zoles with a substituent in 6-position have been cyclised to the corresponding indazolo (2, 3-*b*)-benzothiazoles.

The fact that none of these 2-*o*-azidophenyl benzothiazoles decompose below 140° favours a stepwise mechanism and not a concerted one. As a means of obtaining 2-arylindazoles (VII), all the indazolo (2, 3-*b*) benzothiazoles (IV) have been subjected to desulphurisation by refluxing with Raney Ni in alcohol for 6 hours. In all these cases the expected 2-arylindazoles have been obtained in excellent yields and in pure state.

After the completion of this work, the publication of Suschitzky *et al.*[6], which reported the conversion of 2-*o*-azidophenylbenzothiazole to III (X = H) came to our notice. Neither the method of preparation of III (X = H) nor the physical constants of III and IV (X = H) were mentioned in this report. They obtained 2-phenyltetrahydroindazole on desulphurisation of IV (X = H) in xylene. This result, in contrast to the one obtained in the present work, appears understandable in view of the drastic conditions employed.

Application of this method, for the synthesis of other fused heterocycles from 2-*o*-azidoarylazoles is in progress.

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COPPER (II)-ETHYLENEDIAMINE-SULFADRUGS COMPLEXES

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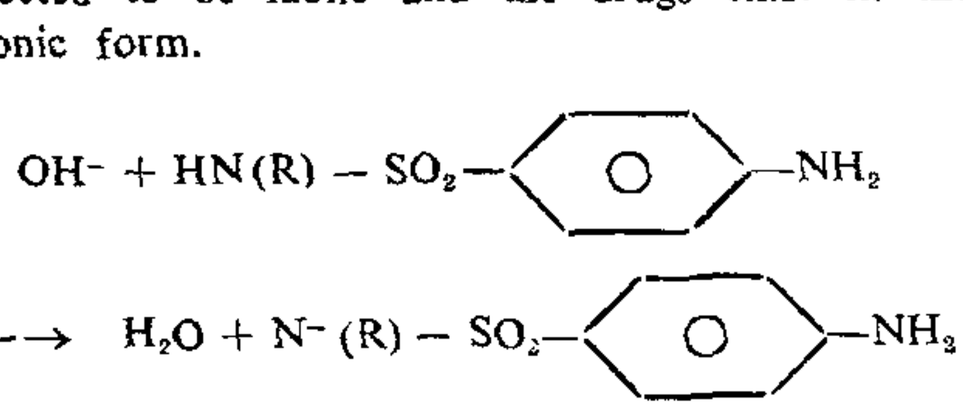
ABSTRACT

Cupper (II) complexes of the composition $Cu(en)_2D_2$ Where en = ethylenediamine and HD = sulfadrugs, *viz.*, sulfathiazole, sulfapyridine, sulfamerazine or sulfadiazine, have been prepared and characterized by analysis, infrared. electronic spectral and magnetic data. The complexes are planar and paramagnetic and the sulfadrug molecules act as anions.

INTRODUCTION

REACTIONS of the sulfadrugs with Zn (II), Cd (II), Hg (II)[1] and Cu (II)[2] have been successfully carried out using high concentrations of metal salts. In alkaline medium, however, the –NH– protons of the sulfadrug molecules are expected to be labile and the drugs exist in the anionic form.



In order to investigate such a behaviour of the sulfadrugs, the present study has been undertaken and some mixed Cu (II) compelxes of sulfadrugs and ethylenediamine are reported.

EXPERIMENTAL

The complexes were prepared by reacting solution of copper (II) chloride (10 m moles) or Copper (II) hydroxide (10 m moles) and ethylenediamine (2 ml) in the minimum amount of water (5 ml) with hot ethanolic solution (25 ml) of sulfadrug (20 m moles) and ethylenediamine (2 ml). The resulting solids were obtained on keeping the reactants for 1 hr., filtered and washed with 50% alcohol and dried at 110° C.

