

SULFONAMIDES. A NEW CLASS OF CHELATING AGENTS OF POTENTIAL
UTILITY IN ANALYTICAL AND SEPARATION CHEMISTRY¹⁾

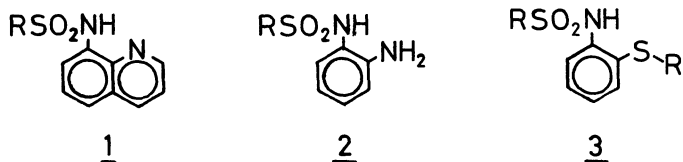
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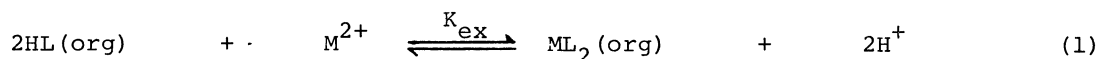
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New sulfonamide chelating agents were synthesized, and the complexation behavior was studied by solvent extraction method. The metal selectivity is strikingly different from the conventional solvent extraction agents. The outlook of this class of reagents in analytical and separation chemistry is discussed.

Primary sulfonamides bear amide protons of comparative acidity to those of phenols. However, only a limited work has been made on their ability to coordinate to metal ions in their anionic form. Sulfonamide complexing agents were first introduced in 1960,²⁾ and there have been altogether fourteen publications since then, all of which appeared in 1960's. The compounds reported are summarized in structures 1~3, where R and R' are simple alkyl or aryl groups. They have been used for the analysis of transition or post-transition metals, as gravimetric (Cu(II)), absorption photometric (Cu(II)), or fluorimetric reagents (Zn(II) and Cd(II)). Obviously, people failed to find any notable characteristics in sulfonamide ligands, and the reagents have quickly passed the memory of analytical as well as coordination chemists. In this communication we would like to show that the sulfonamides are very versatile complexing agents with metal selectivity quite different from the conventional phenolic reagents and have the potential utility in practical metal analysis and separations.



The ligand 1 is a sulfonamide version of 8-hydroxyquinoline. For very lipophilic R such as octyl or *p*-dodecylphenyl, 1 is an excellent solvent extraction agent for transition and post-transition metal ions. The extraction of divalent metals with 1a (HL, R=n-C₈H₁₇) and 1b (R=*p*-CH₃C₆H₄) follows the reaction (1), and the distribution of metal ion is expressed by equation (2).



$$\log D = \log \frac{[(\text{ML}_2)_{\text{org}}]}{[\text{M}^{2+}]} = \log K_{\text{ex}} + 2 \log [(\text{HL})_{\text{org}}] + 2\text{pH} \quad (2)$$

The extraction constant and the half extraction pH ($\text{pH}_{1/2}$) are summarized in Table 1 along with those values of other typical solvent extraction agents. 1a and 1b are more efficient extraction agents than TTA or DBM under low pH conditions.

Table 2 shows the selectivity of metal extraction: 1a and 1b are mono-anionic N,N-coordinating bidentate ligands, while oxine is a mono-anionic N,O-ligand. DBM and dithizone are similarly O,O- and N,S-coordinating ligands, respectively. The metal selectivity is considerably different from each other. The sulfonamide resembles dithizone in that it does not extract iron(III). The ligand 2a ($\text{R}=\text{n-C}_8\text{H}_{17}$) and 3 ($\text{R}=\text{p-CH}_3\text{C}_6\text{H}_4$, $\text{R}'=\text{CH}_3$) behave similar to 1a, but the stability of the metal complexes is considerably lower ($\text{pH}_{1/2}$ higher).

