289. *Studies with Dithizone. Part VIII.*[1] *Reactions with Organometallic Compounds.*

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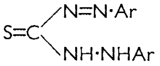
The published reactions of diphenylthiocarbazone (" dithizone," 3-mercapto-1,5-diphenylformazan, HDz) with organometallic compounds of arsenic, tin, lead, and mercury are reviewed. Triethyltin(IV) salts form a 1 : 1 complex, $(C_2H_5)_3SnDz$, and diethyltin(IV) chloride forms a 1 : 2 complex, Et_2SnDz_2. Trimethyl- and triphenyl-lead(IV) salts and dimethyl- and diphenyl-thallium(III) salts form highly coloured complexes R_3PbDz and R_2TlDz respectively (R = Me or Ph). Triphenyltin(IV) salts give a yellow dithizonate of composition Ph_3SnDz. All the dithizone complexes can be extracted quantitatively into an organic phase and used for the determination of the corresponding organometallic compound.

The absorption spectra of dithizone complexes of metallic and organometallic ions are discussed in relation to their structure. There appears to be a linear correlation between the wavelength of maximum absorbancy of a metal–dithizone complex and the logarithm of the stability constant of the corresponding metal–halide complex.

DIPHENYLTHIOCARBAZONE (" Dithizone," 3-mercapto-1,5-diphenylformazan, HDz; I or II, Ar = Ph, R = H) is widely used in trace-metal analysis since, with a limited number of metals, it forms highly coloured inner complexes which are insoluble in water but sufficiently soluble in organic solvents to lend themselves to solvent-extraction procedures.[2] The " dithizone elements " form a compact group in the centre of the Periodic Table whose limits (see Table 1) can be correlated generally with the increasing tendency of the metal to exist as a simple cation of low charge and to form metal–sulphur in preference to metal–oxygen bonds.[3]

(I) 

$S{=}C(N{=}N{\cdot}Ar)(NH{\cdot}NHAr)$

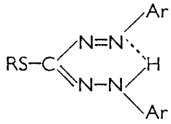
 (II)

TABLE 1. *Elements that form well-established dithizone complexes are enclosed in continuous lines. The broken lines enclose other elements for which the evidence is less certain.*

Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po

Although some of these elements (*e.g.*, copper and mercury) are said to form complexes in two valency states, tin and lead form complexes only in the bivalent state. Thallium(III) and iron(III) are said to oxidize the reagent, although their reactions have not been fully investigated.[2,4] The alleged formation of a red ruthenium complex has been contested.[2,5] Germanium(II) may form a dithizonate * capable of solvent-extraction, but germanium(IV) and gallium(III) do not.[6] Antimony(III) has been shown to form a

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* The terms " dithizonate " and " oxinate " for complexes of metals with dithizone or oxine (8-hydroxyquinoline) are logically incorrect in that they imply that these complexes are derived from dithizonic and oxinic acid respectively. However, this terminology has become almost universally accepted and it is adopted here for the sake of uniformity.

[1] Part VII, *J.*, 1960, 1272.

[2] Iwantscheff, " Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse," Verlag Chemie, G.M.B.H., Weinheim/Bergstr., 1958.

[3] Fischer, *Mikrochem. Mikrochim. Acta*, 1942, **30**, 39.

[4] Dawson, *Analyst*, 1948, **73**, 618; Weber, *Croat. Chim. Acta*, 1957, **29**, 73.

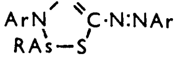
[5] Yaffe and Voigt, *J. Amer. Chem. Soc.*, 1952, **74**, 5043; Steiger, *Mikrochem.*, 1934, **16**, 193.

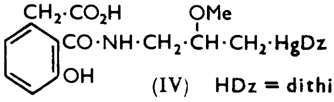
[6] Irving *et al.*, unpublished results.

dithizonate which is orange-red in molten naphthalene[7] and strawberry-red in chloroform and carbon tetrachloride.[8] Dithizone has been used for the solvent extraction of tellurium(IV), ^{129}Te being used as a tracer.[9]

The very great sensitivity of dithizone as an absorptiometric reagent for traces of metals has led a number of authors to consider its application to the detection and determination of organometallic compounds. Tarbell *et al.*[10] found that di-(4-biphenylyl)thiocarbazone reacted with dichloroethylarsine in the presence of bases to give a 1 : 1 complex which they formulated as (III; R = Et). A similar compound was obtained from arsenic(III) chloride and from phenylarsenic(III) oxide, AsPhO.

(III)
Ar = p-C_6H_4Ph
R = Cl, Et, or Ph





(IV) HDz = dithizone

The increasing use of organotin compounds as fungicides and for the treatment of boils[11] has led to studies of their absorptiometric determination with the aid of dithizone.[12] The reagent reacts with triethyltin(IV) salts to give a strongly coloured complex ($\lambda_{max.}$ 435 mμ; ε 23,300) whose composition was not determined. From data in Aldridge and Cremer's paper[12] it is possible to calculate that it must have been the 1 : 1 complex Et_3SnDz. Salts of tri-n-propyl- and tri-n-butyl-tin(IV) are said to form dithizone complexes with spectra similar to that of the triethyltin(IV) complex. By making use of the data quoted for the interaction of diethyltin(IV) salts with dithizone[12] we deduce that a complex ($\lambda_{max.}$ 510 mμ; ε 70,500) has been formed from two molecules of dithizone and one of diethyltin(IV) salts; the probable composition is therefore Et_2SnDz_2. Dibutyl- and dioctyl-tin(IV) salts are said[12] to give dithizone complexes with similar spectra. Tetraalkyltins do not react with dithizone,[12] nor, apparently, does tetraethyl- or tetraphenyl-lead,[6,13,14] although a red compound of unknown composition is said to be formed when solid dithizone and tetraphenyl-lead are ground together.[13]

s-Butylmercury(II) bromide appears to react with dithizone, although this does not seem to have been investigated by the authors:[15] di-s-butylmercury does not react with dithizone,[15] nor does diphenylmercury.[6]

