



SYNTHESIS OF SOME METAL COMPLEXES WITH 1-PHENYL-3-METHYL-4-ACERTHYL-PYRAZOL-5-ONE

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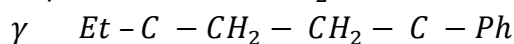
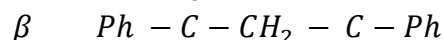
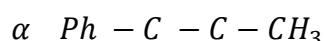
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Abstract: *The ligand; 1-phenyl-3 methyl-4-acetyl Prazol-5-one (HPMAP) may be regarded as a B-diketone. The presence of B-Carbonyl groups with atleast one proton on the carbon between the Ketonic grups, allows Keto – enol tautomerism. The enolic hydrogen is activated by the adjacent c-o groups and conjugate system can arise by a prototropic shift. Thus, under appropriate condition with the ligand, the enolic proton is removed. The compounds which form when the proton is replaced by Zirconium, Hafnium, Uranium and Cerium metals respectively is the subject of this project.*

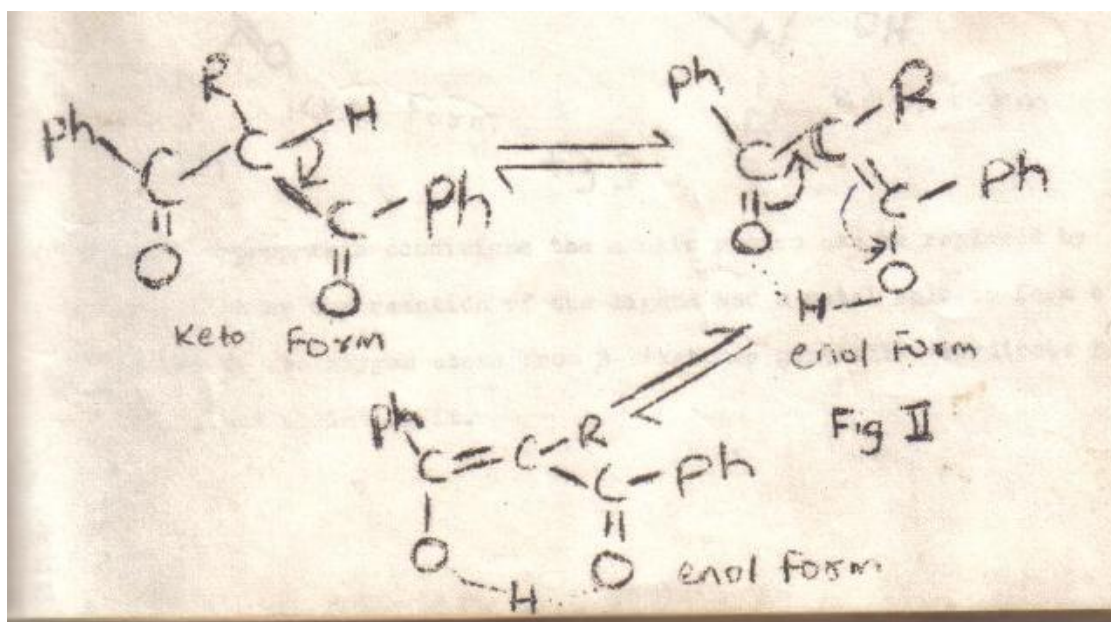
Keywords: Synthesis, Metal complexes, Phenyl, Methyl, Acerthyl, Pyrazol

Introduction

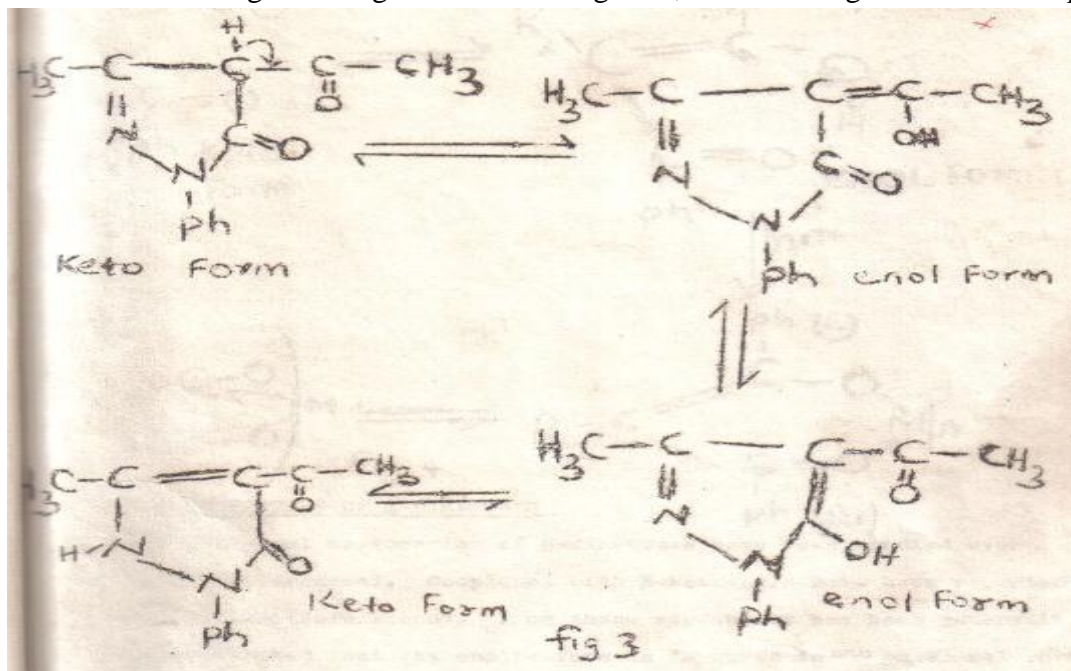
Diketones are classified as α , β , γ diketones according to whether the two carbonyl groups are in the 1,2, 1, 3, and 1,4 positions respectively.