Table 1. $\text{pH}_{1/2}$ ($\log K_{\text{ex}}$) for the Extraction of Divalent Metals with 1a and 1b^{a)}, 25°C

reagent	<u>1a</u>	<u>1b</u>	TTA ^{b)}	DBM ^{c)}	oxine ^{d)}
solvent	kerosene	C ₆ H ₆	kerosene	kerosene	CHCl ₃
Cu ^{II}	1.75(-0.1)	1.20(1.0)	2.50(-1.6)	3.30(-3.2)	1.51(1.77)
Zn ^{II}	5.10(-6.8)	4.20(-5.0)			3.30(-2.41) ^{e)}
Co ^{II}	6.2(-9.0)	5.70(-8.0)			3.21(-2.16) ^{e)}
Cd ^{II}	6.3(-9.2)	5.90(-8.4)			4.65(-5.29) ^{e)}

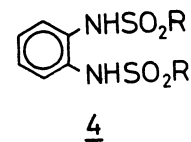
a) $[(\text{HL})_{\text{org}}]=0.02 \text{ mol/dm}^3$ b) thenoyltrifluoroacetone c) dibenzoylmethane
d) $[(\text{HL})_{\text{org}}]=0.10 \text{ mol/dm}^3$; J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, p. 42-43 (1964). e) $\text{ML}_2(\text{HL})_2$ formed^{d)}

Table 2. Selectivity of Extraction, $\Delta\text{pH}_{1/2}$ ($=\text{pH}_{1/2}(\text{M}^{\text{II}}) - \text{pH}_{1/2}(\text{Cu}^{\text{II}})$), 25°C

reagent	solvent	$\text{pH}_{1/2}$				Fe ^{III} extraction ^{a)}
		Cu	Zn	Co	Cd	
<u>1a</u>	kerosene	0	3.3	4.4	4.4	no
<u>1b</u>	C ₆ H ₆	0	3.0	4.5	4.7	no
oxine	CHCl ₃	0	1.8	1.7	3.2	yes
DBM	C ₆ H ₆	0	3.5	3.5	5.1	yes
dithizone	CCl ₄	0	4.1	4.5	4.2	no

a) solvent, CCl₄. "no" : Fe can not be extracted under any conditions.
"yes" : Fe can be extracted under suitable conditions.

The compound 4(H₂L) is a sulfonamide analog of catechol. 4a(R=n-C₈H₁₇) extracts copper(II) and zinc(II) into toluene if the lipophilic uncharged ligand(A) such as 4-benzylpyridine or 1,2-bis(hexylthio)ethane is present. The analysis

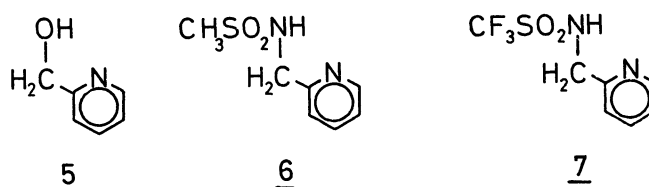


indicated the extraction of ML·A_n type neutral complexes. Many complexes of this type were in fact readily isolable for 4b (R=CH₃) with M=Co(II), Ni(II), Cu(II), Zn(II) and A=NH₃, en, phen. In contrast to catechol, 4 has no affinity to iron (III).

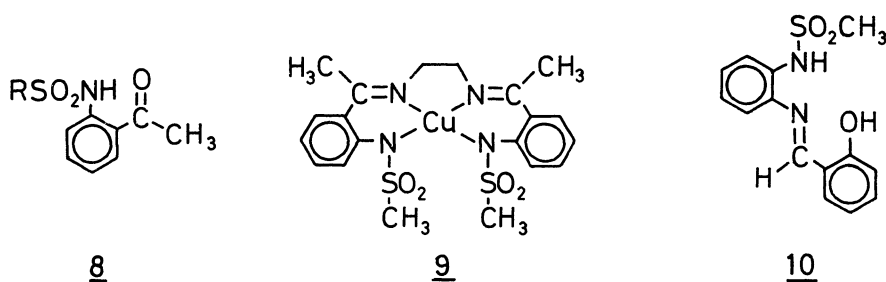
All the sulfonamide complexing agents lacks the affinity to iron(III), aluminium(III) or alkaline earth metals. This seems to suggest that the sulfonamido anion belongs to so-called "soft" bases. However, the selectivity of extraction between zinc(II) and cadmium(II) shows that 1 resembles DBM ("hard" ligand) and is quite different from dithizone ("soft" ligand). The apparent inconsistency is reconciled by the idea that the coordinating atom(amido nitrogen) is indeed hard, but the steric bulkiness of the sulfonamide group hinders the accumulation of the second bulky ligand around the small metal cation. The solvent extraction agents of this type of metal selectivity has long been searched for hydrometallurgical purposes.

