

Homo- and hetero-binuclear complexes of a compartmental Schiff base ligand. Synthesis and characterisation

Kamalendu Dey^{a,*}, Saikat Sarkar^{a,b}, Ranabir Bhowmick^a, Susobhan Biswas^a & Dhananjoy Koner^a

^aDepartment of Chemistry, University of Kalyani, Kalyani 741 235, West Bengal, India

^bDepartment of Chemistry, Santipur College, Santipur 741 404, West Bengal, India

Email: kdehy@klyuniv.ernet.in; kdehy_chem@rediffmail.com

Received 18 February 2005; revised 23 July 2005

Reaction of 3-formylsalicylic acid with diethylenetriamine yields the Schiff base {N,N'-2,2'-bis(aminoethyl)methyl-aminebis(3-carboxysalicylidimine)}(H₄fsadien). The interaction of H₄fsadien with CoCl₂·6H₂O produces [(H₂fsadien)Co^{II}] and silylation and lithiation of which, having two free -COOH groups with Me₃SiCl or trimethylsilyl N,N'-diphenylurea (TDPU) and LiOH, yields disilylated and dilithiated products, [(Me₃Si)₂(fsadien)Co^{II}] and [(Li)₂(fsadien)Co^{II}], in good yield. This disilylated or dilithiated product smoothly reacts with (π-C₅H₅)₂TiCl₂, (π-C₅H₅)₂ZrCl₂, Me₂SnCl₂, Ph₂SnCl₂ and MX₂·nH₂O (where M=Ni²⁺, Cu²⁺, Co²⁺, Pd²⁺, VO²⁺ and X=Cl⁻ or CH₃COO⁻) affording some new homo- and hetero-binuclear complexes, including some organo-derivatives. The reactions of H₄fsadien with FeCl₃·6H₂O and Co(NO₃)₂·6H₂O in access of oxygen also yield di-iron(III) and di-cobalt(III) complexes. The complexes are characterised by elemental analyses, molecular weights, magnetic moment values, molar conductance values and spectroscopic data (IR and electronic) data. In all these complexes, the Schiff base, H₄fsadien, functions as tetrabasic bridging hexadentate/heptadentate ligand using inner compartment of N₂O₂ or N₃O₂ donor set and outer compartment of O₂O₂ donor set.

IPC Code: Int. Cl.⁷ C07F15/06; C07C251/02

In recent years, much attention has been given to the synthesis and characterization of multimetallic complexes in connection with their potential relevance to bioinorganic chemistry¹. The polydentate and compartmental ligands can form such multimetallic clusters by binding two or more metal centres in close proximity²⁻¹⁶. The magnetic interactions and coupling between the metal ions present in such oligometallic clusters play key role in both natural and synthetic catalysts. Recently, some perovskite-intercalated montmorillonite have been obtained by the introduction of cationic form of such binuclear complexes between the clay sheets of nanospecies via an exchange process and their catalytic activity was evaluated¹⁷. In view of these facts, efforts have been made for the synthesis of such compartmental ligands and their multimetallic complexes by controlling the appropriate modification of molecular topology. One such ligand, which can satisfy the conditions of generating multimetal systems, is the present Schiff base ligand (H₄fsadien) derived by the condensation of 3-formylsalicylic acid and diethylenetriamine. The ligand (H₄fsadien) can utilize all the donor sites to

function as a compartmental ligand, the inner compartment being N₂O₂ or N₃O₂ donor ligand and outer compartment being O₂O₂ donor ligand, affording homo- and hetero-bimetallic complexes. In continuation of our earlier work^{18,19} on the mono nuclear complexes of H₄fsadien, we synthesized di-trimethylsilylated and dilithiated products of mononuclear complex, [(H₂fsadien)Co^{II}], namely, [(Me₃Si)₂(fsadien)Co^{II}] and [(Li)₂(fsadien)Co^{II}]. These new products smoothly react with (π-C₅H₅)₂TiCl₂, (π-C₅H₅)₂ZrCl₂, Me₂SnCl₂, Ph₂SnCl₂ and MX₂·nH₂O (where M=Ni²⁺, Cu²⁺, Co²⁺, Pd²⁺, VO²⁺ and X=Cl⁻ or CH₃COO⁻) leading to many new binuclear complexes. The reactions of H₄fsadien with FeCl₃·6H₂O and Co(NO₃)₂·6H₂O have also been studied yielding di-iron(III) and di-cobalt(III) complexes. The present paper reports the results of these investigations.

Materials and Methods

All the chemicals used were of AR grade. The solvents and chemicals were purified and dried before use by standard procedures. 3-Formylsalicylic acid

was synthesized according to Duff and Bills²⁰. Diethylenetriamine was purchased from BDH and used as such. The ligand H₄fsadien was prepared by our previously reported method¹⁹. The mononuclear complex [(H₂fsadien)Co^{II}] was prepared as reported by Dey *et al.*¹⁸.

