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Synthesis and Structure elucidation of metal chelate of Cadmium with ligand 2-amino-1, 4-naphthoquinone and 2-amino-3-chloro-1, 4-naphthoquinone-1 oxime

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Abstract
Metal chelates of Cadmium (Cd) with ligand 2-amino-1, 4-naphthoquinone (ANQ) and 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime (ACNQO) were synthesized. These metal complexes i.e., Cd $(ANQ)_2$ and Cd $(ACNQO)_2$ have been characterized by modern analytical techniques such as elementary analysis, FTIR, electronic spectra, mass spectroscopy, thermogravimetric analysis. These chelates are thermally stable up to 700^0 C and are colored by nature. Ligand and metal chelate were tested for antimicrobial activity on gram-positive and gram-negative bacteria and fungi by Agar Well Diffusion Method and the results are compared to Cisplatin as standard.

Keywords: 2-amino-1,4-naphthoquinone, 2-amino-3-chloro-1,4-naphthoquinone 1-oxime, synthesis, structure elucidation

Introduction

The compound like 2-amino-1,4-Naphthoquinones, 2-amino-3-chloro-1,4-Napthoquinones have an active amino group in the 2-position, which have excellent biological applications which includes antimalarial, antibacterial, antitubercular, antitumor agents larvicides, herbicides and fungicides (Prescott, 1969; Hodnett *et al.*, 1983; Clark, 1984)[1, 2, 3]. So, researches always focused on these molecules, derivatives, metal complexes. Cadmium (Atomic number 48, Atomic weight 112.411, Electron configuration: [Kr] $4d^{10}5s^2$) is bluish white metal having physical properties like malleable, ductile, soft in nature. To complete the Octet rule Cd is easily donate the two electrons in outermost valence shell, so it gives two electrons and form a stable complex, on other hand ligand 2-amino-1, 4-naphthoquinone & 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime are ability to take the electron and form the stable complex, hence synthesis and characterization of these molecules were selected for research. Synthesis of ligand 2-amino-1, 4-naphthoquinone & 2-amino-3-chloro-1,4-naphthoquinone 1-oxime are reported in various methods (Camara *et al.*, 2008; Sharma *et al.*, 2013; Mandke *et al.*, 2017) [4, 5, 6]. This paper summarizes the synthesis and characterization with modern analytical tools of Cd metal chelates with ligands 2-amino-1, 4-naphthoquinone & 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime, also microbiological activities are studied and reported.

Materials Used For Synthesis and Synthesis Process

The ligand 2-amino-1, 4-naphthoquinone was synthesized from 1, 4 naphthoquinone. 1, 4 naphthoquinone which was supplied by Fluca chemicals and ligand 2-amino-3-chloro-1, 4-naphthoquinone-1 oxime was synthesized from 2-amino-3-chloro-1, 4-naphthoquinone which was supplied by Sigma-Aldrich.

Synthesis

Synthesis of 2-amino-1, 4-naphthoquinone from 1, 4-naphthoquione

About 2.0 gm 1, 4-naphthoquinone was dissolved in 50 mL mixture of Tetrahydrofuran: Water (40:10). To this solution 2.5 gm of Sodium Azide (Saturated) was added. Sufficient amount of glacial acetic acid was added in the reaction mixture to acidify the reaction mixture. This reaction mixture was stirred for 6 hours at room temperature. Evaporate the solution to obtain the red-brown solid. Recrystallization was done with the help of Methylene chloride solvent.

Synthesis of 2-amino-3-chloro-1, 4-naphthoquinone-1 oxime from 2-amino-3-chloro-1, 4-naphthoquinone

About 5.0 gm Sodium hydroxide was dissolved in 40 mL of water, to which about 4.1 gm of 2-amino-3-chloro-1, 4-naphthoquinone was added slowly. To this mixture a solution of 2 gm hydroxyl amine hydrochloride dissolved in 40 mL distilled water was added. This entire mixture was warmed at $50\text{-}60^0$C for one hour on water bath. After one hour the reaction mixture was cooled to room temperature and then cooled to about 5^0C in an ice bath. Further to this solution cooled distilled water was added, then it was neutralized by freshly prepared dilute Hydrochloric acid. Dilute hydrochloride acid was added till precipitation is

formed. Filter the precipitate and washed with the cold water. Solid was obtained; the solid was dried on hot plant.

