ARTICLE

Charge Transfer Complexes of Camphor Schiff Base with Acceptors

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ABSTRACT

A new chiral charge transfer (CT) complexes of Schiff base derived from camphor and *o*-aminophenol with π-acceptor as quinol and vacant orbital acceptor as $ZnCl_2$ have been synthesized and characterized. The IR spectra, X-ray, mass, atomic absorption spectrometry, conductivity and elemental analysis are used to elucidate the structure of the charge transfer complexes. The antioxidant activity was measured for the new chiral charge transfer complexes using free radical scavenging 2-diphenyl-1-picryl-hydrazyl (DPPH) assay. The values of IC_{50} were as follows: 4.04 ± 0.01 and 0.81.5 ± 0.004 µg/mL for Schiff base-quinol and Schiff-$ZnCl_2$, respectively. The IC_{50} of ascorbic acid was 6.45 ± 0.30 µg/mL. In addition, the antibacterial activity against three bacterial strains, *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus pneumonia*, was examined using agar disc diffusion method. The antibacterial activity was enhanced in the following order: Zn-Schiff > quinol-Schiff > Schiff-base.

KEYWORDS

Camphor, *o*-Aminophenol, Schiff base, Antioxidant activity, Charge transfer complexes.

INTRODUCTION

Natural chiral drug, camphor (1,7,7-trimethylbicyclo[2.2.1]-hepta-2-one) is cyclic compound and has a ketonic structure. Schiff base metal (II) complexes of aromatic amine posses antiviral, antimalarial, antitumor, antimicrobial and antifungal activities. α-Cyclodextrin inclusion of (*R*)- and (*S*)-camphor compounds has been studied by X-ray crystallography [1]. Schiff bases were synthesized from condensation of methyl hydrazine carbodithioate with (S)-camphor and (R)-camphor [2]. Charge transfer complexes of pyrimidine Schiff bases with some aromatic polynitro compounds were prepared [3]. Schiff base of camphor as a donor with picric acid as acceptor were estimated in methanol at room temperature [4]. Charge-transfer complexes have been made in the reaction of acriflavine with acceptors as tetracyanoquinodimethane dichlorodicyanobenzoquinone quinol and picric acid [5]. Charge transfer complexes formed by the donor of some thiophene –Schiff base and picric acid as π-acceptors and have been studied at different temperatures [6]. *Cinnamomum camphora* plant, belonging to Lauraceae family is a major natural source of camphor. This plant is native to some countries including China, Taiwan and Japan. The

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wood of this tree is subjected to distillation to obtain camphor [7].

The aim of this paper is to investigate the charge transfer (CT) complexes of Schiff base of camphor as a donor (Sch) with quinol (Q) as π-acceptor and $ZnCl_2$ as vacant orbital acceptor, 1:1 stoichiometry of the formed complexes. The synthesized solid charge transfer complexes (Sch-Q, Sch-$ZnCl_2$) were structurally characterized to interpret the behaviour of interactions using elemental analysis, X-ray, mass and IR techniques.

EXPERIMENTAL

(1R)-(+)-Camphor, 2-aminophenol, quinol, $ZnCl_2$ and 2,2-diphenyl-1-picryl-hydrazyl (DPPH) were obtained from Sigma Chemical Co. All other chemicals used were of analytical grade.

Preparation of Schiff-base: Camphor (10 mmol, 1.52 g) was dissolved in 10 mL of methanol and to this solution was added *o*-aminophenol (10 mmol, 1.09 g) in 10 mL of methanol and 1 mL of AcOH. The mixture was refluxed for 9 h. Upon cooling, the black powder of Schiff base was collected by filtration, washed with methanol and dried. Finally, the Schiff base (Sch) was recrystallized from hot methanol to give black crystalline powder.

Preparation of the charge transfer complexes: Charge transfer complex Schiff base with quinol and $ZnCl_2$ were prepared as described previously [8] by mixing a hot saturated methanolic solution of the Schiff base with acceptors. The solid complexes were either separated on standing. The methanol soluble complexes were recrystallized from methanol and dried under vacuum over anhydrous calcium chloride for 24 h.

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). Conductivity meter were recorded on a digital type direct read (Jenway 4510 Conductivity meter). A thermostat (Toshniwal) with an accuracy of ± 0.05 °C was used for maintaining constant temperature.

