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Schiff-base Complexes of Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Characterization and Their Heterobimetallic Adducts with $TiCl_4$

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Schiff-base ligands (L), prepared from salicylaldehyde and ammonia or 1,2-dimethylbutylamine or cycloheptyl amine have been used into *in situ* reaction with the metal ions, Co(II), Ni(II) and Cu(II), in 2 : 1 molar ratio (ligand : metal ion) in ethanol or chloroform to yield metal complexes of the general formula ML_2. The mononuclear complexes were found to behave as Lewis bases in their reactions with the strong Lewis acid $TiCl_4$ to give discrete heterobinuclear base adducts of the type $ML_2{\cdot}TiCl_4$ or polymeric species of the type $[ML_2{\cdot}TiCl_4]_n$, $n > 2$. The complexes yielded have been characterized by their physical and spectroscopic means, and tentative structures have been suggested accordingly.

INTRODUCTION

There is a considerable interest in the coordination chemistry of Schiff-bases with various metal ions, partially due to their capability of acting as multidentate N—N and N—O donors with the formation of mono- or poly-nuclear complexes[1–3]. In addition to their interesting ligational properties, both Schiff-bases and their complexes have important biological and industrial applications[4–7]. Hence, a large portion of the coordination chemistry of Schiff-bases with transition and non-transition metal ions have been reported very recently; their complexes with, *e.g.*, vanadium(IV) and titanium(IV)[8], cobalt(II) and copper(II)[9], zinc(II)[10] and organotin(IV)[11]. As a group of researchers, we took part in the chemistry of Schiff-bases and their coordiantion complexes, as they are rather popular ligands, and several articles have been published so far on their chemistry and their biological activity[12–15].

In this work, we present the synthesis of a new type of Schiff-bases derived from salicylaldehyde and aliphatic amines, *i.e.*, ammonia, 2,3-dimethylbutylamine and cycloheptylamine (Scheme 1) and to use them into *in situ* reactions with Co(II), Ni(II) and Cu(II) metal ions and to react the so formed complexes with $TiCl_4$. To the best of our knowledge and according to the available literature, this work has not been previously attempted.

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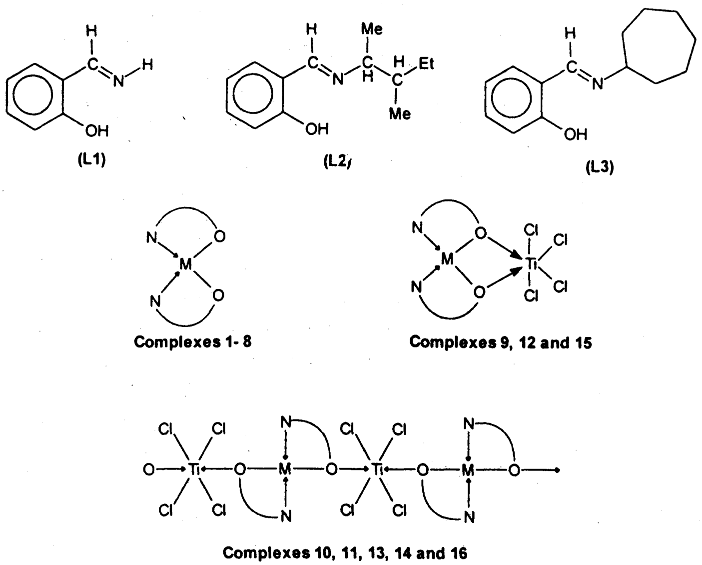

Scheme 1. The Schiff-bases (L1–L3) and the suggested structures of their metal ion complexes and adducts with $TiCl_4$.

EXPERIMENTAL

All the chemicals were of AnalaR grade (BDH, Aldrich or Fluka) and used as such without further purification. The complexes were analysed for carbon, hydrogen and nitrogen using 1106 (Carlo Erba) microanalyser. Infrared absorption spectra were recorded on a Unicam SP-2000 spectrophotometer as CsI discs in the range 4000–200 cm^{-1}. The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker B.M. 6 instrument. The electronic spectra were recorded on a Shimadzu UV/Vis spectrophotometer (range: 200–1100 nm), model 160 Koyoto (Japan) using acetonitrile as a solvent. Conductivity measurements were carried out on 10^{-3} M solutions of the complexes in acetonitrile at room temperature on a digital conductivity meter, model 4070 (Jenway).

