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Ring Isomerism in Cadmium (II) Complexes of Vitamin K3 analog with methyl derivative

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ABSTRACT

2-Hydroxy-3-methyl-1,4-naphthalenedione (Phthiocol),5-Hydroxy-2-methyl-1,4- naphthalenedione (Plumb agin) and their Cadmium (II) complex were synthesized. These two complexes were studied on the basis of a new concept "Ring Isomerism" with thermal, Infrared and Ultraviolet Spectral study. Phthiocolate form five membered ring while Plumbaginate forms a six membered ring chelates with cadmium (II).

Keywords: Phthiocol, Plumbagin, Ring Isomerism, Cadmium (II) Complex.

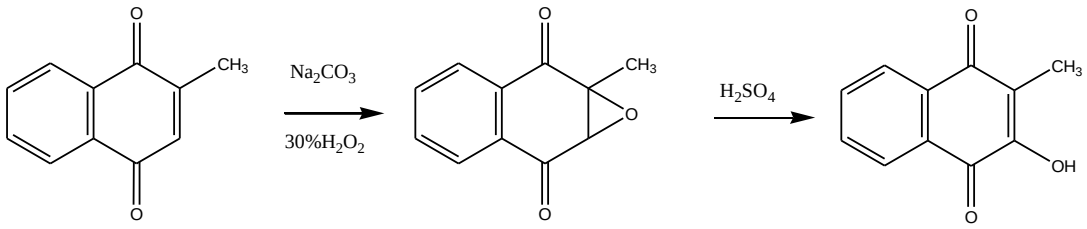
INTRODUCTION

Vitamin K3 analog containing of naturally occurring compounds like Lawsone (2-hydroxy-1,4-naphthalenedione) and Juglone(5-hydroxy-1,4-naphthalenedione)shows an isomeric pairs[1] . Its methyl derivative i.e. Phthiocol[2] and Plumbagin[3], which has natural occurrence as well as are synthesized by known methods[4]. The structural investigations were studied[5] using spectral, analytical[6] electrical dipole moment, dissociation constant, Coordination properties[7-9] etc. These two ligands form five membered and six membered ring in their metal complex.

MATERIALS AND METHODS

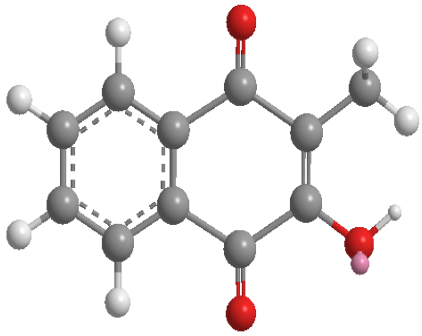
All chemicals used were of A. R. or equivalent Grade. Lawsone and 2-methyl-1,4-naphthalinedione were purchased from Fluka A. G.

Synthesis of Phthiocol[10] :

