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Coprecipitation of a rhodium(VI) oxo hydroxo complex with lithium fluoride

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A matrix system based on lithium fluoride with the $[Rh^{VI}O_2(OH)_4]^{2-}$ dopant ion has been synthesised and studied by ESR and diffuse reflectance spectroscopies.

The possibility of stabilising the highest oxidation states of transition elements is of considerable interest.[1–3] The attention of researchers was focused on Group VIII element derivatives. The highest oxidation states of iron, cobalt, platinum and rhodium were considered elsewhere.[4–7] A matrix system implies a solid compound including doping ions or molecules; the dopant can be located both at lattice sites and in various defects. We consider an increase in the life time of unstable ions or molecules in comparison with those in solutions as the main criterion of successful ‘stabilisation’ in these systems.

The solid-phase synthesis of matrix systems involves the sintering of reagents; however, it is obvious[8] that the higher the sintering temperature, the lower the oxidation state of the ion to be stabilised.

Coprecipitation is another approach to the formation of matrix systems.[9] In this case, constitutional substitution is possible, *e.g.*, for the stabilisation of metal ions that form aqua ions in solutions. For example, this version is implemented in $M^{II}Cl_2$, where M = Ca, Sr, or Ba, and divalent actinide ions act as dopants.[10]

The distinctive feature of the coprecipitation method is that it is applicable to the stabilisation of unstable oxidation states of metals. Previously,[11] we found the formation of the $[RhO_2(OH)_4]^{2-}$ complex, which exists only in strongly alkaline media and in an excess of a strong oxidant. All attempts to concentrate and isolate it from solution as insoluble compounds resulted in the decomposition of the rhodium(VI) complex and the formation of a rhodium(III) superoxo complex.

We encountered this situation in a study of the stabilisation of $[RhO_2(OH)_4]^{2-}$ ions in a lithium fluoride matrix.[12,13] The aim of this work was to study this matrix system and to discuss the distribution of the $[RhO_2(OH)_4]^{2-}$ complex in a LiF crystal (NaCl structure).

The ESR spectra were recorded on a Varian E4 radiofrequency spectrometer in the X-range. Electronic absorption spectra were recorded on an SF-2000 spectrophotometer (200–1100 nm; quartz cells with $l = 10$ mm). Diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda-35 instrument. X-ray diffraction diagrams were obtained on a DRON-3M diffractometer (CuKα radiation, Ni filter).

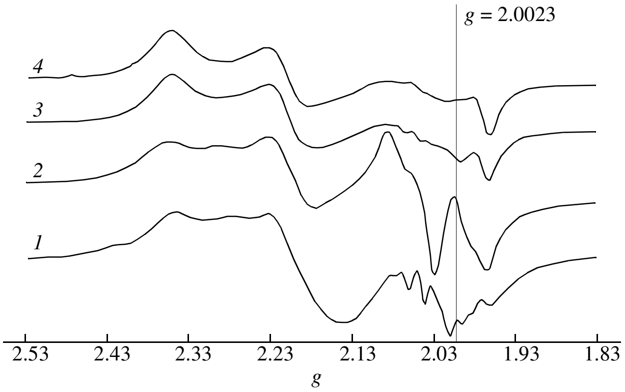

Figure 1 Typical ESR spectra of matrices based on LiF obtained by different procedures for the introduction of fluoride ions: (*1*) KBF_3OH, hydrolysis, (*2*) Na_2SiF_6, hydrolysis, (*3*) dropwise mixing (τ ~ 1–3 h), (*4*) quick mixing (τ ~ 5–10 min).

We attempted to obtain a polycrystalline matrix system with crystals of different sizes. Two methods were used for this purpose: (i) the isothermal evaporation of a solution containing all the components of the desired matrix system; (ii) the controlled addition of the precipitating ion (F^-) to the starting lithium-containing solution.

The former approach was implemented by evaporation of a LiOH solution saturated with LiF and containing the $[RhO_2(OH)_4]^{2-}$ complex in the presence of an excess of BrO^- in a vacuum desiccator with P_4O_{10}. The crystals of a matrix system are precipitated; however, a considerable amount of an X-ray amorphous Rh^{III} superoxo complex, which is formed due to decomposition of the $[RhO_2(OH)_4]^{2-}$ complex, was precipitated simultaneously.

In the latter approach, matrix systems based on LiF were obtained according to the following procedure: a precipitating agent, *viz.*, the F^- ion, was added to a LiOH solution containing the $[RhO_2(OH)_4]^{2-}$ complex and an excess of the BrO^- ion. The coloured crystals that precipitated were separated from the solution, washed with a KOH solution and then with ethanol, and dried in a vacuum desiccator over P_4O_{10}. Note that ethanol reduces rhodium complexes, which exist in alkaline media, to the metal, but the matrix systems obtained remained unchanged on treatment with ethanol.