Dithizone has been used in recent procedures for the analysis of spray residues for organomercurials. The optical absorption peaks of ethylmercury(II) dithizonate and phenylmercury(II) dithizonate in 95% ethanol are reported by Webb *et al.*[16] to be at 480 mμ and at 266 and 475 mμ respectively. Miller *et al.*[17] state that the absorption spectrum of ethylmercury(II) dithizonate in chloroform resembles, but does not coincide with, that of mercury(II) dithizonate, and that ethylmercury(II) dithizonate, phenylmercury(II) dithizonate, and the complex (IV) each have an absorption maximum at 475 mμ. Gran,[18] however, reports 497 mμ for the absorption maximum of phenylmercury(II) dithizonate

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[7] Carlton and Bradbury, *Analyt. Chem.*, 1954, **26**, 1226; Carlton, Bradbury, and Kruh, *Analyt. Chim. Acta*, 1955, **12**, 101.

[8] Burstall, Davies, Linstead, and Wells, *J.*, 1950, 520; Pfeifer and Diller, *Z. analyt. Chem.*, 1956, **149**, 264.

[9] Mabuchi, *Bull. Chem. Soc. Japan*, 1956, **29**, 842.

[10] Tarbell and Bunnett, *J. Amer. Chem. Soc.*, 1947, **69**, 263; Tarbell, Todd, Pauson, Linstrom, and Wystrach, *J. Amer. Chem. Soc.*, 1948, **70**, 1381.

[11] Stoner, Barnes, and Duff, *Brit. J. Pharmacol.*, 1955, **10**, 16; Aldridge and Cremer, *Biochem. J.*, 1955, **61**, 406; van der Kerk and Luitjen, *J. Appl. Chem.*, 1954, **4**, 314; Anon., *Brit. Med. J.*, 1954, **2**, 693.

[12] Aldridge and Cremer, *Analyst*, 1957, **82**, 37.

[13] Steiger, *Mikrochemie*, 1937, **22**, 216.

[14] Griffing, Rozek, Snyder, and Henderson, *Analyt. Chem.*, 1957, **29**, 190; Steiger, *Petroleum Z.*, 1937, No. 27, **33**, 3.

[15] Charman, Hughes, and Ingold, *J.*, 1959, 2530.

[16] Webb, Bhatia, Corwin, and Sharp, *J. Amer. Chem. Soc.*, 1950, **72**, 91.

[17] Miller, Polley, and Gould, *Analyt. Chem.*, 1951, **23**, 1286.

[18] Gran, *Svensk Papperstidn.*, 1950, **53**, 234.

in chloroform. The stoicheiometric composition of these alkyl(or aryl)mercury(II) dithizone complexes has not been rigorously established in every case.

From these observations it is clear that the ions RHg^+ (R = alkyl or aryl) and R_3Sn^+ react as simple univalent cations to give RHgDz and R_3SnDz respectively, that the reactions of R_2Sn^{2+} and R_2Pb^{2+} resemble those of Sn^{2+} and Pb^{2+}, and that the inertness of R_4Sn and R_4Pb resembles that of Sn^{4+}. There seems to be little tendency for excess of dithizone to break the metal–carbon bonds and produce normal dithizone complexes such as $SnDz_2$ or $PbDz_2$.

Since the selective action of dithizone towards a limited number of metals (cf. Table 1) can clearly be extended to include organometallic ions derived from some of them, a point of immediate interest is to ascertain whether this behaviour applies to organometallic salts of all the " dithizone elements," in so far as they are not hydrolysed by water. In this paper we report some results for organometallic derivatives of thallium(III), tin(IV), and lead(IV).

RESULTS

Solutions of dithizone in carbon tetrachloride and other organic solvents were found to react with aqueous solutions of dimethyl- and diphenyl-thallium salts and with trimethyl- and triphenyl-lead(IV) salts to give respectively red and yellow complexes which could be extracted quantitatively into the organic phase if the pH was adjusted within certain limits (cf. Fig. 1, and Table 2). Each complex was characterized by a very simple absorption spectrum with a well-defined peak in the visible region.

