Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(3),** 48-51, March **(2013)** *Res. J. Chem. Sci.*

Synthesis, Spectral characterization and Crystal structure of $[Cd(4\text{-}AAP)_2(NO_2)_2]$ (4-AAP= 4-Aminoantipyrine)

Rajasekar K.[1*], Ramachandramoorthy T.[2] and Balasubramaniyan S.[1]
[1]Department of Chemistry, Government Arts College, Ariyalur-621713, INDIA
[2]PG and Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli-620 017, INDIA

Available online at: www.isca.in
Received 6th January 2013, revised 13th January 2013, accepted 30th January 2013

Abstract

The complex $[Cd^{II}L_2(NO_2)_2]$ (L= 4-aminoantipyrine) was synthesized and the structural aspects of the complex were determined from elemental analysis, EC measurement, IR, NMR spectra and single crystal X-ray diffraction analysis. The spectral and X-ray diffraction studies of the complex indicate that the crystal system is monoclinic with the $P2_1/n$ space group. The cadmium ion in this compound is eight coordinated with two bidentate nitrite groups and two bidentate 4-aminoantipyrine ligands with extended coordination. The nitrite ions and 4-aminoantipyrine molecules are bidentated to the metal ion and form four member chelate rings. The geometry of the complex is distorted dodecahedron.

Keywords: 4-aminoantipyrine, nitrite ion, cadmium complex, crystal structure.

Introduction

Pyrazole is doubly unsaturated five membered ring compound having three carbon and two nitrogen atoms. Several pyrazoline substitution products are used in medicine[1]. 4-aminoantipyrine, an antipyretic agent[2] is one of the pyrazole derivatives. Numerous synthetic compounds containing pyrazole moiety have been focused in the field of Medicinal Chemistry[3]. 4-aminoantipyrine is one of the synthetic drugs[4] and its Schiff bases play a very important role in Inorganic Chemistry because they form stable complexes with most of the transition metals. 4-aminoantipyrine and its formylation derivatives have analgesic[5], anti-inflammatory[6-9], antiviral and antibacterial activities[10]. Getting a single crystal X-ray diffraction structure is very difficult and challenging one for Cd(II) complex with 4-aminoantipyrine. The present study deals with the synthesis and crystal structure of Cd(II) complex with 4-aminoantipyrine and nitrite ion as ligand.

Material and Methods

4-aminoantipyrine was purchased from Alfa Aesar Company. The metal nitrate and the solvents DMSO, DMF, methanol, ethanol used were of Analar grade.

Instrumental analysis: The elemental analysis were carried out by using (Thermo Finnigan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The molar conductance measurements were conducted by using 10^{-3} M complex solutions in acetonitrile on Systronic Conductivity Bridge 304 at 30°C. The IR Spectrum was recorded as KBr pellets on a Shimadzu FT IR -8400S Spectrometer. ^1H and ^{13}C NMR spectrum of 4-AAP and cadmium complex were recorded on a 500 MHz FT NMR Spectrometer using DMSO-d6 as a solvent and TMS as reference.

X-ray intensity data for this compound were collected using a Bruker AXS Kappa APEX II single crystal CCD Diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ=0.71073Å) at room temperature with a crystal dimension of 0.35 x 0.25 x 0.2 mm.[3] Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones. The data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS program[11]. The structure was solved by direct methods of procedure and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program[12].

The positions of all the hydrogen atoms were identified from different electron density map and they were constrained to ride on the corresponding non-hydrogen atoms. The hydrogen atom bound to carbon atoms were constrained to a distance of C-H = 0.93 - 0.97Å and U_{iso} (H) = $1.2U_{eq}$(C) and $1.5U_{eq}$(C). The crystal is monoclinic with $P2_1/n$ space group. Crystallographic data of the complex have been deposited with the Cambridge crystallographic Data Centre as supplementary materials (CCDC number is 882326.

Synthesis of $[Cd^{II}(AAP)_2(NO_2)_2]$: To a solution of 3.22mmol $Cd(NO_3)_2.4H_2O$ 1g in methanol; 6.45 mmol of 4-aminoantipyrine1.32g in methanol was added and the mixture was heated in a microwave oven for about 10 seconds. Then 6.4mmol of sodium nitrite 0.45g in ethanol was added and the mixture was irradiated with microwaves for about 10 seconds. The precipitated colorless complex was filtered, washed with ethanol and dried. The elemental analytical data were in good agreement with the molecular formula arrived for the cadmium complex. The molar conductance value of the complex in acetonitrile is in the range of 63.4 $ohm^{-1}cm^2mol^{-1}$ reveals their

non electrolytic nature. The analytical data are presented in table-1.

