1,5-Bis(2,5-Difluorophenyl)-3-Mercaptoformazan. A New Tetrafluorinated Dithizone Analogue

A. M. Kiwan[a]; H. F. Aly[a]; G. Wanas[a]

[a] Department of Chemistry, University of Kuwait, Kuwait

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ABSTRACT

1,5-Bis(2,5-difluorophenyl)-3-mercaptoformazan (2,2', 5.5'-tetrafluorodithizone, F_4H_2Dz) has been synthesized; its electronic spectra was found to be significantly different from that of dithizone. Its $pH_{1/2}$ in chloroform (8.4) and in carbon tetrachloride (7.4) are lower than the corresponding values (10.6 and 8.8, respectively) for dithizone. The partition coefficient of the reagent is remarkably decreased in chloroform (270) and in carbon tetrachloride (160) due to the presence of fluorine atoms, compared to the corresponding values ($10^{4.89}$ and $10^{4.18}$, respectively) for dithizone. The extraction constants of its complexes with Cd(II), Cu(II), Pb(II), Co(II), Hg(II), and Zn(II) were found to be higher than the corresponding values of dithizone complexes, thus enabling their extraction from more acidic solutions. The new reagent seems also to be slightly more sensitive for Bi(III), Cd(II), Co(II), Cu(II), and Hg(II).

INTRODUCTION

Dithizone (1,5-diphenyl-3-mercaptoformazan, H_2Dz) is a widely

used extractant in trace analysis of metals and organometals [1].

Although it is a very sensitive reagent towards metal ions,

dithizone is not a very selective one. Two methods are generally

used to enhance its selectivity. One is by controlling the metal

extraction equilibria through pH adjustment and/or the introduction

of masking agents, whereas the other involves modifying its

structure by introducing substituents into its phenyl nuclei. The

latter approach has resulted in the preparation of numerous analogues (2), but only a few have been thoroughly investigated.

In an earlier paper (3), we reported the preparation of 2,2'-difluorodithizone and the results of studies of the effect of the two fluorine atoms on its spectra, acidity, and its extraction properties. In this paper, we report our results on the synthesis and properties of a new tetrafluoro-dithizone analogue, 1,5-bis (2,5-difluorophenyl)-3-mercaptoformazan, and describe its extraction behavior.

EXPERIMENTAL

Materials

1,5-bis(2,5-difluorophenyl)-3-mercaptoformazan was synthesized by the nitroformazyl method (4). The nitroformazan was converted to the dithizone analogue by the normal procedure and was finally purified by dissolution in chlorform, extraction with dilute isopiestic ammonia and finally precipitated with dilute isopiestic hydrochloric acid. The solid was washed free of acid, and dried in vacuo. m.p. 167°C. Found: C, 47.56%; H, 2.54%; F, 23.32%; N, 16.93%; the formula $C_{13}H_8F_4N_4S$ requires: C, 47.56%; H, 2.46%; F, 23.15%; N, 17.07%. Infra-red spectra indicated the following: NH stretch, 3100 to 2920 cm^{-1}; NH bend, 1500 cm^{-1}; and NCS, 1205 cm^{-1} in a KBr disc.

Reagent-grade chemicals were used and the usual precautions were taken as with dithizone (1,2).

Procedure

The molar absorptivities of 2,2', 5,5'-tetrafluorodithizone and its metal complexes, their compositions, and the effect of pH on their extractabilities were determined in the usual way as has already been described for dithizone (1). The partition coefficients of 2,2',5,5'F_4H_2Dz in chloroform-water and carbon tetrachloride-water two phase systems and values of pH of half neutralization ($pH_{1/2}$) were determined by methods which had been described previously (5,6).

The extraction constants for Cd(II), Cu(II), Co(II), Ni(II), Pb(II) and Zn(II) complexes were determined by carrying out extraction experiments from perchlorate, acetate, phosphate, and borate solutions at known pH values. The equilibrium concentrations of the complex, M^{n+}--2,2', 5,5'-F_4H_2Dz and H^+ were calculated. The concentrations of the extractant and its metal complexes were determined spectrophotometrically, whereas the concentrations of M^{n+} were obtained from the degree of extraction and the H^+ concentrations from measurements of the pH of the aqueous phase.

