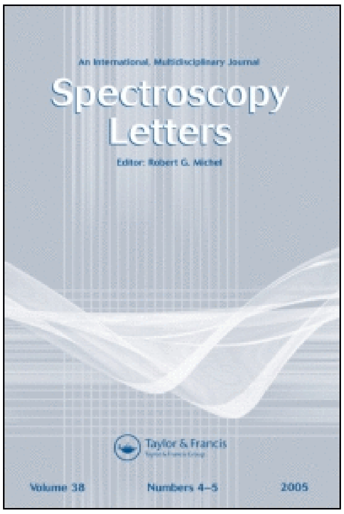

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Molecular Complexes of Macrocyclic Polyamines with π-Electron Acceptors

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MOLECULAR COMPLEXES OF MACROCYCLIC POLYAMINES WITH π-ELECTRON ACCEPTORS

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ABSTRACT

The charge-transfer interaction of macrocyclic polyamines 1,4,8,11-tetraazacyclotetradecane (TACTD); 1,4,8,12-tetraazacyclopentadecane (TACPD) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTACTD) with chloranil (CHL), tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as π-electron acceptors was investigated spectroscopically. Spectral characteristics and stability constants of formed CT complexes are examined and discussed in terms of molecular structure of both electron donor and acceptor as well as solvent polarity. It is deduced that the CT complexes are of strong kind where macrocyclic polyamines-DDQ, TMTACTD-TCNE, -CHL complexes essentially exist in the dissociated state (radical cations and anions D^+, A^-). On the other hand, the TCNE and CHL complexes with TACTD and TACPD exist in a dative structure (D^+-A^-). Solid 1:1 CT complexes are synthesized and characterized.

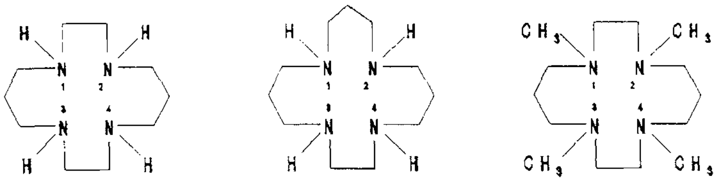
INTRODUCTION

Molecular complexation and structural recognition are key processes in biological systems. For instance, enzyme catalysis, drug action, and ion transfer through lipophilic membrances all involve complexation between two or more distinct molecules⁽¹⁾. Since crown compounds show many features encountered in such biological processes⁽²⁾ (complexing ability, flexibility and selectivity) they may play an important role as substituents for natural occurring molecules in living organisms. Further, these compounds have been used in organic chemistry to study some ionic organic reactions catalyzed by solvolysis of the cationic species(3). For these wide applications extensive studies on charge-transfer complexes of crown compounds such as macrocyclic polyethers with σ- and π-electron acceptors(4-14) have been performed. On the other hand, little attention has been paid to analogous study on macrocyclic polyamines(15-17). Nour and his associates(15-17) investigated the CT interaction of 1,4,8,11-tetraazacyclotetradecane (TACTD) with σ-acceptor, iodine where the formed CT complex was formulated as $(TACTD)I^+.I_3^-$. Since reliable information is still lacking on CT complexes of macrocyclic polyamines with π-electron acceptors. The present article is devoted to collect some information on CT complexes of these donors with some π-acceptors, viz: chloranil (CHL), tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The macrocyclic polyamines used in this work are: 1,4,8,11-tetraazacyclotetradecane (TACTD, I); 1,4,8,12-tetraazacylopentadecane (TACPD, II) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTACTD, III). Spectral characteristics and stabilities of the formed CT complexes were examined and are discussed. Moreover, the solid CT complexes were synthesized and characterized.

EXPERIMENTAL

Materials and Solutions

The macrocyclic polyamines, 1,4,8,11-tetraazacyclotetradecane (TACTD, I); 1,4,8,12-tetraazacyclopentadecane (TACPD, II) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTACTD, III) were supplied by Aldrich Chem. Co and were used as received. The structural formula of these compounds can be represented as follows:



I II III

Scheme 1

The electron acceptors DDQ, TCNE and CHL (Aldrich or Merck reagent grade) were recrystallized from dry dichloromethane, chlorobenzene and dry benzene, respectively. All solvents used were of spectral-grade quality (BDH). Stock solutions of the donors or acceptors were freshly prepared in a dry and deoxygenated solvents prior to use.

