Synthesis and characterization of macrocyclic Cd(II) complexes

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Received 30 July 2007; revised 28 January 2008

Ten new Cd(II) complexes have been synthesized with Cd(ClO4)2·6H2O, Cd(NO3)2·6H2O in chloroform-methanol. The complexes have been characterized by elemental analysis, IR, 1H NMR, UV-vis spectra, magnetic susceptibility, conductivity measurements and mass spectra. On the basis of the spectral studies, four-coordinated tetrahedral geometry may be assigned to these complexes.

IPC Code: Int. Cl.8 CO7F3/08

Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role. Synthetic macrocycles are a growing class of compounds with varying chemistry and sets of donors, with new reports on the transport of transition and post-transition metal ions through bulk liquid membranes using synthetic ionophores. The complexes have no clearly defined melting point and begin to decompose in the temperature range 250-350°C.

**Experimental**

Elemental analysis was carried out on a Leco CHNS model 932 elemental analyzer. 1H NMR spectra were recorded using Bruker Avance DPX-400 NMR spectrometer. IR spectra were recorded on Perkin-Elmer Spectrum RX1 FTIR spectrophotometer on KBr pellets in the wave number range of 4000-400 cm⁻¹. Electronic spectra were conducted on Shimadzu model 160 UV-vis spectrophotometer in the wavelength 200-600 nm. Molar conductivities were measured with a WTW LF model 330 conductivity meter, using prepared solution of the complexes in DMSO-DMF (1:1, v:v) solvents. Electrospray ionization mass spectrometric analysis (ESI–MS) was obtained on the Agilent 1100 MSD spectrometer.

The ligands (Scheme 1) used in the synthesis were prepared from salicylaldehyde derivatives with 2,6-diaminopyridine as known already. All the chemicals and solvents were of analytical grade and used as received.

To a stirred solution of ligands (2 mmol) in chloroform (60 mL) was added Cd(ClO4)2·6H2O or Cd(NO3)2·6H2O (2 mmol) in methanol (40 mL) by dropwise addition. Stirring was then continued for 2 h. Then, the precipitate was filtered and washed with chloroform and methanol and then dried in air. The complexes have no clearly defined melting point and begin to decompose in the temperature range 250-350°C.

**[CdL1](ClO4)2·H2O**

Yield: 0.16 g (13.1%). Anal Caled for CdC21H17N3O10Cl2·H2O: C, 41.2, H, 3.1, N, 6.9. Found: C, 41.3, H, 3.2, N, 6.8. 1H NMR (DMSO-d6, δ ppm): 3.42 (H2O), 4.25 (s, 4H, -OCH2), 7.02-8.04 (m, 11H, Ar-H), 10.38 (s, 2H, HC=N).

**[CdL2](ClO4)2·2H2O**

Yield: 0.11 g (8.5%). Anal Caled for CdC22H19N3O10Cl2·2H2O: C, 41.0, H, 3.6, N, 6.5. Found: C, 41.1, H, 3.7, N, 6.5. 1H NMR (DMSO-d6, δ ppm): 3.42 (H2O), 4.25 (s, 4H, -OCH2), 7.02-8.04 (m, 11H, Ar-H), 10.38 (s, 2H, HC=N).

We report herein the synthesis of ten macrocyclic Schiff base complexes with Cd(ClO4)2·6H2O and Cd(NO3)2·6H2O. Spectral properties of the new compounds have been studied in detail.
NOTES

ppm): $\delta = 2.34$ (t, 2H, $J = 5.3$ Hz) (CH$_2$), $\delta = 3.41$ (H$_2$O), $\delta = 4.32$ (t, 4H, $J = 5.8$ Hz) (OCH$_3$), $\delta = 6.98$-8.03 (m, 11H, Ar-H), $\delta = 10.40$ (s, 2H, HC=N). Selected IR data (KBr, ν cm$^{-1}$): 3371 ν(H$_2$O), 3073 ν(Ar-CH), 2958, 2881 ν(Aliph.-CH), 1657 ν(C=N), 1598 ν[C=N(pyridine)], 1491, 1456 ν(Ar-C=C), 1118, 624 ν(ClO$_4^-$), 1293, 1243 ν(Ar-O), 1162, 1041, ν(R-O), 754 ν(Substituted benzene), 527 ν(Cd-N). Λ = 155 Ω$^{-1}$ mol$^{-1}$ cm$^2$ (in DMSO-DMF (1:1, v:v)). Mass spectra (m/z): 527 [CdL$^2$(ClO$_4^-$)H$^+$].

