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Synthesis and Characterization of Metal Complexes of Curcumin with Alkaline earth metals.

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ABSTRACT

Some Binary complexes of cur cumin with Alkaline earth metals salts have been synthesized by the reaction between M(II) chloride with cur cumin as primary ligand in acetonitrile solution under a nitrogen atmosphere. The composition of the complexes has been characterized by elemental analysis, molar conductivity NMR, IR, UV–Vis spectroscopy and by Magnetic susceptibility measurements. The results reveal that cur cumin ligand coordinates with M(II) in bidentate mode after deprotonation. The spectral data suggest that the coordination of metal ion with ligand is only through diketo oxygen in a bidentate manner. Deprotonation was carried out by adding equimolar amount of triethylammine base. The general formula of the complexes is $[M(Cur)_2]$ where [M = Mg(II) and Ca(II)]. Complexes are Dark Brown colored solids and are having high melting point and insoluble in methanol, distilled water and some organic solvents. The metal complexes are expected to be square pyramidal in geometry based on physicochemical and spectroscopic analyses. Metal to ligand ratio were found to be 1:2 for both of the complexes. The ligand and their metal complexes were partially screened for their antimicrobial activity. The results showed that the metal complexes to be biologically active, while the ligand was inactive. and the results are not included in this paper.

KEYWORDS: Bidentate, Binary complexes, Curcumin, Coordination, Deprotonation

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I. INTRODUCTION

Cur cumin, (bis[4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5-dione) a yellow spice and pigment from Curcumalonga L. (Zingiberaceae), is by far known for its antioxidant [1,3,] anti-inflammatory [4, 5] and anticancer activities [5, 6]. Some studies on cur cumin are based on the ionic structure where the keto-enol equilibrium (Fig. 1) is present or when it is fully in keto form [7-9] with the resulting properties depending on the latter. The strong chelating ability of dike tones has been widely investigated. Synthesis and characterization of some Binary metal ions; therefore, cur cumin could be of great importance in the chelating treatment of metal intoxication and overload [10].So far researchers have prepared transition metal complexes with curcumin but not with Alkali and Alkaline earth metals. we have taken two Alkaline earth metals and prepared Bis complexes. Metals selected by us are also beneficial to the human beings.

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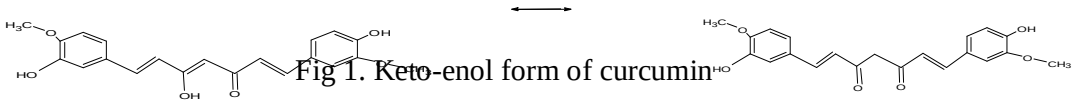


Fig 1. Keto-enol form of curcumin

The formation of various metal complexes with curcumin has been investigated. The stoichiometries of curcumin with some metal ions were also reported [10,12]. Several metal complexes of curcumin have been synthesized, characterized and evaluated for various biological activities. The $[Au(curcumin)_2Cl]$ was a five coordinate gold complex [10], which had anti-arthritic properties and assessed in an adjuvant-induced rat poly arthritis model. The $[Cu(curcumin)_2]$ complexes [11] were most cytotoxic in cultured L929 cells and showed significant reduction in solid tumor volume in as cites tumor bearing mice. In addition, vanadyl, gallium and indium complexes of curcumin[12] have reported for medicinal applications. Curcumin metal complexes (M = Eu, Ce, La, Y, Cr, Pd) showed that curcumin coordinates with metal ions in bidentate mode in deprotonated form. The stoichiometries of curcumin with some metal ions were reported [10, 12.]

E.colihighly affects the urinary tract. The urinary tract comprises the kidneys, ureters, bladder, and urethra as shown in figure. UTIs are diagnosed usually by isolating and identifying the urinary pathogenE.coli from the patient[12-17]

Also, curcumin with other transition metals ions Ni(II), Zn(II), Pd(II), Fe(III), Cr(III), Mn(II), can form strong chelates [10, 18-20]. No other metal curcumin complex motif has been chemically modified to such an extent than vanadyl curcumin.[20–23]. The curcumin, phen ligands and their ternary complexes were screened for their antibacterial activity using the agar diffusion technique [24]

