BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3585—3586 (1973)

The Solid Molecular Complex Formed between Phenothiazinyl Neutral Radical and Bromine

Subray N. **Bhat** and Haruo **Kuroda**

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received July 24, 1973)

The optical and magnetic properties of the phenothiazine-bromine solid complex have been studied by several authors,[1-4] and it has been reported that the solid is a cation radical salt composed of phenothiazine cation radical and bromine anion, although it is diamagnetic at the room temperature. The apparent diamagnetism is considered to be the result of the reduction of paramagnetism by the strong interaction between phenothiazine cations. However, depending on the preparing conditions, possibly by the effect of the oxidizing agents contained in the used solvent, we sometimes obtain a paramagnetic phenothiazine-bromine solid complex. In this note, we will report the properties of this paramagnetic complex.

Experimental

Phonothiazine was recrystallized from an ethanol solution, and then sublimed *in vacuo* (mp 184 °C). A solution of 0.4 g bromine in 20 ml ethyl ether was added slowly to a solution of 1.0 g phenothiazine in 30 ml ethyl ether, cooling the reaction mixture with the ice-salt mixture. The solid precipitate thus obtained, was filtered, washed several times with cold ether, and dried under vacuum. The ethyl ether commercially obtained was distilled once before use, but no special precaution was done to exclude oxygen and other oxidizing agents.[5]

The result of the elemental analysis of the solid complex was as follows; Found: C, 51.64; H, 2.99; N, 4.79; S, 11.27; Br, 30.35%. Calcd[6] for $C_{12}H_9NS\cdot Br$: C, 51.62; H, 3.25; N, 5.02; S, 11.49; Br, 28.63%.

The ESR spectra were recorded by use of JES-ME-X ESR Spectrometer on a powder sample sealed in a glass tube under vacuum. The spin concentration was determined by using DPPH as the reference, and the *g*-value was determined by comparing with the standard signals of Mn^{2+}. The infrared and visible absorption spectra were measured on the powder sample by using the Nujol-mull method.

Results and Discussion

In contrast with the diamagnetic behaviors of the cation radical salt, the solid complex obtained in the present study, showed a strong paramagnetism, and gave a broad ESR signal with a half-width of about 15 Gauss at the room temperature. The *g*-value was 2.0015±0.0005, and the spin concentration at the room temperature was 6.45×10^{19} spin/g. As shown in Fig. 1, the integrated intensity of ESR signal increased on lowering the temperature and, at the same time, there occurred a decrease of the line width. The temperature dependence of the spin concentration nearly obeys the Curie-Weiss law with the Weiss constant of approximately 70 K.

As shown in Fig. 2, the infrared spectrum of this paramagnetic solid complex considerably differs from that of the cation radical salt. In particular, the N–H stretching band which is observed at 3270 cm^{-1} in

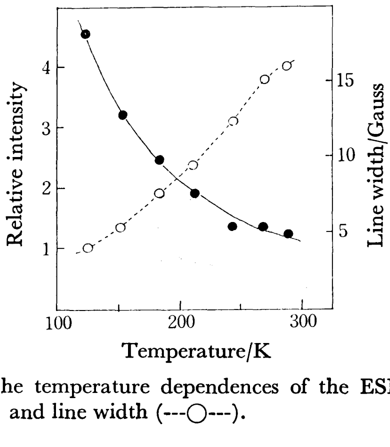


Fig. 1. The temperature dependences of the ESR intensity (—●—) and line width (---○---).

---

[1] G. Lanzi, G. Siragusa, and L. Zanohi, *Il Nouvo Cimento*, **56**, 2179 (1960).

[2] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **40**, 2539 (1967); **42**, 548 (1969).

[3] Y. Matsunaga and K. Shono, *ibid.*, **43**, 2007 (1970).

[4] Y. Iida, *ibid.*, **44**, 663 (1971).

[5] When we carefully excluded oxygen and other oxidizing agents from the solvent, we obtained the cation radical salt.

[6] The values calculated for 2(phenothiazinyl)–Br_2 are as follows: C, 51.81; H, 2.89; N, 5.04; S, 11.53; Br, 28.73%.

