

**Fifth Meeting of the Benelux EPR Society**

**Programme**

**Book of Abstracts**

**List of Participants**

March 20, 1997

Auditorium  
Eindhoven University of Technology  
The Netherlands



### **Local organizer**

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## Scientific Programme

- 10.00 Registration and coffee (*'Voorhof'*)
- 10.25 Opening remarks (*'Collegezaal 2'*)
- 10.30 W. R. Hagen, P. J. M. van Kan, and E. J. Reijerse (University of Nijmegen)  
EPR spectroscopy of the biological meatball cluster
- 11.00 T. Ceulemans, D. Schoemaker (University of Antwerp), D. Vandenbroucke,  
and R. de Keyzer (Agfa-Gevaert)  
Comparative study of hole processes on dye molecules for spectrally sensitized  
AgBr and AgCl microcrystals
- 11.30 M. M. Wienk (Eindhoven University of Technology)  
High-spin cation radicals of oligo-anilines
- 12.00 G. Vanhaelewyn, F. Callens, E. Boesman (University of Ghent)  
EPR and ENDOR of irradiated sugars
- 12.30 Lunch at the Auditorium (*'Senaatszaal'*)
- 14.00 A. J. Hoff (University of Leiden, Huygens Laboratory)  
Electron spin polarization and ESEEM: A tool to measure distances of radical  
pairs
- 14.30 B. Gallez (University of Louvain, Brussels) , R. Debuyst, F. Dejehet  
(University of Louvain, Louvain-la-Neuve), K. J. Liu, T. Walczak, H. M.  
Swartz, (Hanover, NH, USA), F. Goda (Kagawa, Japan), R. Demeure, and H.  
Taper (University of Louvain, Brussels)  
Coated particles of fusinite and carbohydrate chars for in vivo EPR oximetry
- 15.00 J. van der Zee (University of Leiden, Sylvius Laboratory)  
ESR spin trapping investigation of radical formation from the reaction between  
hematin and tert-butyl hydroperoxide
- 15.30 General meeting of the Benelux EPR Society
- 16.00 Poster session and coffee (*'Glazen zaal' in front of 'Collegezaal 11'*)
- 17.30 Closing

## Poster session

E. Goovaerts, S. V. Nistor, and D. Schoemaker (University of Antwerp)  
The heteronuclear (Tl<sup>+</sup>-Pb<sup>2+</sup>) center formed by electron trapping in Tl doped PbCl<sub>2</sub>

S. de Vries (Delft University of Technology)  
Properties of NO reductase

M. van Gastel, J. Mol, J. W. A. Coremans, O. G. Poluektov, E. J. J. Groenen, G. W. Canters, H. Nar, and A. Messerschmidt (University of Leiden)  
A W-band pulsed ENDOR study of single crystals of azurin and fully <sup>15</sup>N enriched azurin

M. van Gastel, J. W. A. Coremans, O. G. Poluektov, G. W. Canters, A. Messerschmidt, and E. J. J. Groenen (University of Leiden)  
A W-band EPR study of axial ligation in azurin and its mutant M121Q

A. P. Spoyalov (Russian Academy of Science, Novosibirsk), R. J. Hulsebosch, S. Shochat, P. Gast, and A. J. Hoff (University of Leiden)  
Evidence that Ala M260 is hydrogen bonded to the reduced primary acceptor quinone Q<sub>A</sub><sup>•-</sup> in reaction centers of Rb. sphaeroides

H. Vrielinck, K. Sabbe, M. Zdravkova, F. Callens (University of Ghent), and H. Vercammen (University of Antwerp)  
Rh<sup>2+</sup> centres in AgCl and NaCl single crystals

E. J. Reijerse (University of Nijmegen), B. M. Weckhuysen, D. E. de Vos, and R. A. Schoonheydt (University of Leuven)  
Pulsed EPR of inclusion complexes and metals in zeolites