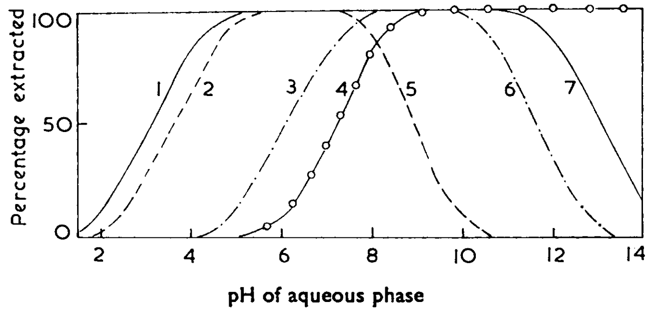

FIG. 1. *Variation with* pH *of the percentage of various organometallic cations extracted by dithizone into carbon tetrachloride.* 1, 7, Ph_2Tl^+. 2, 5, Ph_3Pb^+. 3, 6, Me_3Pb^+. 7, Me_2Tl^+.

TABLE 2. *Extraction of dithizone complexes into carbon tetrachloride.*

Cation	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	pH range for maximum extraction
Me_2Tl^+	525	40·2	8·5 and above
Ph_2Tl^+	520	42·5	5—12
Me_3Pb^+	438	29·9	7·5—10
Ph_3Pb^+	432	31·2	5—8
Ph_3Sn^+	450	24·0	7—11

The composition of each of these new dithizonates was established by one of a variety of methods and each was found to be a 1 : 1 complex. Owing to their sparing solubility Job's method of continuous variations could not be applied to aqueous solutions. This procedure has been applied successfully to the determination of the composition of zinc dithizonate[19] by using a monophase of chloroform (20%), ethanol (70%), and water (10%), but it failed to give unequivocal results for the present complexes. Thus in a monophase buffered at pH 7·9 the absorption bands due to dithizone (455 and 595 mμ), the dithizonate ion (478 mμ), and diphenylthallium(III) dithizonate (495 mμ) overlapped

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[19] Irving, Bell, and Williams, *J.*, 1952, 357.

to such an extent that the calculated Job ordinate never exceeded 0·035 and the extremum could not be located accurately.

To establish the composition of the complexes formed by the ions Me_3Pb^+ and Me_2Tl^+, a solution containing a constant known amount, C_R, of dithizone in carbon tetrachloride was equilibrated with a constant volume of an aqueous buffer containing successively increasing concentrations, C_M, of the organometallic compound. The pH was chosen, after preliminary experiments, to be within the range over which the dithizone complex was known to be quantitatively extracted. Then for a 1 cm. cell the total absorbancy of the organic phase was given by

$$A = [\mathrm{HDz}]\varepsilon_d + [\mathrm{MDz}_n]\varepsilon_c = C_R\varepsilon_d + C_M(\varepsilon_c - n\varepsilon_d)$$

where ε_d and ε_c were the molecular extinction coefficients of dithizone and the complex MDz_n respectively at the wavelength of measurement. The absorbancy of the organic phase increased monotonically with C_M if ε_c was greater than $n\varepsilon_d$. This was the case if measurements were made at the wavelength of maximum absorption of the complex. Absorbancies measured at 620 mμ (the absorption maximum of dithizone in carbon tetrachloride where $\varepsilon_d \gg \varepsilon_c$) decreased monotonically as shown in Fig. 2. At 435 or 450 mμ where $\varepsilon_c > \varepsilon_d$, addition of the organometallic salt caused an increase in the total absorption (Fig. 2). From the volume of dithizone solution required for complete reaction, the composition of the complex could readily be calculated (cf. p. 1475).

FIG. 2. *Spectrophotometric determination of the composition of the complex formed between dithizone and the trimethyl-lead*(IV) *cation.*

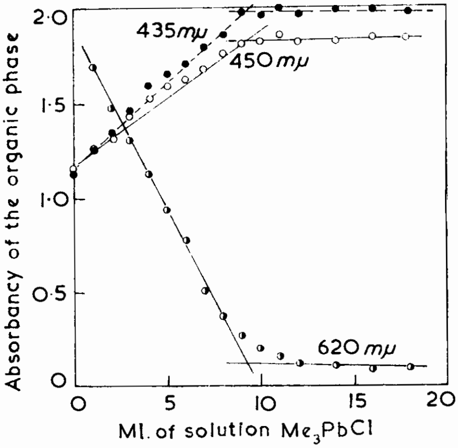
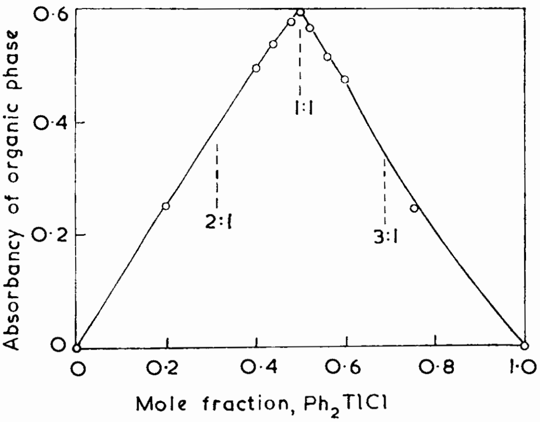


FIG. 3. *Application in a two-phase system of Job's method of continuous variations to the determination of the composition of the complex formed by dithizone with the diphenylthallium*(III) *cation.*



For the diphenylthallium(III) and triphenyl-lead(IV) complexes a modification of Job's method of continuous variations was used. In this procedure the total molar concentration of the reactants is maintained constant, but the uncharged complex is extracted into a water-immiscible phase, carbon tetrachloride in the present case. As in the familiar form of Job's method,[20] some physical property of the complex is measured (in this case the absorbancy in the organic phase) and plotted against the mole ratio of the reactants. For the system diphenylthallium(III) chloride–dithizone, the graph (Fig. 3) takes the form of two straight lines whose intersection at a mole fraction of 0·5 establishes the 1 : 1 stoicheiometry of the complex. A full discussion of the theory of this form of the method of continuous variations has been given.[21]

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[20] Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

[21] Irving and Pierce, *J.*, 1959, 2565.

