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Charge–transfer complex of 2,3-diaminonaphthalene and chloranil: colour development and crystal structure

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Abstract

An intermolecular charge–transfer (CT) complex was obtained from 2,3-diaminonaphthalene as donor with chloranil as acceptor. The crystal structure, as shown by an X-ray analysis, was composed of the donor and acceptor alternatively. The component molecules are stacked on top of each other to form a column along the *a*-axis. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There have been many spectrophotometric investigations concerning intermolecular charge–transfer (CT) complexes. The characteristics of CT complexes can be clarified by their absorption spectra and thermodynamic constants (equilibrium constant K_{CT}, and enthalpy ΔH, and entropy ΔS of formation).

Intermolecular CT complexes have been studied for use as organic electric conductors and organic photoconductors. Thus, a tetrathiafulvalene (TTF)–tetracyanoquinodimethane (TCNQ) intermolecular CT complex has been examined as an organic electric conductors [1,2] and more appropriate combinations of stronger donors and acceptors have been studied in the context of organic metals [3].

Matsuoka et al. have reported some intermolecular CT complexes, such as the combination of carbazoles and naphthoquinones for use as colouring materials [4].

Single crystal X-ray diffraction studies and crystal packing examinations have been employed to determine both the structure and the important intermolecular interactions in the solid state of ethyl carbazole–dicyanonaphthoquinone derivatives [5].

Thus, it is important to study the solid-phase structure in relation to the structures and characteristics of the CT complex Fig. 1. In this paper, the absorption spectra and the solid state structure of the intermolecular CT complex of 2,3-diaminonaphthalene and chloranil was determined by means of X-ray diffraction analysis.

2. Experimental

2.1. Synthesis of intermolecular CT complex

2,3-Diaminonaphthalene **1** and chloranil **2** were each dissolved in methylene chloride at a

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concentration of about 2×10^{-2} mol/litre. After mixing the two solutions, the CT complex was immediately formed. Single crystal was obtained by slow evaporation of a methylene chloride solution of the CT complex.

2.2. X-ray crystallographic analysis

Preliminary experimental and data collection for the X-ray crystal structure determination were performed on an Enraf–Nonius **CAD4**/Turbo diffractometer using Mo K_α radiation ($\lambda=0.71069$ Å). A small single crystal, ($0.5\times0.5\times0.5$ mm), was cut from larger one and glued to a glass fibre with an epoxy resin. Twenty-five reflections in diverse reciprocal space were centered using an automatic search program, and used to obtain cell parameters. After the preliminary cell was confirmed, high-angle data ($2\theta>20°$) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and the systematic absences indicated on orthorhombic space group $P2_12_12_1$ (♯19) [6] with $Z=4$.

Data were collected on this improved unit cell at ambient temperature up to $2\theta=52.64°$. Data reduction, including the correlation for Lorentz-polarization, decay, and absorption, were performed. Crystal structure was solved and refined with full-matrix least-squares by using Mo1EN, the Enra–Nonius structure determination package, resulting in final R_1 and R_W indices of 0.0654 and 0.0637, respectively. Other details of crystallographic data are summarized in Table 1. The final structural parameters are presented in

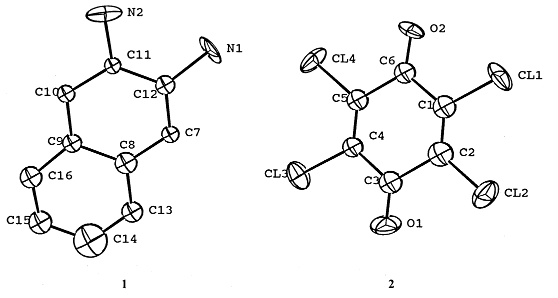

Fig. 1. Molecular structure and atomic numbering of CT complex.

