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Solid state magic angle spinning ^{13}C and ^{31}P NMR of organic ligand stabilized high nuclearity metal clusters

^{13}C and ^{31}P MAS on metal cluster compounds

A.C. Kolbert¹, H.J.M. de Groot¹, D. van der Putten², H.B. Brom², L.J. de Jongh², G. Schmid³, H. Krautscheid⁴ and D. Fenske⁴

¹ Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

² Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands

³ Institut für Anorganische Chemie, Universität Essen; Universitätsstrasse 5-7, D-4300 Essen 1, Germany

⁴ Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstrasse, Geb. 30.45, D-7500 Karlsruhe, Germany

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Abstract. ^{13}C and ^{31}P solid state NMR measurements on the organic ligands in ligated Au_{55} , Ni_8 , Pt_{309} , Cu_{36} and Cu_{70} clusters are reported. The ligands behave like diamagnetic organic molecules, giving rise to relatively narrow lines with excellent cross-polarization efficiency. The resonance lines of the nuclei directly bound to the metal core are systematically broadened in the conducting compounds. No pronounced Knight shifts or evidence of metallic-like relaxation were observed. These results support a model for the electrical conduction involving tunneling between metal cores with the ligands playing the role of a tunneling barrier.

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1. Introduction

High nuclearity metal cluster molecules (MCM) stabilized by organic ligands are interesting materials for solid state study as they exhibit much of the physics of bare metal clusters, but possess a uniformity of size and shape that is hard to achieve for bare clusters in the quantities required e.g. for NMR studies. Aggregates of MCM's might show DC-conductivities up to $\sigma \sim 10^{-1}$ S/cm, or higher [1]. This raises the question: how do the charge carriers propagate through the ligands? Do the charge carriers (which are delocalized over the core [2]) just tunnel through the ligands or are the core electrons (or holes) also delocalized into the supporting organic ligands? Previous NMR experiments on metal cores and ligand atoms connected to the surface revealed a large spatial variation of the Knight shift within the metal core and provided strong evidence for a non-metallic surface layer of the core [2,3]. The present investigation aims at characterizing the propagation of the delocalized metal core wavefunction into the organic surrounding layer by studying the ligands directly with high-resolution solid

state magic angle spinning (MAS) NMR. This technique allows the measurement of both charge and spin density in the ligands through diamagnetic resonance shifts, Knight shifts and relaxation rates T_1^{-1} .

2. Experimental

Five different metal cluster compounds were investigated, see Table 1. Pd_{561} (not yet measured) is listed in the table, to illustrate the trend of increasing conductivity with increasing nuclearity.

Table 1. The room temperature conductivity of the investigated compounds, arranged in increasing nuclearity

compound	conductivity (S/cm)
$\text{Ni}_8(\text{PPh})_6(\text{PPh}_3)_4\text{Cl}_4$	insulator
$\text{Cu}_{36}(\text{P-t-Bu}_3)_{12}\text{Se}_{18}$	insulator
$\text{Au}_{55}(\text{PPh}_3)_{36}\text{Cl}_6$	10^{-5}
$\text{Cu}_{70}(\text{P-Et}_3)_{22}\text{Se}_{35}$	10^{-2}
$\text{Pt}_{309}\text{Phen}^*_{36}\text{O}_{30}$	10^{-3}
$\text{Pd}_{561}\text{Phen}_{37}\text{O}_{200}$	10^{-1}

Ph stands for phenyl (C_6H_5), Phen^* for 1,10-phenanthroline, 4,7-disulphonic acid ($\text{C}_{12}\text{H}_8\text{N}_2\text{S}_2\text{O}_6$), t-Bu for tert-butyl (C_4H_9) and Et for ethyl (C_2H_5). For the Ni_8 and the Cu_{36} cluster an X-ray structure is available. As a general rule it may be assumed that the negative ions (Cl, O, Se) and the phosphorus of the organic ligand are both directly bonded to the metal cores. While the structure of the Pt_{309} cluster is not precisely known, it is thought that the nitrogen lone pairs are involved in the stabilization of the core.

