International Journal of Pharmaceutical Science and Research
ISSN: 2455-4685, Impact Factor: RJIF 5.28
www.pharmacyjournal.net
Volume 1; Issue 7; November 2016; Page No. 45-49

Synthesis and spectral studies of cadmium complexes containing ethylacetate and Acetyl acetone as a ligands

B Divya, K Murali

Department of Chemistry, Vivekanandha Arts and Science College for Women, Sankagiri, Tamil Nadu, India

Abstract

Complexes of Cadmium with Ethylacetate and Acetyl acetone have been prepared and characterized by chemical analyses, molar conductivity, spectroscopic and molar conductance measurements, IR, H^1NMRspectra and C^{13}NMR spectra. The IR and NMR spectral studies of these complexes (Except those Ethylacetate and Acetyl acetone) indicate that they complexes are non-hygroscopic in nature and are soluble in common organic solvents. It has been found that behaves as pentadentate ligands. The Cadmium complexes containing acetylacetonato with cadmium sulphate & ethylacetate yielded complexes assigned square planar structures. From the IR, H^1NMR spectra and C^{13}NMR spectra of Cadmium complexes various parameters have been calculated.

Keywords: cadmium complexes, ethylacetate and acetyl acetone, ethylacetate bis acetyl acetonato cadmium sulphate

1. Introduction

The report on the spectroscopic studies on Bis acetylacetonato cadmium sulphate complex Where alkyl=methyl (or) ethyl indicated that the complex possess square planar structure on cadmium site. When dissolved in different solvent the basic structure of the complex was found to be retained, with this idea, We aim to synthesize bis acetylacetonato cadmium sulphate and conduct spectroscopic studies in the project work with the view of obtaining information of the following points 1.To investigate the structure of the complex in the solid and to know the behavior of the complex

2. Experimental section

2.1 Preparation of Bis Acetylacetonato Ethylacetate cadmium sulphate.

7.6952g of cadmium sulphate was weighed and taken in 100ml beaker. It was dissolved in minimum amount of water and 4ml of Ethylacetate was added to the beaker 6.3ml of acetylacetone and 2.2g of sodium hydroxide were added with constant stirring. From this finally Bis acetylacetanato ethylacetate cadmium sulphate was obtained. The Yellow solid which separated out, was filtered, washed with acetone, dried in vacuum and the recrystalised from water. Melting point.159.

The Crude Sample of (Bis Acetylacetonato Ethylacetate Cadmium Sulphate).

2.2 Coordination number

The coordination number of metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. Numerically coordination number represents the total number of chemical bonds formed between the central metal ion and the donor atoms of the ligands. For example: in K4[Fe(CN)6] the coordination number of Fe(II) is 6 and in [Cu(NH3)4]SO4 the coordination number of Cu(II) is 4.Charge on the complex ion**:** Charge on the complex ion is equal to the sum of the charge on the metal ion and their ligands.

Example

[Cu (NH3)4]2+ can be written as [Cu (NH3)4]2+since NH3 ligand is neutral.

The sum of the charges on the metal ion and the ligands = +2.

This can be determined as shown below,

Charge on the metal ion (Cu2+) = +2.

Charge on the ligand (NH3) = 4 x 0 = 0.

Therefore net charge on the complex ion = +2 +0 = +2.

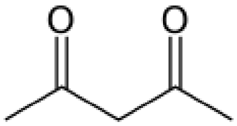
2.3 Naming complexes

The basic procedure for naming a complex:

