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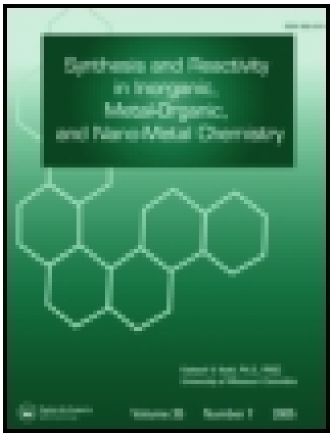

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

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Susannah Seth [a] & Kuttamath Kunniyur Aravindakshan [b]
[a] Department of Chemistry , Malabar Christian College , Kozhikode, India
[b] Department of Chemistry , University of Calicut , India

Published online: 30 Dec 2009.

To cite this article: Susannah Seth & Kuttamath Kunniyur Aravindakshan (2009) Crystal Structure of Spiro 5,5-Dimethyl Cyclohexane1,2,3-trione 2-phenylhydrazone and Spectral Characterization of its Transition Metal Complexes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39:6, 345-350

To link to this article: http://dx.doi.org/10.1080/15533170903095011

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39:345–350, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533170903095011

Crystal Structure of Spiro 5,5-Dimethyl Cyclohexane1,2,3-trione 2-phenylhydrazone and Spectral Characterization of its Transition Metal Complexes

Susannah Seth[1] **and Kuttamath Kunniyur Aravindakshan**[2]
[1]*Department of Chemistry, Malabar Christian College, Kozhikode, India*
[2]*Department of Chemistry, University of Calicut, India*

The synthesis and characterization of spiro5,5-dimethylcyclohexane1,2,3-trione2-phenylhydrazone, phenylazodimedone (AD) and the characterization of its complexes with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been carried out. AD was found to have the hydrazone form with intra-molecular N-H···O hydrogen bond. The complexes were found to have a general formula ML_2/ML_3 when M is a divalent/trivalent metal, respectively, and L is the mono anion of AD. The structure of AD has been arrived at by various spectral techniques and the presence of hydrogen bonding has been verified by single crystal XRD. The complexes were characterized by elemental analyses, magnetic susceptibility measurements, electronic-infrared-^{1}HNMR and mass spectral studies.

Keywords complexes, crystal structure, phenylazodimedone, spectral characterization

INTRODUCTION

Azo betadiketones are obtained by the diazocoupling reaction between diazonium salts and beta diketones. These compounds exhibit keto-enol tautomerism and act as bidentate ligands forming chelates with metal ions. Even though metal complexes of azodimedones with substituted phenyl group have been reported earlier,[1] a detailed characterization and structural specifications have been lacking. Therefore, the present investigation has taken up focusing on the synthesis and geometrical features of spiro5,5-dimethylcyclohexane1,2,3-trione2-phenylhydrazone and its Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) chelates.

EXPERIMENTAL

Synthesis of AD

Aniline (10 mmole, 0.93 mL) was diazotised with $NaNO_2$ (10 mmole, 0.69 g) and 1:1HCl (5 mmole, 5 mL) at a temperature of ~0–5°C. Excess acid was removed by the addition of urea. The mixture was stirred for half an hour maintaining the temperature at ~ 0–5°C. This solution of phenyl diazonium chloride was added drop wise with stirring to a well cooled solution of dimedone (10 mmole, 1.4 g) in ethanol when lemon-yellow colored phenylazo dimedone (AD) precipitated out. The pH of the solution was adjusted to about 6.5 using sodium acetate. The solution was stirred for another half an hour and the precipitate was filtered, washed with water, recrystallized from methanol and dried over anhydrous $MgSO_4$ in a desiccator. The purity of the compound was checked by TLC technique (yield 2.07 g, 85%).

Synthesis of Metal Complexes of AD

The metal salts used for the synthesis were chlorides of Fe(III) and Zn(II) and acetates of Co(II), Ni(II) and Cu(II). The metal to ligand ratio used was 1:2 for divalent metal complexes and 1:3 for trivalent metal complexes. A methanolic solution of the metal salt (1 mmole) was added slowly in drops with stirring to a methanolic solution of phenylazodimedone (3 mmole for Fe (III) and 2 mmole for Co(II), Ni(II), Cu(II) and Zn(II)). This mixture was refluxed for about 2 h on a steam bath. The complex precipitated on cooling and was filtered, washed with water and dried over anhydrous $MgSO_4$ in a desiccator. The complexes were recrystallised from methanol or methanol-dichloromethane mixture.