Metal part and sulphur in the complexes were estimated gravimetrically and nitrogen was analysed by micro-analytical technique using a coleman N-analyzer. Infrared and electronic spectra were recorded on Perkin–Elmer–257 and a Cary–14 model respectively. Magnetic measurements were made on Faraday Balance (Cahn, Magnetic susceptibility Apparatus) using Hg [$CO(NCS)_4$] as calibrant. Diamagnetic currections were applied using

TABLE I

Analytical, magnetic and electronic spectral data of Copper (II)-ethylenediamine-sulfadrug complexes

Compounds	Melting pt. decompn. pt.	Analysis (%)* Metal	Nitrogen	Sulphur	Magnetic moment (μ_{eff}) B.M. temp. 19° C	Electrnoic spectral. λ_{max} mμ
1. Cu $(en)_2$ $(ST)_2$	184° C ST –200° C	8·98 (9·09)	20·30 (20·20)	18·23 (18·47)	1·82	210, 270, 300, 590 ST–250, 310
2. Cu $(en)_2$ $(SP)_2$	216° C Sp –191° C	9·10 (9·25)	20·22 (20·56)	9·18 (9·39)	2·05	215, 275, 305, 570 SP–240, 311
3. Cu $(en)_2$ $(SM)_2$	212° C SM-234° C	8·66 (8·85)	23·69 (23·63)	8·77 (9·00)	1·92	222, 260, 305, 555 SM–270, 305
4. Cu $(en)_2$ $(SD)_2$	213° C SD –253° C	9·26 (9·22)	24·76 (24·59)	9·04 (9·37)	1·99	220, 265, 310, 560 SD–292, 318, 332
5. Cu $(en)_2$ $(ST)_2$**	185° C ST –200° C	8·88 (9·09)	20·47 (20·20)	18·50 (18·47)	2·10	215, 270, 300, 585 ST–250, 310
6. Cu $(en)_2$ $(SP)_2$**	217° C SP –191° C	9·18 (9·25)	20·70 (20·56)	9·59 (9·39)	1·99	215, 272, 305, 570 SP–240, 311
7. Cu $(en)_2$ $(SM)_2$**	214° C SM–234° C	8·68 (8·85)	23·58 (23·63)	9·32 (9·00)	1·93	220, 255, 305, 550 SM–270, 305
8. Cu $(en)_2$ $(SD)_2$**	215° C SD –253° C	9·14 (9·22)	24·35 (24·59)	9·73 (9·37)	1·88	225, 265, 305, 555 SD–292, 318, 332

* Figures in parentheses are calculated values.

** Prepared from $Cu(OH)_2$, others from $CuCl_2$.

Abbreviations: HST = Sulfathiazole, HSP = Sulfapyridine; HSM = Sulfamerazine, HSD = Sulfadiazine.

Pascal's constants. The analytical data and some general characteristics of the complexes are summarized in Table I.

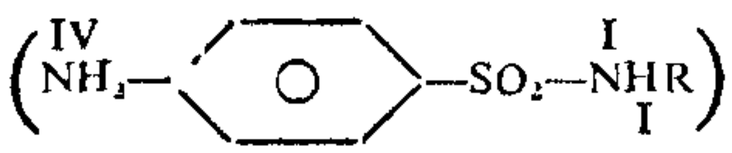
Results and Discussion

All the Cu (II) complexes, presently reported, are either blue or bluish-violet in contrast to green Cu (II) complexes of the sulfadrugs reported earlier[2]. All the complexes are insoluble in water and common organic solvents and melt with decomposition in the range 180–220°. The course of reaction may be as follows :

$$HD + en \longrightarrow [enH^+]\,D^-$$

$$Cu + 2\,en + 2\,D^- \longrightarrow Cu\,(en)_2\,D_2$$

The effect of pH on the UV absorption bands of the sulfadrugs



appearing due to sulfanilamide group and the substituent at N has been studied by Vandenbelt and Doub[3]. The acidic ionization (in alkaline solution) results in a shift of sulfanilamido band (240–270 mμ) towards shorter wavelength with a little change in intensity while, basic dissociation (in acidic solution) decreases the intensity almost to disappearance of the band. In the present complexes, isolated from the basic medium of ethylenediamine, the shift of the characteristic sulfanilamide band to shorter wavelengths indicates the presence of drug anion as above. The absorption bands due to substituents at N^1, *viz.*, thiazole in sulfathiazole, pyridine in sulfapyridine, pyrimidine in sulfadiazine and 4-methyl pyrimidine in sulfamerazine, observed between 280–320 mμ, similarly shift to shorter wavelengths.

