

Cadmium(5^3P_1)-Photosensitized Luminescence of Some Compounds Containing Three Donor Atoms

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The cadmium photosensitized luminescence of some compounds containing three donor atoms (N and/or O) has been investigated by the steady illumination method at temperatures between 453 and 553 K. Broad emission spectra in the visible region were observed with diethylenetriamine (DETA), dipropylenetriamine (DPTA), bis-(2-methoxyethyl) ether (BMOEE), bis-2-methoxyethylamine (BMOEA), and bis-(dimethylaminoethyl) ether (BDAEE). By comparing each of these spectra with the spectra of the corresponding bifunctional compounds, we can resolved these spectra into three component bands for DETA, DPTA, BMOEE, and BMOEA, and into four component bands for BDAEE. The longest wavelength bands were observed for the first time. They can be assigned to different types of 1:1 exciplexes (acyclic, monocyclic, and bicyclic). The enthalpy changes of the chelations were evaluated from the temperature dependences of the intensities of the bands and were found to depend on the type of chelating atom.

Although it is well known that excited triplet mercury^{1,2)} and cadmium³⁾ atoms form complexes with some nucleophilic reagents, such as NH_3 , H_2O , aliphatic amines, alcohols, and ethers, there have been few studies of compounds containing more than two hetero atoms. Recently the cadmium-photosensitized reactions of diamines were studied in detail.^{4,5)} It has been concluded that two kinds of (acyclic and cyclic) exciplexes are formed between an excited cadmium atom and a diamine molecule; these two exciplexes fluoresce with two distinct emission bands. Further, we observed analogous emission bands with a diether and aminoethers,⁶⁾ although their band separations are smaller than those for the diamines. So far we know, there is no report on the cadmium-sensitized luminescence of compounds containing three donor atoms. For such compounds, many types of exciplexes can be formed. Since the position of the emission band from the exciplex depends largely on the kind and the number of the donor atom, it is possible to distinguish clearly between the types of exciplexes. In the present paper, we will report the cadmium-sensitized luminescence of such compounds (triamines, a triether, and aminoethers).

Experimental

Diethylenetriamine (DETA), dipropylenetriamine (DPTA), bis-2-methoxyethylether (BMOEE), bis-2-methoxyethylamine (BMOEA), and bis-2-dimethylaminoethylether (BDAEE) were obtained from commercial sources (G. R. grade). Triamines were used after drying with potassium hydroxide and repeated trap-to-trap distillation. BMOEA, BMOEE, and BDAEE were dried with calcium hydride and used after repeated distillation. The metal used for the source of ground state cadmium atoms was of high purity grade (99.9999%).

The experimental setup has been described in detail previously.^{4,7)} The 326.1 nm resonance line was obtained from a spiral cadmium discharge lamp made of pyrex glass placed in a furnace kept at 523 K and used to excite ground state cadmium atoms in the cell to the 5^3P_1 state. A Hitachi

spectrophotometer (Model 139) equipped with a photomultiplier tube (R 446) was used to monitor the resonance radiation at 326.1 nm and the sensitized luminescence. Since the vapor pressure of these compounds were low at room temperature, a portion of the vacuum line was wound with flexible insulated heating tape to keep the samples at elevated temperatures of sufficient vapor pressures. The resonance line was quenched almost completely by substrates of these pressures. Although the vapor pressures could not measured due to low vapor pressures at room temperature, they were estimated to be higher than 100 Pa for amino compounds and 500 Pa for BMOEE from the quenching rate constants reported for similar compounds.

Results

Figure 1 shows the spectra of the cadmium-sensitized luminescence of DPTA at 453 and 533 K. The spectra were corrected for the wavelength dependence of the sensitivity of the detection system which was determined by using standard fluorescence solutions of quinine sulfate and *N,N*-dimethyl-*m*-nitroaniline and normalized to the same total intensity. By comparing these spectra with the emission spectrum of 1,3-propanediamine, each of the spectra can be separated into the component bands. The separated three bands (bands A, B, and C) at two temperatures are also shown in Fig. 1. In analogy with diamines, bands A and B are assigned to acyclic and monocyclic exciplexes, respectively. Although the two types of the monocyclic exciplex are possible, we can not distinguish them from the band positions, because it was found that the band position does not depend significantly on the size of chelate ring for diamines.⁵⁾ From our recent investigations of the effect of size of the chelate ring on the stability of the cyclic exciplexes between an excited cadmium atom and diamines, we showed that the five-membered cyclic exciplex is most stable and that the stability decreases with increase in the size of the ring. Since it was observed that with 1,6-hexanediamine a cyclic (9 membered) exciplex was not formed, for DPTA there

