Studies of 1,5-Bis(3,4,5-trimethoxyphenyl)- and 1,5-Bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans and Their Reactions with Metal Ions

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1,5-Bis(3,4,5-trimethoxyphenyl)- and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans have been prepared and characterized, and their reactions with metal ions in a two-phase system are reported. The extraction equilibria of their metal complexes with Cd^{II} , Co^{II} , Cu^{II} , Hg^{II} , Ni^{II} , Pb^{II} , Tl^{I} and Zn^{II} as well as their spectral characteristics are also described. The molar absorptivities of Pb^{II} and Zn^{II} complexes with 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan are higher than the corresponding values of their complexes with dithizone. The molar absorptivities of Cu^{II} and Cd^{II} complexes with 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan are also higher than the corresponding values of the dithizone complexes. 1,5-Bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan is more efficient than dithizone in the separation of Cd^{II} from Zn^{II} .

Keywords 1,5-Bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan, 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan, dithizone analogue, metal complex, extraction constant

Dithizone (1,5-diphenyl-3-mercaptoformazan, H_2Dz) is a well-known sensitive reagent for the trace analysis of metals and organometals.¹ It is also effective for the separation of metals from various media prior to their determination by highly sensitive physical methods.² Although it is a sensitive analytical reagent, dithizone is not very selective in its reactions with metals. However, two approaches have been tried to enhance its selectivity: one by controlling the composition of the metal-bearing solution, and the other by modifying its structure. Application of the latter approach has resulted in the synthesis of several dithizone analogues, though only a few of these have been thoroughly investigated.¹ In a preceding paper, the effects of introducing four methyl groups in the phenyl rings of dithizone on the extraction parameters and the spectral characteristics of tetramethyldithizone isomers and their metal complexes were reported.³

This paper reports on the synthesis of two new dithizone analogues, 1,5-bis(3,4,5-trimethoxyphenyl)- and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans, as well as their reactions with metal ions. The substituent effects on the sensitivity and/or selectivity of the two new extractants are assessed.

Experimental

Reagents and chemicals

The 1,5-bis(3,4,5-trimethoxyphenyl)- and 1,5-bis(2-

methoxy-4-methylphenyl)-3-mercaptoformazans were prepared from the corresponding arylanilines by the nitroformazyl method.⁴ The nitroformazan derivatives were converted to the corresponding dithizone 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 1.

Deionized water was used throughout, and the usual precautions were taken, as with dithizone.⁵⁻⁷

Procedures

The spectral characteristics (λ_{max} and ϵ_{max}) of both dithizone analogues were determined in the usual way.⁵⁻⁷ The compositions of metal complexes and their extraction constants were determined as described elsewhere.⁸ The visible spectra of the ligands and their complexes were recorded on a Unicam-SP8000 spectrophotometer and in the infrared on a Unicam-SP1000; a Radiometer 64 pH-meter was used for pH measurements. The elemental analyses were made at the Alfred Bernhardt Microanalytisches Laboratorium, Elbach, Germany.

Results and Discussion

Visible spectra of 1,5-bis(3,4,5-trimethoxyphenyl)- and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans

These are black crystalline solids which are insoluble in water. They are soluble in organic solvents, such as chloroform and carbon tetrachloride, which give green

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Table 1 Elemental analysis, $pH_{1/2}$, characteristic IR and visible spectral data for 1,5-bis(3,4,5-trimethoxyphenyl)- (left column) and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans (right column)

MP/°C	152	160
Elemental analysis		
C %	52.25 (52.28) ^a	59.32 (59.28)
H %	5.57 (5.54)	5.83 (5.83)
N %	12.78 (12.84)	16.35 (16.37)
$pH_{1/2}$ ^b	7.95	12.35
Main IR bands	3450, 3030, 2960, 1600, 1505, 1470, 1430, 1335, 1210, 1175, 1130, 1000, 827, 777	3460, 3040, 2920, 1615, 1510, 1465, 1425, 1300, 1270, 1210, 1170, 1100, 1010, 800, 695
λ_{max1} ($\epsilon \times 10^{-3}$)		
CHCl ₃	654 (51.4)	647 (55.9)
CCl ₄	660 (59.2)	654 (41.4)
C ₆ H ₁₂	659	650 (30.6)
aq. NH ₄ OH	482	484
λ_{max2} ($\epsilon \times 10^{-3}$)		
CHCl ₃		525 (8.6)
CCl ₄	472 (16.8)	484 (14.2)
C ₆ H ₁₂	472	480 (16.4)
λ_{min} ($\epsilon \times 10^{-3}$)		
CCl ₄	540 (11.04)	540 (7.5)
C ₆ H ₁₂	594	540 (9.1)
$R^{\#}(CCl_4)^c$	3.52	3.05
$\Delta R(CCl_4)$	1.79	2.32
$R^{\#}(C_6H_{12})$	2.39	1.87
$\Delta R(C_6H_{12})$	1.26	0.74

a. The theoretical values are in parenthesis.

b. For the system CCl₄/0.5 M NaClO₄ solution.

c. $\Delta R = R_s - R_u$ where R_s and R_u are the peak ratios for the substituted and unsubstituted dithiozone, respectively.

