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Charge Transfer Complexes of N,N'-Dimethylbenzaldehyde Ethylenediimine Schiff Base with Some Electron Acceptors

Awatef S. Assran^{1,2,*}, M. H. M. Abou-El-Wafa²

¹Taif University, Chemistry Department, Faculty of Science, Taif, Saudi Arabia

²Chemistry Department, Faculty of Science at Qena, South Valley University, Qena, Egypt

Email address

a.assran@gmail.com (A. S. Assran)

*Corresponding author

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Abstract

The charge-transfer interactions between the electron donor Bis N,N'-dimethylbenzaldehydeethylenediimine (SB1) and the acceptors tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), Picric acid (PA) and iodine have been studied spectrophotometrically in CH₂Cl₂ solutions. The solid charge-transfer complexes have been isolated and characterized by infrared spectra and elemental analysis. The stoichiometry of the complexes was found to be 1:1 in case of SB1-PA system, 1:2 in case of SB1-TCNE, SB1-DDQ systems and 1:3 in case of SB1-iodine system. Taking this into consideration along with infrared spectra and elemental analysis, the formed CT-complexes have the formulas [(SB1)(PA)], [(SB1)(DDQ)₂], [(SB1)(TCNE)₂] and [(SB)I]⁺ I₃⁻, respectively.

1. Introduction

Schiff's bases, also named as imine compounds, are very important class of compounds which was discovered since more than 150 years via the condensation of primary amines and carbonyl compounds. [1] The diimines, bisimines or bis-Schiff's bases have been synthesized by the reaction of 1 mole diamine with 2 moles of aldehydes or ketones. [2]. A great deal of interest has arisen in the synthesis of noveldiimines as a result of theirbiological activities such as antioxidant [3], anti-inflammatory and anti-analgesics. [4] As well as, they are usedfor formation the charge transfer (CT) complexes. [5] The formation of charge transfer interaction is often determined by appearance of a characteristic absorption band in the visible spectrum. [6, 7] Owing to the significant properties of the charge transfer (CT) complexes, manyresearches have been reported on charge transfer (CT) complexes between n-donors, δ- and π-acceptors in solid state as well as in solution. [8-14] CT-complexes have been documented as an important phenomenon in drug-receptor binding mechanism and in many biological processes. [15, 16] Such CT-interaction stabilizes molecules that intercalate between DNA bases, which can be used for cancer therapy. [17-19] In addition charge-transfer complexes attract an extensive interest in thefields of electronics, solar cells, optical devices and electrical conductivities. [20, 21]

Bazzi et al., have demonstrated that the formation and stoichiometries of CT-complexes between various nitrogen containing donors, n- and π-acceptors depend mainly on the number of donor nitrogen atoms, the type of acceptor, as well as, the

symmetry and structure of both sides. [22, 24] In view of these finding and in continuation to our previous work on the Schiff bases [25–28], this piece of work has devoted with the aim to synthesize some CT- complexes via interaction of symmetrical Schiff base ligand, bis N,N'-dimethylbenzaldehyde ethylenediimine (SB1) with the electron acceptors tetracyanoethane (TCNE), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), Picric acid (PA) and iodine (I₂), using CH₂Cl₂ as a solvent. The obtained results enabled us to examine their physical properties involving spectral behaviors, the inter- or intra-molecular charge transfer, and to trace complexes formation in solutions and to determine the stoichiometric ratios of the formed CT-complexes spectrophotometrically

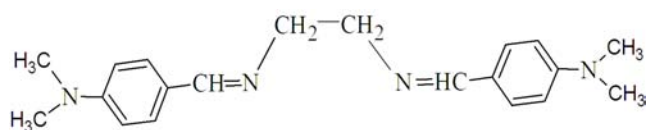


Figure 1. Bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1).

