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Studies on Tetramethyldithizone Isomers and Their Reactions with Metal Ions

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Six bis(dimethylphenyl) analogues of dithizone are prepared, characterized and their reactions with metal ions in a two phase system are reported. The extraction equilibria of their complexes with Cd(II), Co(II), Hg(II), Pb(II), Tl(I), Zn(II), and Bi(III) as well as their spectral characteristics are described. Complete extraction of these metal chelates requires higher pH's than those needed for the unsubstituted dithizone. The molar absorptivities of Bi(III) complexes with bis(3,4-dimethylphenyl)-, and bis(3,5-dimethylphenyl) analogues are higher than the corresponding value of Bi(III) dithizonate. The molar absorptivities of Cu(II) and Hg(II) (in CCl_4) complexes with bis(3,5-dimethylphenyl) analogue are also higher than the corresponding values of the unsubstituted dithizone complexes.

Dithizone (3-mercapto-1,5-diphenylformazan) is a well-known sensitive analytical reagent used for the determination of many metals in various substances.[1] It is also effective for the separation and preconcentration of traces of metals from different materials prior to their determination by highly sensitive methods.[2] The sensitivity and/or selectivity of dithizone are affected by introducing substituents in the phenyl rings. In a preceding paper, the effects of introducing four chlorine atoms (as electron-withdrawing groups) into the phenyl rings of dithizone on the extraction parameters and spectral characteristics of six new tetrachlorodithizone isomers and their metal complexes were reported.[3]

This paper describes the effects of introducing four methyl groups (as electron-releasing groups) into the phenyl rings of dithizone and their spectral characteristics as well as those of their metal complexes.

Results and Discussion

Visible Spectra of Tetramethyldithizone Analogues. These compounds are black crystalline solids which are insoluble in water. They are fairly soluble in

Table 1. Spectral Characteristics of Isomeric Tetramethyldithizones in Chloroform and Carbon Tetrachloride

Compound[a]	Solvent	$\lambda_{\max,1}$	$\lambda_{\max,2}$	$\lambda_{\min}$	$\varepsilon_{\max,1}$[b]	$\varepsilon_{\max,2}$[b]	$\varepsilon_{\min}$[b]	R	ΔR[c]
		nm	nm	nm	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$		
Unsubstituted	$CHCl_3$	605	442	504	41.5	16.0	6.8	2.59[e]	0.0
			440[f]		41.4[f]	15.9[f]	—	2.59[f]	
	CCl_4	620	450	515	34.6	20.0	—	1.73[f]	0.0
2,3-	$CHCl_3$	614	452	510	44.4	12.2	7.2	3.64	1.05
	CCl_4	625	458	528	39.5	15.5	7.6	2.55	0.82
2,4-	$CHCl_3$	625	456	514	50.7	11.8	7.4	4.30	1.71
	CCl_4	632	460	524	48.5	16.2	7.4	2.99	1.26
2,5-	$CHCl_3$	622	455	512	43.6	10.9	6.1	4.0	1.41
	CCl_4	630	460	536	39.0	14.6	4.4	2.67	0.94
2,6-	$CHCl_3$	588	420	484	34.2	12.2	6.5	2.80	0.21
	CCl_4	606	434	500	34.5	14.5	5.9	2.38	0.65
3,4-	$CHCl_3$	618	450	514	50.3	14.2	12.2	3.54	0.95
	CCl_4	627	446	516	43.8	19.0	7.2	2.31	0.58
3,5-	$CHCl_3$	611	446	507	43.4	13.5	7.11	3.21	0.62
	CCl_4	622	452	515	37.5	20.3	7.05	1.85	0.12
2-	$CHCl_3$	610[d]			49.5[d]				
		612[e]	450		43.5[e]			3.38[e]	0.79
								3.32[f]	0.73
	CCl_4	628[g]	460[g]		38.1[g]			2.31[f]	0.58
3-	$CHCl_3$	610[e]	451[e]	506[e]	43.2[e]	14.7[e]	6.5[e]	3.03[e]	0.44
								3.04[f]	0.45
	CCl_4							1.92[f]	0.19
4-	$CHCl_3$	616[e]	452[e]		49.5[e]	13.4[e]		3.76[e]	1.17
								3.74[f]	1.15
	CCl_4	630[g]	456[g]		46.4[g]				
		632[h]			44.2[h]			2.30[f]	0.57

a) Position of methyl substituents on both phenyl rings. b) Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$). c) $\Delta R=R_s-R_u$ where R_s and R_u are the peak ratios for the substituted and unsubstituted dithizone, respectively. d) Ref. 4. e) Ref. 7. f) Ref. 1. g) Ref. 5. h) Ref. 6.

organic solvents such as chloroform and carbon tetrachloride to give green solutions with two distinct absorption bands in the visible region. The positions and intensities of these bands were found to depend on the position of methyl groups in the phenyl rings as well as on the nature of solvents (Table 1). The solutions of these compounds were found to be stable for about one week if they are kept refrigerated.