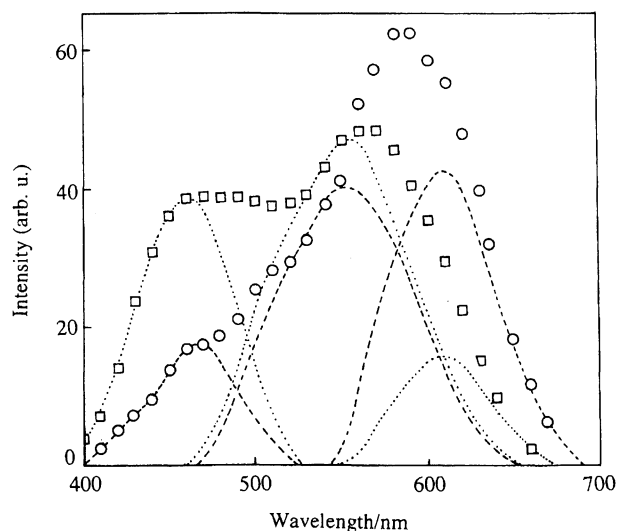


Fig. 1. Sensitivity corrected emission spectra of cadmium-photosensitized luminescence of DPTA at 180 °C (○) and 260 °C (□).

is little probability of formation of a cyclic exciplex (10 membered) by the interaction of two terminal nitrogen atoms. The third band (band C) is a new band; it can be assigned to a bicyclic exciplex formed by coordinating with all the nitrogen atoms of the substrate molecule with an excited cadmium atom from the structure of the substrate. Therefore, the resolved three bands can be assigned to the following three types of 1:1 exciplexes (Chart 1):

Figure 1 shows that the intensity of band A increases and that of band C decreases with increasing temperature. This implies the existence of equilibria among the exciplexes (exciplexes A^* , B^* , and C^* for Bands A, B, and C, Chart 1). The equilibrium between A^* and B^* shifts from B^* to A^* and that between B^* and C^* shifts from C^* to B^* with increasing temperature, as will be discussed later in detail. The emission spectrum for DETA was similar to that for DPTA and can be separated into three component bands. The emission spectra for BMOEE and BMOEA were also separated into three component bands by comparing them with those reported for 1,2-dimethoxyethane and 2-methoxyethylamine, respectively (Fig. 2). The bands were assigned to acyclic, monocyclic, and bicyclic exciplexes in a similar manner to that explained above. Although the first donor atom can not be specified for DETA, DPTA, and BMOEE, the initial attack of an excited cadmium atom must be to the *N*-atom for BMOEA, judging from

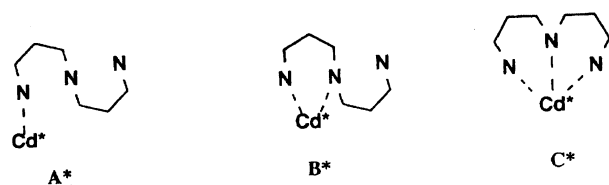


Chart 1.

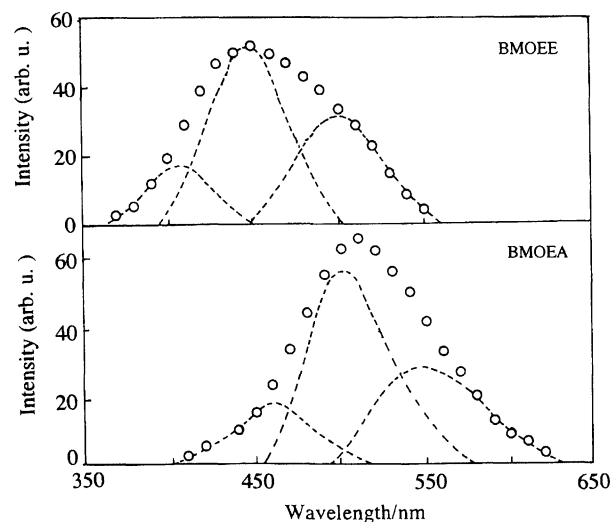


Fig. 2. Sensitivity corrected emission spectra of cadmium-photosensitized luminescence of BMOEE and BMOEA at 180 °C.

the position of band A.