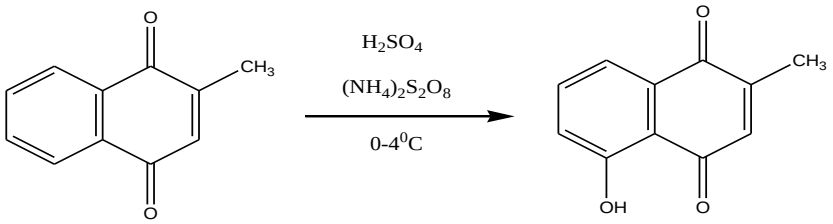


Scheme 1. Synthesis of Phthiocol

The peroxide solution (2 g of anhydrous sodium carbonate in 50 ml of water and 10 ml of 30% H_2O_2) was added in 10 g of 2-methyl-1,4-naphthalenedione dissolved in 20 ml of hot ethanol and mixture was cooled, the pale yellow colored solution. By adding cold water, it gives white crystals of oxide (M. P. 95^0C and Yield 96%). The oxide was treated with 50 ml Con. H_2SO_4 to give deep red colour solution and poured in 200 ml of ice cold water, it gives yellow colored phthiocol. The precipitate was recrystallized with methyl alcohol to give yellow colored needles. Yield, 8.75 g, 80%, m. p. 172^OC. Analysis: Calculated for $C_{11}H_8O_3$: C, 70.21; H, 4.25. Found: C, 70.18; H, 4.30. IR: 1645, 1600, 1182 cm^{-1}.UV in ethanol: 250, 281, 331, 385 nm.^{1}H NMR($CDCl_3$) in δ ppm: (11.72, O-H), (8.09, C-5-H and C-8-H), (7.73, C-6-H and C-7-H), (2.10, C-H).

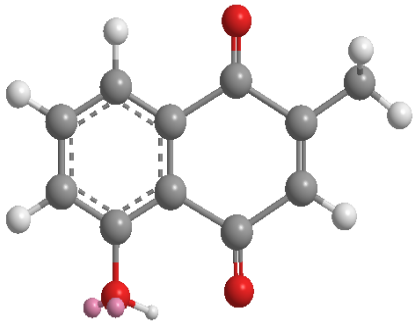


Synthesis of Plumbagin[11]



Scheme 2. Synthesis of Plumbagin

10 g of 2-methyl-1,4-naphthalenedione was dissolved in 100 ml of conc. H_2SO_4 and stirred at below 4^oC in a RB flask. During the stirring of 3 h, 40 g of $(NH_4)_2S_2O_8$ was added. The mixture was then poured in ice. The brown crude product in methanol was isolated by using column chromatography in chloroform. Yield, 2.65 g, 5%, m. p. 76^OC. Analysis: Calculated for $C_{11}H_8O_3$: C, 70.21; H, 4.25. Found: C, 70.22; H, 4.24. IR: 1655, 1630, 1360, 1290, 1235, 1165 cm^{-1}.UV in ethanol: 250, 281, 331, 385 nm. 1 H NMR ($CDCl_3$) in δ ppm: (11.8, O-H), (7.70, C-6-H), (7.62,C-8-H), (7.34, C-7-H), (6.84, C-3-H), (2.20, C-H).



Synthesis of Cadmium(II) complex: To a hot solution of 2.00 mmol of ligand (0.376 g of Phthiocol or Plumbagin) in ethanol (25 ml), an aqueous solution of 1.00 mmol of Cadmium (II) acetate was added. Then an aqueous ammonia solution (1:20 v/v) was added drop wise to adjust the pH of the solution in the range 5 – 5.5, when the complex started to precipitate. This precipitated mixture was refluxed for 3 hr. on an oil bath. The resultant mixture was cooled to room temperature and filtered under suction. The precipitate was washed with cold water followed by hot ethanol and dried in *vacuo* over fused calcium chloride at ambient temperature.

Physical Measurements: The reactant, intermediate compounds and product were characterized by their physical constant and TLC behavior with the authentic sample. The elemental analysis for the percentage of carbon, hydrogen and other elements were performed in the micro analysis using Flash EA, C, H, N and S Analyzer instrument. Thermograms of the metal complexes were recorded on Laboratory constructed Thermo balance with a chromel - alumel thermocouple in air atmosphere up to 700^{o}C with heating rate 10^{o}C min^{-1}. The electronic spectra were recorded on using Shimadzu UV-300 Spectrophotometer model using 1 cm matched quartz cell. The Infra Red spectra were recorded in KBr on FTIR Nicolet – 5700 in the range of wave number 400 – 4000 cm^{-1}. The ^{1}H NMR spectra were recorded on JEOL – 400 MHz IN $CDCl_3$. The structures of ligands and their Cadmium complexes is simulated by using Cambridge software (ChemOffice 2008 – Chem3D ultra 8.0 followed by MM2) for to measure bond length and bond angles.

