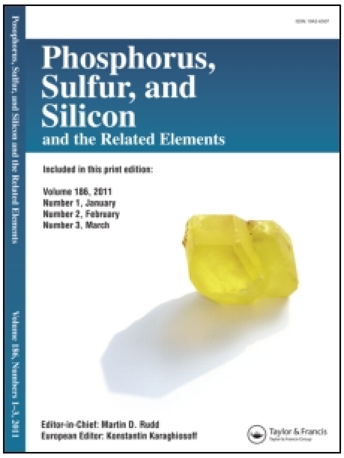

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CHARGE-TRANSFER COMPLEXES OF ALKYLTHIOUREAS WITH π-ACCEPTORS

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CHARGE-TRANSFER COMPLEXES OF ALKYLTHIOUREAS WITH π-ACCEPTORS

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CT-molecular complexes of some dialkylthiourea derivatives with π-acceptors have been investigated. It is concluded that these complexes are of n-π type where the donor site is the sulphur thiocarbonyl group. The stability of the CT complexes has been examined and discussed in terms of molecular structure of donor, nature of π-acceptor and solvent polarity. Solid 1:1 CT complexes of the donors with π-acceptor have been synthesized and characterized.

INTRODUCTION

Charge-transfer complexes of thiourea, alkylthiourears, thiocarbanilides and thioamide with σ-type acceptor, halogen molecules have been investigated.[1–6] Generally, it was suggested that the CT complexes formed are of the type n-σ where the sulphur atom is the donor site. On the other hand Mottaleb *et al.*[7] identified the role of C=S π-electrons of these donors in their CT complex stabilities with I_2. Since the literature does not reveal any information concerning charge-transfer complexes of thiourea and its alkyl derivatives with π-acceptors, the present work is devoted to the study of the charge-transfer interactions of alkylthioureas with some π-acceptors: tetracyanoethylene (TCNE), chloranil (CHL) and 2,3-dichloro-5-6-dicyano-*p*-benzoquinone (DDQ). The aim of this study is to throw some light on the electronic spectral characteristics and stability of the CT complexes formed, as well as to identify the nature of these complexes. Furthermore, the synthesis and characterization of the solid CT complexes is carried out.

RESULTS AND DISCUSSION

Spectral Characteristic of the Formed CT-Complexes in Solution

The absorption spectra of the studied alkylthiourea derivatives-TCNE CT complexes in methylene chloride show a broad absorption band different from that of components. This band can be ascribed to a single intermolecular charge-transfer transition. Typical spectra are shown in Figure 1 for V-TCNE CT-complex in methylene chloride at 10°C. Similar absorption spectra were observed for solutions of other donors with TCNE and CHL in the temperature range 10–30°C. In the case of the CT complexes of donors-TCNE or CHL, the absorption intensities of the CT band increase very slowly with time where the general features of the spectra do not vary, indicating no formation of reaction products. The spectra of

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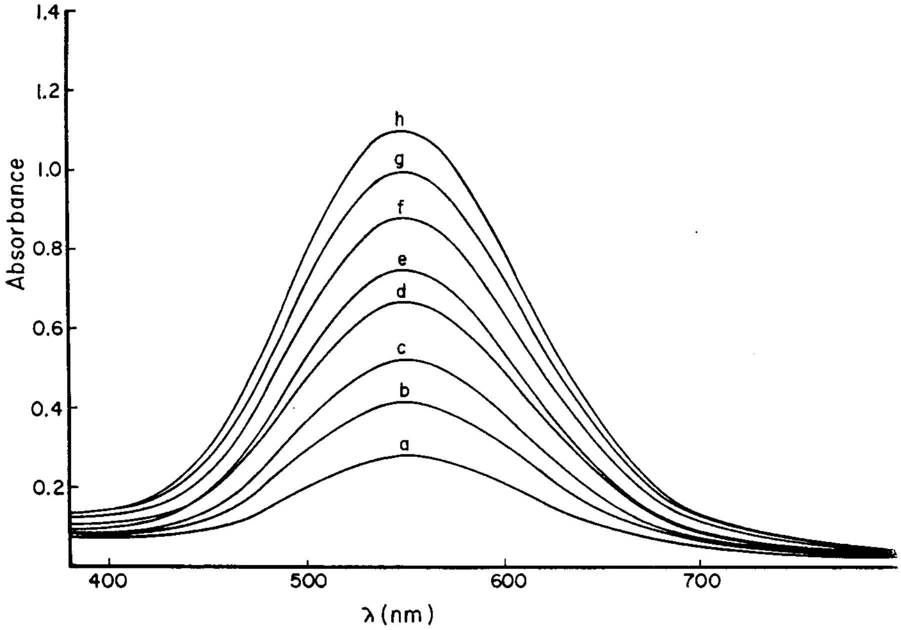


