

TABLE 2 — CHARACTERISATION DATA OF BASE ADDUCTS OF COPPER(II) HYDROXAMATES

Complex	Found (calc.), %		μ_{eff} (B.M.)	Reflectance spectra λ_{max} (nm)
	Cu	N		
CuE ₂ (Py)	10.03 (10.0)	6.96 (6.61)	1.91	675
CuF ₂ (Py) ₂	9.0 (8.64)	11.10 (11.42)	1.97	665
CuE ₂ (3-pic)	9.82 (9.79)	6.67 (6.45)	1.92	680
CuE ₂ (4-pic)	9.94 (9.79)	6.67 (6.45)	2.03	680
CuF ₂ (4-pic) ₂	8.41 (8.37)	10.83 (11.0)	2.03	680
CuE ₂ (Pip)	10.13 (9.91)	6.32 (6.55)	1.96	690
CuF ₂ (Pip) ₂	8.48 (8.50)	11.49 (11.24)	1.98	—

and basicity of the base are the important factors affecting the stability of a particular adduct.

The occurrence of $\nu\text{C}=\text{O}$ around 1550 cm^{-1} in the IR spectra of the adducts ($1540\text{--}1565\text{ cm}^{-1}$) confirms that the chelating group is not acting as monodentate since $\nu\text{C}=\text{O}$ is found in that region in the parent bis-chelates also. Moreover, in the bis-adducts, occurrence of single peaks (including the $\nu\text{C}=\text{N}$) for groups in the base molecules suggests that both the base molecules are in the same environment and hence both are coordinated to the central metal ion.

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Cyclodextrin Inclusion Compounds : Detection of Inclusion by Reflectance Study

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A direct, simple and faster detection of the phenomenon of inclusion of organic compounds in cyclodextrin cavities is possible on the basis of reflectance spectral evidence. Inclusion compounds of α - and β - cyclodextrins with a number of terpenes have been studied. The present study reveals that cyclodextrins can be used as reference standards for reflectance spectral studies on inclusion.

CYCLODEXTRINS, the starch hydrolysis products with amylase, are now well known for their capacity to include a variety of guest compounds¹⁻⁴. The inclusion complex formation can be detected by spectroscopic methods like fluorescence⁵ and nuclear magnetic resonance⁶, and also by polarography⁷. In the present note, we report a method of detection of inclusion for cyclodextrin inclusion compounds in solid state which is based on a change in their reflectance spectra from those of the guest alone and its physical mixture with the host.

Cyclodextrins were obtained commercially. The terpenes used as guest compounds were also obtained commercially and further purified. Their purities were checked by TLC, GC, etc. The complexes were prepared by dissolving about 500 mg cyclodextrin in the minimum amount of water and allowing a measured excess of guest component solution to homogenise with it at about 70°C. A further stirring gave a crystalline inclusion compound which was cooled to about 15°C. This was kept overnight, and the excess untrapped guest was washed with proportional mixtures of dry ethanol and ether for terpenes and acetone for lindane. The complexes thus formed were dried to a constant weight at 120°C.

The dry inclusion compounds and reference standards were then properly ground to obtain a small particle size. The physical mixtures were prepared by mixing both cyclodextrin and the guest in a suitable proportion so as to get a solid solution of these two. The physical mixture (~300 mg) was then placed in a stainless steel cell and a solid cake was obtained by pressing with a steel press.

The solid samples thus prepared for spectral studies were then scanned for reflectance (and absorbance) from 200 nm to 1000 nm on a Carl

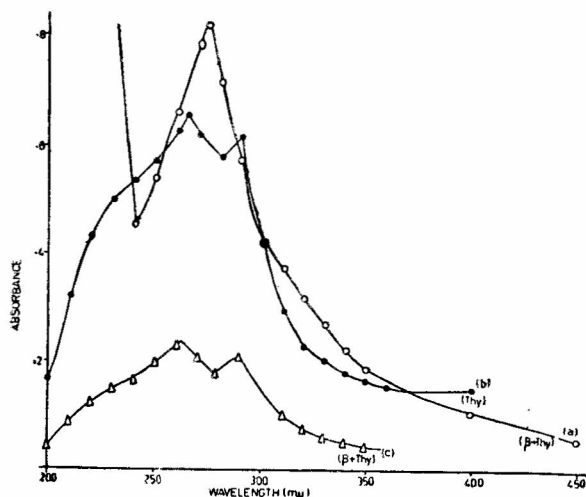


Fig. 1 — Reflectance spectrum of (a) inclusion compound of β -cyclodextrin with thymol, (b) thymol and (c) physical mixture of β -cyclodextrin and thymol.