β -diketones thus have at least one proton on the carbon between the ketonic groups thus making it possible or keto-enol tautomerism to arise as follows:

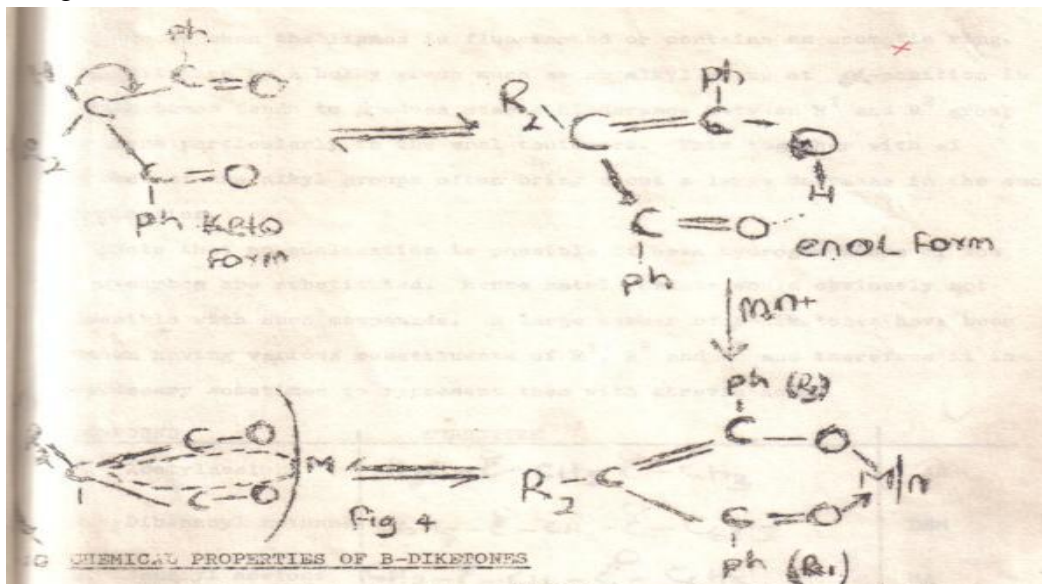


In the case of the ligand being used for investigation, the following tautomerism is possible.





Under appropriate conditions the enolic proton can be replaced by a metal cation by the reaction of the ligand and a metal salt to form a chelate ring. Two oxygen atoms from β -diketones generally coordinate to the metal, thus chelating it.



CHEMICAL PROPERTIES OF β -DIKETONES

The keto-enol tautomerism of β -diketones have been studied over many years (References). Complexes with β -ketoenols have been reported for many metals. (References). From these studies it has been generally noted and accepted that the enolic form is favored in non polar solvents.

It has also been found out that simultaneous conjugation and chelation though hydrogen bonding is responsible for the stability of the enol tautomers.

The ratios of the enol tautomer increases when a $-I$ effort group is substituted at an α -position in β -diketones (eg. When chlorine is substituted at own α -position in β -diketones). The enolisation also increases when the ligand is fluorinated or contains an aromatic ring. Substitution by a bulky group such as an alkyl group at α - position in β -dikotones tends to produces steric hinderance between R^1 and R^2 group protons particularly in the enol tautomers. This together with $+I$ effect of the alkyl groups often bring about a large decrease in the enol proportion.

Note that no enolisation is possible if both hydrogen atoms of the α -carbon are substituted. Hence metal chelate would obviously not possible with such compounds. A large number of β -diketones have been known having various substituent of R^1 , R^2 , and R^3 and therefore it is necessary sometimes to represent them with abbreviations.



S/N	COMPOUND	STRUCTURE	
1.	Acetylacetone	$\text{H}_3\text{C} - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3$	AA
2.	Dibenzoyl methane	$\text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{C} - \text{C}_6\text{H}_5$	DBM
3.	Benzoyl acetone	$\text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} - \text{C}_6\text{H}_5$	BA
4.	Benzoyl trifluoroacetone	$\text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{C} - \text{CF}_3$	BF3A
5.	Dipivoly methane	$\text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{C} - \text{CF}_3$	DIBM
6.	Trifluoro acetyl acetone	$\text{F}_3\text{C} - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3$	TF3A
7.	Benzoyl Trifluoro acetone	$\text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{C} - \text{CF}_3$	BF3A
8.	1-phenyl-3methyl-4acetyl- Pyrazol-5-one	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C} - \text{C} - \text{C} - \text{CH}_3 \\ \quad \quad \\ \text{N} \quad \quad \text{O} \\ \quad \quad // \\ \text{N} \quad \quad \text{O} \\ \\ \text{Ph} \end{array}$	HPMAP
9.	1-phenyl-3-methyl-4benzoyl- pyrazol-5-one	$\begin{array}{c} \text{M}_2 - \text{C} - \text{CH} - \text{C} - \text{Ph} \\ \quad \quad \\ \text{N} \quad \quad \text{C} \quad \quad \text{O} \\ \quad \quad / \quad \quad // \\ \text{N} \quad \quad \text{O} \\ \\ \text{Ph} \end{array}$	HPMB ₂ P

Any of the above named β -diketones can form a metal complex with any of the metals of oxidation (IV).

CLASSIFICATION OF METAL β -DIKETONES

Metal β -diketones can be conveniently classified depending upon the types of bonding of ligand moieties to the atoms

- i. Oxygen bonded.
- ii. Carbon bonded.
- iii. Both carbon and oxygen bonded.
- iv. Olefin bonded.

✓ OXYGEN-BONDED B-DIKETONATO COMPLEXES

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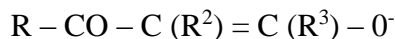
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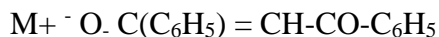
Oxygen-bonded β -diketonato complexes have been studied and in these derivatives the β -ketoenolate anion.



