The Structure of Bis(dithizonato)-zinc(II) and -Cadmium(II)

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One of the present authors, (T. Y.) devised a new method for dyeing the zinc ion in tissues[1]. In order to analyze this dyeing mechanism[2], some information about the structure of bis(dithizonato)zinc(II) became necessary. Though dithizone has been used widely in the field of analytical chemistry and many investigations of the complex compounds with various metals have been carried out[3], information about the structure of metal complexes with dithizone has been very scarce[4,5]. It was thought be interesting and significant to examine various metal complexes with dithizone.

The present paper deals with the preparation methods and structure of bis(dithizonato)zinc(II) and bis(dithizonato)cadmium(II), in comparison with bis(dithizonato)mercury(II), whose structure has recently been determined by the X-ray method[5].

Experimental

Preparation of Bis(dithizonato)zinc(II). — Bis(dithizonato)zinc(II) was prepared according to the method of Pariaud and Archinard[6]. To a solution of zinc acetate (0.5 g.) in aqueous ammonia was added a solution of dithizone (1.7 g.). A dark red precipitate, which formed instantaneously, was filtered off. This precipitate was then dissolved in 30 cc. of chloroform and filtered. The filtrate was evaporated until its volume was reduced by half; then 50 cc. of ethanol was added, and it was evaporated again until crystals began to appear in the solution. This solution was allowed to stand for 3 to 4 hr. Thin plate-like crystals with a green fluorescence were obtained. Recrystallization was made from chloroform-ethanol.

Found: C, 53.16; H, 3.77; N, 19.47. Calcd. for $C_{26}H_{22}N_8S_2Zn$: C, 54.21; H, 3.85; N, 19.43%.

Preparation of Bis(dithizonato)cadmium(II).— Bis(dithizonato)cadmium(II), which had not been isolated as crystals, was prepared by almost the same method as the zinc compound. Here, however, one of two forms of the compound was obtained, depending upon the conditions of the reaction. When a solution of cadmium acetate in aqueous ammonia was poured into a solution of dithizone, a dark red precipitate, which was easily dissolved in chloroform, was formed. By vacuum evaporation of the chloroform solution of this precipitate, however, violet needles which were only slightly soluble in chloroform were obtained. On the other hand, when a solution of dithizone was poured into a solution of cadmium acetate, a dark brown precipitate which was insoluble in chloroform was formed. After this precipitate was thoroughly washed with chloroform, brown powder was obtained. Both forms, the violet and the brown, are soluble in pyridine to give a solution with a strawberry color. After recrystallization from pyridine, both forms yielded a dark red crystalline powder of the same composition.

Found: C, 50.20; H, 3.70; N, 17.69. Calcd. for $C_{26}H_{22}N_8S_2Cd$: C, 50.12; H, 3.56; N, 17.99%.

Elementary analyses of the brown powder and violet needles were also carried out. The results were quite identical with those of the dark red crystalline powder.

Preparation of Bis(dithizonato)mercury(II).—Bis(dithizonato)mercury(II) was prepared by the same method as the zinc compound.

Found: N, 16.02. Calcd. for $C_{26}H_{22}N_8S_2Hg$: N, 15.76%.

Results and Discussion

The analytical results of these metal complexes of dithizone show that the zinc(II) and cadmium(II) compounds, as well as the mercury(II) compound, are composed of one metal ion and two dithizonate ions. The structures of bis(dithizonato)zinc(II) and bis(dithizonato)cadmium(II) have not yet been determined, but the coordination around these metal ions is regarded as tetrahedral, judging from the stereochemistry of these metal ions and the configuration of dithizone. In the molecules of these metal complexes of dithizone, it may be presumed that dithizonate ions are capable of being coordinated to the metal in eight ways, i. e., in four ways through two nitrogen atoms which do not adjoin each other, and in the other four ways through a

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[3] E. B. Sandell, "Colorimetric Determination of Trace of Metals", Interscience Publishers, New York (1959), p. 163; H. Mabuchi and H. Nakahara, This Bulletin, 36, 151 (1963); T. Ashizawa, *Japan, Analyst* (*Bunsekikagaku*), 10, 354, 443, 449 (1961); H. Irving and J. J. Cox, *Proc. Chem. Soc.* 1959, 324.

