

Table II. Characters of the Double-Valued Representations of  $D_5'$

$D_5'$	E	R	$2C_5$	$2RC_5$	$2C_5^2$	$2RC_5^2$	$5C_2'$	$5RC_2'$
A'	1	-1	-1	1	1	-1	<i>i</i>	- <i>i</i>
A''	1	-1	-1	1	1	-1	- <i>i</i>	<i>i</i>
E'	2	-2	$2 \cos(x/2)$	$-2 \cos(x/2)$	$2 \cos x$	$-2 \cos x$	0	0
E''	2	-2	$-2 \cos x$	$2 \cos x$	$-2 \cos(x/2)$	$2 \cos(x/2)$	0	0

$(x = 2\pi/5)$

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### Appendix

The character table for the double group  $D_5'$  does not appear to be readily available in the literature. We have worked out this table, and present the characters of the double-valued representations in this Appendix. The point group  $D_5$  consists of four ir-

reducible representations, generally labeled<sup>28</sup>  $A_1$ ,  $A_2$ ,  $E_1$ , and  $E_2$ . In the double group  $D_5'$ , the number of classes is doubled by multiplication by the operation R, a rotation of  $2\pi$  about the  $C_5$  axis.<sup>24,25</sup> We label the added double-valued representations A', A'', E', and E''. The characters of these new representations are given in Table II.

(23) See, for instance, M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p. 327.

(24) H. A. Bethe, *Ann. Physik*, **3**, 133 (1929).

(25) W. Opechowski, *Physica*, **7**, 552 (1940), has shown that  $C_2$  and  $RC_2$  belong to the same class if, and only if, the group contains another twofold axis perpendicular to the first. This second twofold axis does not occur in the groups  $D_n'$  where  $n$  is odd. Consequently, the elements  $C_2'$  and  $RC_2'$  belong to different classes of  $D_5'$ .

## The Photochromism of Metal Dithizonates

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Twenty-four metal complexes of dithizone have been prepared, characterized, and examined for their photochemical and photochromic behavior in solution. The following nine complexes are photochromic under steady illumination with visible light:  $Pd(HDz)_2$ ,  $Pt(HDz)_2$ ,  $AgHDz$ ,  $Zn(HDz)_2$ ,  $Cd(HDz)_2$ ,  $Hg(HDz)_2$ ,  $Pb(HDz)_2$ ,  $Bi(HDz)_3$ , and  $Bi(HDz)_2Cl \cdot 2HCl$ . Various color changes are observed, ranging from orange  $\rightarrow$  blue to green  $\rightarrow$  yellow. Return reactions are very fast. The photochemical stability of the complexes in benzene solution to ultraviolet light decreases in the order  $Ni(HDz)_2 > Zn(HDz)_2 > Hg(HDz)_2 > Pd(HDz)_2 > Pt(HDz)_2 \sim AgHDz > Pb(HDz)_2 > H_2Dz > Cd(HDz)_2$ . Several generalizations are made regarding the colors and photochromism of dithizone complexes.

### Introduction

Dithizone (diphenylthiocarbazon,  $H_2Dz$ ) has long been used as a reagent for the colorimetric analysis of trace metals.<sup>1,2</sup> However, it is only recently that evidence has begun to accumulate on the properties and structures of the complexes thus formed.<sup>3-5</sup>

Even less is known of the photochemical behavior of the free ligand and its complexes. Although several workers<sup>1-3,6</sup> have noted light sensitivity in this class of compounds and have carried out their experiments in the dark or diffuse light, the possible adverse effects on the analytical applications of these complexes have not been generally recognized, and no detailed investigations of photochemical effects have been made. Around 1950 Irving, *et al.*,<sup>7</sup> and Webb, *et al.*,<sup>8</sup> reported independently that the mercury(II) complex is photochromic. When benzene or chloroform solutions of  $Hg(HDz)_2$  were irradiated or placed in bright sunlight, they changed from their normal orange-yellow color to "an intense royal-blue." They found that the orange-yellow color returned slowly in the dark and that these color changes could be repeated many times. Apparently, these unusual observations were never followed up. We now wish to report on a more detailed study of this system, which has led to the discovery of a large number of photochromic metal dithizonates and a better understanding of the photochemical behavior of these complexes.

(1) G. Iwantschew, "Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse," Verlag Chemie, G.m.b.H., Weinheim/Bergstr., Germany, 1958.

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1959.

(3) H. Irving and R. S. Ramakrishna, *J. Chem. Soc.*, 2118 (1961), and earlier papers in this series.

(4) M. M. Harding, *ibid.*, 4136 (1958).

(5) R. F. Bryan and P. M. Knopf, *Proc. Chem. Soc.*, 203 (1961).

(6) G. Venturolo and A. M. Ghe, *Ann. chim.*, **45**, 1054 (1955).

(7) H. Irving, G. Andrew, and E. J. Risdon, *J. Chem. Soc.*, 541 (1949).

(8) J. L. A. Webb, I. S. Bhatia, A. H. Corwin, and A. G. Sharp, *J. Am. Chem. Soc.*, **72**, 91 (1950).