Many function as a ligand in several ways:

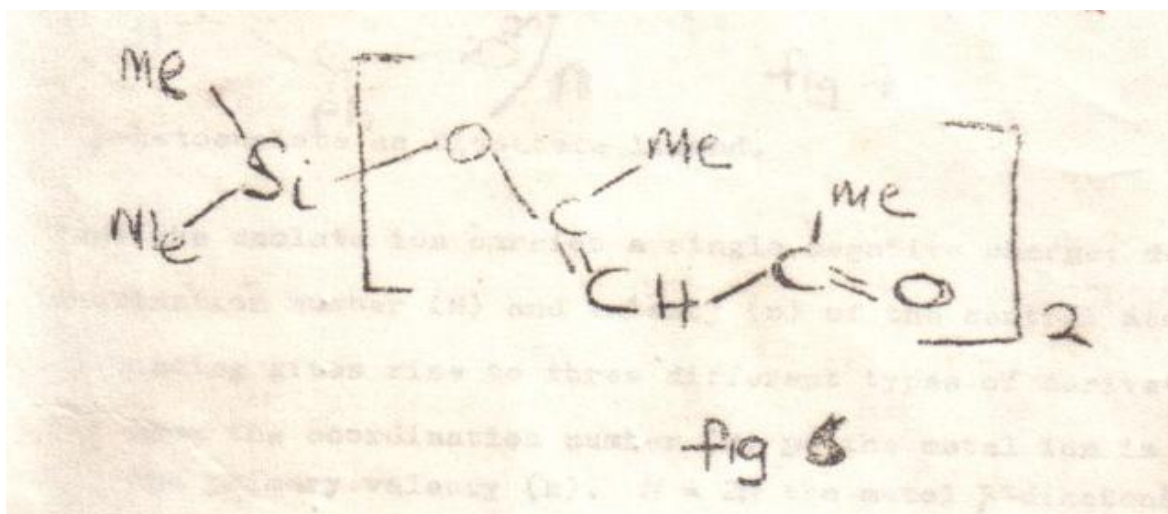
a. β -Ketoenolate as Unidentate Ligand

it can form simple salts with highly electro positive metals which have typical salt- like properties.



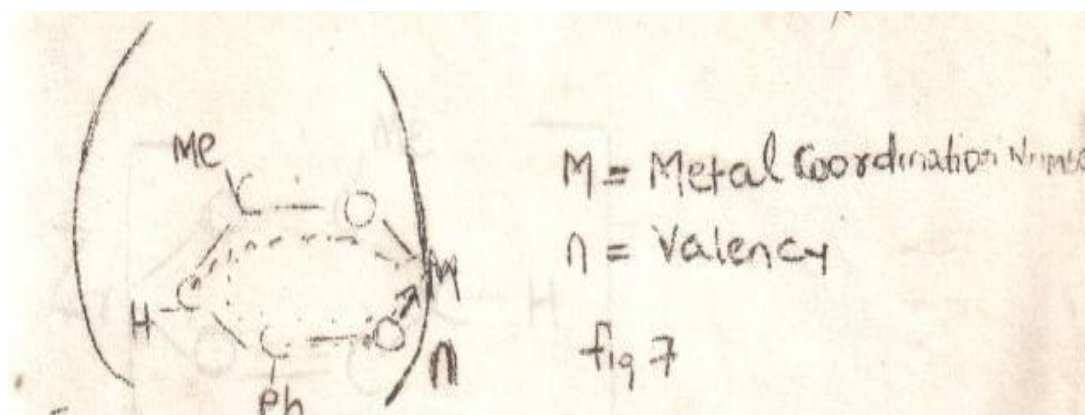
(Metalcation) dibenzoyl moiety

In view of the stability of the 6-membered chelate rings formed by these ligands with metals. It is very rare that β -diketone moiety is linked to the central metal atom through only one carbonyl group. Eg. It has been noted that Si atom has been coordinated tetrahedrally with the acetyl acetone moiety as unidentate ligand eg. See F.g 1



b. β -ketoenolate as Bidentate ligand

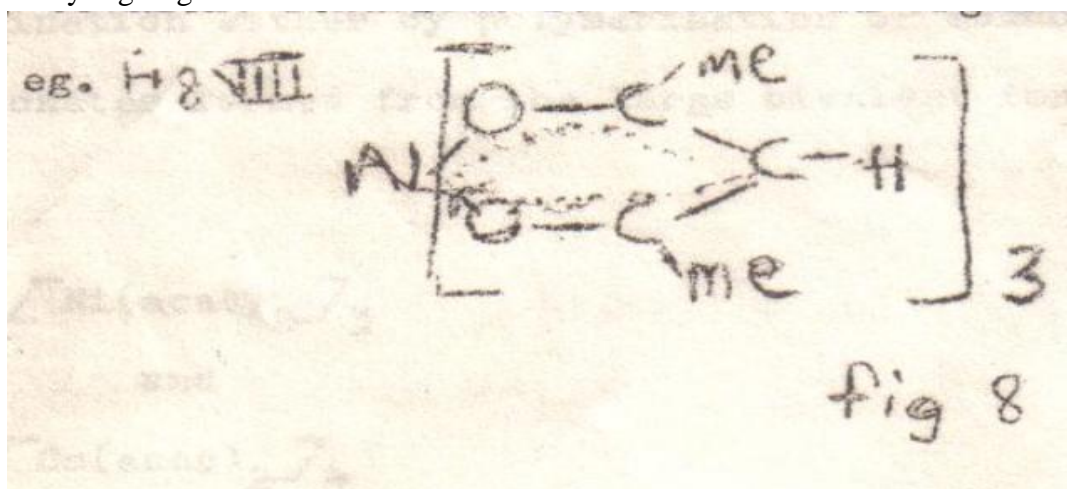
This is the usual type of bonding of β -diketone ligands. A metal replaces the enolic proton of the ligand and a six membered chelate is formed. Delocalization of the electron cloud in the result ant chelate ring has been suggested to account for its certain amount or aromatic character.



