CHELATING BEHAVIOUR OF 2,4,9,11-TETRAPHENYL-1,5,8,12-TETRAAZACYCLOTETRADECA -1,4,8,11-TETRAENE WITH SOME DIVALANT METALS LIKE Cu(II), Ni(II), Fe(II), Co(II) METAL IONS

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Abstract

The synthesis of the metal-ligand complex of Fe(II). Co(II), Ni(II), and Cu(II) of [2,4,9,11-tetraphenyl-1,5,8,12-tetraaza-cyclotetradeca-1,4,8,11 -tetraene] was made by using a method of, metal salt nitrate und1,3-diphenyl-1,3-propanedione. The electronic spectra confirmed the square planar geometry. The observed magnetic moment value of 5.2 B.M. for the complex under discussion suggested the tetrahedral geometry for the Fe $(C_{34}H_{32}N_4)(NO_3)_2$. The electronic spectrum of cobalt complex $Co(C_{34}H_{32}N_4)(NO_3)_2$ exhibited a very weak band in the near-infrared region at 1800 nm, which is characteristic of a square planar Co(II) species. This result was corroborated by its magnetic data (2.02 B.M.). The spectrum of the nickel complex displayed a relatively weak band at 560 with a shoulder at 500 nm. This low-intensity band was described as (d-d) transitions, in square planar complexes. Based on the analytical, spectral (IR, UV-visible), and magnetic data, it is inferred that the bonding of the metal ions takes place through aza group, and the ligand acts as neutral tetradentate.

Key Words

Divalent metals, chelating compounds, Square planar complexes

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Objective of the Study

To find out the broader range of chelation of,4,9,11-tetraphenyl-1,5,8,12- tetra aza cyclo tetradeca -1,4,8,11-tetraene with different divalent metals

Introduction

The discovery[1] that cations and anions form stable complexes with macrocyclic polyamines has opened the door to several broad and fruitful areas of chemical investigations. The interest in these macrocycles was stimulated when it was found that some of them form stable alkali and alkaline earth metal ions and the preferential cation complexation resulted when the relative sizes of the cation and ligand cavity were matched[2]. The design and synthesis of mono-, bi-, and polynuclear complexes of cobalt in its different oxidation states through appropriate choice[3-7] of different ligands are of upsurge interest in coordination chemistry[8-10] are useful organic blockers because of their preparational accessibilities structural varieties and varied denticities. In the present work, we have studied the chelating behavior of 2,4,9,11-tetraphenyl-1,5,8,12 tetra aza cyclo tetradeca-1,4,8,11-tetraene towards Fe(II), Co(II), Ni(II) & Cu(II).
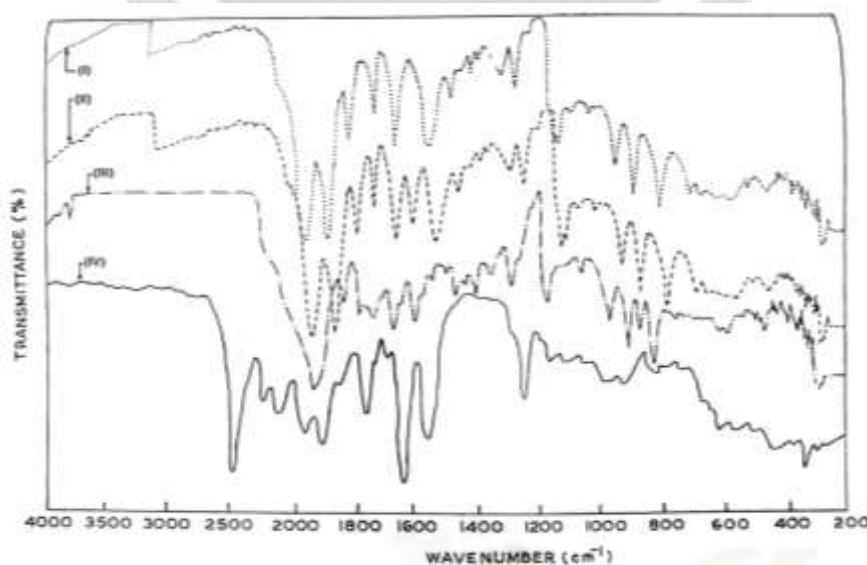
Materials

