Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1187-1190

Synthesis and Crystal Structure of Co(II) Complex with 2,3-*Bis*(2-pyridyl)-5,8-dimethoxyquinoxaline

YU-MIN LIU† and HE LIU*
No.7, Department, Beijing Institute of Pharmacology and Toxicology,
27 Taping Road, Beijing-100 850, P.R. China
Fax: (86)(10)68211656; Tel: (86)(10)66874612; E-mail: hliuamms@yahoo.com

A new polypyridyl ligand, 2,3-*bis*(2-pyridyl)-5,8-dimethoxyquinoxaline and its Co(II) complex have been synthesized and characterized. The crystal structure of Co(II) complex has been elucidated by X-ray diffraction analyses. The ligand acts as a bidentate and the Co(II) center is coordinated to the two nitrogen atoms of the two pyridine group. The formation of infinite quasi one-dimensional chains assisted by the intermolecular face-to-face aryl stacking interactions may have stabilized the crystals of the complex.

Key Words: Polypyridyl bridging ligand, Co(II) complex, 2,3-*Bis*(2-pyridyl)-5,8-dimethoxyquinoxaline.

INTRODUCTION

The research on the coordination chemistry of transition metal complexes with polypyridyl bridging ligands has progressed rapidly in recent years[1,2]. 2,3-Di-2-pyridylquinoxaline and its derivatives represent an important class of chelating agents and have been vigorously developed over the last two decades and the electrochemical and photochemical properties of such polypyridyl metal complexes have been a particular focus. Incorporating a ligand with two chelating sites into the coordination sphere allows systematic construction of large supramolecular assemblies, capable of acting as antenna in the energy conversion schemes, where the photochemical and redox properties of the complexes are strongly dependent on the nature of the ligands. This type of diimine ligands can act as chelating ligands mainly in two ways: by forming a five-membered ring involving N-atoms of the pyridine and the pyrazine rings, or by forming a seven-membered ring involving only the N-atoms of the pyridine rings[3]. In present studies, the authors report the Co(II) complex of a new polypyridyl ligand, 2,3-*bis*(2-pyridyl)-5,8-dimethoxyquinoxaline (L) of Fig. 1.

---

†Department of Catalysis Science & Technology, School of Chemical Engineering & Technology, Tianjin University, Tianjin, 300072, P.R. China.

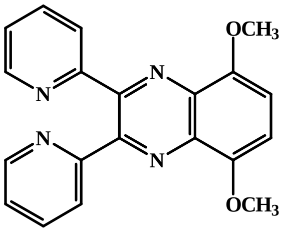

Fig. 1. 2,3-*Bis*(2-pyridyl)-5,8-dimethoxyquinoxaline (L)

RESULT AND DISCUSSION

The ORTEP structure of cobalt complex with atom labeling is shown in Fig. 2. The structure of the complex consists of a neutral mononuclear entity and an uncoordinated CH_3CN molecule. The Co(II) center is coordinated by two nitrogen atoms of the pyridine rings of L, which thus binds Co(II) in a bidentate fashion and four oxygen donors of two NO_3^- anions. The two (Co-N) distances are almost the same: 1.971(3) and 1.976(3) Å; but the (Co-O) distances are quite different for both terminal NO_3^- anions, with the longer bonds being 2.391(3) and 2.492(3) Å and the other two shorter bonds being 1.983(3) and 1.986(3) Å, respectively. The coordination geometry around Co(II) can be described as a distorted octahedral geometry with N(3)-Co(1)-O(6) angle of 167.30(12)º occupying the axial positions. The Co(II) center deviates by 0.2654 Å from the least-squares plane defined by N(4), O(3), O(4) and O(7). The sum of the bond angles [O(3)-Co(1)-O(7) = 89.01(13)º, O(3)-Co(1)-O(4) = 58.10(12)º, O(4)-Co(1)-N(4) = 103.78(12) and N(4)-Co(1)-O(7) = 105.05(12)º] is 355.94, being very close to 360º. In this complex, the Co(II) center is coordinated by the N-atoms of two pyridine rings forming a seven-membered chelate ring. The dihedral angles between the two pyridyl rings and the quinoxaline are 49.5º and 50.8º, respectively and between the two pyridine rings is 75.2º.

As shown in Fig. 3, the distance between parallel neighboring aromatic rings in the cobalt(II) complex is *ca.* 3.4 Å, indicating the presence of significant face-to-face π-π stacking[4] and the strong interaction might be a driving force for the formation of this stacking structure. The intramolecular face-to-face aryl interactions link the adjacent units into an infinite quasi-one-dimensional chain array and this may stabilize the complex in the crystal.