P. van Dam (University of Nijmegen)  
High frequency (130 GHz) EPR on high spin systems

P. J. M. van Kan (University of Nijmegen)  
EPR of iron-sulfur centres in proteins

M. M. Wienk and R. A. J. Janssen (Eindhoven University of Technology)  
High-spin cation radicals of m-phenylene linked methylene phosphoranes

M. Struijk, M. M. Wienk, and R. A. J. Janssen (Eindhoven University of Technology)  
Oligoanilines as building blocks for polaronic organic ferromagnets

**Abstracts of Lectures and Posters**

## EPR SPECTROSCOPY OF THE BIOLOGICAL MEATBALL CLUSTER

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By monitoring column chromatography fractions with EPR we accidentally discovered in 1989 a protein with a novel type of iron-sulfur cluster ( $S=1/2$ ;  $g= 2.0, 1.8, 1.3$ ). Up to this date the protein has kept us and others busy as it proved to be a rich source of spectroscopic problems (cf refs quoted in [1]). We have now solved the crystal structure to 1.7 Å resolution: the 60 kDa protein contains two unusual 4Fe clusters. One cluster is a regular  $[4Fe-4S]^{(2+/1+)}$  cubane in an unusual protein fold and with unusual magnetic properties. The second cluster is a novel structure consisting of four Fe, two  $\mu$ -sulfido bridges, two  $\mu$ -oxo bridges, and a persulfido ligand. This 'meatball cluster' can exist in four oxidation states.

In the 'as isolated' protein the meatball cluster exhibits a very complex EPR spectrum with many features all the way down to an effective  $g$ -value of 17. With the aid of rhombograms for systems with quenched orbital angular momentum the spectrum is analyzed in terms of an  $S=9/2$  system with different rhombicities. The one-electron reduced protein affords a sharp single-feature spectrum in parallel-mode EPR with effective  $g$ -value of 16. It is assigned to the transition within the non-Kramers  $|m_s=\pm 4\rangle$  doublet of an  $S=4$  system.

Upon reduction of the protein with excess dithionite the meatball cluster becomes two-electron reduced ( $S=1/2$ ;  $g=2.0, 1.8, 1.3$ ). The cubane cluster is now one-electron reduced, and  $S=3/2$ . However, the effective  $g$ -values do not fit the rhombogram for  $S=3/2$ . By analogy with cubane model clusters the system is identified as 'spin-admixed'  $S=3/2$ . Differential HYSCORE on wild type protein versus a recombinant that lacks the meatball cluster identifies  $^{13}C$  near the cubane,  $^{14}N$  near the meatball, and protons near both clusters.

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Work supported by the "Flemish Institute for the Encouragement of Scientific and Technological Research in the Industry (IWT)"

Silver halide ( $\text{AgX}$ ) microcrystals used in photographic materials are sensitive only to blue light in the visible region. To extend the spectral sensitivity, dye molecules are adsorbed on the surface of the microcrystals. This process is called spectral sensitization. The adsorbed dye molecules form dye radicals during optical excitation because holes are trapped by the highest occupied molecular orbital of the molecules. In Electron Paramagnetic Resonance (EPR) the radicals show up as a single line with a Lorentzian shape. The formation and decay kinetics of the holes trapped by the dye molecules at the surface of AgBr and AgCl microcrystals was studied using EPR. Previously, only the decay on spectrally sensitized AgBr systems was studied.[1,2] In our experiments, the EPR linewidth decreases when the concentration of adsorbed dye radicals increases. Therefore, the previous analysis of the dye kinetics is incorrect. A more accurate analysis was performed, based on lineshape fitting of the EPR signals. We have extended the study of radical kinetics by recording not only decay curves, but also formation curves during optical excitation. Using our improved analysis, a distinct difference in the formation of dye radicals is observed between the AgCl and AgBr microcrystals. In the case of AgBr there is an equilibrium between dye molecules and radicals. For AgCl a new process is introduced, the formation of doubly oxidized dye molecules. For both systems a model is proposed describing the kinetic behavior of the holes trapped by the dye molecules. The formation and decay curves could be fitted very well. EPR results will be presented to indicate how the two models were arrived at.

