

403. *Studies with Dithizone. Part IX.¹ The Absorption Spectra of Mono- and Di-*p*-bromo-substituted Dithizones and of their Metal Complexes.*

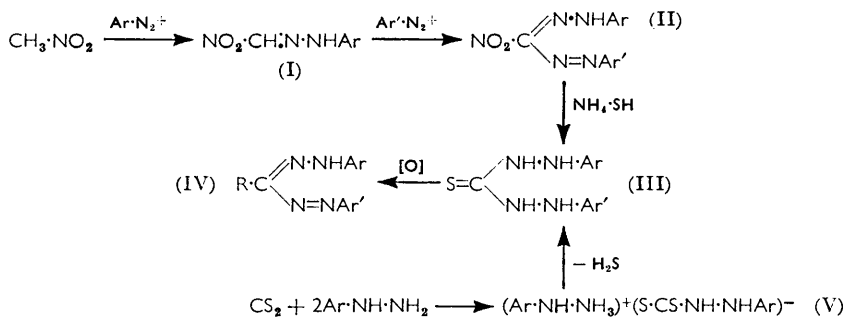
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1(or 5)-*p*-Bromophenyl-3-mercapto-5(or 1)-phenylformazan ("monobromodithizone") has been synthesised and shown to be identical with the monobromination product of dithizone itself. 1,5-Di-*p*-bromophenyl-3-mercaptoformazan ("dibromodithizone") prepared by Fischer's method has been shown to be identical with the material prepared by two other synthetic routes. The absorption spectra of dithizone and of mono- and di-bromodithizone in benzene and carbon tetrachloride have been measured, and the molecular extinction coefficients of the pure reagents determined by the mercury titration method.

The pH range for complete extraction of a number of metal complexes of the three reagents have been determined and values are recorded for λ_{\max} and ϵ_{\max} , the latter being obtained by a new reversion procedure. Values of λ_{\max} increase in the order $\text{Ag}^+ < \text{Hg}^{2+} \approx \text{Bi}^{3+} < \text{Pb}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$, and those of ϵ_{\max} in the order $\text{Ag} < \text{Cu} < \text{Pb} < \text{Hg} < \text{Bi} < \text{Zn}$. Substitution by bromine produces a regular bathochromic shift in values of λ_{\max} for both the reagents and their metal complexes: the value for monobromodithizone is always the arithmetical mean of those for the unsubstituted and the dibromo-substituted reagent. There are no obvious regularities in values of ϵ_{\max} .

Discrepancies between the present extensive data and some results of Pupko and Pelkis are attributed to their use of impure materials.

"DIBROMODITHIZONE" (1,5-di-*p*-bromophenyl-3-mercaptoformazan) (as IV; R = SH, Ar = Ar' = *p*-Br·C₆H₄) was first described by Hubbard and Scott² who prepared it by reducing the nitroformazan (as II) obtained by coupling nitromethane with *p*-bromobenzenediazonium chloride following the general method of Bamberger *et al.*³ They described it as "insoluble in aqueous ammonia" and as possessing "low tinctorial power."



Authentic dibromodithizone was prepared by Irving and Bell⁴ (a) by a modification of Bamberger's method,³ and (b) by the action of sodium hydrogen sulphide upon 3-bromo-1,5-di-*p*-bromophenylformazan (as IV; R = Br, Ar = Ar' = *p*-Br·C₆H₄). It was shown to resemble dithizone in all its reactions, to be soluble in aqueous ammonia, and to have the high molecular extinction coefficient of 30,600 at λ_{\max} 635 m μ .

¹ Part VIII, Irving and Cox, *J.*, 1961, 1470.

² Hubbard and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 2390.

³ Bamberger, Padova, and Ormerod, *Annalen*, 1925, **446**, 260.

⁴ Irving and Bell, *J.*, 1953, 3538.

Dibromodithizone must also have been obtained by Beckett and Dyson⁵ from thio-carbonyl chloride and *p*-bromophenylhydrazine hydrochloride. They describe its colour reaction with plumbous ions but give no details of the preparation or analysis.

More recently Pupko and Pel'kis^{6,7} have reported the preparation of a very large number of analogues of dithizone (as IV; R = SH) both symmetrically (Ar = Ar') and unsymmetrically (Ar ≠ Ar') substituted. However, the values they give for molecular extinction coefficients (generally for solution in benzene) of the reagents are often very different from ours and those of other workers and for reasons given later they appear to be unreliable. For example, their data for molecular extinction coefficients in benzene of a sample of dibromodithizone prepared by Bamberger's method, and of a sample of dithizone itself (Table 1) differ so radically from values found in other solvents that a reinvestigation seemed desirable.

