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Stabilisation of a rhodium(V) complex in the matrix of NaF

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The NaF:Rh^V matrix system was synthesised and studied by ESR and diffuse reflectance spectroscopies.

An experimental method used to increase the stability of metal ions (or complexes) in unusual oxidation states existing in solutions involves their transfer to a solid phase.[1,2] Coprecipitation methods giving so-called matrix systems[3] are popular for the stabilisation of low oxidation states. These methods have almost never been used for the derivatives of platinum metals in the highest oxidation states. Recently, we studied[4] the cocrystallization of a Rh^{VI}–LiF complex. We also presented procedures for the synthesis of this solid system and the results of its study by ESR and diffuse reflectance spectroscopies. Signal intensities in the ESR spectra of the Rh^{VI} complex as a function of the volume of a reducing agent showed that the complex was incorporated into the LiF lattice. The properties of the samples allowed us to state that the stabilisation of the Rh^{VI} complex, which is unstable in solution, can be achieved by its incorporation into a solid phase.

In continuation of this work, we studied the incorporation of a rhodium complex into the NaF lattice, which has the same structural type as LiF (NaCl structure) and found considerable differences between the two matrix systems. This primarily concerns the fact that coprecipitation with NaF is accompanied by selective precipitation of the Rh^V complex from solution, whereas quantitative precipitation of rhodium occurs from the same solution system in the case of LiF. The results obtained are presented in this work.

ESR spectra were recorded on a Varian E4 radio-frequency spectrometer in the X-range. Electronic absorption spectra were recorded on an SF-2000 spectrophotometer (wavelength range 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 (Bregg-Brentano geometry, CuKα radiation, Ni filter).

Since NaF is readily soluble (4.28 g in 100 g of water at 20 °C), matrix systems were obtained by mixing concentrated NaOH solutions and a precipitating agent. For example, a saturated KF solution in KOH (~10 mol dm^{-3}) was added to a NaOH solution (~10 mol dm^{-3}) containing a Rh^{VI} complex in the presence of an excess hypobromite ions. The resulting blue or dark blue precipitate was separated from the mother liquor by centrifugation, washed with ethanol and dried over P_4O_{10} in a exsiccator. Attempts were also made to add dropwise NaOH and KF solutions to a KOH solution (~10 mol dm^{-3}) containing Rh^{VI} complexes.

As opposed to the LiF:Rh^{VI} matrix, the ESR spectrum of the NaF:Rh matrix (recorded after a few days since it had been synthesised) either does not contain any lines or contains only a signal from the Rh^{III} superoxo complex.[†] It was found that, like the LiF-based matrix, the parameters of the ESR signal from the Rh^{III} superoxo complex admixture depend on the precipitation time of the matrix system. After a time, the ‘diamagnetic’ sample kept at room temperature starts to show signals, one of which is characteristic of the $[RhO_2(OH)_4]^{2-}$ complex, similarly to that observed for the LiF:Rh^{VI} matrix, while the other is typical of the rhodium(III) superoxo complex.

According to powder X-ray diffraction data, the unit cell parameter of sodium fluoride (Table 1) does not depend on the rhodium content of the samples.

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

Temperature/°C	*a*/Å
20[a]	4.633(1)
20	4.635(1)
54	4.636(1)
71	4.634(1)
94	4.634(1)
120	4.634(1)
300	4.634(2)

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

The thermal stability of the matrix system based on sodium fluoride was analysed based on ESR and diffuse reflectance spectroscopic data.

We obtained a series of rhodium-containing NaF samples exposed to air at specified temperatures (70, 95, 120, 140 and 300 °C). The exposure was 30 min; the weight of each sample was 0.25 g (weight loss was not recorded). Figure 1 displays the diffuse reflectance spectra; Table 2 shows the results of decomposing the spectra into Gaussian components. One can see that solid samples taken for the study contain several complexes; according to published data,[4] one of these is a Rh^V complex. An increase in the temperature to 70 °C results in a decrease in the intensity of the absorption band of this complex with a simultaneous change in the intensity ratio of all the observed absorption bands, while the concentration of the rhodium(VI) complex changes insignificantly. Subsequent changes in the intensities of absorption bands suggest that the thermal stability of the Rh^V complex is higher than that of the Rh^{VI} complex. The above changes can be associated with disproportionation of the Rh^V complex. According to the data of electronic reflection spectroscopy, the main difference from the LiF:Rh^{VI} matrix is that an increase in the temperature results in an increase in the intensity of an absorption band (at 620 nm). Judging by the position of the line in the diffuse

