

ESR observation of the formation of an Au(II) complex in zeolite Y

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Received (in Cambridge, UK) 8th February 2006, Accepted 20th April 2006

First published as an Advance Article on the web 9th May 2006

DOI: 10.1039/b601900e

Herein we communicate the first time observation of an Au(II) complex stabilized in a zeolite Y supercage, as evidenced by electron spin resonance (ESR); confinement in the zeolite pores obviously stabilizes this unusual oxidation state and prevents it from undergoing disproportionation.

Gold catalysts have attracted much attention in recent years in areas of colloid chemistry, heterogeneous catalysis, fabrication of nanodevices and other applications which depend strongly on the charge state and size of the gold species.^{1–4} Although the divalent state of gold is rare and therefore one of the most interesting oxidation states in transition metal chemistry and biochemistry, only a few paramagnetic Au²⁺ complexes have been reported because of facile disproportionation of Au²⁺ to Au⁰ or Au⁺ and Au³⁺. The gold(II) complexes coordinated by dialkyldithiocarbamate and maleonitrile-dithiolate ligands were synthesized and investigated in solution.^{5,6} van Rens and Schlupp successfully incorporated the [Au(II)-bis(maleonitriledithiolate)] complex into a single crystal of [(*m*-C₄H₉)₄N]₂{Ni(II)-bis(maleonitriledithiolate)} and obtained ESR spectra of an oriented magnetically dilute sample.^{7–9} A ground state hole configuration (B_{1g})²(A_g)¹ was proposed for the Au[1,2-S₂C₂(CN)₂]₂^{2–} complex. It seems that the paramagnetic Au(II) complexes can be stabilized when good σ -donor and π -acceptor ligands are employed to stabilize the metal centre. Zeolites are very promising to act as support for stabilizing cations and metallic species because of the crown-ether-like ring structures in their cages and channels. In this paper we employed ESR spectroscopy to study the anchoring of an Au complex in Y-type zeolites. For the first time we report the observation of the square-planar complex of Au(II) with four nitrogen atoms of two ethylenediamine ligands in the supercage of the zeolite. It can be stabilized following an oxygen pre-treatment between 150 and 250 °C.

The original NaY zeolite (Si/Al = 2.7) was obtained from CU Chemie Uetikon AG in Switzerland. To suppress organic impurities the zeolite was calcined in air at 510 °C for 12 h. An (Na⁺/NH₄⁺)-Y zeolite was prepared by exchanging the NaY zeolite in an aqueous solution of 1 M NH₄NO₃ at 80 °C for 12 h. Gold(III) was introduced into the zeolite by means of cation exchange by the [Au(en)₂]Cl₃ complex ('en' representing ethylenediamine, (H₂N–CH₂–CH₂–NH₂)), which was synthesized following the procedure by Block and Bailar.¹⁰ A gold loading of ca. 2%

was prepared. The original HAuCl₄ was obtained from Chempur in Germany. The exchange reaction is schematically written as follows: 3 Na(NH₄)_(zeolite)⁺ + [Au(en)₂]_{aq.}³⁺ ↔ 3 Na(NH₄)_{aq.}⁺ + [Au(en)₂]_(zeolite)³⁺

It has been demonstrated that it is rather difficult to obtain a fine dispersion of gold species, and that gold species in the supercage of a Y-type zeolite catalyse CO oxidation.¹¹ The Au³⁺ cation is easily reduced. Here we chose ethylenediamine, instead of other more common ligands such as NH₃, Cl[–], H₂O *etc.*, so that because of its large size the [Au(en)₂]³⁺ complex can reside only in the supercages of the zeolite. Before ESR measurements, the gold sample was pretreated under flowing oxygen while slowly increasing the temperature (30° h^{–1}) up to 150 °C. ESR measurements were performed using an X-band Bruker EMX spectrometer. All measurements were performed at *T* = 20 K with a modulation amplitude of 4 G and a microwave power of 1 mW. Spectra were simulated using the Bruker ESR simulation program based on perturbation theory (Simfonia Version 1.25).

