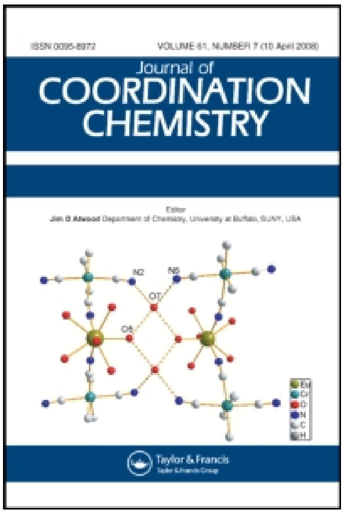

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Crystal structure of 3-acetylcoumarin-*o*-aminobenzoylhydrazone and synthesis, spectral and thermal studies of its transition metal complexes

Kalagouda Gudasi[a]; Ramesh Vadavi[a]; Rashmi Shenoy[a]; Siddappa Patil[a]; M. Nethaji[b]
[a] Department of Chemistry, Karnatak University Dharwad 580 003, India [b] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Crystal structure of 3-acetylcoumarin-*o*-aminobenzoylhydrazone and synthesis, spectral and thermal studies of its transition metal complexes

KALAGOUDA GUDASI*†, RAMESH VADAVI†, RASHMI SHENOY†, SIDDAPPA PATIL† and M. NETHAJI‡

†Department of Chemistry, Karnatak University Dharwad 580 003, India
‡Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Transition metal [Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] complexes of a new Schiff base, 3-acetylcoumarin-*o*-aminobenzoylhydrazone were synthesized and characterized by elemental analyses, magnetic moments, conductivity measurements, spectral [Electronic, IR, ^{1}H and ^{13}C NMR, EPR] and thermal studies. The ligand crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 9.201(5)$, $b = 16.596(9)$, $c = 11.517(6)$ Å, $\beta = 101.388(9)^\circ$, $V = 1724.2(17)$ Å^3 and $Z = 4$. Conductivity measurements indicated Mn(II) and Co(II) complexes to be 1 : 1 electrolytes whereas Ni(II), Cu(II), Zn(II) and Cd(II) complexes are non-electrolytes. Electronic spectra reveal that all the complexes possess four-coordinate geometry around the metal.

Keywords: *o*-Aminobenzoylhydrazide; 3-Acetylcoumarin-*o*-Aminobenzoylhydrazone; 3-Substituted coumarin; Transition metal complexes; Crystal structure; Thermal studies

1. Introduction

Coumarins are widely distributed in the plant kingdom, especially in the families Umbelliferae and Rutaceae [1]. Coumarin derivatives exhibit antibiotic, antifungal, anticoagulating, plant growth regulating and anti-inflammatory activities and are also used as analytical reagents [2]. In particular, coumarins with various substituents at position 3, exhibit a variety of biological properties [3] and are of spectroscopic interest [4]. 3-Acetylcoumarins have been reported to have antimicrobial properties and

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*Corresponding author. Tel.: +91-0836-2460129 (Res); +91-0836-2215286 (Off). Fax: +91-0836-2771275. Email: kbgudasi@rediffmail.com

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are useful synthons for coumarin analogs of chloroamphenicol [5] and 3-coumarinylthiazoles [6].

Aromatic acid hydrazides and their Schiff bases inhibit the growth of tuberculosis mycobacteria [7]. Introduction of a primary amino group ortho on the aromatic acid hydrazide makes it strongly active against tuberculosis mycobacteria; metal complexes of *o*-aminobenzoylhydrazide enhanced the antitubercular activity of the ligand [7].

Considering the biological activity of *o*-aminobenzoylhydrazide [7] and 3-substituted coumarins [5, 6] we aim to design and synthesize a molecule containing both moieties linking through azomethine with a free primary amino group ortho on the hydrazide moiety, so as to enhance its biological activity [7]. Metal complexes of title ligand have been synthesized to examine the role of transition metals in enhancing biological activity of the ligand.

