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Synthesis and Spectroscopic Investigations of Zn(II) and Cd(II) Complexes of Tridentate N-Donor Ligand

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The novel complexes, $[CdL_2](NO_3)_2 \cdot 2H_2O$ (**1**) and $[Zn(L)(H_2O)](NO_3)_2$ (**2**), have been synthesized by reaction of N, N″-*bis*(methyl-2-amino-1-cyclopentene-1-dithiocarboxylate)diethylenetriamine (L), with Cd(II) and Zn(II) salts. The ligand and complexes have been characterized by elemental analysis, IR, ^{1}H NMR, ^{113}Cd NMR spectra. Spectroscopic studies show the ligand coordinates to Zn and Cd in tridentate neutral form *via* three nitrogen atoms. Complex **1** is six-coordinate and complex **2** is four coordinate with one coordinated water molecule. ^{113}Cd NMR confirms a CdN_6 central core for complex **1**.

Key Words: Cd(II) and Zn(II) Complexes, N-donor ligands, ^{113}Cd NMR.

INTRODUCTION

Complexes of d^{10} metal ions, such as zinc(II) and cadmium(II) are of interest since they are involved in many biological processes. About 20 zinc enzymes are known, in which zinc is generally tetrahedrally four-coordinated[1,2]. The d^{10} metal ions do not derive ligand field stabilization energy benefits by assuming certain coordination numbers or geometries. Shape, size and topology of the complexes will hence depend mainly on the steric requirements of the ligands and may show gradual changes between different compounds[3]. Therefore, it was of interest to compare the structural chemistry of the Zn^{2+} complexes to those of other d^{10} metal ions that may compete with Zn^{2+} for binding to donor sites in biological systems. The chemical similarity of zinc(II) and cadmium(II) suggests that the latter may displace the former from the active site in enzymes containing zinc(II). The coordination chemistry of cadmium in both biological and non-biological areas has attracted the interest of many researchers[2-7]. Cadmium(II) adapts a wide variety of stereochemical environments. A review on 200 crystal structures of cadmium(II) complexes showed that cadmium(II) has coordination numbers of 4, 5 and 6 in about 19, 8 and 56 %, respectively[8]. The main impetus for the development of chemistry of cadmium is the fact that cadmium has two important isotopes that are NMR active with spins = ½.

The ^{113}Cd nucleus with natural abundance 12.3 % is an excellent metallobioprobe owing to its favourable NMR properties as compared to some native metal ions, *e.g.*, Zn(II), Ca(II) and Mg(II). Due to the large range in the chemical shift of cadmium (in excess of 900 ppm) and the sensitivity of the chemical shift to the coordination number, donor atom type and ligand geometry, ^{113}Cd NMR has been used widely as a tool for elucidation of structural features in metal coordination chemistry[9,10].

We report here synthesis and spectroscopic studies of new complexes of Zn(II) and Cd(II) with a potentially multidentate N, S-donor ligand. This work is a further step toward the design of a sulfur-nitrogen ligand with suitable competing reactive centers. Presence of competing coordination site in ligand makes the synthesis and studies of its complexes interesting and worthwhile.

EXPERIMENTAL

All chemical and solvents were purchased from commercial sources. Methyl-2-amino-1-cyclopentene-1-dithiocarboxylate (ACDMe) was prepared using the literature methods[11-14]. IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The ^{1}H and ^{113}Cd NMR spectra were recorded with a Bruker Avance DPZ500 spectrometer (at 500.130 and 110.924 MHz, respectively) using TMS and $Cd(ClO_4)_2$ as reference, respectively. The C, H and N analysis were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

Synthesis of ligand: To a solution of ACDMe (0.02 mol, 3.46 g) in methanol (35 mL) was added diethylenetriamine (0.1 mol, 10.31 g). This solution was stirred for 24 h at room temperature. During this period a yellow precipitate was formed. The product was filtered, washed with methanol and dried on $CaCl_2$. Yield: 0.754 g (19 %); m.p. 100-102 °C; Anal. Calcd. for $C_{18}H_{29}N_3S_4$: C, 52.0; H, 7.0; N, 10.1. Found: C, 51.9; H, 7.0; N, 10.2. IR (KBr, cm^{-1}): 3333, 1613, 1588, 1223; ^{1}H NMR ($CDCl_3$, ppm): 1.88 (quintet, 4 H, b-H), 2.59 (s, 6 H, SCH_3), 2.73 (t, 4 H, a-H), 2.83 (t, 4 H, c-H), 2.93 (t. 4 H, e-H), 3.51 (quartet, 4 H, d-H), 12.38 (s, 2 H, NH---S=C). 1H NMR (DMSO, ppm): 1.78 (quintet, 4 H), 2.44 (s, 6 H, SCH_3), 2.67 (t, 4 H), 2.75 (t, 4 H), 2.78 (t, 4 H), 3.43 (quartet, 4 H), 12.17 (s, 2 H, NH---S=C).