Analytical Methods

The percentages of carbon,hydrogen and nitrogen were determined by micro analyses using Vario EL III CHNS analyzer. Electronic spectra were recorded on a JASCO UV-visible spectrophotometer. IR spectra were obtained as KBr discs of the samples on JASCO FT/IR-4100 spectrophotometer. The

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Received 5 March 2009; accepted 13 April 2009.

The authors thank Dr. P. Mohammed Shafi, Professor and Head of the Department of Chemistry, University of Calicut and Sophisticated Analytical Instrument Facility (SAIF) at Kochi, Lucknow, IIT Madras and IIT Bombay for providing physico-chemical data. Thanks are also due to the University Grants Commission, New Delhi for financial assistance.

Address correspondence to Susannah Seth, Dept. of Chemistry, Malabar Christian College, Kozhikode, India. E-mail: susannahseth@yahoo.com

^{1}HNMRspectra were taken by dissolving the sample in $CDCl_3$ on a Varian Mercury NMR instrument at 400 MHz. The ESI mass spectra were measured using Micromass Quattro II triple quadrupole mass spectrometer. The magnetic susceptibilities were determined using Sherwood Scientific Magway magnetic susceptibility balance. The metal percentages of the chelates were estimated from standard analytical procedures,[2] and also by ICP-AES method on IRIS intrepid IIX SP instrument. The single crystal XRD was performed on Bruker AXS –Kappa Apex instrument.

RESULTS AND DISCUSSION

Structure of AD

Analytical Data

Phenylazodimedone has been formed according to the following reaction

$$C_6H_5N_2^+ + C_8H_{12}O \rightarrow C_{14}H_{16}N_2O_2 + H^+$$

The percentages of C, H and N (found: C, 68.69;H,6.11;N, 11.29, calcd., C,11.48;H, 68.35;N, 6.56) showed close agreement with the molecular formula $C_{14}H_{16}N_2O_2$. It registered a sharp melting point at 120°C.

Spectral Data

The electronic, IR, NMR and mass spectra of the AD were utilized to ascertain the structure.

Electronic Spectrum

The electronic spectrum shows all the peaks expected of a monophenyl hydrazone.[3] A weak band at 286 nm and a strong absorption band at 386 nm are clear indications of a hydrazone form. The azo form is excluded as a strong K band,[4] at 270–280 nm, which is characteristic of an azo form is absent in the spectrum of the compound under investigation. The band at 510 nm may be due to a chelated ketonic[5] structure.

IR Spectrum

The IR spectrum of the AD shows almost all bands expected of an azo betadiketone compound. The intense bands in the carbonyl region 1673 and 1623 cm^{-1} confirmed the presence[6] of diketo groups. The shift of these bands to a lower region compared to those expected for β diketones ($\sim$1700 cm^{-1}) may be attributed to the conjugation of the $>C{=}O$ groups with $>C{=}N$ of the hydrazone form. A band at still lower frequency may be due to the stretching of another $>C{=}O$ involved in a hydrogen bonding with $>NH$. No absorption bands were seen $\sim$ 3600 cm^{-1} (free-OH) or $\sim$3500 cm^{-1} (free-NH). However, the presence of a broad band at $\sim$3400 cm^{-1} indicated hydrogen bonded $OH\cdots N$ or $H{-}N\cdots O$ groups. The $\nu C{=}N$ absorption occurs at the same region as that of C=O. In non-conjugated systems, $\nu C{=}N$ absorption normally appears between 1690 and 1650 cm^{-1}. In conjugated systems it shifts to lower frequency. The band at 1590 cm^{-1} may be due to conjugated stretching of C=N.

^{1}H NMR Spectrum

The ^{1}H NMR spectrum supports well the hydrazone structure of AD. In the azo form, there should be a peak corresponding to $- >CH$ group flanked by two $>C{=}O$ groups at $\sim$3.2–3.5 ppm, which was absent in the ^{1}H NMR spectrum of phenylazo dimedone. N-H proton signal of hydrazone group was observed at 15.4 ppm, which gave additional evidence to the hydrazone structure in which the absorption occurs at 3–5 ppm lower than the azo-hydroxy resonance structure. In addition to the above peaks, the unmistatablepeaks,[7] of CH_3 at 1.9 ppm, CH_2 at $\sim$2.6 ppm and aromatic pattern at $\sim$ 7.2–7.6 ppm were also present.

