

## Complex Formation of Platinum(II) and Rhodium(III) Ions with Aminated Silica Surfaces as Studied by C-13 NMR Spectroscopy

SUMIO SHINODA and YASUKAZU SAITO\*

*Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan*

Received March 26, 1982

*Complex formation of Pt(II) and Rh(III) ions with aminated silica surfaces ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$ ,  $\text{NH}_2\text{-CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$ ) has been analyzed by C-13 NMR spectroscopy in both the suspended state (in water; ordinary high-resolution NMR spectrometer with low-power  $^1\text{H}$  decoupling) and the dry state (with CP-MAS techniques). New peaks assignable to Pt(II)-coordinated species appeared for the diamine silica in contact with aqueous  $\text{K}_2\text{PtCl}_4$  solutions, where bis-chelate formation was suggested on the basis that the peaks of uncoordinated species were converted completely to those of coordinated ones at the [Pt]/[ligand] ratio of 0.5; bis-chelate structure was also indicated for  $\text{RhCl}_3$ /diamine silica by diffuse reflectance spectra. While coordinated species did not give high-resolution signals in other cases, they were found detectable with CP-MAS techniques, although the peaks were not fully resolved at 25 MHz. The implications of the associated protonation shifts of uncoordinated ligands are also discussed.*

### Introduction

With the advantages of non-swelling and high rates of attainment of equilibrium, silica gels whose surfaces are modified by chemical bonding of organosilanes have been widely used for the concentration and separation of metal ions [1]. Such a modified surface is also useful for immobilization of soluble complex catalysts [2]. However, attempts to elucidate the structure of the fixed complexes have achieved little, due to the difficulty in the analysis of surface species, although they are fundamental in the understanding and design of such materials.

For aminated silicas, techniques such as electronic absorption [3], electron spin resonance [4], and photo-acoustic [5] spectroscopy have been applied. We have found that the  $^{13}\text{C}$  NMR (CMR) of  $\text{NH}_2\text{-}$

$\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{-Si}\equiv$  groups bonded to silica is observable with satisfactory resolution, when the aminated silica is suspended in polar solvents (water > methanol > chloroform  $\gg$  benzene (virtually no signals)) [6, 7]. Measurement of  $^{13}\text{C}$  spin-lattice relaxation times [8] indicates the presence of hydrogen bonding between the amino and silanol groups [9], or between the amino groups themselves [10].

We report here an application of high-resolution CMR spectroscopy (with ordinary low-power  $^1\text{H}$  decoupling, ca. 15 W) to elucidate the structure of complexes formed on the aminated silicas in water.  $\text{K}_2\text{PtCl}_4$  and  $\text{RhCl}_3$  were adopted as representative diamagnetic salts of transition metals, which are known to form stable square-planar (Pt(II)) and octahedral (Rh(III)) complexes in the bulk of a solution, respectively. The results with cross polarization and magic-angle spinning (CP-MAS) techniques measured for dry powders will also be discussed.

### Experimental

Reagents used were of G. R. grade. Surface modification [6] of silica gel ( $S_{\text{BET}} = 148 \text{ m}^2 \text{ g}^{-1}$ ) with  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$  and  $\text{NH}_2\text{CH}_2\text{CH}_2\text{-NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$  (Shin-Etsu Chem. Ind. Ltd.) gave  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{-silica})$  (N-ligand-silica);  $S_{\text{BET}} = 35 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{-CH}_2\text{CH}_2\text{Si}(\text{-silica})$  (N,N-ligand-silica);  $S_{\text{BET}} = 19 \text{ m}^2 \text{ g}^{-1}$ ), respectively. The amounts of fixed ligand were  $2.8 \text{ mmol g}^{-1}$  for the former and  $2.0 \text{ mmol g}^{-1}$  for the latter (elemental analysis for N).

CMR spectra for the suspended samples were obtained on a Fourier transform pulsed NMR spectrometer (Jeol JNM-FX60 or JNM-FX60Q), operating at 15.04 MHz, with a 20 vol.% 1,4-dioxane/ $\text{D}_2\text{O}$  solution in a coaxial capillary tube used to obtain lock and to provide a reference peak. The chemical shifts are reported in ppm downfield from TMS using the conversion:  $\delta(\text{TMS}) = \delta(\text{dioxane}) - 67.4$  ppm. Before the measurement, the sample ( $0.5 \text{ g}$ )

\*Author to whom correspondence should be addressed.