|$\text{CdL}^2$(ClO$_4^-$)H$_2$O

Yield: 0.82 g (57.1%). Anal Calcd for CdC$_{23}$H$_{35}$N$_3$O$_{10}$Cl$_2$·H$_2$O: C, 41.8, H, 4.0, N, 5.9. Found: C, 41.9, H, 4.2, N, 5.9. $^1$H NMR (DMSO-d$_6$, δ ppm): $\delta = 3.36$ (t, 4H, $J = 4.3$ Hz) (H3), $\delta = 3.44$ (H$_2$O), $\delta = 3.84$ (t, 4H, $J = 4.2$ Hz) (H2), $\delta = 4.26$ (t, 4H, $J = 4.3$ Hz) (H3), $\delta = 7.02$-8.00 (m, 11H, Ar-H), $\delta = 10.40$ (s, 2H, HC=N). Selected IR data (KBr, ν cm$^{-1}$): 3380 ν(Aliph.-CH), 3066 ν(Ar-CH), 2941 ν(Aliph.-CH), 1658 ν(C=N), 1598 ν[C=N(pyridine)], 1498, 1455 ν(Ar-C=C), 1286, 1242 ν(Ar-O), 1161 ν(Cd-N), 752 ν(Substituted benzene), 515 ν(Cd-N). Λ = 179 Ω$^{-1}$ mol$^{-1}$ cm$^2$ (in DMSO-DMF (1:1, v:v)). Mass spectra (m/z): 546 [$\text{CdL}^2$(ClO$_4^-$)H$^+$].

|$\text{CdL}^4$(ClO$_4^-$)$_2$2H$_2$O

Yield: 0.13 g (9.9%). Anal Calcd for CdC$_{23}$H$_{35}$N$_3$O$_{10}$Cl$_2$·H$_2$O: C, 45.4, H, 3.8, N, 12.6. Found: C, 45.5, H, 3.8, N, 12.5. $^1$H NMR (DMSO-d$_6$, δ ppm): 3.40 (H$_2$O), 4.33 (s, 4H, -OCH$_2$), 6.95-8.01 (m, 11H, Ar-H), 10.39 (s, 2H, HC=N). Selected IR data (KBr, ν cm$^{-1}$): 3372 ν(H$_2$O), 3067 ν(Ar-CH), 2969, 2886 ν(Aliph.-CH), 1652 ν(C=N), 1598 ν[C=N(pyridine)], 1452 ν(Ar-C=C), 1162, 653 ν(NO$_3^-$), 1274, 1241 ν(Ar-O), 1146 ν(R-O), 752 ν(Substituted benzene), 531 ν(Cd-N). Λ = 189 Ω$^{-1}$ mol$^{-1}$ cm$^2$ (in DMSO-DMF (1:1, v:v)). Mass spectra (m/z): 579 [$\text{CdL}^4$(NO$_3^-$)$_2$].
|CdL₂(NO₃)₂·2H₂O
Yield: 0.85 g (74.53%). Anal Caled for CdC₂₂H₁₉N₅O₈·2H₂O: C, 46.40, H, 4.04, N, 12.30. Found: C, 46.54, H, 4.11, N, 12.32. ¹H NMR (DMSO-d₆, δ ppm): δ = 2.34 (t, 2H, J = 5.5 Hz) (CH₂), δ = 3.42 (H₂O), δ = 3.84 (t, 4H, J = 6.0 Hz) (OCH₂), δ = 6.99-8.02 (m, 11H, Ar-H), δ = 10.42 (s, 2H, HC=N). Selected IR data (KBr, ν cm⁻¹): 3378 ν(H₂O), 3076 ν(Aliph.-CH), 2937 ν(Aliph.-CH), 1655 ν(C≡N), 1598 ν(C≡N)(pyridine), 1487, 1451 ν(AR-C≡C), 1286, 1242 ν(AR-O), 754 ν(Substituted benzene), 529 ν(Cd-N). Λ = 131 Ω⁻¹.mol⁻¹.cm² (in DMSO-DMF (1:1, v:v)). Mass spectra (m/z): 562 [CdL₂(NO₃)₂²⁺].

|CdL₃(NO₃)₂·H₂O
Yield: 0.69 g (61.1%). Anal Caled for CdC₂₃H₂₁N₅O₈·H₂O: C, 48.9, H, 4.1, N, 12.4. Found: C, 49.0, H, 4.2, N, 12.3. ¹H NMR (DMSO-d₆, δ ppm): δ = 2.39 (t, 4H, J = 5.7 Hz) (CH₂), δ = 3.46 (H₂O), δ = 4.25 (t, 4H, J = 5.4 Hz, OCH₂), δ = 7.00-8.06 (m, 11H, Ar-H), δ = 10.39 (s, 2H, HC=N). Selected IR data (KBr, ν cm⁻¹): 3382 ν(H₂O), 3097 ν(Aliph.-CH), 1654 ν(C≡N), 1598 ν(C≡N)(pyridine), 1488, 1445 ν(AR-C≡C), 1288, 1243 ν(AR-O), 752 ν(Substituted benzene), 535 ν(Cd-N). Λ = 173 Ω⁻¹.mol⁻¹.cm² [in DMSO-DMF (1:1, v:v)]. Mass spectra (m/z): 546 [CdL₃(NO₃)₂⁺].