The extraction constant of $Hg(F_4HDz)_2$ was determined by following a procedure originally suggested by Takei and Kato (7) for the determination of the corresponding values of mercury complexes of some dithizone analogues.

The visible spectra of the tetrafluorodithizone analogue and its complexes were recorded on a Cary 17 spectrophotometer, and the infrared spectra on a Unicam 800 spectrophotometer; a Radiometer pH-meter was used for pH measurements.

RESULTS AND DISCUSSION

Visible Spectra of 2,2',5,5'-tetrafluorodithizone

2,2',5,5'-F_4H_2Dz is a violet-black crystalline powder which resembles dithizone in its appearance. It is very sparingly soluble in water, but dissolves in organic solvents, such as chloroform, to give green solutions with two distinct absorption bands, and in alkali to give orange solution (see Fig. 1). The characteristic absorption spectra of 2,2',5,5'-F_4H_2Dz in some solvents are summarized in Table 1 together with the corresponding data of 2,2'-difluoro-dithizone and dithizone.

The introduction of four fluorine atoms into the phenyl nuclei of dithizone has shifted both its absorption bands towards longer wavelength λ and lowered their molar absorptivities ε remarkably (Table 1). Qualitatively similar effects were observed on introduction of two fluorine (3), chlorine (8) or bromine (7) atoms into the phenyl rings of dithizone.
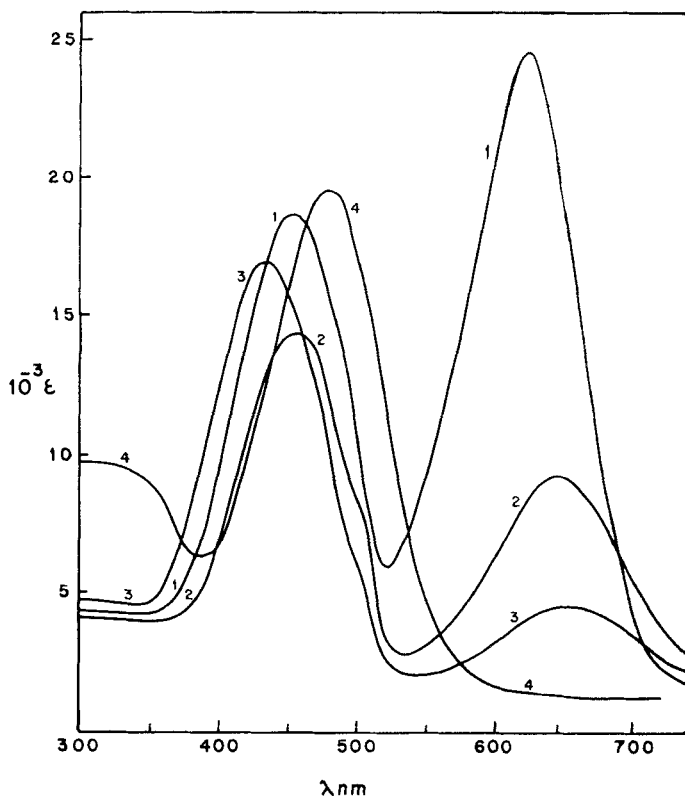
Fig.1 Absorption spectra of 2,2',5,5'-F$_4$H$_2$Dz in (1) CHCl$_3$, (2) CCl$_4$, (3) C$_6$H$_{12}$ and (4) aqueous NH$_4$OH .

The peak ratio R (i.e., the value of ε at the longer λ_{max} divided by ε at the shorter λ_{max}) of 2,2',5,5'-F$_4$H$_2$Dz is also decreased significantly compared to that of dithizone or 2,2'-F$_2$H$_2$Dz (Table 1). In fact, the value of 0.26 in cyclohexane, compared with the corresponding value of 1.13 for dithizone, is the lowest value thus far reported in the literature for a dithizone analogue.