The literature cites very little work on hydrazones derived from 3-acetyl coumarin [8]. In continuation of our earlier work on 3-substituted coumarins [2], we report here studies on synthesis, spectral, thermal and crystallographic studies of 3-acetylcoumarin-*o*-aminobenzoylhydrazone and its metal complexes.

2. Experimental

The complexes were analyzed for their metal content by EDTA titration after decomposition with a mixture of HCl and $HClO_4$. The chloride content of the complexes was determined as silver chloride after decomposition with HNO_3. The elemental analysis (C, H and N) was carried on a Thermoquest CHN analyzer. Magnetic susceptibility measurements were made at room temperature on a Guoy balance using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were made by direct weighing of the ligand for diamagnetic pull. Electronic spectra were recorded on a Carry-Bio-50 Varian in DMSO solution (10^{-3} M) in the range 200–1100 nm. IR spectra were recorded in the 4000–400 cm^{-1} region (KBr disc) on a Nicolet 170SX FT–IR spectrometer. ^1H NMR spectra were obtained in DMSO-d_6 using TMS as an internal reference on a BRUKER AVANCE 300 NMR spectrometer. The EPR spectrum of a polycrystalline sample was recorded at room temperature and also at liquid nitrogen temperature on a Varian E-4-X-band spectrometer using TCNE as a ‘g’ marker. Conductance measurements were recorded in DMSO (10^{-3} M) using an ELICO-CM82 conductivity bridge with cell type CC-01 and cell constant 0.53. TG–DTA studies were carried between 25–1000°C using TGA 7 ANALYSER, Perkin Elmer, US with a heating rate of $10°C\,min^{-1}$ in oxygen.

The chemicals used were of A.R. grade and used without further purification. Methanol was distilled before use. 3-Acetylcoumarin and *o*-aminobenzoylhydrazide were prepared by reported methods [9, 10].

3. Crystallography

The crystal structure of the Schiff base was determined by single crystal X-ray diffraction on a crystal of dimensions $0.14 \times 0.08 \times 0.06\,mm^3$. Data were collected at

293 K on a BRUKER SMART APEX-CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) and scan mode in the range of $2.18° < \theta < 27.35°$. A total of 13321 (3589 independent, $R_{\text{int}} = 0.0592$) reflections were measured. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic temperature factors. Calculations were performed with the SHELXTL programme [11]. Structure solution and refinement based on 3589 independent reflections with $I > 2$ sigma (I) and on 311 parameters gave $R_1 = 0.0485$. ($wR_2 = 0.1315$). The ORTEP [12] of the ligand is shown in figure 1. Crystal data and structure refinement and selected bond lengths and bond angles, are given in tables 1

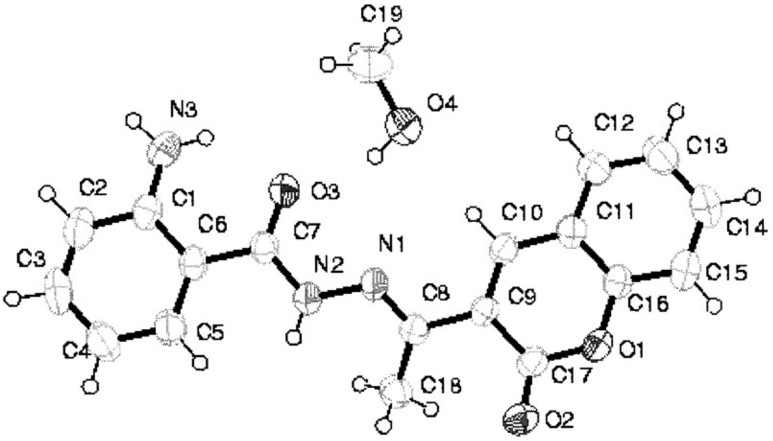

Figure 1. ORTEP diagram of the ligand.