Table I. Preparation and Description of Metal Dithizonates

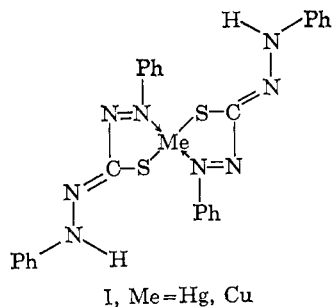
Formula	Method	Yield, %	Color (solid)	M.p., °C.	Theoretical, %					Experimental, %				
					C	H	N	S	Metal <sup>a</sup>	C	H	N	S	Metal <sup>a</sup>
Mn(HDz) <sub>2</sub> ·H <sub>2</sub> O	IA	9	Dark red	220–230	53.60	3.97	19.23	11.00		52.04	3.95	18.02	10.24	
Os(HDz) <sub>3</sub> (?)	IA	<1	Black		Decomposed on recrystallization									
Co(HDz) <sub>2</sub> <sup>b</sup>	II	<1	Black	122–125	Too little sample for analysis									
Ni(HDz) <sub>2</sub>	IA	91	Dark purple	245	54.84	3.89	19.68			54.56	3.52	19.44		
Pd(HDz) <sub>2</sub>														
“Green”	IA	50	Purple	279	50.59	3.56	18.16	10.39	17.3	50.30	3.54	17.87	10.09	15.8
“Violet”	IA	17	Black		50.59	3.56	18.16	10.39		47.23	4.05	12.01	7.83	
“Red”	III	50	Black		50.59	3.56	18.16			47.30	3.66	14.27		
PdDz·2H <sub>2</sub> O	IB	20	Dark red	>280	39.32	3.55	14.11	8.08	26.8	38.93	3.07	13.83	8.11	23.4
Pt(HDz) <sub>2</sub>	IB	50	Black	>280 (subl.)	44.23	3.14	15.87	9.08		41.24	3.10	14.27	8.27	
Cu(HDz) <sub>2</sub>														
“Violet” <sup>c</sup>	IA	70	Black	179–180	54.38	3.86	19.51	11.17	11.1	53.68	4.32	19.74	11.50	8.8
“Brown”	III	50	Brown	141–144	54.38	3.86	19.51		11.1	53.29	4.04	17.70		10.5
CuDz·2H <sub>2</sub> O <sup>e</sup>	IA	32	Black	173–176	44.11	3.98	15.83	9.06	17.9	46.64	3.50	14.16	8.49	17.7
AgHDz·H <sub>2</sub> O <sup>d</sup>	IA	100	Orange-red	223	40.95	3.43	14.69	8.41	28.3	40.78	3.13	14.71	9.01	27.4
Ag <sub>2</sub> Dz <sup>d</sup>	IA	87	Brown	196	33.21	2.14	11.91	6.82	45.9	28.70	2.31	12.19	6.50	45.5
Au(HDz)Cl <sub>2</sub>	IA	94	Dark gray	240	29.82	2.52	10.70			29.91	2.30	10.30		
Au(HDz)(OH) <sub>2</sub>	IA	30	Dark red	182	32.09	2.69	11.51	6.59		31.51	2.60	11.39	6.17	
Zn(HDz) <sub>2</sub> <sup>e</sup>	II	36	Gray-green	236–238	54.21	3.85	19.45	11.13		54.89	3.95	18.43	10.24	
Cd(HDz) <sub>2</sub> <sup>f</sup>	II	99	Orange-brown	251–254	50.11	3.56	17.98	10.29		49.69	3.46	16.79	9.21	
Hg(HDz) <sub>2</sub> <sup>g,h</sup>	II	60	Dark red	228–229	43.89	3.11	15.75			42.58	2.72	15.3		
THDz	IA	72	Dark red	173–179	33.96	2.41	12.19			33.53	2.40	11.84		
Sn <sub>2</sub> O(HDz) <sub>2</sub> ·2H <sub>2</sub> O	IB	1	Red	>200 (subl.)	39.03	3.27	14.00			39.52	3.86	13.97		
Pb(HDz) <sub>2</sub> <sup>f</sup>	IB	7	Red	243–246	43.49	3.08	15.61	8.93		42.57	3.14	15.41	7.33	
Bi(HDz) <sub>3</sub>	IA	94	Green	219	48.04	3.41	17.24	9.86		48.32	3.64	17.24	9.78	
Bi(HDz) <sub>2</sub> Cl·2HCl	II	84	Dark red	206–208	37.71	2.92	13.53	7.74		37.83	2.68	13.62	7.68	

<sup>a</sup> Metal analyses were performed by X-ray fluorescence. <sup>b</sup> J. F. Duncan and F. G. Thomas, *J. Chem. Soc.*, 2814 (1960). <sup>c</sup> R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta*, **8**, 197 (1953). <sup>d</sup> Reference 6. <sup>e</sup> E. Fischer, *Ann.*, **212**, 316 (1882). <sup>f</sup> G. Venturello and A. M. Ghe, *Anal. Chim. Acta*, **10**, 335 (1954). <sup>g</sup> Reference 7. <sup>h</sup> Reference 8.

## Results and Discussion

In Table I are listed the dithizone complexes that were prepared in the course of this study. Standard techniques were generally used in their preparation and most of the purified compounds gave good analyses and sharp melting points. Several new complexes have been prepared and characterized and a number of others have been isolated in the pure state for the first time in this research.

Dithizone is known to form two types of metal complexes, the so-called “primary” and “secondary” dithizonates.<sup>2</sup> In most cases only the “primary” dithizonates have been prepared in this work. These are complexes of the monoanion [C<sub>6</sub>H<sub>5</sub>N=NC(S)=NNHC<sub>6</sub>H<sub>5</sub>]<sup>-</sup>, HDz<sup>-</sup>, Me<sup>+n</sup> + nH<sub>2</sub>H<sub>z</sub> → Me(HDz)<sub>n</sub> + nH<sup>+</sup>. X-Ray investigations of the “primary” Hg(II)<sup>4</sup> and Cu(II)<sup>5</sup> dithizonates have confirmed structure I for these compounds, in which the ligand forms an N,S-chelate ring with the metal atom. Other



“primary” dithizonates have been assumed to contain similar metal–ligand bonding.

The “secondary” dithizonates of Pd(II), Cu(II),

and Ag(I) were also synthesized in order to compare their behavior with the “primary” forms. The “secondary” complexes are formally derived from the dianion [C<sub>6</sub>H<sub>5</sub>N=NC(S)=NNC<sub>6</sub>H<sub>5</sub>]<sup>2-</sup>, Dz<sup>2-</sup>, Me<sup>+n</sup> + (n/2)H<sub>2</sub>Dz → Me(Dz)<sub>n/2</sub> + nH<sup>+</sup>. However, their structures are not known.