Cd chelate with 2-amino-1, 4-naphthoquinone

2 mM of 2-amino-1, 4-naphthoquinone was prepared in methanol and the solution was shake well to form a clear solution (Ligand solution), further reflux the solution for 15-20 minutes. 1 nM of Cadmium sulphate (Cd SO_4 8/3 H_2O, Merck) was prepared in water stirred well to from clear solution (Metal solution). A drop wise the metal solution was added into ligand solution under reflux condition, maintained the temperature of solution about 60^0C. This reaction mixture was heated for half hour under reflex condition. pH of solution was checked and adjusted to pH 6.5 with dilute Ammonia solution. Reflux the reaction mixture continue and pH of the solution was checked and if require pH of solution was adjusted to 6.5. Continued the reflux for two hours, after reflux cool the solution to room temperature and after filtration the solid was obtained. The solid was dried on hot plate and used for further characterization and microbiological studies.

Cd chelate with 2-amino-3-chloro-1, 4-naphthoquinone-1oxime

Dissolved 0.44 gm of 2-amino-3-chloro-1, 4-naphthoquinone-1 oxime (2 mM) in 20 mL of methanol and reflux the solution for about 15-20 minutes to form a clear solution (Ligand solution). Dissolved 0.26 gm of Cadmium sulphate in 10 mL water, the solution was stirred and clear solution was obtained (Metal solution). Drop wise this metal solution was added in ligand solution under reflux condition, during addition temperature was maintained about 60^0C. Further the reaction mixture was heated for half hour under reflex condition. Cool the reaction mixture and pH of solution was checked and adjusted to 6.5-6.7 with dilute Ammonia solution. Reflux was continued and pH of solution was checked, if required the pH of solution was adjusted to 6.5. Continued the reflux for two hours, after reflux the solution was cooled and filtered to obtained the solids. The solid was dried on hot plate and used for further study.

Interpretation of Analytical Data

Instrumental analysis

The synthesized compound was subjected to structural elucidation by elemental analysis, FTIR, Electronic spectra, Mass spectroscopy, Thermogravimetry analysis, X-ray diffraction and metal content by ICP-MS.

Fourier-transform infrared spectroscopic study

FTIR studied was done to evaluation functional groups and confirmation of the structure. FTIR spectra was recorded on Perkin Elmer instrument in KBr matrix with range 4000-400cm^{-1}. Typical functional groups identifications by IR spectroscopy of ligand and metal complex are summarized in Table 1.

Table 1: Typical functional groups by IR spectroscopy of ligand and metal complex,

Compound → Functional group ↓	Typical IR frequencies (cm^{-1}) ↓	Experimental IR frequencies (cm^{-1})			
		ACNQO	ANQ	Cd $(ACNQO)_2$	Cd $(ANQ)_2$
M-O	700-500	--	--	690, 675, 670	703, 695
M-N	700-500	--	--	646, 623, 572, 556	648, 621
C-Cl	850-550 S	770	--	778	--
C-H	900-700 B 1465-1365 B	861, 835, 811, 797,788, 782, 770, 749, 722, 710 1470, 1434, 1421, 1396, 1391, 1379, 1369, 1360	906, 874, 860, 850, 832, 821, 803, 798, 779, 754, 726 1478, 1442, 1419, 1395, 1365	887, 881, 866, 856, 843, 838, 818, 798, 778, 744, 729, 710 1472, 1402, 1384, 1358	876, 796, 757, 725, 703, 695 1473, 1456, 1420, 1377, 1342
C=C	995-790 B 1670-1600 S	994, 967, 926, 861, 835, 811, 797 1675, 1668, 1660, 1653, 1634, 1617, 1603	986, 919, 906, 874, 860, 850, 832, 821, 803, 798 1662, 1615, 1609, 1605, 1600	941, 887, 881, 866, 856, 843, 838, 818, 798 1660, 1648, 1587	998, 988, 973, 962, 876, 796 1682, 1659, 1590,
C-N	1342-1266	1340, 1327, 1315, 1296, 1281, 1270,	1320, 1270	1342, 1331, 1325, 1316, 1310, 1301, 1280	1342, 1315, 1276
N-O	1550-1500 S	1497	--	1523, 1491	--
C=N	1690-1640 S	1675, 1668, 1660, 1653	--	1660, 1648	--
C=O	1870-1650 S	1864, 1830, 1675, 1668, 1660, 1653	1866, 1842, 1686, 1662	1832, 1660, 1648	1843, 1682, 1659
N-H	3500-2800 S	3456, 3273, 3098	3398, 3390	3175	3231
O-H	3700-3584 B	3671, 3612	--	3672, 3612	--

B=Bending, S=Stretching, M=Metal,

For IR frequency evaluation study, Gaussian 09 software was used. Above IR frequencies are matches with literature values. Fig- 1 to 4 indicates the IR spectra for ligand and metal complexes.