Physical Measurements

The electronic absorption spectra of the studied CT complex solutions were recorded with a CECIL CE 599 Spectrophotometer using 1 cm matched silica cells. The apparatus was equipped with a temperature-controlled cell holder, which was adjusted by a Julabo FP 40 thermostat with an accuracy ± 0.01 °C. The IR spectra of the synthesized solid CT complexes were taken on a Shimadzu 408 IR Spectrophotometer. All computions were performed on an Apple IIe microcomputer with the aid of two program based on unweighted linear least-squares fits.

Synthesis of the Solid CT Complexes

The solid CT complexes of the macrocyclic polyamines I-III with the π-electron acceptors (DDQ, TCNE, CHL) were prepared by mixing dichloromethane of each donor (3.5 mmol) with that of DDQ or TCNE or CHL (3.2 mmol). The resulting complex solutions were lefted at room temperature for 3 h. where the solid compound precipitated out. The separated complexes were filtered off, and washed several times with dichloromethane, then dried. The analytical data of these CT complexes (C, H, N and Cl contents) along with some of their physical properties, viz., colour and their decomposition temperatures are listed in Table 1. The C, H, N contents were determined at the microanalytical laboratory, Assiut University, on a PERKIN ELMER 240 C apparatus, whereas the chlorine content was estimated applying the conventional method.

RESULTS AND DISCUSSION

Electronic Spectral Characteristic of the CT Complexes

The electronic spectra of dichloromethane CT complex solutions of the studied macrocyclic polyamines I-III with the π-electron acceptors DDQ, CHL and TCNE are displayed in Figs. 1 and 2. In all cases the same concentration of acceptor as in the test

Table 1: Microanalysis data, colour and decomposition temperatures for the solid molecular complexes of macrocyclic polyamines with π-acceptors (DDQ, TCNE and CHL).

Complex	Colour	Dec. Temp.	Calculated (found)			
			C%	H%	N%	Cl%
TACTD-DQQ	brown	260	50.59 (50.32)	5.66 (5.91)	19.75 (19.48)	16.54 (16.29)
TACTD-TCNE	redish-brown	230	58.52 (58.78)	7.37 (7.66)	34.27 (34.50)	-- --
TACTD-CHL	green	202	43.07 (43.22)	5.42 (5.43)	12.61 (12.53)	31.69 (31.33)
TACPD-DDQ	pale brown	168	51.71 (51.66)	5.94 (5.75)	19.12 (18.79)	16.02 (16.14)
TACPD-TCNE	red	185	59.63 (59.34)	7.65 (7.42)	32.86 (32.72)	-- --
TACPD-CHL	deep brown	212	44.37 (44.52)	5.69 (5.50)	12.23 (11.98)	30.72 (30.93)
TMTACTD-DDQ	buff	148	54.66 (54.49)	6.67 (6.81)	17.46 (17.50)	14.62 (14.47)
TMTACTD-TCNE	yellowish green	222	62.47 (62.51)	8.39 (8.26)	29.26 (29.37)	-- --
TMTACTD-CHL	brown	195	47.82 (47.66)	6.42 (6.70)	11.20 (11.43)	28.15 (28.36)

