Chapter 2

Materials and Methods

2.1 Materials

2.1.1 Chemicals

Fluka

Chromium (III) chloride hexahydrate, $CrCl_3.6H_2O$, A.R. grade

Lanthanum chloride hydrate, $LaCl_3.H_2O$, A.R. grade

Lanthanum oxide, La_2O_3, A.R. grade

Merck

Copper (II) sulphate pentahydrate, $CuSO_4.5H_2O$, A.R. grade

Ferrous sulphate heptahydrate, $FeSO_4.7H_2O$, A.R. grade

Cobalt (II) nitrate hexahydrate, $Co(NO_3)_2.6H_2O$, A.R. grade

Nickel (II) chloride hexahydrate, $NiCl_2.6H_2O$, A.R. grade

Carlo Erba

Mercuric chloride, $HgCl_2$, A.R. grade

Manganese (II) chloride tetrahydrate, $MnCl_2.4H_2O$, A.R. grade

BDH

Nickel (II) sulphate hexahydrate, $NiSO_4.6H_2O$, A.R. grade

Nickel (II) acetate tetrahydrate, $Ni(CH_3COO)_2.4H_2O$, A.R. grade

Samarium oxide, Sm_2O_3, A.R. grade

Gadolinium oxide, Gd_2O_3, A.R. grade

Neodymium oxide, Nd_2O_3, A.R. grade

Ytterbium oxide, Yb_2O_3, A.R. grade

Dysprosium oxide, Dy_2O_3, A.R. grade

Erbium oxide, Er_2O_3, A.R. grade

Praseodymium oxide, Pr_6O_{11}, A.R. grade

Riedel-de Haën

Cadmium (II) nitrate tetrahydrate, $Cd(NO_3)_2.4H_2O$, A.R. grade

UNILAB

Ferric chloride hexahydrate, $FeCl_3.6H_2O$, A.R. grade

AJAX Chemicals

Cobalt (II) acetate tetrahydrate, $Co(CH_3COO)_2.4H_2O$, A.R. grade

Lab-Scan Analytical Science

Sodium hydroxide, NaOH, A.R grade

Hydrochloric acid, HCl

SIGMA

Curcumin or [1,7-bis-(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione], $C_{21}H_{20}O_6$

2.1.2 Solvents

Ethanol, C_2H_5OH, A.R. grade (Lab-Scan Analytical Science)

Methanol, CH_3OH, A.R. grade (Lab-Scan Analytical Science)

Acetone, C_2H_6O, A.R. grade (Lab-Scan Analytical Science)

Water, H_2O

2.2 Instruments

2.2.1 X-ray Fluorescence Spectrometer

The complexes were studied by WDXRF technique using Philips PW2400 X-ray fluorescence spectrometer.

2.2.2 Single crystal X-ray crystallography

Crystal structures were determined with Smart APEX CCD X-ray diffractometer with the SHELXTL NT (version 6.12) program.

2.2.3 Infrared Spectroscopy

All infrared spectra were collected with Perkin Elmer Spectrum GX FT-IR spectrophotometer in the 400-4,000 cm^{-1} range. Solid samples were examined as KBr pellets.

2.3 Syntheses of complexes

Several approaches were tried to synthesize complexes between curcumin and transition elements under suitable conditions.

2.3.1 Finding the suitable solvent for curcumin

Weighed amount, *ca.* 68-70 mg, of curcumin was tested for solubility in 10 ml of various solvents and observed the solubility and color of the solutions.

2.3.2 Varying mole ratio of reactants

Syntheses were carried out by two different methods:

1) Mixing metal salts ($NiCl_2.6H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, and $FeCl_3.6H_2O$) with curcumin in 1:1 and 1:2 molar ratio.

A solution of 5 mM metal salts in water (20 ml) was added to a solution of 5 mM and 10 mM curcumin in methanol (20 ml) or was added to a solution of 5 mM curcumin in acetone (20 ml), stirred for 15 minutes at room temperature. The precipitates were filtered under vacuum and collected to dryness. Results are given in Tables 2-3.

2) This category was carried out in three different media in which curcumin dissolved.

2.1) The complexes were prepared by adding metal salts (Cu(II),

Hg(II), Cr(II) and Ni(II)) 0.05, 0.11, 0.22 mmol, respectively, to a solution of curcumin 0.08 mmol in 10 mM NaOH/H_2O (90 ml), stirred for 15 minutes at room temperature and allowed to crystallize. Results are given in the Table 4.

2.2) The complexes were prepared by adding metal chloride salts (Cu(II), Hg(II), Cr(II) and Ni(II)) 0.05, 0.11, 0.22 mmol, respectively, to a solution of curcumin 0.08 mmol in 50 mM NaOH/H_2O (18 ml), stirred for 15 minutes at room temperature, and allowed to crystallize. Results are given in the Table 5.

2.3) The complexes were prepared by adding metal chloride salts (Cu(II), Hg(II), Cr(II) and Ni(II)) 0.05, 0.11, 0.22 mmol, respectively to a solution of curcumin 0.08 mmol in 10 mM NaOH/50%MeOH (30ml), stirred for 15 minutes at room temperature, and allowed to crystallize. Results are given in the Table 6.

2.3.3 Varying the reaction temperatures

The experimental method was adapted from Sharma's work (Sharma, et al., 1987). The complexes were prepared by mixing curcumin with various metal salts ($NiCl_2.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $MnCl_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $CrCl_3.6H_2O$, $FeCl_3.6H_2O$, $Co(CH_3COO)_2.4H_2O$, $LaCl_3.H_2O$, $HgCl_2$) in the molar ratio 2:1 in ethanol. A solution of 5 mM metal salts in ethanol (50 ml) was added to a solution of 10 mM curcumin (50ml). The mixtures were refluxed for eight hours and allowed to crystallize. Another experiment was carried out without reflux, but stirred for 25 minutes at room temperature and allowed to crystallize.

2.3.4 Addition of NaOH to promote the reaction

A solution of NaOH (2.5, 5, 10, 20, and 50 mmol) in methanol (2 ml) was added to a solution of curcumin 10 mmol in methanol (15 ml), stirred for

10 minutes at room temperature (the red brown mixture was obtained). Then a solution of metal salts ($NiCl_2.6H_2O$, $MnCl_2.4H_2O$, and $Cd(NO_3)_2.4H_2O$) 10 mmol in methanol (15 ml) was added to the mixture solution, stirred for 25 minutes at room temperature (the yellow mixture was obtained), and allowed to crystallize.

2.3.5 Attempts to synthesize curcumin complex with lanthanide elements

A solution of metal oxide (Sm_2O_3, La_2O_3, Gd_2O_3, Nd_2O_3, Yb_2O_3, Dy_2O_3, Er_2O_3 and Pr_6O_{11} 0.10, 0.25, 0.50 and 1.00 ml (50 mg of metal oxide in 3 M HCl (35 ml)) was added to a solution of curcumin 30 mg (or 0.08 mmol) in 10 mM NaOH/50%MeOH (30 ml), stirred for 15 minutes at room temperature. For La_2O_3, Gd_2O_3, Nd_2O_3, Yb_2O_3, Dy_2O_3, Er_2O_3 and Pr_6O_{11} orange precipitates were obtained whereas for Sm_2O_3 yellow and orange precipitates were obtained. The precipitates were filtered, collected to dryness, and allowed to crystallize.