The molecular extinction coefficients of the complexes were calculated by converting a known quantity of highly purified dithizone (see p. 1476) completely into the form of the desired organometallic complex and measuring its absorbancy. The concentration of the solution of pure dithizone in carbon tetrachloride was obtained from its measured absorbancy and the accurately known molecular extinction coefficient.[6,22] In the case of triphenyltin(IV), however, a graphical method was used involving measurements on a series of mixtures of dithizone and the complex (see p. 1476).

EXPERIMENTAL

Materials.—Samples of dimethylthallium(III) iodide, trimethyl-lead(IV) chloride, and triphenyltin(IV) chloride were recrystallized before use. Diphenylthallium(III) chloride, prepared by Meyer and Bertheim's method,[23] was recrystallized three times from pyridine, washed with hot acetone, and kept in a vacuum-desiccator over concentrated sulphuric acid to remove the last traces of base. Tetraphenyl-lead was prepared by Pfeifer's method [24] and from this triphenyl-lead(IV) chloride was made, by following the procedure of Gilman *et al.*,[25] and finally recrystallised from ethanol. Owing to the low solubility of the chloride in water, it was converted into the fluoride by Krause and Pohland's method.[26] For analyses, organic material was destroyed by wet-ashing, and boiling the sample under reflux with nitric acid for halide determinations and with perchloric acid for metal determinations. Halide ions were determined by Volhard's method, and lead by titration with a standard solution of disodium dihydrogen diaminoethanetetra-acetate [27] (Found: Cl, 9·2. $C_{18}H_{15}ClSn$ requires Cl, 9·2. Found: Pb, 45·7. $C_{18}H_{15}FPb$ requires Pb, 45·3. Found: Cl, 12·4. C_3H_9ClPb requires Cl, 12·35. Found: Cl, 9·0. $C_{12}H_{10}ClTl$ requires Cl, 8·95. Found: I, 35·1. C_2H_6ITl requires I, 34·95%).

Dithizone was purified by extracting it from a solution in carbon tetrachloride into metal-free ammonia solution,[28] washing this solution with pure carbon tetrachloride, and finally back-extracting the dithizone into fresh carbon tetrachloride by addition of excess of very pure hydrochloric acid.[28] This cycle was repeated several times until the purity was 98% or better, as indicated by a value of 1·67 or higher [22] for the ratio of the absorbancies at 620 and 450 mμ.

High-grade water, of specific resistance ≮2 megohms/cm., obtained by passing distilled water through a mixed bed of ion-exchange resins, was used throughout. Carbon tetrachloride was purified by Geiger and Sandell's method,[29] and ethanol according to Weissberger and Proskauer's directions.[30] Whenever possible, buffer solutions were prepared from materials obtained by isopiestic distillation; [28] other reagents were of " AnalaR " grade. The customary precautions in cleaning glassware for work with dithizone were observed.[31] Unless otherwise stated, all absorptiometric work was carried out with a Unicam model S.P. 500 spectrophotometer and matched 1 cm. silica cells. Measurements of pH were made with an Electronic Instruments Ltd. model 23 direct-reading pH meter and a Morton electrode system.

Extractibility of Organometallic Dithizonates as a Function of pH.—(a) *Trimethyl-lead*(IV) *dithizonate.* 5 ml. of a solution of dithizone in carbon tetrachloride (0·149mM) were equilibrated with 5 ml. of an aqueous solution (0·078mM) of trimethyl-lead(IV) chloride and 5 ml. of an aqueous buffer by agitation for 30 min. in a ground-glass stoppered Pyrex test-tube. When the phases had separated, the organic layer was removed and centrifuged to remove any droplets of water. The absorbancy of a portion was then measured (1 cm. cell) at 438 mμ [the wavelength previously found for the maximum absorption of the trimethyl-lead(IV) dithizonate] and also at 620 mμ, where the absorption of dithizone is maximal and that of the organometallic complex

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[22] Cooper and Sullivan, *Analyt. Chem.*, 1951, **23**, 613.

[23] Meyer and Bertheim, *Ber.*, 1904, **37**, 2053.

[24] Pfeifer and Truskier, *Ber.*, 1904, **37**, 1125.

[25] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1929, **51**, 3112.

[26] Krause and Pohland, *Ber.*, 1922, **55**, 1287.

[27] Schwarzenbach (trans. Irving), " Complexometric Titrations," Methuen, London, 1957, p. 92.

[28] Irving and Cox, *Analyst*, 1958, **83**, 526.

[29] Geiger and Sandell, *Analyt. Chim. Acta*, 1953, **8**, 197.

[30] Weissberger and Proskauer, " The Technique of Organic Chemistry," Oxford, 1935, Vol. VII, " Organic Solvents," p. 34.