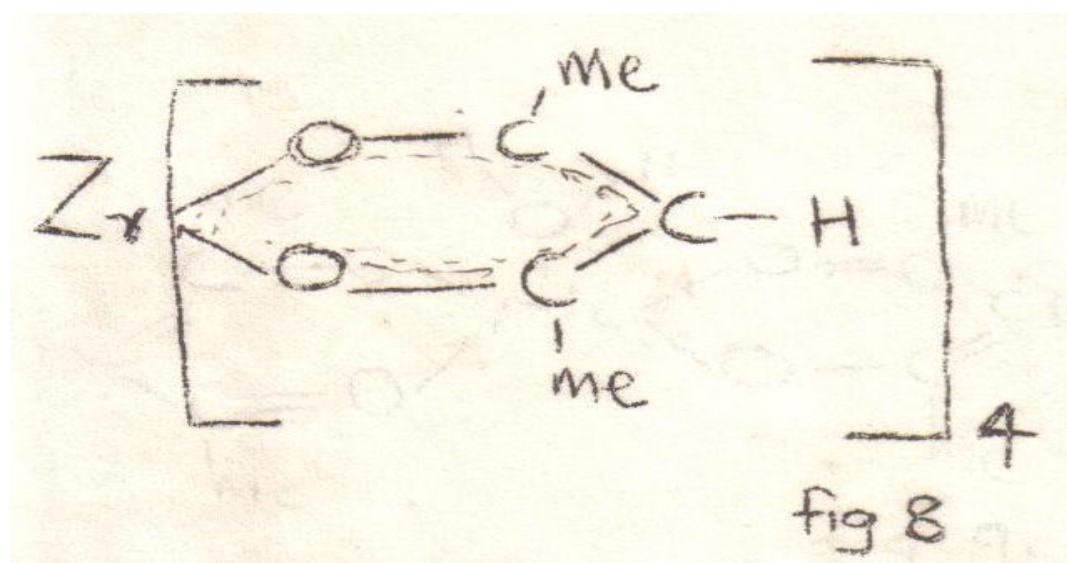
f.g. II β -ketoenolate as Bidentate ligand.

Since the enolate ion carries a single negative charge; depending on the coordination number (M) and valency (n) of the central atom; this type of bonding gives rise to three different types of derivatives firstly:

- when the coordination number (M) of the metal ion is double the primary valency (n), $M=2n$ the metal β -diketonate so formed behaves as an inner complex or neutral molecules. Common examples are $\text{Be}(\text{acac})_2$ and $\text{Al}(\text{acac})_3$ in which the metal atoms are coordinatively saturated. In view of inner-salt formation, these derivatives show predominantly covalent behavior i.e. soluble in organic solvents and volatility. Eg. Fig. III



Here Al has coordination 6 while its primary valency is 3. It forms a neutral complex.

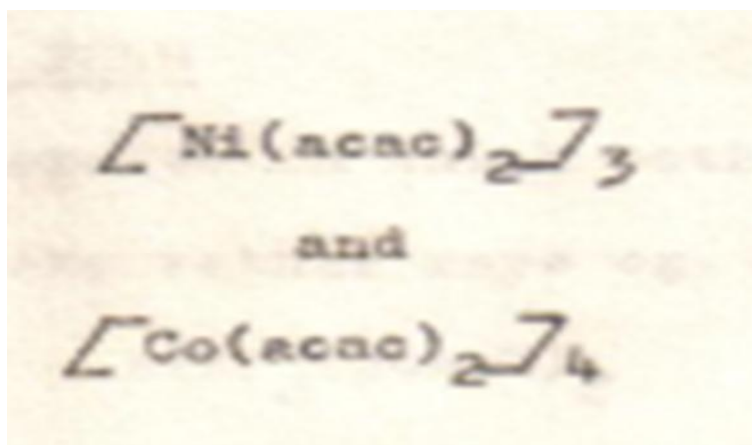


Here Zr has a coordination number 8 satisfied with 4 enolate ligand with its primary valency of 4.

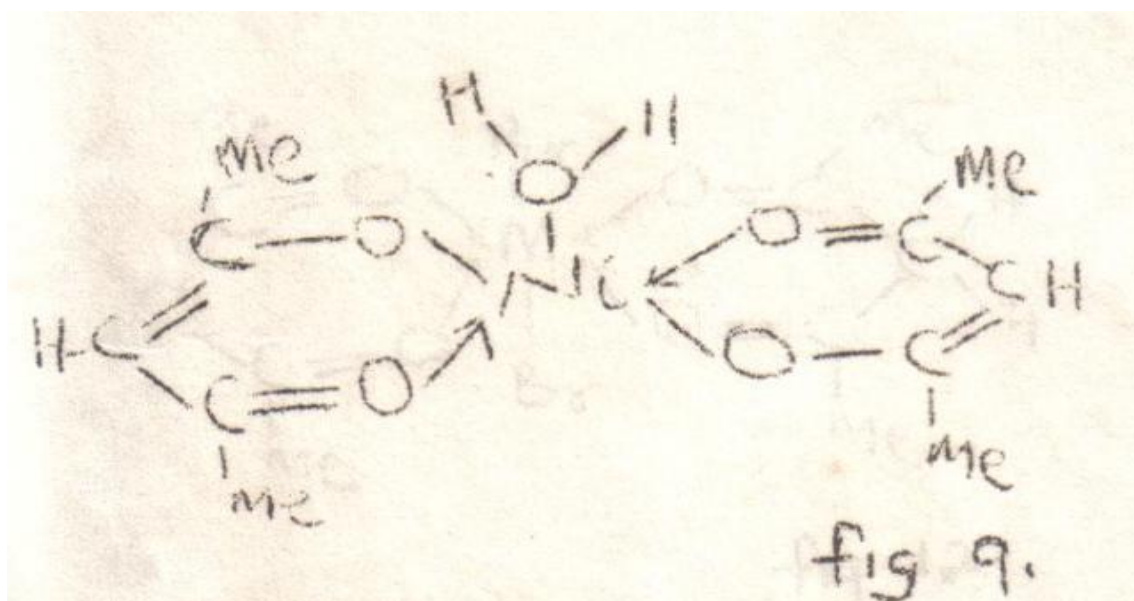
ii. When $M > 2n$

If the coordination number is more than double the primary valency the molecule or complex so formed behaves as a Lewis acid and achieves the desired coordination either by polymerization or adduct formation e.g. Metal β -diketonates formed from the large bivalent ions of transition elements.

Eg.



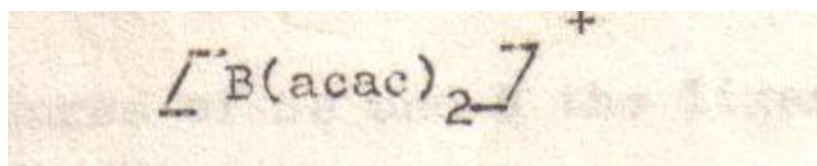
These complexes also behave as covalent compounds and the coordination number of the metal towards oxygen is generally six (6)



iii. When $M < 2n$

When the coordination number of the metal ion is less than double the primary valency a complex ion is formed. The complex so formed is acidic.

E.g.

