + 2g_{\perp})$ should be observed, if the electric fields acting on the paramagnetic ion do not change substantially on going from the liquid to the supercooled state. This is the case, for example, for vanadyl compounds VO^{2+}, where the principal part of the axial field is produced by the bond of vanadium with oxygen. In our case, for $Ag(NO_3)_2$, $g_{\text{av}} = (2.341 + 2 \cdot 2.069) = 2.193$, which differs strongly from the value observed for the liquid, $g = 2.165$. This difference shows that the local electric fields change appreciably in the transition from the liquid state to the supercooled state.

The experimental values we obtained for the g-factors of divalent silver nitrate differ noticeably from the data of Ref. (^{4}). We tried to explain this discrepancy by differences in the acidity of the solutions used. However, changing the concentration of HNO_3 from $10\,M$ to $2.5\,M$ in 1 liter led only to splitting of the hyperfine components of the EPR line; the value of the g-factors did not change.

It follows from the results presented in this work that the EPR spectra in divalent silver compounds show a deep analogy with the EPR spectra in divalent copper compounds $(3d^9, S = 1/2)$. The following features of similarity may be noted: 1. In magnetically concentrated compounds of both ions, strong exchange interactions between d-electrons are observed. 2. In compounds of both ions there is a strong anisotropy of the g-factors. 3. In complex Ag(II) ions with covalently bonded pyridine molecules, a hyperfine structure due to nitrogen nuclei is observed, similar to that recently found for one of the copper compounds (^{6}).

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Note: Figure translations are in progress. See original paper for figures.