The reagents used starting materials were obtained from S.D. Fine Chem. LTD. and work used without further purification. Metal salts nitrate were obtained from E. Merck Ltd. and all other solvents used were of analytical grade.
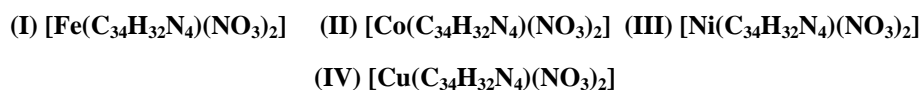
Methodology

The synthesis and characterization of Fe(II), Co(II), and Ni(II) Cu(II) of [2,4,9,11-tetraphenyl-1,5,8,12-tetraaza-cyclotetradeca-1,4,8,11-tetraene] macrocycle were carried out as follows[11-13] Ethylenediamine 6.68 ml (0.1 mol) was dissolved in a minimum quantity of methanol and cooled in an ice bath to about 5°C. To this 12.08 g (0.05 mol) of metal salt nitrate was added with constant stirring followed by 22.42 g (0.1 mol) of 1,3-diphenyl-1,3-propanedione diluted with 10 cm^{-1} of methanol. The solution was slowly heated to reflux for 4 h. The volume of the solution was reduced to half by evaporation at 40°C. The solution was then cooled to 0°C in an ice bath. The dark purple-colored precipitate was filtered under suction through a sintered funnel and washed with a small quantity of ice-cold methanol. The crude product was recrystallized twice from methanol and dried in a vacuum. The melting point of the complex was found to be in the range of 145-260°C. Yield 55-60%. The absorption spectra of the complex in methanol were recorded on a ShimadzuUV-2100 spectrophotometer. The IR spectra were recorded on a Beckman IR-20 spectrophotometer in KBr pellets in 4000-200cm^{-1}. Magnetic moments were recorded at room temperature on a vibrating sample magnetometer (VSM model 155 PrincetonApplied Research). The VSM was calibrated with a high-purity nickel standard showing a saturation moment of 55 emu g^{-1} with an asaturation flux of 5KG. The 'H NMR spectra were recorded at room temperature on a F-16 Varian NMR spectrophotometer.

Result and Discussion

The characteristic band due to ν(C-N) was observed at~1660 cm^{-1} in IR spectra. The appearance of this band along with the absence of the C=O band at ~1700cm^{-1} showed the condensation of the amine with the ketone[14,15]. The macrocyclic complex showed a medium intensity band at 496 cm^{-1} assignable to ν(M-N) vibrations. The presence of 1,3-diphenyl-1,3-propanedione moiety was indicated by the appearance of bands at 2993, 1584, 1419, and 657 cm^{-1}. ^{1}H NMR of the Cu-Complex in DMSO gave singlets in the region 2.24-3.16 ppm and 6.88-7.56 ppm attributable to CH_2 (4H) protons and C_6H_5, (20H) protons of 1.3-diphenyl-1.3-propanedione, respectively. A singlet observed at 3.24-3.52 was assigned to CH_2 (8H) protons adjacent to nitrogen[16]. The observed absorption bands in the visible and ultraviolet regions were recorded. The electronic spectra confirmed the square planar geometry, which showed two intense bands one in the visible region near 19000 cm^{-1} assigned to $^1A_{2g} \leftarrow {}^1A_{1g}$ transition. The observed magnetic moment values were in close agreement with their electronic spectral data[17]. The magnetic moment of 5.2 B.M. of the iron(I1) complex corresponds to four unpaired electrons. The ground state of Fe(II) in high spin oh symmetry[18] is $^5T_{2g}$ whereas in T_d geometry it is SE. Irrespective of the Oh or T_d geometry of the Fe(II) complex, the number of unpaired electrons on the iron will be four, and in both cases, there will be a certain amount of orbital contribution to the spin-only value of the magnetic moment. In practice, the value of the magnetic moment of tetrahedral and octahedral complexes of Fe(II) have magnetic moment values of 5.2 or 5.4 B.M. respectively[19]. The observed value of 5.2 B.M. for the complex under discussion suggested the tetrahedral geometry for the Fe($C_{34}H_{32}N_4$)(NO_3)$_2$. This geometry was also consistent with the composition of the complex: Although four coordinated complexes can have only two possible geometries (tetrahedral or square planar), square planar geometry was however ruled out on the basis that the value of the magnetic moment for such complexes should correspond to two unpaired electrons (> 2.8 B.M.). Tetrahedral geometry was therefore assigned to the iron complex. The electronic spectrum of cobalt complex Co($C_{34}H_{32}N_4$)(NO_3)$_2$ exhibited a very weak band in the near-infrared region at 1800 nm, which was characteristic of a square planar Co(II) species[20]. This result was corroborated by its magnetic data (2,02 B.M.).