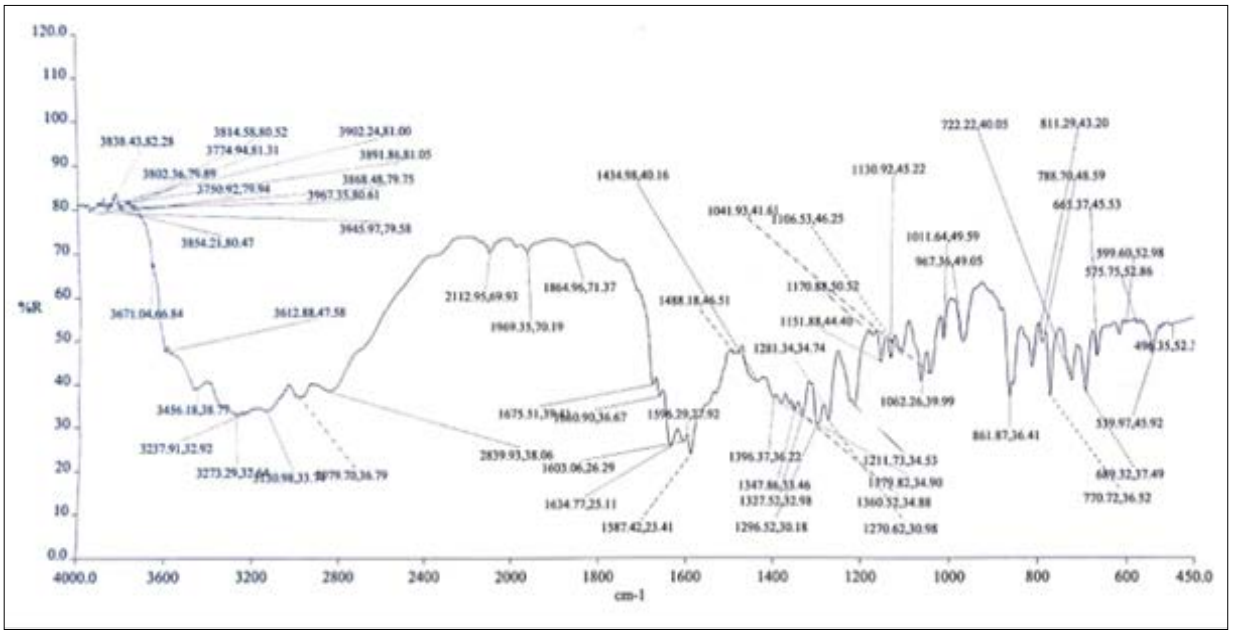


Fig 1: IR spectra for 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime (ACNQO)