The Schiff-bases L1–L3 (Scheme 1) were prepared *in situ* due to their unstability, and used immediately in the complexation with the metal salts.

Preparation of monouclear complexes ML_2

M = Co, L = L2 or L3; M = Cu, L = L3

These were prepared following the method of Sacconi and Ciampolini[16] used for the preparation of isopropyl-, sec.- and tert. butyl-salicylaldimine copper(II) complexes as follows:

Salicylaldehyde (40 mmol, 4.18 mL) in ethanol (20 mL) was added with continuous stirring to the hydrated metal acetate (20 mmol). The reaction mixture was then allowed to stand in a water bath for *ca.* 1 h and then cooled to room temperature. The resulting solid was filtered off, washed with small portions of cold ethanol and dried *in vacuo*. The solid thus formed was redissolved in ethanol (20 mL) and to this was added the corresponding amine (50 mmol) and the mixture was heated under reflux until a complete precipitation of the product was achieved (*ca.* 1.5 h). The solid was filtered off, washed with small portions of ethanol and dried under vacuum for several hours.

M = Co, Ni, Cu, L = L1; M = Ni, L = L2 or L3

These were prepared following the method of Doraswamy and Bhattacharya[17] with some modification, as follows:

Salicylaldehyde (38 mmol, 4.00 mL) was added with continuous stirring to the hydrated metal chloride (18.8 mmol) in a minimum amount of ethanol. The corresponding amine (50 mmol) was then added to the resulting mixture until the pH became 5.5 [and 6.5 for $Ni(L3)_2$]. The mixture was shaken vigorously until the solid product separated off. The solid was then filtered off, washed with water and 50% ethanol and dried *in vacuo*.

Preparation of heterobinuclear complexes $[ML_2{\cdot}TiCl_4]_n$, n = 1 and > 2

A solution of $TiCl_4$ (8.4 mmol, 1.2 mL) in chloroform (12 mL) was added dropwise with vigorous stirring to a solution of the Schiff-base complex ML_2 (8.4 mmol) in a minimum amount of chloroform. The resulting mixture was then allowed to stand aside until complete evaporation of the chloroform. The oily material thus formed was dissolved in methanol and acetone (or petroleum spirit in the case of $Co(L2)_2$] (10 mL) was added dropwise with stirring until complete precipitation of the product. The solid was filtered off, washed with acetone and dried in vacuum.

RESULTS AND DISCUSSION

The physical properties of the mononuclear complexes ML_2 and their heterobimetallic adducts are listed in Table-1, the IR data are listed in Table-2, and the electronic spectra and molar conductivities of the complexes are listed in Table-3. The elemental composition of the complexes prepared is ML_2 and corresponds to 1 : 2 (metal ion : ligand) molar ratio while for the adducts it is $[ML_2{\cdot}TiCl_4]_n$ and corresponds to 1 : 1 ($ML_2{\cdot}TiCl_4$) molar ratio (M = Co, Ni, Cu; n = 1 or > 2).

Infrared spectra: From Table-2, the medium to strong band appearing at 1610–1595 cm^{-1} in the mononuclear complexes **1–8** proves very clearly that the Schiff-bases had been formed during their *in situ* reactions with the metal salts, since this band is attributed to ν(C=N) of the Schiff-base[17, 18]. This band remains almost constant on going to the bimetallic adducts **9–16** (Scheme 1).