We have repeated the preparation of 1,5-di-*p*-bromophenyl-3-mercaptoformazan by Bamberger's method³ and have also synthesised it by Fischer's method,⁸ which involves oxidising the thiocarbazine (as III) obtained by heating the salt (V) that results from the interaction of carbon disulphide and *p*-bromophenylhydrazine. These two preparations were shown by infrared and visible absorption spectrophotometric measurements to be indistinguishable, and identical with the sample previously prepared⁴ from the 3-bromoformazan (IV; R = Br, Ar = Ar' = *p*-Br·C₆H₄). Measurements of the absorption spectra of this "dibromodithizone" after rigorous purification are shown in Tables 3 and 4.

In a recent paper⁹ we have shown that the bromination of dithizone yields an adduct of bromine with a monobrominated dithizone which was found to be 1(or 5)-*p*-bromophenyl-3-mercapto-5(or 1)-phenylformazan (as IV; R = SH, Ar = Ph, Ar' = *p*-Br·C₆H₄) by degradation and infrared measurements. We have now further confirmed its composition by comparison with an authentic specimen prepared by reducing the nitroformazan (II; Ar = Ph, Ar' = *p*-Br·C₆H₄) obtained by coupling nitroformaldehyde phenylhydrazone (I; Ar = Ph) with *p*-bromobenzenediazonium chloride at a controlled pH.

The preparation of the intermediate nitroformaldehyde phenylhydrazone (as I) proved troublesome. It is formed together with the nitroformazan (II; Ar = Ar') when benzenediazonium chloride is condensed with sodium *aci*-nitromethane under rigorously controlled conditions, but none of the published methods proved entirely satisfactory. Bamberger's first procedure¹⁰ was later improved by his school¹¹ but Jensen and Bak¹² characterised this as "capricious" and described a modification in great detail. In our hands a mixture of products (I) and (II) invariably resulted and the proportion of nitroformazan increased with the time the nitroformaldehyde phenylhydrazone and the diazonium solution were allowed to react together. The instruction to wait for four hours before collecting the product¹² must have arisen from a mistranslation of "nach viertelstundigem Stehen . . ." in Bamberger's original paper. By using the procedure detailed in the experimental section we still obtained a mixture of products (I) and (II) but this could be readily separated by taking account of the greater acidity of the nitroformaldehyde phenylhydrazone. This substance was most conveniently purified after conversion of the crude mixture of α - and β -forms into the yellow β -form.

Samples of dithizone, monobromodithizone, and dibromodithizone were exhaustively purified by Cowling and Miller's method,¹³ and their molecular extinction coefficients

⁵ Beckett and Dyson, *J.*, 1937, 1358.

⁶ Pupko and Pel'kis, *Zhur. obschei Khim.*, 1954, **24**, 1640.

⁷ Pel'kis, Dubenko, and Pupko, *Zhur. obschei Khim.*, 1957, **27**, 2190.

⁸ Fischer, *Annalen*, 1878, **180**, 120.

⁹ Irving and Ramakrishna, *J.*, 1961, 1272.

¹⁰ Bamberger, *Ber.*, 1894, **27**, 155.

¹¹ Bamberger, Schmidt, and Levinstein, *Ber.*, 1900, **33**, 2059.

¹² Jensen and Bak, *J. prakt. Chem.*, 1938, **151**, 167.

¹³ Cowling and Miller, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 145.

were obtained by the mercury titration procedure^{4,14,15} after a preliminary study of the pH range over which quantitative extraction of the mercury complexes could be realised. Similar studies were then made of the pH range for complete extraction of complexes with the ions Ag^+ , Hg^{2+} , Bi^{3+} , Pb^{2+} , Zn^{2+} , and Cu^{2+} . The molecular extinction coefficients of these complexes were then measured by a reversion procedure. If A^c is the absorbancy (measured at λ_{max} for the metal complex) of a solution obtained by equilibrating one of dithizone (HDz) of given known concentration in an organic solvent with an excess of an aqueous solution of an n -valent cation, and A_{R}^r is the absorbancy (measured at λ_{max} for the reagent itself) after this solution has been treated with a reagent that reverts the whole of the metal complex, MDz_n , quantitatively into the equivalent amount of dithizone, it can be shown¹⁵ that:

$$A^c = A_{\text{R}}^r (\epsilon_c^c + n \sum k_i \epsilon_i^c) / (n \epsilon_r^r + n \sum k_i \epsilon_i^r) \quad . \quad . \quad . \quad . \quad (1)$$

The subscripts c , r , and i refer to metal complex, reagent, and any adventitious impurities respectively; k_i is the constant of proportionality; the superscripts c and r designate the wavelengths at which the complex and the reagent show their maximum absorption. The plot of A^c against A_{R}^r for reagent solutions of different initial concentrations is a straight line passing through the origin (Fig. 4). The value of $\epsilon_c^c/n\epsilon_r^r$ can be identified with the gradient provided the purity of the reagent used is greater than 95%;¹⁵ this was the case for all the compounds studied in this paper. The value of ϵ_c^c for each metal complex follows from the value of ϵ_r^r previously determined.