2. Experimental

2.1. Material and Methods

All chemicals, solvents and reagents were of extra pure products (Merck, Aldrich, Sigma or B.D.H) and have been used without further purification. The amine used in preparation of the Schiff base is ethylenediamine (EN). The reaction of N,N'-dimethylbenzaldehyde with the amine (EN) led to formation of the Schiff base (SB1) [29]. The acceptors used are Iodine I₂ as δ-acceptor, Tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and Picric acid (PA) as π-acceptors. Melting points (uncorrected) were recorded on melting point apparatus SMP 10. The electronic spectra were measured on a Shimadzu UV-2401PC UV-Vis Recording Spectrophotometer using 1.0 cm matched quartz cells. Infrared spectra of the solid compounds were recorded on KBr pellets using a Jasco FT IR-4010 spectrophotometer. Elemental analyses for C, H, and N of the compounds have been carried out in the micro analytical laboratories at Cairo and Assuit Universities, Egypt.

2.2. Preparation of the Solid CT-complexes

The four solid CT-complexes, [(SB)I]⁺I₃⁻, [(SB1)(TCNE)₂], [(SB1)(DDQ)₂] and [(SB1)(PA)] were prepared by the addition of a saturated solution of bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1) (10 ml) to a saturated solution of each acceptor I₂, TCNE, DDQ or PA (10 ml) in CH₂Cl₂ for (I₂) or in benzene for the others. The resulting precipitate in each case was filtered off, washed with minimum amounts of CH₂Cl₂ or benzene and dried in vacuum over P₂O₅. The complexes were characterized spectrophotometrically (FT-IR and UV-vis) and by elemental analysis.

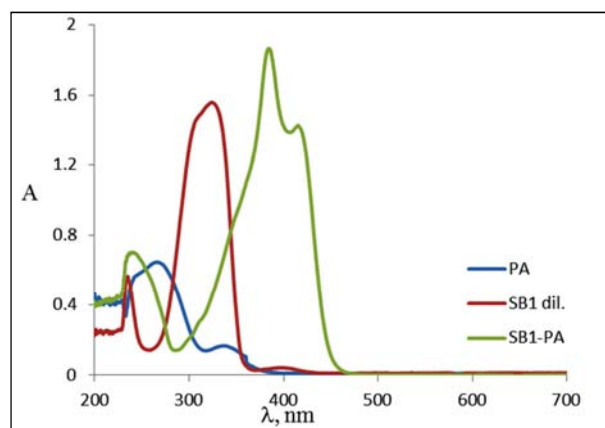
[(SB)I]⁺I₃⁻ dark brown complex, M. p. 225-228°C; (M/W:

1083.87g): Calc. (found) C, 22.16 % (22.55%); H, 2.42% (2.48%); N, 4.56% (5.17%); [(SB1)(TCNE)₂] yellow complex, M. p. 150-155°C; (M/W: 614.66 g): C, 62.69% (62.02%); H, 4.91% (4.51%); N, 27.35% (28.02%); [(SB1)(DDQ)₂] dark brown complex, M. p. 200-210°C; (M/W: 812.48 g): C, 53.22% (53.48%); H, 3.72% (4.350%); N, 13.80% (14.93%); [(SB1)(PA)] orange complex, M. p. 215-220°C; (M/W :551.55g): C, 56.62% (56.03%); H, 5.30% (4.90%); N, 17.78% (18.27%).