100 MHz ^{13}C and 162 MHz ^{31}P cross polarization CP/MAS NMR experiments were performed with a MSL-400 Bruker NMR spectrometer using a 4 mm MAS spinner. The spinning rate around the magic angle was kept constant with a home-made spinning speed controller [4]. The spectra were accumulated with cross-

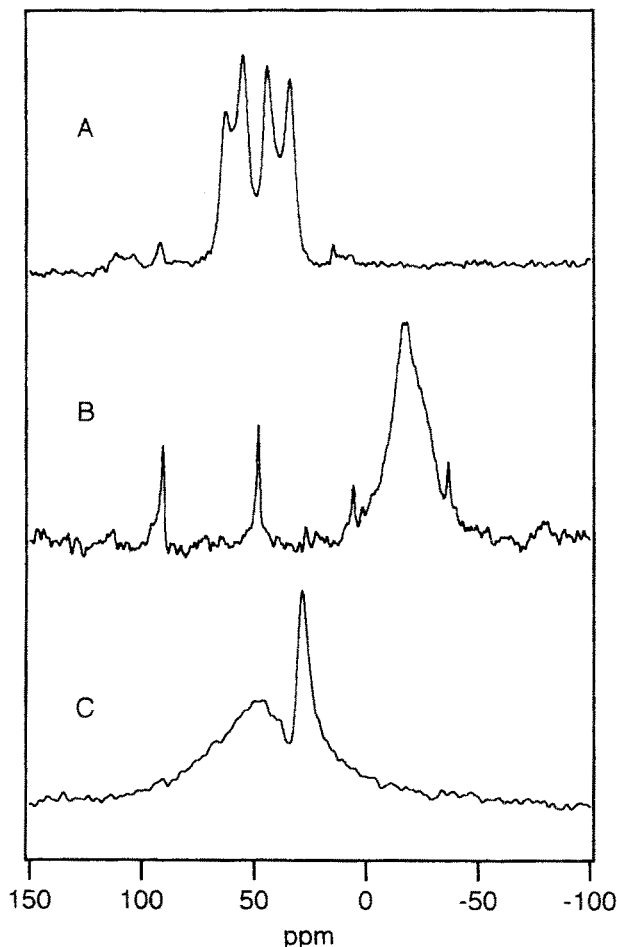


Fig. 1. Proton-decoupled ^{31}P CP/MAS NMR spectra at ambient temperature for the ligands in MCM's. (a) $\text{Cu}_{36}(\text{P-t-Bu}_3)_{12}\text{Se}_{18}$ at $\omega_r/2\pi = 6.0$ kHz (b) $\text{Cu}_{70}(\text{P-Et}_3)_{22}\text{Se}_{35}$ at $\omega_r/2\pi = 6.8$ kHz (c) $\text{Au}_{55}(\text{PPh}_3)_{36}\text{Cl}_6$ at $\omega_r/2\pi = 10.0$ kHz

polarization from the protons and proton decoupling during acquisition. The 90° pulse lengths were 4–5 μs and the cross-polarization times typically 1 ms. ^{13}C chemical shifts are referenced to TMS and ^{31}P shifts are given relative to solid ammonium phosphate.

Chemical shift anisotropies were obtained from the data by analyzing the centerband and sideband intensities with the method developed by Herzfeld and Berger [5].

3. Results and Discussion

Proton-decoupled ^{31}P CP/MAS NMR spectra at ambient temperature for the ligands in Cu_{36} , Cu_{70} and Au_{55} are shown in Fig. 1. Fig. 2. shows the ^{13}C spectra for the same compounds as well as for Pt_{309} .