Mass Spectrum

The mass spectrum of AD was pronounced with the presence of base peak at m/z 245, which is the $(M+1)^+$ ion. The other peaks of importance are at m/z 217 [(M+1)-(C_2H_4)] and one at m/z 152 [(M+1) – C_6H_5NH) which gives additional support to the hydrazone structure where $-HN\cdots N =$ cleavage occurs. Moreover, the absence of an $(M\text{-}N_2)^+$ peak,[8] also points to the absence of an azo group. The other specific peaks are at m/z 124 $(M+1\text{-}(C_6H_5NH\text{+two }CH_3)^+$, and m/z 94 ($C_6H_5N^+H_3$).

Single Crystal XRD Data

The single crystal of the AD has been obtained by slow evaporation of the purified substance in CH_2Cl_2+ CH_3OH mixture at room temperature. The data collection was done by cutting a suitable piece of size 0.3 × 0.2 × 0.2 mm and mounting on a goniometer using glass fiber. 10766 reflections were collected and 2011 were used for structure determination. The structure was solved by direct method using SHELXL software and refined by full matrix least squares against F^2. The computer graphics was of ORTEP model (Figure 1). The general crystal data are tabulated in Table 1. Bond lengths between selected atoms are included in Table 2. The numbering given in parenthesis is in accordance with the ORTEP representation. C(6)–N(1) is a double bond. C(5)–O(2) length is greater than C(7)–O(1). Even though both are carbonyl groups of dimedone moiety, the higher value of C(5)–O(2) may be due the single bond character of the bond as O(2) is hydrogen bonded to H(2) of N(2). Further evidence is provided by the following details of the hydrogen bond. N(2)–H(2). . . . .O(2); bond angle 136.5°;bond length–N(2)–H(2) 0.94 A°; H(2) . . . O(2) 1.00 A°.

Analytical and Spectral Features of the Metal Complexes of AD

Spiro5,5-dimethylcyclohexane1,2,3trione2-phenyhydrazone yielded stable complexes with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). The complexes were amorphous and powdery in nature.

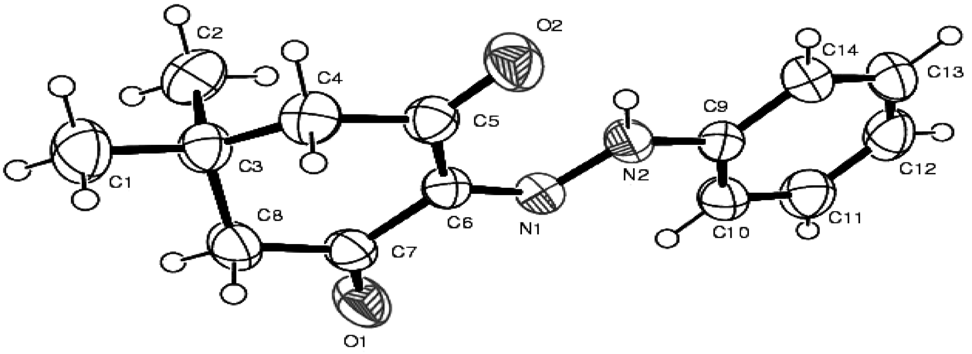

FIG. 1. Ortep representation of phenylazodimedone (AD).

The analytical and spectral characterization were conducted to assign the geometry of the complexes. The formation of the complexes can be represented by the following equation.

$$3\mathrm{LH} + \mathrm{M}^{3+} \rightarrow \mathrm{ML}_3 + 3\mathrm{H}^+$$
$$2\mathrm{LH} + \mathrm{M}^{2+} \rightarrow \mathrm{ML}_2 + 2\mathrm{H}^+$$

Where LH is the ligand AD and L^- is its monovalent ion, $M^{3+}=$ Fe(III) and $M^{2+}=$ Co(II), Ni(II), Cu(II) or Zn(II).

The physico-chemical and electronic spectral data are given in Table 3.

Electronic Spectral and Magnetic Data

The electronic absorption bands of all the complexes bear close resemblance with those of the AD. This showed that no structural alteration has occured to AD on complexation. However, a slight shift in the absorption maxima of > C=O and >C=N bands were seen, and may be because of the involvement of these groups in co-ordination. Trivalent iron has a tendency to have charge-transfer bands in the near UV which have many shoulders extending to the visible region that make the interpretation difficult. The magnetic moment,[9] was typical of an octahedral geometry *viz.* 5.91 B.M. Cobalt (II) complex was brown in color with a pink tinge. This is typical of an octahedral geometry. The band at 512 may be due to $^4T_{lg}(F) \rightarrow {}^4A_{2g}$ of Co(II) in an octahedral environment. But the magnetic moment value of 3.82 B.M was found to be too low for an octahedral geometry. Nickel complex was brown in color and diamagnetic. The bands at 330nm due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition and the charge transfer band at 292nm also indicated the square-planar geometry of the complex. Copper complex was olive green in color as expected and a band,[10] corresponding to the absorption was observed at 686 nm. The explanation of the spectrum was rather difficult owing to the enveloping of bands. However, this can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square-planar geometry. The magnetic moment obtained of 2.10 B.M. was within the range (1.75–2.20 B.M.) expected for magnetically dilute square-planar copper(II) complexes.