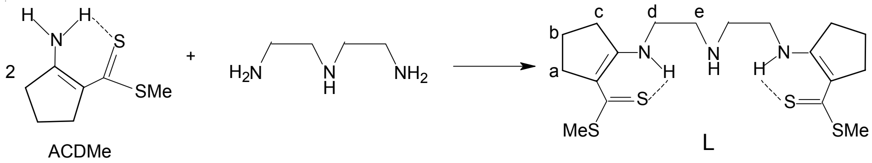
Synthesis of $[CdL_2](NO_3)_2\cdot 2H_2O$ (1): To a stirring solution of ligand (0.5 mmol, 0.208 g) in chloroform (6 mL), a solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.25 mmol, 0.077 g) in ethanol (4 mL, 98 %) was added. A yellow precipitate was formed after 10 min. The mixture was stirred for 2 h to ensure the completion of the reaction. Then the product was filtered and washed with ethanol and chloroform and dried on $CaCl_2$. Yield: 0.170 g (62 %); m.p. 180 °C (dec.); Anal. Calcd. for $C_{36}H_{62}N_8O_8S_8Cd$: C, 39.2; H, 5.6; N, 10.1. Found: C, 39.0; H, 5.3; N, 9.8. IR (KBr, cm^{-1}): 3600-3400, 3265, 1608, 1384; ^{113}Cd NMR (DMSO): 234.5 ppm.

This complex was also obtained from a 1:1 molar mixture of reagents.

Synthesis of [Zn(L)(H_2O)](NO_3)$_2$ (2): Complex **2** was synthesized as **1** with the ligand (0.2 mmol, 0.83 g) and Zn(NO_3)$_2$·6H_2O (0.2 mmol, 0.059 g). Yield: 0.105 g (85 %); m.p. 145 °C (dec.); Anal. Calcd. for $C_{18}H_{31}N_5O_7S_4Zn$: C, 34.7; H, 5.0; N, 11.1. Found: C, 35.2; H, 5.1; N, 10.8. IR (KBr, cm^{-1}): 3100-3000, 3015, 1586, 1384; ^{1}H NMR (DMSO, ppm): 1.82 (quintet, 4 H), 2.46 (s, 6 H, CH_3), 2.71 (t, 4 H), 2.80 (t, 4H), 3.12 (t, 4 H), 3.62 (quartet, 4 H), 8.31 (s,1H), 12.01 (2 H, s).

RESULTS AND DISCUSSION

N,N″-*bis*(methyl-2-amino-1-cyclopentene-1-dithiocarboxylate)diethylenetriamine (L) was obtained by the transamination reaction of methyl-2-amino-1-cyclopentene-1-dithiocarboxylate (ACDMe) with diethylenetriamine (**Scheme-I**). This ligand is conformationally flexible and contains hard and soft donor atoms. The ligand was characterized by elemental analysis as well as IR and ^{1}H NMR spectroscopy. Then the new complexes, [CdL_2](NO_3)$_2$·2H_2O (**1**) and [Zn(L)(H_2O)](NO_3)$_2$ (**2**), were synthesized by reaction of this ligand with Zn(II) and Cd(II) nitrate salts. The stoichiometries of the new complexes have been confirmed by analytical data and known the Cd(II) complex was obtained with 2:1 ligand to metal ratio even in presence of 1:1 molar mixture of reagents. The nature of bonding in the complexes was recognized by spectroscopic data.



Scheme-I

In the IR spectrum of ligand a sharp band at 3333 cm^{-1} is assigned to ν(N-H) of free secondary amine (N'H). The band due to two other NH groups (NH and N″H) falls in lower wavelenght (below 3000 cm^{-1}) because of intramolecular hydrogen bonding (NH---S=C-). This stretching vibration overlaps with the ν(C-H). In the infrared spectra of complexes the band due to N'H shifts to lower frequency than the ligand and indicates participitation of this group in coordination. In the spectra of both complexes the appearance of strong band at 1384 cm^{-1} confirms that an ionic D_{3h} nitrate ion is present[15-17] in these complexes. Complex **1** exhibits an absorption in the 3600-3400 cm^{-1} indicates that lattic water is present. The spectrum of complex **2** shows a broad background band at 3100-3000 cm^{-1} attributed to the presence of coordinated water. The broadness and low frequency of this band are indicative of hydrogen bonding[15,18-21].