FIGURE 1 Electronic absorption spectra of V-TCNE CT complex in CH_2Cl_2 at 10°C. [V] = 0.008, 0.012, 0.016, 0.020, 0.024, 0.028, 0.032, 0.036 mol dm^{-3} for *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*.

methylene chloride solutions of the CT complexes of alkylthioureas with TCNE or CHL are recorded soon after mixing the donor and acceptor under the condition $[D_0] >> [A_0]$ (the solvent is used as a blank in case of TCNE while in case of CHL the same concentration of CHL solution as in the test solution is used as a blank).

On mixing the dialkylthioureas (I–VI) with DDQ, a blue solution is formed whose color instantaneously changes into reddish-brown and finally becomes yellow. The spectra recorded for the yellow (V-DDQ) CT complex solutions (the same concentration of DDQ as in the test solution is used as a blank) show two main bands (λ_{max} = 355 and 385 nm) and a shoulder at 410 nm (cf. Figure 2). The spectra shapes are time dependent, i.e. with elapse of time, the intensity of the shorter wavelength band decreases while those of the other two bands increase. Stability of absorbancies are attained after elapse of 30 min. This behaviour can be interpreted on the principle that, at first the formed CT complex is of the type D-A, i.e. nonbonding structure (outer-sphere type, blue one). This changed to the inner sphere type $D^+ - A^-$, dative structure (reddish-brown) which consequently dissociates into the radicals D^+ and A^- (yellow). The appearance of an isosbestic point at 365 nm in the spectra recorded (Figure 2) clearly indicates the equilibrium dissociation of the dative structure belonging to V-DDQ CT complex to its corresponding radicals:

$$D + A \rightarrow D - A \rightarrow D^+ - A^- \rightleftharpoons D^+ + A^-$$

It is worth mentioning that, the observed high dissociation when compared to the corresponding ones with TCNE or CHL, can be mainly due to the higher electron affinity of DDQ.