Results and Discussion

IR Spectra: IR Spectral data of 4-AAP and its cadmium complex have been presented in table-2. In the spectrum, the strong band at 3325-3431 cm^{-1} indicate the presence of $–NH_2$ group in 4-AAP, which gets shifted to 3429cm^{-1} in cadmium complex indicate the complexation. The value at 1650cm^{-1} indicate s the -C=O in 4-AAP which is shifted to 1630 cm^{-1} in complex. The weak band at 504 cm^{-1} and 445cm^{-1} corresponds to the M-O and M-N bonds respectively. The value at 842 cm^{-1} corresponds to NO_2 group frequency which is present in complex. It is represented in figure-1.

^{1}H- NMR Spectra: In ^{1}H NMR spectra of 4-AAP shows three different peaks for the benzene ring appear as multiplet at δ 7.26 to 7.5. The peaks for C-CH_3, N-CH_3 and $–NH_2$ appears in the region δ 2.1, 2.8, and 4.0 respectively. There is no appreciable change in cadmium complex. All the values are represented in figure-2 and table-3.

^{13}C- NMR Spectra: In the ^{13} C-NMR spectrum the value at 126 to 137 indicate that the three different carbon atoms (Ortho, Para and Meta) of benzene ring. One of the carbon atom in benzene ring attached to the hetero atom of five membered ring of 4-aminoantipyrine. The C-CH_3, C-NH_2 and -C=O groups values are in good agreement with already reported complexes these are all presented in table-4. There is no appreciable change in ^{13}C NMR spectrum of cadmium complex; it is represented in figure-3.

Table- 1
Analytical data of the complexes: found / (calculated) %

Compounds	Colour	Conductance (ohm^{-1} cm^2 mol^{-1})	Yield	C	H	N	M
[Cd $(AAP)_2(NO_2)_2$]	Colourless	63.4	64.45	43.20 (43.21)	4.23 (4.25)	18.30 (18.33)	18.36 (18.40)

Table- 2
IR spectral data of the ligand and its complexes (cm^{-1})

Compound	NH_2	C-H Aromatic	C=O	C=C	M-O	M-N	NO_2
4-AAP	3431	2914	1650	1587	-	-	-
[Cd $(AAP)_2(SCN)_2$]	3429	2925	1630	1587	504	445	842

Table-3
^{1}H-NMR spectral data of the ligand and zinc complex (ppm)

Complexes	NH_2	Aromatic H	N-CH_3	C-CH_3
4-AAP	3.90	7.30-7.50	2.80	2.10
[Cd $(AAP)_2(NO_2)_2$]	4.00	7.30-7.50	2.80	2.10

Table- 4
^{13}C-NMR Spectral data of the ligand and zinc complex (ppm)

Complexes	Aromatic carbons (C1-C4)	C=O	C-NH_2	C-CH_3	CH_3	N-CH_3
4-AAP	120-130	161	136	121	10	40
[Cd$(AAP)_2(NO_2)_2$]	122-136	162	136	120	10	40

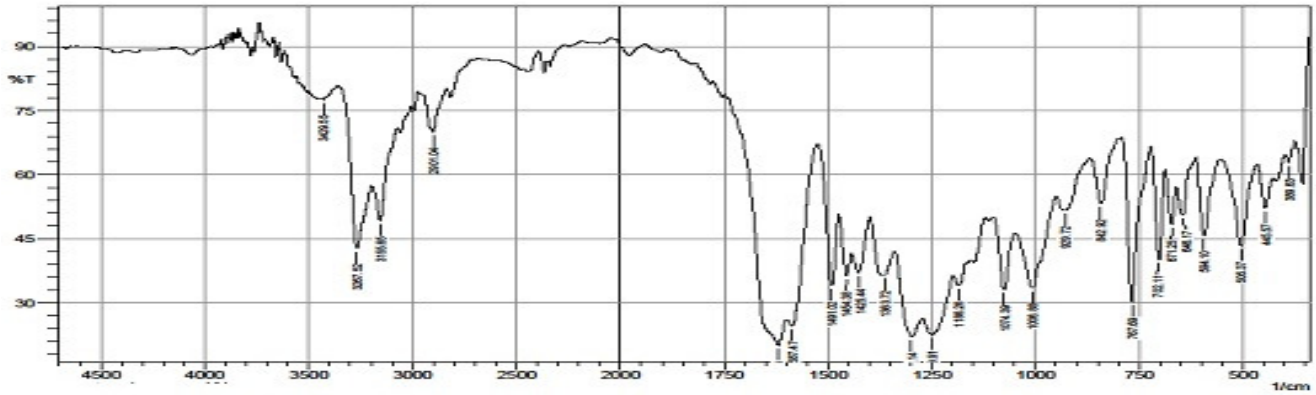

Figure-1
IR Spectrum of [Cd$(AAP)_2(NO2)_2$]