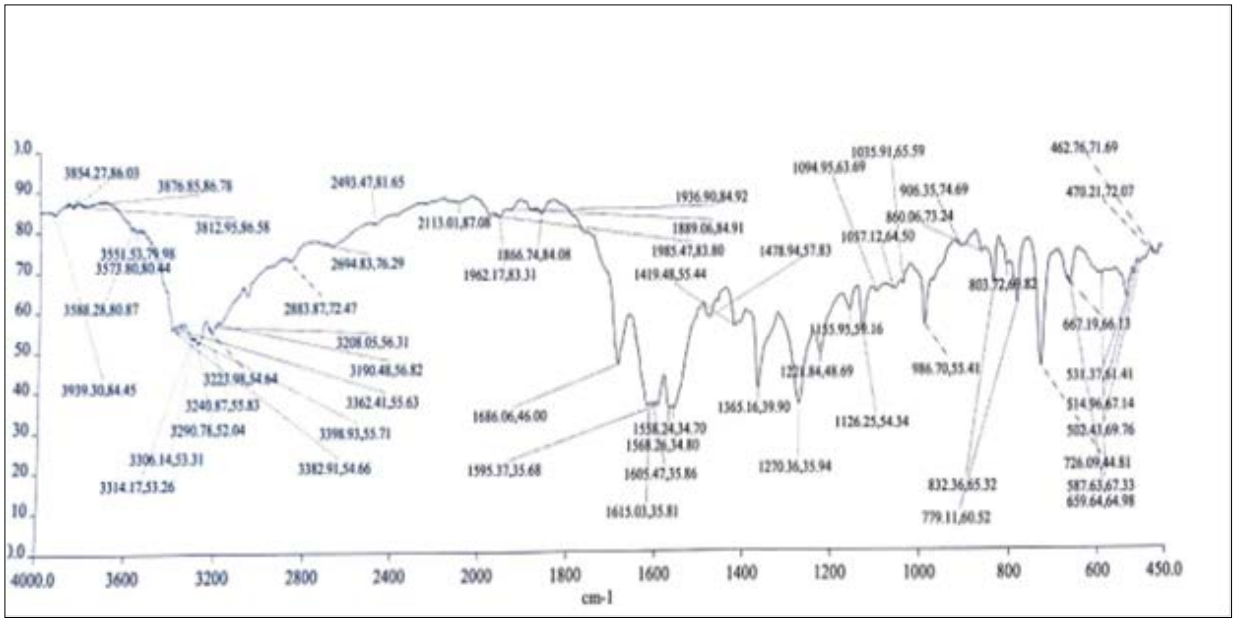


Fig 2: IR spectra for 2-amino-1, 4-naphthoquinone (ANQ)

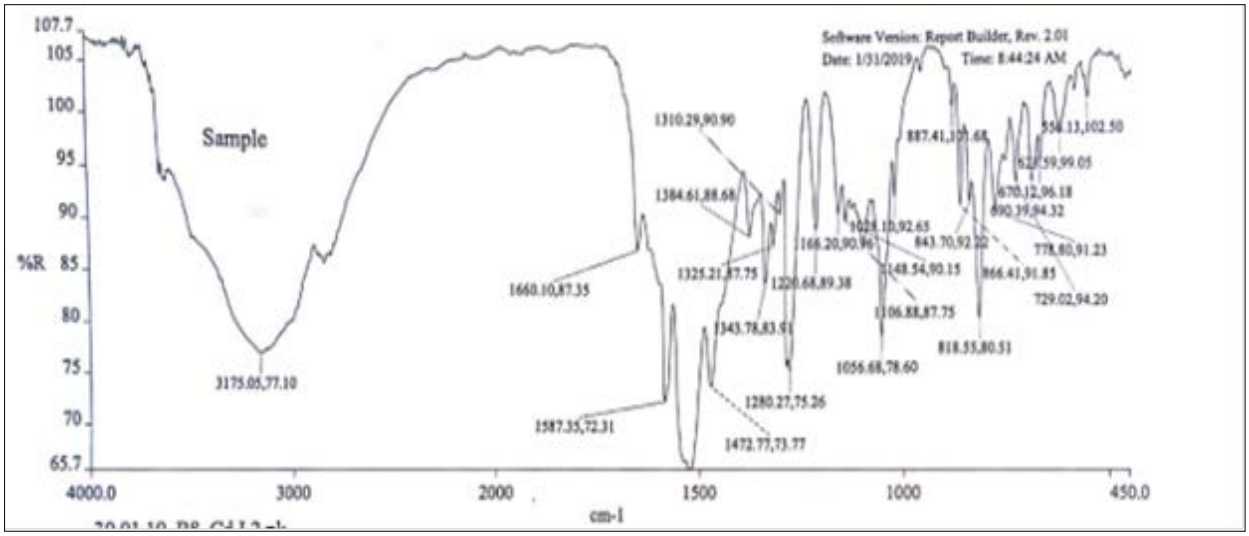


Fig 3: IR spectra for Cd metal complex with 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime (ACNQO)

