

Macrocyclic Complexes of Divalent Transition Metal Ions Derived from 2,2-Dihydroxyindane-1,3-dione and 2,3-/2,6-Diaminopyridines

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A new series of divalent iron, cobalt, nickel and copper complexes have been prepared by the condensation of 2,2-dihydroxyindane-1,3-dione and 2,3-/2,6-diaminopyridines. The complexes have been characterized with the help of various physico-chemical techniques like elemental analyses, IR, electronic spectra, conductance and magnetic susceptibilities measurements. On the basis of these studies a distorted octahedral geometry has been proposed for all the complexes.

Key Words: 2,2-Dihydroxyindane-1,3-dione, Magnetic moments, Electronic spectra.

INTRODUCTION

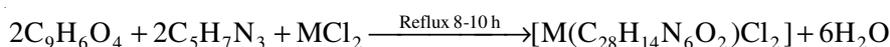
Of late interest in the field of macrocyclic metal complexes has been developed by diagnostic and therapeutic medicinal applications of macrocyclic ligands. A large number of nitrogen/oxygen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications¹. Macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines². Macrocyclic nickel complexes find use in DNA recognition and oxidation³ while macrocyclic copper complexes find use in DNA binding and cleavage⁴. Macrocyclic metal complexes of lanthanides *e.g.*, Gd³⁺ are used as MRI contrast agents⁵. Macrocyclic metal chelating agents are also useful for detecting tumor lesions⁶. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments⁷ as well as NMR shift reagents⁸. Prompted by these, in the present paper synthesis and characterization of divalent iron, cobalt, nickel and copper macrocyclic complexes derived from 2,2-dihydroxyindane-1,3-dione and 2,3 and 2,6-diaminopyridines have been reported.

EXPERIMENTAL

Isolation of complexes: All the complexes were obtained by template synthesis as various efforts to isolate the free ligands were unsuccessful. To a stirring methanolic solution (*ca.* 50 mL) of 2,3-/2,6-diaminopyridine (10 mmol) was added divalent iron, cobalt, nickel and copper salt (5 mmol) dissolved in minimum quantity

of methanol (*ca.* 20 mL). The resulting solution was refluxed for 0.5 h. After that 2,2-dihydroxyindane-1,3-dione (10 mmol) dissolved in (20 mL) methanol added in the refluxing mixture and again refluxed for 8-10 h. On overnight cooling dark coloured precipitate formed which was filtered, washed with methanol, acetone, diethylether and dried *in vacuo*. (Yield 40-65 %). The complexes were found soluble in DMF and DMSO, but were insoluble in common organic solvents and water. They were thermally stable up to *ca.* 250 °C and then decomposed.

The scheme of synthesis of the complexes may be shown by the following reaction:



where M = Fe(II), Co(II), Ni(II) and Cu(II).

RESULTS AND DISCUSSION

The analytical data show the formula for macrocyclic complexes as: $[M(C_{28}H_{14}N_6O_2)Cl_2]$ where M = Fe(II), Co(II), Ni(II) and Cu(II). The tests for anions are positive only after decomposing the complexes, indicating their presence inside the coordination sphere. The measurements of molar conductance in DMSO show that these chelates are non-electrolyte (conductance *ca.* 11-13 ohm⁻¹ cm² mol⁻¹). All the complexes gave satisfactory elemental analyses results as shown in the Table-1.

TABLE-1
ANALYTICAL DATA OF DIVALENT Fe, Co, Ni AND Cu
COMPLEXES DERIVED FROM 2,2-DIHYDROXYINDANE-1,3-DIONE
AND 2,3-/2,6-DIAMINOPYRIDINES. FOUND (CALCD.) (%)

Complexes	Found (calcd.) (%)				Colour	m.w.
	M	C	H	N		
[Fe(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]*	11.0 (11.9)	56.2 (56.6)	2.1 (2.3)	13.6 (14.1)	Brown	593
[Fe(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]**	11.0 (11.9)	56.1 (56.6)	2.0 (2.3)	13.7 (14.1)	Brown	593
[Co(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]*	9.5 (9.8)	55.6 (56.1)	2.5 (2.6)	13.8 (14.0)	Yellow Green	596
[Co(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]**	9.4 (9.8)	55.7 (56.1)	2.4 (2.6)	13.7 (14.0)	Yellow brown	596
[Ni(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]*	9.5 (9.8)	55.8 (56.1)	2.4 (2.6)	13.7 (14.0)	Green	595
[Ni(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]**	9.4 (9.8)	55.7 (56.1)	2.5 (2.6)	13.8 (14.0)	Black	595
[Cu(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]*	10.2 (10.5)	55.4 (55.7)	2.5 (2.6)	13.7 (13.9)	Light green	600.5
[Cu(C ₂₈ H ₁₄ N ₆ O ₂)Cl ₂]**	10.3 (10.5)	55.5 (55.7)	2.5 (2.6)	13.5 (13.9)	Black	600.5

*2,3-Diaminopyridine, **2,6-Diaminopyridine.

