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# Synthesis and characterization of highly conductive charge-transfer complexes using positron annihilation spectroscopy

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# ABSTRACT

Molecular charge-transfer complexes of the tetramethylethylenediamine (TMEDA) with picric acid (Pi-OH), benzene-1,4-diol (QL), tin(IV) tetrachloride (SnCl<sub>4</sub>), iodine, bromine, and zinc chloride (ZnCl<sub>2</sub>) have been synthesized and investigated by elemental and thermal analysis, electronic, infrared, Raman and proton-NMR, energy-dispersive X-ray spectroscopy, X-ray powder diffraction and positron annihilation lifetime spectroscopy, and scanning electron microscopy. In this work, three types of acceptors  $\pi$ -acceptors (Pi-OH and QL),  $\sigma$ -acceptors (iodine and bromine), and vacant *orbital* acceptors (SnCl<sub>4</sub> and ZnCl<sub>2</sub>) were covered. The results of elemental analysis indicated that the CT complexes were formed with ratios 1:1 and 1:2 for QL, SnCl<sub>4</sub>, and ZnCl<sub>2</sub> acceptors and iodine, Pi-OH, and Br<sub>2</sub> acceptors, respectively. The type of chelating between the TMEDA donor and the mentioned acceptors depends upon the behavior of both items. The positron annihilation lifetime parameters were found to be dependent on the structure, electronic configuration, and the power of acceptors. The correlation between these parameters and the molecular weight and biological activities of studied complexes was also observed. Regarding the electrical properties, the AC conductivity and the dielectric coefficients were measured as a function of frequency at room temperature. The TMEDA charge-transfer complexes were screened against antibacterial (Escherichia coli, Staphylococcus aureus, Bacillus subtilis, and Pseudomonas aeruginosa) and antifungal (Aspergillus flavus and Candida albicans) activities.

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# Introduction

The charge-transfer (CT) complexes are known to take part in many chemical reactions such as addition, substitution, and condensation [1,2]. These complexes have had great attention for nonlinear optical materials and electrical conductivity [3–6]. The electron donor–acceptor (EDA) interaction is also important in the field of drug receptor binding mechanisms [7], in solar energy storage [8], and in surface chemistry [9] as well as in many biological fields [10]. On the other hand, the EDA reactions of certain  $\pi$ -acceptors have been successfully utilized in pharmaceutical analysis [11]. For these wide applications extensive studies on CT complexes of  $\pi$ -acceptors have been performed [12]. Various spectroscopic techniques were used to characterize these metallic complexes. Recently, positron annihilation spectroscopy has also been applied to metallic complexes [13–15]. Positron annihilation life-time (PAL) spectroscopy is one of the highly successful techniques

\* Corresponding author. Tel.: +966 502099808. E-mail address: majidadam@yahoo.com (A.M.A. Adam). that have been used to study the structural aspects of different types of materials even at subatomic levels. When a positron is emitted from a <sup>22</sup>Na source and allowed to penetrate the materials, it thermalizes and diffuses to a depth of a few hundred micrometers. The positron either delocalizes or traps in defects, which leads to an increase in its lifetime, or extracts an electron from the surrounding material to form a positronium atom (Ps) with two states, a singlet state (para-Ps, p-Ps) and a triplet state (ortho-Ps, o-Ps). In both cases, the positron will eventually annihilate with an electron and will have a corresponding lifetime for each state at annihilation site. Each lifetime component has a corresponding intensity  $(I_i)$  relating to the number of annihilations occurring at a particular lifetime ( $\tau_i$ ). The measured parameters of the Ps formation in ionic and molecular solids ( $\tau$  and I) depend on the physical and chemical properties of the solids [16,17]. The previous studies show that the Ps is preferentially formed in compounds exhibiting negative charge stabilization at specific sites. These studies also show that the parameters of positron annihilation are sensitive to the liability of the solids to charge-transfer processes and it mainly depends on the nature of the central metal ion [14]. Also, the correlation

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between positron annihilation parameters and the structure of the metallic complexes was observed [14].

The present paper is concerned with the synthesis of the solid CT complexes of tetramethylethylenediamine (TMEDA) (Formula 16) as a donor and Pi-OH, QL, SnCl<sub>4</sub>, iodine, bromine and ZnCl<sub>2</sub> as acceptors. The solid complexes resulted are investigated by spectral, thermal and electrical methods. These tools are enough to detect and characterize the behavior of interaction and the nature of the chelating in these complexes.

# **Experimental methods**

# Materials

All chemicals (N,N,N',N'-tetramethyl-ethane-1,2-diamine, Pi-OH, QL, SnCl<sub>4</sub>, ZnCl<sub>2</sub>, iodine, and bromine) were of reagent grade, were purchased from Aldrich and Fluka Companies, and were used without further purification.

# Synthesis of TMEDA CT complexes

The colored TMEDA CT complexes in solid form with Pi-OH, QL, SnCl<sub>4</sub>, ZnCl<sub>2</sub>, iodine, and bromine acceptors were prepared by mixing 1 mmol of the TMEDA as a donor in pure-grade methanol (25 mL) for all complexes except for (iodine and bromine in chloroform) with 1 mmol of each acceptor. The mixtures were stirred at room temperature for 30 min, and after that, the solid complexes were precipitated separated, and washed with chloroform. The synthesized CT complexes were dried under vacuum over anhydrous CaCl<sub>2</sub>.

## Spectral, thermal, and electrical measurements

The elemental analyses of carbon, hydrogen, and nitrogen contents were performed by the microanalysis unit at Cairo University, Egypt, using a Perkin Elmer CHN 2400 (USA). The molar conductivities of freshly prepared  $1.0 \times 10^{-3}$  mol/cm<sup>3</sup> dimethylsulfoxide (DMSO) solutions were measured for the soluble CT complexes using Jenway 4010 conductivity meter. The electronic absorption spectra of the TMEDA donor and the acceptors (Pi-OH, QL, SnCl<sub>4</sub>, ZnCl<sub>2</sub>, iodine, and bromine) and the resulted CT complexes were recorded in methanol or chloroform solvents within 800-200 nm range using a Perkin-Elmer Precisely Lambda 25 UV/Vis double beam spectrometer fitted with a quartz cell of 1.0 cm path length. The infrared spectra with KBr disks were recorded on a Bruker FT-IR Spectrophotometer (4000–400 cm<sup>-1</sup>). Raman laser spectra of samples were measured on the Bruker FT-Raman with 50 mW of laser at Taif University, Kingdom Saudi Arabia. The <sup>1</sup>H-NMR (200 MHz) spectra were recorded on Varian Gemini spectrophotometers. The thermal studies TG/DTG-50H were carried out on a Shimadzu thermogravimetric analyzer under static air till 800 °C. Scanning electron microscopy (SEM) images and Energy-Dispersive X-ray Detection (EDX) were taken in Joel JSM-6390 equipment, with an accelerating voltage of 20 kV. The X-ray diffraction patterns for the selected CT complexes were recorded on



Formula. 16. Structure of N,N,N',N'-tetramethyl-ethane-1,2-diamine (TMEDA).

X 'Pert PRO PANanalytical X-ray powder diffraction, target copper with secondary monochromate.

The PAL measurements were carried out using a fast-fast coincidence spectrometer [18]. This PAL spectrometer consists of two Bicron BC-418 plastic scintillation detectors and Ortec modules, two 583 constant fraction differential discriminators (CFDD), DB643 delay box (ns D), 414A fast coincidence, and 566 time-toamplitude converter (TAC). The data were acquired using an Ortec 919 multichannel analyzer (MCA). A positron source was prepared using a droplet of <sup>22</sup>NaCl solution dried onto two identical Kapton foils (7.5 µm thick), which were afterward glued by epoxy glue. This source was sandwiched between two identical samples. The lifetime spectra were measured in air at room temperature. More than one million counts were accumulated for each spectrum. and each sample was measured three times. The time resolution of the spectrometer, measured with <sup>60</sup>Co source at <sup>22</sup>Na energy window settings, was  $\sim$ 300 ps (full-width at half maximum). The positron annihilation lifetime is measured experimentally as the time interval between the 1274.5 keV  $\gamma$  ray emitted by the <sup>22</sup>Na radioisotope and one of the annihilation radiations.

The resulting lifetime spectra were analyzed using a computer program LT [19] with a suitable correction for positrons annihilated in the Kapton. The lifetime spectra of studied samples decomposed into two components. All these components were determined with the best-fitting parameter ranging from 1.00 to 1.2. The range of the experimental errors for the PAL parameters  $\tau_1$ ,  $\tau_2$ ,  $I_1$ , and  $I_2$ , determined over multiple measurements, were found to be <2 ps,<15 ps, 1%, and 0.5%, respectively. The mean lifetime of positron was calculated using the following relation:

$$\tau_m = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}.$$
 (1)

AC conductivity for disk shaped was measured, at room temperature, over frequency range from 200 up to 100 kHz. The AC conductivity and the dielectric constant have been measured by the complex impedance technique using a lock-in amplifier (Model SR 510 Stanford Research Systems).