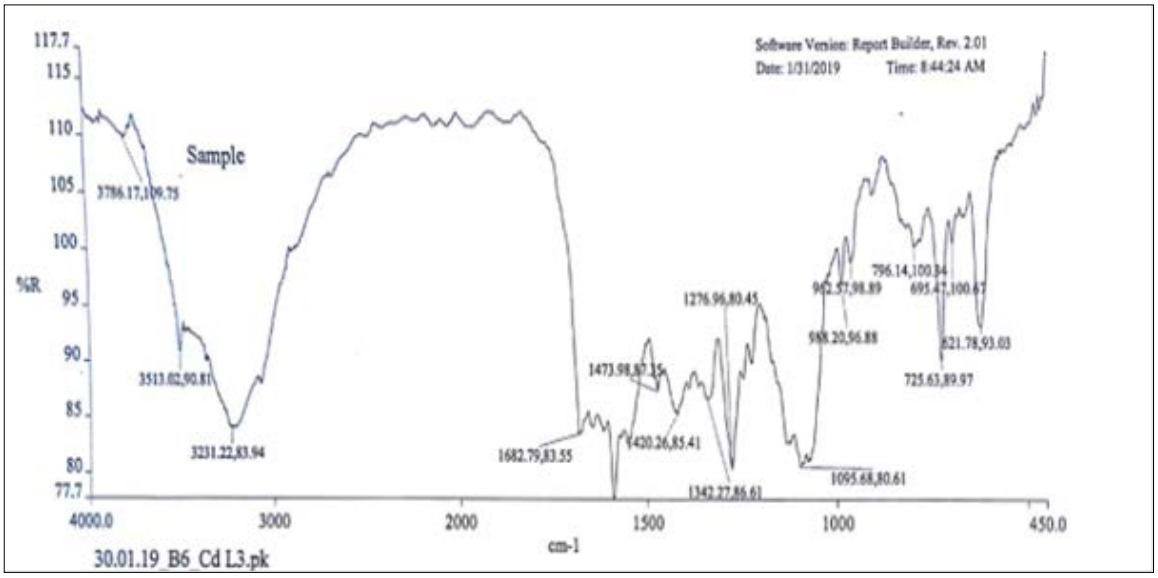


Fig 4: IR spectra for Cd metal complex with 2-amino-1, 4-naphthoquinone (ANQ)

UV spectrophotometric study (Electronic spectroscopy)

Electronic spectroscopic study was conducted to evaluate the UV spectrum of metal chelate and co-relation with ligand. UV spectra had been recorded on Shimadzu instrument in solvent DMSO for metal chelates and UV scan of ligand is recorded in methanol solvents. In UV spectroscopy, a beam of UV-Visible light is passed through the sample solution; a molecule absorb the UV or visible radiations and goes to existed. The electron moves from occupied molecular orbital to unoccupied molecular orbital. Hence this spectroscopy is also called as electronic spectroscopy.

Energy transitions are observed as η→π*, η→σ*, π →π*, σ →π *, σ → σ*.

Table 2: Experimental λ_{max} observed

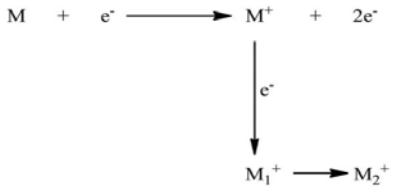
λ → Compound ↓	λ_{max1}	λ_{max2}	λ_{max3}
Cd $(ACNQO)_2$	271 nm	339 nm	431 nm
Cd $(ANQ)_2$	273 nm	442 nm	--

Observed λ_{max} are due to energy transitions of metal complex.

Mass spectroscopic study

Mass spectroscopy is widely used for evaluation of mass to charge ratio of ions. In pharmaceuticals industries these techniques are used for evaluation of mass of molecules.

Mass spectroscopy was used for evaluation of mass to charge ratio i.e., m/z of ligand and metal complex. In this technique sample is converted in vapor phase and high energy electron is bombarded to knock out an electron. Thus, a positively charged ion is produces which is called as molecular ion i.e. M^+



Where,
M^+ = molecular ion
M_1^+ and M_2^+= Fragment ions

Further based on ionization M+1, M+2 ions formed.

The formed ions are analyzed under the electric and magnetic field and recorded and give a mass spectrum. Molecular weight of ligand and metal chelate was evaluated by shimadzu quadrupole mass spectrometer instrument and results are reported in Table 3.