The situation with BDAEE is rather complicated. The more reactive *N* atoms are at the terminal positions and an *O* atom is in the middle. For this compound, five exciplexes can be formed with an excited cadmium atom. As was mentioned in a previous paper,⁶⁾ an excited cadmium atom predominantly attacks the *N*-atom for compounds having *O*- and *N*-atoms, because the quenching efficiency of the $Cd(^3P_1)$ for *O*-atom is much smaller than that for *N*-atom. Actually, no emission band concerning the *O*-atom at 400 nm was observed for this compound. There is still the possibility of the formation of four types of exciplexes, shown as follows (Chart 2): From the results obtained previously,^{4,6)} the emission bands from these exciplexes are expected to appear at about 450 (D^*), 500 (E^*), and 550 (F^*) (Chart 2). From the close examination of normalized emission spectra for BDAEE obtained at several temperatures, they can be separated into four component bands which have the maximum wavelengths corresponding to the above values (Fig. 3). The longest wavelength band can be assigned to exciplex (G^*).

Figure 4 shows the temperature dependences of the ratios of the intensities of four bands (D, E, F, and G) to the total intensity. As is shown in Fig. 4, the proportion of band D increases and that of band G decreases with increasing temperature. These temperature dependences are consistent with a general tendency.

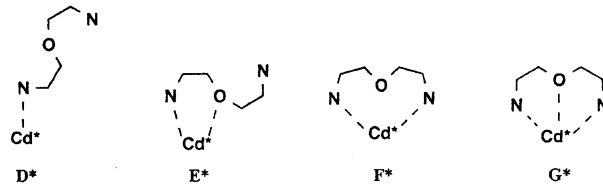


Chart 2.

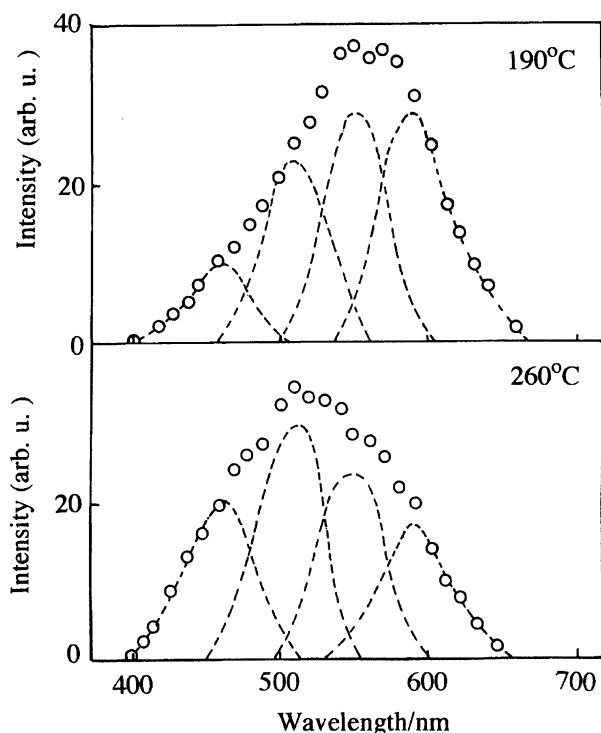


Fig. 3. Sensitivity corrected emission spectra of cadmium-photosensitized luminescence of BDAEE at 190 and 260 °C.