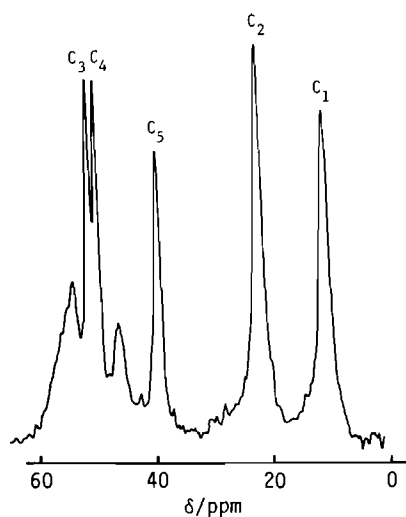


Fig. 1. CMR spectrum of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  groups bonded to silica surface after contact with an aqueous  $\text{K}_2\text{PtCl}_4$  solution. Numbers are designated from the silicon atom;  $[\text{Pt}]/[\text{L}] = 0.2$ , 15 MHz, 60 °C, 25,000 scans.

in an aqueous solution ( $1 \text{ cm}^3$ ) was sedimented in an NMR sample tube ( $10 \text{ mm}\phi$ ) on standing for 5 h, and was fixed with a Teflon plug. It was confirmed that physical adsorption of the metal ions was negligible for all the examined runs, and that after the contact time of 5 h the spectra were reproduced well in the repeated measurements. The CP-MAS spectra were acquired on a Jeol JNM-FX100 spectrometer (25.05 MHz) with external lock (chemical shifts in ppm downfield from TMS) for the samples dried by evacuation.

The amount of platinum or rhodium ion in the supernatant solution was determined by colorimetry with aqueous  $\text{HCl-SnCl}_2$  solutions [11]. Diffuse reflectance spectra were measured with a photometric spectrometer (Shimadzu UV-365) at ambient temperature.

## Results and Discussion

Figure 1 shows the CMR spectrum of N,N-ligand-(silica) immersed in an aqueous  $\text{K}_2\text{PtCl}_4$  solution ( $[\text{Pt}]/[\text{L}] = 0.2$ ). The broad peaks at  $\delta$  46.2 and 55.0 ppm appeared only when the platinum salt had been dissolved in the solution beforehand. In comparison with CMR chemical shifts of Pt(II) complexes possessing ethylenediamine analog as a ligand [12], these peaks are assigned to  $\text{C}_5$  and the superposition of  $\text{C}_3$  and  $\text{C}_4$  for the N,N-ligand coordinated to Pt(II), respectively, where numbers are designated from the silicon atom.

Line broadening due to the exchange of coordinated and uncoordinated ligands was not observed

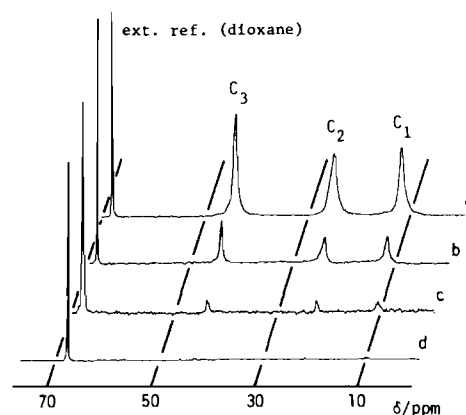


Fig. 2. Effect of the addition of  $\text{K}_2\text{PtCl}_4$  on the CMR spectrum of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  groups bonded to silica surface. Numbers are designated from the silicon atom;  $[\text{Pt}]/[\text{L}] = 0$  (a), 0.1 (b), 0.2 (c), 0.3 (d); 15 MHz, 29 °C,  $\text{H}_2\text{O}$  solvent; scan numbers = 4,000 (a, c), 3,000 (b), 7,000 (d).

up to the probe temperature of 80 °C. Since the peaks of the uncoordinated ligand disappeared at  $[\text{Pt}]/[\text{L}] \cong 0.5$  with less than 0.024% of the total platinum present in the supernatant solution, bis-chelate complex of the type  $[\text{Pt}(\text{N},\text{N})_2]^{2+}$  would be mainly formed on the surface. Relatively high ligand coverage of the present N,N-ligand-(silica) may prevent the mono-chelation [4, 5].

