

Complexes of 1-Hydroxyxanthone with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) & Mg(II)

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Received 19 March 1985; revised and accepted 6 August 1985

Synthesis of 1-hydroxyxanthone complexes of the metal ions Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Mg(II) is reported. The complexes have been characterised on the basis of their elemental analyses, infra red, ^1H NMR and ultra violet spectra. Except for Zn(II) and Mg(II), all the other ions give complexes of the type $\text{ML}_2 \cdot x\text{H}_2\text{O}$ (where L = 1-hydroxyxanthone anion). In the case of Zn(II) and Mg(II), the complexes show the presence of coordinated $-\text{OCH}_3$ groups in addition to the hydroxyxanthone ligand. The stepwise formation constants for the formation of these complexes have also been determined.

The xanthenes constitute a class of compounds that occur extensively in nature. Along with chromones, flavones and juglones, these benzo- γ -pyrone derivatives have the ability to form stable metal complexes. Such complexes have applications in analytical chemistry^{1,2}. This note reports the preparation and stability constants of several metal complexes of 1-hydroxyxanthone. Work done on this ligand is scanty and only the preparation of 1-hydroxyxanthone derivative of the uranyl ion³, and solution studies on the 1-hydroxyxanthone-Cu(II) system⁴ have been reported.

1-Hydroxyxanthone was synthesized by the published procedure⁵. The purity of this compound was checked by its melting point, NMR, and IR data. The IR spectra were obtained in KBr using a Perkin-

Elmer 257 spectrophotometer, and the UV-VIS spectra were obtained on a Pye-Unicam model SP 8000 spectrophotometer. The ^1H NMR spectra were recorded on a Varian T-60 instrument. The pH measurements were carried out using a Corning model 5 pH meter equipped with combination glass and calomel electrodes. The pH meter was calibrated using standard Corning buffer solutions having pH values 7.00 and 4.00 at $25 \pm 1^\circ\text{C}$. The colorimetric determinations were carried out using a Corning model 253 colorimeter. The solvents and chemicals used were of reagent grade. The C and H analyses of these complexes were carried out by M/s Ciba-Geigy Ltd., Geneva.

The Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Mg(II) complexes were synthesized by mixing the appropriate metal acetate solution in methanol with hot methanolic solution of 1-hydroxyxanthone. The mixture was heated on a water-bath for about 15 min and the precipitate obtained was filtered, washed with hot methanol and dried *in vacuo*. The yields were in the range 70-90%. The metal analyses were carried out volumetrically using EDTA (Zn, Mg) or gravimetrically (Cu, Ni, Mn, Co). The analytical data and the electronic spectral data of the complexes are given in Table 1.

The stability constants of the metal complexes were determined by the potentiometric titration technique⁶. Solutions containing 1-hydroxyxanthone ($5.0 \times 10^{-4} M$) in dioxan were titrated with metal acetate solutions in dioxan with carbonate-free 0.01 M KOH at $\mu = 0.1 M$ (KCl) under nitrogen atmosphere. The pH after the addition of 0.2 ml aliquots of alkali was recorded. The pK_a value for the ligand, 1-

Table 1—Analytical Data, Colours and Electronic Spectral Data of the Complexes of 1-Hydroxyxanthone

Complex	Colour	λ_{max} , nm(e)	Found (Calc.), %		
			Metal	C	H
$\text{Cu}(\text{C}_{13}\text{H}_7\text{O}_3)_2$	Yellow	430 (52,000)	13.15 (13.09)	64.05 (64.25)	2.96 (2.88)
$\text{Ni}(\text{C}_{13}\text{H}_7\text{O}_3)_2 (\text{H}_2\text{O})_2$	Yellow	415 (79,000)	11.25 (11.36)	59.40 (60.38)	3.62 (3.48)
$\text{Co}(\text{C}_{13}\text{H}_7\text{O}_3)_2 (\text{H}_2\text{O})_2$	Yellow	418 (60,000)	11.35 (11.40)	59.67 (60.35)	3.53 (3.48)
$\text{Mn}(\text{C}_{13}\text{H}_7\text{O}_3)_2 (\text{H}_2\text{O})_2$	Brown red	427 (38,000)	10.54 (10.71)	61.00 (60.82)	4.01 (3.49)
$\text{Zn}(\text{C}_{13}\text{H}_7\text{O}_3) (\text{OCH}_3) (\text{H}_2\text{O})\text{H}_2\text{O}$	Yellow	411 (32,000)	19.14 (19.03)	48.81 (48.92)	3.06 (4.07)
$\text{Mg}(\text{C}_{13}\text{H}_7\text{O}_3) (\text{OCH}_3) (\text{H}_2\text{O})$	Yellow	415 (31,000)	8.60 (8.55)	60.59 (59.09)	4.36 (4.22)

