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ALIZARINE RED S COMPLEXES OF Mn(II), Co(II) AND Ni(II)

MONTHER Y. AL-JANABI [1], SUBHI S. AL-AZAWE [2] and ALIA SALMAN [1]

[1] *Department of Chemistry, College of Education, University of Baghdad, Baghdad (Iraq)*
[2] *Department of Chemistry, College of Science, University of Baghdad, Baghdad (Iraq)*

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ABSTRACT

The reaction of alizarine red S (ARS) with the divalent metal ions Co^{2+}, Mn^{2+} and Ni^{2+} in aqueous solution at pH 7 gave violet-coloured complexes. IR study of these complexes showed a change in the first C=O and in the phenolic α-OH groups, however, no change was noticed for the SO_3^- and second C=O groups. The absorption maximum in the UV showed a change towards longer wavelength for the complexes compared to the free ligand. Thermoanalysis and TGA of these complexes showed deviation from the free ligand. Also, conductivities of the complexes were measured and their structures were postulated.

INTRODUCTION

Sodium 1,2-dihydroxyanthraquinone-3-sulphonate, trivial name alizarine red S (ARS), has been used with several metal ions to give coloured chelating complexes [1,2]. It has a quinone group, and α- and β-dihydroxy groups, therefore two probable structures were proposed [3]. ARS has been used in complexometric titrations [4,5] as an indicator to determine small quantities of metal ions [6–8]. Also, it was found [9] that when the pH of its solution was equal to 4, one of the protons of the phenolic groups would dissociate, whilst two protons would be dissociated in solutions of pH 7–10. Using amperometric titrations, it was found [10] that when the pH of the solution was 4–6, the cupric ion formed a complex with ARS in a 1 : 1 ratio, and this ratio became 1 : 2 when the pH was 5–6. Other workers [11] found the ratio to be 1 : 1 in solutions of pH 3.20–7.5. In a solution of pH 6–9, Makoto [12] prepared the mixed ligand complex Cu : ARS : 1,10-phenanthroline in a 1 : 1 : 1 ratio, and the same complex was prepared [13] at a pH of 6.5.

Nickel [14–16] and cobalt ions [14,16,17] form complexes with ARS in solutions of pH equal to 7.0 ± 0.1.

Our aim in this research is to prepare solid complexes of ARS with Mn(II), Co(II), Cu(II) and Ni(II) ions and to study them by IR and UV spectroscopy, thermal analysis, conductivity and elemental analysis.

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EXPERIMENTAL

All the chemicals used in this work were of analytical grade A, and α-Al_2O_3, calcined at 1300°C for 3 h, was the reference for DTA. Elemental analysis was performed by the July 14th Nuclear Reaction (Baghdad, Iraq). IR spectra were recorded on a Pye-Unicam SP-2000 IR spectrophotometer, and a Pye-Unicam 292 Mk. 2 pH meter was used to measure the pH of the solution. UV spectra were recorded on a Pye-Unicam SP-8-100 UV/visible spectrophotometer, and conductivity measurements were conducted by Pye-Unicam with a cell constant equal to 1, using dimethylformamide (DMF) as a solvent (10^{-3} M concentration at 25°C). Thermal analysis curves (TG and DTA) were obtained with a Paulik–Paulik–Erdey derivatograph, at a heating rate of 10°C min, in a static (air) atmosphere. Platinum crucibles were used as sample and reference (α-Al_2O_3) holders. The crucibles, each containing 200 mg of powdered sample and the inert reference material were shaken for about 1 min for regular packing.

The preparation of the complexes was as follows. A solution of 1 mmol of MCl_2 (where M is Mn(II), Co(II), Cu(II) or Ni(II)) dissolved in the least amount of distilled water was added to a solution of 1 mmol of ARS, again in the least amount of distilled water. Then, by stirring, 0.1 N NH_4OH was added drop-wise until the solution neutralized (pH 7.0). A violet precipitate appeared, which was filtered, washed several times with distilled water, ethanol, then ether, and dried in a desiccator under vacuum over phosphorous pentaoxide. Results of their elemental analysis are shown in Table 1. It is important to report that cupric ions coordinate to ammonia molecules, as well as to ARS and water molecules. Thus, calculated carbon, hydrogen or nitrogen values are given.

