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Studies on the Reaction of Salicylidenebenzoic-hydrazide (*SBH*) with Ce^{3+}, Th^{4+} and UO_2^{2+}

I. M. Issa†, **Y. M. Temerk***, **A. Z. Abu Zhuri**,
M. S. El-Meligy, and **M. M. Kamal**

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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The stoichiometry and structure of salicylidenebenzoic-hydrazine (*SBH*) chelates with UO_2(II), Ce(III) and Th(IV) in buffer-ethanol mixtures and in pure ethanol is studied applying conductometric titration, visible spectrophotometry and ir-spectrophotometry. The ir-spectra revealed that coordination takes place through the C=O and C=N groups.

(Keywords: Complexes, Ce^{3+}, Th^{4+}, UO_2^{2+}; *Conductometric titration; IR-Spectroscopy)*

Komplexe von Ce^{3+}, Th^{4+} *und* UO_2^{2+} *mit dem Kondensationsprodukt aus Salicylaldehyd—Benzhydrazid (SBH)*

Die Stöchiometrie und die Struktur der *SBH—Me(x)* Chelate in Puffer—Ethanol-Mischungen und in reinem Ethanol wurde mittels Leitfähigkeitsmessungen, UV- und IR-Spektroskopie untersucht. Insbesondere die IR-Messungen zeigen, daß die Koordination über die C=O- und C=N-Gruppierung stattfindet.

Introduction

The chelating properties of hydrazides and their derivatives have become of special interest in recent times due to their biological importance. The antituberculous activity of hydrazides[1] was attributed to their ability to form stable chelates with transition metal ions[2–4].

As given previously[5, 6], the hydrazide rest (—C=O—NH—N) can attain either the ketonic (I) or the enolic form (II).

It was shown that the tendency of the hydrazide to react in the

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† Deceased December 1977.

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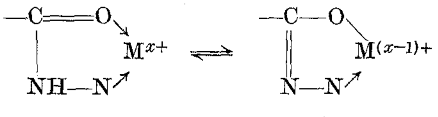
enolic form depends on the anion of the salt used[7], the H^+ ion concentration of the medium and the nature of the substituents attached to the C=O and β—N atom[8]. However, *Issa et al.*[5], have



(I) (II)

indicated that the salt anions and substitution with aliphatic aldehydes or ketone at the β—N atom are of little influence on the type of the reaction. The metal complexes are investigated in ethanol-buffer mixtrues as well as in pure ethanol.

Experimental

Preparation of the Organic Ligand: Salicylidenebenzoic-hydrazide (*SBH*) was prepared by the condensation of salicyaldehyde with benzhydrazide in the usual manner for the preparation of hydrazones[9]. The compound thus prepared was crystallised several times from pure ethanol. The purity of the ligand prepared was checked by elemental analysis.

Preparation of Solutions: A solution of *SBH* ($10^{-2} M$) was prepared by dissolving the appropriate amount of the solid in pure ethanol. The metal salt solutions of Ce(III) and U(VI) were prepared using the perchlorate salts. Th(IV) solutions were obtained from the Analar nitrate reagent. The metal contents of solutions were determined by conventional methods[10]. Buffer solutions consisting of boric acid, Borax, succinic acid and sodium sulfate of *pH* 3-9 were prepared as given by Britton[11].

Preparation of Metal Complexes: The solid complexes with stoichiometric ratio 1:1 and 1:2 were prepared by mixing a hot ethanolic solution of the organic reagent with a similar one of the metal salts. The reaction mixture was then refluxed for 30 min on a water bath. On cooling the complexes separated as fine crystals. The solid was then filtered off and washed several times with hot ethanol, dried and preserved in a desiccator over dried silica gel. The complexes obtained decomposed without melting when heated above 250 °C. The solid complexes are soluble in ethyl and methyl alcohols and acetone, spraingly soluble in water, insoluble in chloroform, carbon tetrachloride and light petroleum.

