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

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Reaction of 3-formylsalicylic acid with diethylenetriamine yields the Schiff base \(N,N'-2,2'-\text{bist}(\text{aminomethyl})\text{methylamine(3-carboxysalicylidimine)})\text{(H}_2\text{fsadien)}\). The interaction of \(\text{H}_2\text{fsadien}\) with \(\text{CoCl}_2\cdot6\text{H}_2\text{O}\) produces \([\{\text{H}_2\text{fsadien}\}\text{Co}^3]\) and silylation and lithiation of which, having two free \(-\text{COOH}\) groups with \(\text{Me}_3\text{SiCl}\) or trimethylsilyl \(N,N'\)-diphenylurea (TDPU) and \(\text{LiOH}\), yields disilylated and dilithiated products, \([\{\{\text{Me}_3\text{Si}\}_2\text{fsadien}\}\text{Co}^3]\) and \([\{\{(\text{Li})_2\text{fsadien}\}\text{Co}^3]\) in good yield. This disilylated or dilithiated product smoothly reacts with \((\pi\text{C}_6\text{H}_5)\text{TiCl}_3\), \((\pi\text{C}_6\text{H}_5)\text{ZrCl}_2\), \(\text{Me}_3\text{SnCl}_3\), \(\text{Ph}_3\text{SnCl}_2\) and \(\text{MX}_2\text{nH}_2\text{O}\) (where \(M=\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Pd}^{2+}, \text{VO}^{2+}\) and \(X=\text{Cl}\) or \(\text{CH}_3\text{COO}^{-}\)) affording some homo- and hetero-binuclear complexes, including some organo-derivatives. The reactions of \(\text{H}_2\text{fsadien}\) with \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) and \(\text{Co(NO}_3\)_2\cdot6\text{H}_2\text{O}\) 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, \(\text{H}_2\text{fsadien}\), functions as tetradentate/heptadentate ligand using inner compartment of \(\text{N}_2\text{O}_2\) or \(\text{N}_2\text{O}_2\) donor set and outer compartment of \(\text{O}_2\text{O}_2\) donor set.

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In recent years, much attention has been given to the synthesis and characterization of multimetallic complexes in connection with their potential relevance to bioinorganic chemistry\textsuperscript{1}. The polydentate and compartmental ligands can form such multimetallic clusters by binding two or more metal centres in close proximity\textsuperscript{2-16}. 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 bimetallic complexes between the clay sheets of nanospecies via an exchange process and their catalytic activity was evaluated\textsuperscript{17}. 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 \((\text{H}_2\text{fsadien})\) derived by the condensation of 3-formysalicylic acid and diethylenetriamine. The ligand \((\text{H}_2\text{fsadien})\) can utilize all the donor sites to function as a compartmental ligand, the inner compartment being \(\text{N}_2\text{O}_2\) or \(\text{N}_2\text{O}_2\) donor ligand and outer compartment being \(\text{O}_2\text{O}_2\) donor ligand, affording homo- and hetero-bimetallic complexes. In continuation of our earlier work\textsuperscript{18,19} on the monoclinic complexes of \(\text{H}_2\text{fsadien}\), we synthesized di-trimethylsilylated and dilithiated products of mononuclear complex, \([\{\text{H}_2\text{fsadien}\}\text{Co}^3]\), namely, \([\{\{\text{Me}_3\text{Si}\}_2\text{fsadien}\}\text{Co}^3]\) and \([\{\{(\text{Li})_2\text{fsadien}\}\text{Co}^3]\). These new products smoothly react with \((\pi\text{C}_6\text{H}_5)\text{TiCl}_3\), \((\pi\text{C}_6\text{H}_5)\text{ZrCl}_2\), \(\text{Me}_3\text{SnCl}_3\), \(\text{Ph}_3\text{SnCl}_2\) and \(\text{MX}_2\text{nH}_2\text{O}\) (where \(M=\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Pd}^{2+}, \text{VO}^{2+}\) and \(X=\text{Cl}\) or \(\text{CH}_3\text{COO}^{-}\)) leading to many new bimetallic complexes. The reactions of \(\text{H}_2\text{fsadien}\) with \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) and \(\text{Co(NO}_3\)_2\cdot6\text{H}_2\text{O}\) 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-Formysalicylic acid...
was synthesized according to Duff and Bills. Diethylenetriamine was purchased from BDH and used as such. The ligand \( \text{H}_2\text{fsadien} \) was prepared by our previously reported method. The mononuclear complex \([\text{H}_2\text{fsadien}]\text{Co}^\text{II} \) was as reported by Dey et al.