Crystal structure: The crystal data and selected bond lengths and bond angle are represented in table 5 and 6. The $[Cd(AAP)_2(NO_2)_2]$ crystallizes in monoclinic space group $P2_1/n$ with four equivalent molecules in the unit cell. In this compound the ligand 4-aminoantipyrine moiety is poitionally distorted over two positions with refined site occupancies of 0.558(9) and 0.442(9) respectively. Suitable similarity restraints were applied during the refinement. The cadmium ion is eight coordinated with one amino group nitrogen atom and one carbonyl group oxygen atom from each 4-aminoantipyrine molecule. Both the ligands (4-aminoantipyrine and nitrite ion) form four membered chelate rings[13] with metal ion. The coordination geometry around Cd(II) centre is dodecahedran[14]. The structure of the complex consists of six oxygen atoms and two nitrogen atoms from the ligands. The average cadmium-oxygen and cadmium-nitrogen distances are 2.620 Å and 2.324 Å respectively. C–H bond length in CH_3 group is 0.96 Å. The carbon atoms C2-C3 and C12-C13 are in the same environment. In benzene ring, C–C and C–H bond lengths are 1.39 Å and 0.93 Å respectively. Cd–N (2.342) and Cd–O (2.474) bond distances are well within the range already reported for cadmium complexes.[15] The highest Cd – O bond angle is 159.32 Å. The values are represented in figure-4.

Table-5
Crystal data and structure refinement of Cd (II) complex

Structural parameters	$[Cd^{II}(AAP)_2(NO_2)_2]$
Empirical formula	$C_{22}H_{26}CdN_8O_6$
Formula weight	610.91
T/K	293(2) *K*
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.293(7)
b (Å)	16.720(9)
c (Å)	14.4633(10)
α (˚)	90
β (˚)	100.69(2)
γ (˚)	90
Volume (Å^3)	2683.7(3)
Z	4
D (mg/m^3)	1.512
μ mm^{-1}	0.865
\F (000)	1240
Crystal size (mm)	0.30 x 0.20 x 0.20
Theta range for data collection	1.88 to 25.00 deg.
Reflections collected / unique	2346 / 4716
[*R* (int) = 0.0273]	
Completeness to theta = 25.00	99.9 %
Data / restraints / parameters	4716 / 3 / 377
Goodness-of-fit on F^2	1.181
Final *R* indices [I>2*σ* (I)]	*R1* = 0.0353,
wR2 = 0.0913	
R indices (all data)	*R1* = 0.0475,
wR2 = 0.1064	
Largest diff. peak and hole (Å^{-3})	
0.541 and -0.674	

Table-6
Selected bond lengths (A˚) and bond angles (˚) in $[Cd^{II}(AAP)_2(NO_2)_2]$

Cd(1)-O(3)	2.345(3)
Cd(1)-O(6)	2.381(3)
Cd(1)-O(4)	2.496(3)
Cd(1)-O(5)	2.553(3)
Cd(1)-O(1)	2.597(2)
N(1)-Cd(1)	2.346(3)
N(4)-Cd(1)	2.340(3)
N(4)-Cd(1)	2.340(3)
N(4)-Cd(1)-O(6)	128.9(11)
N(1)-Cd(1)-O(6)	106.4(12)
N(4)-Cd(1)-O(4)	143.2(10)
N(1)-Cd(1)-O(4)	80.52(9)
N(4)-Cd(1)-O(5)	81.40(10)
N(1)-Cd(1)-O(5)	147.0(10)
N(4)-Cd(1)-O(1)	74.71(9)
N(1)-Cd(1)-O(1)	72.04(9)
N(7)-O(3)-Cd(1)	100.6(2)
N(7)-O(4)-Cd(1)	93.40(2)
N(8)-O(5)-Cd(1)	93.60(3)
N(8)-O(6)-Cd(1)	1.800(3)
O(3)-Cd(1)-N(1)	127.4(9)
O(3)-Cd(1)-O(6)	85.01(12)
O(3)-Cd(1)-O(4)	51.01(9)
O(6)-Cd(1)-O(4)	78.44(11)
O(3)-Cd(1)-O(5)	78.44(10)
O(6)-Cd(1)-O(5)	50.07(11)
O(4)-Cd(1)-O(5)	110.9(10)
O(3)-Cd(1)-O(1)	159.3(9)
O(6)-Cd(1)-O(1)	81.89(11)
O(4)-Cd(1)-O(1)	139.9(8)
O(5)-Cd(1)-O(1)	80.88(9)
C(3)-O(1)-Cd(1)	106.6(2)

