

INTRODUCTION

Day by day Schiff bases and their complexes are more frequently applied for the betterment of human welfare. The importance of the Schiff bases complexes is due to their versatile nature. Literature survey shows that many Schiff bases complexes exhibit biological activities⁽¹⁻³⁾. These biological activities were attributed to the formation of stable chelates with the metal ions present in the cell⁽⁴⁾. In addition, Schiff bases and their metal complexes used in many fields such as oxidation catalysis⁽⁵⁾, electrochemistry⁽⁶⁾. On the industrial scale, they have wide range of applications such as dyes and pigments⁽⁷⁾. Another area of application of these compounds is analytical chemistry where some of Schiff bases are used as ligand in complexometry topic⁽⁸⁾. The presence of azomethine group in Schiff bases made them acting as suitable ligands towards metal ions and forming different coordination compounds^(9,10). The aim of the present work is to prepare a new Schiff base from 2,3-butanedione and hexylamine and then preparation of new complexes by reacting this ligand with Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions. Tentative structures have been proposed on the basis of analytical, spectral, magnetic and conductance measurements.

EXPERIMENTAL

1. Chemicals :

All chemicals as reagent grade (BDH and Fluka) were used as supplied such as CrCl₃.6H₂O, MnCl₂.4H₂O, FeCl₂.4H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O.

2. Analysis and physical measurements :

The metal contents were determined according to the standard procedure⁽¹¹⁾. Melting points were determined by using Richerk Jung Heizbank melting point apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10⁻³M of the complexes in dimethylformamide (DMF) at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 cm⁻¹ range using KBr disc. Electronic spectra were recorded on a Shimadzu 160 spectrophotometer in DMF at 25°C for 10⁻³M solution of the complexes using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Faraday method at room temperature using a Bruker BM6 apparatus.

3. Preparation of the ligand:

An ethanolic solution of 2,3-butanedione (0.861 g, 0.01 mol) was added to an ethanolic solution of hexylamine (2.024 g, 0.02 mol) and refluxed for ~8 hours followed by concentration of the solution, the precipitate was separated by filtration, washed with ethanol and then air-dried (m.p. = 147c⁰).

4. Preparation of the complexes:

All the complexes were prepared by the same general method using the template synthesis⁽¹²⁾ as following :

A mixture of 2,3-butanedione (0.02 mol), hexylamine (0.04 mol) in ethanol was added to an ethanolic solution of metal chlorides (0.01 mol). The mixture of reactants was refluxed for ~ 12 hours. The excess of the solvent was then distilled. The resulting compounds were filtered off, washed with ethanol and then air-dried.

RESULTS AND DISCUSSION

The complexes of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with the ligand appear as powders. They are not soluble in most organic solvents, such as ethanol and acetone but soluble in DMF. The molar conductance of the complexes in DMF are in the range 12-27 ohm⁻¹ cm² mol⁻¹ (Table 1) indicating a non-electrolytic nature, while the chromium complex ($\Lambda_M = 87 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicating a 1:1 electrolytic nature⁽¹³⁾.

Table (1): Analytical and some physical properties of the complexes

Complex	Colour	m.p. °c	Yield %	% Metal	Λ_M ohm ⁻¹ cm ² mol ⁻¹
				Found (Calcd.)	
[Cr(L) ₂ Cl ₂]Cl	Dark Brown	234	73	8.78 (8.29)	87
[Mn(L) ₂ Cl ₂]	Pale Yellow	221	69	8.07 (8.73)	18
[Fe(L) ₂ Cl ₂]	Brown	196	78	9.22 (8.84)	12
[Co(L) ₂ Cl ₂]	Pale Brown	213	59	9.63 (9.29)	13
[Ni(L) ₂ Cl ₂]	Kaki	184	62	8.99 (9.26)	27
[Cu(L) ₂ Cl ₂]	Dark Green	177	70	10.37 (9.95)	19

