interactions but also to other factors like non-ideality in free length[5]. If this contribution is assumed not to vary appreciably for mixtures, with acceptor belonging to the same chloroparaffin series, the maximum deviation in velocity from linearity would increase with an increase in the number of activating chlorine atoms. Table I depicts these values. It can be seen that 'MDV' increases with an increase in the number of chlorine atoms. The following order is followed :

1. in chloromethanes : chloroform > methylene-chloride, and
2. in chloroethanes : pentachloroethane > tetra-chloroethane > trichloroethane > dichloro-ethane.

The same order, for H-bond forming capability of acceptor, was arrived at, by Ewell[1] for these mixtures. The curve between MDV and the number of chlorine atoms, when extrapolated, gave a value of 'MDV' equal to 15 ms^{-2}. This could be taken as the contribution coming from factors other than intermolecular forces (due to H-bonding and dipole association).

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STUDIES ON METAL CHELATES OF SILVER(I), COPPER(I) AND THALLIUM(I) WITH 5-IODO-8-HYDROXY QUINOLINO-4-(*p*-TOLYL) SULPHONAMIDE AND 5,7-DI-IODO-8-HYDROXY QUINOLINO-4-(*p*-TOLYL) SULPHONAMIDE AS POSSIBLE ANTIBACTERIALS

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METAL chelates Ag(I), Cu(I) and Tl(I) with the ligands 5-iodo-8-hydroxy quinolino-4-(*p*-tolyl) sulphonamide (IHQTS) and 5,7-Di-iodo-8-hydroxy quinolino-4-(*p*-tolyl) sulphonamide (DIHQTS) were prepared and characterised by the elemental analyses, infrared spectral study and magnetic susceptibility measurements. These were screened for their antibacterial activity against gram positive *S. aureus* and gram negative *E. coli*. It was found that the metal chelates were more potent than the parent compounds.

Introduction

Quinoline and *p*-toluene sulphonamide have long been associated with medicine[1,2]. They were used as drugs for the diseases like cancer[3], tuberculosis[4], diabetes[5], malaria[6], leprosy[7] and convulsant[8]. They were also found to be active against certain types of bacteria. It has also been found that some drugs have increased activity when administered as metal complexes, more so as metal chelates[9,10]. In the present study we have synthesized the ligands IHQTS and DIHQTS and their metal chelates. The metal chelates of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with DIHQTS have already been reported as antibacterials[11].

Experimental

The chemicals employed were of AnalaR grade. The ligand–metal ratio was determined by conductometric titration and Job's method of continuous variation which showed 1 : 1 complexation. This was also confirmed by elemental analyses.

Preparation of the ligands

The ligands were prepared in two steps :

In the first step 5-iodo-8-hydroxy quinoline was allowed to react with chlorosulfonic acid below 0° C and the product thus obtained was found to be 5-iodo-8-hydroxy quinoline-4-sulfonyl chloride. In the second step an alcoholic solution of the sulfonyl chloride was allowed to react with an alcoholic solution of *p*-toluidine when the required product was formed. DIHQTS was also prepared likewise by taking 5,7-di-iodo-8-hydroxy quinoline as the starting material.

Isolation of the chelates

Reagent solutions were prepared in warm distilled water and were then treated with an appropriate amount of metal salt solutions in distilled water. The pH was maintained between 8–9 by borate buffer. The resulting precipitates of the chelates were filtered, washed well with warm distilled water and dried at 120° C.

The melting points of the chelates were determined by open capillary tubes and were found to be more than 300° C.

Magnetic properties

Magnetic properties of the chelates were determined by Guoy's method. The metal chelates of Ag (I) gave the moment values of 1·85 and 1·86 B.M. with the ligands IHQTS and DIHQTS respectively, showing tetrahedral structure with sp^3 hybridization. The metal chelates of Cu(I) gave the moment values of 2·12 and 2·30 B.M. with the ligands IHQTS and

DIHQTS respectively with dsp^2 hybridization. The structures concluded are hence square planar. The metal chelates of Tl(I) gave the magnetic moments 1·67 and 1·69 B.M. with the ligands IHQTS and DIHQTS respectively, showing tetrahedral configuration with sp^3 hybridization. All the metal chelates are found to be paramagnetic.

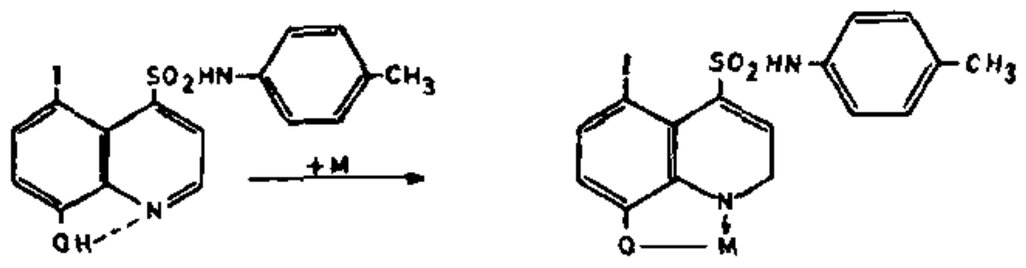
Infrared spectra

On the basis of IR spectra, intramolecular hydrogen bonded chelate structures have been proposed for IHQTS and DIHQTS. On metal chelate formation, however, the bands around 3400 cm^{-1} which appear in all complexes are not present in the original ligand between 3600–3200 cm^{-1} [12, 13]. This is perhaps due to hydrogen bonding. The disappearance of H-bonded –OH in the ligand and its reappearance in the metal chelates is suggestive of O–M–N bond formation where M is a metal atom. The bands between 1600–1490 cm^{-1} are due to aromatic rings. The medium bands at 1595 and 1600 cm^{-1} in the IHQTS and DIHQTS respectively are due to $\nu >C=N-$. These bands shift to lower values with weak intensity suggesting the formation of coordinate bond between M ← N.