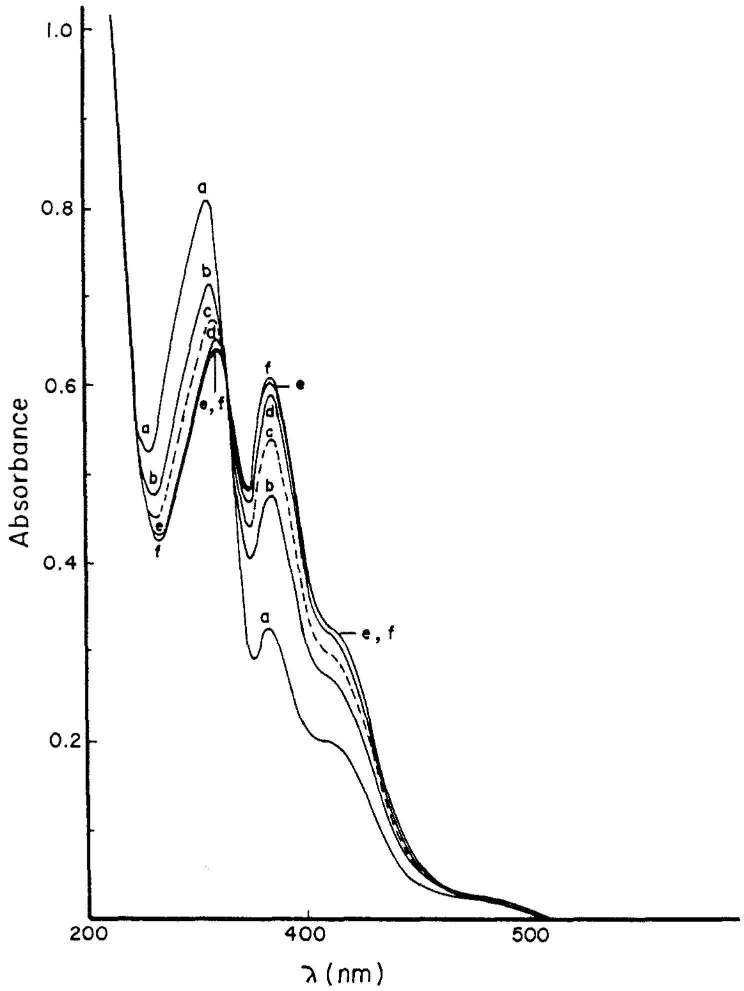


FIGURE 2 Effect of time on the electronic spectra of the CT complex of V (0.03 mol dm^{-3}) with DDQ (2 × 10^{-4} mol dm^{-3}) in CH_2Cl_2 at 20°C. Time (minute) = 0.0, 3, 5, 10, 20, 30 for *a, b, c, d, e, f*.

Determination of the Formation Constants (K_{CT})

The formation constant values of the CT complexes of the studied alkylthioureas with TCNE or CHL have been determined spectroscopically in methylene chloride making use of both Benesi-Hilderband and Scott equations[8,9] under the condition $[D_0] >> [A_0]$ ($[A_0]$ = 0.002 M and $[D_0]$ = 0.008–0.04 M). All calculations were carried out by using a linear least-squares method. The mean K_{CT} and ε_{CT} values obtained are given in Table II. It is evident that the numerical K_{CT} values for the CT complex of alkylthioureas-π acceptor are relatively larger than that known for the π charge-transfer complexes (K_{CT} for some π-complexes of the donors benzene, toluene and hexamethylbenzene vary between 0.13 and 1.33).[10,11] Thus one can conclude that the studied charge-transfer complexes are predominantly of an n-π type. The donor site in alkylthioureas is expected to be the sulphur atom. Ac-

TABLE I

Microanalysis data, colour and melting points for the solid molecular complexes of alkylthioureas with π-acceptors.

Moleculor Complex	Colour	M.P.	% Calculated (Found)			
		°C	C	N	S	Cl
I-DDQ	brown	143 d	43.47	15.59	8.91	19.74
			(43.40)	(15.51)	(8.79)	(19.50)
II-DDQ	reddish-brown	125-27 d	46.52	14.47	8.28	18.31
			(46.71)	(14.52)	(8.41)	(18.12)
III-DDQ	deep red	110 d	49.16	13.49	7.72	17.07
			(49.00)	(13.21)	(7.58)	(17.20)
VI-DDQ	deep red	98-100 d	49.16	13.49	7.72	17.07
			(49.33)	(13.27)	(7.63)	(17.32)
V-DDQ	orange	125	53.96	11.98	6.86	15.17
			(53.69)	(11.72)	(6.66)	(15.01)
VI-DDQ	reddish-brown	110-12 d	57.15	11.59	6.63	14.67
			(57.19)	(11.65)	(6.72)	(14.43)
V-CHL	yellowish-brown	85-87 d	46.93	5.76	6.59	29.20
			(46.65)	(5.91)	(6.45)	(29.03)
VI-CHL	yellowish-brown	71-73 d	50.22	5.58	6.38	28.21
			(50.10)	(5.86)	(6.06)	(28.11)
I-TCNE	deep brown	80	50.75	32.28	12.32	-
			(50.51)	(32.35)	(12.12)	-

d = decompose.

cordingly the CT complexes under investigation are formed by transfer of non-bonding electron from sulphur thiocarbonyl to the antibonding π-orbital of the acceptor. This conclusion can be substantiated by the behaviour that lone pair electrons are better donors than bound π-electrons. Similar conclusion has been reported before for the CT complexes of thiourea derivatives with iodine.[1-7] The results listed in Table II reveals that the formation constant of the CT complex of the various donors with TCNE increases according to the sequence:

dibenzyl < diethyl < dicyclohexyl < dipropyl < dibutyl < diisobutyl

This behaviour is in accordance with the expected high electron donating ability of alkylamino group in the same direction, i.e. high donor ability of the sulphur thiocarbonyl group. This behavior can be considered as a further evidence for n-π nature of the examined CT complexes. On the other hand, the stability of the formed CT complex of the donor V with TCNE is higher than that with CHL. This

TABLE II

λ_{max}(nm), E_{CT}(eV), formation constant (K_{CT}) and molar extinction coefficient (ε_{CT}) for the charge-transfer molecular complexes of alkylthioureas with π-electron acceptors at different temperature in dichloromethane.

