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Synthesis, characterisation& spectral studies of Titanium (IV) complexes with 2'-carboxy phthalianilic acid (2'-CPAA) derived from acid amide and effect on plant growth

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Abstract
A series of transition metal complexes of Co(II), Ni(II), Hg(I), Zn(II), Cu(II) with tridentate ligands (2'-carboxy phthalianilic acid) was prepared by the condensation of phthalic anhydride and anthranilic acid. Metal complexes are reported and characterized based on elemental analysis, IR spectrum, reaction & sensitivity of metal ions with 2'-carboxy phthalianilic acid. Thin layer chromatographic separation & effect of 2'-carboxy phthalianilic acid on germination, seedling growth, chlorophyll and protein contents was examined.

1. Introduction

The development of co-ordination chemistry in the early stages the existence of chelate containing on organic part.However,it is natural molecules or an ion attached to a metal atom by means of more than two donor atoms as established.The ions and natural molecules with the capacity of being attached to a single metal atom through 3,4,5 or more donor atoms are also known. The ions or the natural molecules so attached with the metal atom are called ligands.A group it attached to the same metal ion through to or more of its termed as multidentate ligand.

The research on the development ofmultidentate chelating agents has been done on account of their unique agents has been done on account of their unique and also interesting stereo chemical property the large scale existence in the living organizations & their practical application as separating agents such as ethylene diamine tetra acetic acid (EDTA).These observations have led to the synthesis and the study of a no. of a new variety of chelating agents.

In general each kind of metal can serve the purpose of being a central atom. Transitional elements atoms form complexation as well as chelation comparatively more readily than alkali metals .The chelated complexes have generally been found to be more stable than the similar of rings formed are higher in number.

According to sidgwick the metal that can easily co-ordinate as an acceptor with sulphur are

Cr…….Ni	Cu……GeAs
…RuRhPd	Ag Cd……..SnSb
…OsIrPt	Au Hg Ti Pb Bi

The chemistry of anilic acids and their related compounds has sufficiently been developed in many fields during the last two decades.Keen interest has been shown by various workers in the study of anilic acids & their metal complexes,because of the fact that anilic acids & their metal complexes have multiple use on fungicides lubricants detergent in turbine oils not only this these have been used as rust inhibitors and as analytical reagents. More experimental work is still needed to be done regarding ligand bonding molecular structure and the thermal behaviour of these compounds so as to have a better understanding of the subject.

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2. Materials & Methods

All chemical used were of analytical grade. The elemental analysis were carried out at CDRI,Lucknow.The IR spectra of the complexes were recorded with perkin Elmer spectrophotometer model 651 in KBr or nujolphate at RSIC,CDRI,Lucknow.A stahl type applicator was used for coating adsorbent on glass plates(20x20cm2).Glass chambers (12x24x24cm2) were used for development & the plates were dried in electric air driver .The adsorbent used was silica gel G of B.D.H grade.

2.1 Synthesis of ligands

Synthesis of pure primary amines from amide,passes through the following course of reaction and leads to the formation of acid amide.

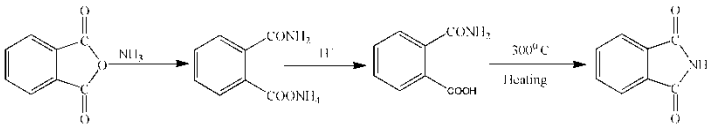

Fig.1: Structure 1

It is prepared by condensation phthalic anhydride and anthranilic acid. The equimolar amounts of the reactants were refluxed with benzene separately,mixed together in a 1000ml beaker and left overnight by which a white product was obtained.It was further purified by carbonate method. The observed yield of white crystalline compound (m.p.-1720C) is 75%. The condensation takes place in the following way.