The existence of the two well-separated absorption bands in the visible spectra of 2,2',5,5'-F$_4$H$_2$Dz, and the manner in which

TABLE 1

Spectral Characteristics of 1,5-bis(2,5-difluorophenyl)-3-mercaptoformazan, F_4H_2Dz;
1,5-di(2-fluorophenyl)-3-mercaptoformazan, F_2H_2Dz; and 1,5-diphenyl-3-mercaptoformazan, H_2Dz

Solvent	2,2',5,5'-F_4H_2Dz			2,2'-F_2H_2Dz			H_2Dz		
	λ_{max}	$10^{-3}\varepsilon$	R	λ_{max}	$10^{-3}\varepsilon$	R	λ_{max}	$10^{-3}\varepsilon$	R
$CHCl_3$	622 457	24.5 17.9	1.37	615 454	35.8 17.9	1.77	605 445	41.4 15.9	2.59
CCl_4	644 456	9.3 13.4	0.69	632 454	25.3 23.7	1.07	620 450	34.6 20.3	1.70
C_6H_{12}	654 432	4.5 17.1	0.26	644 452	8.5 12.7	0.67	623 452	27 23.8	1.13
NH_4OH (aqueous)	480	19.7		473	21.1		470	22	

they are affected by fluorine atoms, suggests that they originate
from the thiol (1) and thione (2) tautomers:
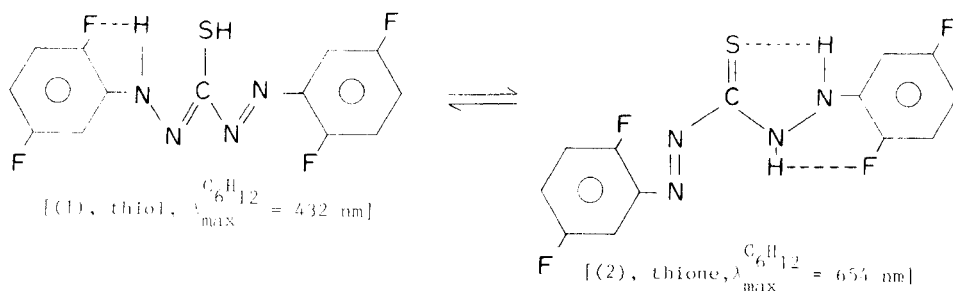
The notion of thiol-thione tautomerism was originally
postulated to account for the two absorption bands of dithizone
(9,10). Since the formazans (3) of the general formula

$$\begin{array}{l} Ar - N = N \\ Ar - HN - N \end{array} \Big\rangle CX$$

$$(3, \lambda_{max} \sim 420 \text{ nm})$$
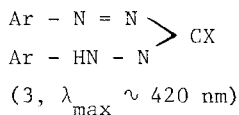
(where X = Cl or alkyl) have a principal absorption band near
420 nm, it is reasonable to assume that the shorter wavelength
band corresponds to the thiol form. The disappearance of the longer
wavelength band on metal complexation (formation of S-M and M-N
bonds), and the bathochromic shift of the shorter wavelength band to
the region of 460 to 540 nm, is consistent with this hypothesis.
The introduction of four fluorine atoms into the phenyl nuclei of
dithizone thus seems to shift the tautomeric equilibria towards
the thiol form. Substitution of hydrogen atoms for two fluorine
(3) or two chlorine (8) atoms were reported to yield a somewhat
similar effect. On the other hand, the introduction of electron-
donating substituents, such as methyl group (1), reverses the
tautomeric equilibria towards the thione form.

Visible Spectra of Metal Complexes

The spectral data for metal complexes of $2,2',5,5'-F_4H_2Dz$ are summarized in Table 2 together with the corresponding data for $2,2'-F_2H_2Dz$ and H_2Dz. Inspection of these data reveals the following trends: (1) the introduction of four fluorine atoms into the phenyl nuclei of dithizone have bathochromically shifted the λ_{max} of its metal complexes, except for the Hg(II) complex; (2) the extent of the bathochromic shift for Zn(II), Cd(II), and Hg(II) complexes runs opposite to the corresponding values of their extraction constants (Table 3); (3) the relative sensitivity of reagent is increased towards some metals, such as Bi(III), Cd(II), Co(II), Cu(II), and Hg(II), as indicated by their relatively higher