*Spectra.* The visible and infrared spectra of the complexes are described in Table II. The visible spectra of the known complexes agreed well with those reported in the literature.<sup>1,9</sup> The outstanding characteristic of the metal dithizonates is the presence of intense visible absorption bands in their solution spectra. All of the complexes display one strong band in the 450–550-mμ region, and frequently one or two other strong bands occur at longer wave lengths. In several complexes a second or third weaker visible band was detected. These weaker visible bands have not been previously reported. Since they frequently occur in the neighborhood of the shorter and longer wave length bands of dithizone, perhaps they should be attributed to traces of the free ligand in the system. The high absorptivities of these strong bands (ε 10<sup>5</sup>–10<sup>6</sup>) and their relative independence of the nature of the metal, as well as similar intense absorption bands in H<sub>2</sub>Dz itself, suggest that these transitions are primarily associated with the delocalized electronic system of the ligand. Several intense visible bands are generally found only in planar complexes, while the tetrahedral and octahedral systems usually have only one band. These additional transitions in the planar systems may result from interaction of the π-electron systems of the coplanar ligands through the central metal atom.

(9) (a) S. S. Cooper and Sr. M. L. Sullivan, *Anal. Chem.*, **23**, 613 (1951); (b) T. Ashizawa, *Bunseki Kagaku*, **10**, 350 (1961).

**Table II.** Visible and Characteristic Infrared Absorption Bands of Metal Dithizonates

Complex	Visible bands, m $\mu$				Infrared bands, cm. <sup>-1</sup> (Nujol mull)			
	Found		Reported <sup>a</sup>		N-H str.	N-H bend	N-phenyl	N-C-S
	$\lambda_{\max}$	Sol-vent <sup>b</sup>	$\lambda_{\max}$	Sol-vent <sup>b</sup>				
Mn(HDz) <sub>2</sub> ·H <sub>2</sub> O	515, 608 sh	A			3350, 3200, 3150 w	1525	1350	1210, 1150
Os(HDz) <sub>3</sub> (?)	390, 520	A			3200 w	1520	1310, 1265	1203
Co(HDz) <sub>2</sub>	410 sh, 545	A	555	A, B	3230	1530	1335	1190, 1167 w
Ni(HDz) <sub>2</sub>	480, 565, 665	B	485, 670	A	3250	1535	1340	1237
Pd(HDz) <sub>2</sub>								
"Green"	450, 570 sh, 640	A	450, 640	A	3230	1534	1340	1230
"Violet"	470, 520	A	470, 510	A		1530	1285, 1257	1215
"Red"	500	A				1535	1330	1210
PdDz·2H <sub>2</sub> O	485	A			3170 vw	1528	1350	1210
Pt(HDz) <sub>2</sub>	430 sh, 488, 710	A	490, 720	A	3260	1528	1335	1217
Cu(HDz) <sub>2</sub>								
"Violet"	545	A	545	B	3220	1530	1340	1212
"Brown"	445	A			3200	1515	1310	1133
CuDz·2H <sub>2</sub> O	445	A	445, 560	A			1325	1200, 1175, 1130
AgHDz·H <sub>2</sub> O	470	A	465	B	3200	1520	1357, 1265	1202, 1128
Ag <sub>2</sub> Dz	490	A			3210	1530	1365 w, 1275	1150
Au(HDz)Cl <sub>2</sub>	540, 570	A	550, 570	A	3180	1545	1343, 1290 w	1238
Au(HDz)(OH) <sub>2</sub>	460, 605 sh	A	460	B	3200	1523	1375, 1262	1190 w, 1128
Zn(HDz) <sub>2</sub>	532	A	532	A, B	3220	1527	1342, 1275 w	1205, 1140 w
Cd(HDz) <sub>2</sub>	518, 605 sh	A	518	A, B	3220	1530	1360	1207, 1157 w
Hg(HDz) <sub>2</sub>	490	A	490	A	3250	1527	1355	1200, 1170 w, 1152 w
TlHDz	515, 605 sh	A	518	B	3200	1517	1357	1130
Sn <sub>2</sub> O(HDz) <sub>2</sub> ·2H <sub>2</sub> O	520	B	522	B	3300, 3200	1520	1310	1216
Pb(HDz) <sub>2</sub>	518, 608 sh	A	520	B	3220	1530	1346, 1275 w	1208, 1155 w
Bi(HDz) <sub>3</sub>	498	A	490	B		1525	1357	1195, 1150
Bi(HDz) <sub>2</sub> Cl·2HCl	500, 620 sh	A			3200	1530	1325	1200, 1135 w

<sup>a</sup> Reference 9b. <sup>b</sup> A = chloroform; B = carbon tetrachloride.

This is not possible in the 1:1 complexes and in those having tetrahedral or octahedral stereochemistry.

The ultraviolet spectra of the metal dithizonates are unexceptional. The usual aromatic bands appear in the 260–280-m $\mu$  region and most of the complexes display weak absorption around 320 m $\mu$ . No bands occur between this wave length and the first visible absorption band in the 450–550-m $\mu$  region.

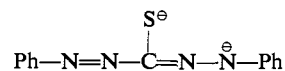
The infrared spectra of the solids (Table II) had characteristic bands in the following regions: 3170–3300 (N–H stretching), 1515–1545 (N–H bending), 1260–1360 (N-phenyl modes), and 1130–1240 cm.<sup>-1</sup> (N–C–S modes). Closer examination of the spectra in the 1000–1600-cm.<sup>-1</sup> region permitted the division of the complexes into four groups, the members of each having very similar spectra. These were: (1) Mn(HDz)<sub>2</sub>·H<sub>2</sub>O, Zn(HDz)<sub>2</sub>, Cd(HDz)<sub>2</sub>, Hg(HDz)<sub>2</sub>, Sn<sub>2</sub>O(HDz)<sub>2</sub>·2H<sub>2</sub>O, Pb(HDz)<sub>2</sub>, and Bi(HDz)<sub>3</sub>; (2) Cu(HDz)<sub>2</sub> "brown," AgHDz·H<sub>2</sub>O, Au(HDz)(OH)<sub>2</sub>, and TlHDz; (3) Ni(HDz)<sub>2</sub>, Pd(HDz)<sub>2</sub> "green," Pd(HDz)<sub>2</sub> "red," PdDz·2H<sub>2</sub>O, Pt(HDz)<sub>2</sub>, and Cu(HDz)<sub>2</sub> "violet"; and (4) Os(HDz)<sub>3</sub> and Co(HDz)<sub>2</sub>. Three complexes, CuDz·2H<sub>2</sub>O, Ag<sub>2</sub>Dz, and Pd(HDz)<sub>2</sub> "violet," had unique spectra, unlike any of the others. These spectral similarities are indicative of structural similarities within the above groups. For example, group 1 contains metals whose complexes would be expected to be either tetrahedral or octahedral. In the third group are complexes of the nickel triad and divalent copper, all of which are probably square-planar. Most of the complexes having only one dithizone residue per metal are found in group 2.