Inspection of the spectral data in Table 1 shows the following:

1) Both $\lambda_{\mathrm{max},1}$ and $\lambda_{\mathrm{max},2}$ of all tetramethyldithizone isomers (except bis(2,6-dimethylphenyl) analogue of dithizone) are shifted towards longer wavelengths. This trend is qualitatively similar to what was found with dimethyldithizone isomers[4–7] and also with the tetrachlorodithizone isomers.[8]

2) The $\varepsilon_{\mathrm{max},1}$ values of all tetramethyldithizone derivatives (except that of bis(2,6-dimethylphenyl) analogue) have increased, whereas the $\varepsilon_{\mathrm{max},2}$ values have decreased. This effect is the opposite to what was found with the tetrachlorodithizone analogues whose $\varepsilon_{\mathrm{max},1}$ values have generally decreased.[8]

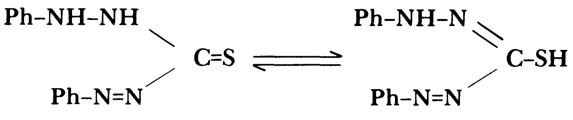
3) As a result of the effects on $\varepsilon_{\mathrm{max},1}$ and $\varepsilon_{\mathrm{max},2}$ mentioned above, all peak ratio (R) values ($=\varepsilon_{\mathrm{max},1}/\varepsilon_{\mathrm{max},2}$) of all tetramethyldithizone derivatives are higher than the corresponding value of the unsubstituted dithizone. Substituent effects on the R values of dimethyldithizone analogues were observed[4–7] where opposite effects on the R values of tetrachlorodithizone analogues has been found.[8]

The existence of two absorption bands in the visible spectra of dithizone solutions in organic solvents are generally attributed to thione–enethiol tautomerism.[1,3,9] The longer wavelength band is attributed to the thione (**1**) whereas the shorter wavelength band corresponds to the thiol tautomer (**2**). It has been also suggested that the peak ratio, R, represents the relative concentration of the two tautomers. The findings that the R values of all tetramethyldithizone isomers are higher than the corresponding values of the unsubstituted dithizone, may then be accounted for by the shifting of equilibria towards the thione tautomer.

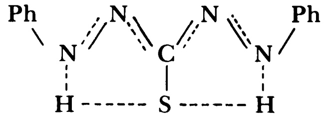
However, some authors have attempted to reconsider the thione–enethiol hypothesis of dithizone; firstly by the preparation of *S*-methyl derivative of dithizone and comparing its spectrum with that of the parent compound. This failed, for while authentic *S*-methyldithizone have been synthesized by Irving and Bell,[10] its initially permanganate pink solution in chloroform (λ_{max} 270 and 550 nm, ε_{550} 1225 m^2 mol^{-1}) isomerizes rapidly by first-order kinetics to a yellow isomer (λ_{max} 280, 420, and 540 nm, ε_{420} 1775 m^2 mol^{-1}) the band at 550 nm becoming less intense as that at 420 nm increases.

Some of the doubts concerning the existence and structure of thiol and thione tautomers of dithizone would be also resolved if *N*-methyl derivatives such as PhNH–N(CH$_3$)–C(=S)–N=N–Ph or PhN(CH$_3$)–NH–C(=S)–N=N–Ph could be prepared. Many authors have attempted such syntheses but without success.[11–13]

The ^{1}H and ^{13}C NMR spectroscopy has also been applied by some authors[14–17] to examine the thione–enethiol hypothesis. Owing to its low solubility in organic solvents, Coleman et al.[14] examined the more soluble analogue 1,5-bis(2-ethylphenyl) thiocarbazone in CDCl$_3$. They observed δ 1.4 (6H, triplet, CH$_3$), 3.0 (4H quartet, CH$_2$), 7.3, 8.1 (8H, multiplet, ArH), and 12.0 (1.6H, singlet, NH). The latter resonance which disappeared on addition of CH$_3$OD, showed no signs of splitting over the range of +50 to −45 °C, and the authors ruled out the hypothesis of tautomeric equilibrium in favor of a single symmetrical species **3** essentially that subsequently established for the solid-state structure by X-ray crystallography.[18]



1 **2**



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Hutton[17] has recently investigated the ^{1}H and ^{13}C NMR spectroscopy of dithizone and seven of its alkyl-substituted analogues and his results showed that their NH singlets at ca. δ 12.50—12.80, always integrated for 2 protons, i.e. confirming Coleman's results.[14]

On the other hand, Wagler and Koch[19] have recently reported a mathematical analysis of the spectra of dithizone in four organic solvents which supports the thione–enethiol tautomerism. Their analysis allowed the calculation of the individual thione and thiol forms and also estimation of the position of tautomeric equilibria in different organic solvents. However, despite that thione–enethiol tautomerism is still unresolved, dithizone (as well as some of its analogues) remains among the best known sensitive analytical reagents.