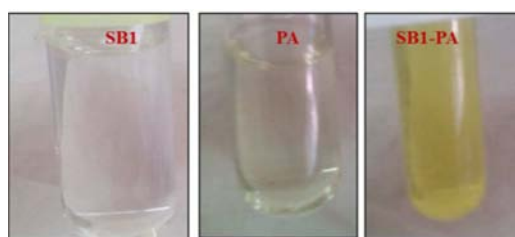
3. Results and Discussions

3.1. Electronic Absorption Spectra

Strong change in colors was observed upon mixing of CH₂Cl₂ solutions of the donor, Bis N,N'-dimethylbenzaldehyde ethylenediimine (SB1) with each of the acceptors iodine, TCNE, DDQ and Picric acid. The new colors are dark brown for SB1-I₂ and SB1-DDQ, light yellow for SB1-TCNE, and orange for SB1-PA reaction mixtures (Figures. 2b, S2b, S3b). These changes in colors represent strong evidence of the charge-transfer interactions between the donor and the acceptors. The electronic absorption spectra of the reactants in each case along with those of the complexes formed between the donor SB1 and each of I₂, TCNE, DDQ and PA are shown in Figures. 2a, S1a, S2a, S3a. Strong absorption bands due to the formed products appeared at 419 and 388 for I₂, 406 nm for TCNE, 526 and 493 nm for DDQ and at 417 and 386 nm for PA, respectively.



(a)



(b)

Figure 2. (a) Electronic absorption spectra of SB1- PA reaction, Color legend: blue line, PA, red SB1 and green, 1:1 SB1-PA mixture, [SB1]=[PA] = 1 × 10⁻⁴ M, (b) Color change of SB1-PA system.

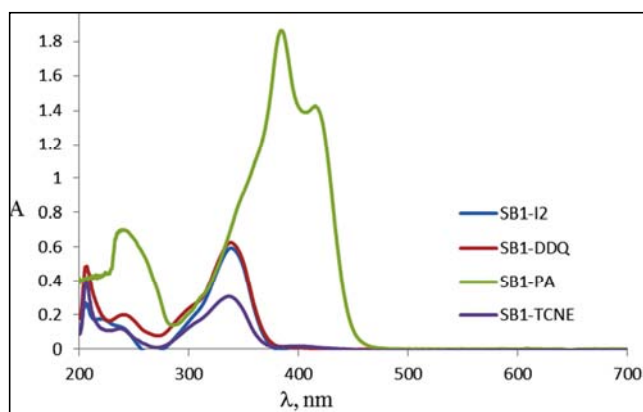
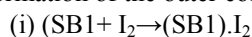


Figure 3. Electronic absorption spectra of SB1-acceptors reactions in CH_2Cl_2 . Color legend: red, $[(SB1)(DDQ)_2]$; purple, $[(SB1)(TCNE)_2]$; green, $[(SB1)(PA)]$ and blue $[(SB1)(I)]^+I_5^-$; $[SB1] = [TCNE] = [DDQ] = [I_2] = 10^{-4}$ M.

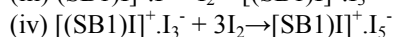
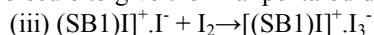
Photometric titration measurements for the four newly prepared complexes in CH_2Cl_2 , namely $[(SB1)(DDQ)_2]$, $[(SB1)(TCNE)_2]$, $[(SB1)(PA)]$ and $[(SB1)(I)]^+I_5^-$ were performed and shown in Figures 4–7 and S4–S7. Interestingly, the measurements show that, the donor-acceptor molar ratio is variable depending on the type of acceptor. These molar ratios were found to be 1:1 in the case of SB1-PA and 1:2 in the case of SB1-DDQ and SB1-TCNE and 1:3 in the case of SB1- I_2 system. Based on this fact, the structures of the four newly formed CT-complexes were formulated to be $[(SB1)(PA)]$, $[(SB1)(DDQ)_2]$, $[(SB1)(TCNE)_2]$ and $[(SB1)(I_2)_3]$. These structures and stoichiometries are in somewhat agreement with the elemental analysis of the formed solid CT-complexes. It should be indicated here that, the absorption of the iodine complex shows two new strong absorptions at 419 and 388 nm. Neither free iodine nor SB1 show these absorptions (Figure. S2a, Table 1). These two absorptions of formed CT-

complex of iodine at 419 and 388 nm are well known to be characteristic for the poly iodide ion of the type I_5^- . [13, 30] Accordingly, the formed CT-complex of iodine is identified as $[(SB1)I]^+I_5^-$. Similar pentaiodide I_5^- species such as $[(TODACOD)I]^+I_5^-$ ((TODACOD) in 1,4,10,13-tetraoxo-7,16-diazacyclooctadecane) are well known in the literature [30] and $[(TMDP)I]^+I_5^-$ ((TMDP) in 4,4'-trimethylenedipiperidine) [31]. The formation of $[(SB1)I]^+I_5^-$ complex proceed in four reaction steps, the first involves the formation of the outer complex.