In order to precipitate matrix systems, a known amount of the fluoride ion was added to a solution of the Rh^{VI} complex over a definite period of time: either the F^- ion from a KF solution in KOH or the F^- ion formed due to alkaline hydrolysis of fluorides. The following fluorides were used: Na_2SiF_6, Li_2SiF_6, KBF_4 and KBF_3OH (KBF_3OH was obtained by the reaction[14] of a saturated KHF_2 solution with H_3BO_3).

If Li_2SiF_6 was used, the formation of a LiF precipitate occurred after the solutions were poured together. The hydrolysis of KBF_4 occurred slowly so that an exposure for one week did not result in a considerable amount of LiF. KBF_3OH was hydrolysed in KOH noticeably faster than KBF_4, which allowed us to obtain sufficiently large crystals; the same is true for Na_2SiF_6. In this approach, the precipitation takes about one week. According to microscopic data, the crystallite size does not exceed 100 μm.

Precipitation with a solution of KF in KOH for 10 min to 2 h followed by drying gives a coloured powder with a crystallite size of no higher than 700 nm.

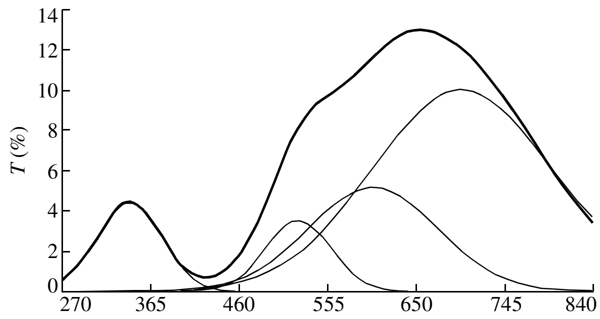

Figure 2 Diffuse reflectance spectrum deconvolution after matrix precipitation (at 20 °C).

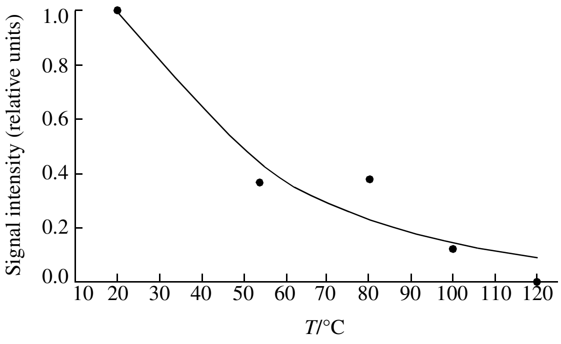

Figure 3 Relative changes in the absorption band intensity of the Rh^{VI} complex in a LiF matrix in electronic absorption spectra as a function of temperature.

A comparison of different procedures showed that the concentration of the Rh^{III} superoxo complex in the samples correlated with the duration of the matrix system preparation.

Figure 1 shows the ESR spectra of solid samples obtained using different approaches; the main signal corresponds to the Rh^{VI} complex [$g_1 = 2.353(2)$, $g_2 = 2.205(1)$, $g_3 = 1.959(1)$]. The *g*-tensor parameters observed are close to those of the Rh^{VI} complex in solution[11] [$g_1 = 2.349(1)$, $g_2 = 2.194(1)$ and $g_3 = 1.973(1)$]. This allows us to believe that the $Rh[O_2(OH)_4]^{2-}$ complex occurred in matrix systems based on lithium fluoride. The use of sodium fluorosilicate as a source of F^- results in a maximum concentration of the rhodium(III) superoxo complex (Figure 1) [$g_1 = 2.093(5)$, $g_2 = 2.043(5)$ and $g_3 = 2.008(8)$].

Thus, attempts to increase the crystallite size by using longer exposures resulted in crystallites up to 100 nm large, but this increased the amount of the rhodium(III) superoxo complex.

The thermal stability of the matrix system based on lithium fluoride was analysed by ESR and diffuse reflectance spectroscopies.

Samples of the LiF:Rh^{VI} system were kept at different temperatures. The starting sample was obtained by the dropwise mixing of KF and LiOH solutions in the presence of $[RhO_2(OH)_4]^{2-}$; the precipitate was dried over P_4O_{10} for 24 h (the rhodium content of the samples was ~1%). After that, 0.2 g portions were kept in air at a specifical temperature (54, 80, 100, 120, 300 or 600 °C) for 30 min. Weight losses were not recorded. According to powder X-ray diffractometry data, all the samples had the same unit cell parameters to within the measurement error (Table 1).

