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Preparation and characterization of the 1:1 inclusion compound γ-cyclodextrin/$[Ni(dmit)_2]^{1-}$

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The preparation of a 1:1 inclusion compound involving γ-cyclodextrin and bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate (III) complex ion, $[Ni(dmit)_2]^{1-}$, is reported. The inclusion complex is characterized by UV-visible and Raman spectroscopy, thermal analysis and X-ray powder diffractometry.

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides with six (α), seven (β) and eight (γ) D(+)-glucopyranose units. A remarkable characteristic of CDs is the presence in their structures of hydrophobic cavities that can host a great variety of guest species, forming rather stable inclusion compounds, that in the case of relatively simple molecules as guests, have been extensively investigated.[1] However, inclusion compounds bearing transition metal complexes as guest species have been only scarcely reported in the literature.[2,3]

H_2dmit, or 1,3-dimercapto-1,3-dithiole-2-thione, is a rather strong acid that gives the anionic ligand 'dmit', which forms very stable metal complexes with several transition metal ions like Zn(II), Ni(III), Pd(II), Pt(II), Cu(III), etc.[4] Such complex anionic species, $[Metal(dmit)_2]^{n-}$, have aroused considerable interest over recent years by virtue of the appreciable electrical conductivity of their salts in the solid state.[5] In fact, mixed valence species like $(NMe_4)[Ni(dmit)_2]_2$, where the complex anions are stacked in the solid, show superconductivity under high pressure and cryogenic temperatures ($T_c = 5$ K at 7 kbar).[5] In the case of $(NBu_4)[Ni(dmit)_2]$, semiconductor behaviour is exhibited when the compound is pure,[6] the conductivity increasing by doping with iodine or bromine.[7] The structure of the anion is depicted in Figure 1(a).

One characteristic of all these compounds is their virtual insolubility in water, regardless of the nature of the cation.[6] Another very important characteristic of such anionic complexes is the remarkable electronic delocalization of the π system that, on the one hand makes it possible to generate species like $[Ni(dmit)_2]^{n-}$ ($n = 0, 1, 2$) by electrochemically reversible steps and, on the other hand, gives origin to highly favourable electronic transitions at unusually low energies.[8,9] The nature of such electronic transitions has been recently clarified by a resonance Raman investigation.[9]

The possibility of enormously increasing the solubility of $[Ni(dmit)_2]^{1-}$ salts in water by its inclusion into γ-CD was first observed by one of the present authors,[10] opening up new possibilities for investigating such species in aqueous media. That was the main motivation that led to the present investigation.

EXPERIMENTAL

Materials

γ-Cyclodextrin supplied by Aldrich was used without purification.

H_2dmit (4,5-dimercapto-1,3-dithiole-2-thione) was prepared according to directions in the literature,[4] which was by the chemical reduction of carbon disulphide with metallic sodium and isolation in the form of its stable zinc complex, $[NBu_4)_2[Zn(dmit)_2]$. $(NBu_4)[Ni(dmit)_2]$ was prepared by the oxidation of $(NBu_2)_2[Ni(dmit)_2]$ in methanol solution with molecular oxygen and characterized by its elemental and thermal analyses as well as by UV-visible and IR spectroscopy. Elemental analysis gave the following results: 38.5%, 1.9%, 5.2% and 8.3% for C, N, H and