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 hexa-chlorobutadiene; 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 osmotometrically.

### Preparation of the precursor complexes, \([\text{Me}_2\text{Si}_2\text{fsadien}]\text{Co}^\text{II} \) and \([\text{Li}_2\text{fsadien}]\text{Co}^\text{II} \)

The complex \([\text{H}_2\text{fsadien}]\text{Co}^\text{II} \) (0.456 g, 0.001 mol) was refluxed with \( \text{Me}_2\text{SICl} \) (0.217 g, 0.002 mol) in THF–hexane mixture (50 mL) in presence of stoichiometric amount of Et_3N 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 \([\text{H}_2\text{fsadien}]\text{Co}^\text{II} \) and trimethylsilyl \( \text{N},\text{N}'\)-diphenylurea (TDPU) (1:2 molar ratio in THF). It can also be prepared by refluxing (2 h) a mixture of the lithiated complex \([\text{Li}_2\text{fsadien}]\text{Co}^\text{II} \) (1 mol) with \( \text{Me}_2\text{SICl} \) (2 mol) in THF-hexane mixture. Lithiation of the mononuclear complex \([\text{H}_2\text{fsadien}]\text{Co}^\text{II} \) was carried out by refluxing a suspension of the complex with \( \text{LiOH} \) (1:2 molar ratio) in methanol or ethanol for 3 h. Colour: light-brown; m.p.: 169-171°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 7.8; \( \mu_{\text{eff}} \) (BM): 4.52.

### Preparation of the complexes \([\text{M}(\text{fsadien})\text{Co}^\text{II} ] \) \( \text{II} \text{H}_2\text{O} \), where \( \text{M}=\text{Ni(II)} \), n=2; (7); \( \text{M} =\text{Cu(II)} \), n=3, (8); \( \text{M} =\text{Pd(II)} \), n=2, (9); \( \text{M} =\text{Zn(II)} \), n=1, (10); \( \text{M} =\text{Co(II)} \), n=3, (11); \( \text{M} =\text{V(II)} \), n=2, (12); \( \text{M} =\text{Mn(II)} \), n=2, (13)

To a refluxed mixture of \([\text{H}_2\text{fsadien}]\text{Co}^\text{II} \) (0.456 g, 0.001 mol) in THF-toluene (80 mL) was added \( \text{M(OAc)}_2\text{H}_2\text{O} \) (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 \([\text{Me}_2\text{Si}_2\text{fsadien}]\text{Co}^\text{II} \) (1) with \( \text{MC}_3\text{H}_2\text{O} \). 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 \([\text{Li}_2\text{fsadien}]\text{Co}^\text{II} \) (2) with the appropriate metal salts in right stoichiometric ratios. Compound (7): Colour: brown; m.p. 278°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 8.88; \( \mu_{\text{eff}} \) (BM): 4.9 (total); compound (8): Colour: light-brown; m.p. 262°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 9.2; \( \mu_{\text{eff}} \) (BM): 6.2 (total); compound (9): Colour: brown; m.p. 298°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 8.9; \( \mu_{\text{eff}} \) (BM): 4.8 (total); compound (10): Colour: brown; m.p. 272°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 5.9; \( \mu_{\text{eff}} \) (BM): 4.45 (total); compound (11): Colour: reddish-brown; m.p. 262°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 7.9; \( \mu_{\text{eff}} \) (BM): 4.4 (per atom); compound (12): Colour: light-brown; m.p. 258°C (d); \( \Lambda_M \) (10^3 M in DMSO, \( \Omega^1 \text{cm}^2 \text{mol}^{-1} \)): 8.8; \( \mu_{\text{eff}} \) (BM): 6.1 (total); compound (13): Colour: yellow;
m.pt. 290°C (d); \( \Lambda_M \) (10^{-3} M in DMSO, \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \)): 9.4; \( \mu_{\text{eff}} \) (BM): 4.49 (total).

