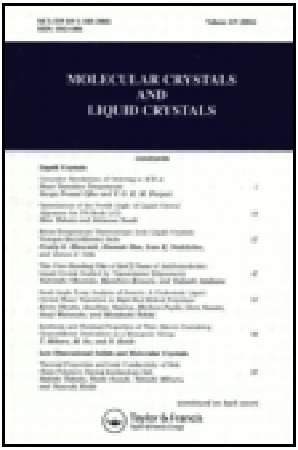

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TOPOCHEMICAL TRANSFORMATIONS OF SUBSTITUTED CYCLOPENTANONE TRANSITION METAL ADDUCTS

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The application of chelation to transition metal ions as a means of controlling the packing motifs of substituted catechols and of substituted malonates has been studied. Substituted malonates have been shown to be capable of solid state photo- or thermally induced decarboxylation or dehydration. It has been shown that chelation with different metallic cations (Ni^{2+}, Zn^{2+}, Cu^{2+}, V^{5+}, Cr^{3+} and VO^{2+} were used) led to differences in solid state packing, and thus reactivity of the benzylidene cyclopentanone framework. The ratio of organic moiety to metallic cations was varied for the copper and vanadyl species leading to solids with different properties to the stoichiometric adducts, leading to the possibility of charge transfer phenomena.

Keywords: topochemical reactions; decarboxylation; chelates

INTRODUCTION

There has been a long-standing interest in the study of the solid state photoreactivity of substituted benzylbenzylidene cyclopentanones (BBCP, **I**) and of dibenzylidene cyclopentanones (DBCP, **II**) [1,2]. The reaction that BBCP and DBCP undergo is [2+2] cycloaddition of the benzylidene non-aromatic double bond, to yield a cyclobutane dimer. Such reactions are topochemical, of the single crystal to single crystal kind. The study of the factors controlling packing in organic crystals, has been expanded by studying the application of chelation [3,4] to transition metal ions as a means of controlling the packing motifs of substituted catechols based on **II**, such as **III** as well as malonic derivatives (e.g. **IV**, **V**). Preliminary work with **IV** has shown that it is capable of solid state

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photo-induced decarboxylation (Fig. 1) which is currently under further investigation.

It was shown that the strategy of using different metal cations for chelation to alter the packing motif may be successful, and resulted in the case that obtains for the catecholic derivatives of DBCP in a semi-conducting coordination polymer. In that study, Ni^{2+}, Zn^{2+} and Cu^{2+} were used. These were chosen because all three had preference towards the same coordination number, 4. Investigation by FTIR showed that of the three chelates two were photodimerisable as was the pristine **III**, whereas the third was photostable [4,5]. Comparison of the fingerprint region of the spectra indicated that there were differences in packing.

In this paper, we present an extension of the study of the use of chelation to metal cations as a crystal engineering device, to the use of adducts to carbonyl group of the cyclopentanone moiety, and to the effect of altering the organic moiety to metal cation ratio, upon packing and thus on solid state properties, including reactivity.

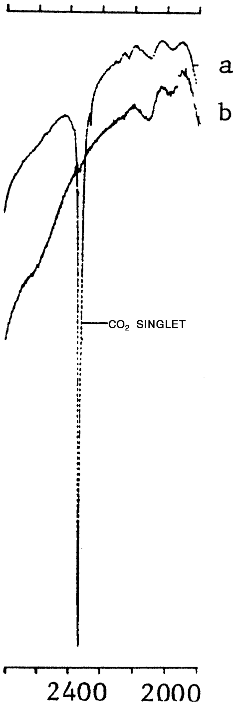


FIGURE 1 FTIR spectra for **IV** (a) after and (b) before photoreaction.