ϵ : molar absorptivity ($l \text{ mol}^{-1} \text{ cm}^{-1}$), $R^{\#} = \lambda_{max1}/\lambda_{max2}$.

solutions with distinct absorption bands in the visible region. The positions and intensities of these bands were found to depend on the nature of the substituents and the type of solvent used (Table 1). The solutions of these compounds were found to be stable for several weeks if kept refrigerated. The spectral data of these new dithione analogues are given in Table 1.

Visible spectra of metal complexes

The metal complexes of both dithione analogues are highly colored and their electronic spectra are characterized by strong absorption bands in the visible region. Table 2 summarizes their spectral characteristics. An inspection of these data indicates that the absorption bands of the metal complexes are remarkably shifted towards longer wavelengths, compared to the corresponding values of metal dithionates. The molar absorptivities of Pb^{II} and Zn^{II} (in CCl₄) with 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan and Cu^{II} and Ni^{II} with 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan are higher than the corresponding values of metal dithionates, suggesting that these analogues are relatively more sensitive than the parent dithione towards those metals. The molar absorptivities of Cd^{II}, Co^{II}, Hg^{II} and Tl^I complexes are either comparable to or slightly lower than the corresponding values of dithione metal complexes.

Extraction equilibria of metal complexes

The metal extraction equilibria may be represented by the following general equations:

Table 2 Spectral characteristics of metal complexes with 1,5-bis(3,4,5-trimethoxyphenyl)- and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans in CHCl₃

Metal	1,5-Bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan		1,5-Bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan		Unsubstituted dithione	
	λ_{max}	($\epsilon \times 10^{-3}$)	λ_{max}	($\epsilon \times 10^{-3}$)	λ_{max}	($\epsilon \times 10^{-3}$)
Cd ^{II}	546	(77.1)	558 (564)	(90.6) 80.4) ^a	517	(88.4)
Co ^{II}	572	(55.4)	558	(57.7)	540	(68.3)
Cu ^{II}	564	(49.7)	556 (568)	(63.2) 66.9) ^a	546	(48.2)
Hg ^{II}	498 (516)	(73.5) 67.2) ^a	524 (516)	(63.5) 60.2) ^a	485	(72.2)
Ni ^{II}	568	(34.3)	602 (604)	(67.8) 58.2) ^a	490 (660)	(30.7) 19.1) ^a
Pb ^{II}	544	(73.3)	548 (548)	(63.4) 60.8) ^a	515	(68.8)
Tl ^I	532	(28.1)	578 (554)	(33) 25.6) ^a	506	(34.8)
Zn ^{II}	560 (560)	(88.7) 100.6) ^a	572 (572)	(87.1) 82.1) ^a	526	(91.1)

Aq. phase 0.5 M NaClO₄. ϵ : molar absorptivity, $l \text{ mol}^{-1} \text{ cm}^{-1}$. a. in CCl₄.

Table 3 Extraction data for the metal complexes with 1,5-bis(3,4,5-methoxyphenyl)- and 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazans in CHCl₃

Metal	1,5-Bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan		1,5-Bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan		Unsubstituted dithizone	
	log K_{ext}	pH _{1/2}	log K_{ext}	pH _{1/2}	log K_{ext}	pH _{1/2}
Cd ^{II}	0.85±0.01 (5)	3.58	1.27±0.08 (5)	3.37	0.39	3.81
Co ^{II}	0.15±0.02 (4)	3.93	-4.55±0.10 (5)	6.28	-2.4	5.2
Cu ^{II}	7.7 ±0.2 (6)	0.15	7.02±0.10 (5)	0.49	7.3	0.35
Hg ^{II}	24.6 ±0.2 (5)	(-8.4)	21.37±0.05 (5)	(-6.7)	26.86	(-9.43)
Ni ^{II}	-4.3 ±0.2 (5)	6.15	-7.1 ±0.2 (6)	7.55	-4.17	6.07
Pb ^{II}	-7.1 ±0.2 (5)	7.55	-0.52±0.04 (4)	4.26	-0.56	4.28
Tl ^I	-5.02±0.15 (4)	9.02	-3.86±0.25 (5)	7.86	-4.17	8.17
Zn ^{II}	0.31±0.02 (5)	3.85	-2.64±0.22 (5)	5.32	0.40	3.80

Figures in parentheses are the number of measurements. pH_{1/2} is calculated from K_{ext} with the assumption that 1.0×10^{-4} M reagent in CHCl₃ is used as extractant. Aq. phase, 0.5 M NaClO₄.

and

where K_{ext} is the extraction constant of a metal complex with 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan (Eq. (1)) or, with 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan (Eq. (2)); subscript o indicates the organic phase. Table 3 gives the extraction constants and the pH_{1/2} values for metal complexes of both dithizone analogues together with the corresponding values for metal dithizonates under the same conditions. The different pH_{1/2} values of the metal-ligand complexes may be considered as indicators of the bonding strength of those ligands towards a particular metal. The following conclusions may be drawn from the data given in Table 3.