1. When naming a complex ion, the ligands are named before the metal ion.
2. Write the names of the ligands in alphabetical order. (Numerical prefixes do not affect the order.) Multiple occurring monodentate ligands receive a prefix according to the number of occurrences: di-, tri-, tetra-, penta-, or hexa.
3. Polydentate ligands (e.g., ethylenediamine, oxalate) receive bis-, tris→-, tetrakis-, etc.
4. Anions end in ido. This replaces the final 'e' when the anion ends with '-ate', e.g. sulfate becomes sulfato. It replaces 'ide': cyanide becomes cyanide.Neutral ligands are given their usual name, with some exceptions: NH_3 becomes ammine; H_2O becomes aqua or aquo; CO becomes carbonyl; NO becomes nitrosyl.
5. Write the name of the central atom/ion. If the complex is an anion, the central atom's name will end in -ate, and its Latin name will be used if available (except for mercury).
6. If the central atom's oxidation state needs to be specified (when it is one of several possible, or zero), write it as a Roman numeral (or 0) in parentheses.
7. Name cation then anion as separate word many metal-containing compounds, co-ordination complexes are so pervasive that the structure and reactions are described in many ways, sometimes confusingly.
8. The atom within a ligand that is bonded to the central atom or ion is called the donor atom. In a typical complex, a metal ion is bound to several donor atoms, which can be the same or different.

9. Polydentate (multiple bonded) ligands consist of several donor atoms, several of which are bound to the central atom or ion. These complexes are called chelate complexes, the formation of such complexes is called chelation, complexation, and coordination
10. The central atom or ion, together with all ligands comprises the coordination sphere. The central atoms or ion and the donor atoms comprise the first coordination sphere.

2.4 Nature of Acetylacetone

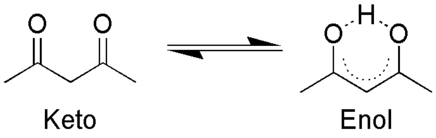


Acetylacetone is an organic compound that famously exists in two tautomer forms that rapidly interconvert. The pair of tautomer's rapidly interconvert and are treated as a single compound in most applications. Although the compound is formally named as the di ketone form, pentane-2, 4-dione, the enol form forms a substantial component of the material, and is actually the favored form in many solvents. It is a colorless liquid that is a precursor to acetylacetonato, a common bidentate ligand. It is also a building block for the synthesis of heterocyclic compounds The acetylacetonato anion, forms complexes with many transition metal ions. A general method of synthesis is to react the metal ion with acetylacetone in the presence of a base (B): Acetylacetone is a weak acid:

$$C_5H_8O_2 \rightleftarrows C_5H_7O_2^- + H^+$$

IUPAC recommended pKa values for this equilibrium in aqueous solution at 25 °C are 8.99±0.04 (I = 0), 8.83±0.02 (I = 0.1 M $NaClO_4$) and 9.00±0.03 (I=1.0 M NaClO4) (I=Ionic strength).Values for mixed solvents are available. Very strong bases, such as organ lithium compounds, will deprotonate acetylacetone twice. The resulting dilithio species can then be alkylated.

2.5 Properties



The keto-enol form has C2v symmetry, meaning the hydrogen is shared equally between the two oxygen atoms. In the gas phase, the equilibrium constant, keto-enol is 11.7, favoring the enol form. The two tautomeric forms can easily be distinguished by NMR spectroscopy, IR spectroscopy, and other methods. The equilibrium constant tends to remain high in nonpolar solvents; the keto form becomes more favorable in polar, hydrogen-bonding solvents, such as water. The enol form is a vinylogous analogue.

Table 1

Molecular formula	**$C_5H_8O_2$**
Molar mass	100.12 g·mol−1
Density	0.975 g/mL[1]
Melting Point	−23 °C (−9 °F; 250 K)
Boiling Point	140 °C (284 °F; 413 K)

2.6 Preparation

Acetylacetone is prepared industrially by the thermal rearrangement of isopropenylacetate.

$CH_2 (CH_3) COC (O) Me \rightarrow MeC (O) CH_2C (O) Me$

Laboratory routes to acetylacetone begin also with acetone. Acetone and acetic anhydride upon the addition of BF_3 catalyst.

$(CH_3CO)_2O + CH_3C(O)CH_3 \rightarrow CH_3C(O)CH_2C(O)CH_3$

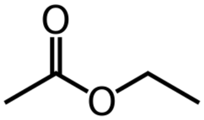
A second synthesis involves the base-catalyzed condensation of acetone and ethyl acetate, followed by acidification.