Apart from the solvent extraction, sulfonamides can offer a vast number of new ligands for possible application in the analytical field. The following would give an idea of their variety in the structure.

2-pyridylmethanol (HL,5) forms a stable CuL₂ complex at pH above 9.³⁾ 2-(Methanesulfonamido)methylpyridine (6) forms the similar copper(II) complex which can readily be isolated from aqueous solution by adding sodium hydroxide to the stoichiometric mixture of 6 and copper(II) salt. Other metal complexes can not be isolated in pure state because of the hydrolysis of metal ions. However, due to the strong electron-withdrawing effect of the trifluoromethyl group, the complexation by 7 of divalent copper, nickel or zinc takes place even under neutral or acidic conditions. Thus, the blue copper complex (CuL₂) precipitates out quantitatively, when copper(II) acetate and 7 are mixed in methanol.

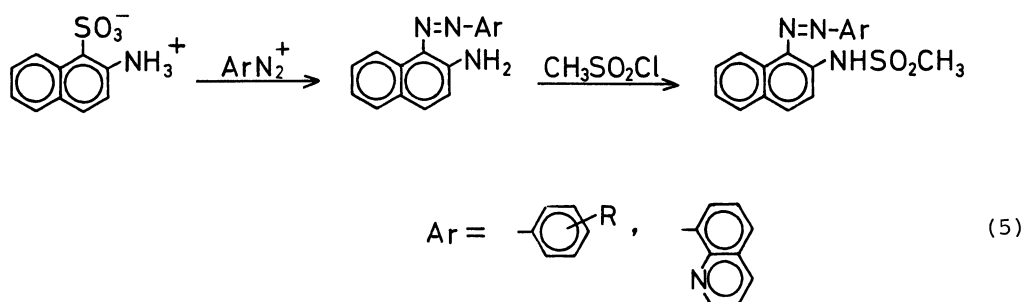
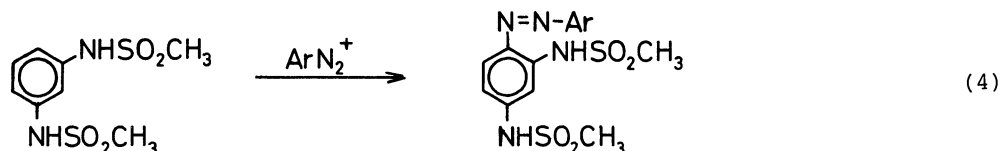


The compound 8 is a sulfonamide version of *o*-hydroxyacetophenone. In the presence of ammonia, the imine complexes were isolated for divalent copper, nickel and zinc. When ammonia was replaced by ethylenediamine, the complex 9 was formed. The ligand 2



can be used to derive a new series of multidentate ligand by condensing with an aldehyde ligand such as salicylaldehyde or picolinaldehyde. The resulting ligand, for example, 10 (H_2L) forms a stable copper(II) complex of the composition $CuL \cdot H_2O$.

The azo dyes containing sulfonamide function can also be readily prepared (reactions (4) and (5)). The dyes form stable complexes with various divalent metals, but the color change on complexation is generally not so distinct as in the corresponding phenolic azo dyes.



Although our study at present is still limited, the evidence collected adequately indicates that the sulfonamide ligands constitute a new class of complexing agents as versatile as traditional phenolic reagents. The sulfonamides are more resistant to oxidation than phenols. They can be rendered various lipophilicity and steric bulkiness by changing the sulfonyl moiety. The ease of large-scale synthesis would make them especially suitable for industrial use. The reagents will meet a wide application in chemical separation and analysis of metal ions in the future.

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References and Notes

- 1) a) Sulfonamide Chelating Agents. 1.
b) Presented at ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979, and the 29 th Symposium on Coordination Chemistry, October 1-3, 1979, Hamamatsu.
- 2) a) J.H. Billman, N.S. Janetos, and R. Chernin, *Anal. Chem.*, 32, 1342 (1960).
b) J.H. Billman, R. Chernin. *Anal. Chem.*, 34, 408 (1962) ; 36, 522 (1964).
- 3) Y. Murakami and M. Takagi, *Bull. Chem. Soc. Jpn.*, 38, 828 (1965).

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