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[1] T. Tani, *Phot. Sci. Eng.* 1975, **19**, 356

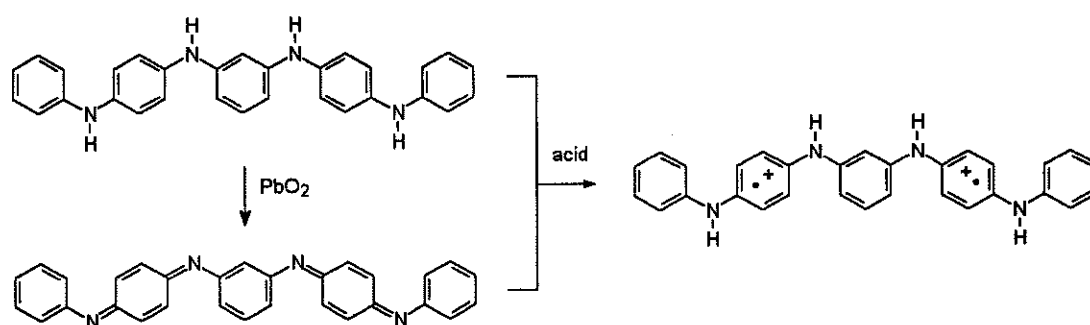
[2] J. Siegel, D. Fassler, M. Friedrich, J.v. Grossman, U. Kempka, H. Pietsch, *J. Phot. Sci.* 1987, **35**, 73

## High-Spin Cation Radicals of Oligoanilines

Martijn M. Wienk

*Contribution from the Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

A series of linear and branched high-spin di- and tri(cation radical)s has been prepared by oxidation of the corresponding oligo-*m-p*-anilines, which are stable under ambient conditions. The formation and properties of the cation radicals has been studied in detail by cyclic voltammetry and UV/visible/nearIR spectroscopy. ESR spectroscopy has provided the zero-field splittings, which are consistent with the topology of the molecules and the localization of the unpaired electrons. Variable temperature ESR experiments reveal that the high-spin states correspond to a low-energy state. The stability of the high-spin *m-p*-aniline oligomers, and the possibility to extend these systems demonstrate that alternating *meta* and *para* aniline oligomers are promising building blocks for future polaronic ferromagnets. We demonstrate that 'acid doping' can be used to prepare high-spin systems: The addition of a single drop of acid to a mixture of a fully reduced and a fully oxidized oligoaniline, produces the corresponding high-spin molecule as the single product:





## EPR AND ENDOR OF IRRADIATED SUGARS

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It has been claimed that the treatment of food with ionizing radiation can destroy harmful microorganisms and extend the shelf life without affecting the quality or flavour [1]. Much research already has focussed on the observation of EPR signals from the harder parts in fruits as seeds, pips and stalks to confirm whether or not irradiation has occurred. EPR signals in some radiation treated fruits like dried grapes, raisins, papayas and dates are said to be sugar-like [2]. Disregarding minor lines, these signals can be roughly described as two broad lines of about the same intensity separated by approximately 2 mT. Irradiated cane sugar bears strongly resembling EPR signals to these in the above mentioned fruit species and is being proposed as an emergency dosimeter [3]. Some research groups already determined the dose response of some particular sugars like glucose, maltose and galactose without further examination of the nature of the defects induced by ionizing radiation [4]. The corresponding spectra are examples of multicomponent spectra. The complexity of these spectra limits their reliable use in EPR applications as dosimetry and detection of irradiated food. If the use of sugar radicals has to be extended for EPR applications then their origin has to be clarified. In the present work preliminary experiments on D-fructose single crystals with EPR and ENDOR are presented. The aim is to give a qualitative idea of the different components that might be present in this and similar systems.

[1] "Radiation Processing", R. J. Woods and A. K. Pikaev, *Appl. Radiat. Chem.* (1994).

