BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 391—395 (1971)

# Inclusion Compounds of Some Charge-Transfer Complexes

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(Received October 3, 1970)

The charge-transfer complex of benzidine and tetracyano-*p*-quinodimethane has been shown to form an inclusion compound with certain molecules such as dichloromethane, dibromomethane and acetone. The molecular volumes of these guest substances are all smaller than 75 cm$^3$/mol, while the substances which are not included have a molecular volume larger than 80 cm$^3$/mol. Besides the size, the molecular shape is also considered to be a primary factor for the formation of the inclusion compound. The heat of formation of the inclusion compound with dichloromethane as a guest was determined to be 11.1±1 kcal per mole of the guest substance by the thermochemical measurements. Similar inclusion compounds were also obtained, when 3,3′-diaminobenzidine, 3,3′-dichlorobenzidine and *o*-tolidine were used in place of benzidine.

In a previous paper,[1] we have reported that benzidine (BD) and tetracyanoquinodimethane (TCNQ) form two types of complexes, the type being determined by the solvent used in the preparation. One is the complex which contains solvent molecules in addition to BD and TCNQ, (BD·TCNQ·S)[2], and the other is the complex which does not contain solvent molecules, BD·TCNQ(n). The amount of the solvent contained in the BD·TCNQ·S complex is as much as those of BD and TCNQ, and several solvents which are different in chemical properties form this type of complexes. In the present paper, the BD·TCNQ·S complex will be shown to possess the characteristics of the inclusion compounds.

A variety of inclusion compounds have been studied[3,4] and are known to possess the following common features.[5] They are composed of two components, host and guest, and the host lattice has cavities to include the guest molecules. Although many kinds of molecules are to be included in the cavity of the same host lattice, the formation of an inclusion compound is normally controlled by the size and shape of a guest molecule. The force binding the guest molecules is intermolecular one and the heats of formation of the inclusion compounds fall usually in the range of 5—12 kcal per mole of the guest substance.

The compounds studied here, whose host lattice is comprised by the organic charge-transfer complexes, are found to possess these characteristics.

## Experimental

*Chemicals.* Benzidine, *o*-tolidine (TL), 3,3′-diaminobenzidine (DABD), and 3,3′-dichlorobenzidine (DCBD) were obtained from commercial sources, and used after purification by recrystallization from ethanol or carbon tetrachloride. Synthesis and purification of TCNQ were described previously.[6]

*Complex Preparation.* BD·TCNQ·S($CH_2Cl_2$): To a solution of 35 mg of BD in 80 m*l* of dichloromethane was added a solution of 44 mg of TCNQ in 120 m*l* of dichloromethane at room temperature, and shiny dark green crystals thus formed were collected.

BD·TCNQ(n) (from Chloroform): Dark green polycrystals were obtained by mixing a solution of 16 mg of BD in 10 m*l* of chloroform with a solution of 23 mg of TCNQ in

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[1] M. Ohmasa, M. Kinoshita, and H. Akamatu, This Bulletin, **42**, 2402 (1969).

[2] For simplicity, the complex of BD with TCNQ which contains solvent molecules will be abbreviated as BD·TCNQ·S, and if the solvent is required to be specified, the notation BD·TCNQ·S (chemical formula of the solvent)is used, *e.g.*, BD·TCNQ·S($CH_2Cl_2$).

[3] L. Mandelcorn, *Chem. Rev.*, **59**, 827 (1959).

[4] F. Cramer, *Angew. Chem.*, **68**, 115 (1956).

[5] J. H. van der Waals and J. C. Platteeum, *Advan. Chem. Phys.*, **2**, 1 (1959).

[6] M. Ohmasa, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **41**, 1998 (1968).

60 m*l* of chloroform at room temperature.

Other complexes including TL, DABD, and DCBD complexes were prepared in a similar manner.

*Measurement of X-Ray Diffraction Patterns.* X-Ray diffraction patterns of powdered samples were measured at room temperature with a diffractometer, Rigaku Denki Geigerflex.