$NaOEt+EtO_2CCH_3+CH_3C(O)CH_3 \rightarrow NaCH_3C(O)CHC(O)CH_3 +2\ EtOH$

$NaCH_3C(O)CHC(O)CH_3 + HCl \rightarrow CH_3C(O)CH_2C(O)CH_3 + NaCl$

Because of the ease of these syntheses, many analogues of acetylacetonates are known. Some examples include $C_6H_5C(O)CH_2C(O)C_6H_5$ (dbaH) and $(CH_3)_3CC(O)CH_2C(O)CC(CH_3)_3$.

2.7 Nature of Ethyl acetate



(Systematically, ethyl ethanoate, commonly abbreviated EtOAc or EA) is the organic compound with the formula CH3-COO-CH2-CH3, simplified to C4H8O2. This colorless liquid has a characteristic sweet smell (similar to pear drops) and is used in glues, nail polish removers, decaffeinating tea and coffee, and cigarettes (see list of additives in cigarettes). Ethyl acetate is the ester of ethanol and acetic acid; it is manufactured on a large scale for use as a solvent. The combined annual production in 1985 of Japan, North America, and Europe was about 400,000 tons. IN 2004, an estimated 1.3M tons were produced worldwide.

2.8 Preparation of Ethyl acetate

Ethyl acetate is synthesized in industry mainly via the classic Fischer esterification reaction of ethanol and acetic acid. This mixture converts to the ester in about 65% yield at room temperature:

$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$

The reaction can be accelerated by acid catalysis and the equilibrium can be shifted to the right by removal of water. It is also prepared in industry using the Tishchenko reaction, by combining two equivalents of acetaldehyde in the presence of an alkoxidecatalyst:

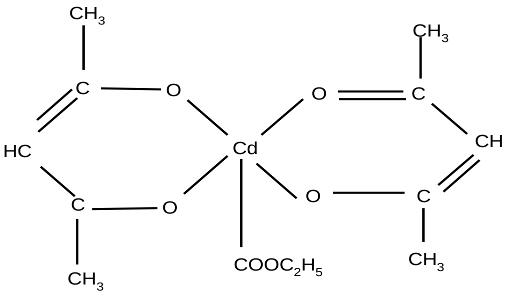
$2CH_3CHO \rightarrow CH_3COOCH_2CH_3$

By dehydrogenation of ethanol. A specialized industrial route entails the catalytic dehydrogenation of ethanol. This method is less cost effective than the esterification but is applied with surplus ethanol in a chemical plant. Typically, dehydrogenation is conducted with copper at an elevated temperature but below 250 °C. The copper may have its surface area increased by depositing it on zinc, promoting the growth of snowflake, fractal like structures (dendrites). Surface area can be again increased by deposition onto a zeolite, typically ZSM-5. Traces of rare earth and alkali metals are beneficial to the process. By products of the dehydrogenation include diethyl ether, which is thought to arise primarily due to aluminum sites in the catalyst, acetaldehyde and its aldol products, higher esters, and ketones. Separations of the byproducts are complicated by the fact that ethanol forms and azoetrope with water, as does ethyl acetate with ethanol water, and methyl ethyl ketone (MEK, which forms from 2-butanol) with both ethanol and ethyl acetate. These azeotropes are "broken" by pressure swing distillation or membrane distillation. After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.0 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of cobalt (II) was 100%, the estimation of cobalt (II), Cr(V) and carbonyl compounds were quantitative, In both the cases the IR spectra of the product agreed with IR spectra of authentic samples.

3. Result and Discussion

The reaction of acetylacetonato with cadmium sulphate & ethylacetate yielded complexes. The general formula [Cd $(CH_3CO\ CHCH_3CO)\ 2\ (CH_2COOC_2H_5)$]. The complexes are non-hygroscopic in nature and are soluble in common organic solvents. It has been found that behaves as pentadentate ligands. If a ligand is capable of forming more than one bond with the central metal atom or ion then ring forming group are described as chelating agents.

$$2CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + CdSO_4 + CH_3COOC_2H$$
$$\downarrow$$