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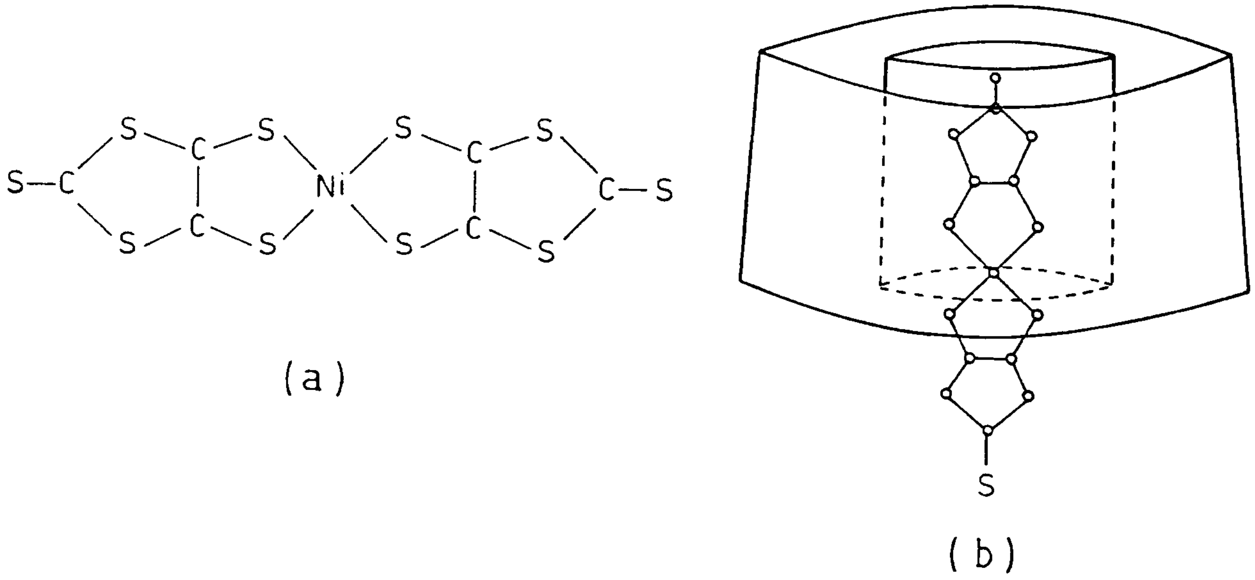

Figure 1 Structures of (a) $[Ni(dmit)_2]^{1-}$ complex ion and (b) γ-CD inclusion compound.

Ni, respectively. The corresponding calculated values are 38.1%, 2.02%, 5.19% and 8.47%.

Preparation of the inclusion compound

$(NBu_4)[Ni(dmit)_2]$ (20 mg, 3.85×10^{-5} mol) was completely dissolved in 10 ml of acetonitrile with the subsequent addition of 40 ml of absolute ethanol. To this solution 50 mg of γ-CD (3.89×10^{-5} mol) was added dropwise with constant stirring. The solution was stirred and heated at 50–60°C for 3 h and then evaporated at 65°C. The greenish residue was dissolved in water (50°C) and filtered. The solution was then evaporated at 65°C and the green powder obtained was then totally soluble in warm water (50°C). The same procedure was used to try to prepare similar compounds, e.g. the inclusion compound of $[Ni(dmit)_2]^{1-}$ and α-CD, and that of $[Zn(dmit)_2]^{2-}$ and γ-CD; in the latter cases a mechanical mixture of the two components was obtained. These experiments suggest that the formation of inclusion compounds with cyclodextrins is governed not only by the geometrical parameters of the cavity, but also by the charge of the ion complex.

The mechanical mixture of γ-CD and the nickel complex in a 1:1 molar ratio was prepared as a blank, by first grinding the complex and then by the addition of γ-CD, with subsequent gentle grinding until a greenish homogenous powder was obtained.

Physical measurements

The Raman spectra of the solids were obtained by using a Jarrel–Ash 25-300 double monochromator Raman spectrometer fitted with a CsGaAs high-gain photomultiplier tube. The spectra were excited with the 488.0 nm line of an Ar^+ laser (Spectra Physics-165) operated at 30 mW. The spectral resolution was 8 cm^{-1}. Use was made of a spinning cell to avoid sample decomposition.

X-ray powder patterns were obtained with a Carl Zeiss–Jena (Model UDR-6) diffractometer with 1.54 Å CuK_α radiation. The scan rate was 2°/min.

The UV-visible spectra of the solid compounds were obtained on a Bomen DA-3 FT-Spectrophotometer using the powder diffuse reflectance technique with a xenon lamp. The spectra were obtained after 64 scans and the resolution was 50 cm^{-1}.

Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained on a Delta Series TGA7 system at a heating rate of 100°C/min in air.

The infrared spectrum of the inclusion compound was also obtained but since it showed only vibrational bands of the γ-CD, it was of no use for the present investigation.