Electron donor	Electron acceptor	λ_{max}(nm)	E_{CT}(eV)	K_{CT}(dm^3mol^{-1}), °C					ε_{CT}($dm^3mol^{-1}cm^{-1}$) at 10°C
				10°C	15°C	20°C	25°C	30°C	
I	TCNE	538	2.36	6.75 ± 0.41	5.62 ± 1.48	4.74 ± 1.55	4.05 ± 0.76	3.24 ± 1.11	2302.43 ± 140
II	TCNE	542	2.29	9.84 ± 1.17	8.44 ± 0.66	7.18 ± 0.76	6.07 ± 0.81	5.27 ± 1.12	1593.54 ± 190
III	TCNE	542	2.29	10.39 + 1.18	9.23 ± 1.48	8.35 ± 1.19	7.54 ± 1.08	7.10 ± 0.79	1711.80 ± 188
IV	TCNE	544	2.28	24.57 ± 0.31	22.26 ± 1.17	19.38 ± 1.55	17.35 ± 1.15	13.98 ± 0.91	698.30 ± 68
V	TCNE	552	2.25	7.39 ± 0.98	5.98 ± 0.79	5.37 ± 0.46	3.46 ± 0.81	3.59 ± 0.76	3119.40 ± 556
VI	TCNE	535	2.32	4.68 ± 1.71	3.75 ± 0.85	3.51 ± 1.21	2.71 ± 0.78	2.29 ± 0.61	1485.17 ± 581
V	CHL	452	2.75	5.71 ± 1.81	5.47 ± 1.63	4.56 ± 1.93	3.95 ± 2.01	-	378.04 ± 216

is in agreement with the high electron affinity of TCNE as compared to that of CHL.

Ionization Potential of the Electron Donors

The ionization potentials of the alkylthiourea compounds (I–VI) were estimated using the empirical relation reported by Aloisi and Pignataro[12] and the values obtained are listed in Tables III and IV. However, their experimental IP values are not available in the literature due to the lack of photoelectron (P.E) data for these compounds, except in case of 1,3-diethylthiourea (I) and 1,3-dibenzylthiourea (VI) where their IP values have been calculated and found to be 8.32 eV[5] and 8.36 eV[7] respectively. These values are comparable with the corresponding calculated ones. Furthermore the calculated IP values for the donor V from CT energies with TCNE and CHL complexes are nearly the same, suggesting that the donor orbital involved in the CT transition is common for the two π-electron acceptor.

Effect of Solvent

In order to examine the solvent effect on the stability of alkylthioureas CT complexes, the CT complex of 1,3-dipropylthiourea (III) with TCNE has been investigated in different solvents of various polarities (CH_2Cl_2, $CHCl_3$, $C_2H_2Cl_2$). Spectral characteristics and the mean K_{CT} values determined for CT complex in these solvents are listed in Table IV. It is evident that the stability of the CT complex increases as the dielectric constant of the solvent is lowered [$C_2H_4Cl_2$(D = 10.65) $\rightarrow$ CH_2Cl_2(D = 9.08) $\rightarrow$ $CHCl_3$(D = 4.08)]. This can be explained on the principle that, the formed complex is strong, i.e. there is large contribution of the dative structure $D^{+}{}_{.} - A^{-}$ to the CT complex ground state. Accordingly, increasing polarity of the medium leads to dissociation of the dative structure owing to the expected high dipole-dipole or dipole-induced dipole interaction along the same

TABLE III

Thermodynamic parameters of charge-transfer complexes formation of alkylthioureas with π-acceptor TCNE and CHL in dichloromethane and calculated ionization potential values of the donor.