In a similar infrared study, Dyfverman<sup>10</sup> recently obtained spectra of 14 primary metal dithizonates

(10) A. Dyfverman, *Acta Chem. Scand.*, **17**, 1609 (1963).

in KBr disks which are essentially in agreement with our results in mulls. He classified the compounds into two groups, based on spectral similarities, which coincide precisely with the above groups 1 plus 2 and 3 plus 4, respectively. Similar structures within the groups were suggested. Duncan and Thomas<sup>11</sup> measured the N–H stretching frequency in carbon tetrachloride of Cu(HDz)<sub>2</sub>, Hg(HDz)<sub>2</sub>, and Co(HDz)<sub>2</sub>, but were also unable to detect this band in CuDz, results which again agree with those reported herein.

The presence of an N–H band in the infrared spectra of the "secondary" silver and lead dithizonates is inconsistent with their formulation as complexes of the dianion



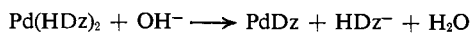
The absence of this band in the spectrum of CuDz·2H<sub>2</sub>O would seem to exclude protonation of nitrogen by water of crystallization. Since the results of the elementary analyses clearly support the compositions Ag<sub>2</sub>Dz and PdDz·2H<sub>2</sub>O, the source of these N–H bands is not clear.

An attempt was made to convert the "secondary" Pd(II) dithizonate into the "primary" form according to the reaction



by shaking a chloroform solution of the "secondary" compound with aqueous hydrochloric acid. After 80 hr., the visible spectrum of the chloroform phase showed that 25% of the "secondary" compound had been converted to the green "primary" form. The reverse reaction

(11) Footnote b, Table I.



does not occur under similar conditions; an isomer of the "primary" compound forms instead.

**Solution Behavior.** Metal dithizonates have very limited solubilities in the usual organic solvents. Saturated solutions in benzene at room temperature are in the concentration range of  $10^{-4}$ – $10^{-5}$  *M* or less. Highest solubility is usually found in chloroform, although carbon tetrachloride, methylene chloride, toluene, tetrahydrofuran, acetone, and ethyl acetate are also satisfactory solvents for spectrophotometric studies. "Secondary" dithizonates are much less soluble than the "primary" compounds.

Most dithizonates are either insoluble or very slightly soluble in ethanol and methanol. They are insoluble in water. The color of alcohol solutions is often different from that of other solvents; it is usually yellow or brown. Dimethylformamide, pyridine, and acetonitrile solutions also tend to have unusual colors, indicative of strong interaction with the solvent. The complexes often cannot be recovered unchanged from these polar solvents.

As expected, pH also has a marked effect on the solution properties of these complexes. For example, when a chloroform solution of "brown"  $\text{Cu}(\text{HDz})_2$  was shaken with aqueous acid it immediately turned violet ( $\lambda_{\text{max}}$  545  $\mu\mu$ ). This change was reversible; upon shaking the chloroform solution with aqueous base, the original brown color returned. The same behavior was noted with the "purple"  $\text{Cu}(\text{HDz})_2$  under the same conditions. Such effects are very common with metal dithizonates and are probably the result of pH dependent structural changes. These phenomena have complicated the interpretation of the photochemistry of these complexes.

**Photochromism.** The 24 metal dithizonates which we have prepared were examined for photochromic properties in the solid and in solution in 16 solvents both at room temperature and at  $-80^\circ$ . Both tungsten and low-pressure mercury light sources were used. In the solid state only  $\text{Hg}(\text{HDz})_2$  was photochromic. The dark red crystals had an orange color when smeared on a porous plate. Under irradiation with visible light, the color changed to brown, finally assuming a violet hue. Return to the orange color was slow, taking several hours.

In solution, 9 complexes were photochromic under these test conditions with visible light. Table III lists the photochromic dithizonates, the conditions (temperature, solvent) under which the phenomenon is observed, and the approximate speed of the return reaction. None of the "secondary" dithizonates is photochromic. Although dithizone itself also displays photochromism, preliminary studies of the color changes, return rates, and photochemical stability of the free ligand suggest that the process follows a very different course from that observed in its metal complexes.

The color change usually observed is from orange or red to blue or violet and is independent of the complexing metal, indicating the primary importance of the ligand in the reaction. The two exceptions are the planar palladium and platinum complexes, in which participation of the metal in the interaction between

the two chelate rings has already been postulated (*vide supra*). The spectrum of the activated form could only be determined in a few cases because of the fast returns and hence the low temperatures necessary to maintain an observable steady-state concentration. Qualitative observations on the blue or violet active forms indicate that their absorption maxima fall in the 570–620- $\mu\mu$  range and that their absorptivities are very high, as in the normal forms.

Although the metal has very little effect on the color of the activated form, it has a marked influence on the rate of return to the normal form. These return rates range from a half-life of about 30 sec. for the mercury compound at  $25^\circ$  to less than 1 sec. for the cadmium and lead compounds at  $-80^\circ$ . At high levels of illumination it is possible to achieve a steady-state system at  $25^\circ$  in benzene containing 80–90% of the total mercury complex in the activated form. Under comparable conditions at  $25^\circ$ , one calculates a steady-state concentration of the active cadmium or lead compound of only about one molecule in  $10^3$  molecules of normal form. No particular significance can be drawn from the order of metals in increasing the apparent return rate:  $\text{Hg} < \text{Pd} < \text{Ag} < \text{Pt} \sim \text{Zn} < \text{Bi} < \text{Cd} \sim \text{Pb}$ . Possible explanations for the metal effect include (1) variations in the metal–ligand bond strengths and bond orders, (2) differences in complex stereochemistry, (3) solvent effects, (4) variations in quantum yields, and (5) different reaction mechanisms.