[31] (*a*) Sandell, " Colorimetric Determination of Traces of Metals," Interscience Publ. Inc., New York, 1950; (*b*) Irving, Cooke, Woodger, and Williams, *J.*, 1949, 1847.

very small. From the latter measurement the absorption due to dithizone at 438 mμ was calculated, and subtracted from the experimental value of the absorbancy at 438 mμ. The pH of the aqueous phase was measured after equilibration. Measurements were repeated with a number of acetate, phosphate, and glycine buffers to cover a wide range of pH values.

(b) *Other organometallic dithizonates.* Similar measurements were carried out with triphenyl-lead(IV) chloride, triphenyltin(IV) chloride, dimethylthallium(III) iodide, and diphenylthallium(III) chloride, where the concentrations of organometallic ions were 0·028, 0·050, 0·081, and 0·033mM respectively, and that of dithizone 0·030, 0·048, 0·149, and 0·039mM respectively. The results are tabulated.

Trimethyl-lead(IV) *chloride.*

pH	5·22	5·91	6·30	6·86	7·17	7·82	8·40	9·64	11·09	12·65
% Extracted	18·5	44·2	57·8	76·6	85·4	97·4	100·0	100·0	71·5	12·6

Tiphenyl-lead(IV) *fluoride.*

pH	3·42	4·21	4·60	4·99	5·37	5·59	5·89	6·24	6·95	7·60	8·04
% Extracted	43·0	73·0	86·7	96·4	103·4	96·5	100·0	96·2	97·4	99·4	93·1
pH	8·20	9·22	9·65								
% Extracted	83·8	33·4	22·0								

Triphenyltin(IV) *chloride.*

pH	3·40	4·05	4·63	5·37	5·89	6·24	6·95	8·04	8·79	9·98	11·14
% Extracted	0	0	12·9	41·7	72·6	98·9	102·1	100·1	103·5	99·0	95·9

Dimethylthallium(III) *iodide.*

pH	5·29	5·76	6·24	6·82	7·28	7·92	8·50	9·37	9·87	10·50	12·45
% Extracted	2·3	5·6	13·8	33·5	52·7	78·7	94·2	98·5	99·6	102·1	104·3

Diphenylthallium(III) *chloride.*

pH	3·44	4·00	4·55	4·90	5·32	5·59	5·89	6·24	6·95	7·38	7·73
% Extracted	65·9	82·6	93·1	94·9	100·7	96·9	96·6	98·7	100·2	100·3	99·6
pH		8·04	8·45	9·22	9·98	10·40	10·60	11·20	11·92	13·10	
% Extracted		100·3	101·9	101·9	97·3	98·4	98·1	101·1	93·5	50·7	

Determination of the Composition of the Dithizone Complexes.—(a) *The two-phase titration procedure.* The extractability curve for trimethyl-lead(IV) dithizonate (Fig. 1) showed it to be completely extracted into the organic phase from buffers in the pH range 7·5—10. Solutions containing x ml. of trimethyl-lead(IV) chloride (0·078 millimole/l.) and $(20 - x)$ ml. of 0·1M-boric acid–borate buffer of pH 8 were equilibrated with 5 ml. of a solution of dithizone (0·149 millimole/l.) in carbon tetrachloride. When values of the absorbancy of the separated organic phase measured at 438 mμ [the absorption maximum of trimethyl-lead(IV) dithizonate] and at 450 and 620 mμ (absorption maxima of dithizone) are plotted against the concentration of trimethyl-lead(IV) chloride (Fig. 2) a sharp change in gradient occurs when 9·2 ml. have been added, indicating the complete interaction of the components. Thus $(9{\cdot}2 \times 10^{-3} \times 7{\cdot}83 \times 10^{-5})$ mole of trimethyl-lead chloride have reacted with $(5 \times 10^{-3} \times 1{\cdot}49 \times 10^{-4})$ mole of dithizone; *i.e.*, 1 mole of trimethyl-lead chloride has reacted with 1·034 moles of dithizone, whence the stoicheiometric formula of the trimethyl-lead(IV)–dithizone complex is Me_3PbDz.

Similar measurements were carried out with dimethylthallium(III) iodide (0·081mM) and a M-ammonia–ammonium chloride buffer of pH 10, measurements being at 450, 525, and 620 mμ. In this case the ratio of dimethylthallium(III) iodide to dithizone was 1 : 0·988, confirming the formula Me_2TlDz.

(b) *The method of continuous variations applied in a two-phase system.*[21] The extractibility curve for diphenylthallium(III) dithizonate (Fig. 1) had shown the complex to be completely extracted into the organic phase in the pH range 5—12. Solutions containing x ml. of diphenylthallium(III) chloride (0·0575 millimole/l.) and $(5 - x)$ ml. of M-ammonia–ammonium chloride buffer of pH 10 were equilibrated with solutions containing $(5 - x)$ ml. of dithizone in carbon tetrachloride (0·0575mM), diluted to 5 ml. with pure organic solvent. After the phases had separated, the organic layer was removed and centrifuged:

Dithizone (mole %)...	20	40	44	48	50	52	56	60	80
Absorbancy, 520 mμ	0·245	0·475	0·515	0·566	0·596	0·578	0·538	0·495	0·249

The absorbancy at 520 mμ [the absorption maximum of diphenylthallium(III) dithizonate] was plotted against the mole fraction of organometallic salt (Fig. 3). The well-defined maximum at 50 moles % of diphenylthallium(III) chloride proves that the stoicheiometric formula of the diphenylthallium(III) complex is Ph_2TlDz.