Table 1. Crystal data and structure refinement for 3-acetylcoumarin-*o*-amino benzoylhydrazone.

Empirical formula	$C_{19}H_{19}N_3O_4$
Fw	353.37
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.2015 (5)
b (Å)	16.5964 (9)
c (Å)	11.5173 (6)
α (°)	90
β (°)	101.388 (9)
γ (°)	90
V (Å^3)	1724.2 (17)
Z	4
T (K)	293 (2)
Absorption coefficient (mm^{-1})	0.097
λ(Mo-Kα) (Å)	0.71073
F(000)	744.0
θ range	2.18–27.35
Limiting indices	$-11 \le h < 10$, $-19 \le k \le 21$, $-13 \le I \le 8$
Reflections collected	13321
Independent reflections	3589 ($R_{\text{int}} = 0.0592$)
Data/restraints/parameters	2923/0/311
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0485$, $wR_2 = 0.1315$

Table 2. Selected bond lengths (Å) and angles (°) for 3-acetylcoumarin-*o*-aminobenzoyl hydrazone.

O(2)–C(17)	1.2028(19)	C(6)–C(7)	1.479(2)
O(3)–C(7)	1.2217(19)	C(8)–C(9)	1.488(2)
N(1)–C(8)	1.2818(19)		
N(1)–N(2)	1.3870(18)		
N(2)–C(7)	1.359(2)		
C(8)–N(1)–N(2)	116.40(13)	C(9)–C(8)–C(18)	120.77(14)
C(7)–N(2)–N(1)	117.57(13)	N(2)–C(7)–C(6)	117.45(14)
C(5)–C(6)–C(7)	121.51(14)	N(1)–C(8)–C(9)	113.82(13)
C(1)–C(6)–C(7)	119.38(14)	N(1)–C(8)–C(18)	125.26(14)
O(3)–C(7)–N(2)	119.98(13)	O(2)–C(17)–O(1)	116.34(13)
O(3)–C(7)–C(6)	122.53(14)		

and 2. The CIF file of the title compound has been deposited at Cambridge Crystallographic Data Center (CCDC). CCDC reference number is 253911.

3.1. *Synthesis of 3-acetylcoumarin-*o*-aminobenzoylhydrazone [ACAB]*

To a methanolic solution of *o*-aminobenzoylhydrazide (1.51 g, 0.01 mol) was added 3-acetylcoumarin (1.88 g, 0.01 mol) and the mixture was stirred for 2–3 h until an orange crystalline product was precipitated. It was filtered, washed with cold chloroform and dried in air. Recrystallization from hot methanol gave shiny orange crystals suitable for X-ray diffraction, m.p. = 115–116°C; yield: 85%.

3.2. *Synthesis of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes*

ACAB (1 mmol) dissolved in 15 mL of methanol was mixed with the corresponding metal(II) chlorides (1 mmol) and refluxed for 2 h to obtain precipitate. The solution was cooled to room temperature, filtered and washed with methanol and air-dried. The products are soluble in DMF and DMSO but insoluble in methanol, ethanol, chloroform and benzene. Attempts to grow single crystals were unsuccessful.

4. Results and discussion

In the crystal structure of ACAB (figure 1), the bond lengths and angles (table 2) in the coumarin moiety are comparable to those of related structures [13, 14]. The bond angles and bond lengths in *o*-aminobenzoylhydrazide moiety are comparable with the analogous compound, di-2-pyridylketone-2-aminobenzoylhydrazone [15]. One hydrogen of N(3) forms a strong intramolecular hydrogen bond with O(3) with a distance of N(3)–H(3B) $\cdots$ O(3) = 2.646(0.006) Å. Another hydrogen of N(3) [H(3A)] is involved in intermolecular hydrogen bonding with the O(4) of another molecule in the unit cell. The ORTEP diagram (figure 1) shows the presence of methanol molecule in the crystal lattice.