EXPERIMENTAL

*Preparation of 1,5-Di-*p*-bromophenyl-3-mercaptoformazan* (IV; $\text{R} = \text{SH}$, $\text{Ar} = \text{Ar}' = p\text{-Br-C}_6\text{H}_4$) [with G. F. WATTS].—Carbon disulphide (8 g., excess) in a little ether was added slowly to a stirred suspension of *p*-bromophenylhydrazine (20 g.) in ether (50 ml.) and methanol (25 ml.). During 45 min. the *p*-bromophenylhydrazinium salt of β -(*p*-bromophenyl)dithiocarbamic acid separated as a white solid (21 g.), m. p. 95–96°. The salt was collected and a portion (16.7 g.) heated cautiously in an open dish at 100° during 20 min., with stirring. Hydrogen sulphide was evolved and the material became viscous and finally liquid. The dish was chilled in ice and the contents were triturated with ethanol; colourless di-(*p*-bromophenyl)-thiocarbamide crystallised. The thiocarbamide was then heated for 2–3 min. with potassium hydroxide (6 g.) in boiling methanol (60 ml.). The deep red solution was poured into 2*N*-sulphuric acid (500 ml.), stirred, and cooled at 0°. *Di*-(*p*-bromophenyl)thiocarbazone separated as a black powder which was washed free from acid by decantation, collected, and dried *in vacuo* [yield 5.2 g.; m. p. 150° (decomp.)]. For analysis it was taken up in ammonia prepared by isopiestic distillation,¹⁶ and after the red solution had been extracted with several portions of chloroform the dibromodithizone was reprecipitated with ice-cold "isopiestic" hydrochloric acid. A portion was further purified by Cooper and Sullivan's procedure¹⁴ (Found: N, 13.3; Br, 38.8. $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_4\text{S}$ requires N, 13.5; Br, 38.6%).

Preparation of Nitroformaldehyde Phenylhydrazone (with F. R. HALE).—Sodium hydroxide (16 g., 0.4 mole) was dissolved in a little water, and ethanol (200 ml.) was added. On addition of nitromethane (24.4 g., 0.4 mol.) a white precipitate of a sodium salt appeared. This was redissolved in ice-cold water (2 l.) and kept at or below 0° until required.

A vigorously stirred diazonium solution from aniline (37.2 g., 0.4 mole) in concentrated hydrochloric acid (120 ml.) and water (250 ml.) containing ice (300 g.) and sodium nitrite (29 g.) was quickly neutralised to litmus by rapid addition of ice-cold sodium hydroxide. The solution of the sodium salt of aci-nitromethane, previously prepared, was then added in one portion. The colour changed through yellow to red, and a red precipitate was formed. Stirring was continued for exactly 15 min. after the addition of the nitromethane, then the precipitate was collected and washed repeatedly with water until no trace of alkali or alkali salts remained.

¹⁴ Cooper and Sullivan, *Analyt. Chem.*, 1951, **23**, 613.

¹⁵ Irving and Ramakrishna, *Analyst*, 1960, **85**, 860.

¹⁶ Irving and Cox, *Analyst*, 1958, **83**, 526.

The red product was dissolved in 2*N*-sodium hydroxide (500 ml.) at 0° and stirred. 3*N*-Hydrochloric acid was then added dropwise. No change appeared at first but later yellow streaks marked each addition of acid. As soon as the solution had acquired a permanent orange-yellow colour the red precipitate (mainly 3-nitro-1,5-diphenylformazan but containing some nitroformaldehyde phenylhydrazone) was collected and the filtrate (still at 0°) treated dropwise with acid until it was just acid to litmus. The yellow precipitate of β -nitroformaldehyde phenylhydrazone, collected and washed with water, had m. p. 83°. A further quantity was obtained from the initial red precipitate by repeating the fractional precipitation.

The yellow β -form could not be recrystallised readily and was converted into the red β -form by dissolution in warm chloroform and removal of the solvent in a current of air: this process was repeated three times. After recrystallisation from light petroleum (b. p. 40–60°) nitroformaldehyde phenylhydrazone formed orange-red needles (3.0 g.), m. p. 79–80°. Bamberger *et al.*¹¹ report m. p. 74.5–75.5°, and Jensen and Bak¹² m. p. 74° for samples heated rapidly from 70°. On slower heating there is partial conversion into the β -form.