Visible Spectra of Metal Complexes: The metal complexes of tetramethyldithizone analogues are highly colored and their electronic spectra are characterized by strong absorption bands in the visible region. Table 2 summarizes their spectral characteristics which indicate the following main features:

1) The metal complexes of bis(2,3-, 2,4-, 2,5-, and 2,6-(dimethylphenyl) analogues of dithizone exhibit λ_{max}'s at shorter wavelengths and have lower values of $\varepsilon_{\mathrm{max}}$ than the corresponding values of unsubstituted

dithizone metal complexes.

2) On the other hand, almost all complexes of bis(3,4- and 3,5-dimethylphenyl) analogues of dithizone exhibit λ_{max}'s at longer wavelengths and have relatively higher ε_{max} values than the corresponding complexes of the unsubstituted dithizone.

3) The molar absorptivities of Bi(III) complexes with bis(3,4-dimethylphenyl)-, and bis(3,5-dimethylphenyl) analogues are higher than the corresponding value with the unsubstituted dithizone. The molar absorptivities of Cu(II) and Hg(II) (in CCl_4) complexes with bis(3,5-dimethylphenyl) analogue are also higher than the corresponding values of the unsubstituted dithizone complexes.

Table 2. Spectral Characteristics of Metal Complexes with Tetramethyldithizone Analogues in Chloroform

Compd.[a] Metal	Unsubs.[c] dithizone		2,3-Dimethyl		2,4-Dimethyl	
	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]
Cd(II)	517 (520)[d]	88.4 (88.0)	506	69.9	518	67.6
Co(II)	540	68.3	I[f]		I[f]	
Cu(II)	546	48.2	530	41.4	540	43.2
Hg(II)	485 484[e]	72.2 71.2[e]	478 478[e]	54.1 55.0[e]	494 486[e]	56.6 62.6[e]
Pb(II)	515	68.8	496	52.6	510	55.6
Tl(I)	506	34.8	500	25.8	514	30.3
Zn(II)	526	91.1	516	68.2	530	74.9
Bi(III)[e]	490	80.0	476	68.4	500	48.5

Compd.[a] Metal	2,5-Dimethyl		2,6-Dimethyl		3,4-Dimethyl		3,5-Dimethyl	
	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]	λ_{max}	$10^{-3}\,\varepsilon_{max}$[b]
Cd(II)	515	63.5	478	52.2	518	84.1	518	82.8
Co(II)	526	60.4	520	18.2	550	63.2	545	48.7
Cu(II)	536	43.8	518	58.4	556	45.9	545	58.1
Hg(II)	484	52.7	440 448[e]	42.3 41.5[e]	498 498[e]	75.3 73.8[e]	491 486[e]	68.4 77.8[e]
Pb(II)	506	50.2	466	45.2	525	70.4	520	63.4
Tl(I)	506	25.7	465	23.4	518	34.3	532	44.0
Zn(II)	526	65.7	488	56.0	538	91.8	534	85.7
Bi(III)[e]	480	65.6	No reaction		500	95.1	496	92.6

a) Position of dimethyl substituents on both phenyl rings are indicated. b) Molar absorptivities ($l\ mol^{-1}\ cm^{-1}$). c) Ref. 7. d) Ref. 1. e) In CCl_4. f) Incomplete reaction.

Table 3. Extraction Data for Metal Complexes with Tetramethyldithizone Analogues from $0.5\ mol\ dm^{-3}$ Sodium Perchlorate Solutions into $CHCl_3$

Compd.[a] Metal	Unsubs.[b] dithizone		2,3-Dimethyl		2,4-Dimethyl	
	$\log K_{ext}$	$pH_{1/2}$	$\log K_{ext}$	$pH_{1/2}$	$\log K_{ext}$	$pH_{1/2}$
Cd(II)	0.34	3.81	−4.21	6.11	−4.13	6.07
Co(II)	−2.4	5.2	−8.62	8.31	−6.60	7.30
Cu(II)	7.3	0.35	0.50	3.75	1.20	3.40
Hg(II)	26.86	−9.43	19.9	−5.95	19.65	−5.83
Pb(II)	−0.56	4.28	−3.30	5.65	−4.68	6.34
Tl(I)	−4.17	8.17	−5.73	9.73	−5.93	9.93
Zn(II)	0.40	3.80	−4.35	6.18	−3.36	5.68
Bi(III)[c]	9.89[c]	0.70[c]	5.30[c]	2.33[c]	2.1[c]	3.3[c]