## **Biological studies**

Antimicrobial activity of the tested samples was determined using a modified Kirby–Bauer disk diffusion method [20]. Briefly, 100 µl of the best bacteria/fungi was grown in 10 mL of fresh media until they reached a count of approximately 108 and 105 cells/mL for bacteria and fungi, respectively [21]. Hundred microliters of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disk diffusion method [22,23].

Of the many media available, National Committee for Clinical Laboratory Standards (NCCLS) recommends Mueller-Hinton agar because it results in good batch-to-batch reproducibility. Disk diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed by the NCCLS [24] for evaluating the susceptibility of filamentous fungi to antifungal agents. Disk diffusion method for yeast developed standard method (M44-P) by the NCCLS [25]. Plates inoculated with filamentous fungi such as Aspergillus flavus at 25 °C for 48 h: Gram (+) bacteria such as Staphylococcus aureus, Bacillus subtilis; Gram (-) bacteria such as Escherichia coli, Pseudomonas aeruginosa were incubated at 35-37 °C for 24-48 h, and yeast such as Candida albicans was incubated at 30 °C for 24-48 h, and then the diameters of the inhabitation zones were measured in millimeters [20]. Standard disks of tetracycline (Antibacterial agent), Amphotericin B (Antifungal agent) served as positive controls for antimicrobial activity,

but filter disk impregnated with  $10 \,\mu$ L of solvent (distilled water, chloroform, DMSO) were used as a negative control.

The agar used is Meuller-Hinton agar that is rigorously tested for composition and pH. Further, the depth of the agar in the plate is a factor to be considered in the disk diffusion method. This method is well documented, and standard zones of inhabitation have been determined for susceptible values. Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated with 10 µL of tested concentration of the stock solutions. When a filter paper disk impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disk into the agar. This diffusion will place the chemical in the agar only around the disk. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disk. If an organism is placed on the agar, it will not grow in the area around the disk if it is susceptible to the chemical. This area of no growth around the disk is known as a "Zone of inhibition" or "Clear zone." For the disk diffusion, the zone diameters were measured with slipping calipers of the National for Clinical Laboratory Standers [22]. Agar-based methods such as Etest disk diffusion can be good alternatives because they are simpler and faster than broth methods [26,27].

# **Results and Discussion**

The analytical data (color, molar ratio elemental analysis) are shown in Table 1. The elemental analysis data (C and H) of the resulted CT complexes were matched with the molar ratio gained from spectrophotometric titrations. The Pi-OH, QL, iodine, and bromine CT complexes have a yellow, light brown, reddish brown, and orange yellow colors, respectively, but SnCl<sub>4</sub> and ZnCl<sub>2</sub> complexes are white with powder fashion. Molar conductance of all the CT complexes in DMSO solvent at  $10^{-3}$  M concentrations were obtained in the range  $48-90 \ \Omega^{-1} \ cm^2 \ mol^{-1}$  and the results indicated them to be electrolytes. These results establish the stoichiometry of these complexes, which are in agreement with the general formulas suggested.

# Electronic and photometric analyses

Photometric titrations of the detectable charge-transfer bands at 410, 294, 360, and 279 nm were performed for the reactions of TMEDA with Pi-OH, QL, iodine, and bromine as follows: 0.25,

0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, or 4.00 mL volumes of a standard solution  $(5.0 \times 10^{-4} \text{ M})$  of the appropriate acceptor (Pi-OH, QL, iodine and bromine) in methanol or chloroform was added to 1.00 mL of  $5.0 \times 10^{-4}$  M TMEDA in chloroform or methanol. The total volume of the mixture was made up to 5 mL. The concentration of TMEDA  $(C_d^o)$  in the reaction mixture was thus fixed at  $1.0 \times 10^{-4}$  M while the concentration of  $\pi$ -acceptors ( $C_a^o$ ) varied from 0.25 to  $4.00 \times 10^{-4}$  M. These concentrations produce donor: acceptor ratios from 4:1 to 1:4. The absorbance of each CT complexes was measured and plotted as a function with the ratio of  $(C_d^o)$ : $(C_d^o)$  according to a known method [28]. It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the formed charge-transfer complexes. To study this solvent effect in a quantitative manner, it was necessary to calculate the values of the equilibrium constant, K, the molar absorptivity,  $\varepsilon$ , and the oscillator strength, f, of the TMEDA complexes in the respective solvent.

The 1:1 modified Benesi–Hildebrand Eq. (2) [29] was used in the calculations of the TMEDA with QL charge-transfer complex,

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon}.$$
(2)

where  $C_a^o$  and  $C_d^o$  are the initial concentrations of the acceptor (QL) and the donor TMEDA, respectively, and *A* is the absorbance of the strong bands at 294 nm for QL. When the  $C_a^o, C_d^o/A$ , values for each 1:1 charge-transfer complex are plotted against the corresponding  $C_a^o + C_d^o$  values. Straight lines are obtained with a slope of  $1/\varepsilon$  and intercept of  $1/K\varepsilon$ .

The spectrophotometric titrations of the intermolecular chargetransfer complexes formed from the reactions of TMEDA with Pi-OH, iodine, and bromine acceptors refereed to formation of 1:2 CT complexes. The 1:2 Eq. (3) [30] was used in the calculations.

$$\frac{C_A^{o^2} C_D^o}{A} = \frac{1}{K\varepsilon} + \frac{1}{\varepsilon} \cdot C_A^o (4C_D^o + C_A^o).$$
(3)

where  $C_A^{o^2}$  and  $C_D^o$  are the initial concentration of the Pi-OH, iodine, and bromine acceptor and donor (TMEDA), respectively, and *A* is the absorbance of the detected CT band. The data obtained  $C_D^o$ ,  $C_A^{o^2}$ ,  $C_A^o(4C_D^o + C_A^o)$ , and  $(C_A^{o^2} \cdot C_D^o)/A$  in methanol were calculated. By plotting  $(C_A^{o^2} \cdot C_D^o)/A$  values versus  $C_A^o(4C_D^o + C_A^o)$ , straight lines were obtained with a slope of  $1/\varepsilon$  and an intercept of  $1/K\varepsilon$ .

The spectroscopic and physical data such as formation constant ( $K_{CT}$ ), molar extinction coefficient ( $\varepsilon_{CT}$ ), standard free energy ( $\Delta G^{\circ}$ ),

Table 1

nalytical and physical data for Pi-OH, QL, SnCl <sub>4</sub> , I <sub>2</sub> , Br <sub>2</sub> , and ZnCl <sub>2</sub> charge-transfer	complexes.
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Compound molecular formula empirical formula (MW.)	Color	Molar ratio	Elemental analysis (%) found (Calcd.)		$\Lambda m \left( \Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1} \right)$
			С	Н	
[(TMEDA)(Pi-OH) <sub>2</sub> ] C <sub>18</sub> H <sub>22</sub> N <sub>8</sub> O <sub>14</sub> 574.44 g/mol	Yellow	1:2	37.42 (37.60)	3.33 (3.83)	65
[(TMEDA)(QL)] C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> 226.35 g/mol	Light brown	1:1	63.49 (63.62)	9.89 (9.72)	48
[(TMEDA)(SnCl <sub>4</sub> )] C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> SnCl <sub>4</sub> 376.74 g/mol	White	1:1	19.35 (19.11)	4.33 (4.25)	90
[(TMEDA)]I·I <sub>3</sub> C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> I·I <sub>3</sub> 623.60 g/mol	Reddish brown	1:1	11.44 (11.54)	2.52 (2.56)	72
[(TMEDA)]-2Br <sub>2</sub> C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> ·2Br <sub>2</sub> 435.84 g/mol	Orange yellow	1:2	16.92 (16.52)	4.02 (3.67)	55
[(TMEDA)(ZnCl <sub>2</sub> )] C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> ·ZnCl <sub>2</sub> 252.56 g/mol	White	1:1	28.26 (28.51)	5.84 (6.33)	88

 Table 2

 Spectrophotometric results of the TMEDA CT complexes for Pi-OH(A), QL(B), I<sub>2</sub>(C), and Br<sub>2</sub>(D).