RESULTS AND DISCUSSION

Solubility

The first evidence for the inclusion of $[Ni(dmit)_2]^{1-}$ into γ-CD, is the solubility of $(NBu_4)[Ni(dmit)_2]$ in water containing γ-CD, while the neat complex is virtually insoluble in pure water. Also relevant is the fact that such solubility is very selective, i.e. the complex is not soluble in aqueous solutions of α-CD or β-CD. Even more remarkable is the observation that $(NBu_4)_2[Ni(dmit)_2]$ is not soluble in an aqueous solution of any of the CDs, i.e. changing from

[Ni(dmit)$_2$]$^{1-}$ to [Ni(dmit)$_2$]$^{2-}$ makes a drastic difference to the inclusion into γ-CD.

Thermal analysis

The TG and DTA curves for γ-CD, (NBu$_4$)[Ni(dmit)$_2$] and for the inclusion compound as well as for the mechanical mixture of the γ-CD/complex are shown in Figures 2 and 3, respectively.

The TG/DTA results show that the weight loss for γ-CD occurs in two steps: at 40–120°C there is a dehydration process, and near 300°C, a decomposition (m.p. 267°C). The same data for the nickel complex show a weight loss in three steps: between 200 and 260°C there is a decomposition (m.p. 191–193°C), whereas the other two steps, at 260–430°C and 430–600°C correspond to the decomposition of the products formed in the first step.

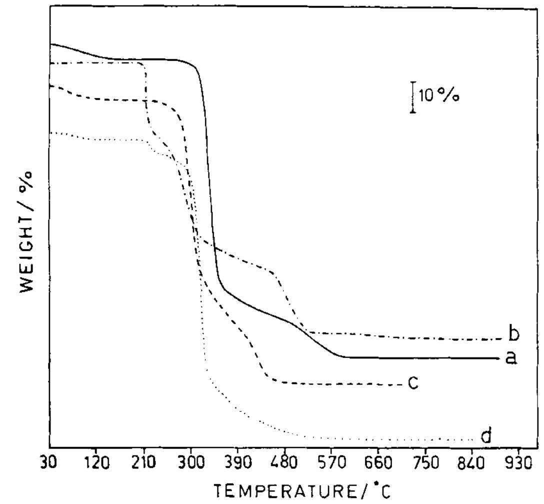

Figure 2 TG curves: (a) γ-CD, (b) (NBu$_4$)[Ni(dmit)$_2$] complex, (c) γ-CD inclusion compound, (d) mechanical mixture.

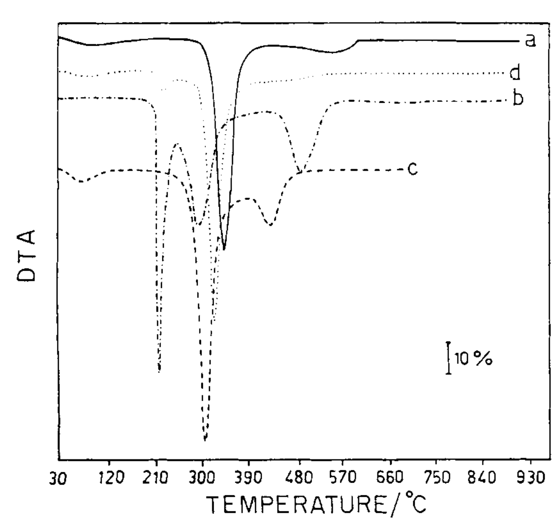

Figure 3 DTA curves: (a) γ-CD, (b) (NBu$_4$)[Ni(dmit)$_2$] complex, (c) γ-CD inclusion compound, (d) mechanical mixture.

As can be observed from the data, the TG/DTA curves for the mechanical mixture (γ-CD and complex) correspond to the superposition of the TG/DTA curves of the isolated components. On the other hand the TG/DTA curves for the inclusion compound show a first step at 30–120°C due to the dehyration of γ-CD, a second step at 170–400°C, corresponding to γ-CD decomposition, and finally a third weight loss from 400 to 550°C. It is worth mentioning that for the inclusion compound the weight loss at 200–260°C, characteristic of the neat complex, is not present, in contrast to that observed for the mechanical mixture. The weight loss at 400–550°C may be due to complex decomposition.