Table 1
Crystallographic data and intensity collection

Formula	$C_{10}H_{10}N_2{\cdot}C_6O_2Cl_4$
Formula weight	404.08
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (♯ 19)
Cell dimensions	
a (Å)	6.866 (3)
b (Å)	14.739 (8)
c (Å)	15.867 (3)
V (Å^3)	1605.6 (1)
Z	4
$D_{calc.}$ (g/cm^3)	1.672
R_1	0.0654
R_W	0.0637

Table 2
Final atomic coordinates and thermal parameter

Atom	*X*	*Y*	*Z*	*B* (Å^2)
Cl 1	0.116 (1)	−0.2444 (4)	0.6297 (4)	3.9 (1)
Cl 2	0.004 (1)	−0.1299 (5)	0.5690 (4)	4.3 (2)
Cl 3	0.087 (1)	0.1786 (4)	0.6485 (4)	3.4 (1)
Cl 4	0.195 (1)	0.0617 (5)	0.8114 (4)	3.6 (1)
O1	0.012 (3)	0.063 (1)	0.5032 (9)	4.4 (4)
O2	0.201 (2)	−0.131 (1)	0.7724 (8)	3.4 (4)
N1	0.072 (3)	−0.747 (1)	0.415 (1)	3.4 (5)
N2	−0.044 (3)	−0.632 (1)	0.545 (1)	3.7 (5)
C1	0.122 (3)	−0.128 (1)	0.631 (1)	2.8 (5)*
C2	0.076 (4)	−0.083 (2)	0.564 (1)	3.4 (6)*
C3	0.051 (3)	0.022 (2)	0.562 (1)	2.8 (5)*
C4	0.107 (3)	0.062 (1)	0.646 (1)	2.2 (4)*
C5	0.147 (3)	0.016 (1)	0.713 (1)	2.4 (5)*
C6	0.161 (3)	−0.086 (1)	0.714 (1)	2.4 (5)*
C7	0.115 (3)	−0.612 (1)	0.326 (1)	1.5 (4)*
C8	0.124 (3)	−0.518 (1)	0.317 (1)	2.4 (5)*
C9	0.082 (3)	−0.459 (1)	0.388 (1)	1.8 (4)*
C10	0.026 (3)	−0.500 (1)	0.464 (1)	1.5 (4)*
C11	0.015 (3)	−0.595 (1)	0.467 (1)	1.3 (4)*
C12	0.068 (3)	−0.651 (1)	0.400 (1)	1.8 (5)
C13	0.178 (3)	−0.479 (1)	0.240 (1)	2.2 (5)
C14	0.185 (4)	−0.387 (2)	0.230 (2)	5.9 (8)
Cl5	0.146 (3)	−0.330 (1)	0.296 (1)	2.8 (5)*
Cl6	0.090 (3)	−0.363 (1)	0.370 (1)	2.5 (5)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) × [$a2\times B(1,1)+b2\times B(2,2)+c2\times B(3,3)+ab(\cos\gamma)\times B(1,2)+ac(\cos\beta)\times B(1,3)+bc(\cos\alpha)\times B(2,3)$].

Table 2. The structure model was drawn using ORTEP, Oak Ridge Thermal Ellipsoid Plot program [7].

3. Results and discussion

2,3-diaminonaphthalene **1** and chloranil **2** were used as donor and acceptor, respectively.

The absorption spectrum of the CT complex **3** in methylene chloride is shown in Fig. 2. The CT complex **3** showed absorption in the range 580–620 nm. This visible band is due to the formation of an intermolecular CT complex. Matsuoka et al. reported that combinations of carbazole analogues and naphthoquinone derivatives gave various dyes absorbing light in the range from the visible to near infrared wavelengths [4].