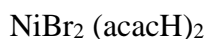


Boron has a primary valency (n) = 3 and has a coordination number 4 ie. Twice the primary valency is greater than its coordination number (M)

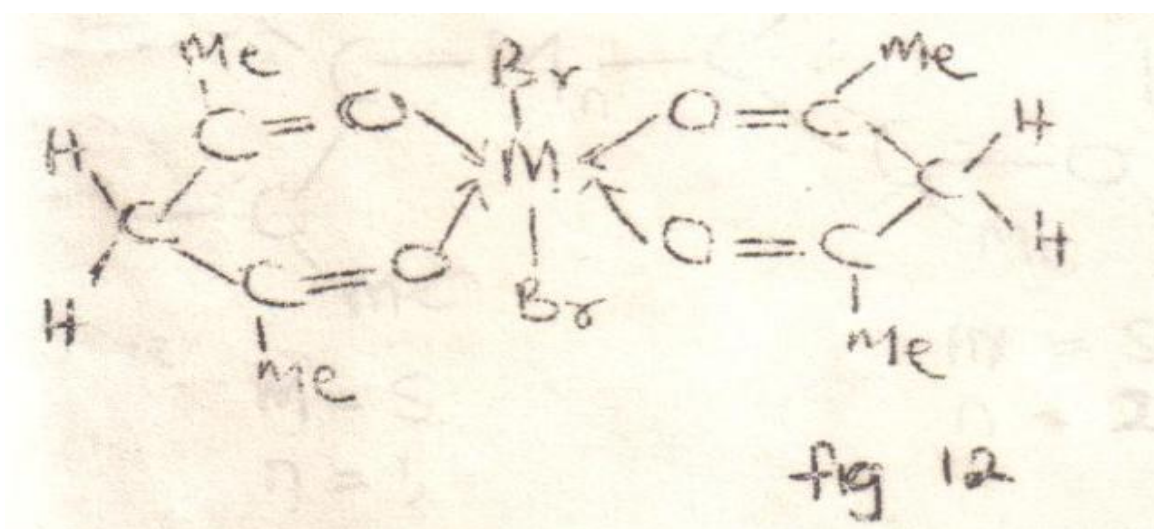
c. β -diketone as Neutral Ligand

KETO FORM

Metal β -diketones in which both carbonyl groups of the ligand act as a donor atom are rather rare eg. Fig. 12

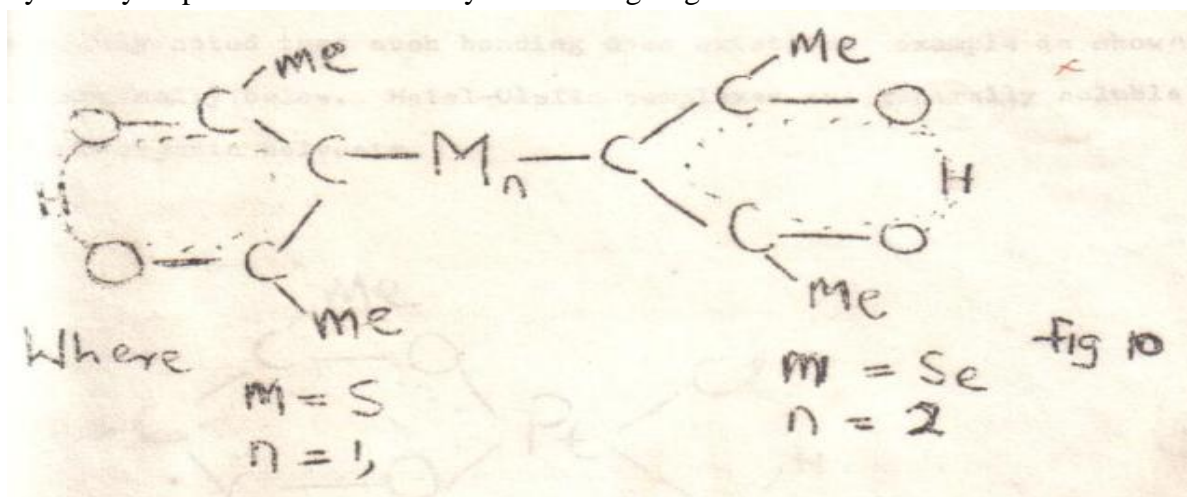


X-ray analysis of this complex revealed an octahedral structure. Fig. 12 shows two neutral acetylacetonate (Keto form) bonded to the metal through all the oxygen atoms.



CARBONATED β -DIKETONATO COMPLEXES

Carbon bonded β -diketone complexes are now well known. For example in β -diketones of Se and S the ligand moiety bonds these elements through the carbon. The metal-carbon bond of these complexes is quite stable as is apparent from their method of preparation in alkali medium. This is due to the coordination tendency usually exhibited by mainly sulphur and sometimes by selenium eg. Fig. 10



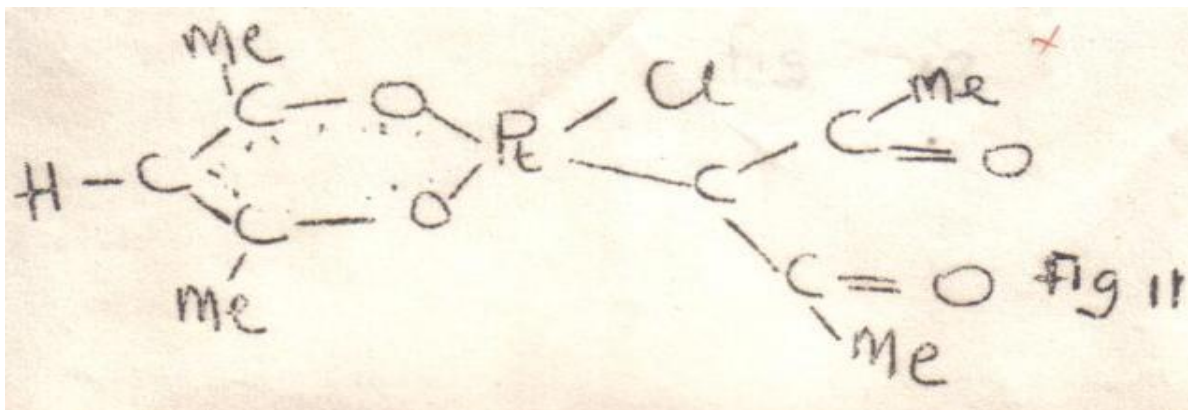
BOTH CARBON-BONDED AND OXYGEN BONDED β -DIKETONATO COMPLEXES