The elemental analyses were carried out on Elementar Vario EL III, Carlo Erba 1108 elemental analyzers at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. The electronic spectra were recorded on a Hitachi 200-20 and Shimadzu UV-2401PC spectrophotometers and infrared spectra (KBr or Nujol or hexachlorobutadiene; more than one media were used for some compounds) on a Perkin-Elmer 1330 and L120-000A FTIR spectrophotometers. The molar conductance was measured using an Elico conductivity bridge. The magnetic susceptibility was determined by the Guoy method. Molecular weights were determined by Rast's method and osmotically.

Preparation of the precursor complexes, [(Me₃Si)₂fsadien]Co^{II} (1) and [(Li)₂fsadien]Co^{II} (2)²¹

The complex [(H₂fsadien)Co^{II}] (0.456 g, 0.001 mol) was refluxed with Me₃SiCl (0.217 g, 0.002 mol) in THF-hexane mixture (50 mL) in presence of stoichiometric amount of Et₃N for 3 h to yield this light-brown compound. The complex is soluble in many organic solvents. It can also be synthesized by refluxing a mixture of the complex [(H₂fsadien)Co^{II}] and trimethylsilyl N,N'-diphenylurea (TDPU) (1:2 molar ratio in THF). It can also be prepared by refluxing (2 h) a mixture of the lithiated complex [(Li)₂fsadien]Co^{II} (1 mol) with Me₃SiCl (2 mol) in THF-hexane mixture. Lithiation of the mononuclear complex [(H₂fsadien)Co^{II}] was carried out by refluxing a suspension of the complex with LiOH (1:2 molar ratio) in methanol or ethanol for 3 h. Colour: light-brown; m.pt.: 169-171°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 7.8; μ_{eff} (BM): 4.52.

Preparation of the complexes

[($\pi\text{-C}_5\text{H}_5$)₂M]Co^{II}(fsadien) [when M=Ti, (3) and M=Zr, (4)]

A mixture of complex (1) (0.456 g, 0.001 mol) and ($\pi\text{-C}_5\text{H}_5$)₂MCl₂ (M=Ti or Zr) (1:1 molar ratio) in THF-toluene (70 mL, 50:50, v/v) was heated under gentle reflux for 5 h and filtered. The volume of the filtrate was reduced under low pressure and cooled to about 5°C with the production of (3) and (4) as yellow brown solid. The compounds were washed with THF-Petroleum ether (40-50°C) (20:80, v/v) and dried *in*

vacuo. Compound (3): Colour: yellow-brown; m.pt. 190°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 8.7; μ_{eff} (BM): 4.4 (total); compound (4): Colour: yellow-brown; m.pt. 208°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 8.9; μ_{eff} (BM): 4.5 (total).

[(R₂Sn)₂]Co^{II}(fsadien) [where R=Me, (5) and R=Ph, (6)]

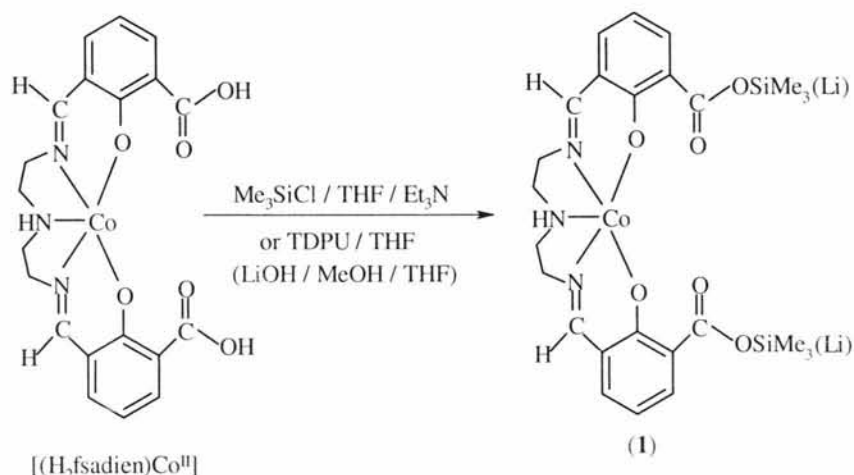
Similarly, the complex [(Me₂Sn)₂]Co^{II}(fsadien) (5) and [(Ph₂Sn)₂]Co^{II}(fsadien) (6) were prepared by the reaction of (1) with Me₂SnCl₂ and Ph₂SnCl₂, respectively as light yellow solid. The rest of the procedures were same as described above. Compound (5): Colour: yellow; m.pt. 210°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.5; μ_{eff} (BM): 4.5 (total); compound (6): Colour: yellow; m.pt. 228°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.2; μ_{eff} (BM): 4.62 (total).

[M(fsadien)Co^{II}] nH₂O, where M=Ni(II), n=2, (7); M=Cu(II), n=3, (8); M=Pd(II), n=2, (9); M=Zn(II), n=1, (10); M=Co(II), n=3, (11); M=VO²⁺, n=2, (12); M=UO₂²⁺, n=2, (13)

To a refluxed mixture of [(H₂fsadien)Co^{II}] (0.456 g, 0.001 mol) in THF-toluene (80 mL) was added M(OAc)₂.nH₂O (0.001 mol) in 30 mL of ethanol and stirred while hot for 30 min. The precipitated coloured compounds were filtered off, washed with aqueous ethanol and then with petroleum ether (40-60°C) and dried *in vacuo*.