TABLE 2

Absorption Data of Metal Complexes with $2,2',5,5'-F_4H_2Dz$, $2,2'F_2H_2Dz$ and H_2Dz in $CHCl_3$

Metal ion	$2,2',5,5'-F_4H_2Dz$		$2,2'-F_2H_2Dz$		H_2Dz	
	λ_{max}	$10^{-3}\,\varepsilon_{max}$	λ_{max}	$10^{-3}\,\varepsilon_{max}$	λ_{max}	$10^{-3}\,\varepsilon_{max}$
Ag^I	466	29	462	29.5	465	33.1
Bi^{III}	506	90.2	494	97.4	490	87.5
Cd^{II}	520	90	508	71.7	520	85.6
Co^{II}	542	59	540	65.9	540	57.9
Cu^{II}	541	44.3	540	65.9	534	41.2
Hg^{II}	476	73.8	480	69.1	480	69.8
Pb^{II}	520	62.3	520	70.7	518	63.6
Tl^I	518	33.1	512	35.9	505	33.6
Ni^{II}	680	15.3	672	38.8	665	19.3
	550	23.6	544	46.7	555	24.7
	490	23.0	476	45.6	480	26.9
Zn^{II}	533	83.3	528	95.6	530	88

TABLE 3

Metal Extraction Equilibria

| Metal	$\log K_{ext}$	pH of half extraction[a]
Ag^+	8.57 (6.0)[b]	
Cd^{2+}	8.25 (0.53)	-0.13 (0.75)[b]
Cu^{2+}	9.68 (6.5)	-0.84 (3.75)
Pb^{2+}	7.52 (-0.89)	0.24 (4.05)
Zn^{2+}	6.66 (0.90)	0.67 (3.80)
Co^{2+}	3.90 (-1.1)	2.05 (4.55)
Hg^{2+}	27.7 (26.8)	

[a]Calculated from K_{ext} with the assumption that 1.0×10^{-4} M F_4H_2Dz in $CHCl_3$ is used as extractant.

[b]Values in parentheses are corresponding values for dithizone.

molar absorptivities compared to the corresponding values of dithizone complexes.

Metal Extraction Equilibria

The tetrafluorodithizone was found to react with metal ions in a stoichiometrically identical manner to dithizone, thus we can describe the equilibria through the equation

$$M^{n+}(a) + nF_4H_2Dz(o) = M(F_4HDz)_n(o) + nH^+(a),$$
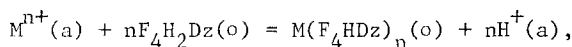
where M^{n+} denotes metal ion and a and o represent aqueous and organic phase, respectively. The extraction constant K_{ext} is then defined by

$$K_{ext} = \frac{[M(F_4HDz)_n]_o [H^+]_a^n}{[M^{n+}]_a [F_4H_2Dz]_o^n} .$$

Values of K_{ext} for various metal complexes of the tetra-
fluorodithizone are presented in Table 3 along with corresponding
values of the dithizone complexes. Also listed are values of pH
of half extraction.

Examination of the data presented in Table 3 indicates that
the introduction of four fluorine atoms into the phenyl nuclei
of dithizone significantly decreases the pH of half extraction of
its metal complexes. This may be partly due to the lower $pH_{1/2}$
values for the tetrafluorodithizone (7.4 in CCl_4 and 8.4 in $CHCl_3$)
as compared with the corresponding values (8.8 in CCl_4 and 10.6
in $CHCl_3$) for dithizone (1). The extraction constants of the
tetrafluorodithizone metal complexes are higher than the
corresponding values of the dithizone complexes, despite the likeli-
hood that the partition constants may in fact be lower. This latter
possibility arises from the observation that the partition coefficients
of $2,2',5,5'-F_4H_2Dz$ itself (270 for $CHCl_3$ and 160 for CCl_4) are
much lower than those of dithizone ($10^{4.89}$ for $CHCl_3$ and $10^{4.18}$
for CCl_4) in the same solvents (1).

ACKNOWLEDGMENT

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