*Calorimetric Measurement.* A conductive twin microcalorimeter made by Oyodenki Co. was used to determine the heats of reaction, $(-\Delta H_2)$ and $(-\Delta H_3)$, for the reactions defined by Eqs. (2) and (3) in the following section. The heats were measured at constant temperature, 25°C and at 1 atm.

The procedures of the measurement are as follows. (i) About 400 mg of the powdered sample was sealed in a thin-wall glass tube. The saturated solution of BD·TCNQ complex in dichloromethane was placed in the reaction vessel and in the reference vessel. The volume of the solution in each vessel was set at 50 m*l*.

(ii) The glass tube containing the sample was placed in the reaction vessel and the vessels were laid in the heat resservoir overnight to achieve the thermal equilibrium.

(iii) The glass tube was then broken and the reaction was started. The difference of the temperature between the reaction vessel and the reference vessel was recorded until the reaction was completed and the temperature of the reaction vessel became constant. It took about 3 hr.

(iv) A certain amount of heat was then generated on the side of the reaction vessel by the standard heater and the difference of the temperature was recorded again.

(v) The areas below the recorded curves for the heat of the reaction and the reference heat were measured and the former heat was calculated by using these areas and the latter heat.

(vi) The heat of reaction calculated in this way was then corrected for the heat generated by breaking the glass tube, which was measured in a blank test.

For this experiment, the BD·TCNQ(n) complex was prepared from chloroform. The special grade dichloromethane from Wako-junyaku Co. was used.

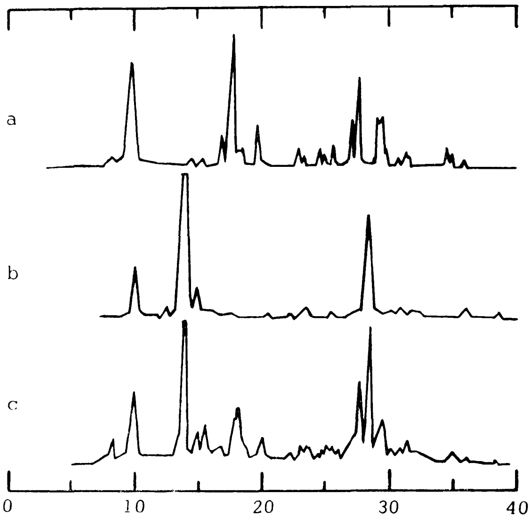

Fig. 1. The X-ray diffraction patterns of powders of BD·TCNQ complexes.
a) BD·TCNQ·S($CH_2Cl_2$)
b) BD·TCNQ(n)
c) BD·TCNQ(n) which was exposed to dichloromethane vapor overnight and then placed in a vacuum for several hours (see the text).

*Thermogravimetric Analysis (TGA).* Thermogravimetric analysis was performed using thermobalance made by Tokyo Koki Seizosho. The heating rate was about 0.75°C/min. Nitrogen gas was slowly streamed about the sample during the measurement.

*Differential Thermal Analysis (DTA).* The differential thermal analysis for the freshly prepared sample of BD·TCNQ·S($CH_2Cl_2$) complex was made with a Rigakudenki DTA apparatus in the air. The heating rate was 2.5°C/min.

*Characterization of BD·TCNQ System.* To know whether the complex prepared in a solvent contains the solvent molecules or not, the infrared absorption spectrum of the complex was examined. As was described in the previous paper,[1] the spectra of BD·TCNQ·S complexes are similar to one another and are quite different from that of BD·TCNQ(n) complex. In the former spectra are observed the absorption bands which are assigned to the vibrational modes of the solvent molecule contained in the complex, while the bands of the solvent molecule are not observed in the latter. These features are employed as criteria for the characterization of the BD·TCNQ complexes.

*Composition of Complexes of TCNQ with TL, DABD, and DCBD.* The ratios, (donor) : (acceptor) : (solvent), of the complex of TL, DABD, and DCBD were calculated from the results of elementary analysis of the complex.

## Results and Discussion

*X-Ray Diffraction Patterns.* The X-ray diffraction patterns for powders of BD·TCNQ system are shown in Fig. 1. The pattern for BD·TCNQ·S($CH_2Cl_2$) (Fig. 1a) is quite different from that of BD·TCNQ(n) (Fig. 1b). It is therefore concluded that these two complexes have different crystal structures.