3.1 IR study of the prepared complex

An infrared spectrum is an important result which gives sufficient information about the compound. The frequency or wave length of the absorption depends on relative masses of the atoms, force constants of the bond and geometry of the atoms. The IR spectrum of pure ethylacetate bis acetyl acetonato cadmium sulphate shows strong 3200-3700cm-1. After complexation with cadmium (ii) ion in the presence of MeOH, the free nitrile was completely absent. The decrease in (C=O) bond order, on co-ordination through the oxygen atom, facilitated by transfer of electron density from the C-O-C moiety. The electron density on the $O{=}C{-}CH_3$ fragment of the ligand is more delocalized in this complex and the =C-O- bond order is raised. The complex gives a (COC) stretch at 1128cm-1297 cm-1 and Vs (COC) at 956 cm-1 has been assigned to v(Cd-s). The IR spectra of the ligands were compared with those of the cadmium complexes in order to confirm the binding mode of the ligands to the cadmium atom in the complexes. The free ligand showed a strong bond in the region 1615-1617 cm-1, v(C=O) is shifted to lower frequencies and appears around 1578-1602 cm-1, indicating coordination of the ethylacetate to the cadmium metal [1, 5]. Spectrum of The bands in the 1507 - 1557 cm-1 region for the above complexes have been assigned to the mixed vibrational mode arising from vC=O and vC=C. a strong band observed at 1343cm-1 in the free H2L has been assigned to phenolic C-O stretching. On complexation, this band is shifted to a higher frequency range 1435vcm-1, indicating coordination through the phenolic oxygen. This has been further supported by the disappearance of the broad band V(OH) around 3000 cm-1 in the complexes indicating deprotonation phenolic proton prior to coordination. IR spectrum of ethyl acetate bisacetyl acetonato cadmium, sulphate.

IR Spectrum

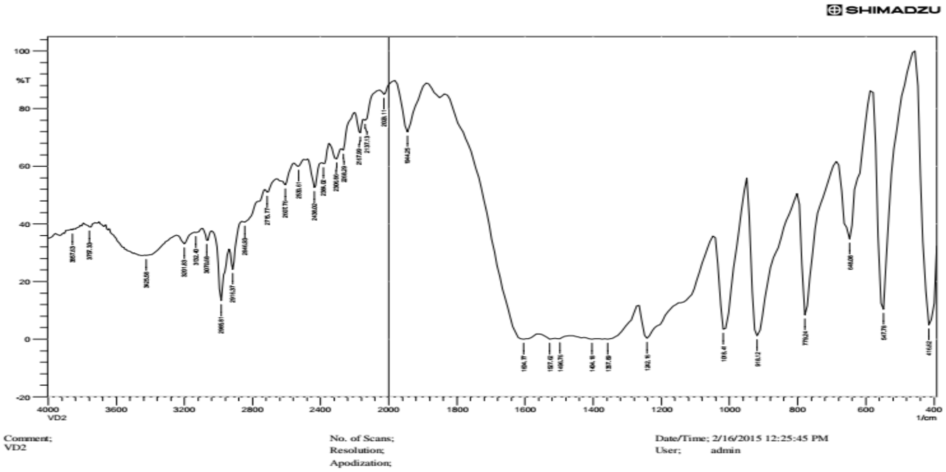


Fig 6

3.2 NMR Studies

H^1NMR Ethylacetate bisacetylacetanato Cadmium sulphate.

H^1 NMR spectrum of ethyl acetate bis acetyl acetonato cadmium sulphate is shown in the following figure. Observed data of ethylacetate bis acetylacetonato cadmium sulphate was compared with reported data. In the H^1 NMR spectrums of ethylacetate bis acetylacetonato cadmium sulphate the 6 aliphatic CH_3, metal protons appear at 8.3 δ as singlet and the 4 aliphatic CH_2 protons appear at 5.04 δ as singlet.