Cu_{36} cluster. The ^{13}C nuclei of the tri-*t*-butyl phosphine ligands yield well-resolved lines at 37 ppm (C) and 33 ppm (CH_3) with $T_1 \sim 0.5$ s. The isotropic shifts are not very different from P-*t*-Bu₃ in solution. The rela-

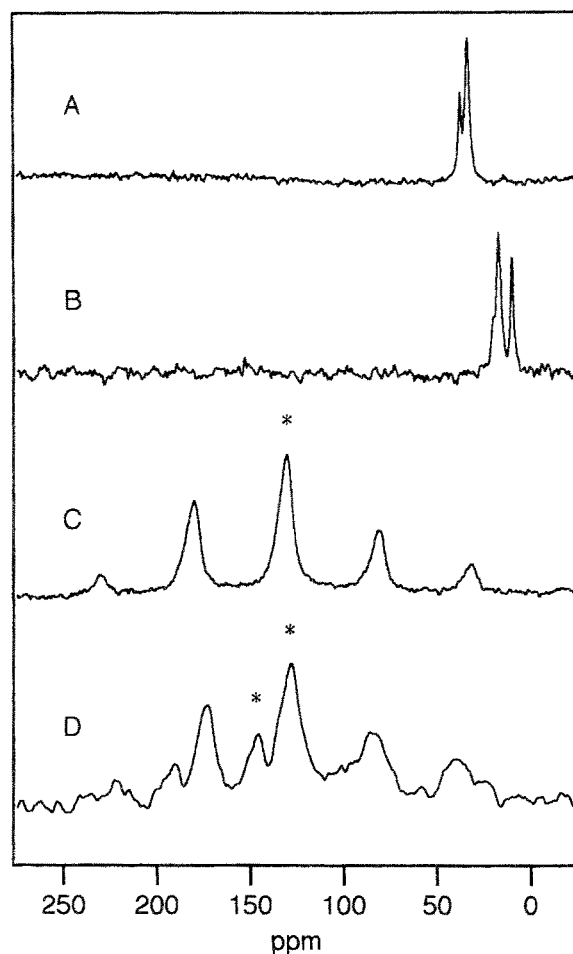


Fig. 2. Proton-decoupled ^{13}C CP/MAS NMR spectra at ambient temperature for the ligands in MCM's. (a) $\text{Cu}_{36}(\text{P-t-Bu}_3)_{12}\text{Se}_{18}$ at $\omega_r/2\pi = 6.0$ kHz (b) $\text{Cu}_{70}(\text{P-Et}_3)_{22}\text{Se}_{35}$ at $\omega_r/2\pi = 6.0$ kHz (c) $\text{Au}_{55}(\text{PPh}_3)_{36}\text{Cl}_6$ at $\omega_r/2\pi = 5.0$ kHz and (d) $\text{Pt}_{309}\text{Phen}^*_{36}\text{O}_{30}$ at $\omega_r/2\pi = 4.5$ kHz. The centerbands are marked by an asterisk

tively short T_1 is probably caused by the rotation of the methyl groups. No sidebands are observed and therefore the overall shift anisotropy is small, in agreement with expectations for these aliphatic carbons. The ^{31}P spectrum consists of a broad ~ 8 kHz wide pattern around 48 ppm with $T_1 = 10$ s, with a rich structure and well resolved peaks at 33, 43, 54, and 62 ppm. The resonance is shifted slightly upfield from the ^{31}P resonance of P-*t*-Bu₃ in solution (~ 62 ppm). The fine structure is caused by a scalar J -coupling of 1.46 kHz with $I = 3/2$ Cu nuclei. Close inspection of the data reveals a small distortion $d = -0.6$ ppm of the J -multiplet, reflecting the effect of J -anisotropy, dipolar interactions between the Cu and P nuclear spins, and the quadrupolar interactions operating on the $I = 3/2$ Cu nuclear spin [6]. Both the strength of the J -coupling and the size of the distortion are well inside the range expected for P-Cu complexes [6].