Complex	$\lambda_{\max}$ (nm)	$E_{\rm CT}~({\rm eV})$	K (l.mol <sup>-1</sup> )	$\varepsilon_{\rm max}$ (l.mol <sup>-1</sup> .cm <sup>-1</sup> )	f	μ	Ip	D	$R_N$	$\Delta G^{o}(25 \ ^{\circ}C) \ \mathrm{KJ} \ \mathrm{mol}^{-1}$
А	410	4.26	$\textbf{8.48}\times \textbf{10}^{7}$	70102	60.55	61.30	11.00	4.81	0.926	45238
В	294	4.05	14334	10661	6.14	20.01	10.74	4.81	0.378	23716
С	360	4.35	$4.7  imes 10^7$	46694	40.33	49.51	11.11	4.81	0.845	38083
D	279	4.35	15667	30211	21.75	36.35	11.11	32.70	0.719	23936

oscillator strength (*f*), transition dipole moment ( $\mu$ ), resonance energy ( $R_N$ ), and ionization potential ( $I_p$ ) were estimated in chloroform or methanol at 25 °C, and the different acceptors were found to have a pronounced effect on the interaction with TMEDA. These calculations can be summarized as follows;

The oscillator strength f was obtained from the approximate formula [31],

$$f = (4.319 \times 10^{-9})\varepsilon_{\rm max} v 1/2 \tag{4}$$

where  $v_{1/2}$  is the band width at half intensity in cm<sup>-1</sup> and  $\varepsilon_{max}$  is the maximum extinction coefficient of the CT band. The oscillator strength values are given in Table 2. The data resulted reveal several items. Firstly, the TMEDA/Acceptor (where Acceptor = Pi-OH, QL, iodine, and bromine) systems show high values of both formation constant (*K*) and molar absorptivity ( $\varepsilon$ ). This high value of *K* reflects the high stability of the 18-crown-6 CT complexes as a result of the expected high rich donation of the TMEDA, which contains two nitrogen atoms fitted with four methyl groups. Secondly, the different values of the oscillator strength, *f*, increase with increase in the dielectric constant (*D*) of the solvent. This result could be explained on the basis of competitive solvent interactions with the acceptors [32,33].

The transition dipole moment ( $\mu$ ) of the TMEDA charge-transfer complexes have been calculated from Eq. (5) [34] and listed in Table 2.

$$\mu(\text{Debye}) = 0.0958 [\varepsilon_{\text{max}} v_{1/2} / v_{\text{max}}]^{1/2}$$
(5)

The transition dipole moment is useful for determining whether transitions are allowed, that the transition from a bonding  $\pi$  orbital to an antibonding  $\pi^*$  orbital is allowed because the integral defining the transition dipole moment is nonzero.

The ionization potential  $(I_p)$  of the TMEDA donor in their CT complexes was calculated using empirical equation derived by Aloisi and Piganatro and Briegleb Eq. (6) [35,36];

$$I_p(eV) = 5.76 + 1.53 \times 10^{-4} v_{\rm CT} \tag{6}$$

where  $v_{CT}$  is the wavenumber in cm<sup>-1</sup> corresponding to the CT band formed from the interaction between donor and acceptor. The electron donating power of a donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the highest occupied molecular orbital.

The energy of the CT complexes  $E_{CT}$  of the TMEDA complexes is calculated using the Eq. (7) [34];

$$E_{\rm CT} = (hv_{\rm CT}) = 1243.667 / \lambda_{\rm CT}(nm) \tag{7}$$

where,  $\lambda_{CT}$  is the wavelength of the complexation band.

Determination of resonance energy  $(R_N)$  [37] theoretically derived from (Eq. (8));

$$\varepsilon_{\rm max} = 7.7 \times 10^{-4} / [h v_{\rm CT} / [R_N] - 3.5]$$
 (8)

where  $\varepsilon_{\text{max}}$  is the molar absorptivity of the CT complexes at maximum CT band,  $v_{\text{CT}}$  is the frequency of the CT peak, and  $R_N$  is the resonance energy of the complex in the ground state, which obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of  $R_N$  for the TMEDA CT complexes under study have been given in Table 2.

The standard free energy changes of complexation ( $\Delta G^{\circ}$ ) were calculated from the formation constants by the following Eq. (9) [38];

$$\Delta G^{o} = -2.303 RT log K_{CT}$$
(9)

where  $\Delta G^{\circ}$  is the free energy change of the CT complexes (kJ mol<sup>-1</sup>), *R* is the gas constant (8.314 J mol<sup>-1</sup> K), *T* is the temperature in Kelvin, and  $K_{CT}$  is the formation constant of the complexes (L mol<sup>-1</sup>) in different solvents at room temperature.

# QL and iodine/TMEDA (1:1) charge-transfer systems

The reactions of TMEDA with the QL as a  $\pi$ -acceptor were carried out in methanol. The electronic absorption spectra of the reactants, TMEDA ( $1.0 \times 10^{-4}$  M), and QL acceptor ( $1.0 \times 10^{-4}$  M) in MeOH along with those of the formed 1:1 CT complex are shown in Fig. 1. The spectrum demonstrates that the formed CT complex has a detectable absorption band around 294 nm for [(TME-DA)(QL)] complex. This band does not exist in the spectra of the reactants in the same behavior. The stoichiometry of the [TME-DA]-acceptor reactions were shown in both cases to be of 1:1 ratio. This was concluded on the bases of the obtained elemental analysis data of the isolated solid CT complexes. In these measurements, concentration of TMEDA was kept fixed, while the concentration of the acceptor was varied over the range of  $0.25 \times 10^{-4}$ - $4.00 \times 10^{-4}$  M as described in the experimental section. Photometric titration curves based on these measurements are shown in Fig. 2. The 1:1 modified Benesi-Hildebrand Eq. (2) was used in calculating the values of the equilibrium constant, K, and the molar absorptivity ( $\varepsilon C_a^o$  and  $C_d^o$  is the initial concentrations of the acceptor (QL) and the donor TMEDA, respectively, while A is the absorbance of the strong band around 294 nm for the TMEDA/QL CT complex. Plotting the values of the  $C_a^o C_d^o / A$  against  $C_a^o + C_d^o$  values for QL acceptor, a straight line is obtained with a slope of  $1/\varepsilon$  and intercept of  $1/K\varepsilon$  as shown in Fig. 3. The values of both K and  $\varepsilon$  associated with these complexes were data obtained throughout these calculations, which are given in Table 2. This complex shows high values of both the formation constant (K) and the extinction coefficients ( $\varepsilon$ ). These high values of *K* confirm the expected high stabilities of the formed CT complexes as a result of the expected high donation of the TMEDA.

# Iodine, bromine and Pi-OH/TMEDA (1:2) charge-transfer systems

New detectable bands in the UV–visible spectra at (290 and 360 nm), 279 and 410 nm are observed immediately on mixing solutions of TMEDA and each of the iodine, bromine and picric acids in chloroform or methanol, respectively. The electronic absorption spectra of the donor TMEDA with acceptors (I<sub>2</sub>, Br<sub>2</sub>, and Pi-OH) have molar ratios (donor:acceptor) of 1:2. Fig. 1 Revealed absorption bands attributed to the CT interaction. The spectrum of the TMEDA/Br<sub>2</sub> system shows one strong absorption band at 279 nm with hyperchromic effect due to the formation of [(TME-DA)]·2Br<sub>2</sub> CT complex, while the corresponding absorption bands associated with the formation of the complex [(TMEDA)(Pi-OH)<sub>2</sub>] was observed at 410 nm. Furthermore, photometric titration measurements based on the characteristic absorptions bands of the CT complexes (Fig. 2) confirmed the molar ratios of the three



Fig. 1. Electronic spectra of [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)]I·I<sub>3</sub>, and [(TMEDA)]·2Br<sub>2</sub> CT complexes.



Fig. 2. Photometric titration curves of [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)]I·I<sub>3</sub>, and [(TMEDA)]·2Br<sub>2</sub> CT complexes.



Fig. 3. The 1:2 and 1:1 modified Benesi-Hildebrand curves for [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)]I·I<sub>3</sub>, and [(TMEDA)]·2Br<sub>2</sub> CT complexes.

mentioned complexes. Photometric titrations between TMEDA and iodine, Br<sub>2</sub>, and Pi-OH in CHCl<sub>3</sub> or MeOH solvent were carried out as follows: concentration of TMEDA (C<sub>d</sub>) were kept fixed at  $1.0 \times 10^{-4}$  M, whereas that of the acceptor (iodine, Br<sub>2</sub>, or Pi-OH)  $C_a$  was changed over a wide range of  $0.25 \times 10^{-4}$ – $4 \times 10^{-4}$  M. The peak absorbances appeared in the spectra that assigned to the formed CT complexes were measured and plotted as a function of the ratio C<sub>d</sub>:C<sub>a</sub> according to the known method [28]. The 1:2 modified Benesi-Hildebrand Eq. (3) was used to calculate the values of the equilibrium constant, K (L mol<sup>-1</sup>), and the extinction coefficient,  $\varepsilon$  (L mol<sup>-1</sup> cm<sup>-1</sup>), for both complexes. The data obtained throughout this calculation are given in Table 2. Plotting values of  $(C_A^o)^2 C_D^o / A$  versus  $C_A^o (C_A^o + 4C_D^o)$  values of Eq. (3), straight lines are obtained with a slope of  $1/\varepsilon$  and intercept of  $1/K\varepsilon$  as shown in Fig. 3. Table 2 has the calculated values of the spectroscopic data such as  $\varepsilon$ , K,  $\mu$ ,  $R_N$ ,  $\Delta G$ ,  $I_p$ , and f, which were deduced from the Eq. 4–9. Generally, these complexes show high values of both the formation constant (K) and the molar absorptivity ( $\varepsilon$ ). These high values of K confirm the expected high stabilities of the formed CT complexes as a result of the expected high donation of the TMEDA. The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it, such as iodine, bromine, or nitro groups.