Figure 2 displays the diffuse reflectance spectrum of the matrix immediately after the precipitation with decomposition into Gaussian components. Absorption band assignments were similar to those made elsewhere.[11,15] Since the ESR spectra of the Rh^{VI} complex in a lithium fluoride matrix and in an aqueous solution are almost identical, we can expect that the absorption bands would shift insignificantly on the passage of the complex from a solution to a solid phase. Therefore, we assign the absorption band at 525 nm to the $[RhO_2(OH)_4]^{2-}$ ion. The intensity of this band decreases with temperature (*T*/°C) under the conditions of these experiments (Figure 3). This is probably due to the decomposition of the complex and correlates with ESR data (Figure 4).

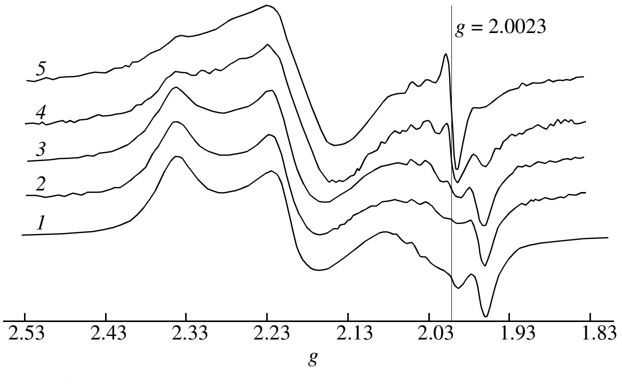

Figure 4 ESR spectra of lithium fluoride samples containing the rhodium complex kept at different temperatures: (*1*) 20, (*2*) 55, (*3*) 80, (*4*) 100 and (*5*) 120 °C.

Table 1 Unit cell parameters of samples obtained by the coprecipitation of LiF and Rh^{VI} complexes and kept at different temperatures.

T/°C	*a*/Å
20[a]	4.035(1)
20	4.039(2)
54	4.039(1)
80	4.040(1)
100	4.040(1)
120	4.038(1)

[a] The sample was obtained by coprecipitation in the absence of rhodium complexes.

Figure 4 shows the ESR spectra of the samples. It is evident that the only signal present in the ESR spectrum immediately after the formation of the precipitate corresponds to the Rh^{VI} complex. Heating to 80 °C does not change the ESR spectrum significantly. Changes in the signal shape are observed only for samples heated to higher temperatures; the signal disappears completely on heating to 300 °C. This is obviously due to the complete conversion of the $[RhO_2(OH)_4]^{2-}$ complex into diamagnetic Rh^{III} compounds that cannot be detected by ESR spectroscopy.

In order to determine the localisation of the Rh^{VI} complex in the matrix system and taking into consideration published data[16] we studied the dissolution of the matrix systems in H_2O_2 and HCl. The amount of the rhodium(VI) complex in a sample was determined from the intensity of ESR signals, since Rh^{VI} stabilised in LiF is paramagnetic but is converted into diamagnetic Rh^{III} upon reduction (by hydrogen peroxide or the chloride ion).

A solid sample was placed in a quartz tube, and an H_2O_2 solution was added. The tube was cooled to 77 K, and the ESR spectrum was recorded. After that, the tube with the compound was unfrozen and a new portion of H_2O_2 was added; the tube was kept for 10 min at room temperature and frozen again. A spectrum was recorded, *etc*.

Figure 5 shows the dependence of the ESR signal intensity on the H_2O_2 volume added. The signal of the Rh^{VI} complex is observed in the spectrum until the compound is dissolved completely. This suggests that the admixture is incorporated into the lithium fluoride lattice during the precipitation rather than concentrated on the crystal surfaces, as it was observed, *e.g.*, during the coprecipitation of the same Rh^{VI} complex with alkaline-earth tungstates and molybdates.[17] If the Rh^{VI} is distributed on the surface, treatment of the matrix system with H_2O_2 results in the instantaneous reduction of Rh^{VI} into Rh^{III} and in the disappearance of ESR signals.