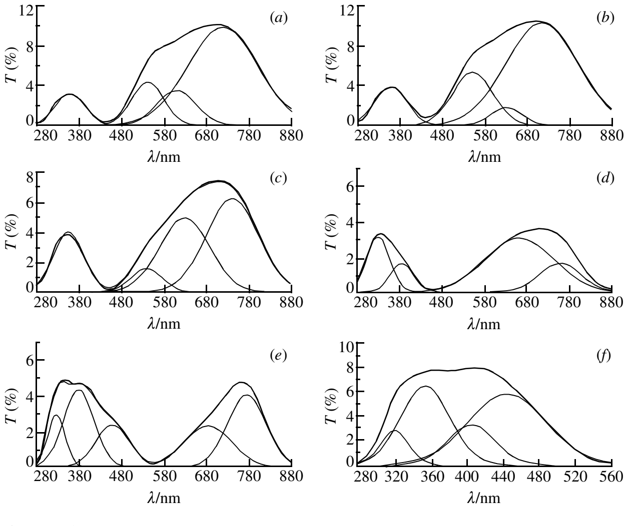

Figure 1 Diffuse reflectance spectra of matrix systems based on NaF kept for a week in air at room temperature (*a*) and for 30 min at temperatures of (*b*) 70, (*c*) 95, (*d*) 120, (*e*) 140 and (*f*) 300 °C.

[†] Small amounts of the Rh^{III} superoxo complex is often present in solution from which the matrix system is precipitated.

Table 2 Decomposition of diffuse reflectance spectra for samples kept at different temperatures.

T/°C	Signal	λ/nm	ε/cm^{-1}	I
20	I	718	13928	2052
	II	610	16393	405
	III	541	18484	415
	IV	358	27933	284
71	I	716	13966	2275
	II	631	15848	280
	III	541	18484	554
	IV	359	27855	439
94	I	744	13441	968
	II	631	15848	738
	III	540	18519	146
	IV	357	28011	367
120	I	759	13175	209
	II	663	15083	646
	III	386	25907	113
	IV	332	30120	222
140	I	776	12887	456
	II	687	14556	322
	III	466	21459	230
	IV	388	25773	389
	V	336	29762	152
300	I	444	22523	614
	II	404	24752	207
	III	353	28329	435
	IV	319	31348	106

reflectance spectrum, the final decomposition products are identical for NaF and LiF matrices.

Figure 2 displays a series of ESR spectra for the samples obtained. A sample undergoes insignificant changes at temperatures up to ~70 °C; the intensity of the ESR signal decreases strongly at higher temperatures probably due to decomposition. Heating to 300 °C results in the complete disappearance of signals from the ESR spectrum, obviously due to the complete decomposition of paramagnetic rhodium complexes into Rh$^{\mathrm{III}}$ compounds that do not give ESR signals.

Dissolution in the presence of H_2O_2 was studied by ESR spectroscopy with samples stored in air at room temperature before the measurements. The measurement procedure is similar to that used for the LiF-based matrix system. Like in the case of LiF:Rh$^{\mathrm{VI}}$,[4] the concentration of paramagnetic centres decreases slowly as the solvent amount increases. The ESR signal disappears only after the complete dissolution of the sample, which suggests that the dopant is distributed in the bulk of the solid sample rather than on the powder surface.

Matrices based on NaF differ from the other compounds studied previously[4–6] as deposition from a solution containing a paramagnetic complex results in a precipitate, which does not give an ESR signal. The absence of the signal from the ESR spectrum can result from several reasons: i, the absence of paramagnetic centres from the system; ii, strong broadening of spectral lines due to spin–spin coupling; iii, considerable splitting in zero field (provided that the spin of the dopant is $S > 1/2$). If the signal is originally absent due to the first or third reason, the appearance of the signal can obviously be explained by disproportionation; hence, it can be expected that two signals would appear in such a case.

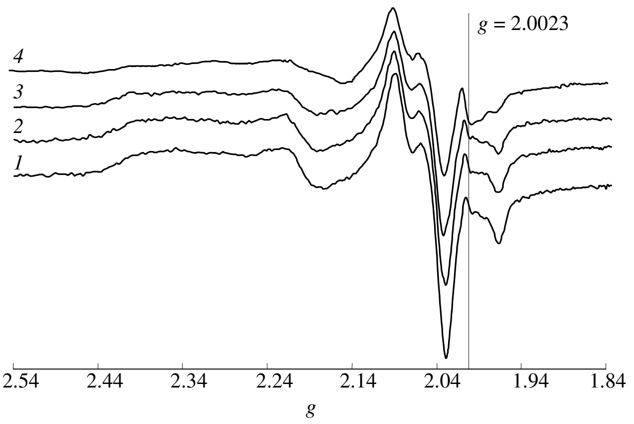

Figure 2 ESR spectra of matrix systems based on NaF kept for a week in air at room temperature (*1*) and for 30 min at temperatures of (*2*) 53, (*3*) 70 and (*4*) 94 °C.