IR Spectra: In the infrared spectra, appearance of a band at *ca.* 1750 cm⁻¹ may be assigned to carbonyl >C=O group which is likely in the different plane and formed by dehydration of *geminal* hydroxyl groups due to heating. A pair of medium intensity bands are present at 3250-3200 cm⁻¹ corresponding to ν(NH₂) stretching frequencies of 2,3-/2,6-diaminopyridine but are absent in the spectra of all the complexes. Further, no strong absorption band was observed near 1700 cm⁻¹ indicating the

absence of $>C=O$ group of 2,2-dihydroxyindane-1,3-dione which was in plane of the molecule. This suggests the condensation reactions of carbonyl groups of 2,2-dihydroxyindane-1,3-dione and amino groups of 2,3-/2,6-diaminopyridine^{9,10}. These results provide strong evidence for the formation of macrocyclic frame¹¹. A strong absorption band in the region *ca.* 1645-1595 cm^{-1} may be attributed to the $C=N$ group. The lower values of $\nu(C=N)$ may be explained on the basis of drift of lone pair density of azomethine nitrogen towards metal atom¹². The bands present in the range *ca.* 1350-1000 cm^{-1} are assigned due to $\nu(C-N)$ vibration. The IR spectra of the complexes do not show any change in the pyridine ring vibrations and rule out the coordination to metal ion through pyridine nitrogen atom¹³.

The far infrared spectra show bands in the region *ca.* 460-425 cm^{-1} corresponding to $\nu(M-N)$ vibrations¹⁴. The bands present at 310-305 cm^{-1} may be assigned as being due to $\nu(M-Cl)$ vibrations¹⁴. However, the absence of various $(M-py)$ vibrations supports the non-involvement of pyridine nitrogen coordination.

Electronic spectra and magnetic measurements

Cobalt complexes: The magnetic moment at room temperature are in the range 4.97-5.01 BM, which corresponds to three unpaired electrons. The solution spectra of cobalt(II) complexes exhibit absorption in the regions *ca.* 8070-9060 (ν_1), 14000 (ν_2) and 21900 cm^{-1} (ν_3). The spectra resemble those reported to be octahedral¹². Thus, assuming the effective symmetry to be D_{4h} , the various bands can be assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)(\nu_2)$, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$. It appears that the symmetry of these complexes is not idealized O_h , but is D_{4h} . The EPR spectra were recorded at liquid nitrogen temperature. The g_{\parallel} = 4.2769 and g_{\perp} = 2.5637. The g -values show pronounced orbital contribution in octahedral geometry¹⁵.

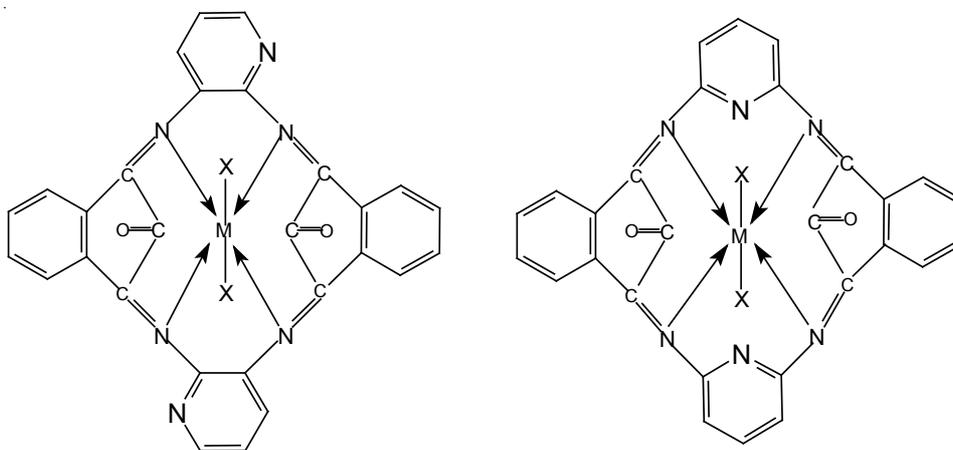
Nickel complexes: The magnetic moment of nickel complexes at room temperature are in the range 2.96-2.98 BM, showing octahedral environment around the Ni(II) ion in all complexes. The solution spectra of Ni(II) complexes exhibit a well discernable band with a shoulder on the low energy side. The other two bands generally observed in the region at *ca.* 16680-17060 cm^{-1} (ν_2) and 27760-28220 cm^{-1} (ν_3), are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$, respectively. The first two bands result from the splitting of one band, ν_1 and are in the range at *ca.* 9700-10300 and 11750-12300 cm^{-1} , which can be assigned to ${}^3B_{1g} \rightarrow {}^3E_g$ and ${}^3B_{1g} \rightarrow {}^3B_{2g}$, assuming the effective symmetry to be D_{4h} (component of ${}^3T_{2g}$ in O_h symmetry)¹⁶. The intense higher energy band at *ca.* 34500 cm^{-1} may be due to a $\pi-\pi^*$ transition of the $(C=N)$ group. The spectra are consistent with distorted octahedral nature of these complexes.