[2] "Establishment of an Eastern Network of Laboratories for Identification of Irradiated Foodstuffs", J. Raffi, E. Andrade, S. Barabassy, F. Callens, B. Kalman, W. Migdal, M. Prost, W. Stachowicz and N. Yordanov, Fourth Report: January 1997.

[3] "Critical evaluation of the sugar-EPR dosimetry system", P. Fattibene, T. L. Duckworth and M. F. Desrosiers, *Appl. Radiat. Isot.* 47, 1375-1379 (1996).

[4] "Applications of Some Polycrystalline Hydrocarbons (Alanine and Sugars) for High-dose Measurement by ESR Spectrometry", V. V. Generalova, A. A. Gromov, M. N. Gursky, A. P. Zhanzhora, N. P. Ilgasova and A. S. Leskov, *Appl. Radiat. Isot.* 44, 791-793 (1993).

## Coated particles of fusinite and carbohydrate chars for *in vivo* EPR oximetry

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Harold M. Swartz<sup>3</sup>, Fuminori Goda<sup>3,4</sup>, Roger Demeure<sup>5</sup>, Henryk Taper<sup>6</sup>.

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The development of oxygen-sensitive paramagnetic materials is being pursued actively because of their potential applications in *in vivo* EPR oximetry. Among these materials, several charcoals and carbohydrate chars present a high interest because of their convenient EPR properties: high sensitivity of the EPR linewidth to the oxygen concentration, simple EPR spectra, and high spin density. However, their potential use in humans is limited by the need to demonstrate that they will not lead to deleterious effects. The strategy used to optimize the biocompatibility of the oxygen-sensitive materials was to decrease the size of the particles and coat them using different suspension or surfactive agents such as arabic gum, poloxamer (Plurion<sup>®</sup> 6800), and polyvinylpyrrolidone. These coated particles of a carbohydrate char and fusinite were characterized *in vitro* for their size, stability, and pO<sub>2</sub> sensitivity. The feasibility of performing pO<sub>2</sub> measurement was checked *in vivo* by inducing ischemia in the gastrocnemius muscle of mice. The use of arabic gum for coating the fusinite particles permits the preservation of the pO<sub>2</sub> sensitivity *in vivo* while other surfactive agents led to a loss of the pO<sub>2</sub> sensitivity *in vivo*. The fusinite coated with arabic gum was also tested in MTG-B tumors induced in mice, demonstrating the possibility for using this material for the monitoring of pO<sub>2</sub> in tumors. The use of small particles of fusinite coated by arabic gum allows to perform intravenous administration of this material and to an accumulation in the liver, while the uncoated fusinite was shown to be toxic when injected intravenously due to the large size of the particles. Histological studies performed 6 months after the injection in muscles of mice did not reveal any form of toxicity with the materials used in the present study. The selection of the size of the particles allows a preferential subcellular localization: the smallest particles ( $\pm 300$  nm) were found in the intracellular medium while the largest particles remained in the extracellular medium.

## ESR SPIN TRAPPING INVESTIGATION OF RADICAL FORMATION FROM THE REACTION BETWEEN HEMATIN AND *tert*-BUTYL HYDROPEROXIDE.

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Various mechanisms have been proposed for the reaction between heme proteins and organic hydroperoxides, including a peroxidase-type mechanism and homolytic cleavage. Electron spin resonance (ESR) spectroscopy was used to investigate the formation of radicals in a hematin/*tert*-butyl hydroperoxide system. Spin trapping studies, using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), showed the formation of peroxy and alkoxy radicals in this system. At higher hematin concentrations an alkyl radical adduct could also be detected, which was identified as the methyl radical by using the spin trap 2-methyl-2-nitrosopropane. Furthermore, the relative contribution of the peroxy and alkoxy radical adducts was determined at various DMPO concentrations using computer simulation. It was found that at low DMPO concentrations both the alkoxy and the peroxy radical adduct could be detected. At higher DMPO concentrations, on the other hand, the alkoxy radical dominated, whereas the peroxy radical adduct decreased to a small portion of the total radical adduct population. Thus the alkoxy radical was the initial radical, produced by homolytic scission of the O-O bond of the hydroperoxide by ferric hematin. Although some *tert*-butyl peroxy radicals could be detected by direct ESR, the majority of the peroxy radicals detected by spin trapping were methyl peroxy radicals, formed in the reaction between methyl radicals (formed by  $\beta$ -scission of the alkoxy radicals) and oxygen.