hydroxyxanthone, was calculated by a similar potentiometric titration carried out in the absence of metal ion. All the titrations were carried out at $25^\circ \pm 1^\circ\text{C}$.

The elemental analyses (Table 1) show 1:2 (metal:ligand) stoichiometry for these complexes when $M = \text{Cu}^{2+}$, Ni^{2+} , Mn^{2+} and Co^{2+} and 1:1 when $M = \text{Zn}^{2+}$ and Mg^{2+} . The complexes are insoluble in common organic solvents but are soluble in DMSO and pyridine. Their melting points are greater than 300°C .

The ligand shows a broad band due to νOH at 3400 and shows $\nu\text{C}=\text{O}$ at 1640 (band positions in cm^{-1}). It is difficult to observe the disappearance of the band due to νOH on complexation due to the presence of water molecules in these complexes. However, there is a downward shift in the carbonyl stretching frequency in these complexes; the exact position is difficult to determine since it overlaps with the aromatic ring stretching vibrations (ca. 1600) of the ligand.

The UV-VIS spectrum of 1-hydroxyxanthone in methanol shows a characteristic absorption maximum at 355 nm, assignable to a $\pi \rightarrow \pi^*$ transition of the carbonyl group. All the metal complexes exhibited the presence of an additional intense charge-transfer band in the range 410-430 nm (Table 1). The weaker bands due to $d-d$ transitions were completely obscured by the intense charge-transfer bands.

The insolubility of these complexes in common organic solvents limited PMR studies, but a few PMR spectra of the diamagnetic complexes were obtained in d_6 -DMSO. The disappearance of the low field hydroxylic proton upon chelation is evident in all these cases. Some unexpected results were obtained in the cases of Zn(II) and Mg(II) complexes where a singlet proton resonance appeared at $\delta = 3.50$ and $\delta = 3.75$, respectively. These peaks do not disappear upon shaking with D_2O and are assigned to coordinated $-\text{OCH}_3$ groups. This formulation is supported by the analytical data of these complexes. However, due to the presence of bands of the ligands in the range of $1000\text{-}1100\text{ cm}^{-1}$, the presence of coordinated $-\text{OCH}_3$ groups could not be detected by IR spectroscopy.

The successive stability constants were determined by the potentiometric titration techniques and calculated by the method of Irving and Rosotti⁶. The

Table 2—Stability Constants of Metal Complexes of 1-Hydroxyxanthone

Metal ion	$\log K_1$	$\log K_2$
Cu(II)	6.25	5.60
Ni(II)	5.56	2.86
Co(II)	5.26	3.55
Mn(II)	4.51	2.71
Zn(II)	6.04	—
Mg(II)	3.75	—

stability constants calculated in this manner are given in Table 2. These values follow the Irving-Williams order for divalent metal ions towards nitrogen donor ligands and are in the sequences: $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)}$; and $\text{Zn(II)} > \text{Mg(II)}$.

Studies on complex formation of these biologically important metal ions may be important in understanding metal ion transport and storage in plants⁷. It is now generally believed that certain carrier molecules are involved in ferrying the metal ions from the soil solution through the root hair cells into the plant. The role of ferrichromes in the uptake of iron by bacteria is well documented⁸. Antibacterial action of 8-hydroxyquinolines against *Bacillus pneumoniae* is supposed to involve the transport of an iron 8-hydroxyquinoline complex and the resultant release of iron inside the bacterial cell. The high stability constants observed for these complexes may be important in explaining the observed antibacterial activity of xanthenes and also their possible relevance in the metal ion metabolism in plants.

The authors acknowledge financial support in the form of a research grant from NARESA, Sri Lanka and they also thank Ciba-Geigy Ltd., Geneva for C and H analyses.

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