The BD·TCNQ(n) and BD·TCNQ·S complexes readily change their structures to each other. When a sample of BD·TCNQ·S($CH_2Cl_2$) is heated on a thermobalance, the weight of the sample begins to reduce at about 50°C and becomes constant at about 120°C. When the heated sample is cooled to the room temperature, its X-ray diffraction pattern becomes identical with that for the BD·TCNQ(n) complex. On the other hand, when a sample of BD·TCNQ(n) is exposed to the vapour of dichloromethane at about 200 mmHg and is laid overnight at room temperature, the X-ray diffraction pattern becomes identical with that for BD·TCNQ·S ($CH_2Cl_2$).

The X-ray diffraction pattern illustrated in Fig. 1c was obtained for the sample of BD·TCNQ(n) which was exposed to the vapour of dichloromethane in the manner described above and then sealed in a vacuum for several hours at room temperature. This pattern is well interpreted as a superposition of the pattern for BD·TCNQ·S($CH_2Cl_2$) complex and that for the BD·TCNQ(n) complex.

These facts show that the solvent molecules contained in the complex are very weakly bound in the crystal lattice. Therefore, it is plausible to conclude that the BD·TCNQ·S($CH_2Cl_2$) complex is a kind of inclusion compounds. If so, this complex is a new family of the inclusion compounds in the sense that its host lattice is composed of a charge-transfer complex.

*Thermodynamic Properties.* The heat of formation of the inclusion compound is rather small, because the guest molecule is bound to the host lattice by the intermolecular force. Many inclusion compounds show the value in the range of 5—12 kcal per mole of the guest molecule.[7–10)]

The heat of formation $(-\Delta H_f)$ of BD·TCNQ·S($CH_2Cl_2$) in the following reaction was measured by the calorimetric method.

$$\begin{aligned}&\mathrm{BD{\cdot}TCNQ(n)(s)} + 1.8\,\mathrm{CH_2Cl_2(g)}\\&\quad = \mathrm{BD{\cdot}TCNQ{\cdot}S(s)};\ \Delta H_f \qquad (1)\end{aligned}$$

where (s) and (g) denote that the substance is in the solid state and in the gaseous state, respectively. It was assumed that one mole of BD·TCNQ·S($CH_2Cl_2$) contains 1.8 mole of dichloromethane.[11)]

Equation (1) is considered to be equivalent to the combination of the following thermochemical equations (2)—(4) according to Hess' law.

$$\begin{aligned}&\mathrm{BD{\cdot}TCNQ(n)(s)} + 1.8\,\mathrm{CH_2Cl_2(l)}\\&\quad = \mathrm{BD{\cdot}TCNQ{\cdot}S(sol)};\ \Delta H_2 \qquad (2)\end{aligned}$$

$$\mathrm{BD{\cdot}TCNQ{\cdot}S(sol)} = \mathrm{BD{\cdot}TCNQ{\cdot}S(s)};\ \Delta H_3 \qquad (3)$$

$$1.8\,\mathrm{CH_2Cl_2(g)} = 1.8\,\mathrm{CH_2Cl_2(l)};\ \Delta H_4 \qquad (4)$$

$$\Delta H_f = \Delta H_2 + \Delta H_3 + \Delta H_4 \qquad (5)$$

Here, (l) denotes that the substance is in the liquid state and (sol) shows that the solid substance is placed in the saturated solution of BD·TCNQ complex in dichloromethane.

The heats of reactions, $(-\Delta H_2)$ and $(-\Delta H_3)$, were measured calorimetrically. The heat of condensation, $(-\Delta H_4)$, was calculated from the value given in a literature.[12)] In the measurement, the sample of BD·TCNQ(n) or BD·TCNQ·S complex was dropped into the saturated solution of BD·TCNQ complex in dichloromethane in order to avoid the effect of dissolution of the solid. The values of $\Delta H_f$, $\Delta H_2$, $\Delta H_3$, $\Delta H_4$ obtained are given in Table 1.