Working Procedure: Conductometric titrations were carried out using a PYE conductance bridge and a conductivity cell of the dipping type. The absorption spectra of the solutions were recorded on a UNICAM S.P. 500 Spectrophotometer. The i.r. spectra of the chelates were recorded on a Beckmann infrared spectrophotometer as KBr disc.

Results and Discussion

Spectrophotometric Measurements

The spectral measurements were carried out in pure ethanol and in *Thiel* buffer solution containing 40% ethanol. Under these conditions,

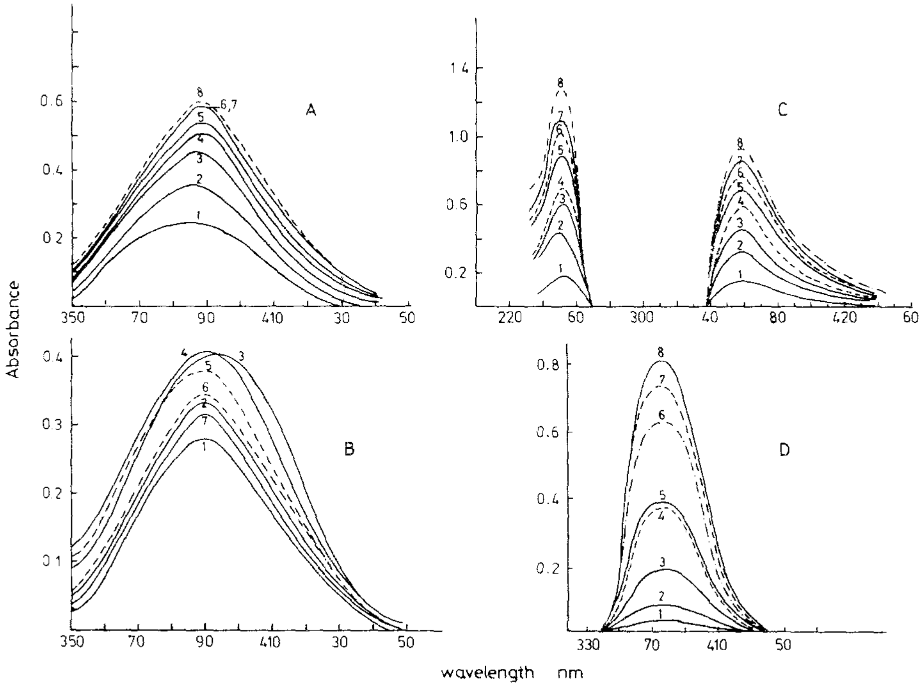


Fig. 1. Absorption spectra of *SBH* complexes. *A* Const. $[Th^{4+}] = 1.0 \times 10^{-4} M$ (in pure ethanol). *1* $[SBH] = 0.3 \times 10^{-4} M$; *2* $0.7 \times 10^{-4} M$; *3* $[SBH] = 1.0 \times 10^{-4} M$; *4* $1.3 \times 10^{-4} M$; *5* $[SBH] = 1.7 \times 10^{-4} M$; *6* $2.0 \times 10^{-4} M$; *7* $[SBH] = 2.5 \times 10^{-4} M$; *8* $3.0 \times 10^{-4} M$, *B* Continuous variation (in pure ethanol) *1* $[Ce^{3+}]$, $[SBH] = 9.0 \times 10^{-5} M$, $3.0 \times 10^{-5} M$; *2* $[Ce^{3+}]$, $[SBH] = 7.2 \times 10^{-5} M$, $4.8 \times 10^{-5} M$; *3* $[Ce^{3+}]$, $[SBH] = 6.0 \times 10^{-5} M$, $6.0 \times 10^{-5} M$; *4* $[Ce^{3+}]$, $[SBH] = 4.6 \times 10^{-5} M$, $7.4 \times 10^{-5} M$; *5* $[Ce^{3+}]$, $[SBH] = 4.0 \times 10^{-5} M$, $8.0 \times 10^{-5} M$; *6* $[Ce^{3+}]$, $[SBH] = 3.0 \times 10^{-5} M$, $9.0 \times 10^{-5} M$; *7* $[Ce^{3+}]$, $[SBH] = 2.0 \times 10^{-5} M$, $10 \times 10^{-5} M$, *C* Const. $[SBH] = 1.2 \times 10^{-4} M$. *1* $[UO_2^{2+}] = 1.5 \times 10^{-5} M$; *2* $3.0 \times 10^{-5} M$; *3* $[UO_2^{2+}] = 4.5 \times 10^{-5} M$; *4* $6.0 \times 10^{-5} M$; *5* $[UO_2^{2+}] = 7.5 \times 10^{-5} M$; *6* $9.0 \times 10^{-5} M$; *7* $[UO_2^{2+}] = 1.05 \times 10^{-4} M$; *8* $1.2 \times 10^{-4} M$. *D* Const. $[Th^{4+}] = 1.5 \times 10^{-4} M$. (*pH* 6.1, 40% ethanol) *1* $[SBH] = 1.0 \times 10^{-4} M$; *2* $1.5 \times 10^{-4} M$; *3* $[SBH] = 2.25 \times 10^{-4} M$; *4* $3.0 \times 10^{-4} M$; *5* $[SBH] = 3.75 \times 10^{-4} M$; *6* $4.5 \times 10^{-4} M$; *7* $[SBH] = 5.25 \times 10^{-4} M$; *8* $6.0 \times 10^{-4} M$