The same complexes were also isolated by the reaction of [(Me₃Si)₂fsadien]Co^{II} (1) with MCl₂.nH₂O. The products were found to be cleaner, provided better yield in this method. The complexes are stable and soluble in coordinating solvents.

All these complexes could be isolated by the reaction of [(Li)₂fsadien]Co^{II} (2) with the appropriate metal salts in right stoichiometric ratios. Compound (7): Colour: brown; m.pt. 278°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 8.88; μ_{eff} (BM): 4.9 (total); compound (8): Colour: light-brown; m.pt. 262°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.2; μ_{eff} (BM): 6.2 (total); compound (9): Colour: brown; m.pt. 298°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 8.9; μ_{eff} (BM): 4.8 (total); compound (10): Colour: brown; m.pt. 272°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 5.9; μ_{eff} (BM): 4.45 (total); compound (11): Colour: reddish-brown; m.pt. 262°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 7.9; μ_{eff} (BM): 4.4 (per atom); compound (12): Colour: light-brown; m.pt. 258°C (d); Λ_M (10⁻³ M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 8.8; μ_{eff} (BM): 6.1 (total); compound (13): Colour: yellow;



Scheme 1

m.pt. 290°C (d); Λ_M (10^{-3} M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.4; μ_{eff} (BM): 4.49 (total).

$[(Cl)(py)Fe^{III}(fsadien)Fe^{III}(py)(Cl)]$ (14)

The Schiff base, $H_4fsadien$ (1.824 g, 0.004 mol) was dissolved in mixed solvent of methanol-pyridine (50 mL, 50:50, v/v) and this solution was added immediately to the hot solution of $FeCl_3 \cdot 6H_2O$ (2.16 g, 0.008 mol) in pyridine (25 mL). The mixture was heated under gentle reflux for 8 h and filtered while hot. On cooling to room temperature, a reddish-pink solid compound separated out. It was filtered off, washed with ethanol and dried *in vacuo*.

The complex is soluble in pyridine, DMSO, DMF but insoluble in water, benzene, ether and chloroform. Colour: reddish-pink; m.pt. 129–132°C (d); Λ_M (10^{-3} M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.2; μ_{eff} (BM): 3.14 (per atom).

$[(NO_3)_2Co^{III}(fsadien)Co^{III}(H_2O)_2]$ (15)

3-Formylsalicylic acid (0.66 g, 0.004 mol) was dissolved in ethanol (30 mL) to which diethylenetriamine (0.2 g, 0.002 mol) in 15 mL of aqueous ethanol was added dropwise while stirring. The mixture turned yellow and heated under reflux on water bath for 2 h. A solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.16 g, 0.004 mol) in ethanol (20 mL) was then added to the hot solution of the ligand $H_4fsadien$ dropwise while stirring followed by heating under gentle reflux for 3 h in the presence of oxygen. During reflux a brown microcrystalline complex was separated out, which was filtered off, washed with ethanol and ether and dried in air.

The compound is slightly soluble in water but highly soluble in coordinating solvents. Colour: brown; m.pt. 210–212°C (d); Λ_M (10^{-3} M in DMSO, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 9.5; diamagnetic.

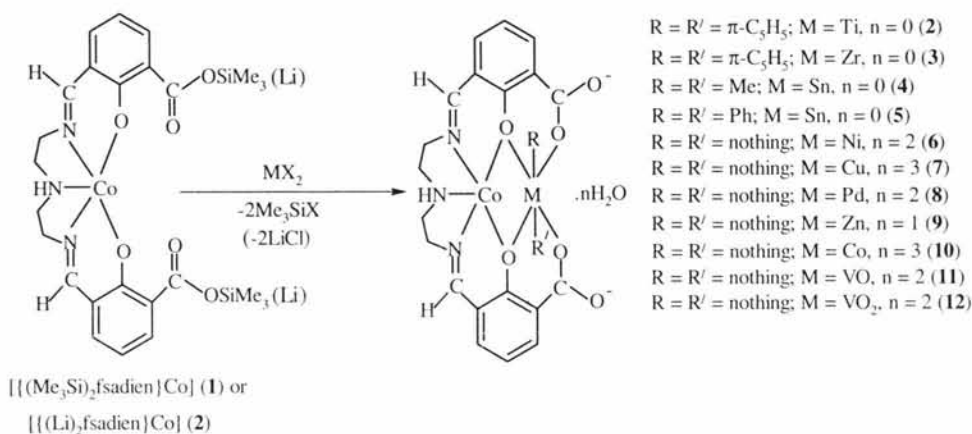
Results and Discussion

The ligand $H_4fsadien$ can function as a compartmental ligand, the inner compartment being N_2O_2 or N_3O_2 donor ligand and outer compartment being O_2O_2 donor ligand, affording homo- and hetero-bimetallic complexes. The chemical composition of the isolated complexes depends to some extent on the nature of the reactants, solvents, temperature, the pH of the solutions and the other conditions of the reactions. The two free $-COOH$ groups present in the mononuclear complex $[(H_2fsadien)Co^{II}]$ can easily be silylated or lithiated leading to the isolation of di(trimethylsilylated) product, $[(Me_3Si)_2fsadien]Co^{II}$ (1) and dilithiated product $[(Li)_2fsadien]Co^{II}$ (2) (Scheme 1). These are very efficient precursors for the synthesis of different types of homo- and hetero-bimetallic complexes including new organo derivatives of titanium(IV), zirconium(IV) and tin(IV) ions.