In the case of TMEDA/iodine, the appearance of the two absorption bands around 360 and 290 nm is well known [39–43] to be characteristic of the formation of the triiodide ion ( $I_3^-$ ). This was also supported by the Raman laser spectrum of the iodine complex. This spectrum shows the characteristic bands for the triiodide ion as  $v_{as}(I-I)$ ,  $v_s(I-I)$ , and  $\delta(I_3^-)$ . These three absorptions do not exist in the spectrum of the donor. However, the  $I_3^-$  ion may be linear ( $D_h$ ) or nonlinear ( $C_{2v}$ ). Group theoretical analysis indicates that the  $I_3^-$ 

with  $C_{2v}$  symmetry displays three vibrations  $v_s$  (I–I), A<sub>1</sub>;  $v_{as}$  (I–I), B<sub>2:</sub> and  $\delta$ , (I<sub>3</sub><sup>-</sup>); A<sub>1</sub>, all are infrared active in good agreement [39–41] with the observed of three Raman bands for [(TMEDA)]I<sup>+</sup>.I<sub>3</sub><sup>-</sup>.

According to the foregoing discussion, a general mechanism is proposed for the formation of  $[(TMEDA)]I^+ I_3^-$  complexes as follows:

 $[\mathsf{TMEDA}] + I_2 \rightarrow [\mathsf{TMEDA}]I^+.I^-$ 

$$[\text{TMEDA}]I^+.I^- + I_2 \rightarrow [\text{TMEDA}]I^+.I_3^-$$

# IR spectral analyses

The infrared spectra of the TMEDA as free donor, Pi-OH/TMEDA, QL/TMEDA, SnCl<sub>4</sub>/TMEDA, ZnCl<sub>2</sub>/TMEDA, iodine/TMEDA, and bromine/TMEDA complexes are shown in Fig. 4(A-G), and their band assignments are given in Tables 3-5. The infrared spectrum of the characteristic bands of TMEDA shows the following absorption bands: (i) 3385, 3374, 2970, and 2943 cm<sup>-1</sup> assigned for the asymmetric stretching vibrational bands of the methyl groups  $(-CH_3 + CH_2$ ), (ii) 2860, 2816, and 2766 cm<sup>-1</sup> due to the symmetric stretching vibrational bands of  $-CH_3 + -CH_2$ , (iii) in the IR spectrum of free donor, the bending deformation bands of methyl groups are assigned at 1684, 1454, 1404, and 1364  $\text{cm}^{-1}$ , (iv) the asymmetric and symmetric stretching bands  $v_{as}(C-N) + v_s(C-N)$  of C-N exist at 1338, 1311, 1299, 1282, and 1267 cm<sup>-1</sup> and 1167, 1138, 1097, 1086, 1043, and 1033 cm<sup>-1</sup>, respectively, (v) both of in-plane bend  $\delta$ (CH) and rocking  $\delta$ (CH) have a detectable bands at 943 and  $876 \text{ cm}^{-1}$  and 836, 788, and  $777 \text{ cm}^{-1}$ , respectively, (vi) bands at 676 and 495 cm<sup>-1</sup> are assigned to out-of-plane bend of the



Fig. 4. Infrared spectra of (A) Free TMEDA, (B) [(TMEDA)(Pi-OH)<sub>2</sub>], (C) [(TMEDA)(QL)], (D) [(TMEDA)]I·I<sub>3</sub>, (E) [(TMEDA)]·2Br<sub>2</sub>, (F) [(TMEDA)(SnCl<sub>4</sub>)], and (G) [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.

 $\delta$ (C–N). These assignments are based on the comparison of the spectra of CT complexes with the spectra of the reactants, (TMEDA) donor, and the acceptors. The spectra of the formed CT complexes contain the main bands for both TMEDA and the acceptor used, and this strongly supports the formation of the [(TMEDA)(Pi-

 $OH_{2}$ ], [(TMEDA)(QL)], [(TMEDA)(SnCl<sub>4</sub>)], [(TMEDA)]I·I<sub>3</sub>, [(TME-DA)]·2Br<sub>2</sub>, and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes. However, the bands associated with spectra of the formed CT complexes show some changes in intensities and in some cases show small shifts in the frequency values compared with those of the free acceptor and the

Characteristic infrared frequencies  $(cm^{-1})$  and tentative assignments of TMEDA free donor and their [(TMEDA)]I-I<sub>3</sub> and [(TMEDA)]-2Br<sub>2</sub> CT complexes.

#### Table 4

Characteristic infrared frequencies (cm<sup>-1</sup>) and tentative assignments of TMEDA free donor and their [(TMEDA)(Pi-OH)<sub>2</sub>] and [(TMEDA)(QL)] CT complexes.

TMEDA	[(TMEDA)]I·I <sub>3</sub>	$[(TMEDA)] \cdot 2Br_2$	Assignments <sup>(b)</sup>
3385	3432	3391	
3374	3013	3017	$v_{as}(C-H)$ ; CH <sub>3</sub> + CH <sub>2</sub>
2970	2949	2940	
2943	2924		
2860	2892	2849	
2816	2827	2768	$v_{s}(C-H); CH_{3} + CH_{2}$
2766	2656	2634	
1684	1785	1663	
1454	1659	1630	
1404	1463	1470	$\delta$ (CH) deformation
1364	1407	1418	
1338	1259	1283	
1311		1235	
1299			$v_{as}(C-N)$
1282			
1267			
1167	1151	1153	
1138	1069	1119	
1097	1042	1058	$v_s(C-N)$
1086		1027	
1043			
1033			
943	992	998	$\delta(CH)$ in-plane bend
876	871	976	
		943	
		896	
836	784	789	$\delta(CH)$ rocking
788			
777			
676	668	590	
495	558	510	$\delta(C-N)$ out-of-plane bend
	459	461	
	408		

TMEDA donor. This could be understood on the basis of symmetry and electronic structure changes in both acceptor and TMEDA in the formed CT complexes compared with those of the free molecules. In the case of [(TMEDA)(Pi-OH)<sub>2</sub>] and [(TMEDA)(OL)] CT complexes, the appearance of a few absorption bands at 2668, 2531, and  $2489 \text{ cm}^{-1}$  and 2699, 2589, and 2365 cm<sup>-1</sup>, respectively, usually comes from stretching vibrations between hydrogen (acceptor) and some nitrogen atoms (TMEDA) [44]. Hydrogen bonding  $(v(OH \cdots N))$  has a significant influence on the peak shape and intensity, generally causing peak broadening and shifts in absorption to lower frequencies. The presence of these bands confirmed that the proton transfer phenomena from the acidic center of each acceptor (Pi-OH and QL) to the lone pair of electron on nitrogen atom to form OH···N hydrogen bonding upon complexation (Formulas 17 and 18). Also, there are some small changes comparing the spectra of the CT complexes and those of the reactants, which could also be notable from the expected changes in the symmetry and electronic configurations of both reactants upon charge-transfer complexation.

The mid-infrared spectra of [(TMEDA)]I·I<sub>3</sub> and [(TMEDA)]·2Br<sub>2</sub> formed CT complex were recorded from KBr disks. The spectral bands are resolved and assigned into their vibrational modes and given in Table 3. As expected, the bands characteristic of the TME-DA unit in both [(TMEDA)]I·I<sub>3</sub> and [(TMEDA)]·2Br<sub>2</sub> CT complexes are shown with small changes in band intensities and frequency values (Formulas 19 and 20).

For the CT complexes  $[(TMEDA)(Pi-OH)_2]$  and  $[(TMEDA)]\cdot 2Br_2$  when the molar ratio is 1:2, it is more likely to propose that the (TMEDA) is arranged in such a way that it is sandwiched between the two acceptor molecules.