FIG. 1. Absorption spectra of complexes of silver and bismuth with dithizone (curve 1, 3.180×10^{-5} M; curve 4, 1.135×10^{-5} M), with monobromodithizone (curve 2, 2.653×10^{-5} M, curve 5, 1.033×10^{-5} M), and with dibromodithizone (curve 3, 2.831×10^{-5} M; curve 6, 1.096×10^{-5} M).

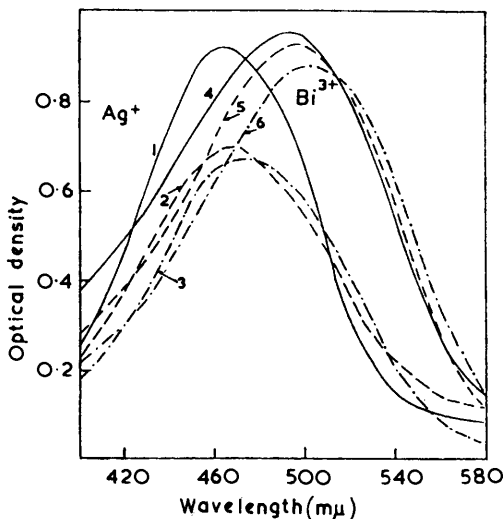
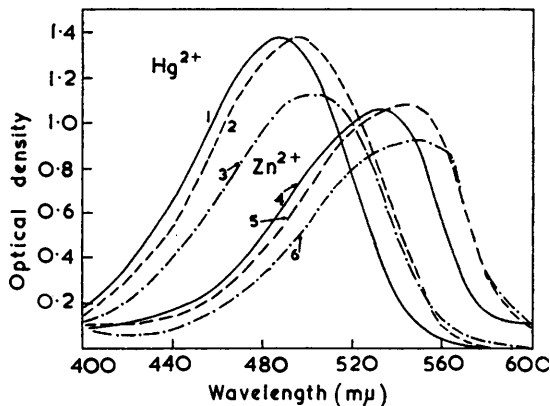


FIG. 2. Absorption spectra of complexes of mercury and zinc with dithizone (curve 1, 1.911×10^{-5} M; curve 4, 1.164×10^{-5} M), with monobromodithizone (curve 2, 1.820×10^{-5} M; curve 5, 1.146×10^{-5} M), and with dibromodithizone (curve 3, 1.580×10^{-5} M; curve 6, 1.048×10^{-5} M).



Preparation of 1(or 5)-p-Bromophenyl-3-nitro-5(or 1)-phenylformazan.—An ice-cold diazonium solution from *p*-bromoaniline (1.29 g., 3 mol.) in the minimum amount of hydrochloric acid was adjusted to pH 4–5 by the addition of solid sodium acetate and added to a vigorously stirred solution obtained by diluting a solution of the nitroformaldehyde phenylhydrazone (0.42 g., 1 mol.) in ethanol (5 ml.) to 700 ml. with water containing ice. After 20 min. the red precipitate of 1(or 5)-*p*-bromophenyl-3-nitro-5(or 1)-phenylformazan was collected, washed, and recrystallised from alcohol and then from chloroform–light petroleum, as a red microcrystalline powder, m. p. 164° (decomp.) (Found: N, 22.3; Br, 23.3. $C_{13}H_{10}BrN_5O_2$ requires N, 22.2; Br, 23.0%).

Preparation of 1(or 5)-p-Bromophenyl-3-mercapto-5(or 1)-phenylformazan.—Dry ammonia was passed through a solution of the nitroformazan (1 g.) in ethanol (40 ml.) until it was saturated at 0°. Hydrogen sulphide was then passed through the (cooled) red solution until an orange colour developed (20 min.). Water was added and the precipitate of monobromodiphenylthiocarbazine was collected and washed. The crude thiocarbazine was then oxidised immediately with methanolic potassium hydroxide as described above. 1(or 5)-*p*-Bromophenyl-3-mercapto-5(or 1)-phenylformazan was finally obtained as a black microcrystalline powder, m. p. 152–153°, which was shown by its infrared and visible absorption spectra to be

identical with the substance obtained by the direct bromination of dithizone⁹ (Found: Br, 23.6. Calc. for $C_{13}H_{11}BrN_4S$: Br, 23.8%).

Absorption Spectra.—(a) Salts of "AnalaR" quality were used for all solutions. Ammonia and hydrochloric acid were purified isopiesticly.¹⁶ Reagent-grade carbon tetrachloride was redistilled over lime immediately before use. Reagent-grade benzene was shaken with successive portions (15% v/v) of concentrated sulphuric acid until the acid layer remained colourless, then twice with 10% sodium carbonate solution, and once with water before being dried over calcium chloride and fractionated; the fraction of b. p. 79.5–80.5° was used.