TABLE 1

Elemental analysis results of the complexes

Complexes	Elemental content (%)				
	C	H	S	Cl	metal
$MnC_{14}H_{13}SO_{11}Na$					
Calculated	35.89	2.77	6.85	–	11.78
Experimental	35.45	2.69	6.63		11.66
$CoC_{14}H_{10}SO_9ClNa$					
Calculated	35.63	2.14	6.78	7.54	12.51
Experimental	36.08	2.23	6.60	7.69	12.45
$NiC_{14}H_{14}SO_{11}ClNa$					
Calculated	34.32	2.44	6.31	6.99	11.63
Experimental	34.12	2.51	6.42	7.12	11.50
Cu					
Calculated					
Experimental	27.10	1.99	6.70	(N = 2.63)	

RESULTS AND DISCUSSION

The usual effect of chelation of organic ligands with metal ions is to shift the UV absorption maxima of the ligands to longer wavelengths. Thus, complexes of ARS with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} showed maximum absorption at 493, 528, 565 and 510 nm, respectively, compared to that of the free ligand at 423 nm (Fig. 1). The shift in absorption alters in accordance with the charge/radius ratio, i.e. $Cu^{2+} < Ni^{2+} > Co^{2+} > Mn^{2+}$. For Cu^{2+} this ratio cannot be calculated exactly because of the Jahn–Teller effect on the radius of the cupric ion.

A lowering of the wave number of the stretching frequency of the C=O bond indicates weakening of the bond and, at the same time, the strengthening of the O–M bond upon coordination. It was noticed that this deviation increased according to the order: $Ni^{2+} > Co^{2+} > Mn^{2+} \approx Cu^{2+}$ (Table 2), which goes along with the increase in crystal lattice energy of the complexes. The stretching frequency for the second C=O bond showed no change from that of the free ligand, i.e. 1665 cm^{-1}, upon the formation of complexes. Therefore, it was concluded that this group did not participate in complexation. The same behaviour was noticed for the SO_3^- group, when its stretching frequencies of 635, 1040 and 1165 cm^{-1} remained unchanged. On the contrary, the stretching frequency of the phenolic α-OH group was noticed to be stronger and broader upon coordination in complexes than that in the free ligand. This is a proof for the coordination of the phenolic α-OH group of alizarine with metal ions.

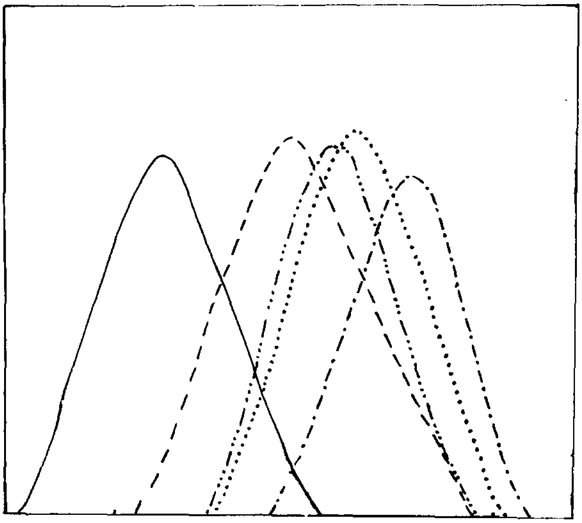

Fig. 1. Absorption spectra of alizarine complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. Free ARS (———); $[MnARS\text{-}(H_2O)_4]$ (— — —); $[CoARS(H_2O)_2]Cl$ (· · · · · ·); $[NiARS\text{-}(H_2O)_4]Cl$(— · —); Cu complex (– · · · –).

TABLE 2

Some IR spectral bands of ARS and its complexes (cm^{-1})

Compound	$\nu_{C=O}$		$\Delta\nu$	$\nu_{\alpha\text{-}OH}$	$\nu_{SO_3^-}$
	first	second			
ARS	1635	1665	–	2900–3590	1165, 1040 635
Mn(II) complex	1620	1665	15	2700–3500	1165, 1040 635
Co(II) complex	1615	1665	20	2700–3500	1165, 1040 635
Ni(II) complex	1600	1665	35	2700–3500	1165, 1040 635
Cu(II) complex	1620	1665	15	2590–3500	1165, 1040 635