Then the next steps are the formation of the inner complex.

(ii) $(\text{SB1}) \cdot I_2 \rightarrow (\text{SB1})I^+ \cdot I^-$ which combines with one iodine molecule to form I_3^- and this reacts with the third iodine molecule to give the final pentaiodide, I_5^- complex.



The absorption of iodine band around 515 nm which is attributed to the $4\pi \rightarrow 10\delta^*$ electronic transition in free iodine [32] was hypsochromically shifted due to its complexation with the added donor, SB1 and the blue shifted iodine bands located around 419 and 388 nm. The observed blue shift in the free iodine band and its split into two bands is obviously due to the perturbation of the $10\delta^*$ molecular orbital of iodine due to the CT-interaction with the donor. The split of the iodine band around 515 nm into two absorptions around 419 and 388 nm is related to the allowed transition in the formed pentaiodide, I_5^- ion. It should be indicated here that the formed I_5^- ion in the CT-complex $[(SB1)I]^+ \cdot I_5^-$ may be of the type $(I_3)(I_2)$ or it may exist as one unit with either linear or bent structures [13]. It is of interest to see that, reaction stoichiometries of SB1 with each of the acceptors under investigation vary from 1:1 to 1:3, depending on the type of donor. For the π -acceptors, the stoichiometry value is 1:1 in the case of PA while it is 1:2 in the case of DDQ and TCNE (Table 1).

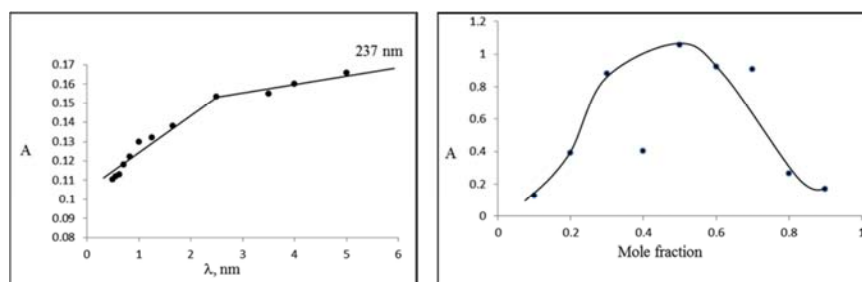


Figure 4. Molar ratio and continuous variation plots for SB1- I_2 reaction in CH_2Cl_2 based on the 237 and 375 nm absorption.

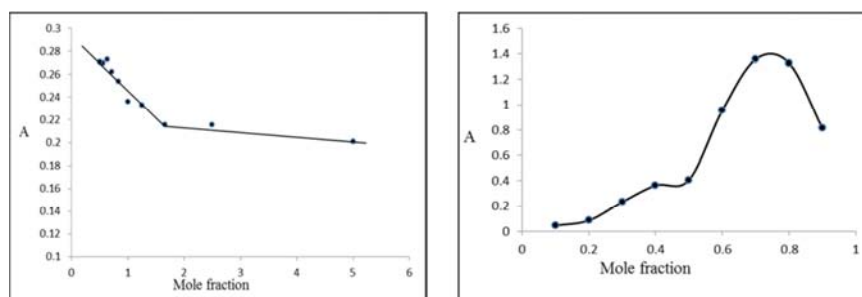


Figure 5. Molar ratio and continuous variation plots for SB1-DDQ reaction in CH_2Cl_2 based on the 303 and 526 nm absorption.