- 1) The K_{ext} values of the Cd^{II}, Co^{II} and Cu^{II} complexes of 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan are slightly higher than the corresponding values of the dithizone complexes. Similarly, the K_{ext} of the Cd^{II} complex of 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan is higher than the corresponding value of cadmium dithizonate.
- 2) The extraction constants of Hg^{II}, Ni^{II}, Pb^{II}, Tl^I and Zn^{II} complexes are lower than the corresponding values of the metal dithizonate complexes.
- 3) 1,5-Bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan seems to be more efficient than either 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan or dithizone in the separation of Cd^{II} from Zn^{II}. Figure 1 compares the extraction (expressed as the distribution coefficient, D_M) of Cd and Zn by the former extractant as a function of pH.

Similar effects were previously observed with 2- and/or 6-substituted dithizone analogues, as suggested by the differences in the K_{ext} values of cadmium and zinc complexes. The log K_{ext} values of cadmium complexes for 2-chloro-⁹, 2-fluoro-¹⁰, 2,6-tetrachloro-⁸, 2,6-tetramethyl-³, and 2,3-tetrachlorodithizones⁸ were found to

Fig. 1 log D_M (distribution coefficient), where M is Cd or Zn vs. pH. Calculated from K_{ext} based on the assumption that 1.0×10^{-4} M 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan is used as the extractant in CHCl₃. Aq. phase: 0.5 M NaClO₄.

be higher than the corresponding values of the zinc complexes.

It is known that Cd^{II} and Zn^{II} have comparable electronic configurations, viz., [Ar] 3d¹⁰ and [Kr] 4d¹⁰, respectively. They are expected to form tetrahedral complexes with dithizone analogues, since they were found with an unsubstituted dithizone.¹¹ The effective ionic radius of Cd^{II} (95 pm) is relatively larger¹² than that of Zn^{II} (74 pm), which seems to have an important effect on their K_{ext} values as well.

The above discussion points out the importance of substitution at C-2 and/or C-6 in generally increasing the values of K_{ext} for cadmium, compared to those of zinc complexes and, thus, enhancing the selectivity of 2- and/or 6-substituted dithizone analogues towards cadmium

and zinc ions.

The effect of introducing methoxy or methyl substituents in the phenyl rings of dithizone on its extraction ability and, hence, the extraction constants of its metal complexes, is also manifested in the $\text{pH}_{1/2}$ value of the substituted analogues. The latter value is a composite parameter comprising the acid dissociation constant (K_a) and the partition coefficient (p_r) of the extractant, *vis.*, $\text{pH}_{1/2} = \log p_r / K_a$. The much higher $\text{pH}_{1/2}$ value of 1,5-bis(2-methoxy-4-methylphenyl)-3-mercaptoformazan (Table 1) than that of either 1,5-bis(3,4,5-trimethoxyphenyl)-3-mercaptoformazan or dithizone (8.63) suggests that the former analogue has a higher partition coefficient and/or a lower acid dissociation constant than either that of dithizone or the latter analogue.

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References

1. H. M. N. H. Irving, "Dithizone", in "Analytical Sciences Monograph", No. 5, The Royal Chemical Society, 1977
2. H. Irving, *Fresenius' Z. Anal. Chem.*, **263**, 264 (1973).
3. A. M. Kiwan, F. M. Hassan and W. Hamdan, *Bull. Chem. Soc. Jpn.*, **62**, 325 (1989).
4. D. M. Hubbard and E. W. Scott, *J. Amer. Chem. Soc.*, **65**, 2390 (1943).
5. E. B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals", Part 1, Chap. 6G, John Wiley and Sons, New York, 1978 and references therein.
6. S. Landry and S. F. Rodendo, *Anal. Chem.*, **26**, 732 (1954).
7. H. Irving and J. J. Cox, *Analyst* [London], **83**, 526 (1958).
8. A. M. Kiwan and G. A. Wanas, *Anal. Chim. Acta*, **144**, 165 (1982).
9. A. M. Kiwan and A. Y. Kassim, *Talanta*, **22**, 931 (1975).
10. A. M. Kiwan and A. Y. Kassim, *Anal. Chim. Acta*, **88**, 177 (1977).
11. A. Mawby and H. M. N. H. Irving, *Anal. Chim. Acta*, **55**, 269 (1971).
12. N. N. Greenwood and A. Earnshaw, "Chemistry of the elements", Chap. 29, p.1400, Pergamon Press, Oxford, 1985.

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