RESULTS AND DISCUSSION

An aqueous solution of Cadmium acetate react with an ethanolic solution of Phthiocol or Plumbagin under reflux condition in a 1:2 mole ratio to yield reddish violet and reddish brown product respectively (Scheme 1).

$$Cd(CH_3COOH)_2 + 2HL \xrightarrow[pH\ 5\text{-}5.5\ by\ NH_4OH]{EtOH\ /\ H_2O} [Cd(L)_2.2H_2O]$$

Scheme 3. Complex formation

The elemental analysis of these two complexes is given in table 1. Which shows the molecular formula of these compound is $Cd(L)_2.2H_2O$.

Table 1. Elemental analysis of the Cd (II) complexes

Sr. No.	Complex	Colour	Yield (%)	Analysis in % (Calculated)		
				Carbon	Hydrogen	Metal
1	Cd(II)Phthiocolate	Reddish Violet	69	48.01 (47.29)	4.06 (3.97)	19.20 (20.11)
2	Cd(II)Plumbaginate	Reddish Brown	75	46.90 (47.29)	4.11 (3.97)	18.99 (20.11)

It is observed that the colour of the complex with plumbagin is darker than that of complex with phthiocol, it may be due to stability of six membered ring present in plumbaginate, which is supported by thermogravimetric analysis. The yield of the plumbaginate complex is also higher than the phthiocolate complex is observed.

Thermal study: The non-isothermal degradation profiles of phthiocol, plumbagin and their Cd (II) complexes are examined for their decomposition character. The results of the thermogravimetric analysis data were compiled in table 2. The phthiocol and plumbagin are thermally stable up to 175^0C and 75^0C respectively, which are close to their melting temperature. Then the sharp loss is observed to decompose[12]. The first step observed in the TG of Cd (II) complex is attributed to loss of coordinated water for both the complexes. While the second step assigned for the continuous loss of ligand to get stable CdO. It is observed that the Cd (II) plumbaginate is more stable than the Cd (II) phthiocolate by 30^0C, it may be due to more stability of six membered ring.

Table 2. Thermogravimetric analysis data of Cd (II) complexes

Complex	Stage of decomposition	Temperature range (^{o}C)	% loss	Assignment
Cd (II) phthtiocolate	I	130-170	6.60	Loss of coordinated water
	II	240-580	68.50	Loss of release of Ligands
Cd (II) Plumbaginate	I	130-160	6.78	Loss of coordinated water
	II	270-590	68.90	Loss of release of Ligand

Infrared study: Both complexes gives broad band in the region 3280 – 3460 cm^{-1}, are attributed to the presence of coordinated water. In case of Cd (II) phthiocolate having five membered ring, it gives more intense band than Cd (II) plumbaginate having six membered chelate ring. The chelated C=O stretching frequency at 1655 cm^{-1} and at 1620 cm^{-1} in phthiocolate and plumbaginate get shifted to lower frequency. It is observed that phthiocolate exhibit higher carbonyl shift than plumbagin. It may be due to less stability of five membered ring in phthiocolate. Similarly the free C=O stretching frequency also show remarkable effect[13-16] in higher frequency in phthiocolate and plumbaginate.

Electronic spectral study: The electronic spectra of the phthiocol, plumbagin and their Cd (II) complexes were recorded in ethyl alcohol, DMSO and n-hexane. From the spectra, it is observed that, the absorptions are shifted to lower wavelength after complexation with respect to benzenoied and quinonoied electron transfer. While the n-π^* absorption maximum is shifted to higher wavelength[12]. The maximum shift is observed in phthiocolates than that of the plumbaginate. This may be due to plumbaginates(six membered chelate ring) are more stable than phthiocolate (five membered chelate ring).