The host:guest molar ratio was obtained from the TG curve, since a NiS residue remains after the thermal decomposition of the complex at above 600°C, and from its mass it is possible to obtain the mass of the nickel complex. By subtracting such mass from the initial mass one obtains the mass of γ-CD, and wich such a procedure a molar ratio of 1.0:1.2 (γ-CD:complex) was obtained. The same procedure was used for the mechanical mixture and neat complex, giving excellent results.

X-ray powder diffraction

The X-ray powder diffractograms of the separated compounds, the inclusion compound and the mechanical mixture are displayed in Figure 4. The peaks observed at ca. 5, 9.5 and 190°C in Figure 4(a) are characteristic of γ-CD, being absent from the diffractograms of the neat complex, and of the inclusion compound, i.e. Figures 4(b) and 4(c), respectively. As expected, such peaks are observed in the diffractogram of the mechanical mixture, i.e. Figure 4(d). In the case of the complex, the main features are observed at 6°C and 10.5°C. Again, such peaks are absent from the diffractograms of γ-CD and the inclusion compound, but present in the diffractogram of the mechanical mixture. Consequently, it can be inferred that the diffractogram of Figure 4(c) is characteristic of a new crystalline material, i.e. the 1:1 inclusion compound of γ-CD with [Ni(dmit)$_2$]$^{1-}$.

Raman spectroscopy

IR spectroscopy was not a convenient technique for investigating the present system since γ-CD absorbs extensively in several regions of the infrared, masking the most relevant spectral features of the complex. On the other hand Raman spectroscopy proved to be one of the techniques of choice for investigating the present system, since γ-CD is a very poor Raman scatterer,

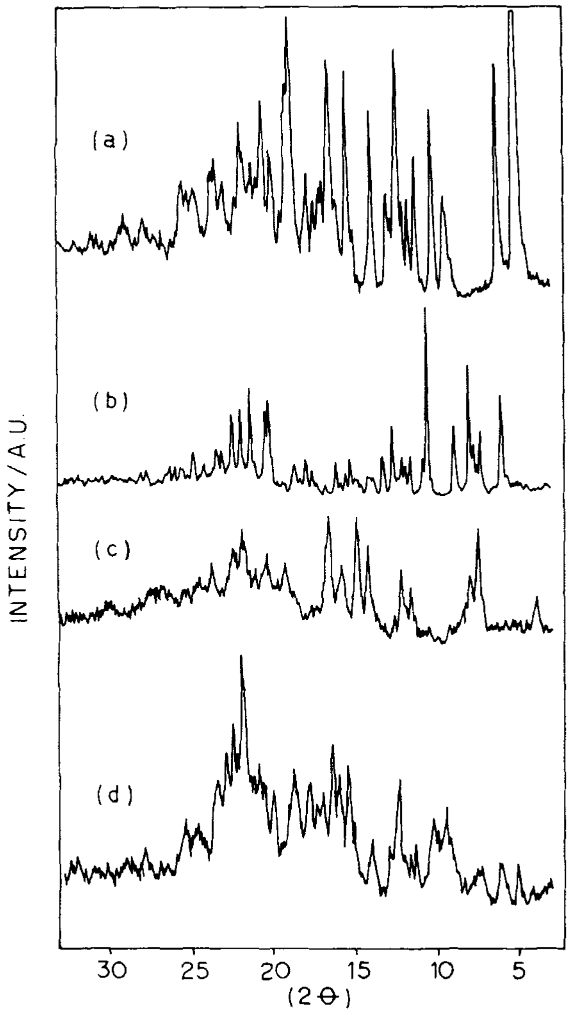

Figure 4 X-ray diffraction patterns of (a) γ-CD, (b) $(NBu_4)[Ni(dmit)_2]$ complex, (c) γ-CD inclusion compound, (d) mechanical mixture.