Cu_{70} cluster. The ^{13}C nuclei of the triethyl phosphine ligands yield well resolved lines of the methylene carbons at 16 ppm and for the methyl carbons at 9 ppm. Again

there is a close correspondence between solution shifts and solid state shifts. No sidebands are observed and therefore the overall shift anisotropy is small as expected. The ^{31}P spectrum consists of a broad ~ 4 kHz wide line around -16 ppm with $T_1 = 11$ s. This shift matches that of the ^{31}P resonance of P-Et_3 in solution (~ -20.1 ppm). The J -coupling with the Cu nuclei, which is well resolved in the Cu_{36} cluster, is now averaged by some mechanism, most likely fast relaxation by metal core electrons. The compound decomposed during the experiments, and the reaction product yields a sharp resonance at 50 ppm with its corresponding sidebands, where the ligand is free from the Cu-cluster.

Au₅₅ cluster. The ^{13}C nuclei of the triphenyl phosphine ligands resonate around 130 ppm with $T_1 = 24$ s. The isotropic shift matches the shifts for PPh_3 in solution (128 - 133 ppm). The line width of ~ 15 ppm is mainly due to the distribution of chemical shifts for the various ^{13}C nuclei, and is associated with the variation in chemical shift within a phenyl ring and between different rings due to local disorder in this aggregate. The overall chemical shift anisotropy was calculated from the line intensities as $\Delta\sigma \sim 200$ ppm with the anisotropy parameter $\eta \sim 0.7$, which is typical for a static aromatic ring. The ^{31}P spectrum comprises a broad (~ 40 ppm or ~ 6 kHz wide) feature at 50 ppm, with a small narrow component at 30 ppm. The latter is attributed to an impurity that is formed in the slow decomposition process of a metal cluster molecule [7], and the broad line is slightly shifted down-field from the ^{31}P resonance of PPh_3 in solution (~ -7 ppm). A hole burning experiment showed that the line is at least partly inhomogeneously broadened (data not shown). The origin of this broadening is not clear at present. The broad ^{31}P resonance provides convincing evidence that the phosphorous is directly bonded to the metal core.

Pt₃₀₉ cluster. The aromatic carbons of the ligands in this conducting cluster molecule give rise to two MAS patterns at 130 and 147 ppm. As for the Au_{55} cluster molecule, the anisotropies are typical for static aromatic carbons. The lines at 147 ppm and 130 ppm most likely originate from ^{13}C nuclei adjacent to the nitrogens and the SO_3 groups respectively.

Ni₈ cluster. The ^{13}C nuclei of the ligands in the Ni_8 cluster resonate over a range from 100 to 190 ppm with $T_1 \approx 10$ s. The individual peaks are not well resolved (data not shown). The ^{31}P spectrum could not be detected with CP/MAS or single pulse excitation. Since the Ni core is weakly ferromagnetic, this may explain why the ^{31}P resonance could not be observed and why the ^{31}C centerband is so broad.

4. Concluding remarks

The three conducting cluster compounds give rise to ^{13}C CP/MAS spectra that are similar to those of comparable

diamagnetic organic molecules. Although the ^{31}P lines are broad, they are not dramatically shifted. In addition, the spin-lattice relaxation times T_1 are long. For the copper clusters, going from the Cu_{36} (insulating) to the Cu_{70} compound (semi-conducting), T_1 even increases slightly. These results strongly argue against unpaired spin density on the ligands.

The mechanism behind the ^{31}P broadening is not clear at present. Different P-sites within the cluster might be at the origin, but also differences between the P-sites of different clusters, due to e.g. surface defects, can be imagined. A remarkable aspect of these systems is that the ^1H T_1 appeared to be rather short in all systems, varying from 0.05 to 0.5 s. This is unusual for materials with rather rigid aromatic molecules. The proton spins, however are strongly coupled by the dipolar interactions. It is therefore not unlikely that the short proton spin-lattice relaxation times are due to paramagnetic relaxation by small fractions of unpaired spin density inside the cores which is communicated through the whole system by spin diffusion.

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