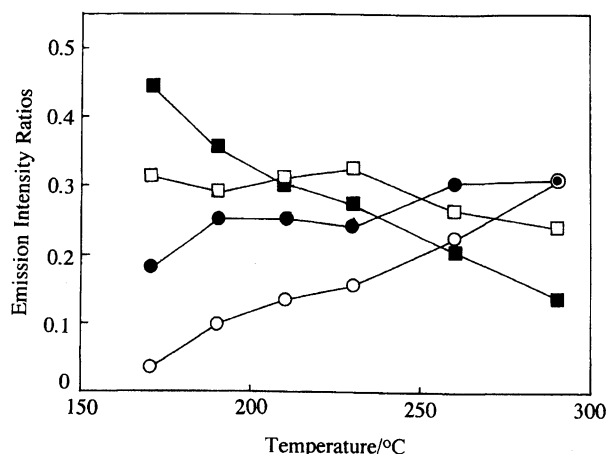


Fig. 4. The temperature dependences of the intensity ratios of four bands (D, E, F, and G) to the total intensity for BDAEE. Band D (○), Band E (●), Band F (□), and Band G (■).

The wavelengths of the peaks of the bands are listed in Table 1.

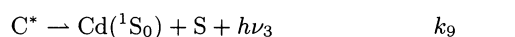
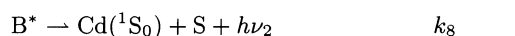
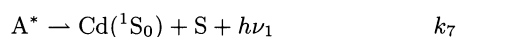
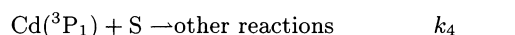
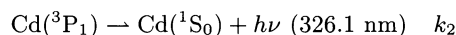
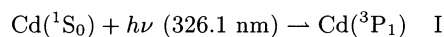
Discussion

To explain the experimental results of the cadmium-sensitized reactions of trifunctional compounds other than BDAEE, the following set of reactions is considered:

Table 1. Peak Wavelengths of Emission Bands

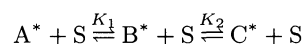
Compounds	Band A/nm	Band B/nm	Band C/nm
DETA	470	560	620
DPTA	460	550	610
BMOEE	400	450	500
BMOEA	460	500	540
BDAEE	460 ^{a)}	510 ^{b)} 550 ^{c)}	590 ^{d)}

a) Band D, b) Band E, c) Band F, d) Band G.



Here, A^* , B^* , and C^* stand for acyclic, monocyclic, and bicyclic exciplexes. In a previous paper,⁸⁾ we showed that a simulation of the temporal profiles of the two emission bands for *N,N,N',N'*-tetramethyl-1,3-propanediamine gave the results that the decay rates of acyclic and cyclic exciplexes are the same. This shows that two exciplexes are in equilibrium under conditions used. Since the conditions of this work are similar to those used previously, we assumed that fast equilibria among three exciplexes are attained in the present system.

As mentioned above, the intensity of band C decreased and that of band A increased with the increase in the temperature. These temperature dependences of the band intensities are similar to those observed for compounds containing two donor atoms. This indicates the existence of equilibria among the exciplexes; they are represented as follows:



The following equations for the intensities of the exciplex emission at high pressures of the substrates, where the cadmium resonance radiation is completely quenched, were derived by a steady-state treatment based on the assumption that fast equilibria among three exciplexes are attained:

$$I(\text{band A}) = I_{\text{total}} \frac{k_7}{k_7 + K_1 k_8 + K_1 K_2 k_9}$$

$$I(\text{band B}) = I_{\text{total}} \frac{K_1 k_8}{k_7 + K_1 k_8 + K_1 K_2 k_9}$$

$$I(\text{band C}) = I_{\text{total}} \frac{K_1 K_2 k_9}{k_7 + K_1 k_8 + K_1 K_2 k_9}$$

Table 2. Ratios of Emission Intensities at 230 °C and Values of ΔH° and $\Delta \tilde{\nu}$

Compounds	I(Band B)	I(Band C)	ΔH°_1	ΔH°_2	$\Delta \tilde{\nu}_1$	$\Delta \tilde{\nu}_2$
	I(Band A)	I(Band B)	kJ mol^{-1}	kJ mol^{-1}	cm^{-1}	cm^{-1}
DETA	12.35	0.14	-37	-33	3420	1730
DPTA	1.53	0.76	-29	-32	3560	1790
BMOEE	2.06	0.46	-21	-19	2780	2220
BMOEA	1.97	0.44	-15	-15	1740	1480
BDAEE	1.56 ^{a)}	1.13 ^{c)}	-18 ^{a)}	-28 ^{c)}	2130 ^{a)}	2660 ^{c)}
	2.09 ^{b)}	0.84 ^{d)}	-30 ^{b)}	-15 ^{d)}	3560 ^{b)}	1230 ^{d)}

a) Band E/Band D, b) Band F/Band D, c) Band G/Band E,
d) Band G/Band F.