The following metal solutions were used. Mercury: $2 \times 10^{-3}M$ from mercuric chloride in 0.25N-sulphuric acid. Zinc: $2 \times 10^{-2}M$ from zinc sulphate heptahydrate in 0.25N-sulphuric acid. Lead: $2 \times 10^{-3}M$ from lead nitrate in 1% nitric acid. Copper: $2 \times 10^{-3}M$ from copper sulphate pentahydrate in 0.25N-sulphuric acid. Silver: $3 \times 10^{-3}M$ from silver nitrate in 0.25N-sulphuric acid. Bismuth: $4 \times 10^{-3}M$ from bismuth nitrate pentahydrate in 1:100 nitric acid. Mixtures of sodium acetate and hydrochloric acid, acetic acid and sodium acetate, potassium dihydrogen phosphate and sodium hydroxide, and citric acid and aqueous ammonia were used as buffer solutions to cover the pH ranges 1–3, 2.4–5.9, 6.0–8.0, and 8.0–10

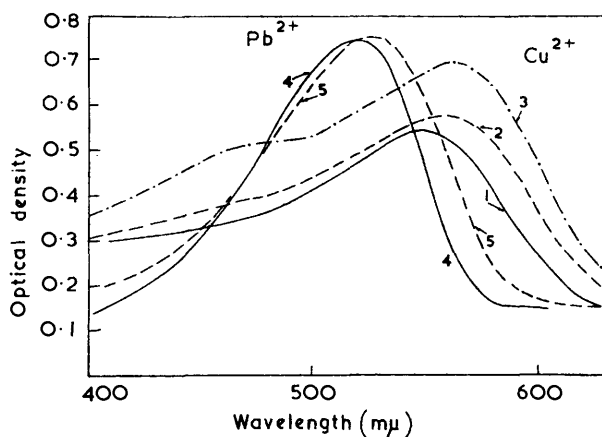


FIG. 3. Absorption spectra of complexes of copper and lead with dithizone (curve 1, $1.211 \times 10^{-5}M$; curve 4, $1.113 \times 10^{-5}M$), with monobromodithizone (curve 2, $1.165 \times 10^{-5}M$; curve 5, $1.081 \times 10^{-5}M$), and copper with dibromodithizone (curve 3, $1.393 \times 10^{-5}M$).

respectively. All buffer solutions were extracted exhaustively with successive portions of a strong solution of dithizone in carbon tetrachloride to remove traces of metallic impurities. Residual dithizone was then removed by extraction with successive portions of carbon tetrachloride.

Dithizone and its analogues were purified by Cowling and Miller's method,¹³ until no further changes in absorption spectra were detectable. An ammoniacal solution of the purest reagent was acidified with pure hydrochloric acid in the presence of the appropriate organic solvent into which it was immediately extracted. Such stock solutions (approx. $10^{-2}M$) were stored in the dark under sulphur dioxide. Immediately before use they were further purified by a cycle of extractions into alkali¹⁴ and diluted as required by pure solvent.

All glass-ware was scrupulously freed from traces of metals as previously described. Absorption spectra were obtained with a Unicam S.P. 700 recording spectrophotometer, but final measurements of absorbancy were made with a Unicam S.P. 500 spectrophotometer and matched 1 cm. silica cells.

(b) The purification of each reagent was continued until the peak ratio (the ratio of the optical densities at the maxima of longer and shorter wavelength) showed no further increase. Data recorded in this paper for reagents and their metal complexes refer only to solutions purified to this degree. Typical absorption spectra of dithizone and its mono- and di-bromo-substitution products have been presented previously.⁹ The concentrations of such solutions were determined by the mercury titration procedure, and the calculated molecular extinction coefficients are summarised in Tables 3 (benzene) and 4 (carbon tetrachloride).

The absorption spectra of metal complexes were obtained by equilibrating solutions of the reagents in the desired solvents with an excess of metal ion dissolved in a buffer chosen from

preliminary experiments (see above) to lie within the range over which the complex is quantitatively extracted. Typical results are shown in Figs. 1—3. The locations of the maxima of the absorption bands are summarised in Table 5.

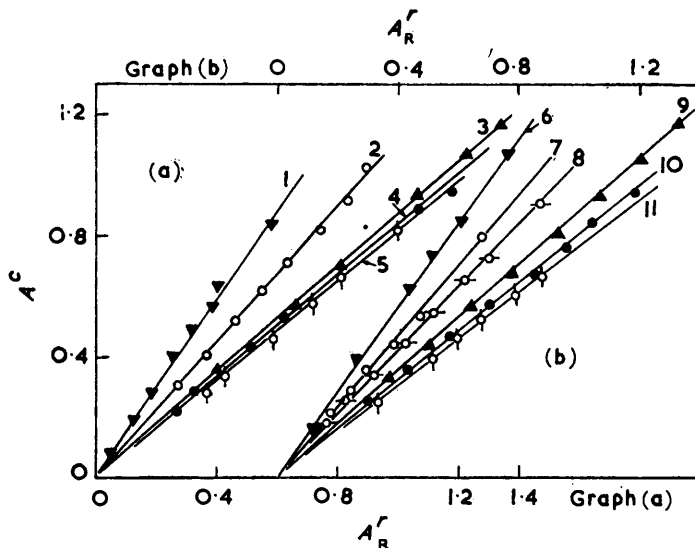
The pH range over which the metal complexes were best extracted was determined by measuring the absorbancy of the organic phase obtained by equilibrating a fixed volume of