Infrared spectroscopy FTIR spectra were collected using a Nicolet 6700 FTIR Advanced Gold Spectrometer with OMNIC 8 software. The FTIR spectra of the investigated drug and its metal complex were recorded as potassium bromide discs (1:200) in the range of 4000-400 cm^{-1}.

The X-ray diffraction patterns for the obtained charge transfer complexes were collected on a PANalyticalX'Pert PRO X-ray powder diffractometer at the Central Lab at Cario University, Egypt. The instrument was equipped with a Ge(III) monochromator and a $CuK_{\alpha 1}$ X-ray source with a wavelength of 0.154056 nm was used.

Atomic absorption spectrometer (Perkin-Elmer 3110) and air compressor detection limit 0.1 ppm and integration time 3 s. The flame used was acetylene-air mixture. A Shimadzu atomic absorption flame spectrophotometer model AA.640-13, slit width 0.2 nm, relative noise 1.0, detection limit 0.6 ppm and integration time 3 s. The flame used was an acetylene-air mixture.

Measuring of antioxidant activity by free radical scavenging DPPH assay: Stock solutions of camphor and complexes (0.5-10 mg/mL) were prepared in dimethyl sulfoxide. The working solutions (10-100 µg/mL) were prepared from the stock solutions using suitable dilution. Ascorbic acid (vitamin C) was used as a reference natural antioxidant. From each working solution, 1 mL was taken to be combined with 2 mL of DPPH solution (0.1 mM). After 30 min incubation in the dark, the absorbance was measured at 517 nm. The percentage of the DPPH radical scavenging was calculated using the equation as given below:

$$\text{Inhibition of DPPH radical (\%)} = \frac{Abs_{control} - Abs_{sample}}{Abs_{control}} \times 100$$

$Abs_{control}$ is the absorbance of DPPH radical + DMSO; Abs_{sample} is the absorbance of DPPH radical + sample.

The calculated IC_{50} value represents the concentration that is required for 50 % inhibition of DPPH.

Antibacterial activity using agar diffusion disc method

Propagation conditions and preparation of inoculums of bacterial strains: The antibacterial activity was appraised against three bacterial species: *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus pneumoniae*. The bacterial cultures were obtained from Bacteriology Laboratory, Botany Department, Faculty of Science, Al-Azhar University, Assuit Branch. The bacterial cultures were maintained in nutrient agar slants at 4 °C. The bacterial strains were inoculated on nutrient broth and left at 36 ± 1 °C in a shaking incubator for overnight. The optical density OD_{600} of cultures was measured to detect the turbidity of the bacterial suspension (inoculum). The bacterial suspension was adjusted to 10^8 CFU/mL (turbidity = McFarland barium sulfate standard 0.5) to be inoculated in a sterile molten nutrient agar (~40 °C). After solidification, the Agar plates were ready for antibacterial activity tests.

Preparation of test compounds and application of antibacterial activity assay: Compounds were dissolved in methanol (100 %). The concentrations of the solutions were 0.5, 1.0, 2.5, 5 and 10 mg/mL. Sterilized 6 mm-discs of filter paper (Whatman, no. 1) were permeated with 10 µL of each of the different dilutions. The discs were loaded and left to dry in aseptic area under laminar-flow cabinet. The ultimate concentrations of each compound of discs were 5, 10, 25, 50 and 100 µg corresponding to respective dilution.

Tetracycline was used as a positive control in antibacterial assay and discs (30 µg) were prepared using suitable dilution. Paper discs impregnated with 10 µL of methanol (100 %) were used as negative control. Tests were performed in duplicate. The discs were spread on Agar plates which were prepared as described in the previous section. The plates were incubated at 37 °C for 24 h. Then, the antimicrobial activity was assessed by measuring the diameter of the zone of inhibition.

Statistical analysis: Experimental results were performed in triplicate and the data are presented as mean ± SD.

RESULTS AND DISCUSSION

Elemental analysis The elemental analysis data (C and H) of the present charge transfer complexes were matched with the molar ratio gained from conductivity, IR and mass spectra.

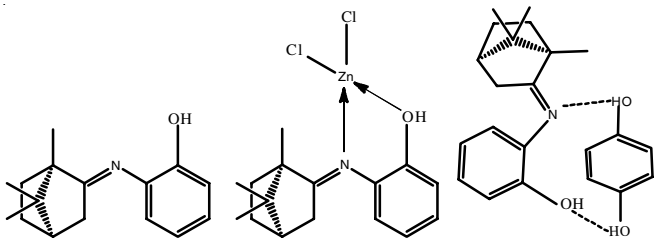
Sch calcd. (%): C 78.65; H 8.66. Found (%): C 78.86; H 8.55, m.f.: $C_{16}H_{21}NO$, m.w. 244.35, colour: black.