Table 3: Molecular weights of ligand and metal complex

Mass spectroscopic data → Compound ↓	Theoretical molecular weight	Experimental data		
		m/z	M+1	M+2
ACNQO	222.63	223	224	225
ANQ	173.17	174	175	--
Cd $(ACNQO)_2$	555.65	556	557	558
Cd $(ANQ)_2$	458.74	459	460	--

Above data is depicted that the experimental data correlates to Theoretical molecular weights.

Elemental analysis

CHN analysis was done to evaluate the elements like Carbon, Hydrogen and Nitrogen. In CHN analysis sample under goes the process of flash combustion and further get oxidized into simple compounds which are detected by thermal conductivity detector or infra-Red spectroscopy. Analysis of ligand and metal complexes were carried out by Perkin Elmer instrument and data is reported in Table 4. Also, the results were compared with the theoretical values.

Table 4: Result of Elemental analysis (CHN)

CHN analysis → Compound ↓	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
ACNQO	53.95	52.99	3.17	3.25	12.58	13.46
ANQ	69.36	69.36	68.67	4.07	4.13	8.09
Cd $(ACNQO)_2$	43.23	43.26	2.18	2.09	10.08	10.83
Cd $(ANQ)_2$	52.36	52.48	3.08	3.24	6.11	6.56

Results of elemental analysis depicted that the experimental

values are good agreements with the theoretical values of ligand and metal complexes.

Metal analysis by ICP MS: Inductively coupled plasma mass spectrometry (ICP-MS)

% Metal content was analyzed with help of ICP MS (Inductive couple plasma mass spectroscopy) and compared with the theoretical values and summarized the data Table 5.

Table 5: Result of Metal content by ICP MS

Metal content → Compound ↓	% Metal content	
	Theoretical	Experimental
Cd L2	20.23	21.95
Cd L3	24.50	24.72

Experimental results of metal contents are matches with the theoretical contents.

Thermogravimetric study

In Thermogravimetric analysis (TGA) sample exposed to temperature and measures the properties like phase transitions, adsorption, absorptions or desorption.

All metal complexes were studied for TGA. The metal complexes were studied for % weight loss against the temperatures.