All the reactions were carried out under dinitrogen atmosphere. The reactivity of the “O-SiMe₃” bond in the complex $[(Me_3Si)_2fsadien]Co^{II}$ (1) and “O-Li” bond in the complex $[(Li)_2fsadien]Co^{II}$ (2) with different substrates was studied leading to the synthesis of many new organotitanium(IV), organo-zirconium(IV), organotin(IV) and also many new homo- and hetero-binuclear complexes involving Ni-Co, Cu-Co, Pd-Co, Zn-Co, Co-Co, VO-Co and VO₂-Co pairs. Since the byproduct, Me_3SiCl is a low-

Table I—Characterisation data of the complexes

Comp.	Mol. wt Found (Calcd.)	Found (Calcd.), %				Solvent	Electronic spectra $\lambda_{\max}$, cm ⁻¹
		C	H	N	M		
[{(Me ₃ Si) ₂ (fsadien)}Co ^{II}] (1) C ₂₆ H ₃₅ N ₃ O ₆ Si ₂ Co	582 (600.69)	52.00 (51.99)	5.92 (5.87)	6.92 (6.99)	9.86 (9.81)	—	—
[{(π-C ₅ H ₅) ₂ Ti(fsadien)}Co ^{II}] (3) C ₃₀ H ₂₇ N ₃ O ₆ TiCo	639 (632.37)	57.00 (56.98)	4.26 (4.30)	6.69 (6.64)	Ti=7.76 (7.57) Co=9.46 (9.32)	—	—
[{(π-C ₅ H ₅) ₂ Zr(fsadien)}Co ^{II}] (4) C ₃₀ H ₂₇ N ₃ O ₆ ZrCo	705 (675.72)	53.29 (53.33)	4.11 (4.03)	6.18 (6.22)	Zr=13.62 (13.50) Co=8.90 (8.72)	—	—
[{(Me ₂ Sn)Co ^{II} (fsadien)] (5) C ₂₄ H ₂₉ N ₃ O ₆ Sn ₂ Co	740 (751.87)	38.37 (38.34)	3.91 (3.89)	5.63 (5.59)	Sn=31.64 (31.58) Co=7.91 (7.84)	—	—
[{(Ph ₂ Sn)Co ^{II} (fsadien)] (6) C ₄₄ H ₃₇ N ₃ O ₆ Sn ₂ Co	— (1000.15)	52.82 (52.84)	3.78 (3.73)	4.17 (4.20)	Sn=23.88 (23.74) Co=5.96 (5.89)	—	—
[Ni ^{II} (fsadien)Co ^{II}]2H ₂ O (7) C ₂₀ H ₂₁ N ₃ O ₈ NiCo	538 (549.04)	43.72 (43.75)	3.81 (3.86)	7.71 (7.65)	Ni=10.92 (10.69) Co=10.58 (10.73)	Nujol	16500; 19500; 25000
[Cu ^{II} (fsadien)Co ^{II}]3H ₂ O (8) C ₂₀ H ₂₃ N ₃ O ₉ CuCo	552 (571.90)	41.96 (42.00)	4.11 (4.05)	7.38 (7.35)	Cu=11.70 (11.11) Co=10.62 (10.30)	Nujol	16200; 16800
[Pd ^{II} (fsadien)Co ^{II}]2H ₂ O (9) C ₂₀ H ₂₁ N ₃ O ₈ PdCo	569 (596.76)	40.31 (40.25)	3.58 (3.55)	7.06 (7.04)	Pd=17.92 (17.83) Co=9.62 (9.88)	Nujol	16600; 20800; 24800
[Zn ^{II} (fsadien)Co ^{II}]H ₂ O (10) C ₂₀ H ₁₉ N ₃ O ₇ ZnCo	530 (537.72)	4.71 (44.67)	3.61 (3.56)	7.86 (7.81)	Zn=12.21 (12.16) Co=10.83 (10.96)	—	—
[Co ^{II} (fsadien)Co ^{II}]3H ₂ O (11) C ₂₀ H ₂₃ N ₃ O ₉ Co ₂	548 (567.29)	42.37 (42.34)	4.11 (4.09)	7.47 (7.41)	Co=20.98 (20.78)	Nujol	18000; 21000
[VO(fsadien)Co ^{II}]2H ₂ O (12) C ₂₀ H ₂₁ N ₃ O ₉ VCu	538 (557.28)	43.15 (43.11)	3.76 (3.80)	7.56 (7.54)	V=9.28 (9.14) Co=10.28 (10.57)	Nujol	14000; 17000; 19000
[UO ₂ (fsadien)Co ^{II}]2H ₂ O (13) C ₂₀ H ₂₁ N ₃ O ₁₀ UCo	742 (760.37)	31.63 (31.59)	2.82 (2.78)	5.56 (5.53)	U=31.72 (31.30) Co=7.66 (7.75)	—	—
[Cl(py)Fe ^{III} (fsadien)Fe ^{III} (py)Cl] (14) C ₃₀ H ₂₇ N ₅ O ₆ Cl ₂ Fe ₂	720 (736.18)	49.01 (48.95)	3.69 (3.70)	9.57 (9.51)	15.62 (15.17)	Nujol	12500; 13158; 15150 (sh); 16400 (sh); 17240 (sh); 18867; 19600; 20800 (sh); 24400; 25640
[(NO ₃) ₂ Co ^{III} (fsadien)Co(H ₂ O)] (15) C ₂₀ H ₂₁ N ₅ O ₁₄ Co ₂	693 (673.29)	35.72 (35.68)	3.11 (3.14)	10.46 (10.40)	17.76 (17.51)	Nujol	11100 (br); 12500; 15600 (sh); 16600 (sh); 17400 (sh); 26000