TABLE 1 — REFLECTANCE CHARACTERISTICS OF CYCLODEXTRIN COMPLEXES

Guest compound	λ_{\max} (nm)	λ_{\max} for physical mixt. with β -cyclodextrin (nm)	λ_{\max} for the inclusion compd. β -cyclodextrin (nm)	Shift in λ_{\max} (nm) ^a
Menthol	240 ^a , 310 ^b	238, 309	250	+10
Camphor	210 ^a , 316 ^b	315	290	-25
Thymol	265 ^a , 290 ^b	263, 290	274	+ 9
Borneol	250 ^a , 300 ^b	303	275	-25
Lindane	300 ^a , 320 ^b , 350 ^b	305	240 ^a , 290 ^b	-10
β -Pinene	—	—	270 [†] , 265 [‡]	—

^aPrimary maximum, ^bsecondary maximum, ^cShift in nearest maximum, [†]With α -cyclodextrin, [‡]with β -cyclodextrin.

Zeiss spectrophotometer using a reflectance measuring attachment for 45/0 geometry, against the dehydrated cyclodextrin reference blanks.

The inclusion compounds of cyclodextrins were best prepared in water, the guest component being dissolved in a miscible solvent. The guest compounds selected for this work were terpenic constituents of essential oils of high purity.

The inclusion of guest in the hydrophobic cavity of cyclodextrins necessarily involves a three dimensional change in the crystal lattice in the solid state⁸. A change in the mode of absorption of light is thus expected. The spectra of inclusion compounds indeed show marked deviation from those of the guest alone and physical mixture with cyclodextrin (Fig. 1). The pattern obtained with the physical mixture is more or less similar to that of the guest component and is markedly different from that of the inclusion compound. The dehydrated (empty) cyclodextrins were found to be better reference standards for scanning the reflectance spectra of

their inclusion complexes as compared to the conventional compounds used for such studies.

The quantitative estimation of terpene content of the inclusion compounds by the reflectance calibration method, though attempted, was however not successful because the content of inclusion is less than the lower limit for such a determination, and also the λ_{\max} values for such an estimation are different for the inclusion compounds and calibrated physical mixtures, as seen from Table 1.

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Complexes of Tin Tetrahalides with 8-Quinolinol N-Oxide

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Tin tetrahalides react at room temperature with 8-quinolinol N-oxide, to form adducts, $\text{SnX}_4 \cdot x\text{C}_9\text{H}_7\text{O}_2\text{N}$; disubstituted derivatives, $\text{SnX}_2(\text{C}_9\text{H}_7\text{O}_2\text{N})_2$ are formed on refluxing in benzene solution. On the basis of IR studies, it is suggested that the ligand coordinates through the N-O group in the adducts, but in the disubstituted derivatives, it coordinates simultaneously through the oxygen atoms of the OH and the N-O groups.

THE analytical applications of 8-quinolinol N-oxide are many^{1,2}. A few of its complexes with metal halides have also been reported³. In continuation of our earlier studies on its coordination behaviour with titanium tetrachloride⁴, we report here the synthesis and characterization of complexes of tin tetrahalides with 8-quinolinol N-oxide.

Precautions were taken to exclude moisture during the preparation of present compounds. Tin tetrahalides were prepared by the halogenation of tin. 8-Quinolinol N-oxide was prepared from 8-quinolinol⁵.

Preparation of adducts — A benzene solution of 8-quinolinol N-oxide was added to a benzene solu-