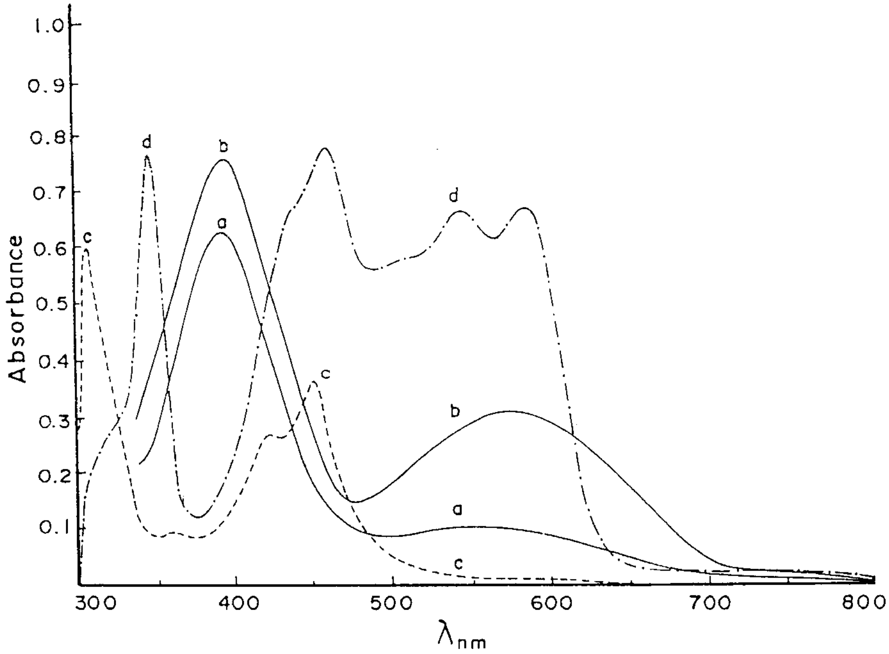


Fig. 1. Electronic spectra of the dichloromethane CT complex solutions of macrocyclic polyamines with CHL and DDQ at 20°C.

a) 5×10^{-4} mol dm^{-3} TACTD + 5×10^{-4} mol dm^{-3} CHL,
b) 5×10^{-4} mol dm^{-3} TACPD + 5×10^{-4} mol dm^{-3} CHL,
c) 5×10^{-4} mol dm^{-3} TMTACTD + 5×10^{-4} mol dm^{-3} CHL,
d) 1×10^{-3} mol dm^{-3} TMTACTD + 2×10^{-4} mol dm^{-3} DDQ.

solution was used as a blank to eliminate any interference from the acceptor spectrum with that of the corresponding formed CT complex.

Within the wavelength range 300-700 nm, the spectra recorded for TCNE and CHL CT complex solutions (in deoxygenated CH_2Cl_2) with donors I and II (TACTD and TACPD, respectively) display two main absorption bands (cf. Figs. 1 and 2, curves a, b). The observed absorption bands for donor I-CHL and TCNE complex solutions are

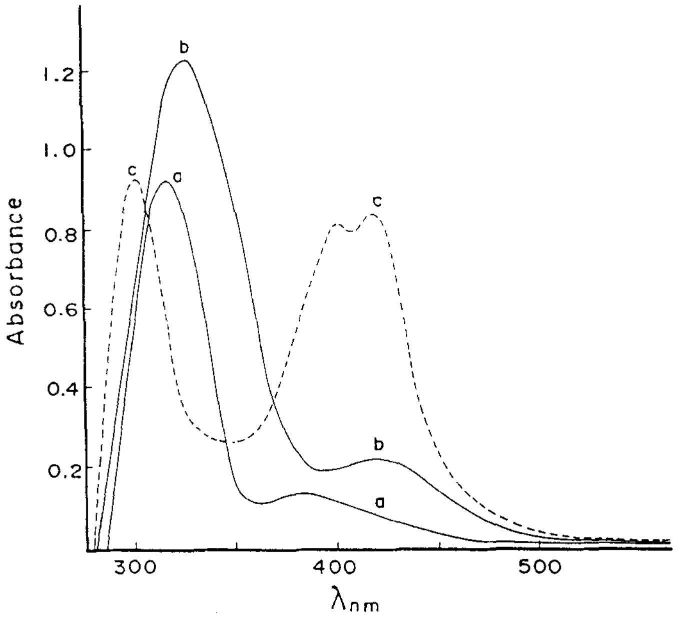


Fig. 2. Electronic spectra of the dichloromethane CT complex solutions of 4x10^{-4} mol dm^{-3} TCNE with 4x10^{-4} mol dm^{-3} macrocyclic polyamines at 20°C.
a) TACTD , b) TACPD , c) TMTACTD

located at 392, 558 nm and at 318, 380 nm, respectively whereas those of II-CHL and TCNE complex solutions are appeared at 400, 573 nm and at 340, 420 nm, respectively. Since the chemical analysis data of the isolated solid I, II-TCNE and CHL CT complexes are in accordance with the formation of a 1:1 CT complex in each case (cf. Table 1), one can ascribe the observed two absorption bands in each complex as double CT transition for one molecular complex. The donor sites of the two CT transition are suggested to be N_1 and N_2 (cf. Scheme 1) since they are characterized by high basicity compared to that of the other two nitrogen atoms N_3 and N_4 (log K values are: 11.585 (N_1), 10.624 (N_2), 1.611 (N_3), 2.415 (N_4) for donor I whereas those of donor II are: 11.081 (N_1), 10.381 (N_2), 5.279 (N_3) and 3.602 (N_4)$^{(18)}$. Furthermore, the stoichiometry of these complexes in solution is ascertained by applying the continuous variation method$^{(19)}$ which gave symmetrical curves with maxima at a mole fraction 0.5 indicating the formation of a 1:1 CT complex in each case (cf. Fig. 3).