Electron donor	Electron Acceptor	$-\Delta H^0$ k cal.mol^{-1}	$-\Delta G^0$ k cal.mol^{-1}	$-\Delta S^0$ cal.mol^{-1}	IP(eV)	$(\frac{b}{a})^2$
I	TCNE	6.25 ± 0.17	1.071± 0.41	18.28 ± 0.60	8.277	0.118
II	TCNE	5.34 ± 0.08	1.281± 0.32	14.33 ± 0.26	8.254	0.101
III	TCNE	3.22 ± 0.16	1.312± 0.28	6.74 ± 0.56	8.254	0.061
IV	TCNE	3.91 ± 0.42	1.794± 0.32	7.43 ± 1.46	8.243	0.074
V	TCNE	6.03 ± 0.45	1.121± 0.98	17.33 ± 1.50	8.323	0.116
VI	TCNE	5.83 ± 0.99	0.865± 0.50	17.53 ± 1.40	8.294	0.109
V	CHL	5.36 ± 0.11	0.976± 0.43	15.49 ± 0.56	8.385	0.085

TABLE IV

λ_{max}(nm), E_{CT}(eV), formation constants (K_{CT}), molar extinction coefficient (ε_{CT}) of the CT molecular complex formation for III with TCNE in various solvents at 10°C.

Solvent	λ_{max}(nm)	E_{CT}(eV)	IP(eV)	K_{CT} (dm^{3}mol^{-1})	ε_{CT}(dm^{3}mol^{-1}cm^{-1})
$CHCl_3$	536	2.32	8.288	16.88 ± 1.81	608.24 ± 67.5
CH_2Cl_2	542	2.29	8.254	9.84 ± 1.17	1593.54 ± 189.7
$C_2H_4Cl_2$	544	2.28	8.243	8.02 ± 0.59	1286.72 ± 79.0

direction. In this respect it is worth mentioning that the solvents employed do not show specific interaction with the formed CT complex.

Thermodynamic Parameters of the CT Complexes

The enthalpy changes (ΔH) and entropy changes (ΔS) connected with the formation of the CT complexes studied were determined from the formation constant values at a series of temperatures making use of the Van't Hoff equation plots (Figure 3). The Free energy change (ΔG) is calculated using the relation $\Delta G = -RT \ln K_{CT}$. The obtained results are given in Table III.

According to Mulliken[13,14] the ratio between the coefficient of the dative to the nonbond wavefunctions ($\psi_{D^+-A^-}$ and ψ_{D-A}, respectively), *b*/a was calculated. The obtained ratio (Table III) is compared to that of many strong CT complex.[15]

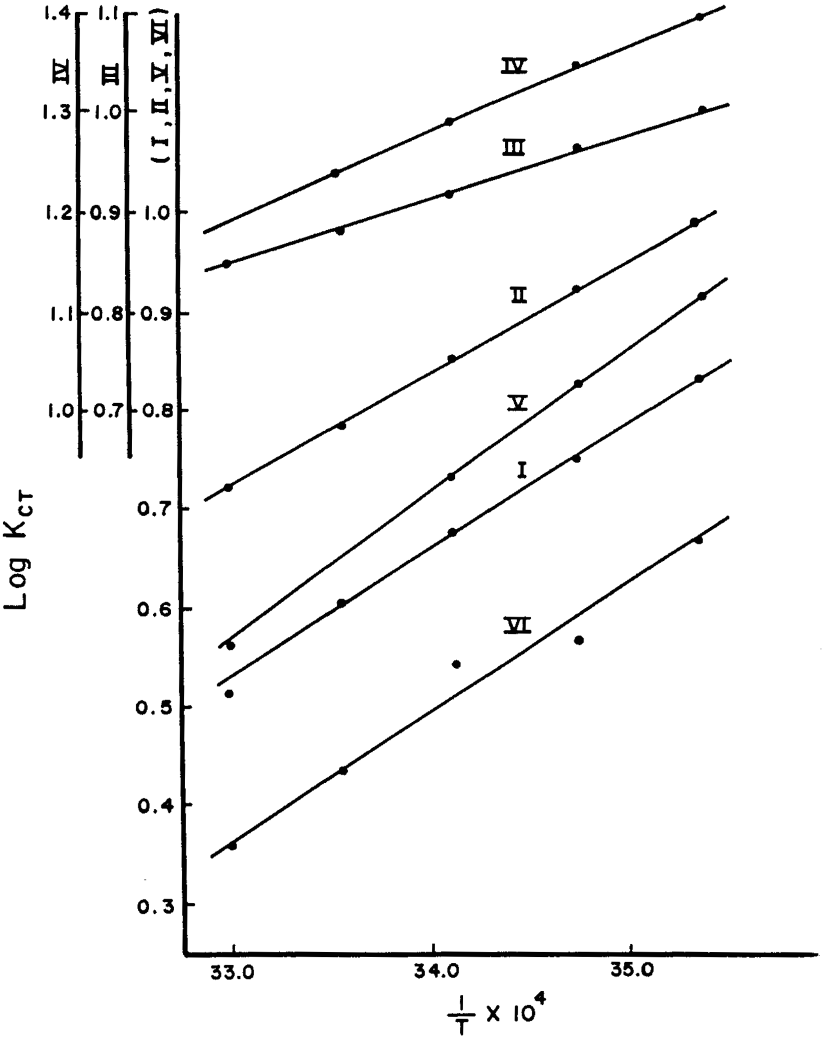
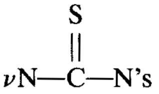