The photochromic property, as measured by the return rate in solution, is very sensitive to the polarity of the solvent and the presence of acids and bases. The strongest photochromic effects are observed in dry, nonpolar solvents, such as benzene, toluene, chloroform, and carbon tetrachloride. Hydroxylic solvents and organic acids and bases are generally the poorest media for observing photochromism. This results from their accelerating effect on the return of the active form. For example, a few drops of ethanol added to a toluene solution of  $\text{Hg}(\text{HDz})_2$  changes the return half-life from 30 sec. at room temperature to less than 1 sec. at  $0^\circ$ . More pronounced effects have been found with acetic acid, triethylamine, and 2,6-lutidine.

Failure to observe spectral changes in the remaining metal dithizonates under present experimental conditions may simply be the result of very high return rates. We are currently pursuing flash photolysis studies<sup>12</sup> on these nonphotochromic systems in the hope of detecting transient activated forms under these more drastic conditions. Flash photolysis also will be used to determine the spectra of the activated forms and the return kinetics of many of the photochromic systems.

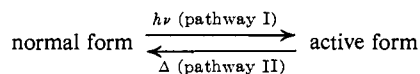
Spectral studies of the metal dithizonates in solution over the temperature range  $-80$  to  $+80^\circ$  failed to produce evidence of thermochromism. The rate of color change from the normal to the active form under conditions (very low temperature) where the return reaction is repressed is a function of the intensity of activating light only. The activation reaction thus

(12) Preliminary results of the flash studies support the assumption that all metal dithizonates are photochromic. In benzene solution at  $25^\circ$ ,  $\text{Ni}(\text{HDz})_2$  has a half-life for return of less than 50  $\mu\text{sec.}$ , and the half-life for  $\text{TiHDz}$  is about 30 msec. Spectral changes similar to those observed in the other photochromic complexes are found.

**Table III.** Photochromic Reactions of Metal Dithizonates

Complex	Solvent	Color and absorption maximum (m $\mu$ )		Temp., °C.	Approx. return time, sec.
		Normal form	Activated form		
Pd(HDz) <sub>2</sub> "Green"	Chloroform	Green (450,640)	Blue (450, 520, 570, 630)	25	5-10
	Benzene	Green	Orange	25	5-10
	Methylene chloride	Green	Orange	-10	1-2
Pt(HDz) <sub>2</sub>	Benzene, carbon tetrachloride	Yellow (490, 708)	Red	25	1-2
AgHDz·H <sub>2</sub> O	Tetrahydrofuran	Yellow (470)	Violet	25	2-5
				10	40-60
Zn(HDz) <sub>2</sub>	Methylene chloride	Red (530)	Violet-blue	25	1-2
	Tetrahydrofuran, ethyl acetate	Red	Violet-blue	-40	<1
Cd(HDz) <sub>2</sub>	Tetrahydrofuran, acetone	Orange (500)	Violet	-80	<1
Hg(HDz) <sub>2</sub>	Benzene, chloroform, methylene chloride	Orange (490)	Blue (605)	25	30-90
Pb(HDz) <sub>2</sub>	Tetrahydrofuran	Red (520)	Blue	-80	<1
Bi(HDz) <sub>3</sub>	Methylene chloride, xylene, ethyl acetate, methanol	Orange (498)	Violet	-30	<1
		Pyridine	Violet	-30	10
BiCl(HDz) <sub>2</sub> ·2HCl	Tetrahydrofuran, methylene chloride	Orange (490)	Blue (605)	-40	2-5

appears to be a strictly photochemical process. On the other hand, the return reaction rate displays the usual temperature dependence and is the same in the light as in the dark, indicating the absence of a photochemical return reaction. Analysis of the time-dependent spectral changes in the return of the mercury and silver complexes has revealed a single isosbestic point between the normal and active forms (Figure 1) showing the absence of reaction intermediates. Therefore, the over-all photochromic reaction of metal dithizonates in solution may be described by the simple expression



in which the steady-state concentration of normal and active forms is a function of both the temperature and the activating light intensity.

In order to test whether free-radical species were produced in the photochromic reaction, a dilute solution of Hg(HDz)<sub>2</sub> in benzene was irradiated with visible and near-ultraviolet light at 25° in the resonant cavity of an electron spin resonance spectrometer. No e.s.r. signals were detected. This system was also insensitive to the presence of free-radical initiators. These results coupled with the strong effect of acids and bases on the systems would suggest that we are dealing with essentially ionic processes and that any excited state species formed in the photochemical reaction must be of extremely short lifetime. More detailed studies of the return reaction of Hg(HDz)<sub>2</sub><sup>13</sup> have confirmed the ionic character of this process.

The activation wave length region of the photochromic metal dithizonates was determined by the use of a 750-w. tungsten projector lamp and a 1000-w. xenon arc source in conjunction with a set of Corning glass filters. The results are shown in Table IV. All photochromic dithizonates are activated by visible light above 450 m $\mu$ , that is, in the region containing the first, or only, visible absorption band. Above 640

(13) L. S. Meriwether, E. C. Breitner, and N. B. Colthup, *J. Am. Chem. Soc.*, **87**, 4448 (1965).

m $\mu$  only the palladium and platinum complexes are activated. This is consistent with the fact that only these two complexes have absorption bands in this