TABLE 1
Single crystal XRD data of AD

Empirical formula	$C_{14}H_{16}N_2O_2$
F.W.	244.29
Temperature	293 K
Wave length (Mo K_α)	0.71073 A°
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions (A°) a = 10.7285: b = 5.845: c = 20.8152	
Inter axial angles (deg) $\alpha = 90.000 : \beta = 96.946 : \gamma = 90.000$	
z value = 4	1.253 Mg/m^3
Density (calc.)	
Volume (A^3)	1295.28 (8)
Reflections collected/used	10766/2011
Residuals (all data) R_1	0.0526, $wR_2= 0$

IR Spectra

The position of the free carbonyl stretching band of AD was only marginally ($\sim$30 cm^{-1}) altered in the IR spectra of complexes, showing that it was still free in the complexes. The band corresponding to hydrogen bonded carbonyl group has been lowered, that may be assigned to

TABLE 2
Bond length between selected atoms

Bond	Bond length (A°)
C(6)–N(1)	1.322
N(1)–N(2)	1.2987
N(2)–H(2)	0.94
C(5)–O(2)	1.2340
C(7)–O(1)	1.2149
C(9)–N(2)	1.406

TABLE 3

Physico-chemical, electronic spectral and magnetic data of complexes

Sl. no.	Compound	Empirical formula (formula weight)	Color	Yield (%)	Decomp. temp. (°C)	Elemental analysis (%) found (calc)				Magnetic moment μ (B.M.)	Electronic spectral bands and assignments λ_{max} (nm)
						C	H	N	M		
1.	[FeL_3]	$C_{42}H_{45}FeN_6O_6$ (785)	Brown	30	165	64.02 (64.22)	5.57 (5.74)	10.26 (10.70)	6.53 (7.12)	5.91	290, 340,(C-T band) 500
2.	[CoL_2]	$C_{28}H_{30}CoN_4O_4$ (545)	Pinkish brown	70	200	61.10 (61.65)	5.15 (5.51)	10.28 (10.27)	10.62 (10.81)	3.82	288,380, 512($^4T_1g(F) \rightarrow {}^4A_2g$), 690
3.	[NiL_2]	$C_{28}H_{30}NiN_4O_4$ (545)	Brown	60	250	61.00 (61.68)	5.41 (5.51)	10.43 (10.28)	10.57 (10.77)	D	292,(C-T band) 330($^1A_1g \rightarrow {}^1B_1g$), 450,564
4.	[CuL_2]	$C_{28}H_{30}CuN_4O_4$ (550)	Olive green	70	215	61.36 (61.41)	5.99 (5.46)	9.98 (10.19)	11.19 (11.56)	2.10	288,384, 686($^2B_1g \rightarrow {}^2A_1g$)
5.	[ZnL_2]	$C_{28}H_{30}N_4O_4Zn$ (551)	Yellow	50	130	60.23 (60.94)	5.98 (5.44)	10.06 (10.16)	11.26 (11.85)	D	288,380,510(ligand transitions)

M = metal; D = diamagnetic; L = monoanion of AD(LH); C-T = charge transfer.

TABLE 4
Significant IR spectral bands of complexes and their assignments

Sl. no.	Compound	Free ν C═O	Chelated νC═O	νC═N	νM─N	νM─O
1.	[FeL$_3$]	1658(s)	1547(m)	1590(m)	554(w)	439(w)
2.	[CoL$_2$]	1660(s)	1546(m)	1595(m)	564(w)	439(w)
3.	[NiL$_2$]	1658(s)	1547(m)	1591(m)	582(w)	447(w)
4.	[CuL$_2$]	1642(s)	1520(m)	1590(m)	519(w)	440(w)
5.	[ZnL$_2$]	1659(s)	1546(m)	1592(m)	553(w)	444(w)

L = mono anion of AD(LH); s = strong; m = medium; w = weak.

metal bonded carbonyl group. A new band at ~440 cm^{-1} may be assigned to νM─O and the band at ~560 cm^{-1} may be assigned to νM–N,[11] respectively. Other bands of AD such as those at 3060 cm^{-1} of aromatic C─H, bands at 2959 and 2850 cm^{-1} of C─H stretch and at 1394 cm^{-1} of geminal dimethyl C─H deformation were retained in the spectra of the complexes. Important bands and assignments are given in Table 4.