No new peak was observed, however, in the high-resolution spectrum of N-ligand-(silica) upon contact with aqueous  $\text{K}_2\text{PtCl}_4$  solutions. As shown in Fig. 2, the peak intensities decreased monotonously with the increase in the amount of the salt, and finally the peaks became hardly detectable at  $[\text{Pt}]/[\text{L}] \cong 0.3$ , where 0.748% of the added platinum exists in the supernatant solution.

Such a difference between the two types of aminated silicas may give insight into the structure of the surface complexes. At the  $[\text{Pt}]/[\text{L}]$  ratio of 0.3, Pt(II) ions may be complexed with 3 or 4 N-ligands per ion [3]. It is quite probable that such a complex formation accompanying 3 or 4 anchors to the surface greatly reduces the mobility of the ligands to broaden out their high-resolution signals.

When complexed with  $\text{RhCl}_3$  in  $\text{H}_2\text{O}$ , not only N- but also N,N-ligand-(silica) gave no high-resolution signals assignable to coordinated species; monotonous decrease in the peak intensities was also observed in these cases. It was distinctly noticed however that as the amount of  $\text{RhCl}_3$  was increased, the  $\text{C}_4$  and  $\text{C}_5$  peaks were shifted significantly to higher field, with appreciable narrowing of line widths (Fig. 3). The observed changes are obviously due to the protonation of the amino groups of N,N-ligand in

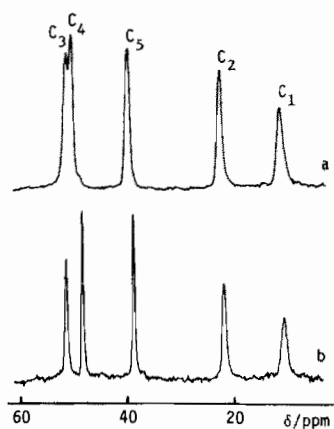


Fig. 3. Effect of the addition of  $\text{RhCl}_3$  on the CMR spectrum of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  groups bonded to silica surface. Numbers are designated from the silicon atom;  $[\text{Rh}]/[\text{L}] = 0$  (a), 0.3 (b); 15 MHz, 29 °C,  $\text{H}_2\text{O}$  solvent; scan numbers = 25,000 (a), 32,000 (b).

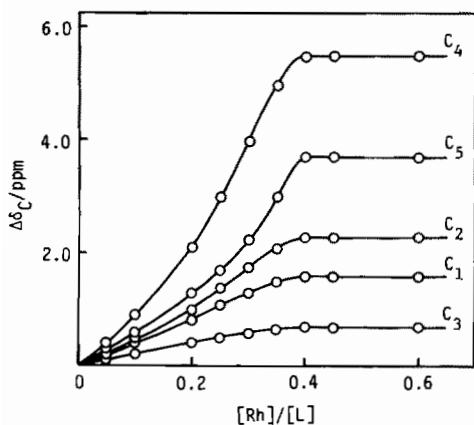


Fig. 4. Effect of the addition of  $\text{RhCl}_3$  on the  $^{13}\text{C}$  chemical shifts of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  groups bonded to silica surface (29 °C,  $\text{H}_2\text{O}$  solvent). Numbers are designated from the silicon atom, and high-field shifts are taken as positive.

view of the agreement in the extent of all the shifts (Fig. 4), as well as line widths [8]. By inspecting Fig. 4 we are able to conclude that all the uncoordinated N,N-ligands are protonated at the  $[\text{Rh}]/[\text{L}]$  ratio of 0.4.

It would be one of the advantages of the present method that the extent of protonation is thus directly determined by spectroscopic analysis. According to this principle, the chemical shifts of the uncoordinated N,N-ligand in Fig. 1 indicate the extent of 30% protonation in comparison with those for 100% protonated state [8]. Regarding N-ligand-(silica), uncoordinated ligands were found completely protonated at  $[\text{M}]/[\text{L}]$  ratios of about 0.2 (M = Pt(II), Rh(III)).