[4] R. F. Bryan and R. M. Knopf, ibid., 1961, 203.

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sulfur atom and one of the four nitrogen atoms. The posibility of behaving as a tridentate may be ruled out because of the steric condition.

According to the crystal structure analysis⁵⁾, the dithizonate ions in the bis(dithizonato)-mercury(II) molecule are coordinated through its sulfur atoms and nitrogen atoms of the azo radicals to the central metal, as shown in Fig. 1. In fact, the crystal structure analysis was carried out with a pyridinated compound. The nitrogen atoms of the pyridine molecules, however, are not linked with the mercury(II) ions but are connected with nitrogen atoms of imino groups of the dithizonate ion by hydrogen bonds. Therefore, the configurations around the mercury(II) ion in the non-solvated crystals, prepared in the present work, may be assumed to be the same as that in the pyridinated compound.

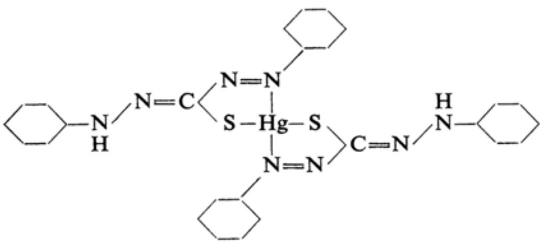

Fig. 1. The structure of bis(dithizonato)-mercury(II).

The infrared spectra of these metal dithizonates and of dithizone itself are shown in Fig. 2. Because the dithizonate ion is coordinated through its sulfur and nitrogen atoms to the mercury(II) ion, the C–S streching and –N=N– stretching absorptions may be shifted to lower frequencies. The N–H stretching vibration was observed by Duncan and Thomas⁷⁾ at 3272 cm^{-1} for the mercury(II) compound in carbon tetrachloride. The present measurement, using the KBr method, reveals that the corresponding absorption band appears at 3260, 3235 and 3232 cm^{-1}, respectively, for the mercury(II), cadmium(II) and zinc(II) compounds. However, these characteristic bands of dithizone have not yet been assigned; it is difficult, therefore, to discuss the coordination from these stretching vibrations at the present stage. Nevertheless, some conclusion may be derived by comparing these spectra. If the coordination type of bis(dithizonato)zinc(II) and bis(dithizonato)cadmium(II) is different from that of bis(dithizonato)mercury(II), the configuration of the dithizonate ion in th zinc(II) or cadmium(II) compound is not the same as in the mercury(II) compound. Accordingly, the skeletal vibrations of zinc(II) or cadmium(II) complexes of dithizone should vary considerably compared with those of the mercury(II) compound. However, as can be seen in Fig. 2, patterns of skeletal vibrations which are