The total disappearance of the band at *ca.* 3430 cm^{-1}, which is attributed to ν(O—H), from the Schiff-base complexes, is a very good indicator to the deprotonation of the phenolic (OH) and the remaining oxygen of the Schiff-base would then bound in a trivalent fashion in the adducts **9–16**. However, the phenolic ν(C—O) band appearing at 1545–1535 cm^{-1} in the mononuclear complexes **1–8** has been shifted to a higher frequency (1568–1560 cm^{-1}) upon forming the adducts **9–16** which means that the Lewis acid $TiCl_4$ had been coordinated to the phenolic oxygen[19, 20]. Additional support to this is the appearance of a new band at 740–715 cm^{-1} which is attributed to ν(M—O—Ti) frequency[21]. The broad absorption band attributable to ν(N—H) for the complexes derived from the Schiff-base (L1), *i.e.*, complexes **1, 4** and **7** appearing at *ca.* 3320 cm^{-1} remains almost constant on going to the adducts **9, 12** and **15**[17], which means that the NH group had no contribution in forming the complexes. The stretching frequencies appeing at 440–415 cm^{-1} and 475–450 cm^{-1} for the complexes **1–16** are attributed to ν(M—N) and ν(M—O), respectivley, whereas the bands appearing at 505–495 cm^{-1} and 492–465 cm^{-1} for the complexes **9–16** are attributed to ν(Ti—Cl) and ν(Ti—O), respectively. These bands represent additional evidence that both the mononuclear complexes and their $TiCl_4$-adducts had been formed[22].

Magnetic measurements and electronic spectra

Cobalt complexes: The mononuclear cobalt complexes **1, 2** and **3** and their adducts **9, 10** and **11** (Scheme 1) showed magnetic properties with μ_{eff} values ranging between 4.16 to 4.38 B.M. (Table-1), which are in good agreement with Co(II) complexes having tetrahedral configuration. The strong electronic spectral bands of all cobalt complexes appearing at 15780–13570 cm^{-1} (Table-3) are attributed to the transitions $^4A_2(F) \rightarrow {}^4T_1(P)(\nu_3)$ in the tetrahedral structures[23, 24]. It should be noted that all cobalt complexes, except complex **1**, showed more than one band for the transitions (ν_3). This was discussed by Sacconi and Ciampolini[17] for similar cobalt complexes to be due to the distortion occurring in the tetrahdedral configuration around cobalt. The transitions ν_1 and ν_2 usually appeared in the near IR, but could not be seen because the spectrometer we used does not exceed the range 200–1100 nm.

TABLE-1
PHYSICAL PROPERTIES OF THE SCHIFF-BASE COMPLEXES AND THEIR ADDUCTS WITH $TiCl_4$

Com. Seq.	Complex[a]	Colour	m.p. (°C)	% Anlaysis, found (calcd.)			μ_{eff} (B.M.)
				C	H	N	
1	$Co(L1)_2$	yellow	350[b]	55.9 (56.1)	4.1 (4.0)	9.3 (9.4)	4.24
2	$Co(L2)_2$	brown	80	66.3 (66.8)	7.8 (7.7)	5.9 (6.0)	4.38
3	$Co(L3)_2$	brown	118	68.0 (68.4)	7.4 (7.3)	5.6 (5.7)	4.25
4	$Ni(L1)_2$	green	340[b]	55.9 (56.2)	4.1 (4.0)	9.2 (9.4)	3.75
5	$Ni(L2)_2$	green	337[b]	66.2 (66.8)	7.8 (7.7)	5.9 (6.0)	3.90
6	$Ni(L3)_2$	green	340[b]	68.0 (68.5)	7.4 (7.3)	5.6 (5.7)	dia.[c]
7	$Cu(L1)_2$	green	350[b]	55.0 (55.3)	4.0 (4.0)	9.2 (9.2)	1.89
8	$Cu(L2)_2$	brown	156	67.5 (67.8)	6.2 (6.0)	5.6 (5.7)	1.91
9	$Co(L1)_2{\cdot}TiCl_4$	green	103	33.6 (34.4)	2.5 (2.5)	5.6 (5.7)	4.26
10	$[Co(L2)_2{\cdot}TiCl_4]_n$	gray	344[b]	46.9 (47.5)	5.5 (5.5)	4.5 (4.6)	4.33
11	$[Co(L3)_2{\cdot}TiCl_4]_n$	brown	340[b]	48.9 (49.4)	5.3 (5.3)	4.0 (4.1)	4.16
12	$Ni(L1)_2{\cdot}TiCl_4$	bright yellow	342[b]	33.8 (34.4)	2.5 (2.5)	5.6 (5.7)	1.69
13	$[Ni(L2)_2{\cdot}TiCl_4]_n$	brown	355[b]	47.2 (47.5)	5.5 (5.5)	4.2 (4.3)	1.67
14	$[Ni(L3)_2{\cdot}TiCl_4]_n$	bright yellow	320[b]	48.9 (49.4)	5.3 (5.3)	4.0 (4.1)	dia.[c]
15	$Cu(L1)_2{\cdot}TiCl_4$	green	334[b]	33.7 (34.1)	2.5 (2.4)	5.6 (5.7)	1.77
16	$Cu(L3)_2{\cdot}TiCl_4$	bright yellow	335[b]	48.7 (49.0)	5.5 (5.5)	4.0 (4.1)	1.86