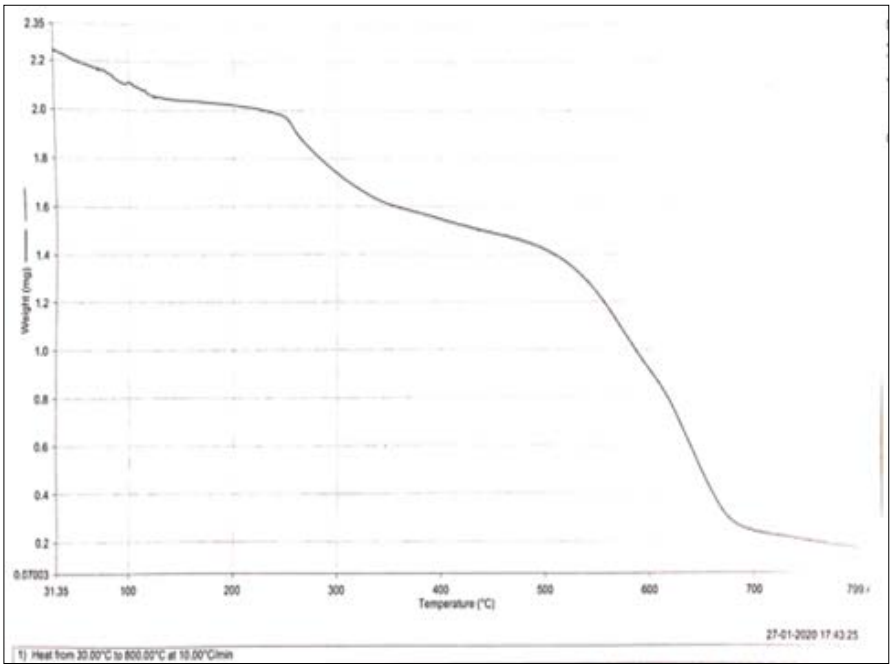


Fig 5: TGA for Cd (ACNQO) $_2$

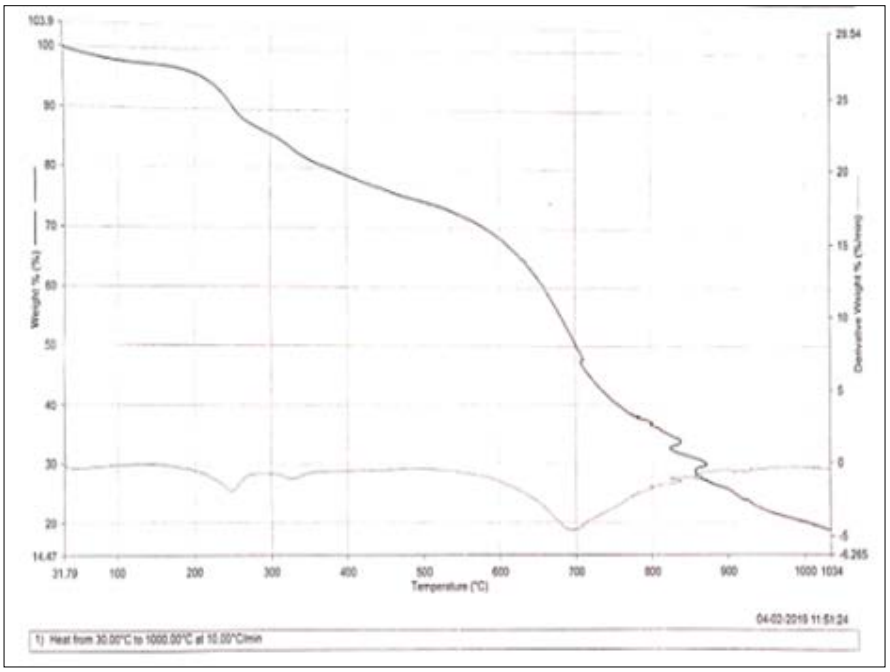


Fig 6: TGA for Cd (ANQ)$_2$

The results of TGA indicated that there is thermal decomposition with weight loss. Cd $(ACNQO)_2$ shows the decomposition at higher temperature (about 670^0C) whereas Cd $(ANQ)_2$ shows decomposition at 780-820^0C. Thermogravimetric analysis data for Cd $(ACNQO)_2$ shows that first weight loss was observed 4.9% at the temperature about 90^0C. Second weight loss was observed at temperature 260^0C and weight loss was observed 14.6%; Third weight loss was observed 53.5% at temperature about 580^0C. Fourth weight loss was observed 74.0% at temperature about 640^0C.

Thermogravimetric analysis data for Cd $(ANQ)_2$ shows that first weight loss was observed 1.1% at the temperature about 60^0C; this is may be due to loss of residual water and solvents. Second weight loss was observed at temperature 240^0C and weight loss was observed 10.4%. Third weight loss was observed 16.6% at temperature 320^0C. Fourth weight loss was observed as 46.7% at temperature 530^0C. Further compound showed slow weight loss due to further decomposition.

X-ray diffraction study

X-ray diffractions study is widely used to identify the crystalline / amorphous nature of compounds. Also, it is used for determination of crystalline form of different type of compounds. This technique has a vast application in pharmaceutical industry and academic fields.

Metal complexes were studied for X-ray diffraction and found that all ligands and metal complexes were observed as "Crystalline in nature". Cd $(ACNQO)_2$ & Cd $(ANQ)_2$ belong to Rhombohedral and hexagonal group respectively. A typical X-ray diffractogram for ligand ACNQO & ANQ and also for metal complex is shown below figures (7 and 8).