Table 3
Bond lengths (Å) with e,s,d values given in parentheses

Cl1–C1	1.72 (3)	C2–C3	1.56 (3)
Cl2–C2	1.73 (3)	C3–C4	1.27 (3)
Cl3–C4	1.73 (2)	C4–C5	1.29 (3)
Cl4–C5	1.73 (3)	C5–C6	1.51 (3)
O1–N1	3.16 (3)[a]	C7–C8	1.39 (3)
O1–N2	3.30 (3)[a]	C7–C12	1.35 (3)
O1–C3	1.14 (3)	C8–C9	1.46 (3)
O2–N1	3.28 (3)[a]	C8–C13	1.41 (3)
O2–N2	3.09 (3)[a]	C9–C10	1.40 (3)
O2–C6	1.17 (3)	C9–C16	1.43 (3)
N1–C12	1.42 (3)	C10–C11	1.41 (3)
N2–C11	1.41 (3)	C11–C12	1.40 (3)
C1–C2	1.27 (3)	C13–C14	1.36 (4)
C1–C6	1.49 (3)	C14–C15	1.37 (4)

[a] Intermolecular hydrogen bond.

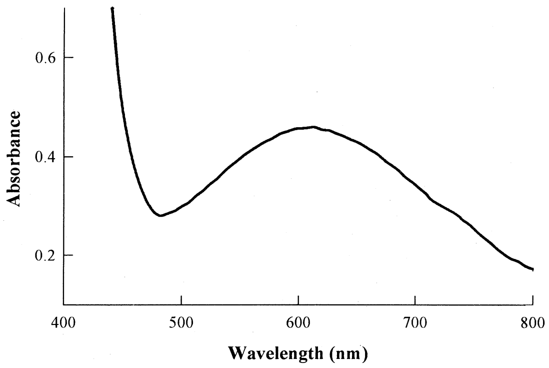

Fig. 2. The absorption spectra of intermolecular CT dye **3**.

To elucidate the packing mode of the donor and acceptor molecule in the crystal, an X-ray structure analysis was carried out. The CT complex **3** arranges in an orthorhombic unit cell of dimensions. $a = 6.866$, $b = 14.739$, $c = 15.867$ Å with $\beta = 111.44°$. The space group is $P2_12_12_1$ (♯19), with four pairs of **1** and **2** residues in unit cell.

Selected bond lengths are given in Table 3. From the results of the intermolecular distance, O1-N1 = 3.16 Å, O1-N2 = 3.30 Å, O2-N1 = 3.28 Å, and O2-N2 = 3.09 Å, the molecules are held together by a weak intermolecular hydrogen bond.

The three dimensional molecular packing of the CT complex in the unit cell is shown in Fig. 3. X-ray study verified the 1:1 composition in the complex. The component molecules are stacked on top of each other to form a column along the *a*-axis with an interplanar Van der Waals distance of 3.43 Å. A stereoview of the crystal packing is shown in Fig. 4.

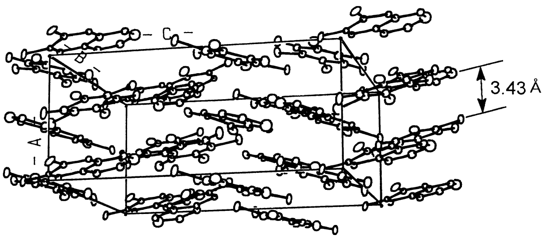

Fig. 3. Unit cell packing diagram of CT complex **3**.

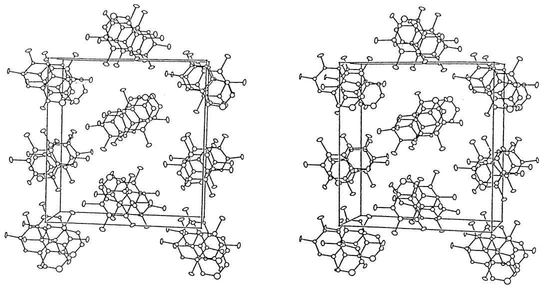

Fig. 4. Stereoview of crystal structure of CT complex **3**.

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