where $I(\text{band A})$, $I(\text{band B})$, and $I(\text{band C})$ are the integrated intensities of bands A, B, and C; I_{total} is the total intensity of bands A, B, and C ($I_{\text{total}} = I(\text{band A}) + I(\text{band B}) + I(\text{band C})$); K_1 and K_2 are the equilibrium constants expressed as follows:

$$K_1 = \frac{[\text{B}^*]}{[\text{A}^*]} \text{ and } K_2 = \frac{[\text{C}^*]}{[\text{A}^*]}$$

The ratios of the intensities of bands A, B, and C are expressed by

$$\frac{I(\text{band B})}{I(\text{band A})} = K_1 \frac{k_8}{k_7}$$

$$\frac{I(\text{band C})}{I(\text{band B})} = K_2 \frac{k_9}{k_8}$$

If the values of k_8/k_7 and k_9/k_8 are independent of the temperature, the values of ΔH° for the equilibria among the exciplexes can be obtained from the slopes of the straight-line plots of $\ln [I(\text{band B})/I(\text{band A})]$ and $\ln [I(\text{band C})/I(\text{band B})]$ vs. $1/T$ (shown in Figs. 5 and 6), and are listed in Table 2. As pointed out in the previous papers,^{4,5)} it is difficult to see how the values of k_7 , k_8 , and k_9 vary with the temperature. Since the ratios of k_8/k_7 and k_9/k_8 are the ratios of the rate con-

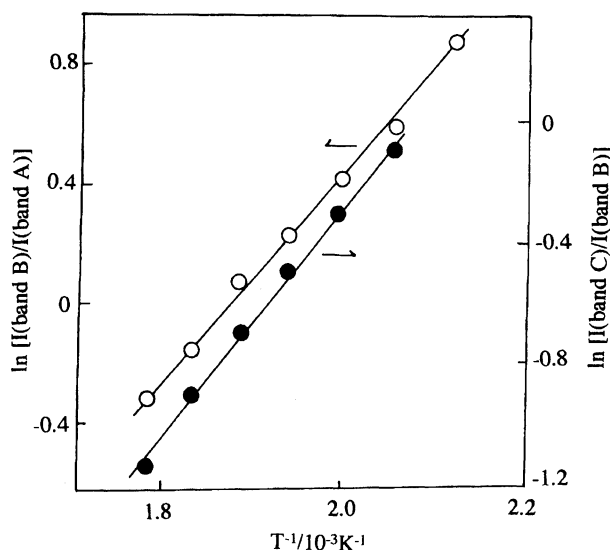


Fig. 5. Plots of $\ln [I(\text{band B})/I(\text{band A})]$ and $\ln [I(\text{band C})/I(\text{band B})]$ against $1/T$ for DPTA.

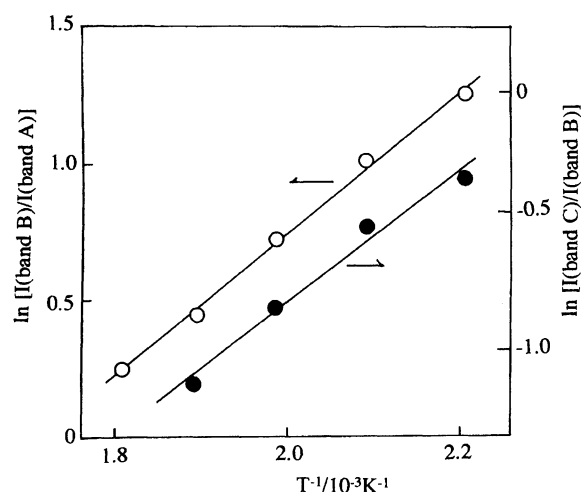


Fig. 6. Plots of $\ln [I(\text{band B})/I(\text{band A})]$ and $\ln [I(\text{band C})/I(\text{band B})]$ against $1/T$ for BMOEE.

stants for similar radiative processes, these ratios are expected to depend little on the temperature.