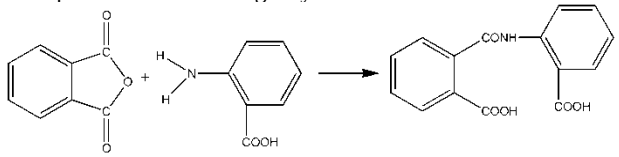

Fig.1: Structure 2

Two carboxylic acids were prepared by condensing the different anhydrides (maleic, succinic, glutaric and phthalic anhydride etc.) with anthranilic acid in the present work. The purification of the products so obtained was done by using conventional methods (boiling with the solvent and bicarbonate method).The formation of single compound during such condensation was confirmed by applying thin layer chromatographic technique. In order to confirm the composition of the products, the compounds were analyzed for carbon, hydrogen and nitrogen .Infra red spectra of the products shows were defined peaks for –CONH (amide I,II and III band) and –COOH group.For the Ti(IV) acids have been used as the gravimetric reagents.The percentage yield was calculated according to:-

Yield % = Actual yield / Theoretical yield

2.2physical and Characterization of Schiff Base

The melting point of the ligands is determined. The synthesized anilic acid were analyzed for their carbon, hydrogen and nitrogen contents to determine their chemical composition, at central drug research, Lucknow. The data is given in the Table 1.

Table 1: Details of Legend Characterization

S.No.	Name & Molecular formula of the ligands	Colour	M.P /D.T.	Elemental Analyses		
				%of C	%of H	%of N
1.	2'-carboxy phthalianilic acid	White	172^0	63.38 (63.75)	3.45 (3.57)	4.85 (4.75)

3. Preparation of Titanium (IV)

3.1Synthesis of Metal Complexes

Metal complexes were prepared by adding the solution of the ligand in appropriate solvent to the solution of the respective metal.Titanium was prepared by dissolving in requisite amount of TiOCl2.8H2O (B.D.H) in distilled water.Metal contents of solution were determined gravimetrically analysis. The study of the visible interaction between the reactants was made by adding the sodium salt of the anilic acid the solutions of different metal ions. The pH of the solution was adjusted by using ammonia (1:1) or dilute acetic acid. The metal hydroxide formation at higher pH range was controlled by adding a very small quantity of sodium,potassium tartarate.

Table 2: Reaction And Sensitivity Of Metal Ions With 2'-Carboxy Phthalinilic Acid

S.N	Metal ions	Alkaline reagent 1% solution	Alcohalic reagent 1% solution	Sensitivity µg/ml	Stability
1	CO ((II)	No Change	No Change	-	-
2	Ni (II)	No Change	No Change	-	-
3	Hg (I)	White ppt.	White ppt.	3.98	Unstable
4	Zn (II)	No Change	No Change		-
5	Cu (II)	No Change	No Change		-
6	Hf(IV)	White ppt.	White ppt.	12.10	Stable
7	Cd (II)	No Change	No Change		-
8	Ti (IV)	White ppt.	White ppt.	8.75	Stable

Complexes of general formula (Ti (L)O(H2O) were isolated by mixing equimolar solution of Ti(IV) and the anilic acid (ligand) in a stoichiometric ratio of 1:1 (ligand) reagent in slight excess).The pH of the solution was adjusted from 5.5 to 6.8 with the help of .01M acetic acid.About 2.0 gram of ammonium nitrate was added for better precipitation.The precipitate was adjusted for half an hour at 500-600and then filtered washed with distilled water many times.The dried precipitate was finally washed by ether and dried 130-1400.

3.2Preliminary information

The study of the visible interaction between the reactants was made by adding the sodium salt of the anilic acid and the solutions of different metal ions. pH of the solution as adjusted by using ammonia (1:1) or dilute acetic acid. The metal hydroxide formation at higher pH range was controlled by adding a very small quantity of sodium potassium tartarate. The effect of various masking agents was also observed. Observations of this study were recorded as given in Table 2.

4. Physical and Characterization of Metal Complexes or Analyses and Instrumentation

The complexes so obtained show satisfactory elemental analyses in Table-1.The complexes isolated above were analyzed for carbon, hydrogen and nitrogen percentages at IIT Kanpur. For the determination of metal as oxide, the complex was dissolved in conc. nitric acid in the complex acid ratio 1:3 & then evaporated to dryness. The process was repeated thrice. The residue thus obtained was diluted with 100ml of distilled water and neutralized by the addition of diluted ammonia solution in the ratio 1:1v/v.