The procedure was repeated with triphenyl-lead(IV) fluoride (0·028mM) and a 0·066M-phosphate buffer of pH 6·3. Absorbancies were measured at 432 mμ (the absorbancy maximum of the complex) and at 620 mμ. In this case a correction had to be made for the contribution to the absorbancy by free dithizone, but the plot clearly established the stoicheiometric formula of the triphenyl-lead(IV) complex as Ph_3PbDz.

Dithizone (mole %)...	20	30	40	45	50	55	60	70	80
Absorbancy, 432 mμ	0·235	0·277	0·364	0·410	0·444	0·460	0·483	0·525	0·567
Absorbancy, 620 mμ	0·002	0·002	0·007	0·005	0·056	0·127	0·224	0·398	0·589

Triphenyltin(IV) chloride was too insoluble in water to enable the composition of its dithizone complex to be determined in this way. Mixtures of x ml. of a 0·050mM-solution of dithizone in carbon tetrachloride with $(10 - x)$ ml. of a 0·050mM-solution of triphenyltin(IV) chloride in carbon tetrachloride were therefore equilibrated with 5 ml. of an aqueous buffer of pH 10, and the absorbancy of the organic phase measured at 450 mμ. The maximum at 50 moles % of triphenyltin(IV) chloride in the plot of absorbancy against molar composition confirmed the formula of the dithizonate as Ph_3SnDz.

Dithizone (mole %)	0	20	30	40	45	50	55	60	70	80	100
Absorbancy, 450 mμ	0·008	0·282	0·422	0·557	0·612	0·647	0·557	0·537	0·416	0·299	0·063

Determination of the Molecular Extinction Coefficients of Dithizone Complexes.—(a) *Trimethyl-lead*(IV) *dithizonate.* A solution of purified dithizone in carbon tetrachloride (5 ml.) was equilibrated with 5 ml. of a glycine–glycinate buffer of pH 7·8 and an excess of trimethyl-lead(IV) chloride crystals. The organic phase was separated, then centrifuged to remove water droplets, and its absorbancy was measured at 438 mμ. In typical results the absorbancy of the original dithizone (1 cm. cells) was 0·639 ± 0·002 at 450 mμ and 1·076 ± 0·003 at 620 mμ. From the absorbancy ratio (1·683 ± 0·003) the purity was 98·8% and the concentration 0·062mM.[22] From the absorbancy of the resulting trimethyl-lead(IV) dithizonate (0·912 ± 0·004), $\varepsilon = 29,320$. The average value from five determinations was $10^{-3}\varepsilon_{max.} = 29{\cdot}9 \pm 0{\cdot}9$.

(b) *Other organometallic dithizonates.* By similar procedures the following results were obtained for $10^{-3}\varepsilon_{max.}$: Ph_3PbDz, 31·2 ± 1·0; Me_2TlDz, 40·2 ± 1·1; Ph_2TlDz, 42·5 ± 1·6.

(c) *Triphenyltin*(IV) *dithizonate.* Aliquot portions (5 ml., an excess) of a solution of dithizone in carbon tetrachloride and x ml. of a standard solution of triphenyltin(IV) chloride in the same solvent were equilibrated with 5 ml. portions of a buffer of pH 10 and $(20 - x)$ ml. of water. Under these conditions the triphenyltin(IV) was completely transferred to the organic phase as its dithizonate together with excess of dithizone, whose absorbancy at 450 mμ was computed from the absorbancy at 620 mμ (where the complex transmits completely) and the known absorption spectrum of the pure reagent. The gradient of the plot of the absorbancy due to triphenyltin(IV) dithizonate alone against the concentration of organometallic salt taken gave $10^{-3}\varepsilon = 24{\cdot}0 \pm 0{\cdot}3$ as a mean of three determinations.

DISCUSSION

Although the stoicheiometric compositions of many of the simple dithizonates have been established, their structures are still in dispute. Those suggested by Fischer[32] (*e.g.*, V; M = a bivalent metal) have been widely used (cf. Sandell[31]), but they can be criticized on many grounds.[2,31b] More probable structures involve metal–sulphur bonds.[31b,33] If, as in other compounds containing the formazan structure,[34] a mesomeric six-membered ring system is formed by hydrogen bonding, each dithizone residue could then occupy only one co-ordination position on the metal atom (as VI). In an alternative formulation (VII) a five-membered chelate ring would occupy two *cis*-co-ordination positions of the metal atom.[6,33] *X*-Ray crystallographic studies support the formulation

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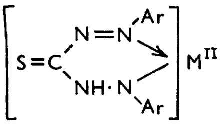
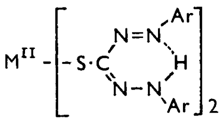
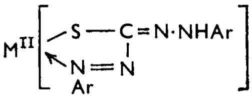
[32] Fischer, *Angew. Chem.*, 1934, **47**, 685; 1937, **50**, 919.
[33] Geiger, *Diss. Abs.*, 1952, **12**, 249.
[34] Irving, Gill, and (in part) Cross, *J.*, 1960, 2087, and refs. therein.