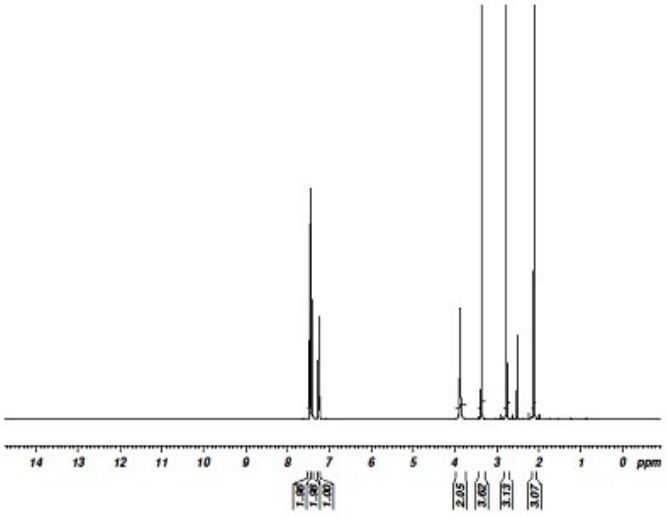

Figure-2
^{1}H NMR Spectrum of $[Cd(AAP)_2(NO2)_2]$

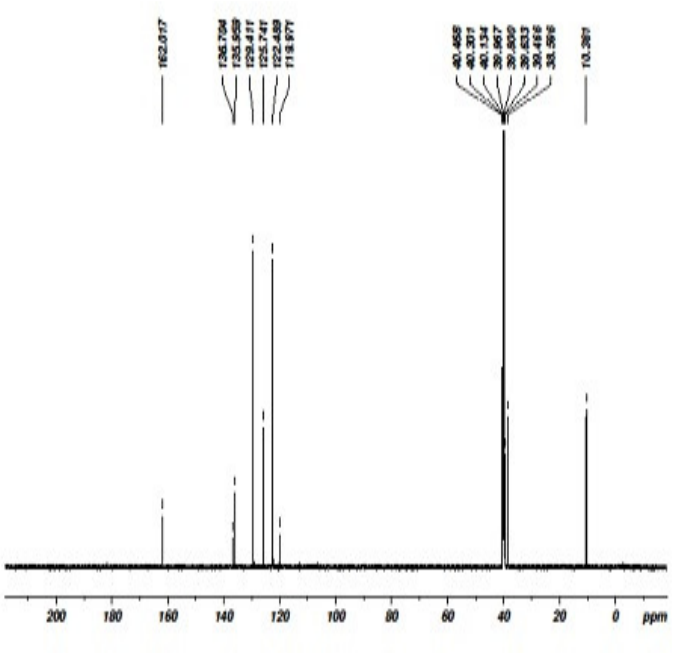

Figure-3
^{13}C NMR Spectrum of [Cd(AAP)$_2$(NO2)$_2$]

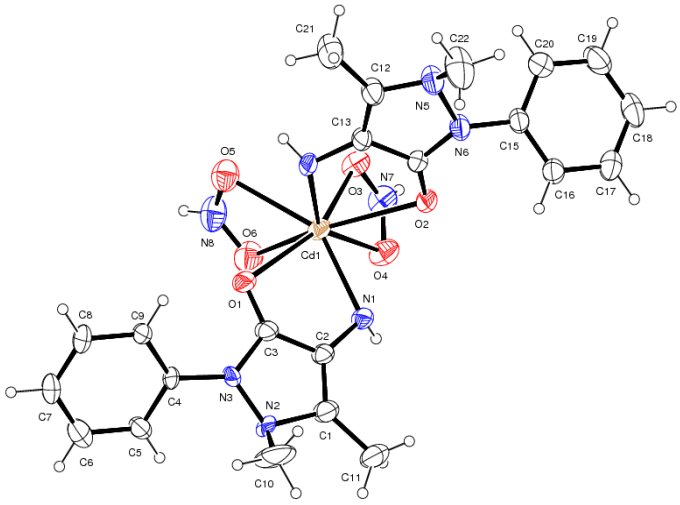

Figure- 4
Ortep diagram of [Cd^{II} (4-AAP) $_2$(NO$_2$)$_2$]