Metal β -diketones in which metal atoms is bonded to the ligands in such a way that one ligand moiety always bonds to the metal via two carbonyl oxygens while the other binds via the 3-c are also quite common. These



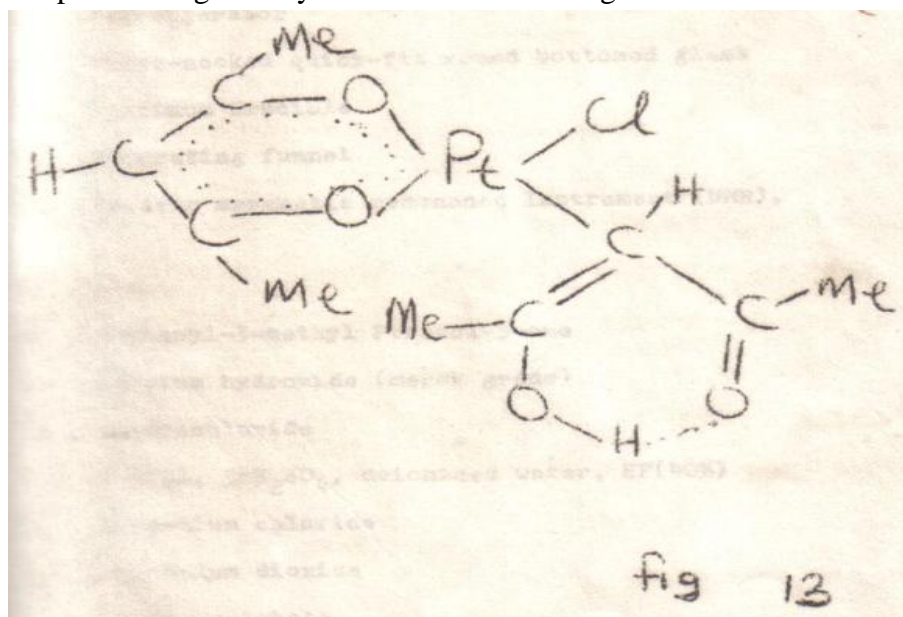
complexes are stable, generally coloured and are soluble in some common organic solvents like ethanol eg. Fig.

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OLEFIN BONDED β -DIKETONATO COMPLEXES:

Although X-ray crystallographic evidence has yet been established for the existence of metal-Olefin bonds in metal β -diketones, it has been generally noted that such bonding does exist; one example is shown mathematically below. Metal-olefin complexes are generally soluble in common organic solvents.



EXPERIMENTAL

APPARATUS

- Gallenkamp (electrothermal) melting point Apparatus
- Heating mentle

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- EB3A vacuum PUMP and compressor
- Hoidolph mechanical stirrer
- Funnel gin
- Refreigerator
- Three-necked quick-fit round bottomed flask
- Platinum Crucible
- Separating funnel
- Nuclear margnetic resonance Instrument (NMR).

REAGENTS

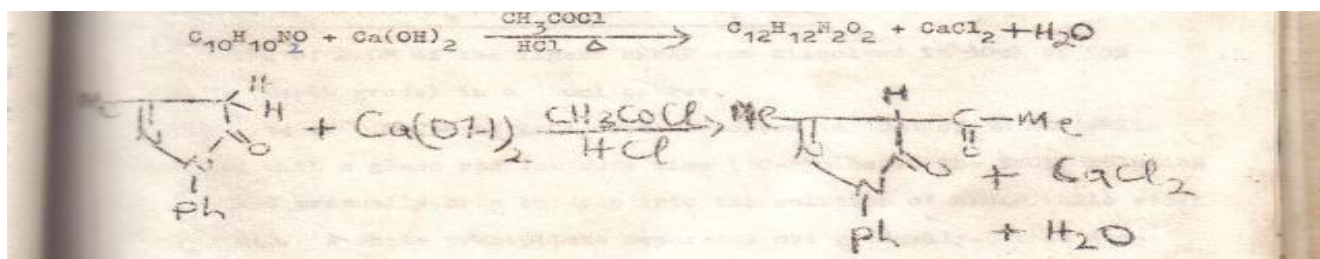
- 1-phenyl-3-methyl Ptrazol-5-one
- Calcium hydroxide (merck grade)
- Acetylchloride
- 3m. Hcl. 3mH₂SO₄, deionised water, HF (40%)
- Zirconium chloride
- Ziroconium dioxide
- Cerium sulphate
- Ethanol (merck grade)
- Acetone
- Zirconium oxy chloride hydrate
- Uranyl acetate.

SYNTHESIS OF THE LIGAND-HPMAP

17.0g of 1-phenyl-3-methyl Pyrazole-5-one were weighed and placed in a three neck-quick first flask equipped with a stirrer, separating funnel and a reflux condenser and dissolved in 100ml 1-4 dioxane (Merck Reagent grade) by application of gentle heat by setting the heat mantle at 1.0. after dissolving; 15g of calcium hydroxide was added while stirring and 7.20 ml of acetyl chloride was added through the funnel dropwise within a minute.

The reaction mixture become a thick yellow paste and increased in temperature within the first few minutes. The mixture was then heated for 30 minutes. The calcium complex (dark brown) was decomposed by pouring the mixture into 300 ml of 3m HCl with stirring while cooling below 0⁰c with chips of ice. This coursed cream coloured crystals to separate. The crystals were filtered with a Buchner funnel connected to a suction pump.

Equation



The crystals were allowed to dry in open air, making sure that impurities did not contaminate it.

Yield = 8 – 10g (crude)

M.P = 62⁰c – 63⁰c

They were recrystallize from water-methanol of equal ratio of volume. The crude ligand was dissolved in methanol while heating and stirring until all dissolved. Deionized water was added gradually still stirring until a white precipitate separated out. This was decanted into a beaker until all crystallized out. This was filtered and dried.