The heat of formation of BD·TCNQ·S($CH_2Cl_2$) per mole of dichloromethane is thus estimated as 11 kcal/mol. This value is reasonable in comparison with that for ordinary inclusion compounds.

Table 1. HEAT OF FORMATION OF BD·TCNQ·S($CH_2Cl_2$) COMPLEX FROM BD·TCNQ(n) COMPLEX AND DICHLOROMETHANE GAS

| | |
|---|---|
| A) Heat of formation per one mole of the complex | |
| $-\Delta H_2$: | 9.1±1 kcal/mol |
| $-\Delta H_3$: | −1.2±1 kcal/mol |
| $-\Delta H_4$:[a)] | 12.0 kcal |
| $-\Delta H_f$: | 19.9±2 kcal/mol |
| B) Heat of formation per one mole of dichloromethane | |
| | 11.1±1 kcal/mol |

a) This value was calculated from the value given in Ref. 12.

The TGA curve and the differential thermogram for freshly prepared sample of BD·TCNQ·S($CH_2Cl_2$) are presented in Figs. 2 and 3, respectively. The amount of the weight loss of the sample shows that the solvent molecules are completely desorbed from the sample during the heating. This was further confirmed by the fact that, as was mentioned before, the X-ray diffraction pattern of the sample after TGA measurement became identical with that of BD·TCNQ(n).

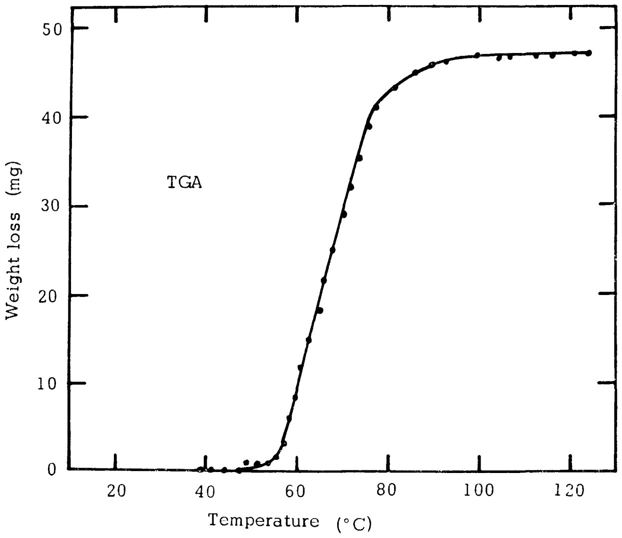

Fig. 2. The thermogravimetric analysis (TGA) curve for BD·TCNQ·S ($CH_2Cl_2$) complex.
Heating rate was about 0.75°C/min. The weight of the sample was 165 mg before the measurement and 118 mg after the measurement.

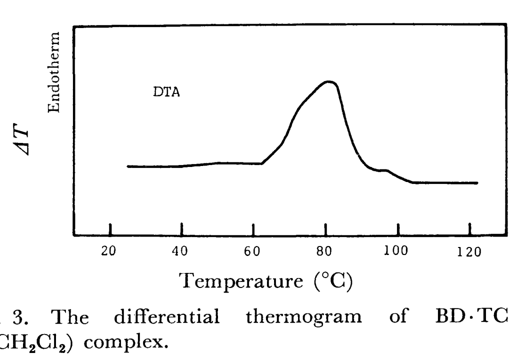

Fig. 3. The differential thermogram of BD·TCNQ·S ($CH_2Cl_2$) complex.
Heating rate was about 2.5°C/min. The weight of the sample was 136 mg before the measurement and 97 mg after the measurement.

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7) R. M. Barrer and A. V. J. Edge, *Proc. Roy. Soc., Ser. A*, **300**, 1 (1967).

8) S. A. Allison and R. M. Barrer, *Trans. Faraday Soc.*, **64**, 549 (1968).

9) R. D. Whitaker, A. J. Barreiro, P. A. Furman, W. C. Guida, and E. S. Stallings, *J. Inorg. Nucl. Chem.*, **30**, 2921 (1968).