*Abstract submitted to Benelux EPR-meeting, Eindhoven, March 20, 1997.*

THE HETERONUCLEAR  $(\text{Tl}^+-\text{Pb}^{2+})^-$  CENTER FORMED BY ELECTRON TRAPPING  
IN Tl-DOPED  $\text{PbCl}_2$

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In pure  $\text{PbCl}_2$ , we have recently demonstrated [1] that free electrons are self-trapped at low temperature, resulting in  $\text{Pb}_2^{3+}$  molecular ions on  $\text{Pb}^{2+}$  nearest neighbors along the  $a$ -axis. The unpaired electron of this self-trapped electron (STEL) center moves in a  $\sigma_g$ -orbital, in a configuration complementary to that of the well-known self-trapped hole  $\text{X}_2^-$ -center (X: halogen) in alkali halides.

In Tl-doped  $\text{PbCl}_2$  single crystals a new trapped-electron center is produced by X-ray irradiation at 80 K, involving a substitutional  $\text{Tl}^+$ -impurity. The strongly anisotropic spectrum was analysed using a low-symmetry spin-Hamiltonian involving the Zeeman interaction, and the hyperfine (hf) interaction with a single  $S=1/2$  Tl-nucleus. The hf interaction with a single  $S=1/2$   $^{207}\text{Pb}$ -nucleus (natural abundancy of 22.1 %) gives rise to an additional set of weaker lines of the same defect, which could be analysed as well. This yields the picture of a heteronuclear diatomic molecule, oriented along the  $a$ -axis –as for the STEL-center– in which the electron is more strongly localised on Pb than on Tl, as can be concluded from comparison with the hf parameters of the STEL center and of  $\text{Tl}_2^+$  defects in alkali halides.

*Work supported by the Fund for Scientific Research – Flanders*

[1] S.V. Nistor, E. Goovaerts and D. Schoemaker Phys. Rev. B 48, 9575 (1993).

## Properties of NO reductase

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A new and relatively simple procedure to purify NO reductase from *Paracoccus denitrificans* using the detergent lauryl maltoside has been developed. The purified enzyme consists of two subunits according to SDS polyacrylamide gelelectrophoresis. Analysis of the content of prosthetic groups indicates the presence of non-haem iron in addition to the presence of haem b and c cytochromes yielding a stoichiometry of haem b: haem c: non-haem iron = 2:1:1. The optical spectrum of reduced NO reductase shows bands of low-spin haem c and haem b with a-band absorbance maxima at 551 nm and 558 nm, respectively. The optical spectrum of oxidized NO reductase shows a broad absorbance band around 590 nm which disappears upon reduction. This latter absorbance is ascribed to a high-spin haem b (charge-transfer) transition. The presence of high-spin haem b is also indicated by the shifts observed in the optical spectrum of oxidized NO reductase in the presence of NO or in the spectrum of reduced enzyme after addition of CO.

The main features of the EPR spectrum of the oxidized enzyme are resonances from a highly anisotropic low-spin haem b ( $g_z = 3.53$ ) and from an anisotropic low-spin haem c with  $g_{z,y,x} = 2.99, 2.28, 1.46$ , the two haemes being present in an approximate 1:1 stoichiometry. Minor signals representing about 1% of the enzyme concentration due to high-spin haem b ( $g = 5.8-6.2$ ) and a novel type of signal with  $g = 2.009$  ascribed to high-spin non-haem ferric iron were also observed.