Analytical data are presented in table 3. The metal-to-ligand ratio in all the complexes was 1 : 1. Conductivity measurements in DMSO (10^{-3} M) suggest the

Table 3. Analytical and electronic spectral data of ACAB and its metal complexes.

	Elemental analysis (%) found (Calcd)							
Compound {empirical formula}	C	H	N	M	Cl	μ_{eff} (BM)	Conductance (λ_m Ohm^{-1} cm^2 mol^{-1})	Electronic spectra (λ_{max}/nm)
ACAB · CH_3OH {$C_{19}H_{19}N_3O_4$}	64.55 (64.58)	5.36 (5.38)	11.86 (11.89)	–	–	–	–	337
[Mn(ACAB)Cl] · Cl {$MnCl_2$ ($C_{18}H_{15}N_3O_3$)}	48.32 (48.34)	3.32 (3.36)	9.38 (9.40)	12.25 (12.30)	15.81 (15.87)	5.82	40	390, 350, 341
[Co(ACAB)Cl] · Cl {$CoCl_2(C_{18}H_{15}N_3O_3)$}	47.88 (47.91)	3.31 (3.33)	9.29 (9.32)	13.02 (13.07)	15.66 (15.73)	4.41	42	685, 615, 370
[Ni(ACAB)Cl] {$NiCl(C_{18}H_{15}N_3O_3$}	52.11 (52.15)	3.35 (3.38)	10.10 (10.14)	14.11 (14.17)	8.50 (8.56)	3.46	0.51	680, 450
[Cu(ACAB)Cl] {$CuCl(C_{18}H_{15}N_3O_3)$	51.53 (51.55)	3.32 (3.34)	9.99 (10.02)	15.12 (15.16)	8.40 (8.46)	1.50	0.43	720–790, 384, 426
[Zn(ACAB)Cl] {$ZnCl(C_{18}H_{15}N_3O_3)$}	51.28 (51.32)	3.30 (3.33)	9.95 (9.98)	15.48 (15.54)	8.38 (8.42)	Dia	0.47	350
[Cd(ACAB)Cl] {$CdCl(C_{18}H_{15}N_3O_3)$}	46.15 (46.17)	2.97 (2.99)	8.94 (8.97)	23.99 (24.03)	7.54 (7.58)	Dia	0.44	375

Dia: Diamagnetic.

Table 4. Diagnostic IR bands in ACAB and its metal complexes.

Compound	$\nu(NH_2)$ asym.	Sym.	ν(C=O) (lactone)	ν(C=O) (amide I)	ν(C=N) (azomethine)	ν(CN) + δ(NH) (amide II)	Amide III
ACAB	3431m	3367m	1696vs	1650m	1618m	1518s	1248s
[Mn(ACAB)Cl] · Cl	3465m	3335m	1670s	1625m	1608s	1522m	1263s
[Co(ACAB)Cl] · Cl	3461m	3333m	1656s	1623m	1606s	1523m	1263s
[Ni(ACAB)Cl]	3446m	3330m	1671s	–	1608vs,br	1514w	no
[Cu(ACAB)Cl]	3440m	3328m	1643s	–	1592vs,br	1496m	no
[Zn(ACAB)Cl]	3465m	3361m	1676s	–	1608vs,br	1515w	no
[Cd(ACAB)Cl]	3468m	3317m	1675s	–	1608vs,br	1514w	no

M = medium; vs = very strong; s = strong; br = broad; w = weak; no = not observed.

non-electrolytic nature for Ni(II), Cu(II), Zn(II) and Cd(II) complexes and 1 : 1 electrolytic nature for Mn(II) and Co(II) complexes [16].