On the other hand, the spectroscopic feature of III-CHL CT complex solution (λ_{max} values = 307, 361 sh, 425 and 450 nm, cf. Fig. 1, curve c) are coincident with those reported earlier for CHL^{-}(20,21). Accordingly, it could be suggested that, the formed III-CHL CT complex is of strong type where it completely dissociates into its radicals III^{+} and CHL^{-}. In terms of molecular structure of the three macrocyclic polyamines under investigation one can deduce that the donor strength of these donors runs according to the order: $I < II < III$, i.e., high basicity along the same direction. This order is in accordance with the observed low excitation energies of the two CT bands in the case of donor II relative to that in the case of donor I (cf. Table 2) as well as the existence of donor III-CHL CT complex mainly in the form of the radicals III^{+} and CHL^{-} as explained above.

Further, the recorded electronic spectra of donor III-TCNE CT complex in dichloromethane show two main absorption bands where the longer wavelength band appears as a doublet (λ_{max} = 399 and 418 nm) while the shorter one located at 302 nm (cf. Fig. 2, curve c). The peak position and shape of the longer wavelength band can be compared with that reported for 1,1,2,3,3-pentacyanoproponide ion, $PCNP^{-}$ produced by interaction of TCNE with water traces present in CH_2Cl_2 solvent in presence of macrocyclic polyamine base (basic hydrolysis)(22). Accordingly, the doublet band appeared at 399 nm and 418 nm could be assigned to absorption of $PCNP^{-}$(23,24). On the other hand, the shorter absorption band (302 nm) could be explained on the principle that the formed III-TCNE CT complex is of strong type, i.e., it exist predominantly in the dissociated state (D^{+}, A^{-}). Thus the above described shorter wavelength band can be ascribed to absorption of tricyanoethenolate anion formed by reaction of water traces present in CH_2Cl_2 with $TCNE^{-}$(25,26).

On using DDQ as electron acceptor, the recorded spectra (cf. Fig. 1, curve d) for dichloromethane CT complex solutions of the donors I-III display a series of absorption bands at 346-8, 440 *sh*, 462-4, 505-7, 540-44 and 580-85 nm. These spectroscopic features are in good agreement with those previously reported for the anion radical DDQ^{-}

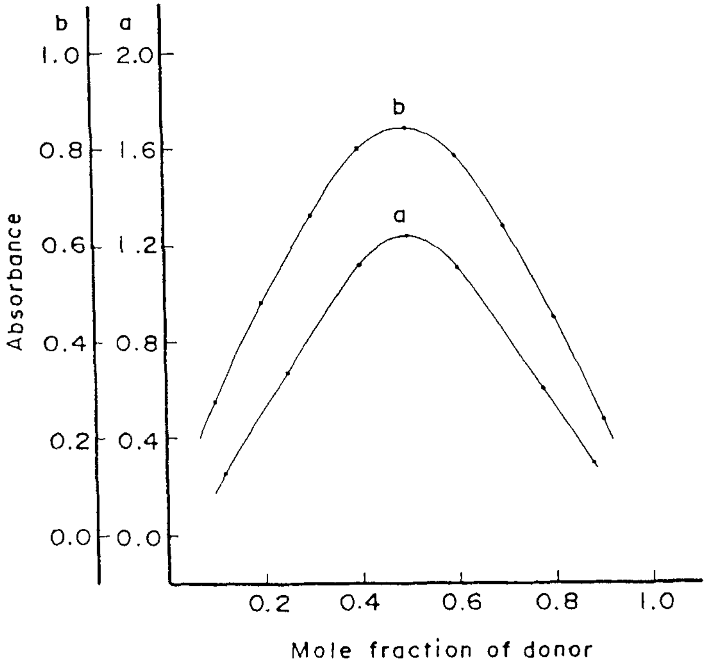


Fig. 3. Continuous variation method for the CT complexes of donor TACPD (II) with π-electron acceptors.
a) TCNE (total molar concentration = 4×10^{-4} mol dm^{-3}, λ_{max} = 340 nm),
b) CHL (total molar concentration = 2×10^{-3} mol dm^{-3}, λ_{max} = 573 nm).