EXPERIMENTAL

2,5-Dibenzylidene cyclopentanone was prepared as previously described. Complexation (adduct formation) with the metal cations was carried out by mixing appropriate amounts of a chloroform-excess methanol solution of DBCP to methanolic or aqueous solutions of the appropriate metal cation, and adding 1–2 ml of dilute aqueous ammonia. Fourier Transform infrared (FTIR) spectroscopy was carried out with a Shimadzu spectrophotometer (FTIR-8501) using the diffuse reflectance, DRIFTS, method (Spectratech attachment). Spectra in this paper are presented as Kubelka-Munk plots. UV-visible spectra were measured in methanol or water solutions using a Shimadzu spectrophotometer.

DISCUSSION

DRIFTS and UV-Vis spectra were used to confirm that complexation (adduct formation) between DBCP and the metal ions used took place. The ions used in this study were Ni^{2+}, Zn^{2+}, Cu^{2+}, V^{5+}, Cr^{3+} and VO^{2+}, used to provide a variety of coordination numbers and possible geometries. Structure **VI** shows the proposed formula for the adduct. Figure 2 shows the DRIFTS spectrum for pristine DBCP, and Figure 3 that for the VO^{2+} adduct prepared from a reaction mixture containing 2:1 molar ratios of metal ion to organic concentrations respectively.

It should be noted that the peak at $1690\,cm^{-1}$ present in Figure 2 which is characteristic of carbonyl groups (C=O stretch) is absent from Figure 3, confirming that the relevant group has been modified by reaction. The advantage of using DRIFTS as opposed to conventional FTIR is that the sample can be used as is, in other words without grinding and without mixing with KBr or other pellet-making material, in which case there is danger of ion-exchange. Comparison of the DRIFTS spectra for adducts made from different metal cations had subtle differences in the bands present in the so-called fingerprint region of the spectrum, *ca* 500–$1300\,cm^{-1}$ which are due vibrational modes involving more than one group, and are characteristic of the crystal structure, in other words are different for different polymorphs. These differences can be attributed to different packing motifs for the DBCP moiety in the presence of different chelating metallic cations. A similar observation has been made previously in the case of chelates with catechol-substituted DBCP.

Figure 4 shows the DRIFTS spectrum for the VO^{2+} DBCP adduct for an organic to metal ion molar ratio of 1:3. The two spectra (Fig. 3 and Fig. 4) are widely different, indicating different packing motifs, necessary to accommodate the extra cations, which are, presumably, present as free

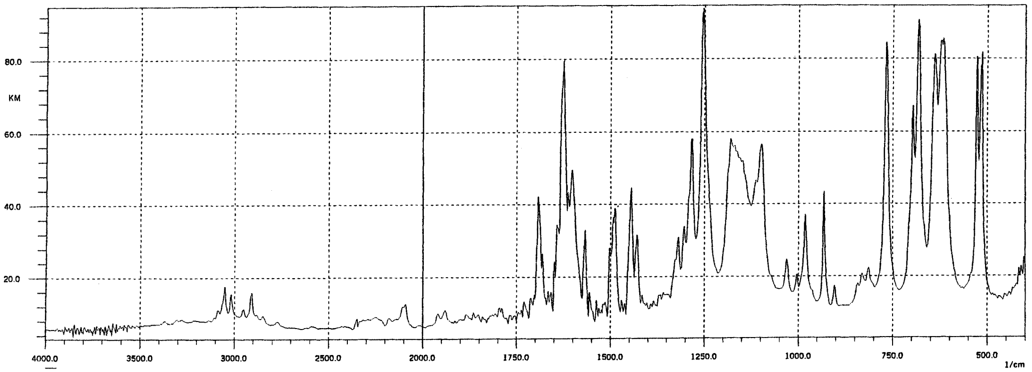


FIGURE 2 DRIFTS spectrum for DBCP (**II**).