The metal contents were analyzed by usual analytical procedures. The results of the analysis are recorded in table no.3.

The elemental analysis reveals that the results of the anilic acids & their complexes are found in accordance with calculated percentage. To confirm the stoichiometry and the structure of the complexes, IR studies were carried out which confirm the same composition for the metal complexes.

Table-3: Characterization of metal complex

Complexes	% Found (calculated)			
2'-CARBOXY PHTHALIANILIC ACID	C	H	N	MO2
	44.05 (44.12)	2.47 (2.73)	3.34 (3.41)	30.06 (30.15)

Table 4: Infra red spectroscopic data of complex

2'-Carboxy Phthalianilic Acid					
S.N	IR	Assignment	S.N	IR	Assignment
1	3100(s)	-NH stretching	13	1220	-C
2	3040(s)	C-H stretching	14	1160	-
3	2960(s)	-	15	1085	-
4	2620(s)	-OH stretching	16	1065	-
5	1685(s)	Amide I band	17	960	-
6	1635	-OHstretching	18	900	-
7	1605	C=C Skeletal in plane vibration	19	830	-
8	1585	Conjugated rings	20	790	-C
9	1530	Amide II band	21	750	-
10	1450	-C-H bending aromatic	22	720	-
11	1365	-C	23	650	N=C=O Bending
12	1320	-	24	560	-

The Infra red spectra of the anilic acid and their complexes were recorded in KBr phase at IIT Kanpur in frequency region 200-4000cm-1.The frequency of compounds obtained under study are complied in Table-4

The following observations were used in the assignment of the peaks.

S = strong; W = Weak; M = Medium; B = Broad; Vs = Very strong; Sh = Shoulder

Thin layer chromatographic separation & detection of 2-carboxy phthalianilic acid and Ti complex. A stahl type applicator was used for coating adsorbent on glass plates (20x20cm2).Glass chambers (12x12x24cm3) were used for development & the plates were dried in electric air drier.

4.1 Adsorbent-The adsorbent used was silica gel G of B.D.H. grade.

4.2 Preparation of thin layer

The TLC plates (thickness of 0.5mm) were prepared by spreading slurry of 50gm of silica gel G in 100ml of distilled water by means of a stahl type applicator and the plates were activated by drying for 24 hours in an oven at a temperature of 60±10C.

4.3 Developers

The developers tried were benzene,toluene methanol,ethyl acetate,chloroform etc. Single or their binary or ternary mixture in different proportion.All these solvents used for the preparing the developing systems were used after suitable distillation.

4.4 Visualization

The chromo-plates were visualized by using iodine vapours. The staring point 1.5cm from the edge of the plate was carefully marked and the finish line 10cm from the application point was also marked. The solutions of the various anilic acids and their complexes were prepared in ethanol (0.1% w/v) and spotted on activated chromo-plates by means of micropipettes manufactured by clay adams (U.S.A). The spots were air dried and the chromo-plates were then put in the chamber for development. Necessary precautions were taken reproducibility of RF value as suggested by Randerath et.al.

(i) The thin layers were carefully prepared by means of stahl type applicator so as to have uniform thickness.

(ii) The activity of the layer was controlled by drying the plates for 24 hours at a constant temperature of 60±10C.

(iii) The degree of saturation the developing chamber was kept constant by keeping the developing solvent in the airtight developing chamber for two hours.The chromo-plates were then kept in the chamber and developing solvent system was developed up to the finish line.

(iv) In each chromatographic run the RF value were checked for reproducibility by making two or more run.

5. Results and Discussion

5.1 Separation of the Legends

First of all single solvent such as ethyl acetate, methanol, ethanol, benzene, toluene, chloroform, acetone and few other solvents were tried in order to separate the anilic acids. But none of these single solvents could achieve the separation of anilic acids. A study of the results given in table no. 5 indicate that when ethyl acetate and methanol were tried developer seven anilic acids could separated .The few spots had slight to medium tailing and also but not compact. When benzene was tried as a developer, only six anilic acids could be separated 2'-CPAA has slight tailing.