After the gold sample had been pretreated with oxygen at 150 °C, a characteristic hyperfine splitting pattern is observed, as shown in Fig. 1B. Similar spectra had previously been reported for the complex of Cu(II) with imidazole in solution.¹² Copper and gold have the same nuclear spin (*I* =), are in the same group of the periodic table, and in their divalent state they both have a d⁹

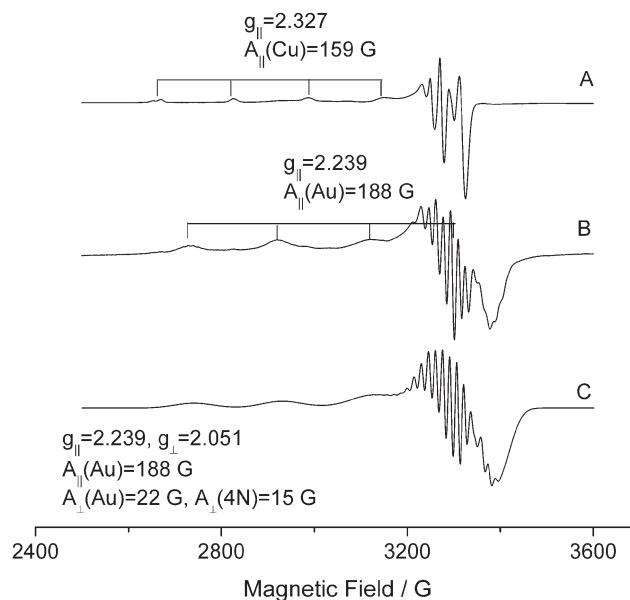


Fig. 1 Experimental ESR spectra of [Cu(en)₂]-Na,NH₄Y (A) and [Au(en)₂]-Na,NH₄Y (B) pretreated with oxygen at 150 °C, and simulated spectra (C) of Au(II)-ethylenediamine in zeolite for emphasizing the *g*_⊥ and *A*_⊥ components.

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electron configuration; thus they show similar properties. It is therefore important to exclude the possibility that our spectrum is due to a Cu^{2+} impurity, so the corresponding $[\text{Cu}(\text{en})_2]\text{Cl}_2$ complex exchanged-(Na/NH_4)-Y zeolite was prepared for comparison. Fig. 1A shows that its ESR spectrum is quite different from that of the gold sample. The $\text{Cu}(\text{II})$ complex easily decomposes after pre-treatment, forming Cu^{2+} ions interacting with the zeolite framework.¹³ There are two spin- isotopes, ^{63}Cu and ^{65}Cu with 69 and 31% natural abundance, respectively, and the latter has a 7% larger magnetic moment. This leads to the observable splitting in the low field component of Fig. 1A but not in the $\text{Au}(\text{II})$ spectrum of Fig. 1B which indicates the presence of a single isotope. Further support that the observed spectrum 1B cannot be attributed to a copper species comes from the maximum impurity of the original gold chemical supplied from Chempur, which is stated to be less than 100 ppm. Comparison of the double integral of the ESR spectrum (Fig. 1B) with that of a spin standard sample reveals a spin concentration of 2.4×10^{-3} spins per gold atom. This demonstrates that 0.2% of all gold ions are ESR active, which is about 20 times more relative to what could be ascribed to an impurity assuming that it consists of Cu only. Therefore, the observed ESR spectrum is Fig. 1B can safely be associated with a gold species.

Pre-treatment was also performed with various other gases at 150 °C. Interestingly, the ESR signal arose only after oxygen pre-treatment. Furthermore, it was also found that the support has a strong effect on the formation of this ESR signal, as certain amounts of NH_4^+ appeared to be necessary in the zeolite, favouring formation and stability of the complex.

$[\text{Au}(\text{en})_2]\text{Cl}_3$ was used to exchange the zeolite in our case, and it is known that the ligands can auto-reduce cations.^{14,15} Au^{3+} is easily auto-reduced to ESR inactive Au^+ (no evidence for Au^0 was detected by ESR at this stage), however the oxygen pre-treatment leads to partial oxidation to ESR active Au^{2+} . Fig. 1C shows the simulated spectrum, demonstrating the agreement with experiment in the characteristic range of the g_{\perp} and A_{\perp} components of the $\text{Au}(\text{II})$ complex. The quadrupole interaction term of gold was not included in the simulation, and all the tensors were assumed coaxial. Simulation yields the spin Hamiltonian parameters $g_{\parallel} = 2.239$, $g_{\perp} = 2.051$, $A_{\parallel}(\text{Au}) = 188$ G, $A_{\perp}(\text{Au}) = 22$ G, $A_{\perp}(4\text{N}) = 15$ G, $A_{\parallel}(4\text{N})$ is not resolved. It reveals that one gold atom interacts with four equivalent nitrogen atoms in our case. These values are in a similar range as those reported for gold(II)-bis(maleonitrile-dithiolate) in a single crystal of the corresponding Ni(II) complex, indicating considerable delocalisation of the 'metal d electrons' to the ligand ($g_1 = 1.98$, $g_2 = 2.00$, $g_3 = 2.11$, $A_x = 35$ G, $A_y = 33$ G, $A_z = 32$ G). The larger hyperfine tensor components of ^{197}Au in $\text{Au}(\text{II})$ -Y are ascribed to a significantly higher d-orbital contribution.