Fig 1: IR Spectra of the Complexes

(I) [Fe(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]   **(II) [Co(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]**   **(III) [Ni(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]**

(IV) [Cu(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]

The intense band at 730, 650, and 620 nm might be assigned to charge transfer bands. The spectrum of the nickel complex displayed a relatively weak band at 560 nm with a shoulder at 500 nm. This low-intensity band was ascribed to (d-d) transitions, in square planar complexes and assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ around 2000, 1000, and 400nm ruling out the tetrahedral or octahedral geometry of the complex[21-27]. This was consistent with the diamagnetic behavior of the complex. Based on the analytical, spectral (IR, UV-visible), and magnetic data, it was inferred that the bonding of the metal ions takes place through aza group and the ligand acted as neutral tetradentate. The geometries assigned to Fe(II), Co(I1), Ni(II) and Cu(Il) complexes are given below;

M = Fe(II), Co(II), Ni(II) & Cu(II)
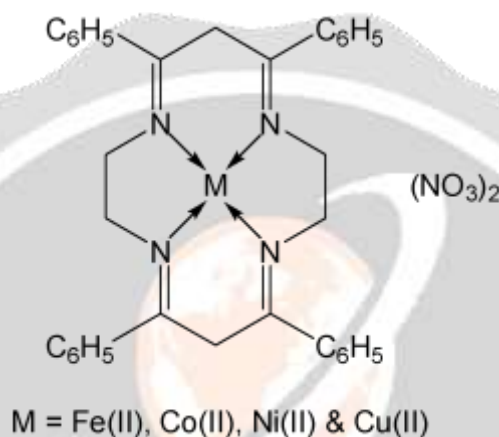
% Found (Calcd.)

[Fe(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]; C-60.20(60.36),H-4.60(4.73),N-12.30(12:42), M-8.10(8.26)

[Co(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]; C-59.90(60.09),H-4.60(4.71),N-12.25(12.37),M-8,50(8.68)

[Ni(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]; C-60.0(60.11),H-4.60(4.71),N-12.20(12.37), M-8.50(8.65)

[Cu(C$_{34}$H$_{32}$N$_4$)(NO$_3$)$_2$]; C-59.50(59.68),H-4.50(4.68),N-12.11(12.28), M-9.10(9.29).

Suggestion

Macrocyclic complexes of transition metal ions having aza groups show some interesting properties and biological functions such as being models for metalloproteins and oxygen carrier systems[28] and a lot of possibilities are there.

Acknowledgment

References

1. CJ. Pederson, Synthetie multidentate macrocyclic compounds, Academic Press, New York (1978).
2. G.A. Melson, Coordination Chemistry of macrocyclic compounds (Plenum NY) 1970.
3. (a) Y.S.Xic, X.T. Liu, M. Zhang, KJ. Wei & Q.L, Llu, Polyhedron 24(2005) 165.
   (b) F.J.Barros,Garcia,Bernalte Garcia,A.M.Lozana Vila, F.L. Giles & E.V. Zahinos Polyhedron 24 (2005) 129.
   (c) U.P. Singh, P. Babbar & A.S. Sharma, Polyhedron 358 (2005) 247.
4. (a) A.Sreekant. U.L. Kaln, C.R. Nayar & M.R.P. Kurup, Polyhedron 23 (2004) 41.
   (b) U.G. Conceiro, O. Castillo, A. Lugue, G. Beobide& P. Roman, Inorg. Chim. Acta 357 (2004) 339.