TABLE 5
Significant ^{1}HNMR spectral assignments of zinc complex of AD

δ(ppm)	Proton assignment
1.2(s,6H)	geminal CH$_3$
2.7(s,4H)	>CH$_2$
7.5(unsymm.)	Aromatic

δ = Chemical shift; s = singlet.

^{1}H NMR Spectrum

^{1}H NMR spectrum of the diamagnetic ZnL$_2$ complex has been recorded and the data are given in Table 5. The prominent feature of the spectrum was the absence of N─H peak at ~15 ppm,[12] which was present in the NMR spectrum of AD. This was a clear indication of coordination through N to metal replacing H. Other peaks were the same as those the ^{1}H NMR spectrum of AD.

Mass Spectrum

The ESI mass spectrum of copper(II) complex (Figure 2) was found to be have very conspicuous M$^+$ (m/z 550)

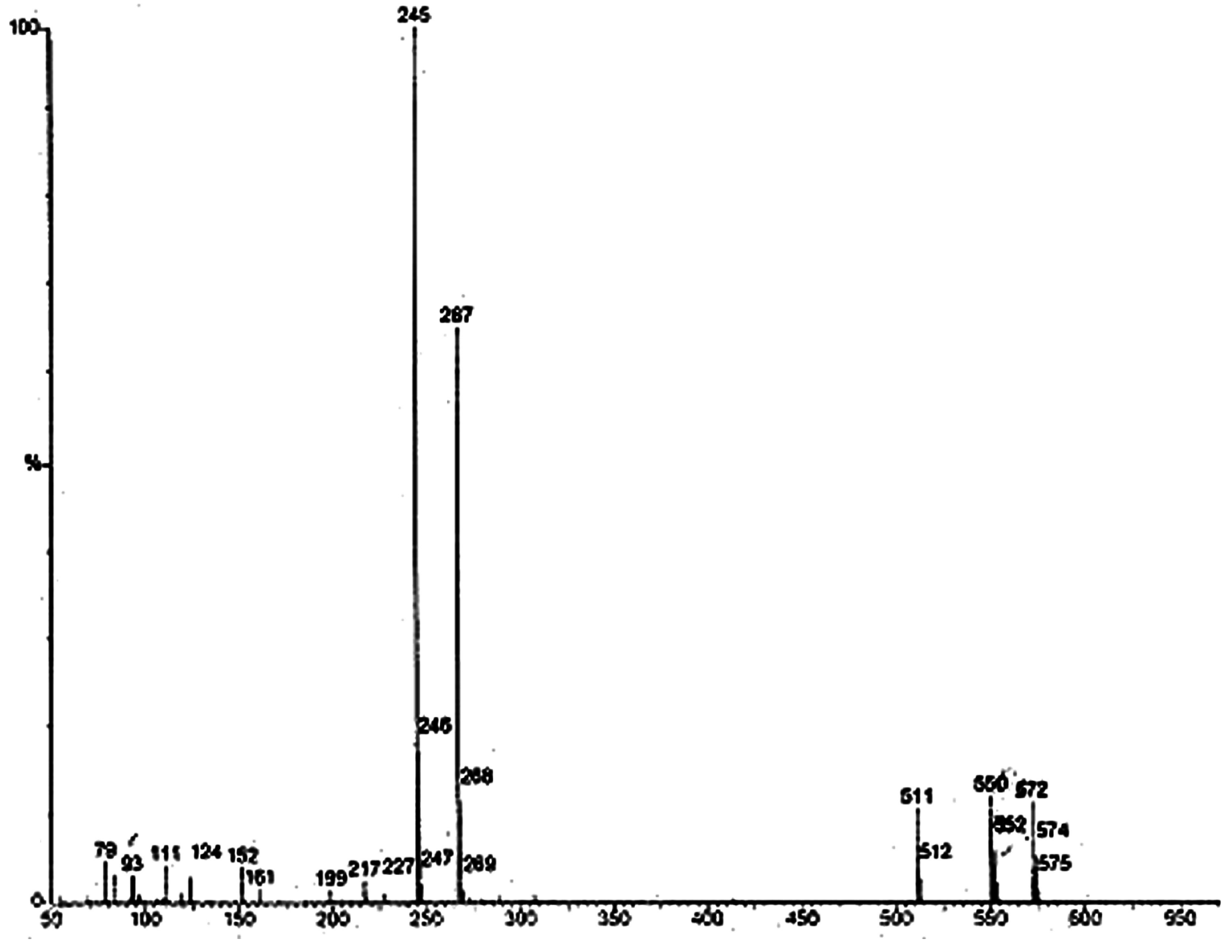

FIG. 2. ESI Mass spectrum of CuL$_2$.

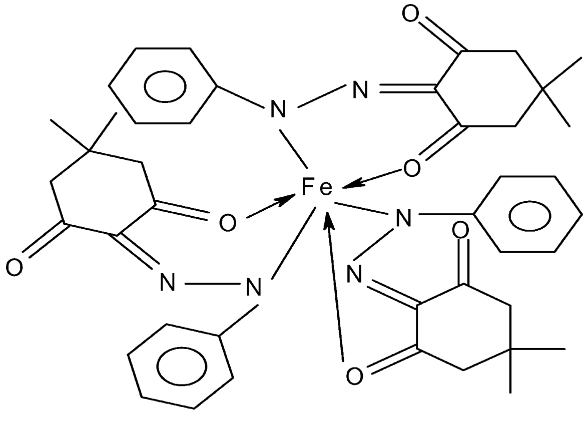

FIG. 3. Tentative structure of FeL_3.

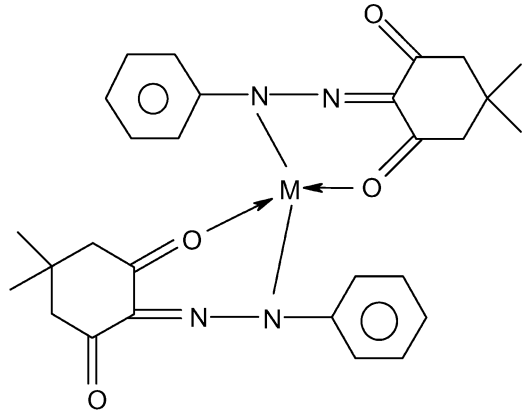

FIG. 4. Tentative structure of ML_2 where M = Ni(II) or Cu(II).

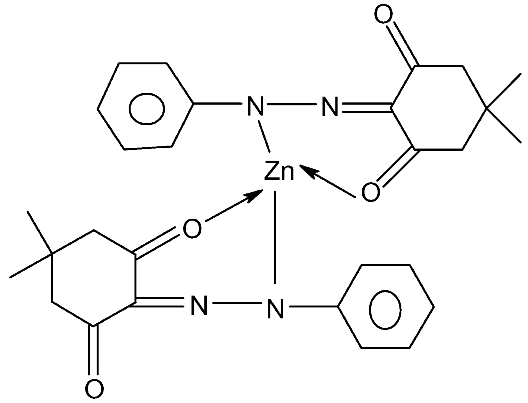

FIG. 5. Tentative structure of ZnL_2.

peak, which confirmed its stoichiometry, ML_2. The base peak (m/z 245) is that of AD. The (M+2) peak must be due to the isotope of copper, ^{65}Cu with an abundance of 30.9 percent.

CONCLUSION

In this communication, the synthesis and characterization of spiro5,5-dimethylcyclohexane1,2,3-trione2-phenylhydrazone (AD) and its Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been discussed. The structure of AD has been confirmed with single crystal XRD data and by other physico-chemical methods. An attempt has been made to suggest the structures of the complexes with the support of mass spectrum of one of the complexes, CuL_2 and other spectral techniques. The single crystals of metal complexes were not obtained despite several attempts. From the available data, it is clear that AD acts as monovalent, bidentate ligand coordinating through nitrogen and also the oxygen of the carbonyl group involved in hydrogen bonding, replacing the H with metal ion. Octahedral/distorted octahedral geometry has been assigned to Fe(III) and Co(II) complexes, and square-planar geometry to Ni(II) and Cu(II) complexes. The four-coordinate Zn(II) complexes may be tetrahedral in geometry. The tentative structures of the complexes are given in Figures 3, 4 and 5.

SUPPLEMENTARY MATERIAL

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No.689573. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic. Data Centre, 12 union Road, Cambridge CB21EZ,UK;fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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