In a similar manner to that mentioned above, the following relations are obtained for BDAEE.

$$\frac{I(\text{band E})}{I(\text{band D})} = K_3 \frac{k_{11}}{k_{10}}$$

$$\frac{I(\text{band F})}{I(\text{band D})} = K_4 \frac{k_{12}}{k_{10}}$$

$$\frac{I(\text{band G})}{I(\text{band F})} = K_5 \frac{k_{13}}{k_{12}}$$

Here, K_3 , K_4 , and K_5 denote the equilibrium constants for the following equilibria (Chart 3): and k_{10} – k_{13} denote the rate constants for the emission processes from the exciplexes D^* , E^* , F^* , and G^* , respectively. The values of ΔH° for the equilibria were estimated from the straight lines shown in Fig. 7, and are listed in Table 2.

As is shown in Table 2, the values of ΔH°_2 are very similar to those of ΔH°_1 for all compounds, and the

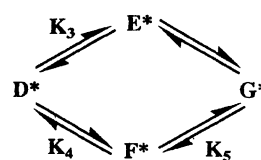


Chart 3.

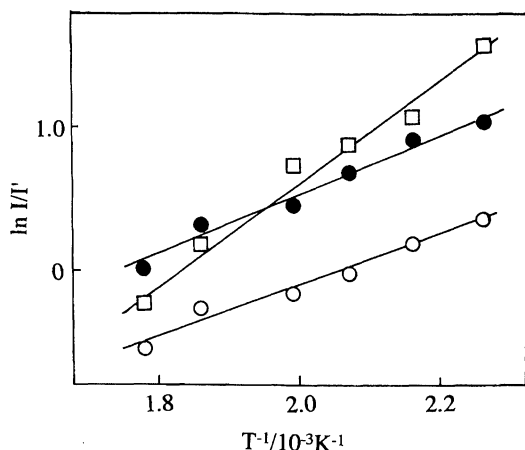


Fig. 7. Plots of $\ln(I/I')$ against $1/T$ for BDAEE, where $I/I' = I(\text{band E})/I(\text{band D})$ (●), $I(\text{band F})/I(\text{band D})$ (□), and $I(\text{band G})/I(\text{band F})$ (○).

values of ΔH°_1 and ΔH°_2 for DETA and DPTA are considerably smaller (more negative) than those for BMOEE and BMOEA. This shows that the attachment of the second and third ligand atoms to an excited cadmium atom are equally exothermic, if they are the same kind of atom, and those of *N*-atoms for DETA and DPTA are more exothermic than those (*O*-atom) for BMOEE and BMOEA. This tendency was perviously pointed out for compounds containing two donor atoms. These are consistent with the observation that the ligand binding energies for the transition metal ions are generally larger for *N*-atoms than those

for *O*-atoms.^{9,10)}

The enthalpy changes qualitatively correlate with the energy differences calculated from the wavelength of the adjacent emission bands. The energy differences calculated from band separations are larger than those estimated from the temperature dependences of the intensity ratios. This difference seems to reflect the difference in the potential energies of the ground states for the configurations corresponding to different types of exciplexes, as pointed out previously.⁶⁾

References

- 1) L. F. Philips, *Acc. Chem. Res.*, **7**, 135 (1974).
- 2) A. B. Callear, *Chem. Rev.*, **87**, 355 (1987).
- 3) T. Tsunashima and S. Sato, *Rev. Chem. Intermed.*, **2**, 201 (1979).
- 4) S. Yamamoto, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **64**, 3335 (1991).
- 5) S. Yamamoto, T. Sakata, and N. Nishimura, *J. Chem. Soc., Faraday Trans.*, **89**, 703 (1993).
- 6) Omar Ahmed, S. Yamamoto, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **66**, 2854 (1993).
- 7) S. Yamamoto, M. Itami, Y. Sueishi, and N. Nishimura, *Chem. Lett.*, **1990**, 1109.
- 8) H. Umemoto, K. Kuwahara, T. Ohnuma, A. Masaki, and S. Yamamoto, *J. Chem. Soc., Faraday Trans.*, **87**, 2897 (1991).
- 9) M. M. Kappes and R. H. Staley, *J. Am. Chem. Soc.*, **104**, 1813 (1983).
- 10) P. J. Marinelli and R. R. Squires, *J. Am. Chem. Soc.*, **111**, 4101 (1989).