10) E. E. Aynsley, W. A. Campbell, and R. E. Dodd, *Proc. Chem. Soc.*, **1957**, 210.

11) The solvent molecules contained in the complex escape slowly from the complex in air at room temperature, so that the composition of the complex changes with time.

As was reported in Ref. 1, the composition of BD·TCNQ·S ($CH_2Cl_2$) determined spectroscopically was (BD) : (TCNQ) : ($CH_2Cl_2$) = 1.0 : 1.1 : 1.6. But this composition is not so accurate, because evaporation of dichloromethane from the solid was not strictly considered.

To find the reliable value of the solvent content, TGA measurement of a freshly prepared sample of BD·TCNQ·S($CH_2Cl_2$) was carried out. The composition of the complex was then calculated from the result of the measurement and was found as (donor) : (acceptor) : (solvent) = 1 : 1 : 1.8. This result is adopted here.

12) "Landolt-Börnstein, Zahlenwerte und Funktionen," Vol. II, part 4, Springer, Berlin (1961), p. 292.

The curves shown in Figs. 2 and 3 indicate that the included dichloromethane molecules were evaporated in one step, which means that all the solvent molecules are bound equivalently in the crystal of BD·TCNQ·S ($CH_2Cl_2$).

*Inclusion of Solvent Molecules in BD·TCNQ System.* It seems that the formation of the BD·TCNQ·S complex is mainly determined by the structural requirement, that is, by the size and the shape of the solvent molecule used in the preparation of the complex. This also indicates that the BD·TCNQ·S complexes are inclusion compounds.

The intermolecular forces between the solvent molecule and the host lattice are not considered to be the determining factor of the formation of the BD·TCNQ·S complex. The molecular volume, the molecular polarizability and the dipole moment of the solvent molecules used in the experiment are compared in Table 2. The type of the complex (solvent contained or not) is also given in the table. The molecular polarizability and the dipole moment are closely related to the dispersion force[13,14] and the electrostatic force which act on the solvent molecule, but these two quantities of the solvents examined so far do not seem to be related to the formation of BD·TCNQ·S complexes. For example, chloroform and 1,1-dichloroethane which give BD·TCNQ(n) complexes have larger molecular polarizability than dichloromethane and ethyl bromide which give BD·TCNQ·S complexes, and the dipole moment of 1,1-dichloroethane is also larger than that of dichloromethane.

Table 2. Molecular volume, molecular polarizability and dipole moment of the solvent used in preparation of BD·TCNQ complexes

| Solvent | Type of complex[a] | Molecular volume[b] | Molecular polarizability[c] | Dipole moment[d] |
|---|---|---|---|---|
| $CHCl_3$ | n | 80.5 | 85.2 | 1.01 |
| $CH_3CHCl_2$ | n | 84.1 | 85.2 | 2.06 |
| $CH_2Cl_2$ | s | 64.0 | 65.0 | 1.60 |
| $CH_3CH_2Br$ | s | 74.6 | 75.6 | 2.03 |
| $CH_2Br_2$ | s | 69.6 | 87.2 | 1.43 |
| $CH_3COCH_3$ | s | 73.6 | 64.5 | 2.88 |
| $CH_3NO_2$ | s | 53.7 | 49.8 | 3.46 |
| $CH_3CN$ | s | 52.2 | 44.1 | 3.92 |
| $CH_2ClCH_2Cl$ | (s)[e] | 80.1 | 86.0 | 1.47 |

a) The type of BD·TCNQ complex prepared in the solvent. n: BD·TCNQ(n), s: BD·TCNQ·S

b) The value in the unit of $cm^3$/mole at 20°C.

c) These values are calculated by the equation, $(4/3)\pi N\alpha = [(n^2-1)/(n^2+2)](M/d)$ where $n$ is refractive index, $M$ is molecular weight, $d$ is density, $N$ is Avogadro's number and $\alpha$ is molecular polarizability. The value of $\alpha$ at 20°C in the unit of $10^{-25}$ $cm^3$ is listed here.

d) debye unit.

e) The complex prepared in this solvent is considered to include solvent molecules partially, because the infrared absorption spectrum of this complex is a superposition of the spectra of BD·TCNQ(n) and BD·TCNQ·S complexes.