The RF values found when benzene-methanol (45:10) used as developer, are given in table No.5 along with RF values of various anilic acids ± 4 or more.

5.2 Separation of Titanium –Anilic Acid Chelates

A thorough study of table No. 6 indicates that when single solvent was used as a developer,the separation of titanium-anilic acid chelates could not be achieved. Benzene,ethyl acetate, toluene, chloroform when used as developer could achieve separation of different titanium anilic acid. The minimum difference in Rf values is ± 4 or more.

5.3 Paper Chromatographic

Paper chromatography was also used to a certain the purity of the compounds.The spots developed on rectangular sheet of whatmann paper no.1. The compounds in alcohalic solution were spotted at a distance of one cm from the bottom of the paper and dried. The paper strips were then placed in jar saturated with the vapours of developing solvent.The top of the jar was covered with a glass plate and the solvent system was allowed to run upto 10 cm. The paper strips were taken out,dried.The spots were visualized by iodine vapours, the spots were single,compact and having no tailing at all and the separation was complete. The compactness and the sharpness of the spots,the absence of any tailing confirms the purity of synthesized products.

Table -5: RF value of 2'-carboxy phthalianilicacid

2'-CARBOXY PHTHALIANILIC ACID	**Ethyl Acetate**	**Methanol**	**Benzene**	**Toluene**	**Chloroform**	**Benzene-Methanol (45:10)**
	78	**80**	**58C**	**58C**	**51b**	**69**

Table-6: Rf value of Titanium 2'-carboxyphthalianilicacid

TITANIUM COMPLEX OF 2'-CARBOXY PHTHALIANILIC ACID	**Ethyl Acetate**	**Methanol**	**Benzene**	**Toluene**	**Chloroform**	**Ethyl Acetate chloroform Benzene (30:20:20)**
	75	**77**	**54**	**53**	**48b**	**65**

6. Result and Discussions

6.1 Titanium Complexes With 2'-Carboxy Anilic Acids

A comparison of the absorption frequency bands in IR spectra of the ligands and their complexes shows that the chelate formation takes place and their metal complexes shows that the chelate formation takes place through the oxygen of the -CONH and carboxylic group.The results of IR spectra are given in table 3 and assignment of the bands based on the available data in literature.

6.2 νN-H frequency at 3100-3140cm^{-1}

Legends have been shifted at 3290-3320cm-1 in the Ti(IV) complexes. The strong peaks at 1680-1690cm-1and 1530-1540 cm-1assigned to amide I and amide II band respectively in the legends have been shifted to 1630-1660cm-1 and 1500-1510cm-1 in the complexes. This decrease in an amide I and II band indicates the co-ordination of the legends to Titanium through oxygen of the –CONH group. The lowering of the amide III bands at 1305-1320cm-1 inanilic acids to1260-1280cm-1 in the complexes further supports the co-ordination through oxygen of the amide group. The strong peaks at 1410-1420cm-1in legends due to νC-O have also been shifted at 1395-1410cm-1in Titanium complexes confirm the bonding of the tridentate legends through carboxyl group.

The absorption related to COOH at 2620-2660 cm-1,1710-1715cm-1 and 1630-1640cm-1 in 2'-carboxy anilic acids disappear in metal complexes, which show deprotonation of carboxylic group on chealation. A very broad band at 3460-3500cm^{-1} in complexes show the presence of –OH of the water molecule in co-ordination or in lattice. A band of medium intensity at 460-465cm-1in the complexes can be attributed to Ti-O stretching frequency. The co-ordination nature of the water molecule is indicated by appearance of rocking modes of medium intensity at 870-880cm-1.In TiOCl2,the band occurs at 870cm-1 has been assigned to Ti=O. The lowering of this band in present complexes may be attributed to the polymerization through Titanyl oxygen.Some new bands in complexes in the region 400-

530cm-1are apparently due to the vibrations of co-ordinated O…….> Ti bonds.

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