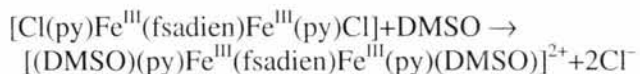


Scheme 2

boiling liquid and miscible with common organic solvents, it is easily removed by low-pressure distillation. In the case of (**2**), the byproduct LiCl can easily be removed. Hence, the new organometallic compounds and homo- and hetero-bimetallic complexes were obtained in very pure form and good yield (Scheme 2).

Elemental analyses and other characterisation data are shown in Table 1, which support their formulations. The molecular weights are also in good agreement with the theoretical values.

The complexes (**1**) and (**3**) to (**15**) are non-conducting in DMSO solvent ($\Lambda_M = 5\text{--}10 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)²². It is interesting to note that the value of Λ_M (in DMSO solution) of the complex (**14**) increases on prolonged standing, which after about 4 days attains a value of $59.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. This may be rationalized by the following equation, which shows the formation of 1:2 electrolyte in solution:



The general trend of the infrared spectra of the present metal complexes are comparable with those published previously with similar types of ligands¹⁹. The N-H stretch in the complexes (**1**) and (**3**) to (**15**) observed as medium-weak broad/or sharp peak in the region^{15,16} $3300\text{--}3100 \text{cm}^{-1}$. The $\nu(\text{C}=\text{N})$ in the complexes is observed around $1645\text{--}1630 \text{cm}^{-1}$ (which is $10 \pm 5 \text{cm}^{-1}$ lower than that observed in free ligand) and lend support for the coordination of imine nitrogen²³⁻²⁶.

The antisymmetric stretching vibration of the carboxylate group of $[(\text{Me}_3\text{Si})_2\text{fsadien}]\text{Co}^{\text{II}}$ (**1**) was

found at 1550cm^{-1} and phenolic $\nu(\text{C}-\text{O})$ at 1538cm^{-1} , which suggest a structure shown in Scheme 2 above. Similarly, carboxylate vibration of the complexes (**3**) to (**15**) observed at 1550cm^{-1} and phenolic $\nu(\text{C}-\text{O})$ at around 1560cm^{-1} suggesting binuclear structure with bridging phenolic oxygen²⁷ as shown in Scheme 2. Band assignments in the region $3100\text{--}3400 \text{cm}^{-1}$ and around 1600cm^{-1} are complicated by the presence of secondary amide and $\text{C}=\text{N}$ chromophoric groups in the present complexes. Besides, absorption of water also appears in $3100\text{--}3500 \text{cm}^{-1}$ range. All these complicate the proper interpretation of the bands in this region.

The infrared band for $\nu(\text{V}=\text{O})$ of the complex (**12**) is observed at 978cm^{-1} , which in all probability to support monomeric $\text{V}=\text{O}$ unit in this chelate²⁷. The infrared spectrum of the dioxouranium(VI) complex (**13**) shows an intense absorption at 898cm^{-1} attributable to the $\nu_{\text{as}}(\text{UO}_2)$ mode^{21,29}. The $\nu_{\text{s}}(\text{UO}_2)$ vibrations in the complex is expected to be weak in intensity, their presence could not be established unequivocally since the ligand absorbs in this region.

Coordination of pyridine in the complex (**14**) is demonstrated by the infrared absorption³⁰ band around 760cm^{-1} . Unidentate nature of NO_3^- (C_{2v}) in the complex (**15**) is demonstrated by the appearance of infrared bands^{31,32} at about $1490, 1250, 1030, 850$ and 755cm^{-1} .

The magnetic susceptibilities of all the isolated complexes were measured in the solid state at room temperature and the calculated magnetic moment values are recorded in Table 1. The complexes (**1**) and (**3**) to (**14**) are paramagnetic while the complex (**15**) is diamagnetic.

