

Co-ordination Polymers based on 2,5-Dibenzylidenecyclopentanone, which are Photochemically Cross-linkable

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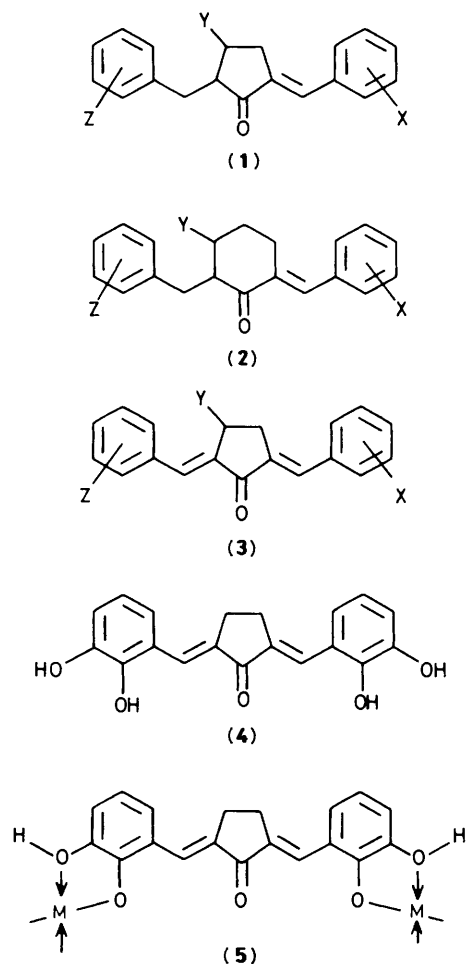
2,5-Bis(2,3-dihydroxybenzylidene)cyclopentanone is topochemically photodimerisable, and i.r. spectroscopic evidence suggests that its packing mode on co-ordination to various metal ions is modified; some of the resulting co-ordination polymers are photochemically cross-linkable, whilst others are photostable.

Much progress has been achieved in the determination of the factors that control the packing of organic molecules in the crystalline state, through the systematic study of closely related structures.^{1,2} One such study employed 2-benzyl-5-benzylidenecyclopentanone (BBCP) (1), 2-benzyl-6-benzylidenecyclohexanone (BBCH) (2), and 2,5-dibenzylidenecyclopentanone (DBCP) (3), and their various analogues.³⁻⁵ A number of these compounds, showed interesting solid state reactivity including [2 + 2] topochemical cycloaddition in a single crystal to single crystal fashion. The relationship between solid state reactivity and crystal packing has been well established, since Schmidt and Cohen's pioneering work with *trans* cinnamic acids.^{1,6} In systems such as BBCP or DBCP, variations in packing and hence reactivity are achieved by varying the nature, position, and number of substituents on the two phenyl rings. This technique is limited by the need for the separate synthesis of each specific compound. The BBCP and DBCP framework can easily be modified [*e.g.* (4)] to act as a chelating agent. Thus, variation in packing motifs and hence reactivity may be achieved for a given organic framework by changing the central metal ion in the complex (5). Organometallic and co-ordination compounds have been of considerable interest⁷ owing to their

potential applicability in electrical or optical devices. Adducts of conjugated ketones (*e.g.* dibenzylidene acetone) with UO_2Cl_2 or SnCl_4 have been prepared and shown to possess different solid state reactivity to the pristine organic molecules.^{8,9}

2,5-Bis(2,3-dihydroxydibenzylidene)cyclopentanone (4) and its 3,4-dihydroxy analogue have been prepared.⁴ Compound (4) was found to act as a chelating bidentate ligand towards Ni^{2+} , Cu^{2+} , and Zn^{2+} ions. The resulting solid was insoluble in all common solvents. This, combined with the chemical structure of (4), suggests that these solids are polymeric in nature. Similar results were obtained for the 3,4-dihydroxy analogue. All metal complexes prepared in this way were polycrystalline.

Comparison of the i.r. spectra of the Ni^{2+} , Cu^{2+} , and Zn^{2+} complexes with (4) indicated significant differences. Furthermore, the spectrum for the pristine organic molecule was significantly different to that of any of the complexes. The differences in the i.r. spectra upon co-ordination to different metal ions cannot be attributed simply to mass changes, since the three metal ions involved have very similar atomic weights, but instead, are probably due to different packing arrangements in the three solids. Similar observations were



made for the 3,4-dihydroxy analogue. The backbone of both (4) and its analogue, consists of a conjugated π -system, and therefore the polymer should possess an extended delocalised system in which the appropriate d orbitals of the metal ions also participate.

Irradiation of pure (4) and of its complexes with u.v. light (500 W low pressure Hg lamp with Pyrex filter) resulted in the [2 + 2] dimerisation of the exocyclic double bond for the pure organic compound and its complex with Ni^{2+} , but not for the other two complexes (see Figure 1 for schematic representa-

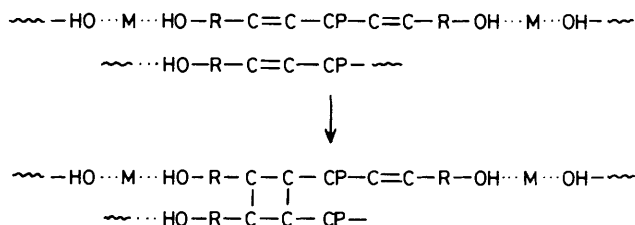


Figure 1. Schematic representation of co-ordination polymer strands and their photochemical cross-linking. R-OH represents the catecholic and CP the cyclopentanone moieties. Although the photoreactive double bonds are presented as being related by translation, thus stacking the metal ions, other configurations are possible, where the metal ions are not aligned.

tion of the reaction and possible packing motif). This reflects the differences in the packing arrangement discussed above. Detection of the dimerisation was carried out by i.r. spectroscopy and t.l.c.¹⁰ The co-ordination complexes obtained thus far were found to be insulators (e.g. for the Ni^{2+} complex, conductivity was ca. 10^{-7} S cm^{-1}). Photodimerisation of selective areas of the solid, which should result in a break in the conjugation system of this polymer, will insert areas of different conductivity within the solid.

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