

## Inorganic Chemistry

## Labile Rh(II) Species Resulting from Oxygen or/and Cu(II) Oxidation of Rh(I) Complexes

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Among the catalysts used for promoting homogeneous oxidations of olefins with molecular oxygen, rhodium complexes seem to be especially efficient. Indeed, several groups have recently reported on the ability of some rhodium complexes to catalyze the oxidation of terminal olefins *via* a direct activation of molecular oxygen [1]. The coordination of both the olefin and O<sub>2</sub> on the same metal center has been

postulated. However, the proposed mechanisms are still largely speculative, especially as far as the metal oxidation level is concerned.

We describe here the EPR characterization of unstable Rh(II) species (d<sup>7</sup>) resulting from a direct oxidation of Rh(I) complexes by molecular oxygen at room temperature. Moreover, the same Rh(II) intermediates are also formed by electron transfer from Cu(II) salts in conditions typical of olefin oxidation. Typically, when O<sub>2</sub> is bubbled through a HAc-EtOH solution of a Rh(I) complex (no EPR signal), the colour turns purple and the build up of an unstable paramagnetic Rh(II) complex can be monitored by EPR. The presence of the same complex is also evidenced after addition of an equimolecular amount of Cu(II) salt to the Rh(I) solution, in the absence of oxygen. In both cases, the concentration of the paramagnetic species decreases with time.

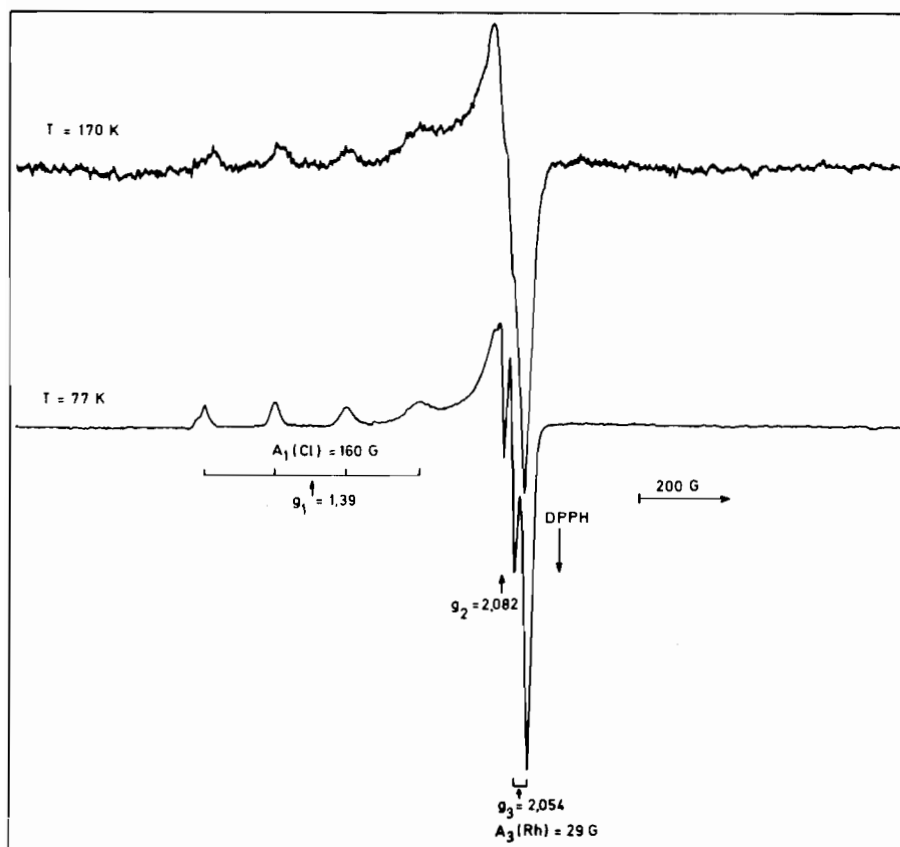


Fig. 1.

The main features of the EPR spectrum of the purple solution at 77 K are seen in Fig. 1. When the spectrum is measured at a higher temperature (up to 250 K), the symmetry of the paramagnetic species remains unchanged. However at temperatures higher than 170 K, the Rh-hyperfine structure disappears and eventually the spectrum of the Figure (measured at 170 K) is observed.

The EPR spectrum is attributed to a Rh(II) complex, the formation of which is totally reproducible. On the basis of experimental and theoretical results published in the case of EPR spectra of  $d^7$  'low spin' elements, we propose a  $C_{2v}$  symmetry for the Rh(II) complex, the unpaired electron being principally located in a  $d_{x^2-y^2}$  orbital. This electron is largely delocalized on the only chloride ion of the complex, on the symmetry axis.

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### Magnetic Resonance Spectra of Some Homo- and Hetero-Dinuclear Paramagnetic Metal Complexes with 1,5-Diphenyl-pentane-1,3,5-Trione

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The spectroscopic and magnetic properties of heterodinuclear transition metal complexes are a topic of current chemical interest, since they can largely expand the number of experimental data on exchange interactions and give new information to correlate the magnetic properties with the structural features of the complexes.

Magnetic resonance spectroscopy has been shown to provide powerful tools for detecting and investigating such chemical species [1, 2]. In particular PMR can provide information on the role of the ligands on the superexchange pathway as well as on the electronic states of the coupled metal pairs, while ESR can be used to obtain the spin hamiltonian para-

eters, which help in the interpretation of the PMR experimental data.

We have considered the complexes formed by the tridentate ligand 1,5-diphenyl-pentane-1,3,5-trione. This ligand is known [3] to form dinuclear antiferromagnetically coupled nickel(II) and cobalt(II) complexes of general formula  $M_2L_2(py)_4 \cdot 4py$  ( $py$  = pyridine). We have also synthesized the manganese(II) and zinc(II) derivatives and solid compounds containing the heterodinuclear complexes. Their ESR and  $^1H$  NMR spectra will be reported and discussed.

#### References

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### ESR Spectra of Some Adducts of Cobalt(II) Acetylacetonate

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We have recently reported that the pattern of  $g$  values in tetragonal octahedral cobalt(II) complexes is dramatically affected by the  $\pi$ -bonding ability of the equatorial and axial ligands [1]. Pursuing our work in this field, we studied several adducts of cobalt(II) acetylacetonate, in order to check how the principal  $g$  values and directions are affected by the nature of the axial substituents. The ESR spectra of  $Co(acac)_2L_2$  [ $L$  = 6-methylquinoline (I); pyridine (II); water (III)] were recorded at 4.2 K and they were interpreted using the method based on the Angular Overlap Model previously developed [2].

Single crystal ESR spectra allowed us to obtain the following  $g$  values:  $g_1 = 5.67$ ,  $g_2 = 4.11$ ,  $g_3 = 1.90$  for (I);  $g_1 = 5.83$ ,  $g_2 = 3.92$ ,  $g_3 = 1.98$  for (II);  $g_1 = 6.84$ ,  $g_2 = 2.74$ ,  $g_3 = 1.88$  for (III). The  $g_3$  direction is close ( $\approx 20^\circ$ ) to the Co-axial ligand bond direction. For (III) also the spectra of the complex diluted in a Mg lattice were recorded. The spectra showed  $g$  values equal to those of the undiluted derivative and a hyperfine structure complicated by second order effects and quadrupolar or nuclear Zeeman interactions. The  $A$  values, obtained through