(VII) for solid mercury(II) dithizonate,[35] but this need not be taken as conclusive evidence that the alternative structure (VI) is not preferred in a solution of the complex in an organic solvent; nor are there any grounds for asserting that all metal dithizonates will adopt the same configuration. However, it would surely be expected that the absorption spectrum of a complex containing the highly symmetrical hydrogen-bonded formazan ring system (as VI) would differ from one containing the chelated structure (VII).


(V)


(VI)


(VII)

In simple formazans, isomerism about –N=N– and >C=N– bonds could lead to four configurational isomers, and two conformations have even been postulated for the hydrogen-bonded isomer (as VI).[36] Equilibrium between the various isomers is known to depend on the nature of the solvent and on the conditions of irradiation, and the kinetics of equilibration have been studied in considerable detail.[37] Although *cis-trans*-isomerism in solutions of *S*-methyldithizone (3-methylthio-1,5-diphenylformazan; II, R = Me) has been observed,[38] and the relative intensity of absorption of dithizone (and its analogues) in various solvents at the two maxima in the visible region (*ca.* 450 and 620 mμ) has been correlated with the position of thiol–thione equilibrium,[6] no time-dependent change in the spectrum of dithizone or of any metal dithizonate has ever been observed. [The reversible photoisomerization of mercury(II) dithizonate is a special phenomenon.] From this we conclude, either that the metal dithizonates exist in solution in a single configuration, or that there is very labile equilibrium between all possible forms.

In the formally uncharged complexes R_3SnDz and R_2SnDz_2 the metal atom can achieve its maximum co-ordination of four by forming respectively one or two metal–sulphur bonds. Further co-ordination is unlikely and chelation by the dithizone residue (as VII) cannot take place. Such complexes must be formulated as (VI) or as some variant in which the hydrogen bond is broken and the groups attached to the carbon atom (position 3) adopt one or other of several possible configurations which, for reasons advanced above, must be in labile equilibrium. On the other hand, in the complexes $SnDz_2$ and $PbDz_2$ formed by the simple ions Pb(II) and Sn(II) the dithizonate ion must act as a bidentate ligand if chelation is to bring the co-ordination number to four, although it is possible that two co-ordination positions might be occupied by water molecules. However, the latter seems improbable, for in the case of mercury(II) dithizonate [35] pyridine of crystallization is attached to the dithizone residue by hydrogen bonding, rather than co-ordinated to the metal; since pyridine is the stronger donor it seems unlikely that water should co-ordinate to the metal where pyridine fails to do so. Chelation of the type (VII) would thus be predicted for the zinc, copper, nickel, and cadmium complexes, MDz_2. Although in view of the characteristic " step " in the formation curves of many mercury complexes with monodentate ligands at $\bar{n} = 2$, mercury might have been exceptional in retaining a covalency of two in $HgDz_2$, it is found to assume a deformed tetrahedral quadricovalent configuration [35] involving nearly collinear metal–sulphur bonds with bidentate chelate rings completed through nitrogen atoms of the formazan residues.

The available spectrophotometric data (Table 3) reveal no uniform pattern of behaviour and we can find no correlation between the wavelength or intensity of absorption of individual dithizonates and the electronic structure of the cation from which they are

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[35] Harding, *J.*, 1958, 4136.

[36] Busch and Schmidt, *J. prakt. Chem.*, 1931, **131**, 182; Ragno and Oreste, *Gazzetta*, 1948, **78**, 228.

[37] Hausser, Jerchel, and Kuhn, *Chem. Ber.*, 1949, **82**, 515; Kuhn and Weitz, *ibid.*, 1953, **86**, 1199.

[38] (*a*) Irving and Bell, *J.*, 1954, 4253; (*b*) Ferguson, B.Sc. Thesis, Oxford, 1957.

derived. The only common feature is the strong absorption band in the visible region between 432 and 550 mμ ($10^{-3}\varepsilon = 8$—46 per unit of dithizone); weaker bands ($10^{-3}\varepsilon =$ 12—19 per unit of dithizone) occur in the near ultraviolet region ($\lambda_{max.}$ 265—280). Complexes of nickel(II), palladium(II), platinum(II), and gold(III) are exceptional in showing weaker absorption throughout the visible region with broad overlapping maxima of comparable intensity between 640 and 710, 450 and 490, and 260 and 282 mμ.

TABLE 3. *Absorption spectra of dithizone complexes in carbon tetrachloride.*

Cation	$\lambda_{max.}$	$10^{-3}\varepsilon$	ex.[b]	Ref.	Cation	$\lambda_{max.}$	$10^{-3}\varepsilon$	ex.[b]	Ref.
Co(II)	542	59·2	29·6	2	Pb(II)	520	68·6	34·3	22
Ni(II)	480	30·4	15·2	2	Bi(III)	490	80·0	26·7	2
Cu(II)	550	45·2	22·6	2	AsCl(III) ...	460	—	—	10
Zn(II)	535	92·6	46·3	22	AsEt(III) ...	510	*ca.* 37	—	10
Pd(II)	450	34·4	17·2	2	PhAs(III) ...	510	*ca.* 34	—	10
Ag(I)	462	27·2	27·2	22	Et_2Sn(IV) ...	438	23·2	23·2	12
Cd(II)	520	88·0	44·0	2	Ph_3Sn(IV) ...	450	23·9	23·9	*a*
In(III)	510	87·0	29·0	2	Et_2Sn(IV) ...	506	70·5	35·3	12
Sn(II)	520	54·0	27·0	2	Me_3Pb(IV)...	438	29·9	29·9	*a*
Pt(II)	490	31·6	15·8	2	Ph_3Pb(IV) ...	432	31·2	31·2	*a*
Au(III)	450	31·6	10·5	2	Me_2Tl(III) ...	525	40·2	40·2	*a*
Hg(II)	485	70·0	35·0	22	Ph_2Tl(III) ...	520	42·5	42·5	*a*
Tl(I)	510	33·2	33·2	2					