the colours of Uranium, Thorium and Cerium chelates with *SBH* vary from reddish brown to deep brown colour. It was found that the maximum colour development is attained at *pH* 6.1 for UO_2^{2+}—*SBH*, *pH* 6.1 for Th^{4+}—*SBH* and *pH* 4.1 for Ce^{3+}—*SBH* chelates.

The spectra of the *SBH*—UO_2^{2+} complex, at *pH* 6.1 (containing 40% ethanol) reveal maximum absorption at $\lambda = 360$ nm and a shoulder near 250 nm. The bands show an increase in intensity with increasing the concentration of either *SBH* or the metal ion. In pure ethanol, the *SBH*—UO_2^{2+} complex exhibits a band with λ_{max} near 410 nm. The bands shows an increase in intensity and an apparent red shift with increasing the concentration of either *SBH* or the metal ion.

The spectrum of the *SBH*—Th^{4+} complex exhibits one band with λ_{max} at 380 nm, in a solution of *pH* 6.1 (containing 40% ethanol) and at 390 nm in pure ethanol. An apparent red shift in the absorption maximum is observed on varying the concentration of the organic ligand, which indicates the probable formation of complexes containing higher ratios of the ligand.

The spectrum of the *SBH*—Ce^{3+} complexes at *pH* 4.1 is characterised by two bands with λ_{max} at 355 and 260 nm. This refers to the probable existence of two types of complexes. In pure ethanol, the spectrum shows one absorption band with $\lambda_{max} = 390$ nm. An apparent red shift is observed for high concentration of ligand or metal ion. Representive absorption spectra of the chelates are shown in Fig. 1.

SBH shows three bands at 225, 295 and 330 nm, which undergo a red shift on complexation owing to an enhanced charge transfer through the hydrazide rest (—C=O—NH—N). On the other hand, the band due to the ligand disappears gradually upon the addition of increasing amounts of metal ion to a constant concentration of ligand. This leads to the appearance of a characteristic absorption band which may be attributed to the chelate formation.

Stoichiometry of the Complexes

The composition of the complexes formed in solution were examined by the molar ratio[12], straight line[13], continuous variation[14], slope ratio[15] and the limiting logarithmic methods[16]. The results obtained indicate the probable formation of two types of complexes with stoichiometric ratio 1:1 and 1:2 (*M*:*L*) for the three metal ions investigated, as shown in Fig. 2.

The apparent stability constants ($\log \beta$) of the complexes formed were determined from the spectral data using molar ratio[11], continuous variation[14] and straight line[13] methods (Tab. 1).