Diagnostic IR bands are given in table 4. The Schiff base showed two bands of medium intensity at 3431 and 3367 cm^{-1} ascribed to NH stretching frequencies of asymmetric and symmetric modes of primary amine, respectively [17]. These frequencies appeared to slightly lower wavenumber compared to 2-aminobenzoylhydrazone of 1,3-dione [17] probably due to involvement of free amino group in intramolecular hydrogen bonding with oxygen of C=O of hydrazide moiety as confirmed by crystallographic studies. A sharp band at 3646 cm^{-1} is due to OH stretching of lattice held methanol. Three bands at 1696, 1650 and 1618 cm^{-1} were assigned to ν(C=O) lactone [8], ν(C=O) hydrazide (amide I) [15], and ν(C=N) [8], respectively. The lowering of the ν(C=O) hydrazide frequency compared to 3-acetylcoumarin-*o*-hydroxybenzoylhydrazone [8] reveals the involvement of oxygen in hydrogen bonding. The ν(C=O) of lactone shifts to lower wavenumber by 20–53 cm^{-1} in all complexes indicating involvement of lactone oxygen in coordination [8]. The amide I band [ν(C=O)] in Mn(II) and Co(II) complexes shifts to lower frequency by 25–27 cm^{-1} revealing coordination of uncharged amide oxygen. On the other hand, in Ni(II), Cu(II), Zn(II) and Cd(II) complexes the amide I band disappears indicating the involvement of oxygen via enolization. The ν(C=N) band in Ni(II), Cu(II), Zn(II) and Cd(II) complexes shifts to lower frequency by 10–26 cm^{-1} as a broad band in all the complexes, indicating coordination of azomethine nitrogen; broadening is probably due to the formation of a new C=N bond [17] due to enolization and deprotonation. Two strong bands at 1518 and 1248 cm^{-1} in ACAB are attributed to amide II and amide III bands [18]; these bands shift to slightly higher wavenumber in Mn(II) and Co(II) complexes, further supporting amide oxygen coordination [18]. In Ni(II), Cu(II), Zn(II) and Cd(II) complexes amide II band shifts to lower frequency, with decreased intensity due to deprotonation during complex formation [19]. The tentative structure for the complexes showing the bonding sites in ligand are shown in figures 2 and 3.

^{1}H and ^{13}C NMR spectral data of ACAB and its zinc(II) complex are listed in table 5. The ^{1}H NMR spectrum of the Schiff base in DMSO-d_6 showed two broad singlets at 10.59 and 6.22 ppm corresponding to one and two protons of N(2) and N(3) (figure 1), respectively. A sharp singlet at 8.23 ppm is assigned to C(10)H. Three doublets in the downfield region at 7.88, 7.56 and 6.76 ppm are ascribed to C(5)H, C(15)H, and C(2)H, respectively. Triplets at 7.66, 7.21, and 6.59 ppm are attributed to protons of C(13), C(3) and C(4), respectively. One doublet of C(12)H and a triplet of C(14)H merge to give a

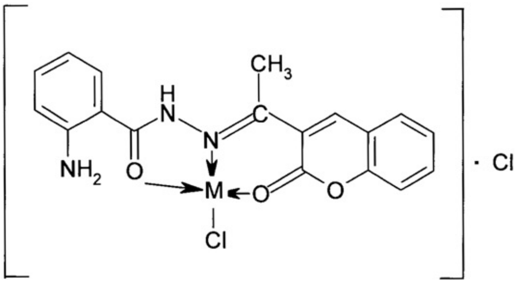

Figure 2. Tentative structures for Mn(II) and Co(II) complexes.

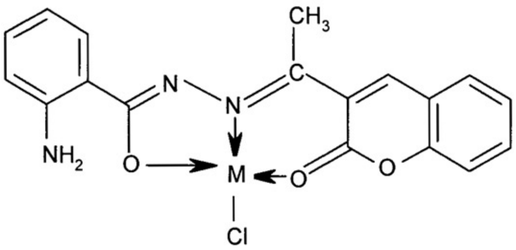

Figure 3. Tentative structures for Ni(II), Cu(II), Zn(II) and Cd(II) complexes.

Table 5. ^{1}H and ^{13}C NMR spectral data of ACAB[a] and its zinc(II) complex (δ ppm).