^{1}H NMR spectrum of ligand has been recorded in both $CDCl_3$ and DMSO-d_6 and the results have been given in the experimental section according to alphabeting in **Scheme-I**. Since the complexes are poorly soluble in $CDCl_3$, their NMR spectra were run in DMSO-d_6. It was not possible to obtain satisfactory ^{1}H NMR data for complex **1**, because the high donor capacity of the DMSO leads to dissociate the complex. In the NMR spectrum of the ligand NH and N″H protons appear as a singlet in downfield due to intramolecular hydrogen bonding. The signal due to N'H that falls in higher field was overlapped by the other peaks. In complex **2** the signal of N'H is shifted downfield and appeared at 8.31 ppm. This shift is due to coordination of this nitrogen to metal and charge donation from it to Zn(II) acceptor. The lack of a shift in the position of the signal attributable to NH and N″H is due to weakening of hydrogen bonding upon coordination of these groups to Zn(II). The presence of only one set of resonances in ^{1}H NMR spectrum of this complex indicates that coordination environments of two NH and N″H are equivalent.

^{113}Cd NMR spectrum of complex **1** in DMSO solution shows two sharp singlets at 31.6 and 234.5 ppm. The singlet at 31.6 ppm is due to dissociation of complex and presence of cadmium(II) nitrate in DMSO solution[9]. The signal at 234.5 ppm is due to complex **1**. It is well known that the ligand bond to cadmium through nitrogen cause decreased shielding and the absorption at *ca.* +200 indicate a CdN_6 central core[9,22-24]. On the basis of ^{113}Cd NMR data it appears reasonable to assume coordination number for complex **1** is six and two ligand were coordinated through three nitrogen atom. In this complex cadmium nucleus is deshielded due to the presence in a environment of only nitrogen atoms, poor shielding donors.

In conclusion the ligand synthesized in this research coordinates to Cd(II) and Zn(II) in tridentate neutral form *via* three nitrogen atoms. Therefore complex **1** is six-coordinate and two ionic nitrate and two hydrated water is also present. Complex **2** is four coordinate with one coordinated water molecule and two ionic nitrate is also present.

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REFERENCES

1. S. Hansen, L.K. Hansen and E. Hough, *J. Mol. Biol.*, **231**, 870 (1993).
2. F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesi and A. Lorenzotti, *Polyhedron*, **18**, 3041 (1999).
3. H. Fleischer, *Coord. Chem. Rev.*, **249**, 799 (2005).
4. C. Santini, *Inorg. Chem. Commun.*, **7**, 834 (2004).
5. A.S. Al-Shihri, *Spectrochim. Acta Part A*, **60**, 1189 (2004).
6. D. Haffar, T. Douadi, S. Chaffa, M.A. Khan and G. Bouet, *Transition Metal Chem.*, **29**, 245 (2004).
7. M.A. Ali, A.H. Mirza, M. Nazimuddin, R. Ahmed, L.R. Gahan and P.V. Bernhardt, *Polyhedron*, **22**, 1471 (2003).
8. H. Sigel and R.B. Martin, *Chem. Soc. Rev.*, **23**, 83 (1994).
9. M.F. Summer, *Coord. Chem. Rev.*, **86**, 43 (1988).
10. K.H. Chung, E. Hung, Y. Do and C.H. Moon, *J. Chem. Soc. Dalton Trans.*, 3363 (1996).
11. T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano and H. Asaba, *J. Org. Chem.*, **34**, 730 (1969).
12. B. Bordas, P. Sohar, G. Matolcsy and P. Berencsi, *J. Org. Chem.*, **37**, 1727 (1972).
13. K. Nag and D.S. Joardar, *Inorg. Chim. Acta*, **14**, 133 (1975).
14. D.M. Baid, *J. Chem. Edu.*, **621**, 169 (1981).
15. S. Gourbatsis, N. Hadjiliadis, S.P. Perlepes, A. Garoufis and I.S. Butler, *Transition Met. Chem.*, **23**, 599 (1998).
16. S. Aime, M. Botta, U. Casellato, S. Tamburini and P.A. Vigato, *Inorg. Chem.*, **34**, 5825 (1995).
17. U. Casellato, P.A. Vigato and M. Vidali, *Coord. Chem. Rev.*, **36**, 183 (1981).
18. S. Gourbatsis, S.P. Perlepes, N. Hadjiliadis and G. Kalkanis, *Transition Met. Chem.*, **15**, 300 (1990).
19. K.K.M. Yusuff and A.R. Karthikeyan, *Transition Met. Chem.*, **18**, 435 (1993).
20. N. Raman, A. Kulandaisamy and C. Thangaraja, *Transition Met. Chem.*, **28**, 29 (2003).
21. M.A. El-Gahami, Z.A. Khafagy, A.M.M. Ali and N.M. Ismail, *J. Inorg. Organomet. Polym.*, **14**, 117 (2004).
22. C. Pettinari, F. Marchetti, A. Cingolani, S.I. Troyanov and A. Drozdov, *Polyhedron*, **17**, 1677 (1998).
23. D.L. Reger, S.S. Mason, A.L. Rheingold and R.L. Ostrander, *Inorg. Chem.*, **32**, 4904 (1996).
24. N.G. Charles, E.A.H. Griffith, P.F. Rodesiler and E.L. Amma, *Inorg. Chem.*, **22**, 2717 (1983).

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