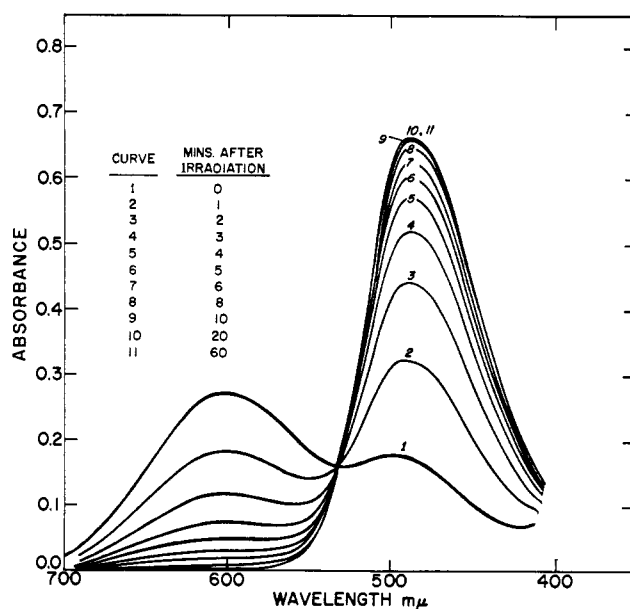


Figure 1. Visible spectrum of return reaction of  $9.4 \times 10^{-6} M$  Hg(HDz)<sub>2</sub> after irradiation in benzene at 25°.

region and shows that activation can occur in more than one of the visible absorption bands. Irradiation in the 300-360-m $\mu$  region produced a detectable photochromism in four of the nine complexes, including those having the slowest return times. Thus the higher energy, near-ultraviolet region can induce photochromism, but the effect is substantially weaker than in the visible region, presumably because of the low absorptivity of the complexes in the near-ultraviolet.

**Photochemical Stability.** In the course of studying the photochromism of metal dithizonates, we have discovered a number of interesting irreversible photochemical reactions. The most important of these are listed in Table V. Since all of the complexes are

**Table IV.** Activation Wave Length Region of Metal Dithizonates

Complex	Solvent	Temp., °C.	Irradiation region <sup>a</sup>		
			300-360 m $\mu$	>450 m $\mu$	>640 m $\mu$
Pd(HDz) <sub>2</sub>	Benzene	10	+	++	++
Pt(HDz) <sub>2</sub>	Benzene	10	-	++	++
AgHDz·H <sub>2</sub> O	Tetrahydrofuran	-80	+	+++	-
Zn(HDz) <sub>2</sub>	Methylene chloride	-80	-	+++	-
Cd(HDz) <sub>2</sub>	Tetrahydrofuran	-80	-	+	-
Hg(HDz) <sub>2</sub>	Benzene	25	+	+++	-
Pb(HDz) <sub>2</sub>	Tetrahydrofuran	-80	-	+	-
Bi(HDz) <sub>2</sub> Cl·2HCl	Tetrahydrofuran	-80	+	+	-
Bi(HDz) <sub>3</sub>	Methylene chloride	-80	-	++	-

<sup>a</sup> Relative intensity of photochromic effect: +++, very strong; ++, strong; +, weak; -, none.

**Table V.** Light-Induced Irreversible Color Changes of Metal Dithizonates

Complex	Solvent	Color and absorption maximum (m $\mu$ )	
		Before irradiation	After irradiation
Mn(HDz) <sub>2</sub> ·H <sub>2</sub> O	Chloroform, methylene chloride	Red (515, 608 sh)	Blue (515, 608)
Pd(HDz) <sub>2</sub> "violet"	Acetone	Violet	Red
Cu(HDz) <sub>2</sub> "violet"	Acetone	Violet (545)	Brown (450)
AuCl <sub>2</sub> HDz	Chloroform	Violet	Blue
Cd(HDz) <sub>2</sub>	Chloroform	Pink (518, 605 sh)	Violet (518, 605)
	Benzene	Green (455, 485 sh, 530 sh, 620)	Pink
TIHDz	Chloroform	Orange-red (515, 605 sh)	Red-violet (515, 605)

stable to visible light above 400 m $\mu$ , these experiments were made with low-pressure Hg arc sources. The conversions of the "violet" Cu(HDz)<sub>2</sub> to the "brown" form and the "green" Pd(HDz)<sub>2</sub> to the "red" form were also carried out on a preparative scale, and the products were isolated and characterized (see Table I). Similar color changes have been observed with several dithizonates resulting from changes in solvent and pH, which suggest that the same products are formed by the photochemical and the chemical routes. Unfortunately, this conclusion is supported by spectral data only, since attempts to isolate the new products from the chemically modified systems resulted either in reversion of the complex to the starting material or decomposition products.

Visible spectra of the manganese, cadmium, and thallium complexes are very similar, each possessing a strong band around 515 m $\mu$  and a weak shoulder at about 605 m $\mu$ . In each case, near-ultraviolet irradiation of the complexes in solution produced a decrease in the 515-m $\mu$  band and a strong increase in the intensity of the 605-m $\mu$  band producing color changes from orange to blue. Exactly the same phenomenon occurs in many of the photochromic dithizonate systems under visible light. It would thus appear that under some conditions the "active" photochromic forms may be stable. However, there is no proof that both the stable and the unstable species absorbing at 605 m $\mu$  have the same structure. They could be isomers.

It was of interest to establish the stability of metal dithizonates to ultraviolet light. Benzene solutions (0.001%) of AgHDz, Hg(HDz)<sub>2</sub>, Pd(HDz)<sub>2</sub>, Zn(HDz)<sub>2</sub>, and dithizone were exposed for the same length of time to gradually shorter wave lengths of the near-ultraviolet spectrum, using cut-off filters every 20 m $\mu$  from 400 to 300 m $\mu$ . Irradiation with light above 400 m $\mu$  caused no decomposition in the solutions. With

the exception of dithizone and AgHDz they were unaffected by light above 360 m $\mu$ , and only after a considerable exposure to irradiation of wave length >340 m $\mu$  did they decompose. However, very rapid decomposition took place when the solutions were exposed to wave lengths down to 320 and 300 m $\mu$ . Since all of the complexes possess a weak absorption band at 320 m $\mu$ , photochemical instability must reside in this band.