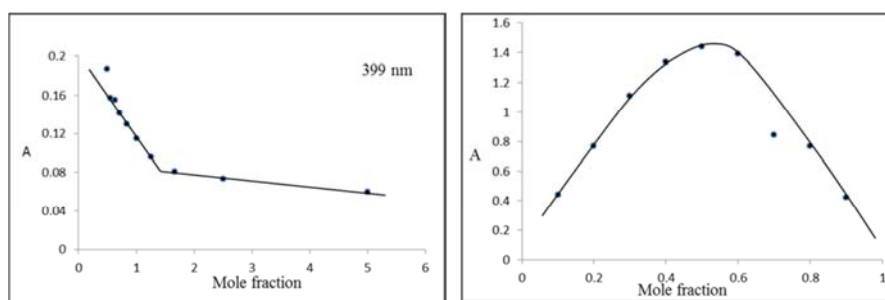


Figure 6. Molar ratio and continuous variation plots for SB1-PA reaction in CH_2Cl_2 based on the 399 and 405 nm absorption.

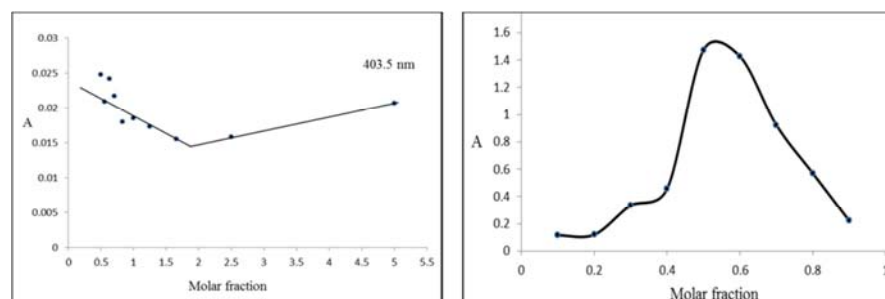


Figure 7. Molar ratio and continuous variation plots for SB1-TCNE reaction in CH_2Cl_2 based on the 403.5 and 406 nm absorption.

Table 1. Spectroscopic data for the CH_2Cl_2 solutions for CT-complexes of SB1 and acceptors I_2 , TCNE, DDQ and PA.

CT-Complex	Color	Absorption ^a (nm)	
		MR ^b	CV ^c
[(SB1)(PA)]	Orange	338 s	417 s
[(SB1)(DDQ) ₂]	Dark brown	303 sh	526 s
		338 s	493 s
[(SB1)(TCNE) ₂]	Yellow	403.5 m	406 s
[(SB1)(I)] ⁺ .15 ⁻	Dark brown	344 s	419 s
		237 m	388 s

^a The reactants SB1, PA, DDQ, TCNE and iodine have no measurable absorptions in the region of study with used concentrations: ^b Molar ratio method: ^c continuous variation method: m, medium; s, strong; sh, shoulder

Such noticeable variations of CT-interaction stoichiometries, are relatively due to many factors such as, the donor molecular symmetry, the type of electron withdrawing groups or atoms Cl, NO_2 , or $\text{C} \equiv \text{N}$, $\text{O}=\text{C}$, as well as the steric hindrance between reactants.

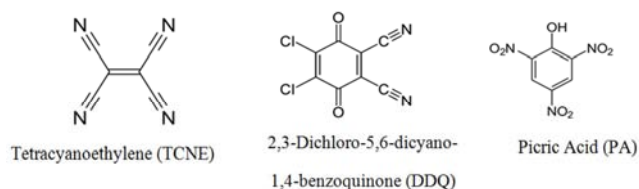


Figure 8. The names and the structure of acceptors.