The IR spectra of the ligand exhibits a band at 1624 cm⁻¹ assignable to $\nu(\text{C}=\text{N})$ stretching vibration. In all the complexes, no peaks corresponding to unreacted primary amines or carbonyl groups were

present. All the complexes show a absorption band in the region 1597-1610 cm^{-1} (Table 2), attributable to the azomethine groups. This observation indicates the involvement of the nitrogen atom of the azomethine $\nu(\text{C}=\text{N})$ group in the complexes and also indicating that the $\text{C}=\text{N}$ band of the ligand was shifted to a lower frequency by about 14-27 cm^{-1} , suggesting the coordination through N atom of the azomethine group⁽¹⁴⁻¹⁷⁾. The presence of bands at 416-457 cm^{-1} in all the complexes (Table 2), originates from the $\nu(\text{M}-\text{N})$ (azomethine) vibration and substantiates this coordination. The coordination of the chloride ions to the metals could not be inferred from the infrared absorption spectra since M-Cl band located beyond the limits of our instrument (at the far infrared spectra) while the chromium (III) complex show a new band located at 574 cm^{-1} for chloride ion. The position of this band suggested the ionic nature and the non-involvement of this group in coordination⁽¹⁸⁾, and therefore remained outside the coordination sphere. This observation were in good agreement with the conductance value of the chromium (III) complex and which have been supported the given formula for this complex.

The electronic spectrum of the chromium (III) complex has two bands, one at 13717 cm^{-1} and the other at 25252 cm^{-1} , which are assigned to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ transitions, respectively. The transition ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ is usually not observed in the visible region due to involvement of the charge transfer band at 34965 cm^{-1} . The observed magnetic moment value of 3.74 BM and the electronic spectrum of the complex support the octahedral structure for the complex⁽¹⁹⁾. The high spin d^5 Mn(II) octahedral complex (μ_{eff} 5.91 BM) exhibits complex spin forbidden transitions from the ${}^6\text{A}_{1g}$ ground state. The Mn(II) complex shows four absorptions characteristic of electronic transitions to the excited states ${}^4\text{T}_{1g}({}^4\text{G})$, ${}^4\text{A}_{1g}({}^4\text{G})$, ${}^4\text{E}_g({}^4\text{D})$ and ${}^4\text{T}_{1g}({}^4\text{P})$ at 19531, 24937, 28490 and 32051 cm^{-1} , respectively. These values and also the magnetic moment value for Mn(II) complex were well in accord with those having octahedral structure with five unpaired electrons^(19,20). The electronic spectrum of the iron(II) complex shows absorption band at 11947 cm^{-1} assignable to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition consistent with an octahedral geometry for iron(II) complex⁽²¹⁾. The room temperature magnetic moment (5.07 BM) corresponds to an octahedral geometry of iron(II)^(21,22). The cobalt (II) complex has two bands, one at 20618 cm^{-1} and the other at 15698 cm^{-1} , which are assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition, respectively. From the position of these bands and the magnetic moment value of 4.68 BM, the geometry of the cobalt complex suggested the geometry of the complex as octahedral^(19,23). d-d transitions of the nickel complex at 16025 and 23809 cm^{-1} , corresponding to the transition of ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and

${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in the octahedral field were noted. Magnetic moment value of 2.93 BM supports the hexacoordinated configuration of the nickel complex^(19,24). The spectrum of copper(II) complex showed a broad band at 17857-19531 cm^{-1} , which indicates that this complex is a distorted octahedral. The magnetic moment of 1.92 BM supports the geometry of the complex⁽²⁵⁾.

Table (2): Important I.R spectral bands (cm^{-1}), magnetic moments and electronic spectral data of the complexes

Complex	ν (C=N)	ν (M-N)	μ_{eff} (B.M)	d-d transitions (cm^{-1})
[Cr(L) ₂ Cl ₂]Cl	1597	420	3.74	13717 , 25252
[Mn(L) ₂ Cl ₂]	1605	416	5.91	19531 , 24937 , 28400 , 32051
[Fe(L) ₂ Cl ₂]	1604	425	5.07	11947
[Co(L) ₂ Cl ₂]	1603	424	4.68	15698 , 20168
[Ni(L) ₂ Cl ₂]	1604	441	2.93	16025 , 23809
[Cu(L) ₂ Cl ₂]	1610	457	1.92	17857- 19531

CONCLUSION

Based on the reported results, it may be concluded that the ligand acts as a bidentate molecule and the nitrogen of the azomethine group takes part in coordination. All the complexes are found to be mononuclear. The coordination number six is attained by coordination with the two chloride ions. Based on the physicochemical and the spectral studies; the tentative structures suggested for the complexes are shown in figures 1 and 2.