The infrared spectrum of the TMEDA donor was compared with those of the [(TMEDA)(SnCl<sub>4</sub>)] and [(TMEDA)(ZnCl<sub>2</sub>)] complexes

TMEDA	[(TMEDA)(Pi-OH)2]	[(TMEDA)(QL)]	Assignments <sup>(b)</sup>
3385	3297	3031	$v_{as}(C-H)$ ; $CH_3 + CH_2$
3374	3101	2987	
2970	3059	2958	
2943	2993		
2860	-	2873	$v_{s}(C-H); CH_{3} + CH_{2}$
2816		2829	
2766		2791	
-	2668	2744	v(OH· · · N), hydrogen
	2531	2699	bonding
	2489	2589	
-	1846	-	$v(NO_2)$ , Pi-OH
1684	1611	1513	$\delta$ (CH) deformation
1454	1541	1479	v(C=C)
1404	1489	1373	
1364	1431		
	1365		
1338	1330	1255	$v_{as}(C-N)$
1311	1268	1226	
1299			
1282			
1267			
1167	1162	1161	$v_s(C-N)$
1138	1080	1141	
1097		1093	
1086		1021	
1043			
1033			
943	1003	896	$\delta$ (CH) in-plane bend
876	973		
	919		
	844		
836	789	826	
788	741	796	
777		762	$\delta$ (CH) rocking
676	709	511	$\delta$ (C–N) out-of-plane
495	546	438	bend
	519		$\delta(ONO)$
	441		

(Formulas 21 and 22) in order to ascertain the complexation sites that may be involved in chelation (Table 5). In the spectra of the complexes (Fig. 4), the infrared spectra of these complexes exhibited non-ligand bands in the regions  $460-570 \text{ cm}^{-1}$ , assignable to v(M–N) vibrations [44].

# Raman spectral analyses

Fig. 5A-E shows the Raman spectra of [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(SnCl<sub>4</sub>)], [(TMEDA)]I·I<sub>3</sub>, [(TMEDA)]·2Br<sub>2</sub>, and [(TME-DA) $(ZnCl_2)$ ] CT complexes in the (4000–50 cm<sup>-1</sup>) frequency ranges. As one can see from Fig. 5 concerning the [(TMEDA)(Pi-OH)<sub>2</sub>] complex, vibrations at 1633, 1612, 1548, 1530, and 1346 cm<sup>-1</sup> clearly correspond to the symmetric vibrational modes of v(C = C) of Pi-OH and bending deformation of  $\delta$ (CH). The difference intense bands at 1315 and 1273  $\rm cm^{-1}$  and 1177 and 1083  $\rm cm^{-1}$  have been assigned to  $v_{as}(C-N)$  and  $v_s(C-N)$  stretching vibrations, while the frequencies component at 943 and 827 cm<sup>-1</sup> has been attributed to the in-plane bend deformation and rocking overtone vibration of CH<sub>3</sub> and CH<sub>2</sub> groups. Assignments of the  $\delta$ (CN) out-of-plane and  $\delta(ONO)$  of Pi-OH acceptor vibrational bands exist at 706. 329, and 206 cm<sup>-1</sup>. On examining the Raman spectra of the [(TME-DA)(SnCl<sub>4</sub>)], and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes in comparison with TMEDA, it was found that the spectra of the Sn(IV) and Zn(II) complexes exhibited non-ligand bands in the regions 470-505 and 380–212 cm<sup>-1</sup>, assignable to v(M-N) and v(M-Cl) vibrations, respectively [44]. Resonance Raman spectroscopy has been used to study the reaction of iodine with the interesting TMEDA donor.

Characteristic infrared frequencies  $(\rm cm^{-1})$  and tentative assignments of TMEDA free donor and their [(TMEDA)(SnCl\_4)] and [(TMEDA)(ZnCl\_2)] CT complex.

TMEDA	[(TMEDA)(SnCl <sub>4</sub> )]	[(TMEDA)(ZnCl <sub>2</sub> )]	Assignments <sup>(b)</sup>
3385	3418	3001	$v_{as}(C-H)$ ; CH <sub>3</sub> + CH <sub>2</sub>
3374	3088	2976	
2970	3029	2930	
2943	2966		
2860	2769	2895	$v_s(C-H)$ ; $CH_3 + CH_2$
2816	2736	2819	
2766			
1684	1632	1467	$\delta$ (CH) deformation
1454	1458	1353	
1404	1408		
1364	1351		
1338	1288	1290	$v_{as}(C-N)$
1311	1232	1247	
1299		1200	
1282			
1267			
1167	1146	1170	$v_{\rm s}({\rm C-N})$
1138	1119	1127	
1097	1049	1023	
1086			
1043			
1033			
943	990	953	$\delta(CH)$ in-plane bend
876	972		
836	832	831	$\delta$ (CH) rocking
788	771	801	
777		766	
676	669	587	$\delta$ (C–N) out-of-plane
495	565	499	bend
v(M-N)			
		468	
		439	



Formula. 17. Suggested structure of [(TMEDA)(Pi-OH)<sub>2</sub>] charge-transfer complex.



Formula. 18. Suggested structure of [(TMEDA)(QL)] charge-transfer complex.

The results indicate that the complex [(TMEDA)]I·I<sub>3</sub> is formed. Maki and Forneris [42] assigned the lines of Raman spectra of  $I_3^-$  at 111



Formula. 19. Suggested structure of [(TMEDA)]I·I<sub>3</sub> charge-transfer complex.



Formula. 20. Suggested structure of [(TMEDA)]·2Br<sub>2</sub> charge-transfer complex.



Formula. 21. Suggested structure of [(TMEDA)(SnCl<sub>4</sub>)] charge-transfer complex.



Formula. 22. Suggested structure of [(TMEDA)(ZnCl<sub>2</sub>)] charge-transfer complex.

and 161 cm<sup>-1</sup> to the symmetric and anti-symmetric stretching vibrations, respectively, and the observed bending vibration at 213 cm<sup>-1</sup> is weak broad in the Raman spectrum. In the literature, the Raman spectrum of the band for free bromine exhibited at a very intense wavenumber 310 cm<sup>-1</sup>. In the Raman spectrum of [(TMEDA)]·2Br<sub>2</sub> CT complex, the halogen vibration band, v(Br–Br), is shifted in the lower frequency direction at 166 cm<sup>-1</sup>.

# <sup>1</sup>H–NMR spectral analysis

<sup>1</sup>H–NMR data were expressed in parts per million (ppm), and they were referenced internally to the residual proton impurity in DMSO (dimethylsulfoxide). The <sup>1</sup>H–NMR spectra of the [(TME-DA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)(SnCl<sub>4</sub>)], and [(TME-DA)(ZnCl<sub>2</sub>)] CT complexes (Fig. 6) are consistent with the proposed structures (Formulas 17, 18, 21 and 22). The <sup>1</sup>H–NMR spectral data of TMEDA and their CT complexes were reported in Table 6.

In the TMEDA free donor, the peak at 2.243 ppm corresponds to (12H; 4CH<sub>3</sub>) twelve protons of four methyl groups, and beside, peak



Fig. 5. Raman spectra of (A) [(TMEDA)(Pi-OH)<sub>2</sub>], (B) [(TMEDA)]I-I<sub>3</sub>, (C) [(TMEDA)]-2Br<sub>2</sub>, (D) [(TMEDA)(SnCl<sub>4</sub>)], and (E) [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.

in the same zone at 2.384 ppm corresponds to the four protons of 2CH<sub>2</sub>. The discussion of the downfield status for the protons concerning  $-CH_3$  and  $-CH_2$  group is due to the formation of intermolecular CT complexes. Compared with the <sup>1</sup>H–NMR spectrum data of pure TMEDA, Pi-OH, and QL moieties, the <sup>1</sup>H–NMR spectra of the [(TMEDA)(Pi-OH)<sub>2</sub>] and [(TMEDA)(QL)] exhibit a down field chemical shift at 2.170–2.860 ppm and 3.126–3.756 ppm of 4CH<sub>3</sub> and 2CH<sub>2</sub> protons, respectively. According to this discussion, it can be said that the electronic environments of the TMEDA protons change with the formation of the Pi-OH and QL CT complexes. The weak broadening signals exhibited at 9.442 and 8.731 ppm were assigned to the protons of v(O-H...N) interactions for Pi-OH and

QL, respectively, via intermolecular hydrogen bond, which are shifted relative to the value of pure Pi-OH and QL acceptors. On the other hand, the proton signals of aromatic rings for both Pi-OH and QL were shifted slightly up field, from 8.624 ppm (pure Pi-OH) to 8.599 ppm (after complexation) and from 6.579 ppm (free QL) to 6.552 ppm (after complexation).

The [(TMEDA)(SnCl<sub>4</sub>)] and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes were characterized by IR, Raman, and <sup>1</sup>H–NMR spectra and elemental analysis. After complexation, the protons of both  $-CH_3$ and  $-CH_2$  groups, the signals for CH<sub>2</sub> (2.444 and 2.809 ppm) and CH<sub>3</sub> (2.7059–3.408 ppm) hydrogens are shifted slightly up field in comparison with the same signals found in TMEDA.