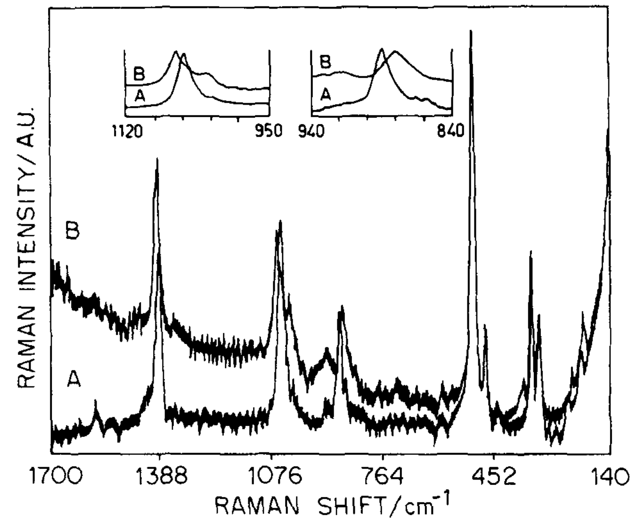

Figure 5 Raman spectra in the solid state: (A) $(NBu_4)[Ni(dmit)_2]$ complex, (B) γ-CD inclusion compound. The insets are expanded views of the spectra in (A) and (B).

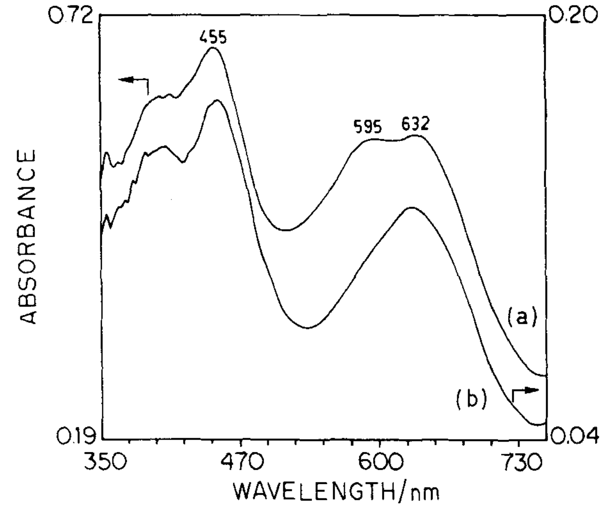

Figure 6 UV-visible diffuse reflectance spectra of (a) $(NBu_4)[Ni(dmit)_2]$ complex, (b) γ-CD inclusion compound.

while the complex anion, by virtue of a pre-resonance enhancement,[10] shows up quite distinctively in the spectrum.

The Raman spectra of the neat complex and of its inclusion compound in γ-CD are displayed in Figures 5(a) and 5(b), respectively. The modes that show up, in both spectra, are essentially the modes of the complex anion enhanced by a pre-resonance effect.[10] This insets in Figure 5 highlight the most significant differences in the Raman spectra of the neat complex and of the inclusion compound; the modes at 1053 and 893 cm^{-1}, that were assigned to $\nu(C{=}O)$ and $\nu(C{-}S)$ stretching, respectively.[7,11] In the inclusion compound these modes are shifted to 1063 and 883 cm^{-1}, respectively. The relatively small magnitude of the shifts indicates that the anionic complex inside the γ-CD cavity conserves its highly planar and delocalized structure. This is also confirmed by the fact that the enhanced modes are the same in both the neat complex and in the inclusion compound, i.e. the chromophoric moiety is not significantly disturbed by the inclusion. In Figure 1(b) is shown schematically a proposed structure for the inclusion compound.

UV-visible spectroscopy

The UV-visible spectra of $(NBu_4)[Ni(dmit)_2]$ and of its inclusion compound in γ-CD are shown in Figures 6(a) and 6(b), respectively. The main difference between these spectra is the absence in the spectrum of the inclusion compound of the intense absorption, present at ca. 595 nm in the spectrum of the neat complex. It would be rather speculative to propose an interpretation for that fact, since the assignment of that particular transition is still rather controversial.

CONCLUSION

From the analysis of the observed results it is clear that the species $[Ni(dmit)_2]^{1-}$ is included in the cavity of γ-CD, forming a 1:1 inclusion compound that is highly soluble in water. It is also clear that the structure of the complex is not significantly disturbed by the inclusion. In view of the growing interest in metal–dmit anionic species, due to the appreciable conductivities of their salts in the solid state, there is also increasing interest in investigating them as discrete species in solution. The possibility, demonstrated in the present work, of including them in CDs opens up new and interesting ways of performing such investigations.

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