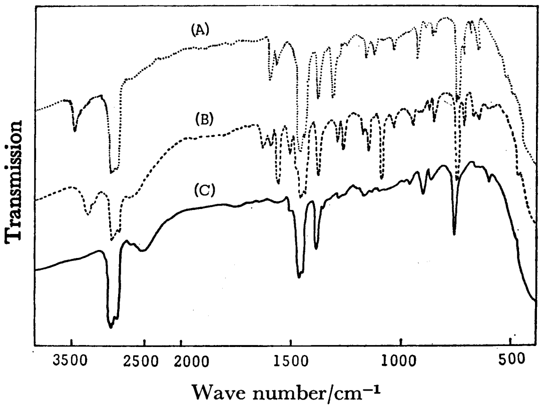


Fig. 2. Infrared absorption spectra of the phenothiazine (A), the cation radical salt, phenothiazine bromide (B) and the paramagnetic complex (C).

the case of the cation radical salt and at 3440 cm^{-1} in the case of pure phenothiazine, is missing in the spectrum of the paramagnetic complex. This seems to indicate that the hydrogen atom attached to nitrogen has been taken off from phenothiazine molecule. In the region below 500 cm^{-1}, the complex gives a broad band at 305 cm^{-1}, which can be attributed to Br–Br stretching vibration.[7,8]

The visible absorption spectrum of the paramagnetic complex is shown in Fig. 3, together with the spectrum of the cation radical salt. In the latter, the 20×10^3 cm^{-1} band has been attributed to the one corresponding to the 18×10^3 cm^{-1} band of the phenothiazine cation, and the near-infrared band at 11×10^3 cm^{-1} to the charge-transfer band associated with the interaction between phenothiazine cations.[4] The spectrum of the paramagnetic complex is considerably different from this; the first band is located at 8×10^3 cm^{-1}, and the second one at about 18×10^3 cm^{-1}.

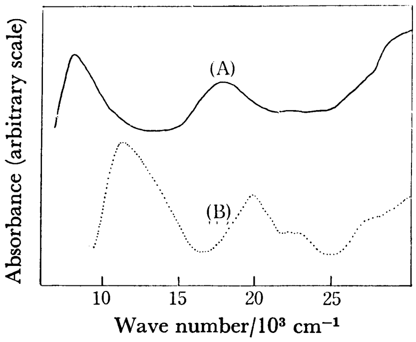
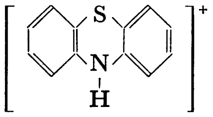
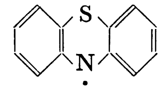


Fig. 3. Powder absorption spectra of the paramagnetic complex (A) and cation radical salt (B).

It has been reported that the oxidation of phenothiazine in solution gives either phenothiazine cation radical (I) or phenothiazinyl neutral radical (II) depending on the condition of oxidation.[9–11] The latter exhibits a strong visible absorption band at about 16×10^3 cm^{-1}.



(I)



(II)

The strong paramagnetism and the absence of the N–H stretching band in the infrared spectrum, seem to indicate that phenothiazine is in the state of the phenothiazinyl neutral radical in the paramagnetic solid complex obtained in the present study. If this is the case, the solid is likely to be composed of the phenothiazinyl radical and bromine molecule with the mole ratio, 2: 1. This is in accord with the appearance of the Br–Br stretching band in the infrared spectrum. As for the visible spectrum, one could assign the 18×10^3 cm^{-1} band to the one due to phenothiazinyl radical and the 8×10^3 cm^{-1} band to a charge-transfer band.

Thanks are due to the Japan Society for the Promotion of Science for giving the fellowship to one of the authors (S.N.B.).

---

[7] The Br–Br stretching band is infrared inactive in the free bromine molecule, but known to appear in a molecular complex such as the benzene–Br_2 complex.[8]

[8] W. B. Person, C. F. Cook, and H. B. Friedrich, *J. Chem. Phys.*, **46**, 2521 (1967).

[9] B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. T. Satcliffe, *Chem. Commun.*, **1966**, 161.

[10] C. Jackson and N. K. D. Patel, *Tetrahedron Lett.*, **1967**, 2265.

[11] M. Kamiya, T. Mitsui, and Y. Akahori, This Bulletin, **46**, 1577 (1973).