Sch-Q calcd. (%): C 74.55; H 7.48. Found (%): C 74.76; H 7.70, m.f.: $C_{22}H_{27}NO_3$, m.w. 353.45, colour: deep brown.

Sch-$ZnCl_2$ calcd. (%) C 50.62; H 5.58; N 11.86. Found (%) C 50.11; H 5.13, m.f.: $C_{16}H_{21}NOZnCl_2$, m.w. 379.633, colour: black.

Conductivity: The addition of the acceptors to donor solution increased the molar conductivity values as the donor: acceptor molar ratio increased, which indicates that charge transfer complexes in these systems have higher mobility than donor. The slope of the corresponding mole ratio plots changes at the point where the donor to acceptor mole ratio corresponds to about a 1:1 complex between Sch:Q and Sch:$ZnCl_2$.

Mass spectra: The mass spectrum of the Schiff base displayed a molecular peak at *m/z* 239 (12.01). The Schiff base fragments observed in the mass spectrum confirm the assigned structure of the charge transfer complexes (**Scheme-I**). The peaks at 239,227, 112, 98, 85 and 71 were characteristic and assigned to the fragments which correspond to the sequential loss of NH, C_9H_{14}, CH and CH_2 respectively. Mass spectrometry was applied to appear the main fragmentation routes of charge transfer complexes. The differentiation in fragmentation was caused by the nature of the attached between acceptors and donor, while the peaks assigned to Sch-Q *m/z* 349 (0.23), Sch-$ZnCl_2$ *m/z* = 375(8.63). The different competitive fragmentation pathways of the donor and charge transfer complexes give the peaks at different mass numbers show in Table-1. The intensities of these peaks reflect the stability and abundance of the ions [9].



Scheme-I: Structural of Schiff base and charge transfer complexes with $ZnCl_2$ and Q

TABLE-1
MASS SPECTRA DATA OF SCHIFF BASE, Sch-Q AND Sch-$ZnCl_2$ CHARGE TRANSFER COMPLEXES

Compound	*m/z*
Sch	244(2.67), 239(12.01), 227(2.07), 112(4.46), 98(19.59), 85(25.70), 71(45.74)
Sch-Q	363(4.60), 359(0.32), 349(0.23), 317(3.86), 305(6.42), 259(4.53), 247(3.01), 229(2.35)
Sch-$ZnCl_2$	379(2.02), 375(8.63), 363(16.32), 329(2.04), 305(10.11), 288(3.83), 87(9.56)

Infrared spectroscopy: IR spectrum of the charge transfer complexes compared with the spectrum of the donor and acceptors where shift vibrations band to the number of wavelengths lower or higher depending on the type of interaction charge transfer. The donation method from Schiff base donor to quinol can occur from the lone pair of electron on the oxygen of atoms and the azomethine nitrogen of Schiff base and have been identified as the donation source in most studied donors. The band of ν(OH) observed at 3376-3305 cm^{-1} in the free Schiff base appeared at 3262 cm^{-1} were shifted to frequency 3158 cm^{-1} for Sch-Q complex and become more broadening. The observed shift in the ν(O-H) band upon complexation clearly indicated the -OH moiety of the acceptor participated in the CT bonding with Sch. IR spectra of Sch-Q is characterized by medium bands that appear at 2598-2363 cm^{-1}, which does not appear in the IR spectrum of Sch or of the quinol. This peaks are due to hydrogen bonding in the complex between OH, azomethine group of Sch and two OH group of Q [6,8]. This result caused to the protonation of the OH^+ group of Sch from of quinol (Fig. 1, Table-2). The infrared spectra of Schiff base with $ZnCl_2$ are presented in Fig. 1 and their band assignments are given in Table-2 and Fig. 1. Small shifts in both wavenumber values and band intensities between free donor and the charge transfer complex are recorded, this fact is owing to the structure configurations upon complexation. The infrared spectra of this charge transfer complex shown non-ligand bands in the regions 570-460 cm^{-1}, assignable to ν(Zn–N) vibrations [10].

