

The Electronic Spectra of Cationic Amine Complexes of the Nickel(II) Ion adsorbed on the Surface of Silica Gel

By B. J. HATHAWAY* and C. E. LEWIS

(Department of Chemistry, University of Essex, Colchester)

TRANSITION-METAL complex cations can be adsorbed on the surface of silica gel, in the sodium form, by exchange with the sodium cations.¹ In the past such systems have been described as involving an electrostatic attraction for the ion by the surface.² A study of the electronic spectra of these systems has shown that under certain circumstances the complex cation may interact with the surface, even at room temperature, with the probable formation of a bond to the surface.

From aqueous solutions of $\text{Ni}(\text{en})_3(\text{NO}_3)_2$, the $\text{Ni}(\text{en})_3^{2+}$ cation (en = ethylenediamine) can be adsorbed onto the surface of silica gel and the diffuse reflectance spectra of air-dried samples (Figure 1) indicate that the same species, namely $\text{Ni}(\text{en})_3^{2+}$ is present on the surface as was originally present in the aqueous solution. At this stage the cations are associated with the surface by an electrostatic attraction. Dehydration of the gels at room temperature by prolonged evacuation (24 hr. at 10^{-4} torr), a process which is known to remove physically adsorbed water,³ results in marked changes in the electronic spectra (Figure 1). The spectra still suggest a broadly octahedral environment for the nickel(II) ion but the bands are shifted to lower energy suggesting the displacement of ethylenediamine by oxygen ligands. As water has been removed from the system and as the changes in spectra can be rapidly reversed by rehydration (exposure to water vapour) it is unlikely to be water that is displacing the ethylenediamine from the co-ordination shell of the nickel(II) ion. It is suggested that the removal of water from the surface enables the $\text{Ni}(\text{en})_3^{2+}$ cations to react with the surface and bond it to the surface. A comparison of the electronic spectrum of the surface-bonded species with that of nickel ethylenediamine complexes of known structure⁴ suggests that the nickel ion environment is *cis*- $\text{Ni}(\text{en})_2\text{O}_2$ implying that the surface is acting as a chelate oxygen ligand.

The structure of the surface complex depends very much on the nature of the ligands co-ordinated to the transition-metal ion prior to adsorption, with $\text{Ni}(\text{dien})(\text{NO}_3)_2$ and $\text{Ni}(\text{dien})_2(\text{NO}_3)_2$ (dien = diethylenetriamine) changes in the spectra of adsorbed cations also occur upon evacuation, but with these cations the nickel(II) ion is not present in even an approximately octahedral, tetrahedral, or square coplanar environment.⁵ The spectra by comparison with that of the non-aqueous solution

spectrum⁶ of $\text{Ni}(\text{Et}_4\text{dien})\text{Cl}_2$ (Figure 2, Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) in which state

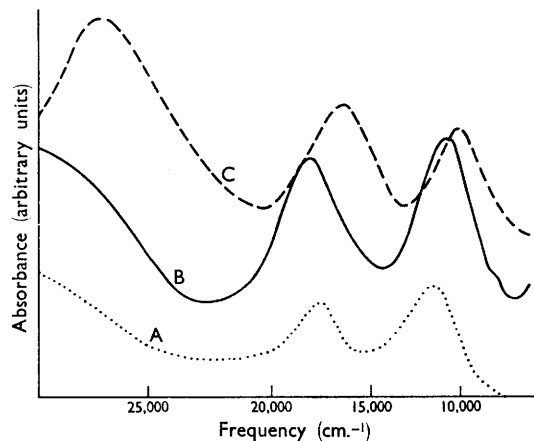


FIGURE 1. The electronic reflectance spectra of A, $\text{Ni}(\text{en})_3(\text{NO}_3)_2$; B, $\text{Ni}(\text{en})_3^{2+}$ on air-dried silica gel; C, $\text{Ni}(\text{en})_3^{2+}$ on silica gel after evacuation for 24 hr.

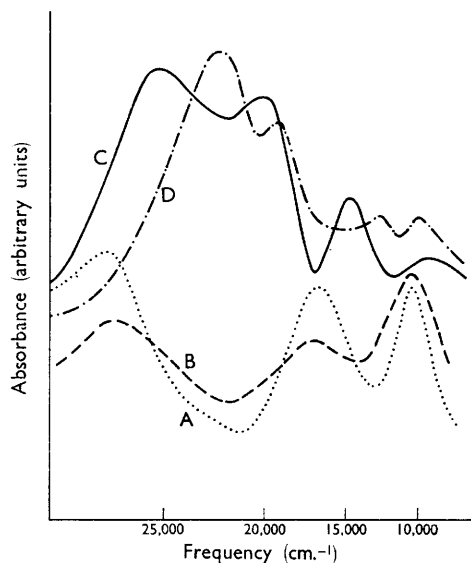


FIGURE 2. The electronic reflectance spectra of A, $\text{Ni}(\text{dien})_1(\text{NO}_3)_2$; B, $\text{Ni}(\text{dien})_1(\text{H}_2\text{O})_n^{2+}$ on air-dried silica gel; C, $\text{Ni}(\text{dien})^{2+}$ on silica gel after evacuation for 24 hr. D shows the non-aqueous solution spectra of $\text{Ni}(\text{Et}_4\text{dien})\text{Cl}_2$ for comparison.

it is paramagnetic, suggest a five-co-ordinate configuration, probably trigonal bipyramidal. The band positions of this complex are at lower energy than those of the surface complex [considered as Ni (dien) O₂], consistent with the relative position of the respective ligands in the spectrochemical series.⁷ The Ni(dien)O₂ surface complex has a magnetic moment of approximately 3.0 B.M. consistent with a spin-free five-co-ordinate nickel(II) ion environment.^{5,6} A five co-ordinate environment for a nickel(II) ion in a complex is generally obtained by using bulky ligands which are unable to assume an octahedral co-ordination. Attempts to prepare five-co-ordinate complexes of unsubstituted (dien) were unsuccessful, Stuart models indicate that (dien) is unlikely to impose five-co-ordination on the nickel(II) ion on its own and suggests that it is a steric requirement of the surface which imposes five-co-ordination on the adsorbed Ni(dien)²⁺ ion. The magnitude of the interaction

with the surface is emphasised by the formation of a similar surface complex using both a mono- or bis-(dien) complex of nickel(II). An examination of a Stuart model of a silica gel surface (based on β -tridymite⁸) indicates that suitable adsorption sites are available involving adjacent oxygen atoms capable of chelating to the nickel ion.

These and other results suggest that the environment adopted by a given ion depends on a fine balance of effects involving the particular transition metal ion used, the number and nature of ligands co-ordinated to it, the role of water on the surface, and the steric requirements of the surface. The particular role of surface water in determining the ion-surface interaction is being used to elucidate the factors involved in the preparation of catalysts consisting of dispersed metallised gels.

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