[a] For L1, L2 and L3, see Scheme 1.
[b] Complexes melt with decomposition.
[c] Complexes have no magnetic properties (diamagnetic).

TABLE-2

SELECTED IR BANDS[a] (cm^{-1}) OF THE COMPLEXES

Com. Seq.	ν(C=N)	ν(C—O)	ν(M—O)[b]	ν(M—N)	ν(M—O—Ti)	ν(Ti—Cl)	ν(Ti—O)[b]	ν(N—H)
1	1605 s	1540 m	455 m	435 s				3315 br
2	1595 s	1542 m	475 br	440 s				
3	1610 s	1540 m	472 br	415 m				
4	1605 s	1535 s	460 w	430 m				3328 br
5	1610 s	1540 m	463 br	430 w				
6	1605 m	1535 m	460 br	420 w				
7	1600 m	1538 m	470 br	430 br				3328 br
8	1610 m	1540 m	475 br	435 br				
9	1605 s	1565 m	455 br	430 m	755 w	495 br	480 w	3315 m
10	1595 s	1568 m	475 m	435 m	735 w	495 w	465 w	
11	1601 s	1560 m	460 m	420 m	730 w	490 br	475 w	
12	1605 s	1560 m	462 m	425 w	760 m	505 w	485 w	3320 br
13	1605 s	1565 m	465 m	430 w	755 m	495 w	470 w	
14	1610 s	1560 m	450 m	415 m	740 m	500 w	475 w	
15	1610 s	1562 m	460 m	425 m	720 m	500 w	470 m	3325 br
16	1610 s	1565 m	475 m	430 m	760 m	505 m	492 w	

[a] For IR spectra, s = strong; m = medium; w = weak and br = broad, bands.

[b] Absorption bands for M—O and Ti—O frequencies could be reversed.

TABLE-3

ELECTRONIC SPECTRA AND MOLAR CONDUCTIVITY OF THE COMPLEXES (IN CH_3CN)

Complex Seq.	Spectra (cm^{-1})	Λ_M mol^{-1} cm^2 ohm^{-1}
1	14225, 29320	9.2
2	13570, 14520, 30030, 33100	8.5
3	14025, 14770, 29800	7.0
4	4490*, 9780, 15820, 31010	7.4
5	4485*, 9768, 15765, 32300	7.5
6	14320, 15820, 16010, 22100, 34000	8.6
7	15050, 31010	7.9
8	14380, 15120, 29870	10.0
9	14285, 14770, 15780, 29300	12.1
10	13990, 14490, 14890, 31390	11.8
11	13890, 14380, 15380, 29800	14.1
12	9890, 15870, 16200, 21780, 33890	6.2
13	9790, 15680, 15980, 22350, 34010	12.0
14	14900, 15760, 21850, 32000, 34100	11.8
15	14020, 29800	7.2
16	14200, 31200	9.9