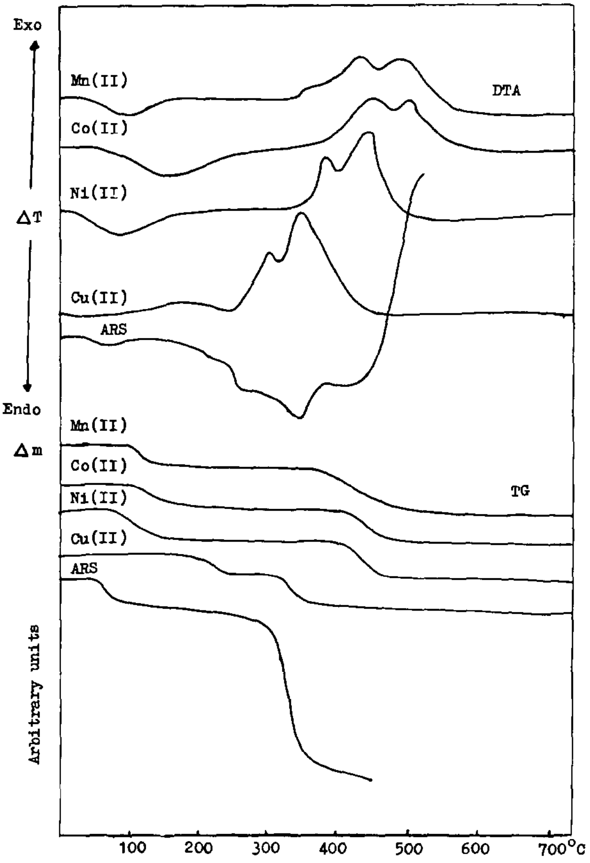

Fig. 2. TG and DTA curves of alizarine complexes with Mn(II), Co(II), Ni(II) and Cu(II).

TABLE 3

Results of thermoanalytical study of ARS complexes

Complex	Lost H_2O (%)		Decomposition temperature (° C)		No. of H_2O molecules lost
	Calculated	Experimental	T_i	T_f	
Mn(II)	3.8	3.5	90	200	1
	4.0	3.65	340	550	1
Co(II)	3.8	3.5	90	230	1
	3.9	3.6	380	550	1
Ni(II)	3.54	3.5	80	150	1
	4.0	3.6	360	500	1
Cu(II)		3.0	190	250	
		3.6	300	390	

Molar conductivity of 10^{-3} M solutions of complexes dissolved in DMF at 25°C was found to be 9×10^{-6}, 53×10^{-6}, 25×10^{-6} and 10.5×10^{-6} Ω^{-1} cm^{-2} mol^{-1} for the metal ions Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. It seems to be that complexes of Mn^{2+} and Cu^{2+} are non-ionic, while those of Co^{2+} and Ni^{2+} are 1 : 1 ionic.

Figure 2 depicts the TG and DTA curves of ARS and its prepared complexes, while Table 3 shows the numerical values for T_i, T_f, percentage and weight lost during the thermogravimetric analysis of the complexes. The ARS curve exhibited shows that there is a rather different behaviour between the free ligand and its metal complexes, such as loss of moisture between 80 and 100°C. This is manifested by the wide endotherm on the DTA curve. The horizontal plateau on the TG curve shows the thermal stability of the anhydrous ARS, which melts and starts decomposition, leaving a white material that remains stable up to 550°C. The final product was examined and found to be sodium oxide.

The DTA curve of each metal complex shows one endotherm peak representing a loss of one water molecule: between 80 and 180°C for Mn^{2+}, Co^{2+} and Ni^{2+} complexes; for the Cu^{2+} complex it was between 220 and 300°C. Loss of the second water molecule occurs between 320 and 380°C for the Cu^{2+} complex, while for the other three complexes it was between 390 and 500°C. Losing the second water molecule is accompanied by a split exotherm peak, which means there is a change in the crystal lattice energy. Lowering the coordination number of the central ions forces them to have a new hybridization and configuration. No more loss in weight occurred, even when the complexes were heated to 700°C. When the final products were cooled they were found to be polymers. No effect was noticed on these polymers when distilled water was added to them.

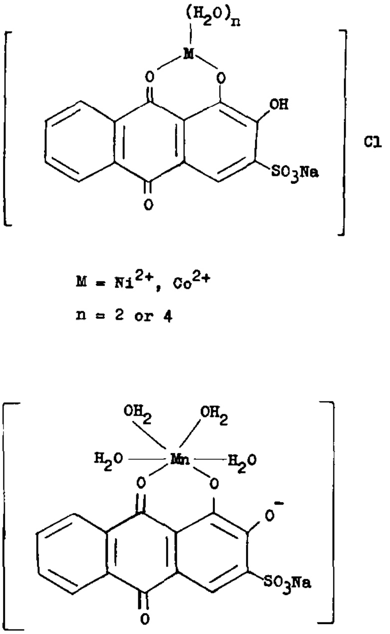

Fig. 3. Proposed structures of alizarine complexes with Mn(II), Co(II) and Ni(II).

The proposed structures [18] of alizarine red S complexes of Co^{2+}, Mn^{2+} and Ni^{2+} are shown in Fig. 3.

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