# Thermal analysis

To make sure about the proposed formula and structure of the new TMEDA CT complexes,  $[(TMEDA)(Pi-OH)_2]$ , [(TMEDA)(QL)],  $[(TMEDA)(SnCl_4)]$ ,  $[(TMEDA)]I\cdotI_3$ ,  $[(TMEDA)]\cdot2Br_2$ , and  $[(TMEDA)(ZnCl_2)]$ , thermogravimetric (TG) analysis was carried out for these complexes under static air flow. TG curves are shown in Fig. 7A–F. Table 7 gives the maximum temperature values,  $T_{max}/^{\circ}C$ , together with the corresponding weight loss for each step of the decomposition reactions of these complexes. The obtained data strongly support the structure proposed for the TMEDA complexes under investigation.

The thermal decomposition of the [(TMEDA)(Pi-OH)<sub>2</sub>] complex proceeds approximately with very strong one main degradation step. This stage occurs at a maximum temperature of 191 °C with weight loss of 62.59%, which is very close to the theoretical value of 62.39% corresponding to the loss of  $H_{22}N_8O_{14}$  moiety as will be described by the mechanism of the decomposition. The final thermal product obtained at 800 °C is few carbon atoms (18C). Accordingly, the mechanism for the thermal decomposition of the Pi-OH complex, [(TMEDA)(Pi-OH)<sub>2</sub>], is follows:

# $[(TMEDA)(Pi - OH)_2] \stackrel{191^{\circ}c}{\rightarrow} H_{22}N_8O_{14}(loss) + 18C \ (residue).$

The TGA curve of [(TMEDA)(QL)] CT complex indicates that the mass change begins at 125 °C and continuous up to 800 °C. The main mass loss at  $TG_{max}$  = 191 °C is a wide broad peak that corresponds to the liberation of most organic moiety of both TMEDA and QL molecules (obs. = 96.44%, calc. = 94.54%). The final decomposition of the organic moiety led to residual carbon atoms.



Fig. 6. <sup>1</sup>HNMR spectrum of (A) Free TMEDA, (B) [(TMEDA)(Pi-OH)<sub>2</sub>], (C) [(TMEDA)(QL)], (D) [(TMEDA)(SnCl<sub>4</sub>)], and (E) [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.



Fig. 6 (continued)

 $[(TMEDA)(QL)] \stackrel{191\degree c}{\rightarrow} C_{11}H_{22}N_2O_2(loss) + 1C \ (residue).$ 

To establish the proposed formula and structure for each of the complexes under investigation, thermogravimetric (TG) analysis was carried out for the two solid charge-transfer complexes [(TME-DA)]I-13 and [(TMEDA)]·2Br2 under static air flow. The data obtained support the proposed structures of the two complexes and indicate the following:

(i) The thermal degradation of the [(TMEDA)]I-I3 complex takes place in two degradation stages, Fig. 7 and Table 7. The first stage of decomposition occurs at a maximum temperature of 253 °C. This stage of degradation is accompanied by weight of loss 39.26% corresponding to the loss of one iodine molecule. Theoretically, the loss of these molecules corresponds to a weight loss of 40.70%. The second decomposition stage occurs at the maximum temperature of 343 °C. The weight loss at this step is 60.31% due to the loss of  $C_6H_{16}N_2I_2$  in agreement with the theoretical weight loss value of 59.30%. According to the above discussion the decomposition mechanism of the [(TMEDA)2]I-I3 complex is as follows:

 $[(TMEDA)]I\cdot I_3 \overset{253^{^\circ}c}{\rightarrow} I_2 + C_6H_{16}N_4I_2$ 

 $C_{11}H_{28}N_4I_2 \overset{343^\circ c}{\rightarrow} C_{11}H_{28}N_4I_2 + zero(residue).$ 

From this mechanism of decomposition, we can deduce that iodine molecules play an important role as a catalysis in the decomposition processes.

(i) The thermal decomposition of [(TMEDA)]·2Br<sub>2</sub> complex proceeds with two main degradation steps. The first stage of the decomposition occurs at the maximum temperature of 150 °C is accompanied by weight loss of 26.26% correspond to the loss of the two methane and half bromine molecules. Theoretically, the losses of these molecules correspond to a weight loss of 25.67%, which agrees with the experimental result. The second decomposition stage occurs at the maximum temperature of 326 °C. The weight loss at this step is 73.74% associated with the loss of C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>3</sub>. The theoretical weight loss value is 74.27%. Accordingly, the following mechanism was proposed for thermal decomposition of the [(TMEDA)]·2Br<sub>2</sub> complex:

 $[(TMEDA)] \cdot 2Br_2 \xrightarrow{150^\circ c} 1/2Br_2 + 2CH_4(loss) + C_4H_8N_2Br_3$ 

 $C_4H_8N_2Br_3 \stackrel{326^{^\circ}c}{\longrightarrow} C_4H_8N_2Br_3 + zero(residue).$ 

TG thermogram of [(TMEDA)(ZnCl<sub>2</sub>)] is shown in Fig. 7. Table 7 gives the maximum temperature values,  $T_{max}/^{\circ}C$ , together with the corresponding weight loss for each step of the decomposition reaction. The data obtained support the proposed structure and indicate that the thermal decomposition of this complex proceeds with two main degradation steps. The first stage of decomposition occurs at a temperature maximum of 357 °C. The found weight loss associated with this step is 49.03% and may be attributed to the decomposition of TMEDA donor. The second stage of decomposition occurs at a temperature maximum of 569 °C. The weight loss found at this stage equals to 41.09%, corresponds to the loss of remaining TMEDA molecule. The continuous of weight loss in the decomposition diagram of [(TMEDA)(ZnCl<sub>2</sub>)] complex can be discussed as follows: The zinc metal is hard and brittle at most temperatures, but becomes malleable between 100 and 150 °C. Above 210 °C, the metal becomes brittle again and can be pulverized by beating. The [(TMEDA)(SnCl<sub>4</sub>)] complex start decomposing at 239 °C with T<sub>max</sub> at 342 °C with simultaneous decomposition. The

<sup>1</sup>H-NMR spectral bands (ppm) and tentative assignments of TMEDA free donor (1), Pi-OH (2), QL (3) and their [(TMEDA)(Pi-OH)<sub>2</sub>] (4), [(TMEDA)(QL)] (5), [(TMEDA)(SnCl<sub>4</sub>)] (6), and [(TMEDA)(ZnCl<sub>2</sub>)] (7) CT complex.

ppm							Assignments <sup>(b)</sup>
1	2	3	4	5	6	7	
				2.170			
2.243	-	-	2.860	2.283	2.809	2.444	12H; 4CH <sub>3</sub>
				2.750			
2.384	-	-	3.446	3.126	3.167	2.705	4H; 2CH <sub>2</sub>
			3.756	3.347	3.408	3.168	
-						3.328	2H; Aromatic ring
-	8.624	6.579	8.599	6.552	-		
-	-	8.590	9.442	8.731	-		H; OH of Pi-OH or QL

decomposition steps seem to be consistent with a mass loss of obs. = 68.68% and calc. = 68.48% due to loss of  $C_6H_{16}N_2Cl_4$  as a gaseous molecules. The difference between the observed weight loss and complex at all (100%) was devoted to the residual tin metal.

# **Biological evaluation**

Biological activities were observed in terms of antimicrobial activities of target charge-transfer complexes against gram-positive



Fig. 7. TG curves of (A) [(TMEDA)(Pi-OH)<sub>2</sub>], (B) [(TMEDA)(QL)], (C) [(TMEDA)]I-I<sub>3</sub>, (D) [(TMEDA)]-2Br<sub>2</sub>, (E) [(TMEDA)(SnCl<sub>4</sub>)], and (F) [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.

The maximum temperature,  $T_{max}/^{\circ}C$ , and weight loss values of the decomposition stages for the [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)(SnCl<sub>4</sub>)], [(TMEDA)]I-l<sub>3</sub>, [(TMEDA)]-2Br<sub>2</sub>, and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.