Copper complexes: The magnetic moments of copper complexes are in the range 1.99-2.01 BM. The absorption spectra of the copper complexes exhibit bands in the region *ca.* 17840-19660 cm^{-1} with a shoulder on the low energy side at *ca.* 14630-16070 cm^{-1} and show that these complexes are distorted octahedral^{12,16}.

Assuming tetragonal distortion in the molecule, the d -orbital energy level sequence for these complexes may be: $x^2 - y^2 > z^2 > xy > xz > yz$ and the shoulder can be assigned to: $z^2 \rightarrow x^2 - y^2$ (${}^2B_{1g} \rightarrow {}^2B_{2g}$) and the broad band contains both the $xy \rightarrow x^2 - y^2$ (${}^2B_{1g} \rightarrow {}^2E_g$) and $xz, yz \rightarrow x^2 - y^2$ (${}^2B_{1g} \rightarrow {}^2A_{2g}$) transitions¹⁷. The band separation of the spectra of the complexes is of the order 2500 cm^{-1} , which is consistent with proposed geometry of the complexes¹⁸. Therefore, it may be concluded that all the complexes of Cu(II) metals of this series are distorted octahedral. The complexes of Cu(II) exhibit an anisotropic ESR spectrum characteristic of tetragonal copper. The g -values are $g_{\parallel} = 2.1769$ and $g_{\perp} = 2.0637$. The EPR spectrum of Cu(II) complex in solution does not show any change¹⁵.

Iron complexes: The magnetic moments of iron complexes are in the range 5.10-5.50 BM. This suggests that the electronic configuration of iron in the complex is $3d^6, 4s^0$. The complexes are high spin. Hence electronic spectral bands (10510 and 12200 cm^{-1}) may be assigned to the transitions, respectively, as follows: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (10510 cm^{-1}), ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (12200 cm^{-1}). These bands are indicative of octahedral geometries¹⁸.

Proposed structure: Therefore based on various physico-chemical techniques like elemental analyses, conductivity measurements, magnetic moments, electronic and IR spectral studies the following structures (Fig. 1) may be proposed for these complexes.



where $M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$, $X = \text{Cl}$

Fig. 1

REFERENCES

1. W. Ma, Y. Tian, S. Zhang and J. Wu, *Transition Met. Chem.*, **31**, 97 (2006).
2. M. Rosignoli, P.V. Bernhardt, G.A. Lawrence and M. Maeder, *J. Chem. Soc. Dalton Trans.*, 323 (1997).

3. J.G. Muller, X. Chen, A.C. Dadiz, S.E. Rokita and C.J. Burrows, *Pure Appl. Chem.*, **65**, 545 (1993).
4. J. Liu, T.B. Lu, H. Deng, L.N. Ji, L.H. Qu and H. Zhou, *Transition Met. Chem.*, **28**, 116 (2003).
5. A.D. Watson and S.M. Rocklodge, in ed.: C.B. Higgins, *Magnetic Resonance Imaging of the Body*, Raven Press, New York (1992).
6. C. Kosmos, D. Snook, C.S. Gooden, N.S. Courtenay-Luck, M.J. McCall, C.F. Meares and A.A. Epenetos, *Cancer Res.*, **52**, 904 (1992).
7. J. Seto, S. Tamura, N. Asai, N. Kishii, Y. Kijima and N. Matsuzawa, *Pure Appl. Chem.*, **68**, 1429 (1996).
8. W. Dong, R. Yang and L. Yan, *Indian J. Chem.*, **40A**, 202 (2001).
9. S.S. Nivasan and P. Athappan, *Transition Met. Chem.*, **26**, 588 (2001).
10. Q. Zeng, J. Sun, S. Gou, K. Zhou, J. Fang and H. Chen, *Transition Met. Chem.*, **23**, 371 (1998).
11. A.K. Mohamed, K.S. Islam, S.S. Hasan and M. Shakir, *Transition Met. Chem.*, **24**, 198 (1999).
12. D.P. Singh, K. Kumar and C. Sharma, *Spectrochim. Acta*, **75A**, 98 (2010).
13. D.P. Singh and V.B. Rana, *Polyhedron*, **14**, 2901 (1995).
14. M. Shakir, K.S. Islam, A.K. Mohamed, M. Shagufta and S.S. Hasan, *Transition Met. Chem.*, **24**, 577 (1999).
15. J.F. Wertz and J.R. Bolton, *Electron Spin Resonance*, McGraw-Hill, New York (1986).
16. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, edn. 2 (1984).
17. S. Chandra and R. Kumar, *Transition Met. Chem.*, **29**, 269 (2004).
18. A.B.P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817(1971).