In octahedral Cu (II) complexes, a band around 800 mμ due to $^2T_{2g} \leftarrow {}^2E_g$ transition[4] blue-shifts considerably due to Jahn–Teller effect as the stereochemistry of Cu (II) complexes departs from octahedral to square planar. In general, the amine complexes of Cu (II) are blueish-violet and have been shown to have planar geometry. Cu $(en)_2^{2+}$ complexes show a *d-d* transition band around 550 mμ (18·2 kK)[5] in solid state and 545 mμ in solution[6]. Cu $(en)_2$ $(ClO_4)_2$ and Cu $(en)_2$–$(SCN)_2$ are isostructural and square planar. They show similar visible absorption bands around 520 mμ (19·2 kK) and 515 mμ (19·4 kK) respectively in solid state[7]. Since Cu $(en)_2D_2$ complexes

absorb between 550–590 mμ and are either blue or bluish-violet, they are predominantly planar or at the most 'pseudo-octahedral with weakly co-ordinated drug anion.

All the Cu $(en)_2D_2$ complexes are normal paramagnetic and the μ_{eff} lies between 1·80–2·10 BM in agreement with the observed values for one unpaired electron in Cu (II) complexes[8].

Infrared spectra of the complexes show several bands in the 3500–3000 cm^{-1} due to ν NH from drug and *en* molecules. Although one of the series of the complexes has been prepared from copper (II) hydroxide but the close similarity of i.r. spectra of copper (II) chloride complexes indicates absence of OH group. When ν NH, δNH_2, phenyl ring, SO_2 asym., SO_2 Sym. and τNH_2 vibrational modes of the sulfanilamide part[9] (appearing in the regions 3500–3000, 1660–1620, 1600–1500, 1350–1300, 1150–1120 and 680–670 cm^{-1} respectively) in the sulfadrugs and Cu $(en)_2D_2$ complexes are compared, after eliminating the bands due to ethylenediamine, no significant changes are observed. It appears that the electron density has uniformly distributed itself over the entire drug molecule. In the case of sulfamerazine and sulfadiazine complexes, however, the SO_2 asymmetric band shows lowering of ~ 10 cm^{-1}, which may be due to the slight decrease of electron density over-SO_2-group.

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EFFECT OF SUBSTITUTION AND ITS LOCATION ON LIQUID CRYSTALLINE PROPERTIES OF CHOLESTERYLBENZOATE AND CHOLESTERYL CINNAMATE

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ABSTRACT

Cholesteryl 2- and 3-methoxybenzoates are non-mesomorphic, cholesteryl 2-nitrobenzoate is monotropic smectic and enantiotropic cholesteric. Cholestery 4-nitrocinnamate exhibits enantiotropic smectic and cholesteric mesophases, whereas cholesteryl 4-chlorocinnamate is only cholesteric. The mesomorphic properties are explained by comparing these compounds with other related compounds.

THE detailed study of many mesogenic homologous series has helped to evolve some general rules for the effect of chemical constitution in the nematogenic and smectogenic compounds[1]. The effect of chemical constitution on cholesteric mesophase has been also reported recently[2,3]. Dave and Vora[4] and Barral *et al.*[5], have reported *ortho*, *meta*, and *para* substituted benzoates of cholesterol and some substituted benzoates and cinnamates of cholesterol, respectively. From the study of substituted benzoates of cholesterol[4] it was observed that effect of same substituent at different locations is quite interesting. Generally the order of thermal stability is para > parent compound > meta > ortho. All the substituted benzoates of cholesterol reported exhibit mesomorphism. Some more substituted benzoates and cinnamates of cholesterol are reported here which are compared with other known compounds. Transition temperatures of these compounds are recorded in Table I.

Reference to Table I shows that methoxy group in the 4-position of cholesteryl benzoate, enhances cholesteric thermal stability quite appreciably but