

Structures of Secondary Metal Dithizonates

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Summary On the basis of i.r. spectroscopic results, general formulae for the dithizonates of monovalent and bivalent metals are suggested.

We have recorded the i.r. spectra of the secondary dithizonates of Ag^I, Hg^{II}, and Cu^{II} in the region 4000—400 cm⁻¹ in the solid state (Nujol and hexachlorobutadiene mulls) and in solution (CS₂: 700—1400 and 2600—3500 cm⁻¹, C₂Cl₄: 1200—1800 cm⁻¹).

Above 1350 cm⁻¹ we observed absorption bands due to the phenyl group (3070, 1600, 1485, and 1455 cm⁻¹) but no bands due to NH, C=N, or N=N groups.

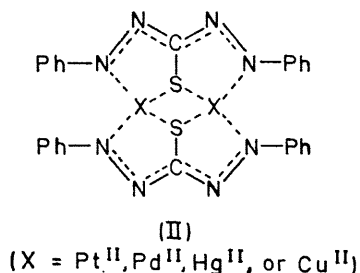
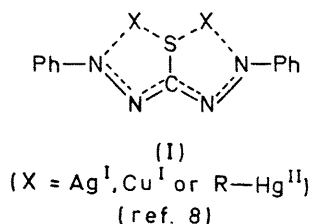
The i.r. spectrum of CuDz that had been subjected to treatment with D₂O was identical with that of the original material, in chloroform, CS₂, and C₂Cl₄. Evidently, neither

an N-H group^{1,2} nor co-ordinated water is present in secondary copper dithizonate.

Meriwether and his co-workers³ observed absorption bands at about 3200 and 1530 cm⁻¹ in the spectra of Ag₂D and PdDz. According to our results, these bands are characteristic of primary dithizonates; we have not observed such bands in the spectra of Ag₂Dz, HgDz, or CuDz.

Dithizone skeletal vibration bands are present in the region 1150—1205 cm⁻¹ (Ag₂Dz: 1150 and 1190 cm⁻¹; CuDz: 1150, 1175, and 1205 cm⁻¹). Similar bands in the spectra of primary dithizonates have been assigned to ν(N-C-S) vibrations.³ These bands are present in the spectra of di-(1-naphthyl)thiocarbazone and di-(2-naphthyl)-thiocarbazone metal complexes (our results).

Deformation vibrations $\gamma(\text{C-H})$ in the phenyl group give rise to single bands at 750 and 690 cm^{-1} indicating that all



the phenyl groups in the molecule of the secondary dithi-

zonate are in equivalent positions; in the spectra of the primary dithizonates there are double bands at 750 and 690 cm^{-1} .

It has been shown that CuDz is diamagnetic.⁴ The dithizone to copper ratio was 1:1 in Cu^{II}Dz as well as in Cu^IHDz.⁵ Moreover, the visible spectra of these compounds are very similar. The molar absorptivity of CuDz is 20,000 l/mole cm^{-1} ,⁶ while that of CuHDz is $21,200 \pm 300$ l/mole cm^{-1} (our results) in CCl_4 at λ 450 and 480 nm, respectively.

CuHDz is also diamagnetic.⁷ However, the i.r. spectrum of CuHDz is quite different from that of CuDz; the spectrum of CuHDz contains a $\nu(\text{N-H})$ band at 3220 cm^{-1} , a $\nu(\text{C=N}) + \delta(\text{N-H})$ band at 1525 cm^{-1} (very strong), and a $\delta(\text{N-H})$ band at 1435 cm^{-1} .

On the basis of the above results, we suggest formula (I) for the secondary dithizonates of monovalent metals and formula (II) for those of bivalent metals.

According to formula (II), interaction between two copper atoms as well as superexchange in the Cu-S-Cu bridge may be responsible for the diamagnetism of CuDz.⁹

It is noteworthy that bivalent metals which can achieve a square-planar co-ordination form secondary dithizonates.

(Received, March 10th, 1971; Com. 201.)

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