The experimental spectrum shows a clear axial characteristics and coincides well with the simulated spectrum of $\text{Au}(\text{II})$ with N_4 , suggesting that an $\text{Au}(\text{II})$ - N_4 square planar type coordination accounts for the observed ESR spectrum. Three of the expected four hyperfine transitions in the parallel region are visible whereas the fourth component overlaps with A_{\perp} features and is not resolved. The multiplet spectrum in the perpendicular regime is due to both the hyperfine interaction with gold and the superhyperfine interaction with the nitrogen ligands. Some small differences between the experimental and simulated spectra might

be related to a slight non-axiality or inequivalence of the nitrogen nuclei interacting with gold. The pronounced axial nature of the spectrum clearly excludes tetrahedral or other higher symmetries.

Even though the low yield of $\text{Au}(\text{II})$ reveals a delicate balance of trends it is noteworthy that the species is stable in its somewhat unusual oxidation state for several months. Isolating individual complexes in the pore structure of the zeolite obviously prevents disproportionation. Complexation by ethylenediamine provides further stabilization. Nevertheless, auto-reduction of the gold-ethylenediamine complex led to stable gold nanoparticles in zeolite supercages, as reported by Guillemot and Horváth *et al.* and proven by TEM microtomy and ^{129}Xe NMR studies.¹⁵⁻¹⁷ $[\text{Au}(\text{en})_2]\text{Cl}_3$ enters only the supercages of the zeolite during the ion-exchange process because the dimensions of the gold complexes do not allow them to enter the sodalite cages or the hexagonal prisms. Eventually, by further treatment, gold nanoparticles can be formed for catalytic applications.

We further investigated the stability of the $\text{Au}(\text{II})$ complex in the zeolites and found that the temperature employed in oxygen pre-treatment strongly influences the ESR signal. The intensity of the split signal decreases when the oxygen pre-treatment temperature increases to 200 °C, and disappears completely at 250 °C (results not shown). The gold(II) species is very sensitive to H_2 even at RT, and is completely destroyed by H_2 treatment at 100 °C, as shown in Fig. 2B. A single ESR peak at $g = 2.008$ appears after H_2 reduction at 100 °C. It is tentatively attributed to defects of the support or to gold nanoparticles,^{18,19} which needs further evidence. However an interesting finding is that the ESR signal of the $\text{Au}(\text{II})$ complex can partly be recovered when the H_2 -treated sample is treated again with oxygen at 150 °C (Fig. 2C). This shows that the $\text{Au}(\text{II})$ -complex is still intact and has only switched its oxidation state. It suggests strongly that the complex may be suitable as a redox catalyst, and that oxygen treatment can convert inactive Au^+ to paramagnetic Au^{2+} species. However, further increasing the oxygen treatment temperature to 250 °C irreversibly annihilates

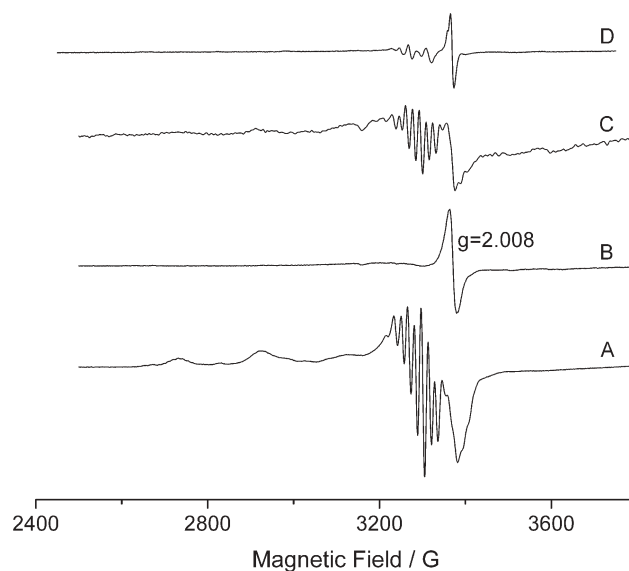


Fig. 2 ESR spectra of $\text{Au}(\text{II})$ -ethylenediamine in zeolite pretreated with oxygen at 150 °C (A), followed by H_2 at 100 °C (B) and followed by oxygen again at 150 °C (C) and 250 °C (D).

the multiplet signal. Instead, a new set of signals is observed, which has also been found with the pure NH_4Y zeolite after pre-treatment at high temperatures.

In summary, employing ESR, we observed for the first time the formation of the square-planar $\text{Au}(\text{II})$ complex with N_4 in the supercage of a Y-zeolite. The complex is stabilized in the supercage of the Y-zeolite after oxygen treatments between 150 and 250 °C. This finding will be of great interest for heterogeneous catalysis.

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