    (c) U. Ray, B. Chand, G. Mostafa, J. Cheng, T.H. Lu, and C.Sinha, Polyhedron 22(2003) 2587.

5.   (a) U.G. Makhankova, O.Y. Vassilyeva, V.N. Kozozay, J. Reedijk, G.A. Vanelbada, J. Jezicrska& B.W. Skelton,Eur. J. Inorg. Chem. (2002) 2163.
    (b) C. Demuno, F. Cipriani, D. Armentano, M. Julve& J.A. Real, New J. Chem. 25 (2001) 1031.

6.   (a) D.M. Ciutin, Y.B. Dong, M.D. Smith, T. Barclay & H.C. Zurloye, Inorg, Chem. 40 (2001) 2825.
    (b) C. J. Matthews, L.K. Thompson, S.R. Parsons, Z.Xu, D.O.Miller& L.S.Heath, Inorg.Chem.40(2001) 4448.

7.   F.A. Cotton, G. Wilkinson, C.A. Murrilo& M. Bochmann, Advanced Inorganic Chemistry 6h Edn. (John Wiley & Sons, New York) 1999, p. 598.

8.   V. Alexander, Chem. Rev. 95 (2003) 205.

9.   (a) T.K. Karmakar, S.K. Chandra, J. Ribas, G, Mostafa, T.H. Lu & .K. Ghosh, Chem, Commun. (2002) 2364.
    (b) R. Paschke, S. Liebsch, C. Tschierske, M.A. Oakley & E. Sinn, Inorg, Chem. 42 (2003) 8230.

10. S.H. Rahman, R. Ghosh, D. Bose, H.K. Fun and B.K. Ghosh, Ind. J. Chem. 43A (2004) 1901.

11. C.T. Lin, D.B. Rorabacher, G.R. Cayley and D.W. Margerum, Inorg. Chem. 14 (1975) 919.

12. R.W. Hay & P.R. Norman, Inorg. Chim.Acta. 45(1980)L139.

13. R.W. Hay & R. Bembi,Inorg. Chim.Acta 65(1982)L227.

14. M.S. Holtzman & S.C. Cummings, Inorg. Chem. 15 (1976) 660.

15. W.A. Welsh, G.J.Reynolds&P.M.Henry, Inorg.Chem.16(1977)2558

16. V.F. Bystrov, Progress in NMR spectroscopy 10, (1976) 41.

17. M. Shakir, S.P. Varkey & P.S.Hameed,J.Chem, Res.11(1993)2964.

18. CJ. Ballhausen and H.B. Gray, Molecular orbital theory (W.A. Benjamin, New York (1965).

19. B.N. Figgis, Introduction to ligand fields (Wiley Eastern, New Delhi) 1966, pp 278, 312.

20. G.W. Everctt (Jr.) & R.H. Holm, J. Am. Chem, Soc. 88 (1966) 3444.

21. P. Pallavicini, M. Boiocchi, G. Daearroa, and C. Manganona, New J. Chem.

22. M.G.B. Drew, S. Nag and D. Datta, Inorg. Chim. Acta 361 (2008) 417.

23. J.P. Naskar, S. Chowdhury, M.G.B.Drew& D. Datta, New J.Chem. 26(2002) 170.

24. T. Punniyamurthy. S. Valusamy and J. Iqbal, Chem. Rev. 105(2005) 2329

25. R. Bal, M. Tada, T. Sasaki and Y. Iwasawa, Angew Chem, Int. Ed. 45 (2006) 448.

26. P.R. Reddy &Addla Shilpa, Ind. J. Chem; 49A (2010) 1003.

27. J.H.Li, J.T. Wang,L.Y.Zhang,Z.N.Chen,7.W.Mao&L.N.Ji.J.Coord.Chem.62(200

28. M.B.H. Howlader, M.S. Islam and M.R. Karin, Ind. J.Chem. 39A (2000) 407.

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