II.EXPERIMENTAL

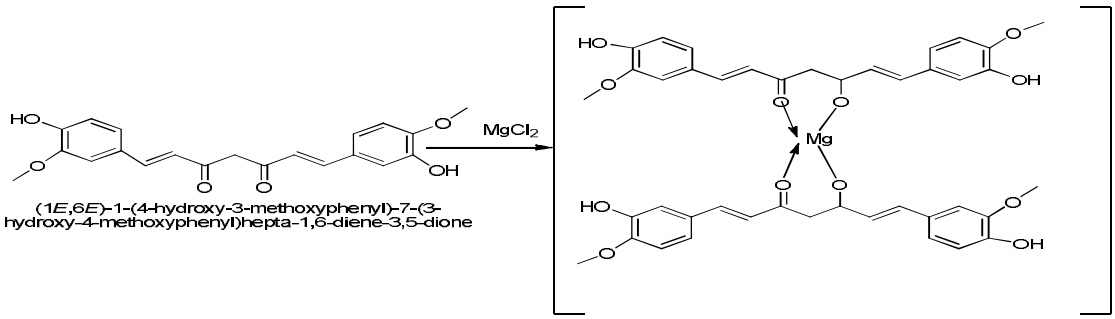
2.1. Chemicals and instruments

Curcumin, Magnesium chloride and Calcium chloride, were purchased from Sigma-Aldrich and used as received. All solvents were of reagent grade and used without further purification. IR spectra were recorded as KBr pellets on a Bruker FTIR1003-3610 alpha-P spectrometer. Electronic absorption spectra were measured on a Perkin Elmer Lamda 650 UV-Vis spectrophotometer. NMR measurements were performed on a Bruker 400 MHz Multinuclear spectrometer. Samples were dissolved in d6-DMSO with TMS as internal reference. Magnetic susceptibility measurements of the paramagnetic complexes were carried out on a Sherwood Scientific magnetic susceptibility balance. The complexes were also characterized by elemental analysis (CHN ANALYSER Model : LECO TruSpec CHN(S)

2.2. Synthesis of the binary complexes of curcumin with MCl_2

a. The Mg(II)–Bis-curcumin complex was synthesized by mixing equi-molar amounts of Mg(II) chloride (0.095 g, 1.0 mmol) and curcumin (0.37 g, 1.0 mmol) in acetonitrile and the mixture was heated at RT for 24 hr under a nitrogen atmosphere. After 24 h, the complex solution was concentrated and the solid residue was separated by filtration and washed several times by methanol/acetonitrile to remove un reacted curcumin,

b. The Ca(II) Bis-curcumin complex was synthesized by mixing equimolar mixtures of (0.111g mmol of $CaCl_2$) and curcumin (0.37 g, 1.0 mmol) in acetonitrile and the mixture was heated at RT for 24 hr under a nitrogen atmosphere. After 24 h, the complex solution was concentrated and the solid residue was separated by filtration and washed several times by methanol/acetonitrile to remove un reacted curcumin.



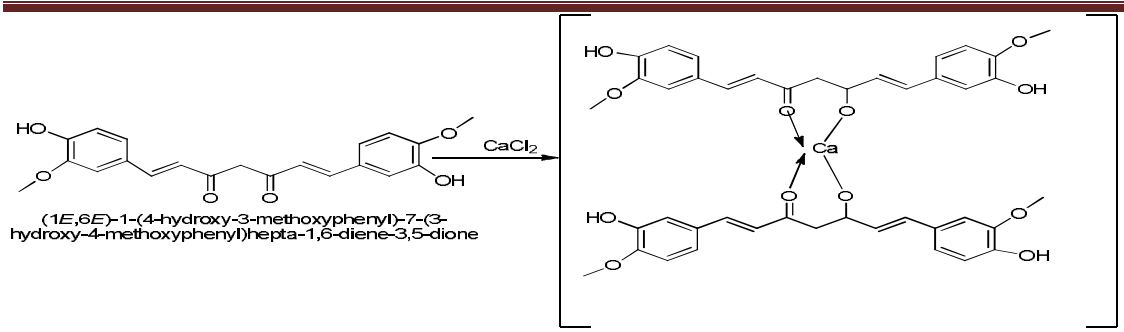


Figure.2 depicts the molecular structure of (η^6-*p*-cymene)RuCl(Curc).[35]