Yield: 6 -7g pure

M.P. = 35⁰C - 57⁰C

DISCUSSION:

It was discovered that during the decomposition with 3m HCL while stirring; the crystals could separate without cooling it below 0⁰c with ice clips but takes longer time and also low yield is obtained.

SYNTHESIS OF Zr (PMAP)₄ COMPLEX FROM ZrCl₄ SALT

2.1624g of 0.0m of the ligand HPMAP was dissolved in 50ml of 95% ethanol (Merck grade) in a 100ml beaker. 0.58258g of 0.0025m of ZrCl₄ was dissolved in 10ml of 3m HCl while stirring with a glass rod for sometime (10-15mins). The ZrCl₄ solution was poured gradually drop by drop into the solution of HPMAP while stirring vigorously. A white precipitate separates out gradually. This was filtered with a sintered glass funnel connected to a suction pump. The white crystals were dried in open air protected from dust particles and impurities.

Yield = 2.1230g

Melting Point = 190 – 191⁰c

AN ATTEMPT TO SYNTHESIZE HF (PMAP)₄ FROM HFO₂ SALT

STOCK SOLUTION OF HFO₂

Solubility

Con. HCl	Con. H ₂ SO ₄	Aquaragia	Con. HNO ₃	40% HF
HFO ₂ insoluble	Insoluble	Insoluble	Insoluble	Soluble with heating

2.16242g of 0.01M of the ligand HPMAP was dissolved in 50ml of 95% ethanol (merck grade) in 100ml beaker.



0.79076g of 0.0025M of HFO_2 was poured into a round bottom flask with a three neck quick first equipped with a reflux condenser and 10ml of cone HCl added. Heat was applied for 3 hours in order to dissolve it. After the 3 hours the HFO_2 remained undissolved. It was repeated for another 3 hours and there was no positive result. The conc. HCl was evaporated and the HFO_2 heated to dryness.

The salt HFO_2 was reweighed and the dissolving was repeated with 40% HF.

1.00g HFO_2 was poured into a platinum crucible and 20ml or 40% was added. This was heated and evaporated to dryness on a hot plate adjusted to high. 10ml of Con. HCl was added and heated to dryness and another 10ml of Conc. HCl was added and also evaporated to dryness.

The salt was cooled in a desiccator. 0.79076g of 0.0025M of this salt was added to 10ml 3M HCl while stirring. The salt did not dissolve in the 3M HCl. It was repeated with 3M H_2SO_4 and it did not dissolve and the reaction was abandoned.

DISCUSSION: (1) My adviser suggested that it is likely I have reconverted the HFCl_4 to HFO_2 by evaporating the dryness and heating excessively, department to repeat the experiment.

SYNTHESIS OF ZrO (PMAP)₂ FROM ZrOCl₂ · 8H₂O

2.16242 of 0.01M of the ligand HPMAP was dissolved in 50ml of 95% ethanol (merck grade) in 100ml beaker.

1.61125g of 0.005M of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 10ml of 3m HCl while stirring with a glass rod for some times (10-15 mins). The ZrOCl_2 solution was poured gradually into the solution of HPMAP while stirring. This was later evaporated to concentrate it. Few drops of NH_3 solution were added dropwise, a white precipitate appeared. This is also $\text{Zr}(\text{HPMAP})_4$ complex. This was filtered with a sintered glass funnel connected to a suction pump. The white crystals were left to dry in open air protected from contamination.

Yield = 2.4139g

Melting Point = 196⁰c

SYNTHESIS OF U (PMP)₂ FROM URANYLACETATE SALT

2.16242g of 0.01m of the ligand (HPMAP) was dissolved in 75ml of 95% ethanol (merck grade) while stirring with a glass rod in 100ml beaker.

2.12075g of 0.005m of Uranyl acetate was dissolved in 15ml of deionised water while stirring with a glass rod until it dissolved completely. The solution of Uranyl acetate was poured gradually drop by drop into the solution of the ligand while stirring vigorously and continuously too. A faint orange colour precipitate with fine crystals appeared. This was allowed to settle for few minutes and filtered with a sintered glass funnel attached to a suction pump. The orange crystals were collected and dried in open air protected from dust particles.

Yield 4.5031g

Melting Point 222⁰c -223⁰c

SYNTHESIS OF Ce (PMP)₄ FROM Ce(IV) SULPHATE SOLUTION IN WATER

2.16242g of 0.01m of the ligand HPMAP was in 75ml of 95% ethanol (merck grade) while stirring with a glass rod in a 100ml beaker.

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1.01075g of 0.0025m of Cerium (IV) sulphate (yellow crystals) was dissolved in 15ml of deionized water with stirring. The solution of cerium (IV) sulphate was poured into the ethanolic solution of the ligand in a running droplets manner while stirring vigorously. A dark precipitates separates out. This was filtered with a sintered glass funnel attached to a suction pump. The crystals were collected and were allowed to dry in open air protecting it from dust particles.

Yield 1.2110g

M.P. 216⁰c – 218⁰c

SYNTHESIS OF Ce(PMAP)₄ FROM Ce(IV) SULPHATE SOLUTION IN HOF 3M HCl

2.1624g of 0.01m of the ligand HPMAP was dissolved in 75ml of 95% ethanol (merck grade) while stirring with a glass rod. 1.01075g of 0.0025m of Cerium (IV) sulphate was dissolved in 15ml of deionised water with stirring. The solution of cerium (IV) sulphate (Yellow) was heated on a hot plate until it started boiling, the colour of the solution changes from red wine colour to orange and nearly fading to colourless. This was poured into the solution of the ligand from a separating funnel drop by drop until the reaction mixture was completed. A dirty white precipitates separates out. This was filtered with sintered glass funnel attached to a suction pump. These was dried in open air.