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

The Schiff base, \( \text{H}_4\text{fsadien} \) (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 \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) (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); \( \Lambda_M \) (10^{-3} M in DMSO, \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \)): 9.2; \( \mu_{\text{eff}} \) (BM): 3.14 (per atom).

\[ [(\text{NO}_3)_2\text{Co}^\text{III}(\text{fsadien})\text{Co}^\text{III}(\text{H}_2\text{O})_2] \text{(15)} \]

3-Formy salicylic acid (0.66 g, 0.004 mol) was dissolved in ethanol (30 mL) to which diethyleneetriamine (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 \( \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) (1.16 g, 0.004 mol) in ethanol (20 mL) was then added to the hot solution of the ligand \( \text{H}_4\text{fsadien} \) 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); \( \Lambda_M \) (10^{-3} M in DMSO, \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \)): 9.5; diamagnetic.

Results and Discussion

The ligand \( \text{H}_4\text{fsadien} \) can function as a compartmental ligand, the inner compartment being \( \text{N}_2\text{O}_2 \) or \( \text{N}_3\text{O}_2 \) donor ligand and outer compartment being \( \text{O}_2\text{O}_2 \) donor ligand, affording homo- and heterobimetallic 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 \( [(\text{H}_4\text{fsadien})\text{Co}^\text{III}] \) can easily be silylated or lithiated leading to the isolation of di(tri-methylsilylated) product, \( [(\text{Me}_3\text{Si})_2\text{fsadien}]\text{Co}^\text{III}] \) (1) and dilithiated product \( [(\text{Li})_2\text{fsadien}]\text{Co}^\text{III}] \) (2) (Scheme 1). These are very efficient precursors for the synthesis of different types of homo- and heterobimetallic 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 \( [(\text{Me}_3\text{Si})_2\text{fsadien}]\text{Co}^\text{III}] \) (1) and “O-Li” bond in the complex \( [(\text{Li})_2\text{fsadien}]\text{Co}^\text{III}] \) (2) with different substrates was studied leading to the synthesis of many new organotitanium(IV), organozirconium(IV), organotin(IV) and also many new homo- and hetero-bimetallic complexes involving Ni-Co, Cu-Co, Pt-Co, Zn-Co, Co-Co, VO-Co and VO-Co pairs. Since the byproduct, \( \text{Me}_3\text{SiCl} \) is a low-
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<td>N</td>
<td>M</td>
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<td>57.00</td>
<td>4.26</td>
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<td>673.29</td>
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<td>(17.51)</td>
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</table>
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 ($\Lambda_m$ 5–10 $\Omega^{-1}$ cm$^{-1}$)22. It is interesting to note that the value of $\Lambda_m$ (in DMSO solution) of the complex (14) increases on prolonged standing, which after about 4 days attains a value of 59.5 $\Omega^{-1}$ cm$^{-2}$ mol$^{-1}$. This may be rationalized by the following equation, which shows the formation of 1:2 electrolyte in solution:

$$[\text{Cl(py)Fe}^{III}(fsadien)Fe^{III}(py)C]+\text{DMSO} \rightarrow [\text{(DMSO)(py)Fe}^{III}(fsadien)Fe^{III}(py)(\text{DMSO})]^2^+2\text{Cl}^-$$

The general trend of the infrared spectra of the present metal complexes are comparable with those published previously with similar types of ligands. The N-H stretch in the complexes (1) and (3) to (15) observed as medium-weak broad/or sharp peak in the region 3300–3100 cm$^{-1}$. The v(C-O) in the complexes is observed around 1564–1630 cm$^{-1}$ (which is 10±5 cm$^{-1}$ lower than that observed in free ligand) and lends support for the coordination of imine nitrogen.