TABLE I. pH ranges for maximum extraction of metal complexes of brominated dithizones.

| Metal | pH range for max. extraction | Buffer and pH |
|------------------------|------------------------------|---|
| Hg ²⁺ | 1 | H ₂ SO ₄ , 1 |
| Ag ⁺ | 2—2.5 | H ₂ SO ₄ , 2 |
| Cu ²⁺ | 1.8—2.8 | NaOAc-HCl, 2.6 |
| Zn ²⁺ | 6.5—8.0 | KH ₂ PO ₄ -NaOH, 7.40 |
| Pb ²⁺ | 8.6 | Citric acid-NH ₃ , 9.00 |
| Bi ³⁺ | 9.0 | NH ₄ citrate-KCN, 9.60 |

stock reagent solution with an excess of metal ions dissolved in buffers whose pH was later measured. The pH range over which the absorbancy was constant or maximal was taken as

FIG. 4. The reversion method for determination of molecular extinction coefficients of metal-dithizone complexes. (a) Complexes with 1,5-di-p-bromophenylthiocarbazon (lower scale). (b) Complexes with 1(or 5)-p-bromophenyl-5(or 1)-phenylthiocarbazon (upper scale).



1 & 6, Zn²⁺; 2 & 7, Hg²⁺; 3 & 9, Bi³⁺; 4 & 10, Ag⁺; 5 & 11, Cu²⁺; 8, Pb²⁺.

the optimum pH range for extraction. These were found to be much the same for the brominated reagents as for dithizone itself (Table I).

The molecular extinction coefficients of the various metal—dithizone complexes were

TABLE 2. Gradients of lines obtained in the reversion method for measuring molecular extinction coefficients.

| | Hg ²⁺ | Zn ²⁺ | Cu ²⁺ | Pb ²⁺ | Ag ⁺ | Bi ³⁺ |
|--------------------------|------------------|------------------|------------------|------------------|-----------------|------------------|
| Dithizone | 1.044 | 1.329 | 0.650 | 0.961 | 0.812 | 0.815 |
| Monobromodithizone | 1.106 | 1.383 | 0.744 | 1.010 | 0.776 | 0.873 |
| Dibromodithizone | 1.139 | 1.431 | 0.792 | — | 0.766 | 0.853 |

determined by the reversion procedure as follows: x ml. of dithizone solution ($3.72 \times 10^{-5}M$) and $(10 - x)$ ml. of carbon tetrachloride were equilibrated with 10 ml. of a solution of bismuth ions ($4.459 \times 10^{-5}M$) and 10 ml. of an ammonium citrate-potassium cyanide buffer of pH

9.70 for 10 min. After centrifugation of the organic layer to remove any water droplets its absorbancy was measured at 490 $m\mu$ ($\lambda_{max.}$ for the bismuth complex) and at 620 $m\mu$ ($\lambda_{max.}$ for dithizone—to confirm the absence of residual reagent). 5 ml. of the organic phase were then shaken with 5 ml. of 2*N*-sulphuric acid pre-saturated with carbon tetrachloride. The absorbancy of the organic phase was determined at 620 $m\mu$ (to obtain the value of A_R^*) and at 450 $m\mu$ (to give a value for the peak ratio of the reverted dithizone). Typical results are shown below with corresponding data for mono- and di-bromodithizone complexes of bismuth.

| Initial concn. of reagent (10^5M) | Dithizone 3.72 | | | | Monobromodithizone 4.15 | | | | Dibromodithizone 4.35 | | | |
|--|-------------------|---------|-------|---------|----------------------------|---------|-------|---------|--------------------------|---------|-------|---------|
| | A^c | A_R^* | A^c | A_R^* | A^c | A_R^* | A^c | A_R^* | A^c | A_R^* | A^c | A_R^* |
| Wavelength ($m\mu$) | 490 | 620 | 490 | 620 | 496 | 628 | 496 | 628 | 500 | 635 | 500 | 635 |
| Absorbancy | 0.889 | 1.089 | 0.510 | 0.620 | 1.175 | 1.333 | 0.678 | 0.786 | 1.152 | 1.340 | 0.693 | 0.820 |
| | 0.809 | 0.982 | 0.412 | 0.503 | 1.056 | 1.210 | 0.562 | 0.642 | 1.053 | 1.235 | 0.571 | 0.663 |
| | 0.714 | 0.861 | 0.324 | 0.388 | 0.930 | 1.018 | 0.438 | 0.505 | 0.925 | 1.073 | 0.470 | 0.538 |
| | 0.605 | 0.738 | — | — | 0.801 | 0.931 | 0.330 | 0.370 | 0.819 | 0.950 | — | — |