M.P. = 219⁰c - 218⁰c

Yield = 3,1025g

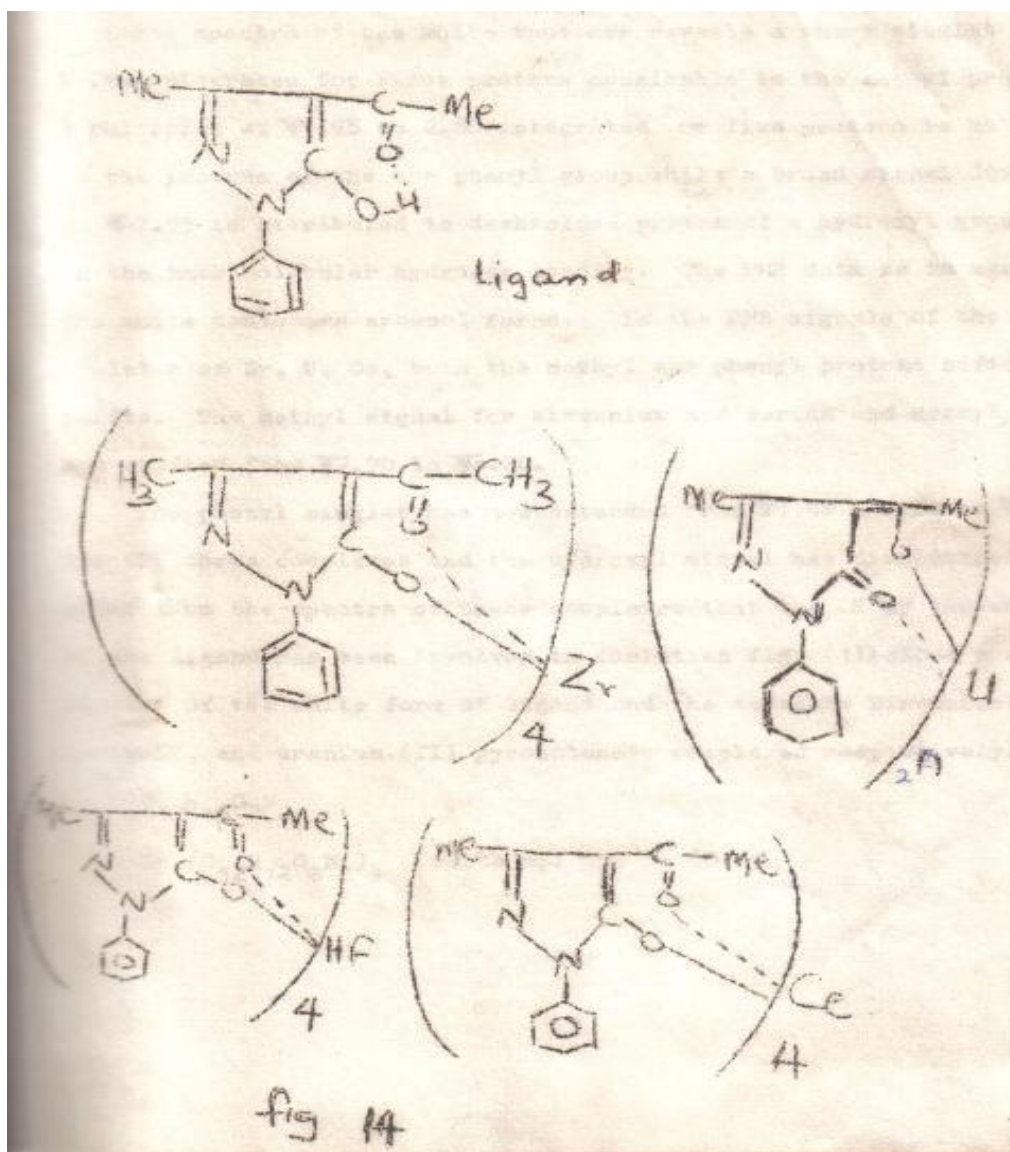
SYNTHESIS OF Ce(PMAP)₄ FROM Ce(IV) SULPHATE IN 3M H₂SO₄

2.16242g of 0.01m of the ligand HPMAP was dissolved in 75ml of 95% ethanol (merck grade) with stirring with a glass rod in a 100ml beaker.

1.01075g of 0.0025m of cerium (IV) sulphate (yellow crystals) were dissolved in 15ml of 3M H₂SO₄ with stirring for about 15mins.

The solution of cerium (IV) sulphate was poured into a separating funnel and introduced into the solution of the ligand drop by drop while stirring vigorously, a white precipitate appears. This was filtered and on washing with H₂O it re-dissolves.

TENTATIVE STRUCTURES OF THE LIGAND AND THE STRUCTURES:



Discussion

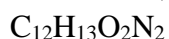
Proton Magnetic Resonance (PMR) Spectra

The spectra of the white tautomer reveals a sharp singlet at $\gamma 7.90$ integrated for three protons ascribable to the methyl protons, a multiplet at $\gamma 1.98$ to 2.80 integrated α five protons is attributed to the protons of the one phenyl group while a broad signal down field at $\gamma 2.95$ is attributed to deshielded proton of a hydroxyl group involved in



the intramolecular hydrogen bonding. The PMR data is in agreement that the white tautomers are enol forms. In the PMR signals of the tetrakis chelates of Zr, U, Ce, both the methyl and phenyl protons suffer upfield shifts. The methyl signal for zirconium and cerium and uranyl complexes has shifted from γ 7.90 to γ 8.20.

The phenyl singlet has now extended from γ 1.98 – 2.80 to γ 1.80 – 3.10 for the three complexes and the hydroxyl signal has disappeared. It is clear from the spectra of these complexes that the OH of the enolic form of the ligand has been involved in chelation fig. (1)f below are the PMR spectra of the white form of ligand and the tetrakis Zirconium (IV), Cerium IV, and Uranium (II) pyrozonate complexes respectively.



Zr ($C_{12}H_{12}O_2N_2$) White mp. 59⁰ - 60⁰

Compound	Methyl Proton	Phenyl Proton	Hydroxyl
$C_{12}H_{13}O_2N_2$	7.90 sh, S	1.98 – 2.80 S	-2.95br, S
Zr ($C_{12}H_{12}O_2N_2$) ₄	8.20 sh, S	1.80 – 3.10 S	
U Zr ($C_{12}H_{12}O_2N_2$) ₂	8.20 sh, S	1.80 – 3.10S	
Cr Zr ($C_{12}H_{12}O_2N_2$) ₄	8.20 sh, S	1.80 – 3.10S	

Conclusion

The ligand HPMAP was synthesized. Complexes of this ligand with Zirconium, Uranium and Cerium were made. Some Physical Properties as melting points and NMR data were obtained. No IR, UV and elemental analysis was done due to lack of facilities.

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