It is well known that the width of an ESR line is determined by spin–spin relaxation (interaction between magnetic centres) and spin–lattice relaxation (interaction of magnetic centres with the crystal lattice). The spin–spin interaction in magnetically diluted systems should not vary considerably in the range 77–300 K,[18] whereas the spin–lattice relaxation should increase

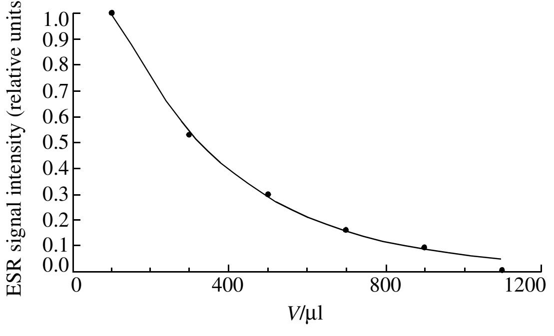

Figure 5 Relative change in the concentration of the Rh^{VI} complex in a LiF sample as a function of the volume of hydrogen peroxide added.

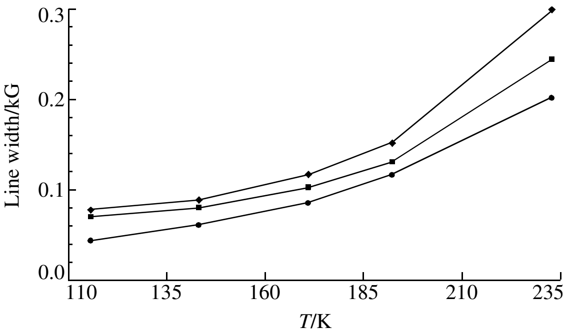

Figure 6 The temperature dependence of the widths of ESR signal components of the Rh^{VI} complex in a lithium fluoride matrix.

with temperature, which should result in a considerable line broadening.

Figure 6 demonstrates the dependence of the widths of three ESR signal components for the Rh^{VI} complex in the LiF matrix on temperature (in the range 115–235 K). The line widths in the spectrum cannot be determined at higher temperatures because it is impossible to resolve line components in the spectrum mathematically.

The above results suggest that $[RhO_2(OH)_4]^{2-}$ ions are arranged on the surface of LiF crystals. Two variants of distribution in the bulk of the crystals should be discussed: constitutional substitution (*e.g.*, when a solid solution is formed) and the concentrating of paramagnetic species near crystal lattice extended defects.

If a solid solution is formed and the dopant is distributed statistically, the local concentration of the dopant approximately equals its mean concentration in the crystal. In this case, a noticeable line broadening in the ESR spectrum due to spin–spin coupling can be expected at concentrations of paramagnetic species above 1%. If the dopant is preferentially distributed near extended defects, the local concentration of the dopant can considerably exceed its mean value. Thus, if the dopant is distributed near defects, spin-spin relaxation should affect the line width in the ESR spectrum even at a low mean dopant content, since the distance between the magnetic centres is small. Accordingly, the threshold total concentration starting from which dilution does not affect the line width is much lower than that for a solid solution. Figure 7 shows the concentration dependence of line widths in the ESR spectrum. One can see that the widths of different components of the signal of the Rh^{VI} complex do not change within the calculation error. Data presented in Figure 6 suggest that the model involving a statistical distribution of doping ions in the LiF lattice should be preferred. They support the assumption that the rhodium(VI) complex forms a solid solution in the lithium fluoride matrix.

It can be assumed that a $[LiF_6]^{5-}$ fragment is replaced by an octahedral Rh^{VI} complex with charge neutralization by the replacement of some F^- ions by O^{2-} ions. The size of the octahedral rhodium complex is close to that of the $[LiF_6]^{5-}$ fragment, which makes this assumption quite probable. The fact that crystal lattice parameters do not depend on the rhodium complex content of the matrix can be due to (i) a small rhodium content (~1%), and (ii) the similarity of the fragment sizes noted above.

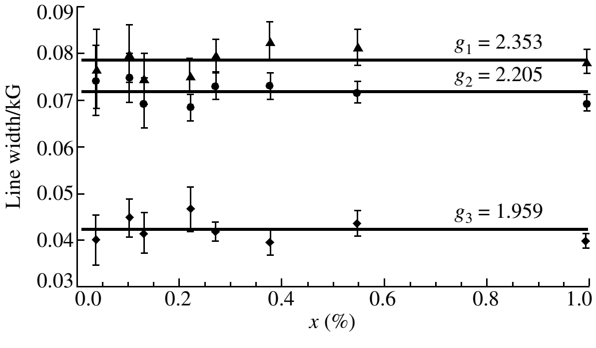

Figure 7 The concentration dependence of the line width in the ESR spectrum of the Rh^{VI} complex in LiF matrix for different signal components: $g_1 = 2.353(2)$, $g_2 = 2.205(1)$, $g_3 = 1.959(1)$ (solid lines indicate the mean values).

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