Similar measurements were carried out with other metals by using the following reversion agents. Mercury: A solution containing potassium hydrogen phthalate (25 g.) and potassium iodide (60 g.) in a litre of distilled water with a few drops of sodium thiosulphate solution to reduce any free iodine. Lead: *N*-hydrochloric acid. Copper: 0.5*N*-sodium thiosulphate. Silver: 6% (w/v) potassium iodide in 0.25*N*-sulphuric acid. Zinc: *N*-hydrochloric acid. The experimental results are plotted in Fig. 4. From the gradients of the best straight lines through the experimental points the values in Table 2 were calculated for the ratios ϵ_c/ϵ_R^* .

RESULTS AND DISCUSSION

The positions of the two absorption bands in the visible spectra of dithizone and its mono- and di-bromo-substitution products are given in Table 3 together with values for the respective molecular extinction coefficients. Table 3 also includes values for the peak ratios, *i.e.*, the ratio of the molecular extinction coefficients at the longer and the shorter wavelength maxima. This ratio is well known to be a sensitive criterion of purity since the common impurity in laboratory and commercial samples of thiocarbazonones is an oxidation product whose absorption is negligible near 630 $m\mu$ and increases as the wavelength falls to 450 $m\mu$ and below: the immediate effect is to produce a decrease in the measured peak ratio.

TABLE 3. *Absorption data for mercaptoformazans in benzene.*

| Reagent | $\lambda_{max.}$ | $10^{-3}\epsilon_{max.}$ | $\lambda_{min.}$ | $10^{-3}\epsilon_{min.}$ | $\lambda_{max.}$ | $10^{-3}\epsilon_{max.}$ | Peak ratio |
|----------------------|------------------|--------------------------|------------------|--------------------------|------------------|--------------------------|-------------------|
| Dithizone | 450 | 20.6 ± 0.1 | 514 | 5.56 | 620 | 37.1 ± 0.2 | 1.80 |
| | 450 ^b | 45.9 ^b | — | — | 620 ^b | 79.0 ^b | 1.72 ^b |
| Monobromodithizone | 456 | 20.1 | 520 | 5.79 | 626 | 36.9 ± 0.6 | 1.84 |
| Dibromodithizone ... | 464 | 22.4 | 527 | 7.19 | 635 | 40.9 ± 0.4 | 1.83 |
| | 454 ^b | 19.0 ^b | — | — | 638 ^b | 23.0 ^b | 1.21 ^b |

^a Value of ratio of $\epsilon_{max.}$ for the two absorption maxima. ^b Data from Pupko and Pel'kis (refs. 6, 7). All other data from the present paper. The extinction coefficients are mean values of two independent determinations on different samples.

TABLE 4. *Absorption data for mercaptoformazans in carbon tetrachloride.*

| Reagent | $\lambda_{max.}$ | $10^{-3}\epsilon_{max.}$ | $\lambda_{min.}$ | $10^{-3}\epsilon_{min.}$ | $\lambda_{max.}$ | $10^{-3}\epsilon_{max.}$ | Peak ratio |
|----------------------|------------------|--------------------------|------------------|--------------------------|------------------|--------------------------|-------------------|
| Dithizone | 450 | 20.3 | 515 | 5.48 | 620 | 34.6 | 1.70 ^a |
| | 450 | 21.4 | 515 | 5.4 | 620 | 36.4 | 1.70 ^b |
| Monobromodithizone | 458 | 21.0 | 520 | 5.84 | 628 | 34.5 | 1.64 |
| Dibromodithizone ... | 464 | 19.6 | 526 | 6.07 | 635 | 31.4 | 1.60 |

^a Ref. 14. ^b Ref. 18.

While Pupko and Pel'kis's values of $\lambda_{max.}$ for dithizone are confirmed by ours, the values they give for dibromodithizone are substantially different. Their values for molecular extinction coefficients are in serious disagreement with ours and with those of

all other workers.^{17,18} Values they have reported for each of a large number of other analogues of dithizone differ from the results of other workers to much the same extent. Pupko and Pel'kis state that all their measurements were made with solutions of the same concentration (6.6×10^{-5} mole/l.). This appears to imply that these solutions had been prepared by weighing solid reagents: but their papers make no reference to any attempts to purify their crude preparations. If 1 cm. cells were used in their work, the stated concentration implies also that optical densities up to 4.0 were measured.