All of these factors are expected to play an important role in the electron donation process from the nitrogen electron pairs of the donor SB1 and the aromatic ring of each acceptor. Such a comparison in I_2 is invalid, since I_2 is an n-electron donor. To know more regarding the properties of the CT-complex [(SB1)(PA)] where the reaction stoichiometries

are 1:1, the formation constant, K_c , and the absorptivity, ϵ'_c for the complex were calculated using the modified Benesi-Hildebrand equation [33] for the 1:1 reaction;

$$[A_0][D_0]/A = 1/K_c\epsilon'_c + ([A_0] + [D_0])/ \epsilon'_c$$

Where A is the absorbance of the CT-transition of [(SB1)(PA)] at 399 nm. $[A_0]$ and $[D_0]$ are the initial concentrations of the acceptor and the donor, respectively. Straight line is obtained from the plot of $[A_0][D_0]/A$ vs. $[A_0] + [D_0]$ confirming our conclusion of the formation of 1:1 complex, Figure 9. The obtained values of K_c and ϵ'_c of the [(SB1)(PA)] are $6.66 \times 10^3 \text{ L mol}^{-1}$ and $0.025 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. The high value of ϵ'_c is characteristic for CT-complexes.

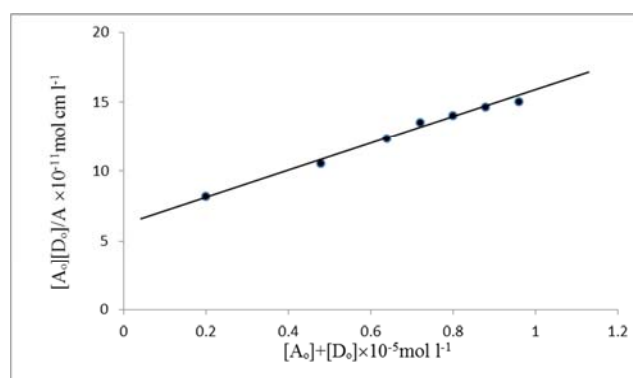


Figure 9. The plot of $[A_0][D_0]/A$ values against $[A_0] + [D_0]$ for SB1-PA reaction in CH_2Cl_2 based on the 399 nm absorption.

3.2. Infrared Absorption Spectra

Infrared spectra of the electron donor bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1) and its CT-complexes [(SB1)(TCNE)₂], [(SB1)(DDQ)₂], [(SB1)(PA)]

and $[(SB1)I]^+I_3^-$ are shown in Figure 10 and their infrared band assignments are given in Table 2. In the spectra of the CT-complexes main bands of both the donor and the acceptors are observed. This is a clear indication of the formation of the CT interactions. See Figures S8-S11. Interestingly, the characteristic beaks $\nu(C-H)$, $\nu(C=N)$, $\nu(C \equiv N)$ and $\nu(C-N)$ of the free base bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1) show some changes in both band intensities, band number and

wavenumber values upon complexation, Table 2. The $\nu(C \equiv N)$ for the free TCNE and DDQ occur at 2220 and 2231 cm^{-1} , respectively and at 2204 and 2217 cm^{-1} upon complexation. Similar changes are observed for the $\nu(C=C)$ vibrations for all free acceptors TCNE, DDQ and PA where, $\nu(C=C)$ peaks are at 1480, 1553 and 1550 cm^{-1} , respectively, corresponding to 1553, 1545 and 1565 cm^{-1} upon complexation. These changes could be related to both electronic and symmetry changes upon complexation.

Table 2. Fourier transform infrared spectroscopy (FTIR) and tentative band assignments for bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1), and CT-complexes. $[(SB1)(TCNE)_2]$, $[(SB1)(DDQ)_2]$, $[(SB1)(PA)]$ and $[(SB1)I]^+I_3^-$.