	^{13}C			^{1}H	
Carbon position	ACAB	Zn(II) complex	Proton position	ACAB	Zn(II) complex
C(1)[b]	150.52	150.47	–	–	–
C(2)	115.25	115.36	C(2)H	6.76 (d, $J=8.1$ Hz)	6.76 (d, $J=8.1$ Hz)
C(3)	133.28	133.35	C(3)H	7.21 (t, $J=7.5$ Hz)	7.21 (t, $J=7.5$ Hz)
C(4)	116.86	116.85	C(4)H	6.59 (t, $J=7.4$ Hz)	6.59 (t, $J=7.4$ Hz)
C(5)	133.08	133.01	C(5)H	7.88 (d, $J=7.5$ Hz)	7.86 (d, $J=7.5$ Hz)
C(6)	115.76	115.76	–	–	–
C(7)	160.14	161.10	–	–	–
C(8)[b]	150.52	150.47	–	–	–
C(9)	119.66	124.17	–	–	–
C(10)	142.39	144.41	C(10)H	8.23 (s)	8.24 (s)
C(11)	117.14	119.63	–	–	–
C(12)	127.80	129.68	C(12)H	7.42 (m)	7.41 (m)
C(13)	125.66	125.70	C(13)H	7.66 (t, $J=7.7$ Hz)	7.65 (m)
C(14)	130.06	130.07	C(14)H	7.42 (m)	7.41 (m)
C(15)	116.97	117.14	C(15)H	7.56 (d, $J=7.7$ Hz)	7.58 (d, $J=6.8$ Hz)
C(16)[c]	154.30	154.17	–	–	
C(17)[c]	154.30	155.30	–	–	
C(18)	17.04	17.19	C(18)H	2.30 (s)	2.32 (s)
C(19)	49.46	–	C(19)H	3.16 (d, $J=5.1$ Hz)	–

[a] Chemical shifts of protons of N(2), N(3) and O(4) are not included in table.
[b] These carbons appeared as a single line both in ACAB and the Zn(II) complex.
[c] These carbons appeared as a single line in ACAB.

multiplet at 7.42 ppm, which corresponds to two protons. In the upfield region, a sharp singlet at 2.31 ppm is ascribed to protons of C(18), the integral area of which accounts for three protons. ^{13}C NMR spectrum shows signals at 154.30 and 150.52 ppm, the former assigned to C(16) [20] and C(17), and the latter due to C(l) and C(8) [20]. The C(18) signal was observed at 17.04 ppm as expected for sp^3 hybridized carbon. The signal at δ 160.14 was assignable to C(7) [19]. These assignments were made by comparing ^{1}H and ^{13}C NMR spectrum of the title compound with 3-acetylcoumarin [21] and methyl anthranilate [22]. One quartet and a doublet in the ^{1}H NMR at 4.11 and 3.16 ppm are due to protons of O(4) and C(19) of lattice held methanol [23]. Lattice held methanol carbon, C(19), was observed at 49.4 ppm [23].

In the ^{1}H NMR spectrum of the Zn(II) complex, disappearance of NH clearly indicates deprotonation of amide NH via enolization, further confirmed by appearance of C(7) signal in the ^{13}C NMR spectrum of zinc(II) complex downfield by 0.94 ppm indicating involvement of oxygen in coordination. The free NH_2 signal shifts upfield by 2.79 ppm revealing breakdown of hydrogen bonding upon complexation. Other signals in the ^{1}H NMR of the Zn(II) complex did not show any shift. In ^{13}C NMR spectrum of Zn(II) complex, the shift of C(9) and C(17) carbons by 5 and 1 ppm, respectively, indicate participation of lactone oxygen in coordination.

On the basis of IR and NMR studies, one can expect free rotation across C(8)–C(9). This change in conformation will facilitate ligand coordination through carbonyl oxygen, azomethine nitrogen and lactone oxygen.