However, if the absence of the signal results from its considerable broadening due to spin–spin coupling, the signal can appear if the number of paramagnetic centres decreases in time. Such a change cannot occur stepwise, and a decrease in the ESR signal intensity with time (like line narrowing) will be observed. Therefore, the second of the above reasons is unlikely. Studies on the thermal stability of NaF-based matrix systems show that heating does not result in noticeable changes in the ESR spectral line. This supports the assumption that the metal atom in the rhodium complex trapped by NaF during cocrystallisation from solution has an even number of electrons or no unpaired electrons.

The ESR spectrum contains two signals; one of them corresponds to the Rh$^{\mathrm{VI}}$ complex [$g_1 = 2.337(4)$, $g_2 = 2.196(3)$, $g_3 = 1.961(1)$]. The nature of the second signal [$g_1 = 2.088(2)$, $g_2 = 2.041(1)$, $g_3 = 2.028(1)$, $\delta_1 = 0.044$, $\delta_2 = 0.055$, $\delta_3 = 0.029$, where δ is the line width in kG] is unclear. A complex described previously[6] and designated as **V**, as its structure could not be proved, had similar magnetic-resonance parameters: $g_1 = 2.098(1)$, $g_2 = 2.052(1)$, $g_3 = 2.016(1)$. Complex **V** is formed in solution upon the reduction of a Rh$^{\mathrm{V}}$ complex by hydrogen peroxide. A signal with similar g-tensor parameters is also observed for the complex formed upon sorption on a $Ca(OH)_2$ surface[2,3] [$g_1 = 2.089(1)$, $g_2 = 2.039(1)$ and $g_3 = 2.014(1)$]; however, the line width is much greater ($\delta_1 = 0.070$, $\delta_2 = 0.070$, $\delta_3 = 0.042$) than that of the NaF-based matrix system. The similarity of g-tensor parameters allows us to believe that the signal in the ESR spectrum corresponds to the same complex in all the three cases; most likely, the minor differences in the g-tensor parameters are due to changes in the environment. The decrease in the line width can be due to a decrease in the spin–spin coupling, *i.e.*, an increase in the degree of magnetic dilution and a decrease in the mutual influence of paramagnetic centres.

The intensity of signals in the ESR spectrum is proportional to the concentration of paramagnetic centres, *i.e.*, the intensity ratio of two signals equals the concentration ratio of paramagnetic centres. The results of resolving ESR spectra for NaF-based matrix systems show a 3:1 ratio with the predominance of the rhodium(VI) complex. Such an intensity ratio of the complexes cannot be explained by the formation of mononuclear complexes since in this case one has to assume that the formation of Rh$^{\mathrm{II}}$ occurs ($4Rh^{5+} \rightarrow 3Rh^{6+} + Rh^{2+}$), which is impossible in the absence of strong reducing agents. It is more probable that a binuclear rhodium complex with a formal oxidation state of 3.5+ is formed, namely $5Rh^{5+} \rightarrow 3Rh^{6+} + Rh_2^{3.5+}$. The notation $Rh_2^{3.5+}$ is arbitrary, as data on the complex structure are unavailable. Disproportionation involving a large number of Rh$^{\mathrm{V}}$ complexes is only possible if they are localised in the matrix because disproportionation is a cooperative process. In other words, it is very likely in this case that trapped Rh$^{\mathrm{V}}$ is located near extended defects. This is also indirectly evidenced by the broadening of Rh$^{\mathrm{VI}}$ ESR spectral lines in comparison with the same signal in the LiF matrix, despite the smaller paramagnet content in the matrix system based on NaF.

Note that, after reaching a steady state, the content of paramagnets and their concentration ratio in the NaF do almost not change in time.

Thus, the following assumptions can be made on the basis of available data: NaF precipitated from an alkaline solution containing Rh$^{\mathrm{V}}$ and Rh$^{\mathrm{VI}}$ complexes selectively traps the Rh$^{\mathrm{V}}$ complex. Probably, almost all the rhodium contained in solution is captured owing to the equilibrium between the Rh$^{\mathrm{VI}}$ and Rh$^{\mathrm{V}}$ complexes in the starting solution. Storage of the NaF matrix results in decomposition of the Rh$^{\mathrm{V}}$ complex to give two types of paramagnetic centres, *i.e.*, disproportionation of Rh$^{\mathrm{V}}$ occurs. This makes it possible to explain the absence of a signal from the ESR spectrum of freshly prepared matrix systems based on NaF and the changes observed on storage and heating of these systems.

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