The analysis of steady-state kinetic measurements of the NO reductase activity shows a sigmoidal relation between rate of NO reduction and NO concentration, consistent with a model describing sequential binding of two molecules of NO to the reduced enzyme. At high NO concentrations substrate inhibition occurs ( $K_i(\text{apparent}) = 13.5 \text{ mM}$ ) suggested to be due to binding of NO to oxidized enzyme.

The absence from the EPR spectrum of signals originating from ferric non-haem iron and ferric high-spin haem b in stoichiometric amounts with respect to the enzyme concentration is suggested to be due to an antiferromagnetic coupling between these two centers. The steady-state kinetic behaviour and the optical and EPR spectroscopic properties of the NO reductase are incorporated into a tentative structural and mechanistic model.

A W-BAND EPR STUDY OF AXIAL LIGATION IN AZURIN AND  
ITS MUTANT M121Q

M. van Gastel, J.W.A. Coremans, O.G. Poluektov, G.W. Canters,  
A. Messerschmidt and E.J.J. Groenen

Crystals of the blue-copper proteins azurin and M121Q, a mutant of azurin in which methionine-121 is replaced by glutamine, have been studied by W-band ESE detected EPR at 1.2 K. Resolution and sensitivity of EPR at 95 GHz have enabled the determination of the complete g-tensors. The non-axiality of these tensors, larger for M121Q than for azurin, will be discussed in relation to the bonding between the copper ion and the axial ligands.

## Evidence that Ala M260 is bound to the Primary Acceptor Quinone $Q_A^-$ in Reaction Centers of *Rb. sphaeroides*.

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### Abstract

The binding of the primary quinone anion radical  $Q_A^-$  in reaction centers (RCs) of *Rhodobacter (Rb.) sphaeroides* species was investigated with Electron Spin Echo Envelope Modulation (ESEEM). The ESEEM spectra, at two microwave frequencies, of Zn-substituted RCs of *Rb. sphaeroides* R26 showed interactions of the unpaired electron of  $Q_A^-$  with two nitrogen nuclei in the protein matrix. From the analysis of the experimental data the nitrogen nuclear quadrupole resonance (NQR) parameters were determined:  $e^2qQ/h=1.52$  MHz,  $\eta=0.82$  and  $e^2qQ/h=3.04$  MHz,  $\eta=0.66$ , which are assigned to the  $^{14}\text{N}^{\delta(1)}\text{-H}$  group of His M219 and the peptide  $^{14}\text{N}$  of Ala M260. The ESEEM spectrum of  $Q_A^-$  in reaction centers of the *Rb. sphaeroides* mutant W(M252)Y shows that the nitrogen of Trp M252 is not interacting with  $Q_A^-$ , that of the mutant H(M266)C shows that manipulating the Fe-binding site strongly affects the  $Q_A$ -binding site.

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## Rh<sup>2+</sup> centres in AgCl and NaCl single crystals

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Rh<sup>3+</sup> in AgX (X=Cl,Br) acts as a deep electron trap and is routinely used to increase contrast and decrease sensitivity of photographic emulsions. The EPR and ENDOR analysis of the solution-grown AgX:Rh microcrystals is feasible [1,2] but difficult. As no large AgX single crystals can be grown from aqueous solution, melt-grown silver and alkali halide single crystals on the one hand and solution-grown alkali halide single crystals on the other hand are used as model systems for the AgX microcrystals.

In this work, results of an EPR and ENDOR study on Bridgman AgCl and NaCl and solution-grown NaCl single crystals doped with rhodium are presented. A comparison of the Rh<sup>2+</sup> ENDOR spectra for the three crystals is made. The superhyperfine and quadrupole tensors for the axial Cl ligands will be discussed in detail. It will be shown that the primary Rh centres in AgCl and NaCl Bridgman crystals have the same orthorhombic symmetry. The model, proposed earlier by Van Robbroeck and by Olm et al. [3,4] for AgCl:Rh, seems also valid for Bridgman NaCl:Rh<sup>2+</sup>. In the solution-grown crystal however, the primary centre stable at room temperature has tetragonal symmetry and will be identified as a non-locally compensated (RhCl<sub>6</sub>)<sup>4+</sup> complex.