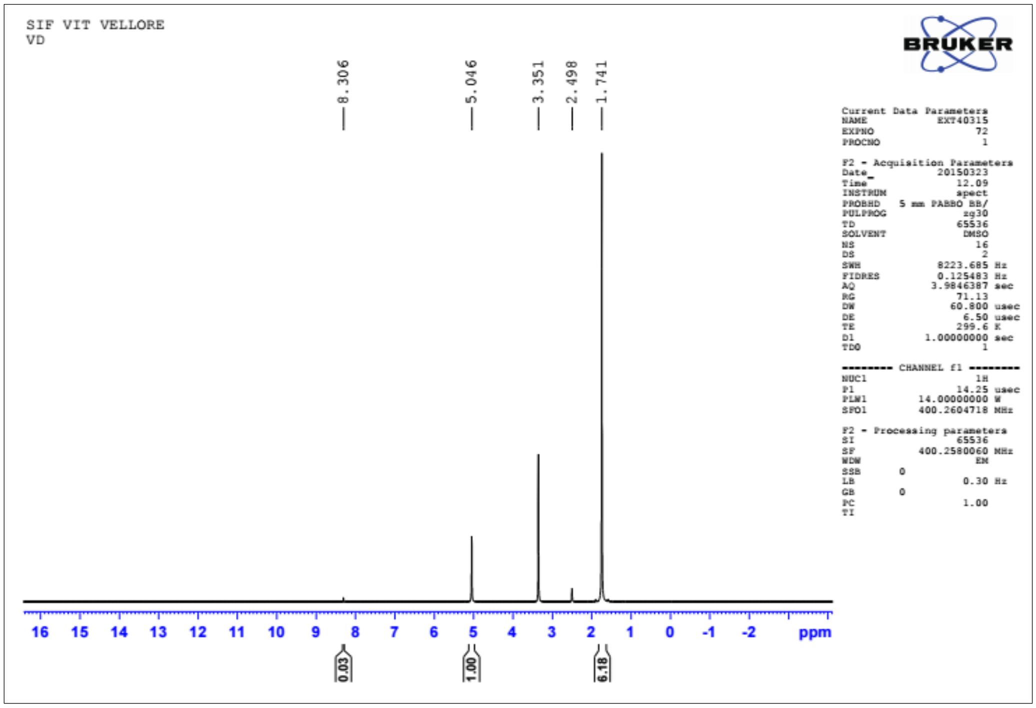


Fig 7

3.3 C^{13} NMR spectrum of Ethylacetate bisacetylacetanato Cadmium sulphate

C^{13} NMR Spectrum of ethylacetate bis acetylacetonato cadmium sulphate are shown in the following figure. Observed data ethyl acetate bis acetyl acetonato cadmium sulphate was compared with the reported data. There are present in the table.

Table 2

Group	Expected value δ	Observed value δ
Carbonyl O=C	190-220	190.2
Aliphatic C	42-49	40