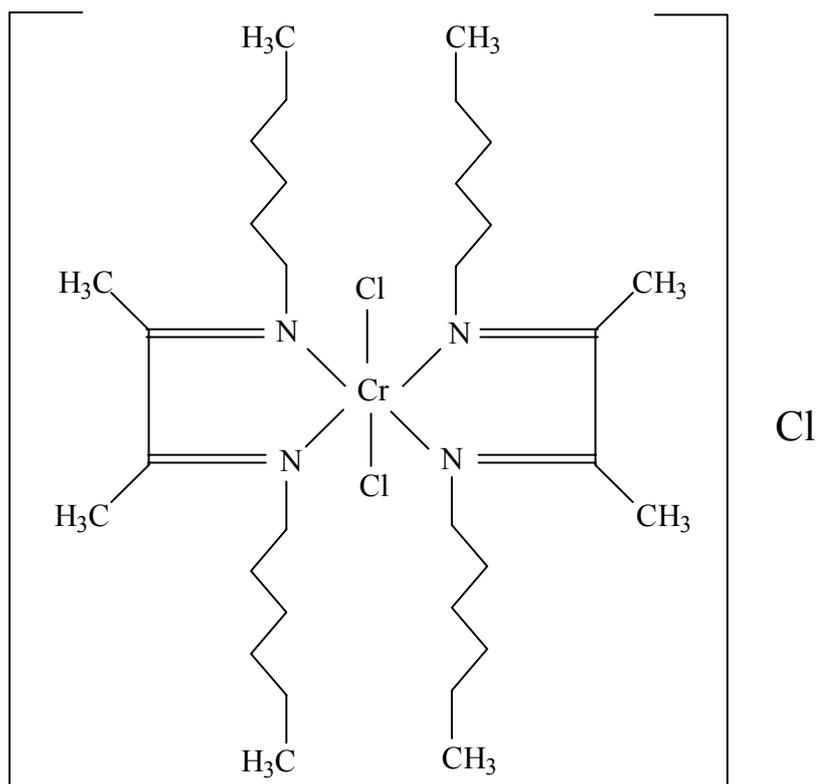


Fig.1 : Suggested structure of the chromium(III) complex

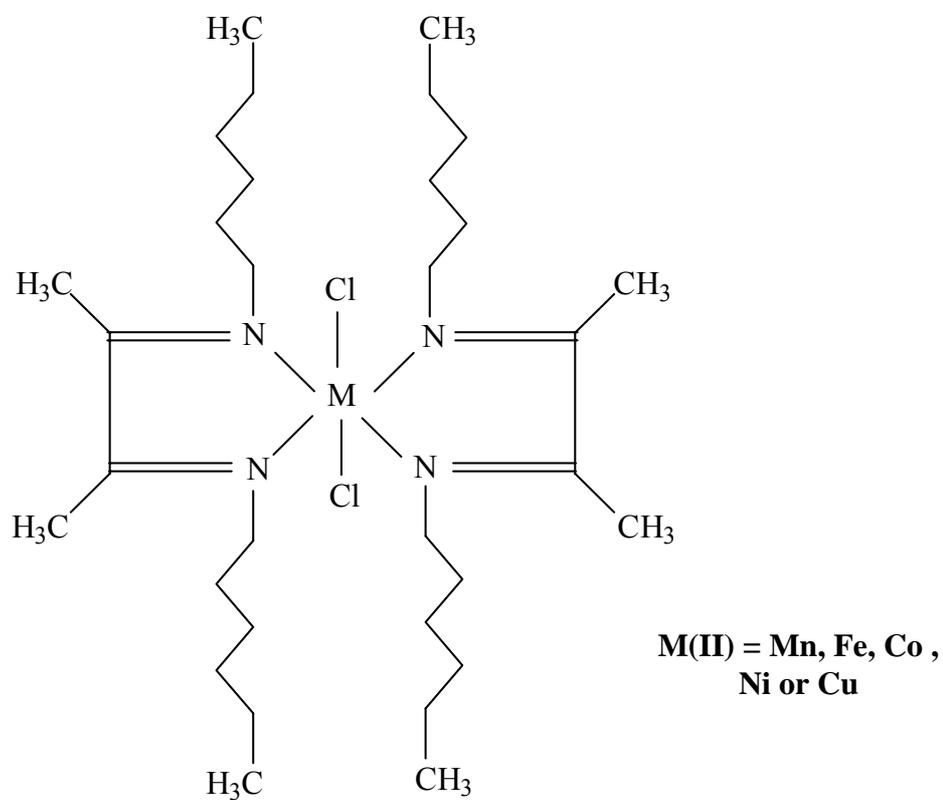


Fig.2: Suggested structure of the complexes

REFERENCES

1. Panchai P.K., Pansuriya P.B. and Patel M.N., *J. Enzy. Inhib. Med. Chem.*, 21(4): 453-458 (2006).
2. Gupta M.K., Singh H.L., Varshney S., and Varshney A.K., *Bioinorg. Chem. and Appl.*, 1(3-4): 309-320 (2003).
3. Singh H.L., Khungar B., Tripaati U.D., and Varshney A.K., *Main Group Met. Chem.*, 24: 5 (2001).
4. Chohan Z.H., Farooq M.A., and Iqbal M.S., *Met.-Based Drugs*, 7: 133 (2000).
5. Djebbar S.S., Benali B.O., and Deloume J.P., *Trans. Met. Chem.*, 23: 443 (1998).
6. Hamada Y.J., *IEEE Trans. Electron Devices*, 44: 1208 (1997).
7. Taggi A.E., Hafez A.M., Wack H., Young B., Ferraris D. and Lectka T., *J. Am. Chem. Soc.*, 124: 6626-6635 (2002).
8. Saitou S., Kumaki S., and Hasegawa Y., *Bunseki Kagaku*, 54(11): 1027-1032 (2005).
9. Khandar A.A., Yazdi S.A.H., Khatamian M., McArdle P., and Zarei S.A., *Polyhedron*, 26(1): 33-38 (2007).
10. Tamburini S., Tomasin P., Vigato P.A., Casnati A., and Domiano L., *Inorg. Chim. Acta*, 54(2): 209-212 (1997).
11. Vogel A.I., "A Text-Book of Quantitative Inorganic Analysis". 3rd Ed., Longman, New York (1972).