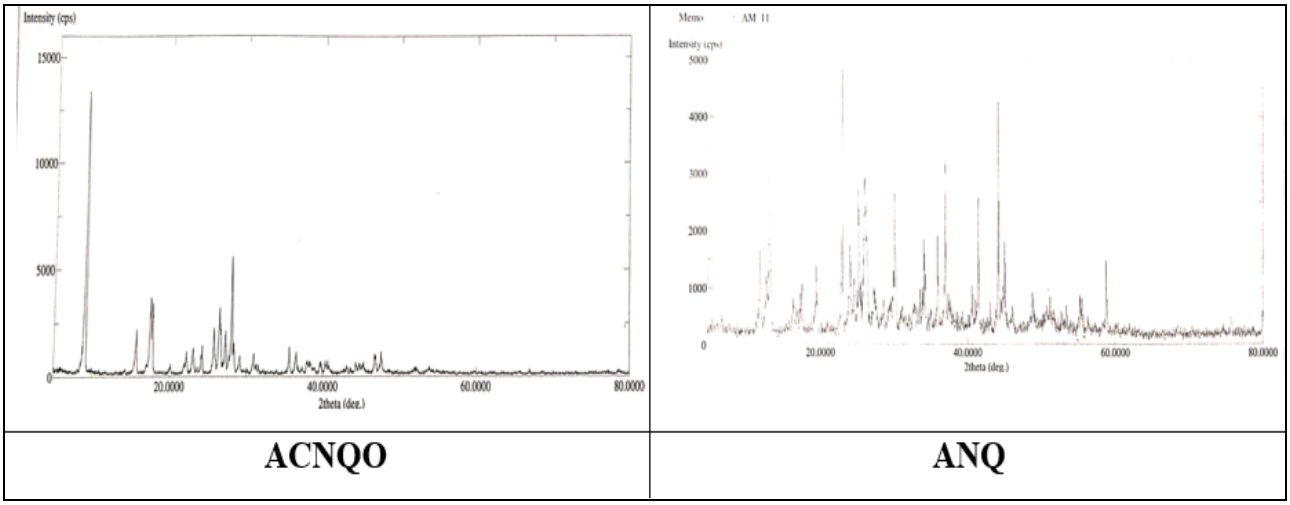


Fig 7: X-ray diffract gram for ligands (ACNQO & ANQ)

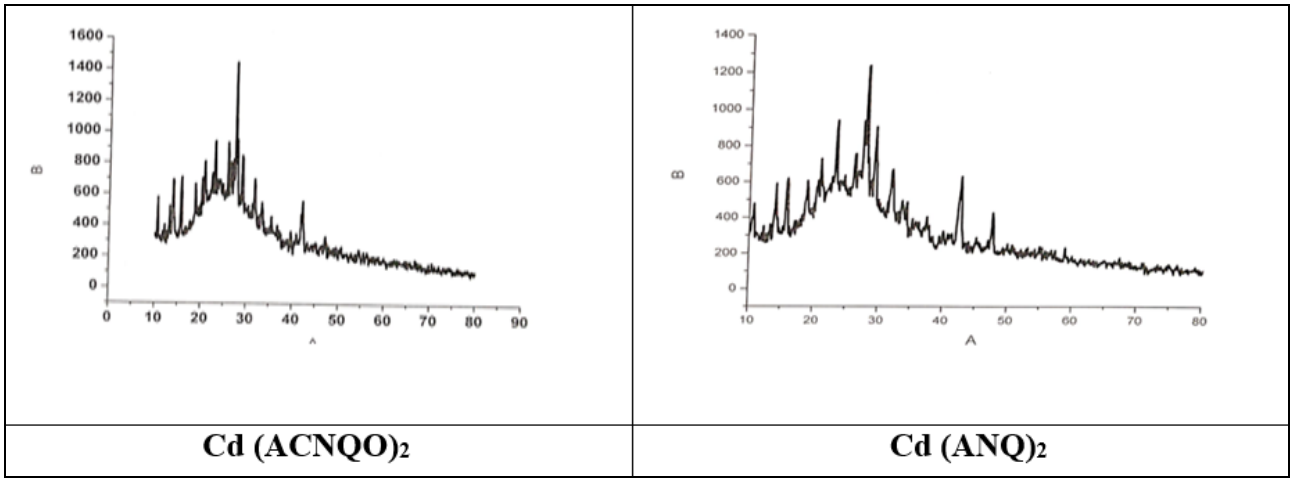


Fig 8: X-ray diffract gram for Metal complexes (Cd $(ACNQO)_2$, Cd $(ANQ)_2$)

Conclusions

Ligand 2-amino-1, 4-naphthoquinone (ANQ) and 2-amino-3-chloro-1, 4-naphthoquinone 1-oxime (ACNQO) were synthesized and also metal chelates were synthesized. These ligands and metal complexes were characterized by elemental analysis, FTIR, Electronic spectra, Mass spectroscopy, Thermogravimetry, Differential scanning calorimetry, X-ray diffraction and metal content by ICPMS. The metal chelates were found crystalline in nature. Microbiological activities were found good than standard Cisplatin which was used as standard. All results of structure elucidations show good agreement with the theoretical values. Thermal analysis depicted that the metal chelates are decomposed with high temperatures above 600^0C.

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