It is common knowledge that commercial samples of dithizone often show a purity of 85% or less based on mercurimetric titration and Cooper and Sullivan's values for the peak ratio of the purest known samples of dithizone. Several cycles of extraction by aqueous ammonia and reacidification in contact with a solvent are needed to bring the purity, as judged by the peak ratio, to its maximum value.^{13,14,18} That Pupko and Pel'kis's sample of dithizone was impure follows from the low value they report for its peak ratio (Table 3), but no simple explanation can be put forward to explain why they found a value for ϵ_{\max} more than twice as great as that found by any other worker in this field.^{14,17,18} The very low peak ratio recorded for dibromodithizone shows that their sample was grossly impure: this conclusion is supported by the low values they record for the value of ϵ_{\max} at 638 m μ .

Date for solutions in carbon tetrachloride are summarised in Table 4. In this solvent the intensities of absorption at the longer wavelength maxima are slightly lower than in benzene and values of peak ratios are uniformly lower. But the general similarity of data for the two solvents lends further weight to our criticisms of Pupko and Pel'kis's work.

From Tables 3 and 4 it is clear that the introduction of *p*-bromine atoms into diphenylthiocarbazone produces a bathochromic shift in the position of each of the prominent absorption bands in the visible region. The value of λ_{\max} for monobromodithizone is the arithmetic mean of the values for dibromodithizone and dithizone itself. This confirms a generalisation made by Pupko and Pel'kis from a wider range of compounds which, as pointed out above, do not appear to be individually reliable. Pupko, Dubenko, and Pel'kis also stated (a) "that with the introduction of electron-acceptor substituents in the phenyl groups of dithizone the molar coefficient of extinction is decreased, the latter having a value several times less than that of dithizone" and (b) "when haloids are introduced into the phenyl groups of 1,5-diphenylthiocarbazones the intensity of the long-wave maximum is decreased with a simultaneous increase in the intensity of the short-wave maximum."⁷ The present data provide no support for such generalisations.

TABLE 5. *Absorption spectra of various metal complexes of 3-mercaptoformazans in carbon tetrachloride.*

| Metal | | Ag ⁺ | Hg ²⁺ | Bi ³⁺ | Pb ²⁺ | Zn ²⁺ | Cu ²⁺ |
|--------------------|-----------------------------|-----------------|------------------|------------------|-------------------|-------------------|-------------------|
| Dithizone | λ_{\max} (m μ) | 462 | 490 | 490 | 520 | 536 | 548 |
| | $10^{-3}\epsilon_{\max}$ | 29.1 | 72.2 | 84.6 | 66.5 ^a | 92.0 ^a | 45.0 ^a |
| Monobromodithizone | λ_{\max} (m μ) | 468 | 496 | 496 | 526 | 544 | 558 |
| | $10^{-3}\epsilon_{\max}$ | 26.7 | 76.1 | 90.0 | 69.4 | 95.1 | 49.6 |
| Dibromodithizone | λ_{\max} (m μ) | 472 | 502 | 500 | — | 552 | 566 |
| | $10^{-3}\epsilon_{\max}$ | 24.0 | 71.5 | 80.3 | — | 89.7 | 49.7 |

^a Data from ref. 17.

From values of the ratio $\epsilon_c^e/n\epsilon_r^e$ from Table 2 and the values of ϵ_r^e given in Table 4 it was possible to calculate values for the molecular extinction coefficients of various metal-dithizone complexes. These are summarised in Table 5 together with the position of the maximum of the prominent absorption band. For each reagent it was found that λ_{\max} increased in the order Ag⁺ < Hg²⁺ \approx Bi³⁺ < Pb²⁺ < Zn²⁺ < Cu²⁺. There is again a

¹⁷ Iwantschiff, "Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse," Verlag Chemie, Weinheim, 1958.

¹⁸ Weber and Vouk, *Analyst*, 1960, **85**, 40.

bathochromic shift for each metal caused by bromine-substitution, and the value of λ_{max} for the complex of any metal with monobromodithizone is the arithmetic mean of the values for the dibromodithizone and dithizone complex. Values of ϵ_{max} increase in the order $\text{Ag} < \text{Cu} < \text{Pb} < \text{Hg} < \text{Bi} < \text{Zn}$ for each reagent, but there is no systematic trend in individual values as a result of bromine substitution in the parent reagent.

The brominated dithizones appeared to be more soluble than dithizone in aqueous alkali, pointing to a higher acidity of the thiol grouping. The complex of lead with dibromodithizone and of cadmium with either mono- or di-bromodithizone formed red and orange flocks respectively, almost insoluble in carbon tetrachloride. Saturated organic solutions of these metal complexes decomposed too rapidly to permit accurate measurements of their absorption spectra.

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