- [1] H. Vercammen, T. Ceulemans, D. Schoemaker, P. Moens and D. Vandenbroucke, proc. of the IS&T's 49th Annual Conference, Minneapolis, May 19 - 24, 54 (1996)
- [2] P. Moens, H. Vercammen, D. Vandenbroucke, F. Callens and D. Schoemaker, proc. of the IS&T's 49th Annual Conference, Minneapolis, May 19 - 24, 56 (1996)
- [3] L. Van Robbroeck, PhD. thesis, UIA (1995)
- [4] M.T. Olm, J.R. Niklas, J.M. Spaeth and M.R.C Symons, Phys. Rev. B **38** (7), 4343 (1988)

<sup>#</sup> On leave from the Institute of Catalysis, Academy of Sciences, Sofia, Bulgaria

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## Pulsed EPR of inclusion complexes and metals in Zeolites

*E.J. Reijerse, B.M. Weckhuysen, D.E. de Vos, and R.A. Schoonheydt*

The most active and selective redox catalysts are often found in nature in the form of metallo-enzymes. The active center usually contains a metal ion in unsaturated coordination. It has been demonstrated that in zeolites metal complexes with relatively high catalytical activity can be stabilized [1,2]. In this study we present a 2D-ESEEM study of several Cu complexes in zeolite Y with aminoacids as ligands. In particular the nitrogen ESEEM of a Cu(histidine)<sub>2</sub><sup>+</sup> complex is analyzed in terms of the quadrupole and hyperfine parameters of the remote imidazole nitrogen. The data are compared to Cu(hist) interactions reported in inorganic complexes and proteins.

In addition, the structure of several Manganese species stabilized in zeolite A is studied using 1D and 2D ESEEM. The data are interpreted in terms of water coordination and symmetry of the complex.

[1] W.J. Mortier, R.A. Schoonheydt, *Prog. Solid State Chem.* 1985, 16, 1

[2] D.E. de Vos, P.P. Knops-Gerrits, R.F. Parton, B.M. Weckhuysen,  
P.A. Jacobs, R.A. Schoonheydt, *J. Inclusion. Phys. Mol. Recogn. Chem.*  
1995, 21, 185

## High Frequency (130 GHz) EPR on High Spin Systems

*P.J. van Dam, A.A.K. Klaassen, E.J. Reijerse and W.R. Hagen*

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High frequency EPR spectrometers ( $\nu > 100$  GHz) have mainly been used so far to resolve  $g$ -tensors with small anisotropy. Few groups have studied high spin systems with such a spectrometer. We present here some HF-EPR experiments on integer spin systems (Ni(II),  $S = 1$ ) with large zero field splitting parameters to demonstrate the usefulness of high frequency EPR for such systems. These compounds will serve as model complexes for biological systems to be studied later.