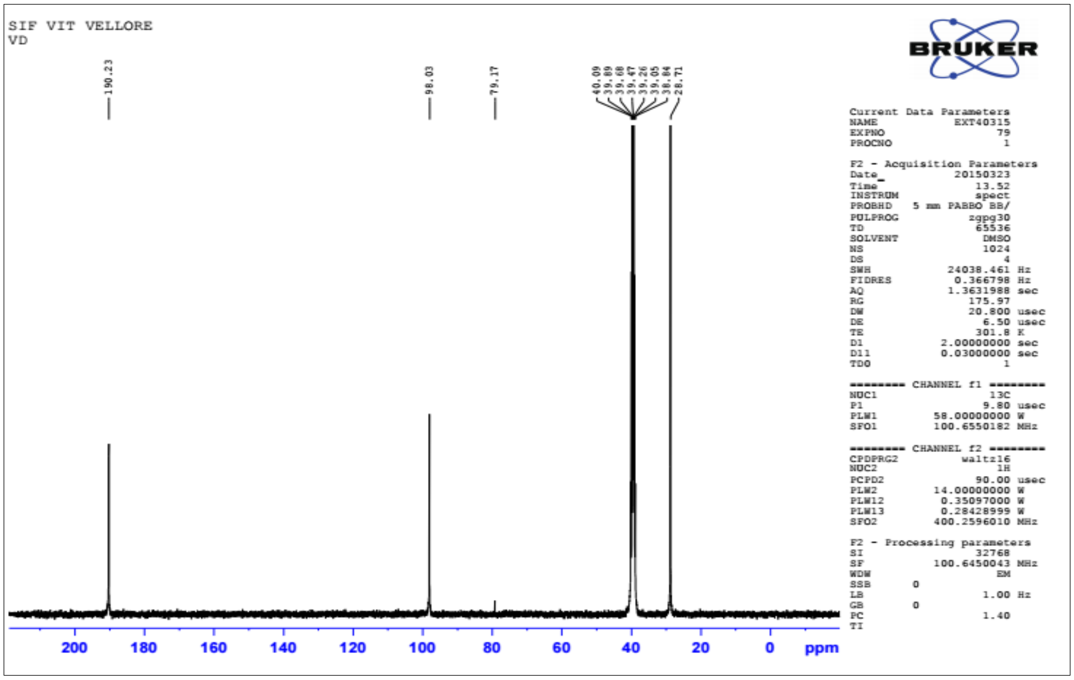


Fig 8

4. Conclusion

It has been found that the Cadmium complexes of ligands moieties are enhanced more in the presence of IR spectrum of ethyl acetate bisacetyl acetonato cadmiumsulphate when compared to H^1 NMR spectrum of ethyl acetate bis acetyl acetonato cadmium sulphate. The micelles act as a ligands in the present study.

5. Acknowledgment

With immense pleasure I express my heartful gratitude to Dr.

K.MURALI M.Sc. M.Phil. Ph.D., Assistant Professor in Chemistry, Vivekanandha Arts and Science College for Women, Sankagiri-637 303, for his inspiring guidance, clear and explicit instruction and constant encouragement during the course of this work. At last I thanks to my friend R. KALAIVANI M.A., for his kind help in processing the complete this work in computer.

6. References

1. Nareshkumar K, Ramesh R, Polyhedron. 2005; 24:1885.
2. Thomas JM, Raja R. Annu. Rev. Mater. Res. 2005; 35:315.
3. Martinez R, Ramon DJ, Yus M. Tetrahedron. 2005; 8:1009.
4. Mohamed GG, Abd El-Wahab ZH. Spectrochim. Acta. 2005; A61:1059.
5. Singh OI, Damayanthi M, Singh NR, Singh RKH, Mohaptra M, Kadam RM. Polyhedron., 2005; 24:909.
6. Jayabalakrishnan C, Bertagnolli H, Natrajan K, Appl organometal chem., 2006; 20:203.
7. Venkatachalam G, Ramesh R. Inorg Chem commun. 2006; 9:703.
8. Deligonul N, Tumer M, Sein S, Trans. Met. Chem. 2006; 31:920.
9. Ledox N, Allart B, Schaubroeck D, Monsaert S, Drozdzak R, Voort PVD, *et al.* J. Org. Me. Chem., 2006; 691:5482.
10. Nakabayyashi Y, Iwamoto N, Inada H, Yamauchi O. Inorg. Chem. Commun. 2006; 9:1033.
11. Manivannan S, Prabakaran R, Balasubramaniam KP, Dhanpal R, Natrajan K, Karvembu A, *et al.* Organometal chem., 2007; 21:95.
12. Asadi M, Asadi Z. Trans. Met. Chem., 2007; 32:387.
13. Priyarega S, Prabakaran R, Aranganayagam KR, Karvembu R, Natrajan K. Organometal chem., 2007; 21:788.
14. Krishnaraj S, Muthukumar M, Visvanathamurthi P, Sivakumar S. Trans. Met. Chem., 2008; 33:643.
15. Abou-Melha KS, Faruk H. Journal of Coordination Chemistry. 2008; 61:12.
16. Reddy V, Patil N, Angadi SD. E-Journal of Chemistry. 2008; 5:577.
17. Pandey RN, Nag AK, Rasayan. J Chem., 2009; 2:990.
18. Kwanruthai Wongsaprom, Santi Maensiri, Chang mai. Journal of. Sci. 2013; 40(1):99.
19. Ajith Sinthuja S. The International journal of science & technoledge. 2014; 2(10):1-3.
20. Hasan Saral, Ozgur Ozdamar, Ibrahim Uçar, Yunus Bekdemir, Muhittin Aygun. Journal of Molecular Structure. 2016; 1103:9-19.