EPR spectra of the Cu(II) complex at room temperature and liquid nitrogen temperature showed identical features. The room temperature EPR spectrum is depicted in figure 4. From observed g values of the Cu(II) complex at RT and LNT ($g_{\parallel} = 2.19$, $g_{\perp} = 2.16$ and $g_{\mathrm{av}} = 2.17$), it is evident that the unpaired electron lies predominantly in the $d_{x^2} - d_{y^2}$ orbital with some d_{z^2} character being mixed with it because of low symmetry [24]. The $g_{\parallel}$ value ($g_{\parallel} = 2.19 < 2.3$) indicates a larger percentage of co-valency [25]. The G value ($G = 1.17$) being less than 4 indicates interaction between copper centers in the solid state.

Electronic spectra of all complexes in DMSO (10^{-3} M) were scanned in the region 250–1100 nm. The electronic spectrum of ACAB showed a strong band at 337 nm attributed to $\pi \rightarrow \pi^*$ transition. The Mn(II) complex exhibits three bands at 390, 350

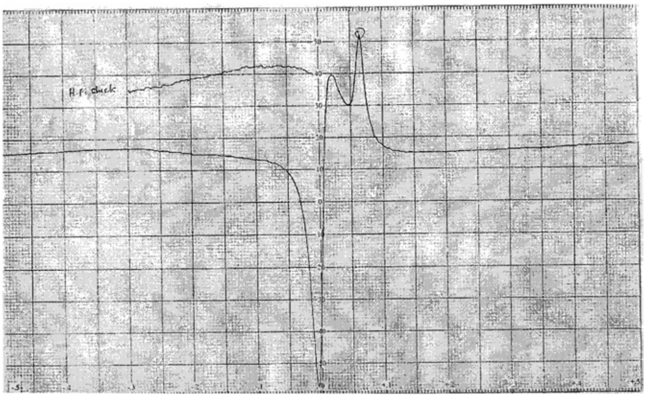

Figure 4. EPR spectrum of Cu(II) complex.

and 341 nm assigned to the transitions, $^6A_1 \rightarrow 4E$, $^6A_1 \rightarrow {}^4T_2(D)$ and $^6A_1 \rightarrow {}^4E(D)$, respectively. These transitions indicate tetrahedral geometry around Mn(II) [19]. A broad band at 685 nm followed by a shoulder at 615 nm were observed in the electronic spectrum of the Co(II) complex. The former was attributed to $^4A_2(F) \rightarrow {}^4T_1(P)$ and the latter to spin–spin coupling [19]. A broad band centered at 370 nm was probably due to charge transfer. These transitions reveal tetrahedral geometry around Co(II). The Ni(II) complex shows two bands at 680 and 450 nm assigned to $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) and charge transfer transitions, respectively, in consistent with tetrahedral geometry around Ni(II) [19]. In the electronic spectrum of the Cu(II) complex, a broad band in the region 720–790 nm was observed and assigned to the combination of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions. These transitions indicate square-planar around Cu(II) [19]. Two more bands were observed at 384 and 426 nm and are assigned to charge transfer transitions. The bands observed at 350 and 375 nm in Zn(II) and Cd(II) complexes are probably due to charge transfer transitions.

Effective magnetic moments of 5.82, 4.41 and 3.46 BM were observed for Mn(II), Co(II) and Ni(II) complexes, respectively. These values are within the range for high spin tetrahedral complexes [19]. The copper(II) complex showed an effective magnetic moment of 1.50 BM, which is less than the spin only value indicating some metal–metal interaction in the crystalline state, supporting the EPR observation.