The antisymmetric stretching vibration of the carboxylate group of [(Me$_2$Si)$_2$fsadien]Co$^{II}$ (1) was found at 1550 cm$^{-1}$ and phenolic v(C-O) at 1538 cm$^{-1}$, which suggest a structure shown in Scheme 2 above. Similarly, carboxylate vibration of the complexes (3) to (15) observed at 1550 cm$^{-1}$ and phenolic v(C-O) at around 1560 cm$^{-1}$ suggesting binuclear structure with bridging phenolic oxygen as shown in Scheme 2. Band assignments in the region 3100-3400 cm$^{-1}$ and around 1600 cm$^{-1}$ are complicated by the presence of secondary amide and C=N chromophoric groups in the present complexes. Besides, absorption of water also appears in 3100-3500 cm$^{-1}$ range. All these complicate the proper interpretation of the bands in this region.

The infrared band for v(V-O) of the complex (12) is observed at 978 cm$^{-1}$, which in all probability to support monomeric V=O unit in this chelate. The infrared spectrum of the dioxouranium(VI) complex (13) shows an intense absorption at 898 cm$^{-1}$ attributable to the v$_{\nu 2}$ (U=O) mode. The v$_{\nu 1}$ (U=O) 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 absorption band around 760 cm$^{-1}$. Unidentate nature of NO$_2$ (C$_2$) in the complex (15) is demonstrated by the appearance of infrared bands at about 1490, 1250, 1030, 850 and 755 cm$^{-1}$.

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 [Cl(py)Fe$^{II}$(fsadien)-Fe$^{III}$(py)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 Vanderbout$^{33}$ 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)salicylidine (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 $\mu_{\text{eff}}$ values. Nevertheless, the following tentative structure (I) may be proposed for the di-iron(III) complex (14) following the work of Borer and Vanderbout$^{33}$ 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 occurs$^{35}$ in the range $14 \times 10^3 - 16 \times 10^3$ 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$^{23,35,39}$ attributable to $d$-$\pi^*$ and $\pi$-$\pi^*$ 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 [$(\text{NO}_3)_2\text{Co}^{III}$(fsadien)-Co$^{III}$(H$_2$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)$^{12,43}$.

All the bimetallic complexes from (7) to (13), synthesized in this study, are paramagnetic. It has been concluded that cobalt(II) ion occupies the $\text{N}_3\text{O}_2$ 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 \( \text{N}_2\text{O}_2\) compartment and cobalt(II) change its position from inner \( \text{N}_2\text{O}_2\) compartment to outer \( \text{O}_2\) compartment. In this situation nickel(II) complex (7), copper(II) complex (8) and palladium(II) complex (9) may attain square planar geometry using inner \( \text{N}_2\text{O}_2\) 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 (\( d^8\)-system) in these complexes\(^44\)-\(^46\). 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 \( ^4A_{2g} \rightarrow ^2T_{1g} \) transition of cobalt(II) in an octahedral geometry\(^44\)-\(^46\). 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 \( ^1A_{1g} \rightarrow ^1A_{2g} \) (\( d_{x^2-y^2} \rightarrow d_{z^2} \)) transition in square planar geometry\(^44\)-\(^46\).

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 field\(^44\)-\(^46\).

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 dioxouranium(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 \( ^1T_{1g} \rightarrow ^1T_{1g} \) (P) transitions respectively, in an octahedral field\(^49\). 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 \( [\text{VO(isatien)}\text{Co}^2]\text{H}_2\text{O} \) (11) may be considered as the presence of five-coordinated \( d^5 \)-system and octahedral/five-coordinated \( d^5 \)-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 pyramidal\(^30\) oxo-uranium(IV) and trigonal bipyramidal or octahedral cobalt(II) ion in the complex (12) (\( \lambda_{\text{max}} \) for \( \text{VO}^2- \): 14,000; 17,000 and 19,000 cm\(^{-1}\) suggesting square pyramidal structure; for electronic spectral data of Co(II) see above).

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