(346, 435, 456, 508, 547 and 584 nm)(27-29). Thus one can deduce that the formed DDQ-macrocyclic polyamines CT complexes are of strong type, i.e., they completely dissociate to the corresponding radicals DDQ$^-$ and polyamines$^+$.

Thermodynamic Properties

The formation constant values (K_{CT}) and molar extinction coefficients (ϵ_{CT}) of the 1:1 I, II-CHL CT complexes in the temperature range 10-25°C were determined from spectral measurements for a series of nine solutions containing varying donor concentration and a constant acceptor concentration (CHL), cf. Fig. 4. This was

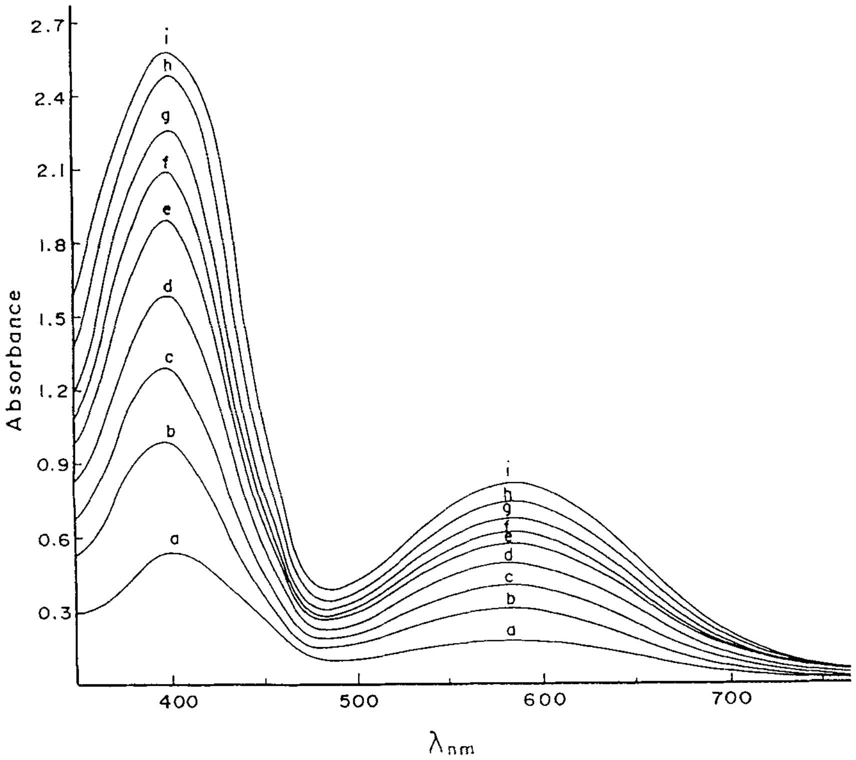


Fig. 4. Electronic spectra of the dichloromethane TACPD-CHL CT complex solutions at 20°C. [CHL] = 1×10^{-3} mol dm^{-3}, [TACPD] = 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0×10^{-3} mol dm^{-3} for a, b, c, d, e, f, g, h and i, respectively.

performed through the application of the Scott equation(30) where the absorbance values were determined at the λ_{max} of the longer wavelength CT band. All calculations were carried out using a linear least squares methods. The obtained K_{CT} and ϵ_{CT} values are listed in Table 2. In general, the obtained high K_{CT} values of the studied CT complexes suggest that such complexes are of the strong kind. The observed high stability of donor II CT complex compared to that of donor I could be ascribed to the high donor character

Table 2: Spectral characteristics, formation constants (K_{CT}) and enthalpy changes (ΔH) values for CT complexes of macrocyclic polyamines with chloranil in various solvents at different temperatures.