Results and Discussion

The experimental analytical data agreed with those of the calculated values indicating the metal-ligand ratio as 1 : 1.

The overall study clearly indicates that the metal chelates are of the general formula ML. The reaction may be given as below :



Similar reactions occur with DIHQTS also. The structures are in close agreement with those of the previous workers[14].

Screening for antibacterial activity

The antibacterial properties of the complexes were studied by the usual cup plate agar diffusion technique[15] against the gram positive *Staphylococcus aureus* and gram negative *Escherichia coli*. Solutions were prepared in a solvent containing equal amounts of dioxane and isopropyl alcohol. Four holes (5 mm diameter) were cut in the agar medium enriched with culture and 0·1 ml of 1% solutions of the compounds were put in these holes. The petridishes were allowed to remain in the refrigerator at 4–8° C for about one hour and then transferred to an incubator (37° C) and after 24 hours of incubation, the zones of inhibition were measured. The control with solvent under identical conditions, however, showed no activity. The results are depicted in Table I.

TABLE I

Sl. No.	Compound	Zones of inhibition in mm against *S. aureus*	Zones of inhibition in mm against *E. coli*
1.	IHQTS	10	..
2.	Ag–IHQTS	10	..
3.	Cu–IHQTS	16	12
4.	Tl–IHQTS	..	18
5.	DIHQTS	11	13
6.	Ag–DIHQTS	..	..
7.	Cu–DIHQTS	18	..
8.	Tl–DIHQTS	13	19

Compounds No. 3 and 7 are more active against *S. aureus* than the parent compounds while compounds No. 2 and 8 are either equally active or a little more than the parent compounds. Compounds No. 4 and 6 are inactive against *S. aureus*. Compounds No. 1, 2, 6 and 7 are inactive against *E. coli*. Compounds No. 4 and 8 are more active than parent compounds against *E. coli*. Compounds No. 3 and 5 were also found active against *E. coli*.

Thus in general we can say that the antibacterial activity is enhanced on complexation of the ligands with metals.

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FLAVONOIDS OF THE INFLORESCENCE OF *VERNONIA ELAEGNIFOLIA*

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Vernonia elaegnifolia DC. (syn. *Conyza elaegnifolia*) belonging to the Compositae is a climbing shrub with creamy-white inflorescence[1]. *V. cinerea* and *V. patens* have been reported[2] to contain luteolin-7-0-glucoside and quercetin-3-0-methylether, while the flowers of (*V. cinerea* have subsequently been found to contain luteolin, chrysoeriol, luteolin-7-0-glucoside and isoorientin[3]. As there is no record of any phytochemical work on *V. elaegnifolia*, the inflorescence of the same has been examined for flavonoids and the results are presented in this note.

Fresh inflorescence of *V. elaegnifolia* collected from the Bishop Heber College Campus, Tiruchirapalli, was extracted with hot 80% alcohol under reflux. The aqueous concentrate was worked up in the usual way and partitioned into petrol, ether and ethyl acetate solubles. The petrol fraction did not afford any crystalline solid. The ether fraction on concentration yielded a yellow solid which on crystallisation from MeOH came out as yellow needles, m.p. 277–279° (yield 0·02%), $C_{15}H_{10}O_6$, tetraacetate, m.p. 185–187°, tetramethylether, m.p. 151–153°, dull yellow under UV with or without NH_3 and was identified as kaempferol and the identity confirmed by λ_{max} and characteristic diagnostic shifts noticed on addition of appropriate seagents[4], R_f and direct comparison with authentic samples of kaempferol and its derivatives,

The ethyl acetate fraction afforded yellow needles (aq., MeOH), m.p. 263–265° (yield 0·06%), appeared purple under UV changing to yellow on fuming with NH_3, had λ_{max} (MeOH) 268, 302, 314 sh, 355 nm exhibiting bathochromic shifts of 62 nm, 42 nm and 6 nm (band II) with NaOMe, $AlCl_3$ (with and without HCl) and NaOAc respectively, did not answer the Hörhammer–Hansel test, positive to Molisch's test and could be hydrolysed by 7% H_2SO_4 (100°, 2 hr) to kaempferol and D-galactose in equimolar amounts. Based on these data, the glycoside has been characterised as kaempferol-3-0-galactoside and the identity confirmed by co- and mixed PC with an authentic sample from *Melochia umbellata*[5].

Luteolin, its 7-0-glucoside and 6-C-glucoside, chrysoeriol and quercetin-3-methylether have been reported from two *Vernonias* by previous workers[2,3]. Although flavonols as their 3-0-glycosides are reported to be common in this family[6], this is perhaps the first instance of isoloation of a rare bioflavonoid, kaempferol,3-0-galactoside recorded to be pharmacologically active[7] from *Vernonia*.

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