[a] Present work. [b] The figures in cols. 4 and 9 headed " ex." are values of $10^{-3}\varepsilon$ divided by the number of molecules of dithizone in each complex.

It has been pointed out [39] that for complexes of 8-hydroxyquinoline with a number of uni-, bi- and ter-valent cations the molecular extinction coefficient divided by the number of oxine residues is substantially constant ($10^{-3}\varepsilon$ 2·24 ± 3%) irrespective of the nature or valency of the cation. By contrast, individual values of $10^{-3}\varepsilon$ for dithizonates vary from 92·6 for zinc dithizonate to 23·2 for triethyltin(IV) dithizonate. Even after recalculation on the basis of the number of dithizone residues involved Fig. 4 (Table 3), the variations are still very large (30,000 ± 50%) and demonstrate clearly the specific effects of different metals in modifying transition probabilities in the absorbing species. The wide range of values also supports the suggestion that the configuration of the ligand [*e.g.*, as (V), (VI), or (VII)] is unlikely to be the same for all metal dithizonates. A comparison with the spectrum of *S*-methyldithizone [38a] (II; R = Me) is suggestive, for this substance cannot possibly contain the ring systems postulated by structures (V) or (VII): it is perhaps significant that the molecular extinction coefficient is very low (10,000).

Some regularities in the effect of substitution on spectra may be noted: (*a*) The addition of alkyl groups without change of net charge [Sn(II) to Ph_2Sn(IV); Tl(I) to Me_2Tl(III)] increases the intensity of absorption. (*b*) The addition of alkyl groups with concurrent decrease in charge provokes a decrease in molecular extinction coefficient [*e.g.*, Sn(II) to Et_3Sn(IV); Pb(II) to Me_3Pb(IV)]. (*c*) Replacement of Me (or Et) by Ph causes an increase in $\varepsilon_{max.}$ which is small for tin ($\Delta\varepsilon$ +700), large for lead ($\Delta\varepsilon$ +1300) and thallium ($\Delta\varepsilon$ +2300), and very large for mercury ($\Delta\varepsilon$ +8400 to 16,300).[6]

We have recently commented [40] on the fact that the small number of simple cations that react selectively with dithizone to form complexes are generally those of class (*b*) metals, *i.e.*, those for which the stability of their halide complexes increases in the order $F^- \ll Cl^- < Br^- < I^-$. It was further noted that the absorption maximum of the metal–dithizone complex shifts towards shorter wavelengths as the strength of the metal–chloride (bromide or iodide) bond increases. There is a roughly linear relation between $\lambda_{max.}$ and $\log_{10} K$, where K is the stability constant of the 1 : 1 complex (Ref. 40, Fig. 2). There are no data for the strengths of the metal–ligand bonds in any dithizone complexes, but in so far as d_π–p_π bonding is equally effective in reinforcing the strength of σ-bonds between a

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[39] Irving and Williams, *Analyst*, 1952, **77**, 813.

[40] Irving and Cox, *Proc. Chem. Soc.*, 1959, 324.

class (*b*) metal and chlorine (bromine or iodine) and a class (*b*) metal and sulphur, it is reasonable to expect that the hypsochromic shift is associated with a stronger bond between the metal and the ligand, it being always assumed that this is bonded through a sulphur atom. Increase of valency (in the present case by the loss of an inert pair of electrons) will reduce the radius of a metal ion and favour d_π–p_π overlap. This may account for the hypsochromic effect in the series Pb(II) [520 mμ ⟶ Me_3Pb(IV) (438 mμ) or Ph_3Pb(IV) (506 mμ)]; Sn(II) [(520 mμ) ⟶ Et_2Sn(IV) (506 mμ) or Et_3Sn(IV) (438 mμ) or Ph_3Sn(IV) (450 mμ)], where, for reasons stated above it seems likely that co-ordination through sulphur atoms is not accompanied by the formation of a chelate ring. In the series Tl(I) ⟶ Me_2Tl(III) (525 mμ) or Ph_2Tl(III) (520 mμ), where there is a small bathochromic effect, the preservation of a co-ordination number of four must involve co-ordination through both sulphur and nitrogen (or, in the case of the thallous ion, oxygen from water as well).

It will be apparent that the interpretation of the spectra of metal dithizonates is far from complete, and the hope of being able to use differences in spectra to distinguish between alternative structures has not been realized. However, the distinctive spectra and high molecular extinction coefficients of the different organometallic dithizonates, coupled with their characteristic pH range for extraction, can form the basis for a variety of analytical determinations and separations which will be described elsewhere.

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