*Calculated bands (not observed) assigned to $^3T_1(F) \rightarrow {}^3T_2(F)$

Nickel complexes: The nickel complexes **4** and **5** (Scheme 1) showed magnetic properties with μ_{eff} values of 3.75 and 3.90 B.M., respectively, which are assigned to nickel(II) complexes with tetrahdedral structures. These values are somehow higher than the expected ones for Ni^{2+} complexes, probably due to some orbital contributions, whereas complex (6) appeared to be diamagnetic with, most possibly, square-planar configuration around nickel. The electronic spectra of these complexes were in good agreement with the suggested structures, in which complexes **4** and **5** showed two bands at 9768 and 9780 cm^{-1}, and 15765 and 15820 cm^{-1} (Table-3) which are attributed to the transitions $^3T_1(F) \rightarrow {}^3A_2(F)(\nu_2)$ and $^3T_1(F) \rightarrow {}^3A_2(F)(\nu_3)$, respectively, which is again assigned to a tetrahedral structure around nickel. The transitions $^3T_1(F) \rightarrow {}^3T_2(F)(\nu_1)$ were calculated for complexes **4** and **5** and found to be 4490 and 4485 cm^{-1}, respectively[25, 26]. The complex **6** showed a splitted band at 14320, 15820 and 16010 cm^{-1} which is attributed to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ in the square-planar configuration[27]. The binuclear nickel adduct **14** has electronic spectral bands at 14900 and 15760 cm^{-1} due to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, and a single band at 21850 cm^{-1} due to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$. The adducts **12** and **13** showed μ_{eff} value of 1.69 and 1.67 B.M., respectively indicating the presence of mixed properties for both the tetrahedral and the square-planar configurations[28]. This argument was supported by the electronic spectra obtained for these adducts (Table-3). Hence, the first electronic band in both adducts which appeared at 9890 and 9790 cm^{-1}, respectively, is attributed to the transitions $^3T_1(F) \rightarrow {}^3A_2(F)(\nu_2)$ in the tetrahedral structure (similar to those for complexes **4** and **5**). Also two bands for each adduct appeared at 15870 and 16200 cm^{-1} and 15680 and 15980 cm^{-1}, respectively, usually attributed to the transitions $^3T_1(F) \rightarrow {}^3A_2(F)(\nu_3)$ is the tetrahedral structure and also attributed to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ in the square-planar structure[28] [the first transitions being similar to those for complexes **4** and **5** while the second transitions being similar to those for complexes **6** and **14**]. The third band for adducts **12 and 13**, appearing at 21780 and 22350 cm^{-1} is attributed to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$ in the square-planar structure (similar to those for complexes **6** and **14**). As a conclusion, it seems very likely that adducts **12** and **13** possess both the tetrahedral and the square planer structures, in the solid state (the magnetic measurements) and in solution (the electronic spectra), in such random proportion that could not be determined easily.

Copper complexes: The mononuclear copper complexes **7** and **8** and their $TiCl_4$-adducts **15** and **16** gave μ_{eff} values of 1.77–1.91 B.M. (Table-1), assigning the presence of a single electron in the Cu^{2+} configuration with some orbital contributions for complexes **7, 8** and **16**. The electronic spectra of these complexes (Table-3) showed similar observations concerning their structures. For instance, the electronic spectra of these complexes were similar to each other and appeared in the range 14020 to 15120 cm^{-1} with a splitting occurring in the case of complex

8. However, this band is attributed to the transitions $^3B_{1g} \rightarrow E_g$ in the square-planar structure[29], since the tetrahedral structure does not, usually, give electronic band in the range 20000–10000 cm^{-1}.

Conductivity measurements

All the mononuclear complexes and their $TiCl_4$-adducts showed conductivity values ranging between 6.2–14.1 $mol^{-1}\ cm^2\ ohm^{-1}$ (Table-3) in acetonitrile at room temperature, indicating non-conductive species, since 1 : 1 conductive species usually give conductivity ranging between 120–160 $mol^{-1}\ cm^2\ ohm^{-1}$ in the same solvent.[30]

Structural elucidation

From the data obtained above, it is unambiguous now that mononuclear complexes **1–8** possess either the tetrahdral or square-planar structures. Their adducts with $TiCl_4$ **9–16** may be divided into two categories according to their solubility; the adducts **9, 12** and **15** possess the discrete heterobimetallic shape, while the adducts **10–14** and **16** possess the polymeric heterobimetallic shape, since they are insoluble in any of the solvents, CH_2Cl_2, C_2H_5OH, CH_3COCH_3, CH_3NO_2 and even DMSO, but only slightly soluble in CH_3CN. According to this, one can suggest the structures drawn in Scheme 1 for both types of complexes.

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