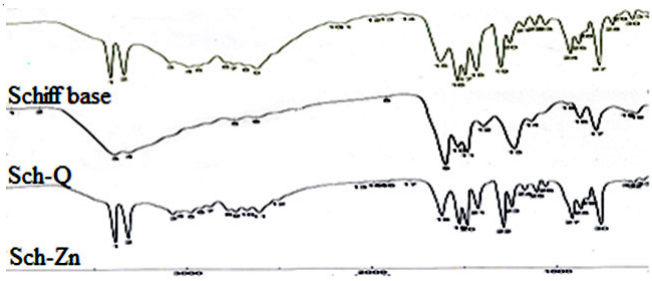


Fig. 1. Infrared spectra of Schiff base, Sch-Q andSch-$ZnCl_2$ charge transfer complexes

TABLE-2
INFRARED DATA OF SCHIFF BASE, Sch-Q AND Sch-$ZnCl_2$ CHARGE TRANSFER COMPLEXES

Sch	Sch-Q	Sch-$ZnCl_2$	Functional group
Wavenumber (cm^{-1})			
3376	3375	3375	–OH
3303	3298	3303	
–	2593	–	H-bonding
3055-2590	3045-2710	3056-2589	Alkane
1605	1646	1661	Azomethine

X-ray diffraction: The structure of charge transfer complexes were studies by using PANalytical X'Pert PRO X-ray powder diffractometer, the indexed diffractograms obtained in the rang of $5° < 2\theta > 70°$. The size particle charge transfer complexes were determined by using Deby- Scherrer equation:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the apparent particle size of the grains, λ is the X-ray wavelength used (1.5418 Å), K is a constant (0.94 for Cu grid) and β is the full-width at half-maximum (FWHM) of the X-ray diffraction line (additional peak broadening) in radians, θ is half the scattering angle (the Bragg diffraction angle).

Bragg's Law can calculate d value by using eqn. 2:

$$d = \lambda/2 \sin\theta \quad (2)$$

where d is the the inter planar spacing between atoms.

The result of X-ray spectra for Sch-Q and Sch-$ZnCl_2$ complexes containing the data of θ, β, d and D are presented in Table-3. From these results, the scattering peak of Sch-Q and Sch-$ZnCl_2$ complex occurred at 18.33° and 19.15° in the diffraction pattern, respectively. The X-ray of donor differ from the charge transfer complexes at 8.603°. The appearance of a sharp and strong Bragg peak of the donor and its complexes indicates the formation of a well-defined distorted crystalline structure.

TABLE-3
X-RAY SPECTRAL DATA OF THE HEXAMINE CHARGE TRANSFER COMPLEXES

Complex	2θ (°)	d value (Å)	FWHM	Relative intensity (%)	Particle size (D) (nm)
Sch	8.603	10.270	0.20	100	7.267
Sch-Q	18.33	4.784	0.25	100	5.876
Sch-$ZnCl_2$	19.15	4.631	0.22	100	3.459

Atomic absorption spectroscopy: The atomic absorption data was acquired by aspirating aqueous single element standard solution. Wavelength of zinc was 213.9 nm, best concentration was 1 ppm. The presence of zinc in charge transfer complex has been confirmed by atomic absorption spectrometry, the absorbance of Sch-Zn solution were give result at the specific wavelength of zinc. This indicate the reaction of $ZnCl_2$ with Schiff base compound.

Free radical scavenging activity measurements: The free radical scavenging activity of different concentrations from camphor and complex compounds was compared with that of ascorbic acid using DPPH scavenging assay (Fig. 2). The stable DPPH radical has a deep purple colour which converted to a yellowish colour diphenlypicrylhyrazine derivative due to reducing by an antioxidant. In a concentration-dependent reaction, an antioxidant decreases the intensity of the DPPH purple colour which could be measured by absorbance at 517 nm.

Neither camphor nor Schiff-base showed any scavenging toward DPPH. The increase complex compounds enhanced the scavenging of DPPH. The most scavenging activity was detected in Zn-Schiff complex as compared to that of Ascorbic acid (Fig. 1a). The values of IC_{50} is shown in Fig. 1b. The smallest IC_{50} value indicated the highest potency of antioxidant properties of the compound. The values of IC_{50} were ordered as follows: 4.04 ± 0.01 and 0.81.5 ± 0.004 µg/mL for Schiff base-quinol and Schiff base-Zn, respectively. The IC_{50} of ascorbic acid was 6.45 ± 0.30 µg/mL.