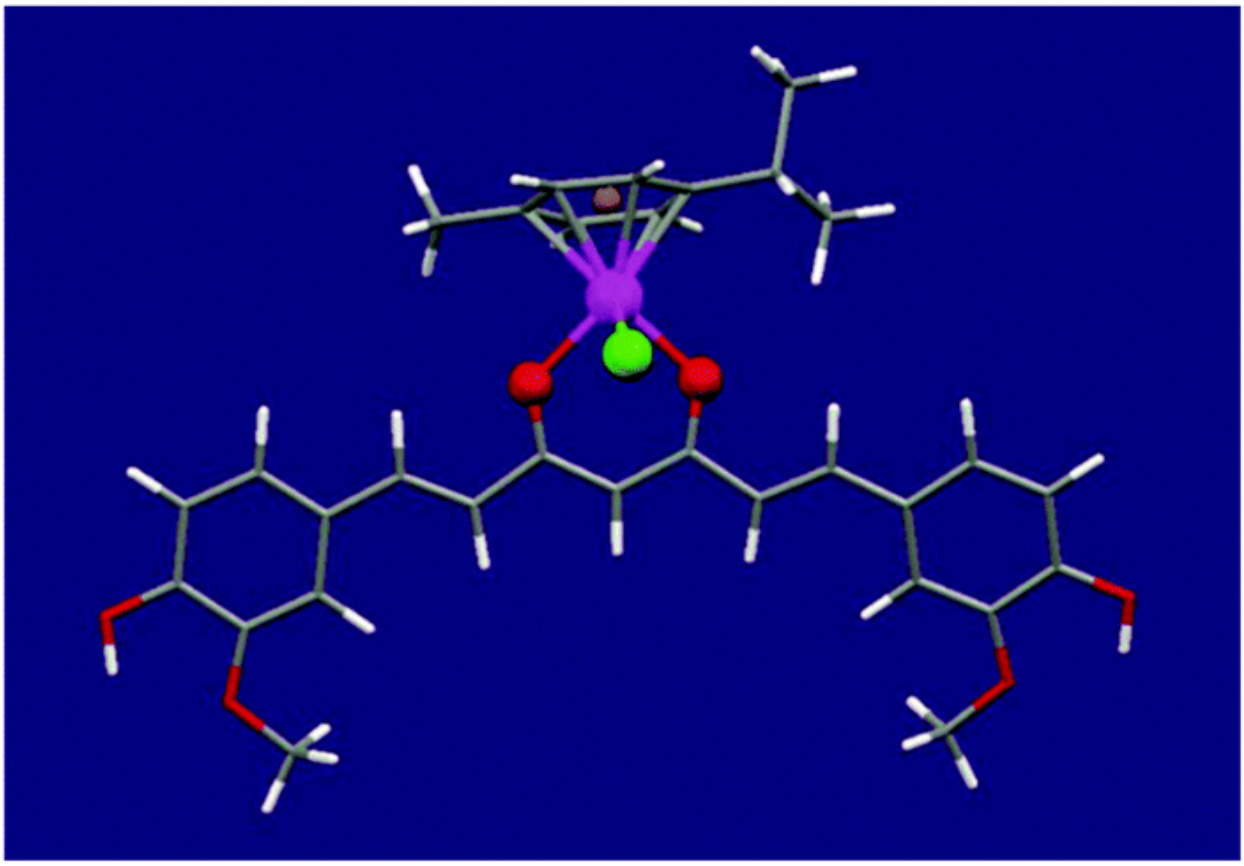


Fig. 2 Molecular structure of (η^6-*p*-cymene) RuCl(Curc). Reproduced from ref. 35. Copyright 2012 American Chemical Society.

III. RESULTS AND DISCUSSION

3.1 Characterization of the metal-cur cumin ligand and complexes

Both complexes were stable at room temperature and were soluble in DMF and DMSO and partly soluble in methanol and ethanol. Solubility is very low in other solvents Both complexes have brownish-red colour with high melting points and are photosensitive crystalline solids..

3.2 U V-Vis spectra of cur cumin

UV-Vis spectra was recorded in DMSO. In this spectra there are two peaks due to л--л* and n-л* transitions because of ligand to metal and charge transfer transitions [31,32]

3.3 The IR spectra of cur cumin

Fig. 2, shows stretching vibrations at 1628 cm^{-1} attributed predominantly to the overlapping stretching vibrations of alkenes (C=C) and carbonyl (C=O) character. Infrared of cur cumin ligand show stretching vibration at 3508 cm^{-1} due to O-H groups, C=C aromatic stretching vibration at 1597 cm^{-1} and high intensity band at 1589 cm^{-1} attributed to the mixed vibrations including stretching carbonyl bond vibrations ν(C=O), νC=O band of the free cur cumin is shifted from 1628 cm^{-1} to 1627-1597 cm^{-1} depending on the metal used . The υ (OH) of the two phenolic groups in cur cumin showed broad band in the 2900–3508 cm-1 region. The IR spectra of the complexes exhibited new bands at 968, 970 cm^{-1} assigned to υ(M-O) stretching frequency, respectively