The presence of some functional groups in the solvent molecule is not again the determining factor for the formation of BD·TCNQ·S complexes, because 1,1-dichloroethane gives a BD·TCNQ(n) complex, although dichloromethane and ethyl bromide give BD·TCNQ·S complexes.

Unlike the factors mentioned above, there is a close correlation between the molecular volume of the solvent molecule and the formation of BD·TCNQ·S complexes. As is seen in Table 2, the molecular volumes of chloroform and 1,1-dichloroethane which give BD·TCNQ(n) complexes are larger than those of the solvents which are found to be included in BD·TCNQ system. Therefore it is likely that the formation of the BD·TCNQ·S complex is controlled by the size of the solvent molecule on the one hand.

On the other hand, the molecular shape of chloroform and 1,1-dichloroethane is pyramidal, while that of dichloromethane is regarded as a triangle, if the van der Waals' radius of hydrogen atom is neglected. The shape of other solvent molecules which form BD·TCNQ·S complexes can also be regarded as triangular. Acetonitrile molecule is the only exception which is a linear one. Although both chloroform and dichloromethane molecules are composed of carbon, hydrogen and chlorine atoms and are methane type molecules, chloroform molecule is not included in the BD·TCNQ system, while dichloromethane gives a BD·TCNQ·S complex. This shows that the molecular shape of the solvent is another important factor, which determines the formation of the BD·TCNQ·S complex. 1,2-Dichloroethane whose molecular volume is as large as that of chloroform is partially included in the BD·TCNQ system as is shown in Table 2. This fact also indicates the importance of the molecular shape of the solvent.

*Complexes of TCNQ with TL, DABD, and DCBD.* The charge-transfer complexes of TL, DABD, and DCBD with TCNQ were expected to form inclusion compounds with certain solvents such as dichloromethane, because the molecular structures of these donors are similar to that of BD. Some of these complexes were prepared using dichloromethane or chloroform as a solvent. Their compositions were determined by analyzing the results of elementary analysis. The results are presented in Table 3. As is seen in the table, the system of TL·TCNQ contains a considerable amount of dichloromethane or chloroform and these complexes are considered to be inclusion compounds. The complex of DABD·TCNQ prepared in dichloro-

Table 3. Composition of the complexes of TCNQ with TL, DABD and DCBD

| Donor | Solvent used in preparation | Mole ratios[a] |
|---|---|---|
| TL | $CH_2Cl_2$ | 1 : 1.00 : 1.23 |
| TL | $CHCl_3$ | 1 : 1.07 : 0.52 |
| DABD | $CH_2Cl_2$ | 1 : 1.00 : 0.45 |
| DCBD | $CH_2Cl_2$ | 1 : 0.80 : 0.16 |

a) (Donor) : (Acceptor) : (Solvent)

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[13] F. London, *Z. Phys. Chem.*, **B11**, 222 (1930).

[14] D. F. Evans and R. E. Richards, *Proc. Roy. Soc., Ser. A*, **223**, 238 (1954).

methane is also regarded as an inclusion compound for the same reason. The complex of DCBD·TCNQ, however, contains a small amount of dichloromethane, and it is questionable that the complex is an inclusion compound. As is shown in Table 3, the amount of TCNQ is less than that of DCBD by a small amount which is nearly the same as the amount of the included solvent. The solvent molecules in this complex, therefore, may be trapped in the vacancies of the TCNQ molecules.

Tolidine·TCNQ system forms an inclusion compound with chloroform in contrast to the BD·TCNQ system. The physical properties of TL·TCNQ·S($CHCl_3$) are similar to those of BD·TCNQ·S($CH_2Cl_2$).[15] It seems, therefore, that the structure of the donor molecule is also an important factor for the formation of the inclusion compounds of this type.

The authors wish to thank Professor Nobufusa Saito for the use of his laboratory thermal analysis facilities and Mr. Kenji Nakada for his kind help in the DTA experiments.

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15) M. Ohmasa, M. Kinoshita, and H. Akamatu, This Bulletin, **44**, 395 (1971).