

## LETTERS TO THE EDITOR

## SPECTROSCOPIC STUDIES OF THE ELECTRON DONOR-ACCEPTOR INTERACTION BETWEEN CHLORANIL AND ANILINES

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AROMATIC amines are known to form electron donor-acceptor (EDA) complexes with a number of electron acceptors<sup>1-3</sup>. Although, the anilines possess considerable donor strength because of their low ionization potentials, these molecules can not be classified into  $n$ -donors or  $\pi$ -donors due to the lone pair orbital on the nitrogen atom of the amino group entering in conjugation with the  $\pi$ -orbital of the benzene ring. Electron donating properties of aniline increase when a methyl group is introduced either at the nitrogen atom or in the benzen ring<sup>4</sup>. Nagakura and Coworkers<sup>5</sup> reported the formation of  $\pi$ - $\pi$  type EDA complex between aniline and chloranil (CA) at temperatures below 200° K. Mukherjee and Chandra<sup>6</sup> determined the formation constants of the 1:1 EDA complexes of anilines with CA and suggested that the charge transfer takes place mainly from the amino part of the aniline molecule in these complexes. The energies of interaction may provide valuable information regarding  $n$  or  $\pi$ -donor character of anilines. Unfortunately, the energies of interaction were not available in these systems. We have, therefore, examined the interaction of CA with aniline, *m*-toluidine, *o*-toluidine, *p*-toluidine, diphenylamine and N,N-dimethylaniline in chloroform solution with a view to evaluating the energies of interaction in these systems.

The anilines (BDH, analar) were purified by standard methods and stored in the dark. Chloranil and chloroform were purified by the method described in earlier<sup>7</sup>. Spectral measurements were made on a Beckman DU spectrophotometer attached with variable temperature cell compartment using ground glass stoppered silica cells of 1 cm path length. Equilibrium constants of formation  $K$  and molar extinction coefficients  $\epsilon$  of the EDA complexes were calculated graphically employing the modified Scott equation<sup>8,9</sup>. The absorbances of a series of solutions with varying donor concentration and fixed acceptor concentration were measured at the charge-transfer band maximum. The donor concentrations were sufficiently high as required by Person's criteria<sup>10</sup>. Freshly prepared stock solutions of the donor and acceptor were used in all the measurements. The enthalpies of formation  $\epsilon H$  were determined from the equilibrium constants at various temperatures in the range 15° C. The  $K$  and  $\epsilon$  values of the complexes have an uncertainty less than  $\pm 10\%$ .

All the anilines on mixing with CA in chloroform solution exhibited new and broad absorption bands in ( $\lambda_{CT}$ ) the visible region characteristic of EDA complexes and well-separated from those of the individual components. Absorbance measurements at the  $\lambda_{CT}$  of the EDA complexes yielded linear modified Scott equation<sup>8,9</sup>, plots indicating the formation of 1:1 complexes in these systems. These plots were used to evaluate  $K$  and  $\epsilon$  values of the EDA complexes. Since the absorbances of aniline+CA solutions changed slowly on standing, measurements were made on fresh solutions. The spectroscopic and thermodynamic data for the EDA complexes are summarised in table 1. The  $\lambda_{CT}$  and  $K$  values for the EDA complexes studied here agree with the data reported earlier<sup>6</sup>. However, the

TABLE I

*Spectroscopic and thermodynamic data for EDA complexes of anilines with CA in chloroform solution*

Electron donor	$I_p$ (eV)	$\lambda_{CT}$ (nm)	$K^*$ (l mole <sup>-1</sup> )	$\epsilon$ (l mole <sup>-1</sup> cm <sup>-1</sup> )	$-\Delta H$ Kcal mol <sup>-1</sup>	$\Delta\nu_{1/2}$ (cm <sup>-1</sup> )	$f$
Aniline	7.70	530	1.1	1533	5.6	7053	0.047
<i>m</i> -Toluidine	7.66	550	1.6	1500	6.1	7756	0.050
<i>o</i> -Toluidine	7.62	560	1.7	1000	6.8	6833	0.031
<i>p</i> -Toluidine	7.48	575	2.3	1429	7.0	5669	0.035
Diphenylamine	—	650	1.3	795	7.2	5657	0.019
N, N-Dimethylaniline	7.20	675	2.6	1000	7.8	6533	0.028

\*At 34° C; data are given at one temperature only for the sake of brevity.