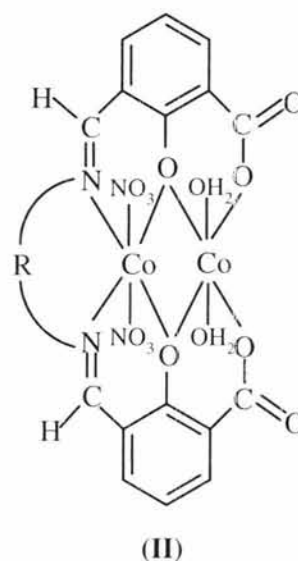
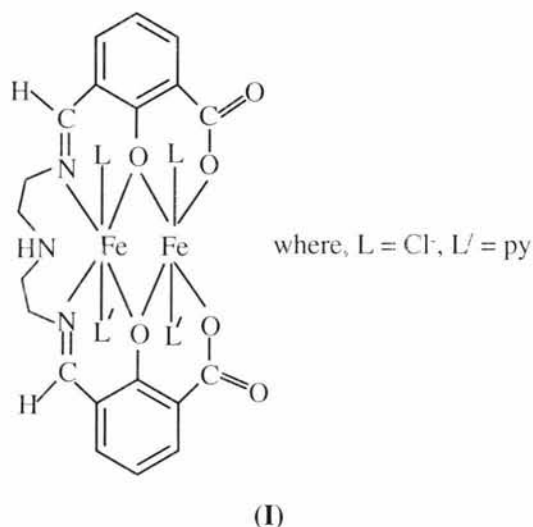
The di-iron(III) complex $[\text{Cl}(\text{py})\text{Fe}^{\text{III}}(\text{fsdien})\text{Fe}^{\text{III}}(\text{py})\text{Cl}]$ (**14**) has the room temperature magnetic moment value of 3.14 B.M. (per iron atom), which is lower than 5.2–6.0 B.M. expected for a iron(III) complex and suggestive of the presence of antiferromagnetic exchange interaction in the complex. Unfortunately, we could not study the temperature dependence of the magnetic susceptibilities and also the Mössbauer spectra of the chelates due to non-availability of such facilities in our laboratory.

Borer and Vanderbout³³ have reported the synthesis and structural predictions on the iron(III) triketonates having room temperature magnetic moments similar to those observed for the present di-iron(III) complex (**14**) under discussion. Kahn *et al.*³⁴ also studied the reactions of iron(III) ion with bis(3-carboxy)salicylidineimine (a Schiff base derived from ethylenediamine and 3-formylsalicylic acid) and their results are also comparable with the present results. However, presence of mixed-spin state of iron cannot be ruled out on the basis of the present data, which might also help to account the lower μ_{eff} values. Nevertheless, the following tentative structure (**I**) may be proposed for the di-iron(III) complex (**14**) following the work of Borer and Vanderbout³³ and Kahn *et al.*³⁴.

The electronic absorption spectrum of the di-iron complex (**14**) in nujol mull shows bands at 25,640, 24,400, 20,800 (sh), 19,600, 18,867, 17,240 (sh), 16,400 (sh), 15,150 (sh), 13,158 and 12,500 cm^{-1} . The absorption of the low-spin complexes occurs³⁵ in the range 14×10^3 – 16×10^3 cm^{-1} , which are absent in the high spin complexes. The spectral data of the present iron(III) complex (**14**) may be assigned following the well-known theoretical treatments on the subject^{36,37}.

The low intensity bands in the region 12,000–15,000 cm^{-1} may be ascribed to the spin forbidden $d-d$ transitions. The bands appearing above 25,000 cm^{-1} (with high intensity) may be assigned to charge transfer bands^{23,35,38,39} attributable to $d \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The electronic spectra of high and low-spin iron(III) complexes have been discussed thoroughly elsewhere^{23,35–41}. The electronic spectral data collected for the complex (**14**) support oxo-bridged binuclear complex formation, which is in line with the interpretation of magnetic moment value and infrared spectral data.

The di-cobalt(III) complex $[(\text{NO}_3)_2\text{Co}^{\text{III}}(\text{fsdien})\text{Co}^{\text{III}}(\text{H}_2\text{O})_2]$ (**15**) is found to be diamagnetic suggesting the formation of cobalt(III) complex. The UV-vis



spectrum of the complex in nujol mull shows several bands at 26,000, 17,400 (sh), 16,600 (sh), 15,600 (sh), 12,500, 11,100 (br) cm^{-1} . Appearance of two bands in the range 15,000–28,000 cm^{-1} is assignable to distorted octahedral structure of cobalt(III) complex (**15**) and plausible structure for the complex is shown in structure (**II**)^{42,43}.

All the bimetallic complexes from (**7**) to (**13**), synthesized in this study, are paramagnetic. It has been concluded that cobalt(II) ion occupies the N_3O_2 inner compartment attaining thereby a trigonal bipyramidal structure. In view of the fact that for a given ligand, corresponding stability constant of complexes of a bivalent ion of the first transition series are usually in the “Irving-Williams order”.