In order to assess the effect of the central metal on the photochemical stability of the metal dithizonates, a series of comparative experiments was made under controlled conditions. Benzene solutions (0.001%) of nine complexes were prepared, sealed in identical test tubes, and rotated together on a drum before a powerful light source, filtered by a water cell and a 340-m $\mu$  cut-off filter. A 0.001% solution of dithizone in benzene was run with each set of samples as a standard to monitor the output of the light source. Results of these experiments are shown in Table VI. If the relative stability of the dithizone solution is taken as unity (100% decomposition in 11 hr.), the order of stability of the metal dithizonates is the following: Cd(HDz)<sub>2</sub> (0.5) < Bi(HDz)<sub>3</sub> (0.6) < Pb(HDz)<sub>2</sub> (1.5) < Pt(HDz)<sub>2</sub> (4.3) < AgHDz (4.5) < Zn(HDz)<sub>2</sub> (6.0) < Pd(HDz)<sub>2</sub> (6.5) < Hg(HDz)<sub>2</sub> (7.0) < Ni(HDz)<sub>2</sub> (12.0). In general, formation of a metal complex has a strong stabilizing effect on the light tolerance of the ligand. This might perhaps be attributed to the harmless dissipation of excitation energy in the photochromic process, as is observed in various ultraviolet absorbers.<sup>14</sup>

### Conclusions

Twenty-four dithizonates of 16 different metals have been prepared and fully characterized by micro-

(14) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

**Table VI.** Relative Stabilities of Metal Dithizonates to Irradiation of Wave Length  $> 340 \text{ m}\mu$

Complex <sup>a</sup>	Total irradiation, <sup>b</sup> hr.	Decomposition, %
Ni(HDz) <sub>2</sub>	89.0	70
Hg(HDz) <sub>2</sub>	62.0	85
Pd(HDz) <sub>2</sub>	50.5	70
Zn(HDz) <sub>2</sub>	25.0	38
AgHDz·H <sub>2</sub> O	35.0	70
Pt(HDz) <sub>2</sub>	29.0	60
Pb(HDz) <sub>2</sub>	13.0	80
H <sub>2</sub> Dz	11.0	100
Bi(HDz) <sub>3</sub>	6.0	97
Cd(HDz) <sub>2</sub>	5.5	100

<sup>a</sup> 0.001% solutions of the compounds in benzene, except for Cd(HDz)<sub>2</sub> and AgHDz·H<sub>2</sub>O, which were used as saturated solutions in benzene at a lower concentration. <sup>b</sup> Samples were mounted on a rotating drum, such that exposure to the light source represented only 25% of the total hours of irradiation.

analysis and infrared and visible spectra. Complexes of the same stereochemistry generally have very similar infrared spectra.

It has now been demonstrated that solution photochromism is a general property of metal dithizonates. These photochromic systems possess several unique characteristics, including: (1) very rapid dark return rate; (2) reversible change from one color to another; (3) activation by visible light; (4) long-term stability to visible and near-ultraviolet light of wave length above about  $350 \text{ m}\mu$ ; (5) photochemical forward and thermal return reactions. Free-radical intermediates do not take part in either the forward or return process. Photochromism is probably an inherent property of the ligand since it occurs in the presence of a variety of metals. The central metal atom determines the photochemical stability, rate of the return reaction, and, in some cases, the colors of the complexes.

The following paper<sup>13</sup> describes a kinetic and spectral study of the photochromic process and discusses possible reaction mechanisms.

### Experimental Section

*Preparation of Metal Dithizonates.* Three basic methods were used for the preparation of the complexes. Method I was used for preparing most of the "primary" and all of the "secondary" complexes. Some of the primary complexes were synthesized by method II. Method III was a special irradiation procedure used for obtaining the "red" Pd(HDz)<sub>2</sub> and the "brown" Cu(HDz)<sub>2</sub> from the "green" Pd(HDz)<sub>2</sub> and "violet" Cu(HDz)<sub>2</sub>, respectively. Commercial dithizone was purified according to the procedure of Billman and Cleland.<sup>15</sup> All other chemicals and solvents used were commercially available reagent grade.

*Method I.* For the primary complexes, a 100-ml. aqueous solution containing 3.7–4.4 mequiv. of a suitable salt of the metal (nitrate was used when possible, otherwise, chloride, sulfate, or acetate) was prepared and the pH of the solution was adjusted to the optimum extraction pH described in the literature.<sup>2,16</sup> This mixture was then extracted with a solu-

(15) J. H. Billman and E. S. Cleland, *J. Am. Chem. Soc.*, **65**, 1300 (1943).

(16) H. Freiser, *Chemist-Analyst*, **50**, 62 (1961).

tion of 3.5 mmoles of dithizone dissolved in 200 ml. of chloroform (IA) or 1000 ml. of carbon tetrachloride (IB) by shaking the aqueous solution with portions of the organic solution in a separatory funnel at room temperature until no unreacted dithizone could be detected. The reaction usually took place readily and the complex extracted quantitatively into the organic phase. This phase was separated, dried, and evaporated to dryness. The residue was recrystallized from chloroform or carbon tetrachloride and the pure product was dried in a vacuum drying apparatus over phosphorus pentoxide at 80° for several hours. The same procedure was followed for the "secondary" complexes except that a 50-fold molar excess of the metal salt was used and the precipitated product was filtered off, washed with water, and dried under vacuum.

*Method II.* The chloride salt of the metal (2 mequiv.) was dissolved in absolute ethanol to form a nearly saturated solution. To this a suspension of 2 mmoles of dithizone in 100 ml. of benzene was added rapidly with constant stirring. This mixture was refluxed for 1–2 hr. After cooling, the solution was concentrated by evaporating part of the solvent, and the product was allowed to crystallize. Purification was achieved by recrystallization from chloroform and drying under vacuum at 80°.

*Method III.* A solution of 200 mg. of the complex in 500 ml. of acetone (Cu(HDz)<sub>2</sub>) or chloroform (Pd(HDz)<sub>2</sub>) was irradiated with stirring in a Pyrex glass flask with a 500-w. Hanovia low-pressure mercury arc for several hours. The progress of the reaction was followed by examining the visible spectra of aliquots of the solution. After complete conversion to the new complex, irradiation was discontinued and the solid product was isolated by evaporation of the solvent. The elemental composition of the product was identical with that of the starting material, but changes in the physical properties and the visible and infrared spectra demonstrated that isomerization of the original complex had occurred.