|CdL₄(NO₃)₂·3H₂O
Yield: 0.67 g (54.3%). Anal Caled for CdC₂₃H₂₁N₅O₈·3H₂O: C, 44.7, H, 4.4, N, 11.3. Found: C, 44.8, H, 4.3, N, 11.4. ¹H NMR (DMSO-d₆, δ ppm): δ = 3.46 (H₂O), δ = 3.81 (t, 4H, J = 5.4 Hz) (OCH₂), δ = 4.26 (t, 4H, J = 5.0 Hz) (CH₂OPh), δ = 6.97-8.04 (m, 11H, Ar-H), δ = 10.40 (s, 2H, HC=N). Selected IR data (KBr, ν cm⁻¹): 3375 ν(H₂O), 3066 ν(AR-C≡C), 2937 ν(Aliph.-CH), 1655 ν(C≡N), 1598 ν(C≡N)(pyridine), 1487, 1451 ν(AR-C≡C), 1286, 1242 ν(AR-O), 754 ν(Substituted benzene), 529 ν(Cd-N). Λ = 131 Ω⁻¹.mol⁻¹.cm² (in DMSO-DMF (1:1, v:v)). Mass spectra (m/z): 562 [CdL₂(NO₃)₂²⁺].

Results and discussion
We have found during the present investigations that during the reaction of the Schiff base macrocyclic ligands (dissolved in chloroform) with cadmium(II) perchlorate or cadmium(II) nitrate (dissolved in methanol), the [1+1] macrocycle Schiff-base complexes are formed. The macrocyclic complexes were characterized by elemental analysis, mass, IR and UV-vis spectrometry and conductivity measurements. The mass spectra of complexes play an important role in confirming the monomeric [1+1] ligands and metal salt nature of complexes. On the bases of the spectral studies, four-coordinated tetrahedral geometry may be assigned to these complexes (Scheme 2). The ligand is soluble in

Scheme 2
DMSO, DMF, CHCl₃, CH₂Cl₂ and CH₃CN but insoluble H₂O, EtOH and MeOH. The complexes are stable in air, partly soluble in DMF, DMSO and insoluble in CHCl₃, CH₂Cl₂ and CH₃CN. The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate, and acetonitrile.

IR of Cd(II) complexes were recorded in KBr pellet from 4000 to 400 cm⁻¹. The IR spectra of all complexes show ν(C=N) bands at 1650-1665 cm⁻¹ and it is found that the ν(C=N) bands in the complexes shift by about ca. 30 cm⁻¹ to lower energy regions compared to that in the free ligand (L)²⁵. This phenomenon appears to be due to the coordination of azomethine nitrogen to the metal ion²⁶. The broad bands in the range 3380-3370 cm⁻¹ and a weak band between 649-624 cm⁻¹ which are due to ν(Cl-O) of uncoordinated perchlorate anions²⁸. The absorption of the nitrate counterions, at ca. 1384 cm⁻¹ is attributed to the presence of the ionic nitrate²⁹. The fragmentation mass spectra of the complexes play an important role in conforming the monomeric [1+1] (dicarbonyl and diamine) nature of the complexes.

The mass spectra of the complexes exhibited almost the same values as that of the ligand. Although we expected a shift on the position of CH=N signal for the NMR spectra of the complexes, no significant shift could not be observed²⁵,²⁷,²⁸,³².

The molar conductivities of the compounds in DMSO-DMF (1:1, v:v) are range 131-194 Ω⁻¹mol⁻¹cm² reported for 1:2 electrolytes²⁵,²⁷,²⁸,³².

The ¹H NMR spectra of the complexes showed a singlet at ca. 10.4 ppm due to the imine protons, multiplied in the range ca. 7.0-8.0 ppm due to the aromatic protons, and H₂O proton at ca. 3.4 ppm. The other entire proton values are also shown in the experimental section. The ¹H NMR spectra of the complexes exhibited almost the same values as that of the ligand. Although we expected a shift on the position of CH=N signal for the NMR spectra of the complexes, no significant shift could not be observed²⁵,²⁷,²⁸,³².

The ¹H NMR spectra of the complexes were recorded in DMSO-d₆ solution show that they are NMR active. However, ¹³C NMR of the complexes could not be obtained because of the low solubility degree of the complexes in common solvents. The ¹H NMR spectra of the free ligands showed a singlet at ca. 10.4 ppm due to the imine protons, multiplied in the range ca. 7.0-8.0 ppm due to the aromatic protons, and H₂O proton at ca. 3.4 ppm. The other entire proton values are also shown in the experimental section.
References