In order to study the thermal behavior of cationic complexes [Mn(II) and Co(II)] and neutral complexes [Ni(II), Cu(II), Zn(II) and Cd(II)] we have chosen Mn(II) and Ni(II) complexes as representative. The Mn(II) and Ni(II) complexes decompose in two steps. In the Mn(II) complex the weight loss of 16.0% (Calcd 15.87%) in the first step (250–380°C) corresponds to loss of chloride and a coordinated chloride. In the second step (380–535°C), the ligand is lost with a mass loss of 71.7% (Calcd 71.6%). The plateau obtained at 535°C with a residual weight of 16.0% (Calcd 15.9%) corresponds to MnO. For the Ni(II) complex, the first weight loss of 8.3% (Calcd 8.46%) (250–295°C) accounts for the loss of coordinated chloride. The weight loss 77.16% (Calcd 77.26%) observed in the second step (295–505°C), corresponds to loss of ligand. The plateau obtained with the residual weight of 18.0% (Calcd 18.03%) above 505°C corresponds to formation of NiO.

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References

[1] J Banerji, K.P. Dhara, A.K. Das, A. Chatterjee. *Indian J. Chem.*, **27B**, 21 (1988).
[2] K.B. Gudasi, S.D. Dhumwad, T.R. Goudar. *Indian J. Chem.*, **33A**, 782 (1994).
[3] G. Feurer. In *Progress in Medicinal Chemistry*, G.P. Ellisand, G.B. Westand (Eds), pp. 10, 85, North Holland, London (1974).
[4] R. Clinging, F.M. Dean, L.E. Houghton. *J. Chem. Soc.*, **C**, 897 (1970).
[5] H.S. Bevinakatti, V.V. Badiger. *J. Heterocycl. Chem.*, **17**, 1701 (1980).
[6] A.K. Panigrahi, M.K. Raut. *J. Indian Chem. Soc.*, **48**, 665 (1971).

[7] A. Maiti, S. Ghosh. *J. Inorg. Biochem.*, **36**, 131 (1989).
[8] V.K. Revankar, V.H. Arali, V.B. Mahale. *Indian J. Chem.*, **29A**, 889 (1990).
[9] E. Knoevenagel. *Berichte*, **31**, 720 (1898).
[10] K.K. Narang, J.P. Pandey, V.P. Singh. *Polyhedron*, **13**, 529 (1994).
[11] G.M. Sheldrick. *SHELXL 97 Programme for the Solution of Crystal Structures*, University of Gottingen, Germany (1997).
[12] C.K. Jhonson, *ORTEP REPORT ORNL-3794*, Oak Ridge National Laboratory, Tennessee.
[13] M.B. Mahendra, H. Doreswamy, M.A. Sridhar, J.S. Prasad, V.P. Narodia, Y.T. Naliapara, A. Shah. *Anal. Sci.*, **119**, x33 (2003).
[14] M.K. Kokila, Puttaraja, M.V. Kulkarni, N.C. Shivaprakash. *Acta Cryst.*, **C52**, 2078 (1996).
[15] S. Ianelli, P. Mazza, M. Orcesi, C. Pelizzi, G. Pelizzi, F. Zani. *J. Inorg. Biochem.*, **60**, 89 (1995).
[16] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[17] S. Ghosh, A. Maiti. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **90**, 185 (1987).
[18] T.F. Zafiropoulos, J.C. Plakatouras, S.P. Perlepes. *Polyhedron*, **10**, 2405 (1991).
[19] N. Nawar, N.M. Hosny. *Chem. Pharm. Bull.*, **47**, 944 (1999).
[20] F. Fulop, M. Siemenov, K. Pihlaja. *Tetrahedron*, **48**, 531 (1992).
[21] SDBS web: http://www.aist.go.jp/RIODB/SDBS (27-08-2004). SDBS No. 23888 HSP-44-727.
[22] SDBS web:http://www.aist.go.jp/RIODB/SDBS (27-08-2004), SDBS No. 730 HSP-40-980.
[23] E. Gottlieb, V. Kotlyar, A. Nudelman. *J. Org. Chem.*, **62**, 7512 (1997).
[24] B.J. Hathaway, B.E. Billing. *Coord. Chem. Rev.*, **5**, 143 (1970).
[25] D. Kivelson, R. Neiman. *J. Chem. Phy.*, **35**, 149 (1961).