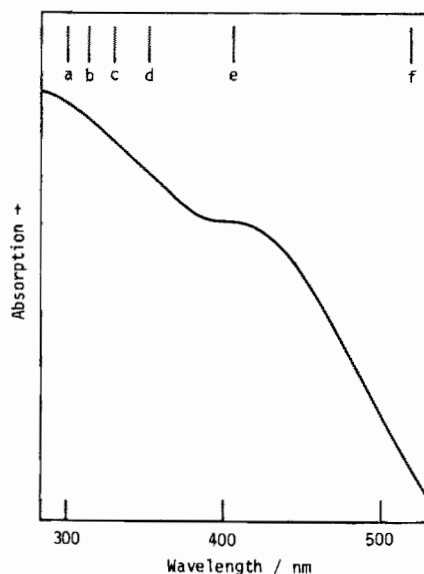


Fig. 5. Diffuse reflectance spectrum of the complex formed by the contact of  $\text{RhCl}_3$  with  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  ligands bonded to silica surface ( $[\text{Rh}]/[\text{L}] = 0.25$ ). Lines show the positions of the peak maximum of d-d transition for various Rh(III) complexes (en = ethylenediamine) [15, 17, 18]: (a)  $[\text{Rh}(\text{en})_3]^{3+}$ , (b)  $\text{cis-}[\text{Rh}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ , (c)  $\text{cis-}[\text{Rh}(\text{OH})_2(\text{en})_2]^+$ , (d)  $\text{cis-}[\text{RhCl}_2(\text{en})_2]^+$ , (e)  $\text{trans-}[\text{RhCl}_2(\text{en})_2]^+$ , (f)  $[\text{RhCl}_6]^{3-}$ .

The failure to detect high-resolution CMR signals of the Rh(III)-coordinated N,N-ligand-(silica) is in contrast to the Pt(II) case. In an attempt to elucidate the structure of the Rh(III) complex formed on the surface, diffuse reflectance spectra were measured. It was observed that upon contact with an aqueous  $\text{RhCl}_3$  solution, a broad peak with its maximum near 410 nm appeared, whose intensity became greater as the added amount was increased ( $[\text{Rh}]/[\text{L}] = 0-0.3$ ). The position and shape of this peak scarcely altered by drying the sample, but a considerable increase was observed for its absorbance. In Fig. 5 a spectrum for a dried sample is presented.

By comparing the positions of the peak maximum of d-d transition for various Rh(III) complexes (Fig. 5), it is suggested that the complex of the type  $\text{trans-}[\text{RhCl}_2(\text{N,N})_2]^+$  (Fig. 6) is formed on the surface, although some chloro ligands would be hydrolyzed to account for the protonation of the remaining uncoordinated ligands. As only 0.838% of the total rhodium is present in the supernatant solution at  $[\text{Rh}]/[\text{L}] = 0.4$ , 80% of N,N-ligand is to be used for the bis-chelate formation. The coordination of fifth and sixth ligands in the bis-chelate Rh(III) complex would restrict the motion of the diamine ligand more than in the Pt(II) case. This additional nature may make it difficult to detect the high-resolution signals of the surface Rh(III) complexes.

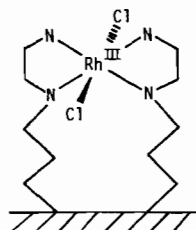


Fig. 6. Proposed structure of the complex formed between  $\text{RhCl}_3$  and  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  ligands bonded to silica surface.

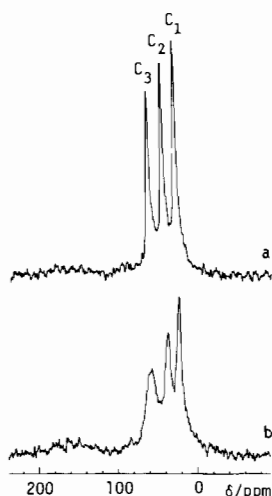


Fig. 7. CP-MAS CMR spectrum of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}\equiv$  groups bonded to silica surface (a), and its change by contact with  $\text{K}_2\text{PtCl}_4$  (b;  $[\text{Pt}]/[\text{L}] = 0.2$ ). Numbers are designated from the silicon atom; 11 scans; /ms contact time.