*Photochromism Tests.* The dithizonates were evaluated for photochromic properties by the following procedures. The complex was dissolved in an organic solvent to produce a solution of optical density  $\sim 1$  in the visible. The solution was divided into two Pyrex glass tubes, one of which was exposed to irradiation while the other was used as a control. A visual difference in color between the sample and the control immediately after removing the former from the light source was taken as positive evidence of photochromism. Both a GE RS-2 275-w. sunlamp and a GE 100-w. tungsten lamp (microscope 100 T8 1/2/9-120V) were used as light sources.

If solubility permitted, the complexes were tested in all of the following solvents: methanol, ethanol, benzene, toluene, xylene, carbon tetrachloride, chloroform, methylene chloride, ethyl acetate, dimethylformamide, formamide, tetrahydrofuran, dioxane, acetone, acetonitrile, and pyridine. After evaluation at room temperature, similar tests were carried out after cooling the solution in an ice or Dry Ice-ethanol bath. Solvents used for these cold experiments were methylene chloride, toluene, xylene, acetone, and tetrahydrofuran.

For the determination of the activation wave length regions a similar series of qualitative tests was per-

formed, using as sources a 750-w. tungsten source in a 35-mm. slide projector with a water filter (for the infrared radiation) plus a Corning 2-64 cut-off filter for wave lengths  $>640\text{ m}\mu$  or a Corning 3-72 cut-off filter for wave lengths  $>450\text{ m}\mu$ . For the wave length range 300–360  $\text{m}\mu$ , a 1000-w. high-pressure xenon arc light source was used in conjunction with a Corning 7-54 band-pass filter and a 1-cm. thickness of an aqueous solution containing 50 g./100 ml. of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

*Photochemical Stability Studies.* A GE BH-6 1000-w. high-pressure mercury arc source at a distance of 15 cm. was used for the stability studies. The dithizonate solutions to be tested (3.5 ml.) were sealed in identical 4-ml. Pyrex glass tubes. Twelve of these tubes were mounted on a drum which was mounted vertically and rotated slowly in front of the source. A maximum of three tubes of each solution was prepared and exposed for different periods. The per cent decomposition of the exposed samples was determined by comparing the optical density at the visible maximum with that of an unexposed portion of the same solution. The complexes decomposed to colorless or weakly absorbing

products. The following Corning filters were used along with a water filter for the different wave length regions:  $>400\text{ m}\mu$ , 3-73;  $>360\text{ m}\mu$ , 3-75;  $>340\text{ m}\mu$ , 0-52;  $>320\text{ m}\mu$ , 0-54.

Infrared spectra were determined in mineral oil mulls on a Perkin-Elmer Model 21 recording infrared spectrophotometer with sodium chloride optics. A Bausch and Lomb Spectronic 505 spectrophotometer was used for the ultraviolet and visible spectroscopy. Melting points were determined in an aluminum block and are uncorrected. Metal analyses on the complexes were done by X-ray emission. A Varian V-4500 electron spin resonance spectrometer was used for the e.s.r. experiment.

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## Kinetic and Infrared Study of Photochromism of Metal Dithizonates

L. S. Meriwether, E. C. Breitner, and N. B. Colthup

*Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut. Received April 1, 1965*

*Infrared and kinetic studies of the photochromism of  $\text{Hg}(\text{HDz})_2$ ,  $\text{Ag}(\text{HDz})$ , and  $\text{Bi}(\text{HDz})_3$  in solution at 25° and lower temperatures have been carried out. The thermal return reaction of  $\text{Hg}(\text{HDz})_2$  in benzene at 25° follows first-order kinetics and also shows a direct linear dependence on total complex and water concentration. N-Deuteration of the complex produces a threefold decrease in the return rate. A structure is proposed for the activated form of  $\text{Hg}(\text{HDz})_2$ , and a mechanism for the return to the normal form is presented involving a cis-trans isomerization of an azomethine group and a rate-determining proton shift.  $\text{Ag}(\text{HDz})$  and  $\text{Bi}(\text{HDz})_3$  display behavior essentially identical with that of the mercury complex.*

### Introduction

In the preceding paper<sup>1</sup> we discussed the photochromic and photochemical behavior of a large number of metal dithizonates. In view of the unique characteristics of these photochromic systems, it is of interest to determine the structures of the activated forms of the complexes and the mechanisms of the reactions involved. To this end a technique has been developed for following the infrared spectral changes of the complex solutions under irradiation, and a kinetic study of

the return reaction of mercury and silver dithizonate has been carried out. Both the N-protonated and N-deuterated complexes have been examined. The results of these studies and their mechanistic consequences are the subject of this paper.

### Results

*Infrared Spectra.* The infrared spectrum of  $\text{Hg}(\text{HDz})_2$  in either carbon disulfide or carbon tetrachloride at  $-15^\circ$  was essentially the same as that of the solid. Carbon disulfide was used as solvent for study of the region above  $3000\text{ cm}^{-1}$  and below  $1300\text{ cm}^{-1}$ , and carbon tetrachloride was used for the region above  $3000\text{ cm}^{-1}$  and below  $1700\text{ cm}^{-1}$ . The complex is much more soluble in carbon disulfide.

Significant changes were observed in the solution spectra under irradiation with visible light. Figure 1 shows the infrared spectra of the normal and activated forms of  $\text{Hg}(\text{HDz})_2$  in carbon disulfide solution at two different concentrations. In the saturated solution only a partial conversion to the activated form was achieved, but the dilute solution was converted practically quantitatively to the activated form under the same experimental conditions. In Figure 2 the normal and activated spectrum of  $\text{Hg}(\text{HDz})_2$  is shown in carbon tetrachloride solution. This result was obtained by using different cell thicknesses for the various bands of the spectrum.

(1) L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Am. Chem. Soc.*, **87**, 4441 (1965).