Complexes	Decomposition	$T_{\rm max}/^{\circ}{\rm C}$	Lost	% Weight loss	
			Species	Found	Calc.
[(TMEDA)(Pi-OH) <sub>2</sub> ]	First step	191	$H_{22}N_8O_{14}$	62.59	62.39
	Total loss			62.59	62.39
	Residue		18C	37.41	37.61
[(TMEDA)(QL)]	First step	191	$C_{11}H_{22}N_2O_2$	96.44	94.54
	Total loss			96.44	94.54
	Residue		1C	3.56	5.45
[(TMEDA)]I·I <sub>3</sub>	First step	253	I <sub>2</sub>	39.26	40.70
	Second step	343	$C_6H_{16}N_2I_2$	60.31	59.30
	Total loss			99.57	100
	Residue		-	-	-
[(TMEDA)]·2Br <sub>2</sub>	First step	150	$\frac{1}{2}Br_2 + 2CH_4$	26.26	25.67
	Second step	326	$C_4H_8N_2Br_3$	73.74	74.33
	Total loss			100	100
	Residue		-	-	-
[(TMEDA)(ZnCl <sub>2</sub> )]	First step	357	$C_4H_{12}N_2Cl$	49.03	48.90
	Second step	569	$C_2H_4Cl$ + melt of Zn metal	41.09	-
	Total loss			90.12	-
	Residue		Zn metal	9.88	-
[(TMEDA)(SnCl <sub>4</sub> )]	First step	342	$C_6H_{16}N_2Cl_4$	68.68	68.48
	Total loss			68.68	68.48
	Residue		Sn metal	31.32	31.52

# Table 8

Inhibition zone diameter (mm) of the target compounds against tested microorganisms.

	Sample	Inhibition zone diameter (mm/mg sample)								
		Bacillus subtilis (G <sup>+</sup> )	Escherichia coli (G <sup>-</sup> )	Pseudomonas aeruginosa (G <sup>-</sup> )	Staphylococcus aureus (G <sup>+</sup> )	Aspergillus flavus (Fungus)	Candida albicans (Fungus)			
	Control: DMSO Antifungal agent	0.0	0.0	0.0	0.0	0.0	0.0			
Standard	(Tetracycline)	34	32	34	30	-	-			
	(Amphotericin B)	-	-	-	-	18	19			
	[(TMEDA)(Pi-OH)2]	9	9	9	10	0	0			
	[(TMEDA)(QL)]	24	23	28	28	16	17			
	[(TMEDA)]I·I <sub>3</sub>	9	10	9	9	0	0			
	[(TMEDA)]·2Br <sub>2</sub>	10	10	10	10	0	0			
	[(TMEDA)(ZnCl <sub>2</sub> )]	13	14	15	13	0	0			
	[(TMEDA)(SnCl <sub>4</sub> )]	19	16	21	20		0			

Gram reaction. Solvent: DMSO.

(B. subtilis and S. aureus) and gram-negative (E. coli and P. aeruginosa) and tow strains of fungus (A. flavus and C. albicans). Results from the agar disk diffusion tests for antimicrobial activities of target compounds are presented in Table 8 and illustrated in Fig. 8. The diameters of zone of inhibition (in mm) of the standard drug tetracycline against gram-positive bacteria B. subtilis and S. aureus and gramnegative bacteria E. coli and P. aeruginosa were found to be 34, 32, 34, and 30 mm, respectively, while the standard drug amphotericin B against A. flavus and C. albicans gave 18 and 19, respectively. Under identical conditions, Table 8 shows that [(TMEDA)(Pi-OH)<sub>2</sub>] complex has (9, 9, 9, 10, 0, and 0 mm), [(TMEDA)(QL)] complex has (24, 23, 28, 28, 16, 17 mm), [(TMEDA)<sub>2</sub>]I·I<sub>3</sub> has (9, 10, 9, 9, 0, and 0 mm), [(TMEDA)]·2Br<sub>2</sub> complex has (10, 10, 10, 10, 0, 0 mm), [(TMEDA)(ZnCl<sub>2</sub>)] complex has (13, 14, 15, 13, 0, 0 mm), [(TME-DA)(SnCl<sub>4</sub>)] complex has (19, 16, 21, 20, 0, and 0 mm), respectively, for B. subtilis, E. coli, P. aeruginosa, S. aureus, A. flavus, C. albicans. All complexes were found to be efficient antibacterial agents except for [(TMEDA)(QL)] complex, which is efficient both antibacterial and antifungal agents.

# X- ray powder diffraction studies

The X-ray powder diffraction patterns for the new TMEDA charge-transfer complexes [(TMEDA)]2Br<sub>2</sub>, [(TMEDA)(Pi-OH)<sub>2</sub>],



**Fig. 8.** Antibacterial and antifungal activity [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)].<sup>1</sup>2Br<sub>2</sub>, [(TMEDA)(SnCl<sub>4</sub>)], and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes as inhibition zones (mm).



Fig. 9. XRD spectra of (A) [(TMEDA)]·2Br<sub>2</sub>, (B) [(TMEDA)(Pi-OH)<sub>2</sub>], (C) [(TMEDA)(QL)], and [(TMEDA)(ZnCl<sub>2</sub>)] CT complexes.

Table 9					
The resulting indexing of the system	(TMEDA)(ZnCl <sub>2</sub> )	complex	and	the	resulting
lattice parameters a, b, c, B, volume V.					

	h	k	1	d-Obs	2 <i>θ</i> −Obs	2 <i>θ</i> −Cal	DELTA
	-1	0	1	8.6384	10.232	10.210	0.022
	1	0	0	7.4625	11.850	11.847	0.003
(TMEDA)(ZnCl <sub>2</sub> )	0	1	1	6.2380	14.187	14.188	-0.001
	-1	1	1	5.7252	15.465	15.458	0.007
System: monoclinic	-1	0	2	5.2126	16.996	16.978	0.018
a = 12.0138(13) Å	-2	0	2	4.3192	20.541	20.501	0.010
b = 7.6379(6) Å	-1	2	1	3.4926	25.483	25.472	0.011
c = 10.9273(58)	1	2	3	2.5032	35.845	35.847	-0.002
$\beta = 98.50(12)^{\circ}$	1	3	0	2.4900	36.040	36.049	-0.009
$V = 991.67 \text{ Å}^3$	3	0	3	2.4875	36.079	36.069	0.010
	5	1	2	1.9941	45.447	45.450	-0.003
	6	1	0	1.9167	47.392	47.387	0.005
	2	3	3	1.9115	47.502	47.511	-0.009
	-6	0	3	1.8552	49.066	49.070	-0.004
	1	4	1	1.8501	49.210	49.215	-0.005
	-3	4	2	1.6702	54.930	54.927	0.003

[(TMEDA)(QL)], and [(TMEDA)(ZnCl<sub>2</sub>)] are depicted in Fig. 9. Inspecting these patterns, we notice that the systems (TMEDA)(QL) and (TMEDA)(ZnCl<sub>2</sub>) are well crystalline compared with [(TMEDA)]·2Br<sub>2</sub>, which has high background and less intensity. To get structural data about these systems, we tried to index the diffraction patterns applying the CRYSFIRE system [45]. It is a powder-indexing wizard in the form of a family of DOS scripts and programs for running eight indexing programs automatically. The indexing results revealed that all patterns are monoclinic systems but with different lattice constants, and the results are given in Tables 9–11. For the system (TMEDA)(Pi-OH)<sub>2</sub>, no satisfactory indexing could be obtained, which may be due to the Table 10

The resulting indexing of the system (	(TMEDA)(QL) complex	and the resulting	lattice
parameters <i>a</i> , <i>b</i> , <i>c</i> , $\beta$ , volume <i>V</i> .			

	h	k	l	d-Obs	2θ-Obs	2 <i>θ</i> -Cal	DELTA
	1	0	1	6.9485	12.730	12.693	0.037
	$^{-1}$	1	1	6.1101	14.485	14.509	-0.024
(TMEDA)(QL)	$^{-1}$	0	2	5.9894	14.779	14.772	0.007
	-2	0	2	5.2069	17.015	17.044	-0.035
System: monoclinic	2	0	1	4.6248	19.175	19.178	-0.013
a = 13.0854(123) Å	-3	0	1	4.3569	20.367	20.348	0.019
b = 7.5334(85) Å	3	0	0	4.0340	22.017	22.027	-0.010
$c = 12.0273(78) \text{ \AA}$	2	1	1	3.9398	22.550	22.543	0.007
$\beta = 112.42(74)^{\circ}$	-2	0	3	3.8935	22.821	22.848	-0.027
$V = 1096.02 \text{ Å}^3$	1	1	2	3.8333	23.185	23.202	-0.017
	-3	1	2	3.5932	24.758	24.759	-0.001
	0	2	1	3.5667	24.945	24.939	0.006
	-3	0	3	3.4648	25.691	25.687	0.004
	-2	0	4	2.9947	29.811	29.796	0.015
	3	2	0	2.7482	32.515	32.503	0.012

heavy overlapping of the diffraction peaks. Single crystal for this system should be used for its structural determination, which is a further work.