$\epsilon$  values differ in most complexes. The present values of  $K$  and  $\epsilon$  appear to be reliable since the donor concentration employed was sufficiently high and satisfied Person's criteria<sup>10</sup>. Table 1 shows that the  $\lambda_{CT}$  values of the EDA complexes decrease with increase in the ionisation potential of the donor. This agrees with the Mulliken's theory<sup>11</sup>. The  $K$  values also vary in the same direction as the  $\lambda_{CT}$  values with the exception of diphenylamine. This may be due to the reduced overlap between the molecular orbitals of the donor and acceptor molecules because of the bulky phenyl groups on the nitrogen atom in diphenylamine. The  $\Delta H$  values reported in table 1 are new and significant and are high enough to be comparable to other  $n$ -donor- $\pi$ -acceptor complexes<sup>1</sup>, indicating that the anilines behave as  $n$ -donors towards CA. Mukherjee and Chandra<sup>6</sup> arrived at a similar conclusion and proposed that the charge transfer takes place mainly from the amino part of the aniline molecule in these complexes.

A direct relationship between half band width,  $\Delta\nu$  and the strength of the complexes (as measured by  $\Delta H$ ) was observed by a number of workers<sup>12-14</sup> and was attributed to the large resonance interaction in the complexes. Also, the intensity of the charge-transfer band (measured by  $\epsilon$  or  $f$ ) was found to increase with the increase in the strength of interaction<sup>13-15</sup>. However, the  $\Delta\nu^{1/2} \Delta H$  and  $\epsilon$  or  $f - \Delta H$  relation is anomalous in aniline-CA systems. The larger values of  $\Delta H$ ,  $\Delta\nu^{1/2}$  and  $f$  indicate that these complexes are quite strong and suggest that the anilines probably behave as  $n$ -donors in these systems.

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## PLATINUM (II AND IV) COMPLEXES WITH NS AND NO DONOR LIGANDS

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IN recent years there has been considerable interest in the synthesis of new platinum (II and IV) complexes due to their anticancer properties<sup>1</sup>. Kidani *et al*<sup>2,3</sup> have recently reported that platinum (II) heterochelate with cyclohexyldiamine and oxalate ion shows higher anticancer activity as compared to the homochelate complexes with cyclohexyldiamine. This prompted us to synthesize new platinum (II) heterochelates of the type  $[PtL(BB)]$  and  $[PtL(B)_2]$  (where  $L = 2$ -aminoethanol or 2-aminoethanethiol,  $BB =$  oxalate or malonate ion,  $B =$  formate or acetate ion). These complexes undergo oxidative addition reactions with chlorine and bromine and as a result the platinum (IV) complexes of the type *trans*- $[PtX_2L(BB)]$  and *trans*- $[PtX_2L(B)_2]$  are formed. Syntheses and characterisation of all these complexes are reported in this preliminary communication.

*General method of syntheses of the complexes, platinum(II) complexes:*  $K_2PtCl_4$  (0.001 mol) was dissolved in 8 ml of water. To this an aqueous solution of  $K_2C_2O_4$  (0.001 mol in 2 ml) was added and the pH of the solution was adjusted to 8.5 with dilute KOH solution. An ethanolic solution of 2-aminoethanol or 2-aminoethanethiol (0.001 mol in 5 ml) was added to the above solution and the mixture was refluxed on a water bath for one hour. The solvent was evaporated partially on the water bath and the mixture was cooled to 25°C. The separated precipitates were filtered, washed with ethanol (1:1) and dried *in vacuo*. Similar procedure was adopted for other acids.

*Platinum (IV) complexes:* The appropriate platinum (II) complex (0.002 mol) was suspended in 4 ml water and  $Cl_2$  was passed through the suspension for