FIGURE 3 Van't Hoff's plots for CT molecular complexes of alkylthioureas (I–VI) with TCNE in CH_2Cl_2.

Characterization of the CT-Complexes

The results of chemical analysis (C, N, S and Cl contents) of the different isolated CT-complexes are reported in Table I, where the results clearly indicate the formation of 1:1 CT-complexes in each case. A comparison of the recorded IR spectra of the free donors and acceptors with those of the CT-complexes gives some information on the nature of these complexes:

i) The νNH's, νC=S's,



$$\nu N{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}N\text{'s}$$

and δNH's for the free donors are shifted to lower frequencies in the CT molecular complexes. This is in accordance with charge migration from the donors to the acceptors (DDQ, TCNE and CHL).

ii) The νC≡N of DDQ (at 2235 cm^{-1}) and of TCNE (at 2220 cm^{-1}) as well as νC—Cl of DDQ and CHL (at 802 cm^{-1} and 760 cm^{-1} respectively) are shifted toward lower frequencies in their molecular complexes with dialkylthioureas. This behaviour is indicative of an electron transfer from HOMO of the donor thiourea to LUMO on the acceptor. The magnitude of the shift in the νC—Cl of DDQ on its CT complex formation with the different dialkylthioureas runs according the sequence:

dibenzyl (22 cm^{-1}) < diethyl (27 cm^{-1}) < dicyclohexyl (37 cm^{-1})
< dipropyl (47 cm^{-1}) < dibutyl (54 cm^{-1}) < diisobutyl (57 cm^{-1}).

This is in accordance with the deduced high stability of the formed TCNE CT complex as dialkyl group is changed along the same sequence (cf. Table II).

EXPERIMENTAL

Materials and Solutions: Thiourea derivatives were synthesized according to the method described in the literature.[3] The prepared compounds are: 1,3-diethylthiourea (I); 1,3-dipropylthiourea (II); 1,3-dibutylthiourea (III); 1,3-diisobutylthiourea (IV); 1,3-dicyclohexylthiourea (V) and 1,3-dibenzylthiourea (VI). The electron acceptors TCNE, CHL and DDQ (Aldrich grade products) were recrystallized from chlorobenzene, dry benzene and dry methylene chloride respectively. All solvents used were spectral-grade (BDH). Stock solutions of the donors or acceptors were freshly prepared in the proper solvent prior to use.

Physical Measurements: Electron spectra were recorded with a CECIL CE 599 recording spectrophotometer equipped with a temperature-controlled cell holder thermostated with an accuracy of ±0.05°C. IR spectra of the solid CT complexes were taken on a PERKINELMER 599 B IR spectrophotometer. Computations were performed on an Apple IIe microcomputer with the aid of two programs based on unweighted linear least-squares fits.

Preparation of Solid Complexes: Saturated solutions of the donors (2.2 mmol) in dichloromethane were mixed with the saturated one of the π-acceptor DDQ or TCNE or CHL (2.0 mmol) in dichloromethane and refluxed for ½–1 h. Then the solution was evaporated to a small volume where the solid CT complexes were separated as fine crystals on cooling. The precipitates were collected and recrystallized from absolute ethanol and dried. The analytical results of the prepared complexes (C, N, S and Cl) along with the physical properties viz colour and melting points are listed in Table I.

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