# SEM and EDX studies

Surface image using SEM (Fig. 10A–F) demonstrates the porous structures of the surface of prepared charge-transfer complexes. Analysis of these images shows the size of pores to be quite different with different acceptors. The chemical analysis results by EDX for the formed charge-transfer complexes show a homogenous distribution of each acceptor. SEM examinations checked the surfaces

The resulting indexing of the system (TMEDA).2Br<sub>2</sub> complex and the resulting lattice parameters a, b, c,  $\beta$ , volume V.

	h	k	L	d-Obs	2 <i>θ</i> −Obs	2 <i>θ</i> −Cal	DELTA
	-1	0	1	8.0056	11.043	11.031	0.012
	2	0	0	5.7293	15.453	15.435	0.018
(TMEDA)-2Br <sub>2</sub>	2	0	1	4.5742	19.390	19.400	-0.010
	0	2	0	4.2290	20.990	20.971	0.019
System: monoclinic	1	2	0	3.9679	22.388	22.371	0.017
a = 11.6454(45) Å	3	0	0	3.8238	23.243	23.241	0.002
b = 8.4653(18) Å	-2	1	2	3.6239	24.545	24.559	-0.014
c = 9.6213(72) Å	3	1	0	3.4871	25.524	25.539	-0.015
$\beta = 99.89 \ (3)^{\circ}$	-3	1	1	3.4479	25.819	25.799	-0.020
$V = 934.38 \text{ Å}^3$	3	0	1	3.3531	26.562	26.569	-0.017
	2	1	2	3.5667	28.420	28.413	0.007
	-1	2	2	3.1378	28.452	28.430	0.022
	4	0	3	1.9623	46.226	46.223	0.003
	3	4	1	1.7897	50.988	50.992	-0.004

of these CT complexes that show a small to medium particles, which has tendency to agglomerate formation with different shapes in comparison with the starting materials. The chemical compositions of the free TMEDA donor and charge-transfer complexes were determined using energy-dispersive X-ray diffraction (EDX). In the EDX profile of these complexes (Fig. 10A–F), the peaks of the essential two elements such as carbon and nitrogen, beside oxygen, and subsidiary elements, which constitute the molecules of [(TMEDA)(Pi-OH)<sub>2</sub>], [(TMEDA)(QL)], [(TMEDA)(SnCl<sub>4</sub>)], [(TMEDA)]I·I<sub>3</sub>, [(TMEDA)]·2Br<sub>2</sub>, and [(TMEDA)(ZnCl<sub>2</sub>)] chargetransfer complexes, are clearly identified confirming the proposed structures.

# Electrical conductivity studies

The frequency dependence of AC conductivity of SnCl<sub>4</sub> and ZnCl<sub>2</sub> CT complexes at T = 306 K is shown in Fig. 11. The AC conductivity tends to increase slightly with increasing frequency. This can be attributed to the enhancement of the conduction carriers by applied external field. For these two complexes, the dielectric constant and dielectric loss ( $\varepsilon'$  and tan $\delta$ ) were measured as a function of frequency of applied electric field at T = 306 K (see Figs. 12 and 13). It has been found that both complexes have similar variation trend of the dielectric constant against frequency, where the dielectric constant tends to sharply decrease with the increase in applied field with low frequency. This may be due to the polarization resulting from the heterogeneous structure. In the range of high frequency, the dielectric constant seems likely to be



Fig. 10A. SEM/EDX of [(TMEDA)(Pi-OH)2] CT complex.



Fig. 10B. SEM/EDX of [(TMEDA)(QL)] CT complex.



Fig. 10C. SEM/EDX of [(TMEDA)(SnCl<sub>4</sub>)] CT complex.



Fig. 10D. SEM/EDX of [(TMEDA)]I-I<sub>3</sub> CT complex.



Fig. 10E. SEM/EDX of [(TMEDA)]·2Br<sub>2</sub> CT complex.

frequency independent. Such behavior can be attributed to the low charge carrier's mobility, which hinders the frequency change and cannot follow the frequency change. The results indicated that the dielectric loss of  $SnCl_4$  and  $ZnCl_2$  CT complexes is continuously decreasing with frequency in the range of studied frequency.



Fig. 10F. SEM/EDX of [(TMEDA)(ZnCl<sub>2</sub>)] CT complex.



**Fig. 11.** Frequency dependence of AC conductivity at T = 306 K for SnCl<sub>4</sub> (A) and ZnCl<sub>2</sub> (B) charge-transfer complexes.

## Positron annihilation studies

The measured two lifetime components representing  $\tau_1$  (for *p*-Ps with lifetime = 125 ps, and free and bound positrons with lifetime = 150–500 ps) and  $\tau_2$  (for *o*-Ps with lifetimes > 900 ps) with the associated formation probabilities  $I_1$  and  $I_2$ , respectively. Figs. 14 and 15 show the PAL parameters  $\tau_1$ ,  $\tau_2$ ,  $I_1$ , and  $I_2$  as a function of the type of CT complex. The relatively poor time resolution (~300 ps) of the used spectrometer makes the decomposition of the shortest-lived lifetime component  $\tau_1$  somewhat impossible. The results show that the Ps was formed ( $I_2$ ) with a range of 12.0–34.1 for studied CT complexes. The Ps formation in these CT complexes with high intensities may be due to their Lewis base that depends on the complex electronic configuration, and the layers between the donor and acceptor. The wide range of  $I_2$  value may be due to the different electron affinities of electron acceptors. The  $\tau_2$  lifetime component ascribed to the annihilation of *o*-Ps



**Fig. 12.** Frequency dependence of dielectric constant ( $\varepsilon'$ ) at *T* = 306 K for Sn Cl<sub>4</sub> (A) and Zn Cl<sub>2</sub> (B) charge-transfer complexes.

indicates that there is one type of vacant. The results indicate that the  $\tau_2$  value of Pi-OH CT complex is comparable with the value of Br<sub>2</sub> CT complexes due to their same donor-to-acceptor molar ratio of 1:2. The  $\tau_2$  values are decreased by 27%, 17%, and 10% for ZnCl<sub>2</sub>, QL, and SnCl<sub>4</sub>, respectively, due to the different electron acceptor power and acceptor configuration in each case.

The  $\tau_1$  and  $I_1$  values, ascribed mainly to the number of positrons annihilated in bulk or trapping centers, ranged from 303 ps to 344.2 ps and from 65.9% to 88.1%, respectively. The results show two distinct groups. The QL and ZnCl<sub>2</sub> CT complexes, with high  $\tau_1$  value and low  $I_1$  value, represent the first group. The second group (Pi-OH, Br<sub>2</sub> and SnCl<sub>4</sub> complexes) has low  $\tau_1$  value and high  $I_1$  value. Both groups are also defined using the calculated mean lifetime. Each complex in the second group has distinguished properties that can affect the PAL parameters. These properties are the high powerful acceptor of Pi-OH, vacant orbitals of SnCl<sub>4</sub>, and high



**Fig. 13.** Frequency dependence of dielectric loss ( $\varepsilon$ ") at *T* = 306 K for Sn Cl<sub>4</sub> (A) and Zn Cl<sub>2</sub> (B) charge-transfer complexes.



Fig. 14. The o-Ps lifetime component and its intensity for CT complexes.

molecular weight of Br<sub>2</sub> complexes. Also, the different ionization potential of the complexes of both groups can be considered as a factor for this classification.

The results reveal that there are good positive or negative correlations between all PAL parameters and the complex molecular weight with the range of linear correlation coefficient = 0.73– 0.88. This indicates that the molecular weight affects the mass fraction of the donor component in the complex and consequently the fraction of positrons annihilation in that part of the complex as previously reported [17]. The average diameter of the inhibition zone of the tetracycline and CT complexes against the four types



**Fig. 15.** The  $\tau_1$  lifetime component and its intensity for CT complexes.

of bacteria was calculated, and the relative inhibition zone diameter was calculated by normalizing the diameters of CT complex with the diameter of the standard. Then, the linear correlation between the biological activity of CT complexes and the PAL parameters was calculated. The results indicate that the PAL components, especially the short one ( $\tau_1$ , with linear correlation coefficient = 0.73), are affected by the biological activity of the CT complex. Therefore, it can be used as a probe for the complex biological activity. This observed correlation can be explained as follows: firstly, the increasing the complex biological activity increases the delocalized electrons over the whole chelating ring, and these delocalized electrons affect the PAL parameters; secondly, the dependence of the biological activity on the complex molecular weight (linear correlation coefficient = -0.74) that already has a strong correlation with the PAL parameters.

# Conclusion

The positron annihilation lifetime parameters were found to be dependent on the properties of the CT complex such as the acceptor power, number of layers between the donor and acceptor, donor-to-acceptor molar ratio, and ionization potential of the complexes. The molecular weight of the complex affects the mass fraction of the donor component and consequently the fraction of positrons annihilation in that part of the complex. The positron annihilation lifetime components are affected by the biological activity of the metal complex due to the increasing delocalized electrons.

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