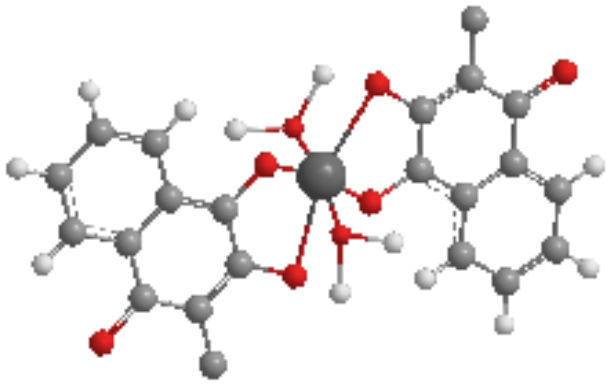


Figure 1. Octahedral structure of Cd (II) complex with phthiocol having five membered chelate ring

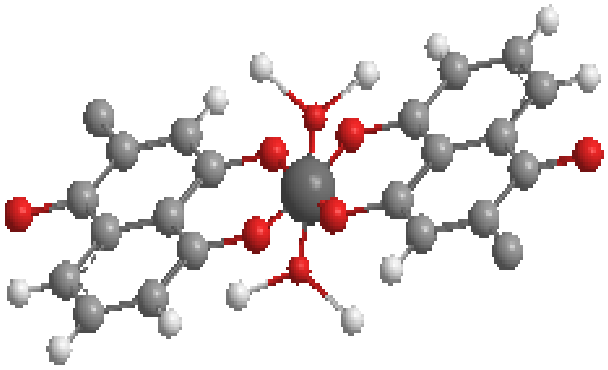


Figure 2. Octahedral structure of Cd (II) complex with plumbagin having six membered chelate ring

APPLICATIONS

The new concept of ring isomerism was applied for cadmium complex.

CONCLUSIONS

Ring Isomerism is a new concept, which studied with the help of cd (II) complex of phthiocol and plumbagin a isomeric pair of ligands. They form a five and six membered chelate ring respectively. Which show slightly differ in their properties like colour, decomposition temperature, physical constants, electron transformation etc.

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REFERENCES

[1] R. J. Andeson and M. S. Newman, *j. Biol. Chem.*,**(1993),**101, 773.
[2] R. H. Thomson, "*Naturally Occurring Quinones"* 2nd Edn,Accademic Press, London**(1971)**
[3] P. Fluckiger, *NeuesHandwaterbuchdee*
[4] F. Radt (Ed.), "*Elesvier's Encyclopaedia of Organic Chemistry",* Amsterdam **(1952)** Series III, 12B, Elsevier,
[5] S. B. Padhye, and B. A. Kulkarni, *J. Univ. Poona*, **(1974)**, 27, 46.
[6] P. Babula, D. Huska, P. Hanustiak, J. Baloun, S. K. V. Adam and et al, *Sensors*,**(2006)**, 6, 1466
[7] S. D. Gaikwad and C. S. Gaikwad, *J. Chem. Pharma. Res*., **2010**, 2(4), 106-111
[8] Gaikwad S. D., Kanase D. G., Kelkar V. D., Kulkarni B. A., *Synth. React. Inorg.Met. Org. Chem.,* **1996**, 26(9) 77-87
[9] Sanjay Gaikwad, *Res., Rew., JC*, **2013**, Vol 2 (3) 10-15.
[10] L. F. Fieser, J. Biol. Chem., **1940**, 133, 391.
[11] Saenz de Buruaga, *Verdu, Anale. Soc. Espan. Fis. Quim*. **1934**, 32,830.
[12] Dandawate F. V., Kodilikar J. G., Kelkar V. D. and Kulkarni B. A., *Thermochim. Acta*., **1994,** 241, 103.
[13] H. E. Cox, *Analyst*, **1938**, 63,397.
[14] S. Gaikwad, C. Gaikwad, S. Khansole and R. Kankariya *Bulletin of Pure and Applied Sciences.*

2010, Vol.29C (No.1):P.1-10
[15] S. B. Padhye, S. Y. Rane and S. G Gupta, *Inorg. Nucl. Chem. Lett.*, **1978,** 14, 83,
[16] Rane S. Y., Padhye S. B., Khan E. M. and Garge P. L., *Sunth. React. Inorg.Met. Org. Chem.*, **1988,** 18, 609.