The values of the formation constants were calculated for different media in order to find out the optimum conditions for maximum stability; maximum stability is attained in pure ethanol. Change in ionic strength by addition of different concentrations of $NaClO_4$ (0.1 *M*-1.0 *M*) to the ethanol-buffer mixture shows no effect on the stability constant. It is clear from the results listed in Tab. 1 that the stability of the complexes formed are in the following order:

$$Ce^{3+} > UO_2^{2+} > Th^{4+}$$

Conductometric Measurements

Solutions of $10^{-3}\,M$ of metal chloride were titrated with $10^{-2}\,M$ solution of *SBH*. The conductance-molar ratio curves (Fig. 3) are characterised by breaks denoting the formation of 1:1 and 1:2 complexes. From these results it is concluded that the reaction between the metal ions and complexing agent under investigation occurs via the formation of a coordination linkage with the oxygen of the carbonyl group and the nitrogen of the azomethine linkage. *SBH* behaves as a bidentate ligand:

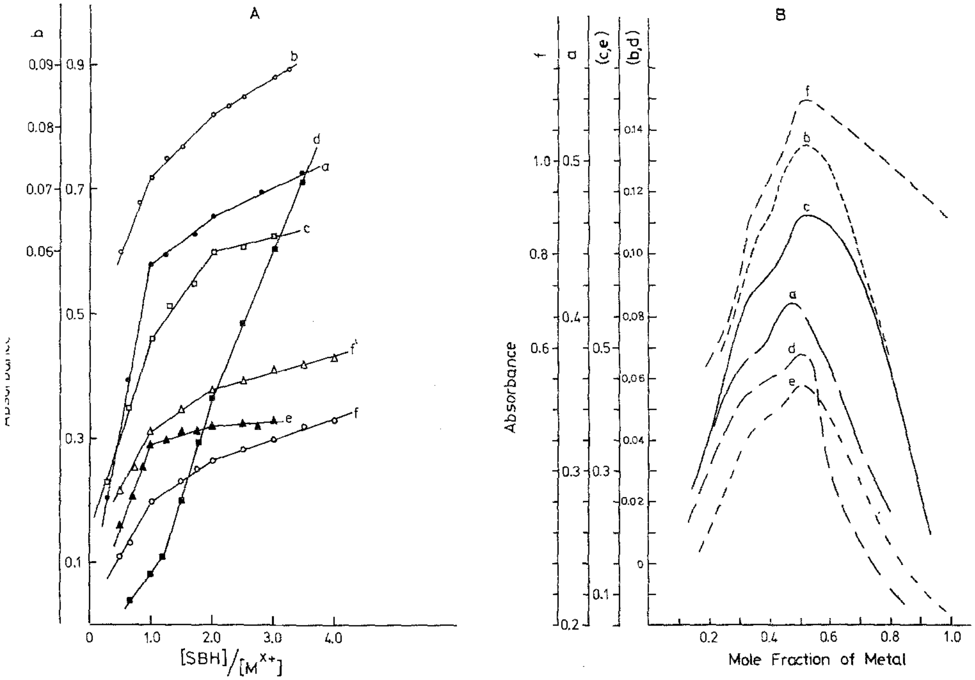
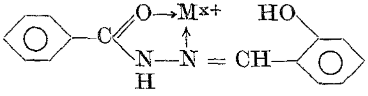


Fig. 2. Stoichiometry of *SBH* complexes. *A* Molar ratio, *B* Continuous variation. *a* *SBH*—Ce^{3+} (ethanol, $\lambda = 390$ nm); *b* *SBH*—Ce^{3+} (*pH* 4.1, 40% ethanol, $\lambda = 355$ nm); *c* *SBH*—Th^{4+} (ethanol, $\lambda = 390$ nm); *d* *SBH*—Th^{4+} (*pH* 6.1, 40% ethanol, $\lambda = 380$ nm); *e* *SBH*—UO_2^{2+} (ethanol, $\lambda = 410$ nm); *f* *SBH*—UO_2^{2+} (*pH* 6.1, 40% ethanol, $\lambda = 360$ nm); *f* *SBH*—UO_2^{2+} (*pH* 6.1, 40% ethanol, $\lambda = 250$ nm)



(I)