Conclusion

The data obtained from elemental analysis, IR spectroscopy and single crystal X-ray diffraction analysis indicate that the formula of the cadmium complex is [Cd^{II}(4-AAP)$_2$(NO$_2$)$_2$] in which cadmium ion has the coordination number eight. The geometry of the complex is dodecahedron.

Supplementary Material: Crystallographic data of the complex have been deposited in the Cambridge Crystallographic Data Centre CCDC (number–882326 (http://www.ccdc.ac.uk/services/structure deposit/)

Acknowledgement

The authors thank the Principal and Management of Bishop Heber College, Tiruchirappalli for encouragement and support and the Director and technicians of SAIF, IIT- Chennai, for the X-ray diffraction analytical work.

References

1. Bhutani S.P., Organic Chemistry, 1st Edn., Ane Books, India, 112 **(2007)**

2. Acheson R.M., Introduction to Heterocyclic Compounds, 4th Edn., John Wiley and Sons, New York, 354-364 **(2009)**

3. Agarwal R.K., Singh I. and Sharma D.K., Synthesis, Spectral and Biological properties of Copper(II) Complexes of Thiosemicarbazones of Sciff Bases derived from 4-Aminoantipyrine and Aromatic Aldehyde, *Bio.Chem.Appl*., 1-10 **(2006)**

4. Bansal Raj K., Heterocyclic Chemistry, 4th Edn., New Age International Publisher, New York, 454 **(2010)**

5. Joule J.A. and Mills K., Heterocyclic Chemistry, 4th Edn., Black Well Publishing Company, 439 **(2008)**

6. Yogesh Kumar Vaghasiya, Rathish Nair, Mayur Soni, Shipra Baluja and Sumitha Chanda, Synthesis, Structural Determination and Antibacterial Activity of Compounds derived from Vanillin and 4-Aminoantipyrine, *J.Serb.Chem.Soc*., **69(12),** 991-998 **(2004)**

7. Anupama B., Padmaja M. and. Gyananakumari C., Synthesis, Characterization, Biological Activity and DNA Studies of Metal Complexes with 4-Aminoantipyrine Schiff Base Ligand, *E-Journal of Chemistry*., **9(1),** 389-400 **(2012)**

8. Elemike E.E., Oviawe A.P. and. Otuokere I.E., Potentiation of the Antimicrobial Activity of 4-Benzylimino-2, 3-Dimethyl-1-Phenylpyrazal-5-One by Metal Chelation, *Research Journal Chemical Sciences,* **1(8),** 6-11 **(2011)**

9. Ahamed A. Fadda. and. Khaled. M.Elattar., Synthesis of Novel Azo Disperse dyes Derived from 4-Aminoantipyrine and their Applications to Polyester Fabrics, *American Journal of Organic Chemistry,* **2(3)**, 52-57 **(2012)**

10. Raman N., Dhaveethu Raja J. and Sakthivel A., Synthesis, Spectral Characterization of Schiff base Transition metal comp [lexes, DNA cleavage and antimicrobial activity studies, *J.Chem.Sci.,* **119(4)**, 303-310 **(2007)**

11. Madison., Wisconsin, Bruker APEX2, SAINT-Plus. and XPREP., Bruker AXS Inc., USA **(2004)**

12. Sheldrick G.M., *Acta Cryst*., **(A) 64 (2008)**

13. Josifina Pons, Jordi Garcia-Anton., Ruben Jimenez., Xavier Solans, Merce Font-Bardia., Josep Ros., Preparation and structural characterization of a Cd(II) complex with unusual geometry, *Inorganic Chemistry Communications,* **10**, 1554 **(2007)**

14. Huheey J.E., Keiter E.A. and Keiter R.L., Inorganic Chemistry, Principle of Structure and Reactivity 4th Edn., Addition- Wiley Publishing Company, New York, 508 **(2000)**

15. Sabbani Supria., Simple inorganic complexes but intricate hydrogen bonding networks: synthesis and crystal structures of [M(opda)2(NO3)2] (M= Zn and Cd), *J.Chem. Sci*., **2,** 112–122 **(2009)**