Because of the recent advances in the CP-MAS NMR spectroscopy of solids [13], we applied these techniques to N- and N,N-ligand-(silica), as well as metal-fixed ones ( $[\text{M}]/[\text{L}] = 0.2$ ;  $\text{M} = \text{Pt}(\text{II}), \text{Rh}(\text{III})$ ). Figure 7 gives the spectra for N-ligand-(silica) with and without platinum(II) ions on its surface. It is clearly seen that the peak for C<sub>3</sub> carbon is broadened markedly in the former spectrum, which would be induced by the overlap of the C<sub>3</sub> peak of the Pt(II)-coordinated ligands. The peaks are, however, not fully resolved because of rather broad line-widths of the uncoordinated ligand itself (about 150 Hz at half maximum).

This is also the case for Pt(II)/N,N-ligand-(silica), and the situation is more severe for the Rh(III) cases due to the smaller coordination shifts [14, 15].

For the precise analysis of the structure of the surface complex it may be necessary to observe directly the CMR signals of the coordinated species. It is also the merit of the present approach that the extent of protonation can be evaluated without analyzing any equilibrium formula. This feature may serve as a plain molecular basis for metal-ion separation with chemically-modified silicas, where gradient elution with continuous change of pH is used frequently [16].

### Acknowledgment

The authors thank the Application Center of Jeol Ltd. for the measurement of CP-MAS NMR spectra.

### References

- 1 R. E. Sturgeon, S. S. Berman, S. N. Willie and J. A. H. Desaulniers, *Anal. Chem.*, **53**, 2337 (1981), and references therein.
- 2 F. R. Hartley and P. N. Vezev, in 'Advances in Organometallic Chemistry', F. G. A. Stone and R. West Eds., Academic Press, New York (1977), vol. 15, p. 189.
- 3 K. B. Yatsimirskii, A. P. Filippov and G. A. Karpenko, *Dokl. Akad. Nauk SSSR (Fiz. Khim.)*, **251**, 652 (1980).
- 4 T. J. Pinnavaia, J. G. Lee and M. Abedeni, in 'Silylated Surfaces', D. E. Leyden and W. Collins Eds., Gordon and Breach, New York (1980), p. 333.
- 5 L. W. Burggraf, D. S. Kendall, D. E. Leyden and F.-J. Pern, *Anal. Chim. Acta*, **129**, 19 (1981).
- 6 K. Tanaka, S. Shinoda and Y. Saito, *Chem. Lett.*, 179 (1979).
- 7 K. Tanaka, S. Shinoda, N. Takai, H. Takahashi and Y. Saito, *Bull. Chem. Soc. Jpn.*, **53**, 1242 (1980).
- 8 S. Shinoda and Y. Saito, *J. Colloid Interface Sci.*, in press.
- 9 F. J. Boerio and J. W. Williams, *Appl. Surface Sci.*, **7**, 19 (1981).
- 10 R. S. Davidson, W. J. Lough, S. A. Matlin and C. L. Morrison, *J. Chem. Soc., Chem. Commun.*, 517 (1981).
- 11 E. B. Sandell, 'Colorimetric Determination of Traces of Metals', 3rd Ed., Interscience, New York (1959).
- 12 L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, **14**, 3007 (1975).
- 13 D. E. Leyden, D. S. Kendall and T. G. Waddell, *Anal. Chim. Acta*, **126**, 207 (1981).
- 14 C. Burgess and F. R. Hartley, *Inorg. Chim. Acta*, **14**, 37 (1975).
- 15 F.P. Jakse, J. V. Paukstelis and J. D. Petersen, *Inorg. Chim. Acta*, **27**, 225 (1978).
- 16 J. R. Jezorek and H. Freiser, *Anal. Chem.*, **51**, 366 (1979).
- 17 M. P. Hancock, *Acta Chem. Scand.*, **A31**, 678 (1977).
- 18 R. D. Gillard and L. R. H. Tipping, *J. Chem. Soc., Dalton Trans.*, 1241 (1977).