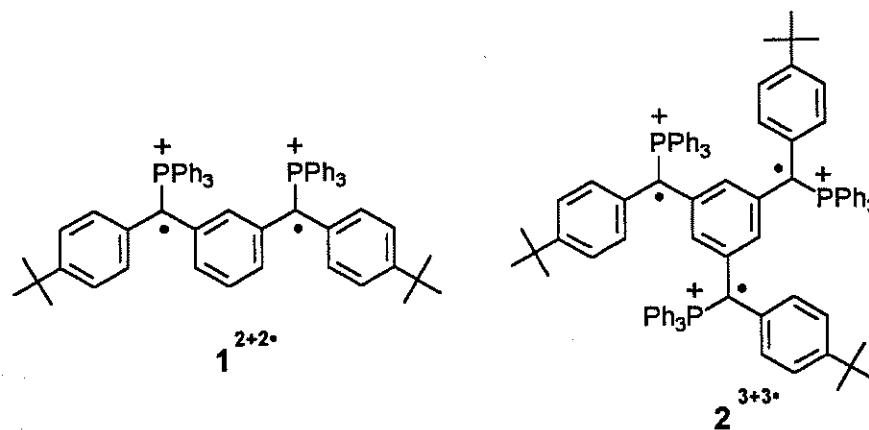
One complex,  $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3(\text{NO}_3)_2$  has an intermediate ZFS ( $D = 0.831 \text{ cm}^{-1}$ ,  $E = 0 \text{ cm}^{-1}$ ), while the second sample,  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2$ , has large ZFS values ( $D = 2.24 \text{ cm}^{-1}$ ,  $E = 0.38 \text{ cm}^{-1}$ ). The spectra at 130 GHz show the complete spectra as would be expected for  $h\nu > D$ . Remarkable is the double quantum line in the spectra. At Q-band this line is only a weak feature but at D-band frequency it appears as the strongest line in the spectrum. Also the microwave power dependency of this double quantum line is not as has been described previously in literature.

## High-Spin Cation Radicals of Methylene Phosphoranes

Martijn M. Wienk and René A. J. Janssen

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Novel di(cation radical)s ( $1^{2+2\cdot}$ ) and tri(cation radical)s ( $2^{3+3\cdot}$ ) are prepared by oxidation of the corresponding 1,3-phenylenebis[[(4-*t*-butylphenyl)methylene]triphenyl phosphorane] and 1,3,5-benzenetriyltris[[(4-*t*-butylphenyl)methylene]triphenyl phosphorane] precursors. The oligo(cation radical)s are investigated in frozen solutions using ESR spectroscopy. The di(cation radical) has a triplet state as evidenced from a  $\Delta M_s = \pm 2$  ESR transition exhibiting hyperfine coupling to two identical phosphorus nuclei and is characterized by zero-field splitting parameters  $D = 350$  MHz and  $E = 0$  MHz. The corresponding tri(cation radical) possesses a quartet state with  $D = 262$  MHz and  $E = 0$  MHz, and exhibits a  $\Delta M_s = \pm 3$  transition.



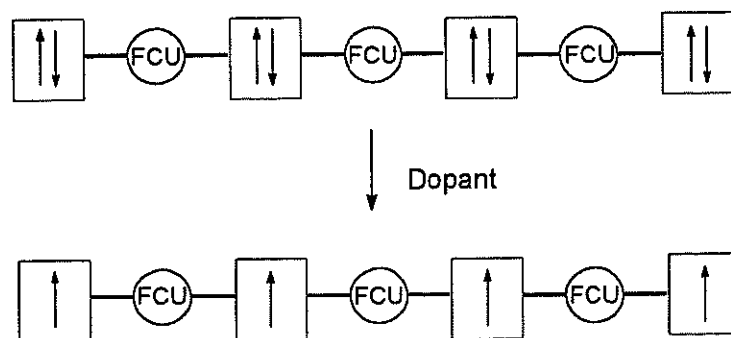
Temperature dependent studies (4 - 100 K) reveal that the ESR intensities follow Curie's law, consistent with high-spin ground states. The stability of these oligo(cation radical)s is assessed via cyclic voltammetry at room temperature in THF solution.

## Oligoanilines as Building Blocks for Polaronic Organic Ferromagnets

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Polaronic organic ferromagnetism has first been proposed by Fukutome *et al.* based on PPP quantum chemical calculations. Two structural aspects of such a hypothetical polymer were envisaged: (i) The polymer itself does not contain unpaired electrons but spins are generated by oxidative or reductive doping. (ii) The dopable subunits are connected by a ferromagnetic coupling unit; schematically:



Here we describe our first results on the synthesis and oxidation of oligo-*N*-methylanilines that may serve as building blocks for such a polaronic organic ferromagnet. These systems offer a combination of synthetic accessibility and intra molecular spin alignment in one and two dimensions after oxidation to an intermediate oxidation state.

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