Therefore, it may so happen that during the synthesis of hetero binuclear complexes (7) to (9), nickel(II), copper(II) and palladium(II) might take up the inner N_2O_2/N_3O_2 compartment and cobalt(II) change its position from inner N_3O_2 compartment to outer O_2O_2 compartment. In this situation nickel(II) complex (7), copper(II) complex (8) and palladium(II) complex (9) may attain square planar geometry using inner N_2O_2 compartment. On the other hand, cobalt(II) may attain a pseudo-octahedral geometry by the addition of water molecules (see infrared spectral discussion above). Room temperature magnetic moment values (Table 1) may be discussed accordingly. As square planar nickel(II) and palladium(II) are diamagnetic, the magnetic moment values observed for the complexes (7) and (9) account the presence of pseudo-octahedral cobalt(II) ion (d^7 -system) in these complexes⁴⁴⁻⁴⁶. The electronic spectra of the complexes (7) and (9) in nujol mull show bands at 16,500, 19,400 and 25,000 cm^{-1} (sh) for (7) and 16,600, 20,800 and 24,800 cm^{-1} (sh) for (9). The band at 16,500 and 16,600 cm^{-1} may be attributed to the $^4A_{2g} \rightarrow ^4T_{1g}$ transition of cobalt(II) in an octahedral geometry⁴⁴⁻⁴⁶. The bands at 19,400 and 25,000 cm^{-1} assignable (tentatively) to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transition in a square planar field^{47,48} for the nickel(II) complex (7). A band at 20,800 cm^{-1} for the palladium(II) complex (9) is assigned to the $^1A_{1g} \rightarrow ^1A_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) transition in square planar geometry^{47,48}.

The magnetic moment value of 6.20 B.M. (total) for the complex (8) containing copper (II) and cobalt(II) ion suggest negligible metal-metal interaction^{44,45}. The electronic spectrum of (8) possesses two bands (16,200 and 16,800 cm^{-1}) which can be assigned to the $d-d$ transitions of the 'inside' copper(II) and the $^4T_{1g} \rightarrow ^4A_{2g}$ transition of cobalt(II) in an octahedral field⁴⁴⁻⁴⁶.

The complexes (10) and (13) show magnetic moment values of 4.45 and 4.49 B.M. respectively which tentatively suggest the presence of octahedral cobalt(II) in these complexes. Zinc(II) and dioxo-uranium(VI) being diamagnetic. Electronic spectral data also support this interpretation as discussed above.

The complex (11) has two absorption bands, one at 18,000 cm^{-1} and the other at 21,000 cm^{-1} . These could be assigned to $^4T_{1g} \rightarrow ^4A_{2g}$ and $^4T_{1g} \rightarrow ^4T_{2g}$ (P) transitions respectively, in an octahedral field⁴⁹.

Magnetic moment value (Table 1) per cobalt(II) ion also supports it.

The magnetic moment value of 6.1 B.M. (total) for the complex $[VO(fsadien)Co^{II}]2H_2O$ (11) may be considered as the presence of 5-coordinated d^1 -system and octahedral/five-coordinated d^7 -system. In absence of cryomagnetic data we are unable to say about the possible antiferromagnetic interactions between the two metal centres. Electronic spectral data also suggest the presence of square pyramidal⁵⁰ oxovanadium(IV) and trigonal bipyramidal or octahedral cobalt(II) ion in the complex (12) (λ_{max} for VO^{2+} : 14,000; 17,000 and 19,000 cm^{-1} suggesting square pyramidal structure; for electronic spectral data of Co(II) see above).

Acknowledgement

This work is financially supported by University of Kalyani. We are grateful to Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow for elemental analyses and some spectroscopic measurements. Facilities provided by the Department of Science and Technology, Govt. of India, New Delhi under Funds for Improvement in Science and Technology are also gratefully acknowledged.

References

- 1 Halcrow M A & Christou G, *Chem Rev*, 94 (1994) 2421.
- 2 Winpenny R E P, *Chem Soc Rev*, 27 (1998) 447.
- 3 Gheroghe R, Kravtsov V, Simonov Y A, Costes J-P, Journaux Y & Andruh M, *Inorg Chim Acta*, 357 (2004) 1613.
- 4 Tuna F, Patron L, Journaux Y, Andruh M, Plass W & Trombe J-C, *J Chem Soc Dalton Trans*, (1999) 539.
- 5 Utz D, Heinemann F W, Hampel F, Richens D T & Schindler S, *Inorg Chem*, 42 (2003) 1430.
- 6 Sakamoto M, Manseki K & Ōkawa H, *Coord Chem Rev*, 219-221 (2001) 379.
- 7 Nag J K, Das D & Sinha C, *Proc Indian Acad Sci (Chem Sci)*, 113 (2001) 11.
- 8 Ikeda K, Ohba M & Ōkawa H, *J Chem Soc Dalton Trans*, (2001) 3119.
- 9 Makode J T & Aswar A S, *Indian J Chem*, 43 A (2004) 2120.
- 10 Naik A D & Revankar V K, *Indian J Chem*, 43 A (2004) 1447.
- 11 Black D, Blake A J, Finn R L, Lindoy L F, Nezhadali, Rongnghi G, Tasker P A & Schröder, *Chem Commun*, (2002) 340.
- 12 Patole J, Padhye S, Padhye S, Newton C J, Anson C & Powell A K, *Indian J Chem*, 43 A (2004) 1654.
- 13 Verani C N, Rentschler E, Weyhermüller T, Bill E & Chaudhuri P, *J Chem Soc Dalton Trans*, (2000) 251.
- 14 Deoghoria S, Wong W T, Chandra S K, *Indian J Chem*, 42 A (2003) 1004.