12. Wu J.C., Tang N., Liu W.S., Tan M.Y., and Chan A.S.C., *Chin. Chem. Lett.*, 12: 757-760 (2001).
13. Geary W.J., *Coord. Chem. Rev.*, 71: 81-122 (1971).
14. Sonmez M., and Sekerci M., *Polish J. Chem.*, 76: 907 (2002).
15. Sonmez M., *Polish J. Chem.*, 77: 397 (2003).
16. Sonmez M., and Sekerci M., *Synth. React. Inorg. Met.-Org. Chem.*, 33: 1747 (2003).

17. Sonmez M., and Sekerci M., Synth. React. Inorg. Met.-Org. Chem., 34: 489 (2004).
18. Bellamy L.J., "The Infrared Spectra of Complex Molecules". 3rd Ed., Methuen, London (1966).
19. Huheey J.E., Keiter E.A., and Keiter R.L., "Inorganic Chemistry, Principles of Structure and Reactivity". 4th Ed., Harper Collins College Publishers, New York (1993).
20. Chandra S. and Gupta L.K., Trans. Met. Chem., 27: 329 (2002).
21. Lobana T. S., Cheema H.S., and Sandhu S.S., Polyhedron, 4(4): 717-721 (1985).
22. Chaudhary A., Jaroli D.P. and Singh R.V., Met.-Based Drugs, 8(6): 347-353 (2001).
23. Lever A.B.P., "Crystal Field Spectra and Electronic Spectroscopy". Wiley Inter. Science, New York (1970).
24. Chandra S., and Gupta K., Synth. React. Met. Org. Chem., 31(4): 661-672 (2001).
25. Rajib L.D., Benerjee I., Subhadra G., and Mukherjee A.K., Indian J. Chem., 41A: 1380-1384 (2002).