Compd.[a] Metal	2,5-Dimethyl		2,6-Dimethyl		3,4-Dimethyl		3,5-Dimethyl	
	$\log K_{ext}$	$pH_{1/2}$	$\log K_{ext}$	$pH_{1/2}$	$\log K_{ext}$	$pH_{1/2}$	$\log K_{ext}$	$pH_{1/2}$
Cd(II)	−3.69	5.85	−3.21	5.61	−0.89	4.45	−1.10	4.55
Co(II)	—		−5.26	6.63	−3.29	5.65	−5.16	6.58
Cu(II)	0.80	3.59	5.30	1.35	7.63	0.18	3.38	2.31
Hg(II)	20.39	−6.20	19.45	−5.73	21.76	−6.88	22.85	−7.43
Pb(II)	−4.25	6.13	−4.0	6.0	0.50	3.75	−1.55	4.78
Tl(I)	−5.66	9.66	−5.24	9.24	−4.78	8.78	−2.97	6.97
Zn(II)	−3.75	5.88	−3.05	5.53	−1.25	4.63	−3.15	5.58
Bi(III)[c]	3.5[c]	2.83[c]	—		9.05[c]	0.98[c]	8.97[c]	1.01[c]

a) Position of dimethyl substituents on both phenyl rings are indicated. b) Ref. 7. c) In CCl_4.

Table 4. Elemental Analysis and Some Characteristic IR Data for Tetramethyldithizone Analogues

Bis(dimethylphenyl) analogue	Mp θ_m/°C	Elemental analysis[a]		Main IR bands (KBr)/cm^{-1}
		C/%	H/%	
2,3-	152	65.20	6.51	3460, 2910, 1595, 1585, 1490, 1465, 1415, 1280, 1260, 1235, 1190, 1140, 1090, 1050, 780, 700, 580, 465
2,4-	143	65.45	6.38	3440, 2915, 1605, 1505, 1435, 1385, 1215, 1165, 1145 1095, 805
2,5-	136	65.27	6.45	3440, 2910, 1630, 1465, 1450, 1250, 1230, 1190, 1145, 1095, 805, 585, 450
2,6-	138	65.18	6.40	3410, 3280, 3175, 2960, 1290, 1260, 1200, 1150, 1095, 1020, 930, 860, 790, 765, 630, 575, 510, 465
3,4-	125	65.52	6.27	3420, 2910, 1485, 1450, 1315, 1255, 1215, 1175, 1140, 815, 460
3,5-	128	65.15	6.42	3440, 2910, 1600, 1490, 1315, 1245, 1190, 1160, 1120, 840, 770, 660, 475

a) The theoretical results are 65.35% C, and 6.45% H.

Extraction Equilibria. The metal extraction equilibria may be represented by the following general equation:

$$n(CH_3)_4H_2Dz + M^{n+} \rightleftharpoons M[(CH_3)_4HDz]_n + nH^+$$

Table 3 lists the extraction data from which the following conclusions may be drawn:

i) The extraction constants, K_{ext} of tetramethyldithizone metal complexes are considerably smaller than those of the unsubstituted dithizone or the tetrachlorodithizone complexes.[8]

ii) Complete extraction of the metal chelates require higher pH's than those needed for the unsubstituted dithizone complexes as suggested by their higher $pH_{1/2}$.

iii) Unlike bis(2,6-dichlorophenyl) analogue of dithizone,[8] the bis(2,6-dimethylphenyl) analogue of dithizone can extract Cu(II) rather more efficiently than the other tetramethyldithizone isomers (except bis(3,4-dimethylphenyl) analogue.

iv) Bis(3,5-dimethylphenyl) analogue seems more efficient than the unsubstituted dithizone in the separation of Cd(II) from Zn(II).

Experimental

Reagents and Chemicals: The bis(2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylphenyl) analogues of dithizone were prepared from the corresponding arylamines by the nitroformazyl method.[20] The nitroformazan derivatives were converted to the tetramethyldithizone analogues and were finally purified by crystallization from chloroform-cyclohexane mixtures. The elemental analysis data, melting points and some characteristic IR frequencies are given in Table 4.

Deionized water was used throughout, and the usual precautions were taken as with dithizone.[3,21,22]

Procedures. The spectral characteristics (λ_{max} and ε_{max}) of the tetramethyldithizone isomers and their metal complexes were determined in the usual way.[3,21,22] The composition of metal complexes and their extraction constants were also determined as described elsewhere.[8]

The visible spectra of ligands and their complexes were recorded on a Unicam SP8000 spectrophotometer and the infrared spectra on a Unicam SP1000, a Radiometer 64 pH-meter was used for pH measurements. The elemental analyses were done at the Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, F. R. G.

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