- 15 Kavalakoglu E, Elmali A & Elerman Y, *Z Naturforsch*, 57 B (2002) 323.
- 16 Sharma K, Sharma M, Singh A & Mehrotra R C, *Indian J Chem*, 42A (2003) 493.
- 17 Ladavos A K, Kooli F, Moreno S, Skaribas S P, Pomonis P J, Jones W & Poncelet G, *Appl Clay Sci*, 13 (1998) 49.
- 18 Dey K, Bhowmick R, Sarkar S, Biswas S & Koner D, *Synth React Inorg Met-Org Nano Met Chem*, 35 (2005) 285.
- 19 Dey K, Sinha Roy A K, Mallik A K & Nandi K K, *Synth React Inorg Met-Org Chem*, 22 (1992) 145.
- 20 Duff J C & Bills E J, *J Chem Soc*, (1932) 1987.
- 21 Dey K, Biswas A K & Sinha Roy A K, *Indian J Chem*, 20A (1981) 848.
- 22 Geary W J, *Coord Chem Rev* 7 (1971) 81; Rosenblum M, Sauter J O & Jowells W G, *J Am Chem Soc*, 85 (1963) 1450.
- 23 Prince R H & Stoller D A, *Inorg Chim Acta*, 10 (1974) 89.
- 24 Prince R H, Stoller D A & Woolley P R, *Inorg Chim Acta*, 9 (1974) 51.
- 25 Drew M G B, Grinshaw J, Mellory P D A & Nelson S M, *J Chem Soc*, (1976) 1388.
- 26 Sharma B D, Roy K R, Sievers R E & Bailar J C (Jr), *J Am Chem Soc*, 86 (1964) 14.
- 27 Dey K & Maiti R K, *Indian J Chem*, 14 A (1976) 602.
- 28 Lever A B P, *Inorg Chem*, 4 (1965) 1042.
- 29 Cattalini L, Degetto S, Vidali M & Vigato P A, *Inorg Chim Acta*, 6 (1972) 173.
- 30 Torihara T, Ōkawa H & Kida S, *Bull Chem Soc Japan*, 51 (1978) 3236.
- 31 Galihouse B M, Livingstone S E & Nyholm R S, *J Chem Soc*, (1957) 4222; *J Inorg Nucl Chem*, 8 (1958) 75.
- 32 Bannister E & Cotton F A, *J Chem Soc*, (1960) 2276.
- 33 Borer L L & Vanderbout W, *Inorg Chem*, 18 (1979) 526.
- 34 Zarembowitch J, Kahn O, Saud J & Galy J, *Inorg Chim Acta*, 65 (1982) L 35.
- 35 Nishida Y, Oshio S & Kida S, *Bull Chem Soc Japan*, 50 (1977) 119.
- 36 Froster D & Goodgame D M L, *J Chem Soc*, (1965) 454.
- 37 Lever A B P, *Inorganic Electronic Spectroscopy*, 2nd Edn (Elsevier, Amsterdam) 1984.
- 38 Drew M G B, Grinshaw J, Mellory P D A & Nelson S M, *J Chem Soc*, (1976) 1388.
- 39 Rastogi D K, Dua S K, Rama V B & Sahni S K, *J Inorg Nucl Chem*, 40 (1978) 1323.
- 40 Dey K & De R L, *Z Anorg Allg Chem*, 402 (1973) 120.
- 41 Dey K, De R L & Roy K C, *Indian J Chem*, 10 (1972) 864.
- 42 Reiff W, Long G J & Baker W, *J Am Chem Soc*, 90 (1968) 6347.
- 43 Okamura M Y & Klotz D M, *Inorganic Biochemistry*, edited by G L Eichson (Elsevier, Amsterdam) 1975, Chap. II.
- 44 Yu Z W, Tao R J, Zhou X Y, Jim O M & Liao D Z, *Polyhedron*, 13 (1994) 951.
- 45 Ōkawa H, Nishida Y, Tanaka M & Kida S, *Bull Chem Soc Japan*, 50 (1977) 127.
- 46 Torihara N, Ōkawa H & Kida S, *Chem Lett*, (1979) 683.
- 47 Yamada S, Nishikawa H & Yoshida E, *Bull Chem Soc Japan*, 39 (1966) 994.
- 48 Larkworthy L F, Murphy J M & Philips D H, *Inorg Chem*, 7 (1968) 1936.
- 49 Zhou X Y, Yu Z W, Rao R J, Hau H X, Jin D M & Liao D Z, *Polyhedron*, 11 (1992) 3041.
- 50 Sakamoto M, Ohsavi M, Yamato K, Nakayama Y, Matsumoto A & Ōkawa H, *Bull Chem Soc Japan*, 65 (1992) 2514.