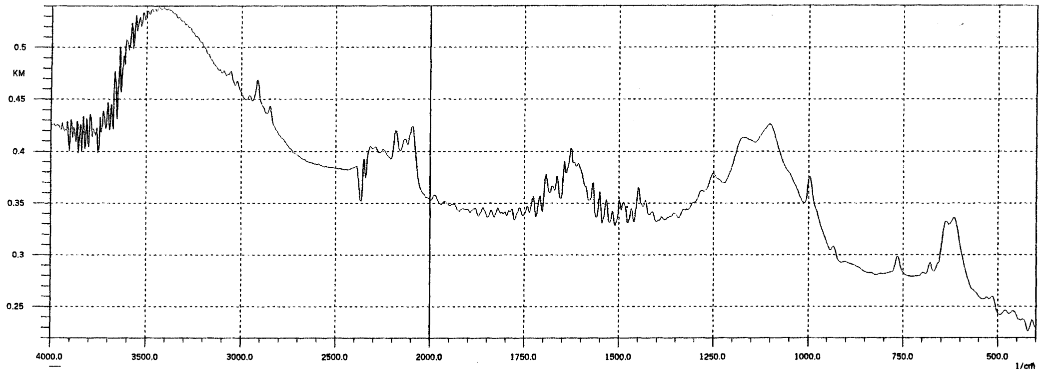


FIGURE 3 DRIFTS spectrum for DBCP: VO^{2+} 1:2 adduct.

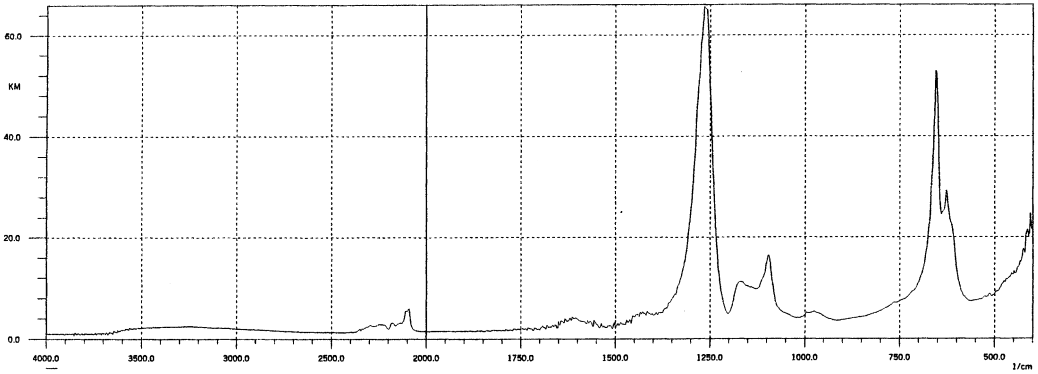
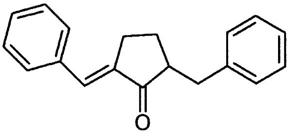
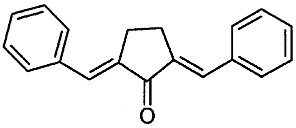


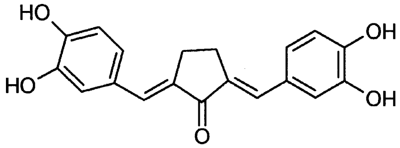
FIGURE 4 DRIFTS spectrum for DBCP: VO^{2+} 1:3 adduct.



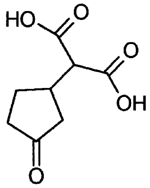
I



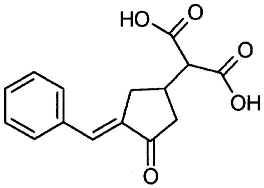
II



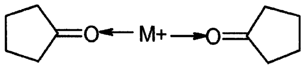
III



IV



V



VI

cations in the solid. Whereas the 2:1 adduct was green in colour, the 3:1 sample was pink, raising the possibility of charge transfer interactions between the delocalised π electrons of the DBCP framework, and the empty d orbitals of the cation.

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