Donor	Solvent	λ_{max} nm	E_{CT} ev	K_{CT} ($dm^3\ mol^{-1}$), °C				ϵ_{CT} $dm^3\ mol^{-1}\ cm^{-1}$	$-\Delta H$ $K\ J\ mol^{-1}$
				10	15	20	25		
TACTD	CH_2Cl_2	558 392	2.223 3.164	131.77±5.7	116.28±6.1	104.01±7.7	93.06±5.4	1137.88±42.2	16.18±0.2
TACPD	CH_2Cl_2	573 400	2.165 3.101	325.33± 3.1	290.66±1.3	255.43±2.0	220.96±1.1	2519.64±7.9	18.02±0.8
TACPD	$CHCl_3$	590	2.103	222.93± 2.9	201.11±3.0	184.12±1.9	161.07±3.9	1950.65±9.1	14.89±0.9
TACPD	$C_2H_4Cl_2$	570	2.177	454.77± 1.2	399.49±1.4	349.04±2.1	306.53±1.8	2757.9 ±4.8	20.16±0.6

of II relative to that of I (the overall basicity, log β_4 is 26.235 and 30.343 for donors I and II, respectively)(18). This is due to the large size of the hydrocarbon chain of donor II relative to that of donor I. From this dependence of the CT complex stability on donor molecular structure (nitrogen basicity), it seems reasonable to deduce that the formed CT complexes are of n-π type where the nitrogen atoms are the donor sites for the CT interaction. However, it is difficult to determine the formation constant values of donor I, II-TCNE complexes due to the large dependence of absorption intensities of the appeared two bands by elapse of time. Further, the determination of K_{CT} values of the formed CT complexes of donors I-III with DDQ as well as those of donor III with TCNE and with CHL could not be possible owing to the existence of these complexes predominantely in the dissociated state (radical cations and anions D^+, A^-) as described before. Thus the recorded spectra of these complexes are perturbed by those of the radical anions, i.e., they do not exhibit well defined CT bands.

The computed K_{CT} values at a series of temperatures (10-25°C) were utilized to determine the enthalpy change (ΔH) of the CT complex formation using Van't Hoff plots where the obtained results are listed in Table 2. It can been seen that the interaction of CHL with donor II is more exothermic than that with donor I which agrees with the above deduced high stability of the former complex compared to that of the latter one.

Effect of Solvent

The formed CT complex of donor II with CHL was investigated in different solvents of various polarities ($CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$) at a series of temperatures. Spectral characteristics and the obtained K_{CT} values are given in Table 2. It is evident that the K_{CT} value increases as the dielectric constant of the solvent is increased ($CHCl_3$, D= 4.806 → CH_2Cl_2, D= 9.08 → $C_2H_4Cl_2$, D= 10.65). This trend can be interpreted on the basis that the formed CT complex is of strong n-π type, i.e., the contribution of the dative structure wave function $\Psi_{D^+-A^-}$ in the ground state of the CT complex is large. Accordingly, the dative structure D^+ - A^- would be more stabilized in solvents of high dielectric constants owing to increasing dipole-dipole or dipol-induced dipole interactions.

Characterization of the Solid CT Complexes

The stiochiometry of various synthesized solid charge-transfer complexes was assigned on the basis of their elemental analyses data (C, H, N and Cl contents) cited in Table 1. These data reveal the formation of a 1:1 CT complex in each case.

Comparison of the important IR spectral bands of free donors I-III and the π-acceptors (DDQ, TCNE, CHL) with the corresponding ones appeared in the IR spectra of the obtained CT complexes show strong pattern due to the corresponding radical anions DDQ$^{\cdot-}$, TCNE$^{\cdot-}$ and CHL$^{\cdot-}$. Namely, the vibration frequencies of $C \equiv N$ group for DDQ and TCNE observed at 2240 cm^{-1} and at 2260, 2230 cm^{-1} respectively are shifted to 2210 and to 2210-2207, 2185 cm^{-1} in the corresponding IR spectra of their complexes. Also, the C=O, C-C-CN and C-Cl stretching vibration frequencies appearing at 1675, 898 and 802, 720 cm^{-1}, respectively in the IR spectra of free DDQ are displayed at 1630-1610, 890-875 and 785-775 cm^{-1} in its complexes. Further, the group of frequencies connected to C=O (at 1690, 1679 cm^{-1}) and to C-Cl (at 750, 710 cm^{-1}) of the free CHL are displayed at lower energies in the IR spectra of its complexes (appeared at 1685, 1630-1625 cm^{-1} and at 740-710 cm^{-1} respectively). The observed shift to lower energies, indicates a high charge density on these groups as a result of charge transfer from the highest occupied molecular orbitals (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. Based on the above findings one can deduce that, the described characteristic bands for the applied π-acceptors (DDQ, TCNE, CHL) in the IR spectra of their complexes are comparable to those of their anion radicals as previously reported(29-31). This is in accordance with the strong nature of such CT complexes as deduced from examination of their electronic spectral characteristics and from high K_{CT} values of the formed CHL CT complexes.