Table 1. *The apparent stability constants of SBH chelates*

Type of complex	log β			$-\Delta G^*$kcal/mol		
	Pure ethanol	Buffer + Ethanol	Buffer + Ethanol + $NaClO_4$	Pure Ethanol	Buffer + Ethanol	Buffer + Ethanol + $NaClO_4$
1 Th^{4+} : 1 *SBH*	5.20	5.07	5.07	7.09	6.91	6.91
1 Th^{4+} : 2 *SBH*	11.55	11.25	11.09	15.83	15.42	15.12
1 UO_2^{2+} : 1 *SBH*	6.34	6.14	5.87	8.65	8.25	8.06
1 UO_2^{2+} : 2 *SBH*	11.76	11.38	11.40	16.12	15.52	15.62
1 Ce^{3+} : 1 *SBH*	7.45	6.23	6.22	10.16	8.54	8.54
1 Ce^{3+} : 2 *SBH*	11.56	11.40	11.36	15.76	15.62	15.49

The increase in conductance upon titrating metal ion solutions by the ligand is probably due to the liberation of the coordinated chloride ions through interaction of the ligand with the metal salt, thus increasing the number of ionic species in solution.

$$MCl_x + L \rightleftharpoons ML^{x+} + xCl^-$$

In case of the 1:1 Th(IV)—*SBH* complex, the decrease in conductance is brought about by the increased weight and volume of the metal ion after being incorporated in a complex. This results in a decrease of its diffusion coefficient and hence of its conductivity.

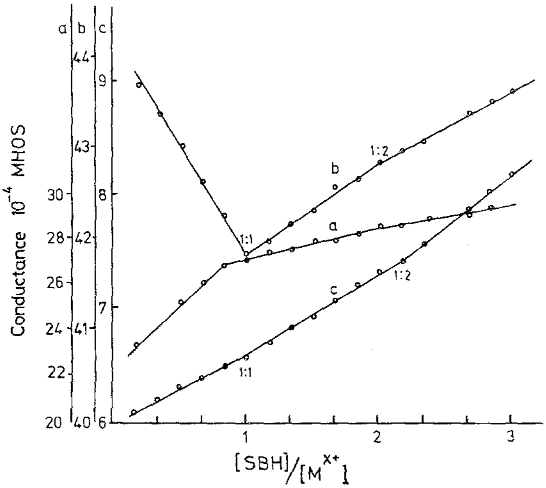


Fig. 3. Conductance-molar ratio curves. *a* *SBH*—Ce^{3+}; *b* *SBH*—Th^{4+}; *c* *SBH*—UO_2^{2+}

IR Spectra

The infrared spectra of the solid complexes compared to those of the organic ligand show that the ir bands due to the C=O and C=N, lying at 1,665 cm^{-1} and 1,615 cm^{-1} respectively, are shifted to red (Tab. 2), therefore the coordination to the metal ion takes place through these functional groups. The existence of the ν_{HN} band at 3,250 cm^{-1} in the spectra of complexes indicates coordination of the ligand in the ketonic form. But the bands due to the OH group (3,400 cm^{-1}) are still observed in the spectra of the chelates. This result favour formula (I), i.e. the OH group does not participate in chelate formation. The hydrogen atom of the OH group is involved in an intramolecular hydrogen bond with the nitrogen of the azomethine centre as indicated by the broadening of the OH band at 3,400 cm^{-1}. The existence of the hydrogen bond would decrease the tendency of the hydrogen atom to be displaced by the metal ion. On the other hand it brings about an increase of electron density on the N-atom by charge transfer of electron from the phenyl ring and oxygen atom of the OH group.

Generally, the ir spectra certify that the *SBH* would behave as a bidentate ligand coordinating via the carbonyl oxygen and β—N atom.

Table 2. *Some IR bands of SBH and its metal chelates*

Ligand	Th^{4+} 1:2	UO_2^{2+} 1:2	Ce^{3+} 1:2	Assignment
1615	1580	1560	1550	$\nu_{C=N}$
1665	1610	1600	1590	$\nu_{C=O}$
3250	3250	3250	3250	ν_{NH}
1295	1295	1295	1295	$\nu_{C—N}$

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