Screening of antibacterial activity: Different concentrations of camphor, Schiff-base, Schiff base-quinol and Schiff base-Zn were investigated for their antibacterial effects using agar disc diffusion method. Standard antibiotic tetracycline was used for comparison attempts. The results of the sensitivity of *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus pneumonia* are tabulated in Table-4.

Camphor showed no antibacterial activity towards any of the tested strains. The most resistant bacterial strain was *Staphylococcus aureus* and sensitive only to the highest concentrations (50-100 µg/disc) of Schiff-base, quinole Schiff base

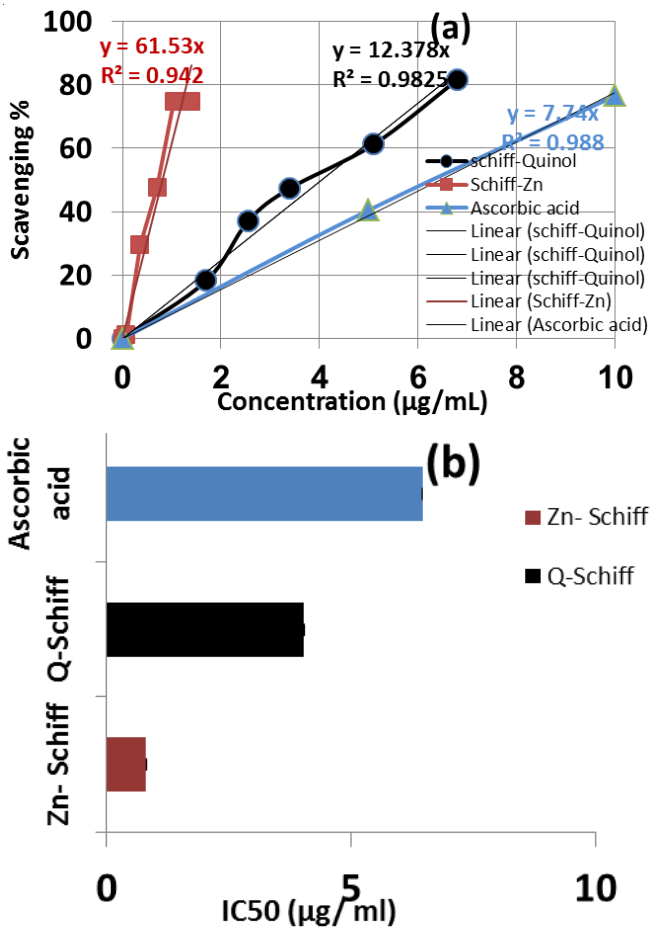


Fig. 2. DPPH scavenging percentages quinol- Schiff base, Zn-Schiff base and ascorbic acid (a). The IC_{50} of quinol-Schiff base, Zn-Schiff base and ascorbic acid (b)

TABLE-4
INHIBITION ZONES (mm) OF *Eucalyptus* METHANOLIC EXTRACT, CAMPHOR, SCHIFF BASE, QUINOL SCHIFF BASE AND Zn-SCHIFF BASE TOWARDS *Escherichia coli*, *Streptococcus pneumonia* AND *Staphylococcus aureus*

	Inhibition growth zone (mm)			
	Concentration (µg/disc)	*E. coli*	*S. aureus*	*S. pneumonia*
Camphor	5	–	–	–
	10	–	–	–
	25	–	–	–
	50	–	–	–
	100	–	–	–
Schiff base	5	–	–	–
	10	–	–	–
	25	–	–	10
	50	–	7	11
	100	7	8	12
Schiff base-Quinol	5	–	–	9
	10	10	–	10
	25	14	–	14
	50	15	13	15
	100	17	13	18
Schiff base-Zn	5	11	–	11
	10	12	–	12
	25	12	12	20
	50	17	19	26
	100	18	19	27
Tetracycline (30 µg)		25 ± 2	38 ± 1.5	32 ± 2.5

*no inhibit zone was noticed

and Zn-Schiff base with inhibition zones ranged from 7 to 19 mm (Table-4). On the other hand, the most sensitive bacterial strain was *Streptococcus pneumonia* to the plant extract and the Schiff derivatives. The widest inhibition zone was recorded for the effect of Zn-Schiff (100 µg/disc) toward *Streptococcus pneumonia* with value equal to 27 mm.

The antibacterial activity was enhanced in the following order: Zn-Schiff base > quinol-Schiff base > Schiff-base.

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