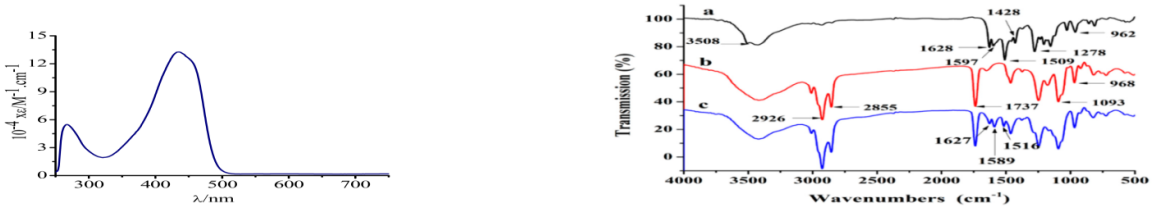


Fig. 3. FTIR and UV-Vis spectra of curcumin and its complexes

3.4 NMR spectra of complexes

Chemical shifts data δ (ppm) of cur cumin free ligand: 2.517(DMSO), 3.365 and 3.855 514 (6H; -OCH_3), 3.83 (^{1}H; C_1), 6.737 (1H; C_3), 6.825 (1H; C_9), 7.173 (1H; C_{10}), 7.338 (1H; C_6), 7.594 (1H; C_4), 5.35 (1H; -OH phenol) and 6.45 (^{1}H; -OH enol). The ^{1}H NMR spectrum of [$M(Cur)_2$] complex in Fig.3 showed signals due to curcuma The previous results of the NMR studies showed that cur cumin exists in solution as keto-enol tautomers [28-30]. in with respective shift ,3.840 (6H; -OCH_3), 5.714 (^{1}H; C1), 6.667 (^{1}H;C3), 6.768 (1H; C9), 7.079 (^{1}H; C10), 7.271 (1H; C6), 7.489 ^{1}H NMR spectrum of [$Mg(Cur)_2$] complex. (^{1}H; C4), 9.86 (^{1}H; ArOH phenol

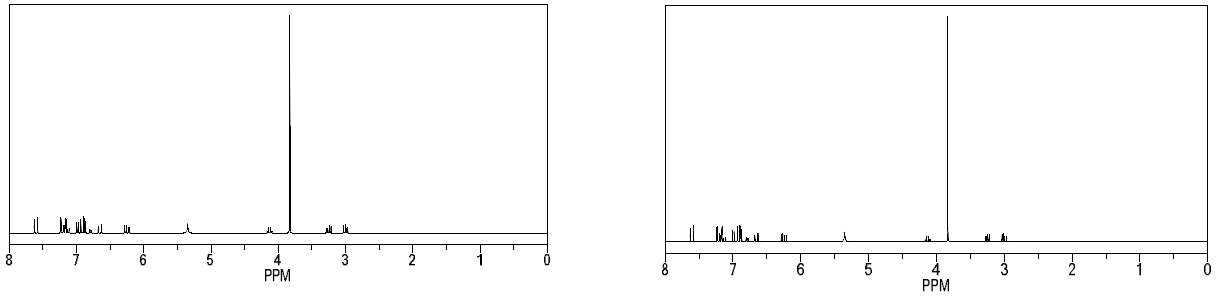


Fig.4 NMR spectra of Mg and Ca complexes.

Table.1;.'Elemental analysis, Conductivity and Magnetism of compounds'.

Ligand/ Complex	Percentage C% Observed (calculated)	Percentage H% Observed (calculated)	Percentage Metal Observed (calculated)	Conductivity (Ohm^{-1} cm^2)	Magnetism (In B.M)
Curcumin	68.47(68.3)	5.43(5.35)	--------	5-10	0.00
$[Mg(cur)_2]$ $C_{42}H_{42}MgO_{12}$	66.11(65.71)	5.55(5.61)	3.19(3.22)	10-20	1.78
$[Ca(cur)_2]$ $C_{42}H_{42}CaO_{12}$	64.76(65.9)	5.44(5.55)	5.15(5.10)	15-25	0.89

The formation of the binary complexes of cur cumin with metal salts was confirmed on the bases of elemental analysis observed values are in agreement with the calculated ones.

3.5 Conductivity and Magnetometry

The conductivity, Λ_M value of the complex in water is 53-85 Ohm^{-1} cm^2 mol^{-1}, which indicated that the complex is a 1:1 electrolyte [25]. The complexes are non-electrolytes with very low conductivity in methanol The magnetic moment values are 1.08 and 1.23 BM for $[Ca(Cur)_2]$ and $[Mg(Cur)_2]$ complexes, this indicates diamagnetic nature of the complexes. with square planar geometry. keto and enol configurations and stretching vibrations around aromatic νC-C bonds of keto and enolic form of cur cumin [26].

IV.CONCLUSION

New binary Bis complexes using cur cumin as a primary ligand with Alkaline earth metals like Magnesium and Calcium have been synthesized and characterized. by various techniques like IR, UV-Viv, NMR, Conductivity, Magnetism, and Elemental analysis. The complexes have square planar geometry with no conductivity and and magnetism. They have excellent antibacterial activities

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