# ESR Spectra and Electronic Structure of Oxidized Forms of Organorhodium Chelates

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Fig. 1. ESR spectrum of $EtRh(dmgH)_2^+$ solution in acidified (0.1 $M$ in $HClO_4$)methanol–toluene mixture (1:1) at −60 °C.

While oxidized forms of the organocobalt chelates $[RCo(chel)L]^{+**}$, have been intensively studied in recent years and found to be essentially compounds of the tetravalent metal [1–4], little is known of similar rhodium complexes [5]. We could not obtain ESR spectra of $[RRh(salen)H_2O]^+$ by analogy from the corresponding cobalt species (*i.e.* after low temperature oxidation of the related organorhodium-(III) chelates in solutions of perchloric acid in aqueous methanol [3]).

Here we report for the first time the recording of ESR spectra of alkylrhodium chelates in oxidized form (*viz.* those of the $(dmgH)_2$ and salen series) and discuss the electronic structure of these labile complexes.

## Experimental

The starting organorhodium(III) chelates, RRh-$(dmgH)_2py$ (R = Et) and RRh(salen)py (R = Et or n-Bu), were prepared *via* known routes [6, 7] and characterized by IR spectra, gaseous products of pyrolysis, *viz.* the R–H olefins, and TLC behaviour (on $SiO_2$, solvent system MeOH–py 20:1). The complexes were oxidized at −78 °C in $CH_2Cl_2$ with $Br_2$ or in MeOH or MeOH–PHMe mixtures with $(NH_4)_2$-$Ce(NO_3)_6$, in some cases with the methanolic media having been acidified with (0.1 $M$) $HClO_4$. Changes in colour were observed from yellow to greenish-brown in the case of $RRh(dmgH)_2py$ and to green for RRh(salen)py. Retention of the coordination sphere in the course of the oxidations was proved by the regeneration of the initial complex after

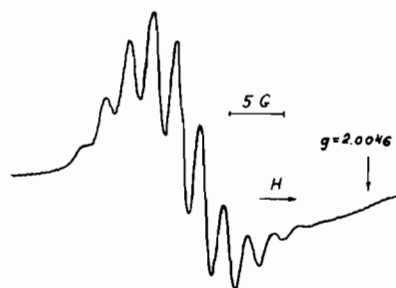reduction with $Fe(CN)_6^{4-}$ or ferrocene at −78 °C (identification by TLC).

ESR spectra of liquid (at −50 ÷ −80 °C) and frozen (at −196 °C) solutions after oxidation were recorded on X-band spectrometers.

## Results and Discussion

ESR spectra of $EtRh(dmgH)_2^+$* (concentration of the complex *ca.* 1 × 10⁻³ *M*) were observed both in liquid and frozen solutions, their parameters being almost identical in all the media used. Nevertheless, the spectrum in the acidified methanolic solutions (Fig. 1) was by far superior in quality to the other liquid phase spectra, evidently due to higher stability of the species in this medium (*vide infra*). It consists of ten hyperfine (*hf*) components, which must indicate splitting at four equivalent nitrogen nuclei and a rhodium one with $a_{Rh} \cong a_N$. A successful computer simulation using the model system of four equivalent nuclei with I = 1 and one with I = ½, assuming their *hf* constants to coincide, provided convincing evidence for this interpretation. In the frozen solutions an asymmetric line was observed (Fig. 2, a). Neither deuteration of the solvent (use of $CD_3OD$), nor that of the ethyl ligand in the complex, resulted in appreciable improvement of the spectra.

ESR spectra of $RRh(salen)^+$ could be recorded only in frozen non-acidified methanolic solutions

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**In this conventional formula R stands for alkyl, chel for a tetradentate or bis-bidentate dianion ligand derived from a Schiff base or an α-dioxime respectively, and L is an axial base ligand. Hereafter the following symbols are used for chelating ligands: $(dmgH)_2$ = bis-dimethylglyoximate and salen = N,N'-ethylene-bis(salicylideneiminate).

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*The oxidized species evidently retains the original axial base (py) in the $CH_2Cl_2$ medium while in the acidified methanol it should be replaced by MeOH (or $H_2O$). As to the oxidations of $RRh(dmgH)_2py$ (and RRh(salen)py as well) in non-acidified methanol, it is unclear whether the substitution occurs. Fortunately, due to the close similarity of the ESR spectra in these media, we need not take account on any change of axial base in the following discussion. ESR spectra of related cobalt complexes were also found to be unaffected by substitution of an axial base [2, 4]. For this reason it is omitted here and below.