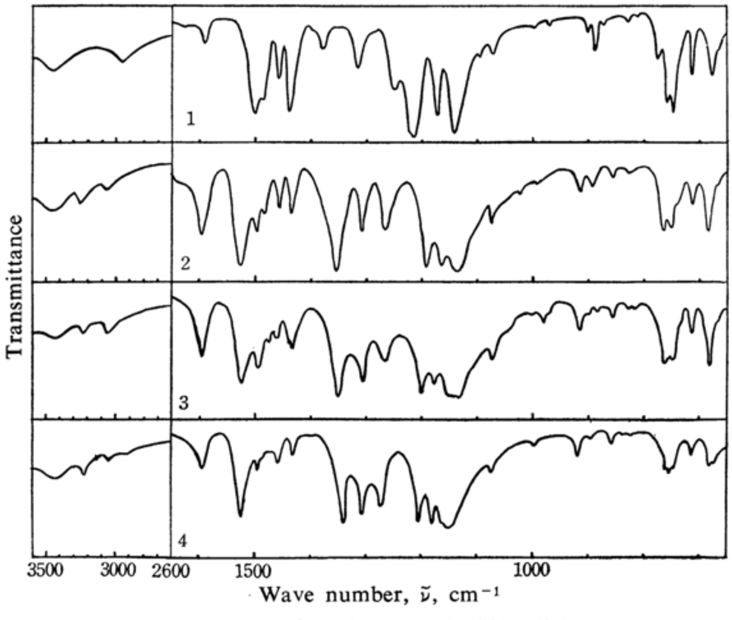

Fig. 2. Infrared spectra in KBr disk.

1 Dithizone
2 Bis(dithizonato)mercury(II)
3 Bis(dithizonato)cadmium(II)
4 Bis(dithizonato)zinc(II)

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7) J. F. Duncan and F. G. Thomas, *J. Chem. Soc.*, **1960**, 2823.

expected to appear from 1000 cm^{-1} to 1300 cm^{-1}, are very similar, and the peaks for the corresponding vibrations are found to be shifted regularly in the order of the atomic number. It may, therefore, be concluded that the configurations and the mode of the coordination of dithizonate ions are all identical in these metal complexes of dithizone. Consequently dithizonate ions are presumed to be coordinated through the sulfur atom and nitrogen atom of the azo radical to the zinc(II) or the cadmium(II) ion as well as to the mercury(II) ion.

The visible and ultraviolet absorption spectra of these complexes in pyridine were determined and are shown in Fig. 3. The spectra of the zinc(II) and mercury(II) complexes in chloroform were found to be almost identical with the spectra of the same complexes in pyridine. As may be seen in Fig. 3, these curves are essentially similar, and maxima of the corresponding bands are shifted to a higher frequency in the order: zinc(II)<cadmium(II) <mercury(II). The order agrees with the current view about the strength of the perturbing effect of the metal ions on the ligand. The rather close similarity of the spectra and the regular shift of the absorption bands seem to be in agreement with the above-mentioned conclusion that the mode of the coordination of dithizonate ions is quite similar among the complexes of the three metal ions.

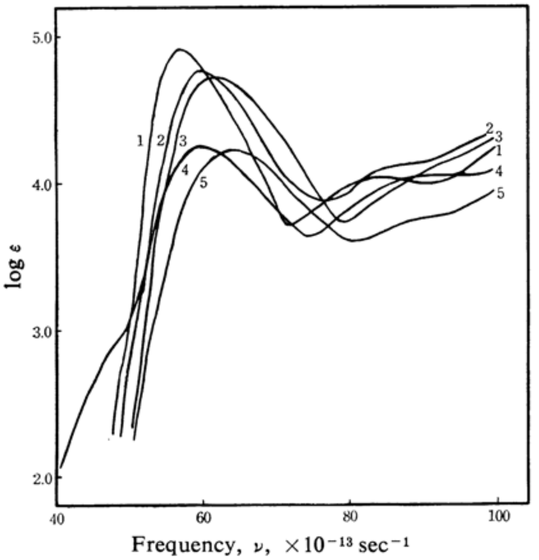

Fig. 3. Absorption spectra in pyridine.
1 Bis(dithizonato)zinc(II)
2 Bis(dithizonato)cadmium(II)
3 Bis(dithizonato)mercury(II)
4 Dithizone
5 Dithizone in aqueous ammonia

Summary

Two forms of bis(dithizonato)cadmium(II) have newly been isolated. Upon recrystallization from pyridine, both the forms yielded the same dark red crystalline powder. A comparison of their infrared and ultraviolet spectra shows that the mode of coordination and the configuration of zinc(II) and cadmium(II) are the same as in the mercury(II) complex.

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