SB1	$[(SB1)(TCNE)_2]$	$[(SB1)(DDQ)_2]$	$[(SB1)(PA)]$	$[(SB1)I]^+I_3^-$	Assignments
-	-	-	-	3316	$\nu(H_2O)$; KBr
2878	2361, 2334,	2982, 2365, 2359	2365, 2347, 2900	2902, 2665	$\nu(C-H)$; SB1, PA, $\nu(O-H)$; PA
-	2204	2217	-	-	$\nu(C \equiv N)$; TCNE, DDQ
1641, 1610	1649	1653	1666, 1636, 1602	-	$\nu(C=N)$; SB1, PA
1555	1599	1600	1565	1578, 1527	$\nu(C=C)$; free SB1
-	-	-	1491	-	$\nu(N-O)$; PA
1445, 1433	1432	1440	1438	1455, 1433, 1411	$\nu(CH_2)$; SB1 free and complexed SB1
1232	1226	1232	1263	1285, 1231	$\nu(C-N)$; SB1
1186, 1172, 1130	1186	1189, 1175	1190, 1162	1171	$\nu(C-C)$; SB1
-	-	728	-	-	$\nu(C-Cl)$; PA

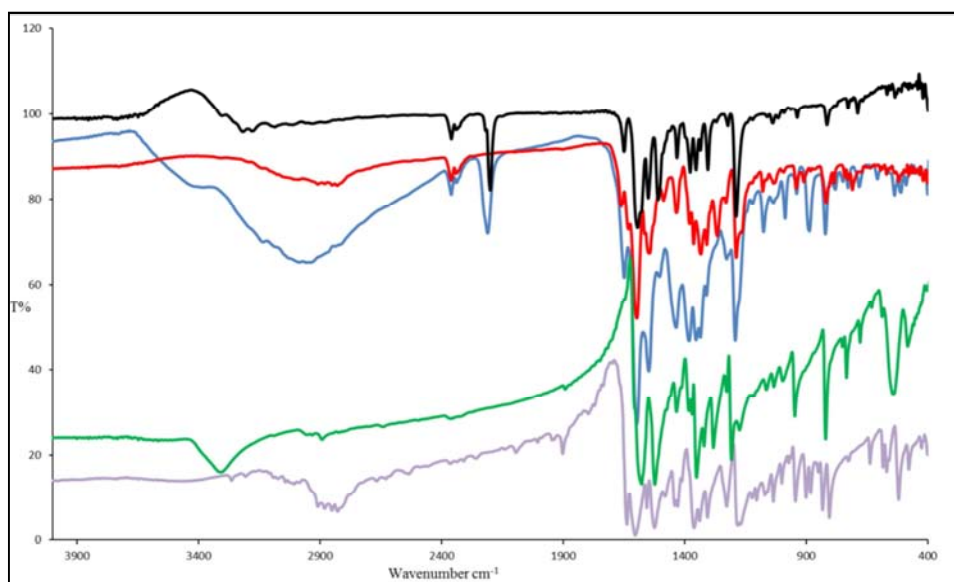


Figure 10. FT- infrared spectra of bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1) move line; $[(SB1)(DDQ)_2]$ blue line; $[(SB1)(TCNE)_2]$ black line; $[(SB1)(PA)]$ red line; and $[(SB1)I]^+I_3^-$ green line.

4. Conclusion

Four new charge transfer complexes of Bis N, N'-dimethylbenzaldehyde ethylenediimine (SB1) and the acceptors tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), Picric acid (PA) and iodine have been prepared and have been studied spectrophotometrically. Photometric measurements of these compounds showed that, the donor-acceptor molar ratio is variable depending on the type of acceptor. These molar ratios were found to be 1:1 in the case of SB1-PA and 1:2 in the case of SB1-DDQ and SB1-TCNE and 1:3 in the case of SB1-I₂ system. Depending on the results of photometric titration, elemental analysis and Infrared absorption spectra,

the structures of the newly formed CT-complexes were formulated to be $[(SB1)(PA)]$, $[(SB1)(DDQ)_2]$, $[(SB1)(TCNE)_2]$ and $[(SB1)(I_2)_3]$.

Acknowledgments

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