TABLE 1. Comparison of ESR Parameters for Oxidized Forms of Ethylcobalt and Ethylrhodium Chelates EtM(chel)[+].

a) chel = $(dmgH)_2$, liquid $(a_M, a_N, g_{iso})$ and frozen $(g_{\parallel}, g_{\perp})$ solutions

| M | $10^4\ a_M$, cm$^{-1}$ | $10^4\ a_N$, cm$^{-1}$ | $g_{iso}$ | $g_{\parallel}$ | $g_{\perp}$ | Reference |
|---|---|---|---|---|---|---|
| Co | 13.6 ± 0.05 | 2.28 ± 0.05 | 2.0292 ± 0.0003 | 2.031 ± 0.002 | 2.028 ± 0.002 | [4] |
| Rh | 2.31 ± 0.03 | 2.31 ± 0.03 | 2.015 ± 0.002 | ⟨g⟩ = 2.015 | | This work |

b) chel = salen, frozen solution

| M | $10^4\ a_M$, cm$^{-1}$ | | | g | | | Reference |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | |
| Co | 74.4 | 39.0 | 25.1 | 2.213 | 2.090 | 1.993 | [3] |
| Rh | – | – | – | 2.157 | 2.021 | 1.937 | This work |
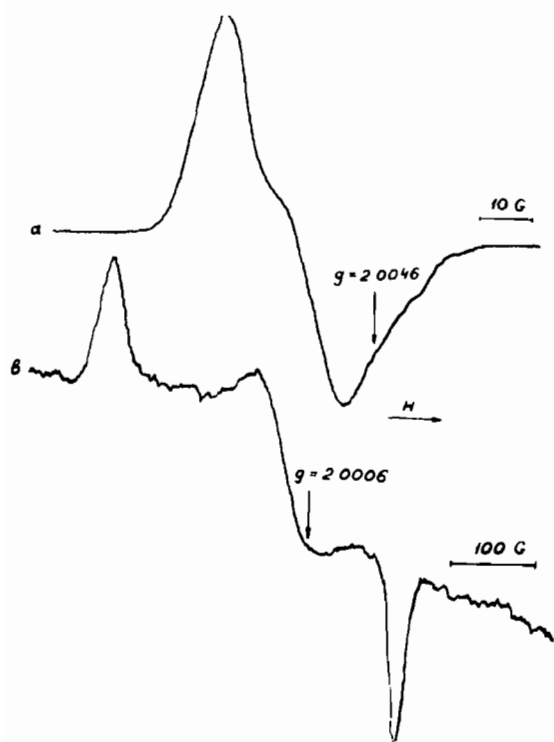


Fig. 2. ESR spectra of (a) EtRh(dmgH)$_2^+$ and (b) n-BuRh-(salen)[+] in frozen methanol solutions at −196 °C.

(concentration of the complex *ca.* $5 \times 10^{-4}\ M$)*. The complexes with R = Et and n-Bu gave identical spectra (Fig. 2, b) with unresolved *hf* structures and g-tensor anisotropy along three axes.

*Failure of the experiments in the acidic medium might be caused by poor solubility of perchlorate salts of the oxidized species (*cf.* [3]).

ESR parameters of the complexes studied, as well as those of their cobalt analogues (taken from Refs. [3, 4]), are summarized in Table I. As can be seen the respective values of g-factors and *hf* splittings at nitrogen nuclei for the related pairs of cobalt and rhodium species are very close. This means that in the oxidized forms of rhodium complexes, just as in their cobalt analogs, an unpaired electron is localized mainly at the metal ion (mostly at the $4d_{x^2-y^2}$ orbital). Thus the species under consideration have the structure of organorhodium(IV) chelates.

Furthermore, in the case of the EtM(dmgH)$_2^+$ pair where *hf* splitting at either metal atom has been observed in liquid phase ESR spectra, the splitting constant at rhodium is far less than for that at cobalt. This fact can be explained if one takes into account the similarity of the electronic structures of both complexes and considers the difference of magnetic properties of Co$^{4+}$ and Rh$^{4+}$ ions. The *hf* splitting due to the metal atom in isostructural compounds of cobalt and rhodium must be proportional to the magnetogyric ratios for $^{59}$Co and $^{103}$Rh nuclei. Hence for a rhodium complex it should be 7.5 times less than for a similar cobalt complex. Thus, in the case of EtRh(dmgH)$_2^+$ such an estimate of $a_{Rh}$ based on the value of $a_{Co}$ = 13.6 × 10$^{-4}$ cm$^{-1}$ for the related cobalt complex [4] would give 1.8 × 10$^{-4}$ cm$^{-1}$. The reasonable agreement between this rough estimate and the experimental value ($a_{Rh}$ = 2.3 × 10$^{-4}$ cm$^{-1}$) provides eventual support to our conclusion.

A progressive change of the ESR spectra of EtRh-(dmgH)$_2^+$ in liquid solutions was observed indicating a decomposition of the complex. In the acidified methanol solution this process was very slow at −80 °C, while at −50 °C the initial spectrum gradually decreased and disappeared within a few hours; a

single line signal with g = 2.009 ± 0.002 and $\Delta H \cong 7G$ emerged simultaneously. The non-acidified methanol solution is considerably less stable. This observation probably reveals high electrophilic reactivity (in this case towards hydroxide ion) of organorhodium(IV) complexes resembling that of their cobalt analogs [1]. The dichloromethane solution is even more labile: noticeable changes of the ESR spectrum were recorded in half an hour at −80 °C. In the case of EtCo(dmgH)$_2^+$ comparable rates of decomposition were observed under similar conditions at much higher temperature (above −30 °C). This comparison shows that organorhodium(IV) chelates are far less stable than are their cobalt analogs. A probable cause is the greater electrophilic reactivity of the former. Such a trend could be also expected from the higher potentials of their formation as measured in [5].

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