REFERENCES

1. J.W.H.M. Uiterwijk, S. Harkema and D. Feil, J. Chem. Soc. Perkin Trans. **II**, 721 (1978).
2. R.M. Kellogg, Top. Curr. Chem., **101**, 111 (1982).
3. J.S. Bradshaw and J.Y.K. Hui, J. Heterocyclic Chem., **11**, 649 (1974).
4. Y. Jayathirtha and V. Krishnan, Proc. Indian Acad. Sci., **86** A (5), 465 (1977).

5. Y. Jayathirtha and V. Krishnan, Z. Naturforch., **33** A (2), 243 (1978).
6. Y. Jayathirtha and V. Krishnan, Natl. Acad. Sci. Lett. (Indian), **I** (10), 365 (1978).
7. Y.A. Serguchev, L.M. Mostovaya and T.I. Petrenko, Teor. Eksp. Khim., **15** (6), 736 (1979); C.A. **92**, 163267F (1980).
8. R. Malini and V. Krishnan, Bull. Soc. Chim. Belg., **89** (5), 359 (1980).
9. R. Malini and V. Krishnan, J. Phys. Chem., **84** (5), 551 (1980).
10. V. Krishnan and R. Malini, J. Chim. Phys. Phys. - Chim. Biol., **78** (6), 503 (1981).
11. Y. Jayathirtha and V. Krishnan, Indian J. Chem., **20** A (3), 249 (1981).
12. J. Muchova and V. Holba, Collect. Czech. Chem. Commun., **48** (4), 1158 (1983).
13. R. Malini and V. Krishnan, Spectrochim. Acta, **40** A (3), 323 (1984).
14. A.M. Nour El-Din, Spectrochim. Acta, **42** A (5), 637 (1986).
15. E.M. Nour and L.A. Shahada, Spectrochim. Acta, **44** A (12), 1277 (1988).
16. E.M. Nour and L. Shahada, Spectrochim. Acta, **45** A (10), 1035 (1989).
17. E.M. Nour, G. Abdel-Wahed, S. Abdel-Khalik and M. El-Essawi, Indian J. Chem., **29** A (1), 73 (1990).
18. M. Micheloni, A. Sabatini and P. Paoletti, J. Chem. Soc. Perkin **II**, 828 (1978).
19. P. Job, Ann. Chim. Phys., **9**, 113 (1928).
20. Y. Iida, Bull. Chem. Soc. Jpn., **43**, 2772 (1970).
21. T. Yamaoka and S. Nagakura, Bull. Chem. Soc. Jpn., **44**, 1780 (1971).
22. W.J. Middleton, E.L. Little, D.D. Coffman and V.A. Engelhardt, J. Am. Chem. Soc., **80**, 2795 (1958).
23. H.J. Shine and R.D. Goodin, J. Org. Chem., **35**, 949 (1970).
24. P.G. Farrell and R.K. Wojtowski, J. Chem. Soc. (c), 1394 (1970).
25. O.W. Webster, W. Mahler and R.E. Benson, J. Am. Chem. Soc., **84**, 3278 (1962).
26. C.L. Dickinson, D.W. Wiley and B.C. Mckusick, J. Am. Chem. Soc., **82**, 6932 (1962).
27. Y. Idia and Y. Matsunga, Bull. Chem. Soc. Jpn., **40**, 231 (1967).
28. Y. Iida, Bull. Chem. Soc. Jpn., **44**, 2615 (1971).

29. J.S. Miller, P.J. Krusic, D.A. Dixon, W.M. Reiff, J.H. Zhang, E.C. Anderson and A.J. Epstein, J. Am. Chem. Soc., **108**, 4459 (1986).

30. R.L. Scott, Recl. Trav. Chim. Pays. Bas, **75**, 787 (1956).

31. M.R. Mahmoud, H.M.A. Salman and A.A. Ahmed, Cand. J. Appl. Spectrosc., **37**, 170 (1992).

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