EXPERIMENTAL

All the reagents for syntheses were obtained commercially and used without further purification or purified by standard methods prior to use. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR

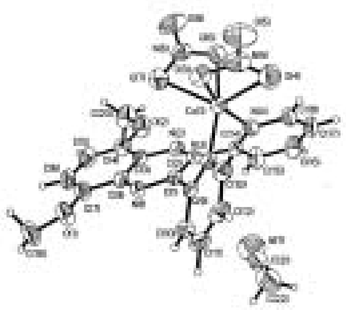

Fig. 2. Molecular structure of the Co(II) complex

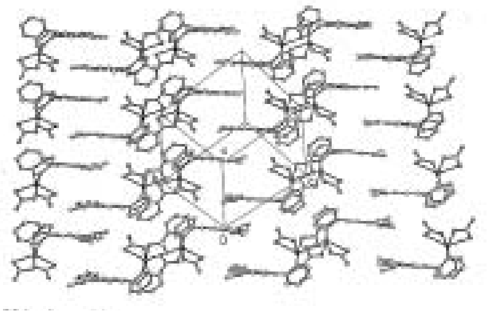

Fig. 3. Molecular packing in a unit cell showing the quasi one-dimensional structures with π-π stacking

spectra were measured on a 170SX (Nicolet) FT-IR spectrometer with KBr pellets and electronic spectra on a Hitachi UV-3010 spectrometer.

The ligand, 2,3-bis(2-pyridyl)-5,8-dimethoxyquinoxaline (L) was synthesized as described previously[5].

A solution of freshly prepared 1,4-dimethoxy-2,3-phenylenediamine (0.8 g, 4.7 mmol) in ethanol (20 mL) was added to a solution of 2,2'-pyridyl (1.0 g, 4.7 mmol) in ethanol (40 mL) under argon and the mixture was heated at reflux for 4 h. Upon cooling, the light yellow cubic crystals of ligand were separated out. (yield: 1.6 g, 89%) m.p. 230-231ºC. ^1H NMR ($CDCl_3$): δ 4.07 (s, 6H), 7.07 (s, 2H, 7.19-7.21 (m 2H), 7.74-7.81 (m, 2H), 8.03 (m, 2H), 8.32 (d, 2H, J = 4.2 Hz). Anal. (%) Calcd. for $C_{20}H_{16}N_4O_2$: C, 69.75; H, 4.68; N, 16.27.

To a solution of $Co(NO_3)_2{\cdot}6H_2O$ (29 mg, 0.1 mmol) in CH_3CN (5 mL) was added a solution of ligand (34 mg, 0.1 mmol) in $CHCl_3$ (5 mL) to give a red solution. After stirring for 0.5 h the solution was filtered. Single crystals suitable for structure determination were obtained by slow evaporation of the solvent. Yield: 45 mg, 70 % (Found: C, 46.35; H, 3.31; N, 17.19. Anal. (%) Calcd. for $C_{22}H_{19}N_7O_8Co$: C, 46.49; H, 3.37; N, 17.25%). IR (ν_{max} KBr, cm^{-1}): 2931w, 1660vs, 1064m, 1570w, 1051m, 1461s, 1387vs, 1353m, 1110s, 842m.

Crystal data: $C_{22}H_{19}N_7O_8Co$, Mr = 568.37, Ticlinic, P_1^{-}, a = 7.9957(13) Å, b = 12.026(2)Å, c = 13.262(2) Å, V = 1200.1(3) Å, D_x = 1.573 g cm^{-3}, Z = 2, μ = 0.779 mm^{-1}, T = 298(2) K. A colourless crystal of the title compound with dimensions of 0.40 × 0.15 × 0.02 mm was mounted on a glass fiber in a random orientation. The data was collected by a Bruker Smart 100 CCD diffractometer with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using a ω scan moe in the range of $1.60 \leq \theta \leq 26.44^o$. A total of 5671 reflections were collected with 4840 unique ones (R_{int} = 0.0327), of which 3561 with $I > 2\sigma(I)$ were considered as observed and used in the succeeding refinements. Unit cell dimensions were obtained with least-squares refinements. The structure was solved by direct methods with SHELXL-97 program[5] and all the data were corrected by using semi-empirical absorption corrections (SADABS) method. All the other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was carried out by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms of F^2. The hydrogen atoms were added theoretically and riding on the concerned atoms and refined with fixed thermal factors. The final refinement gave R = 0.0576, wR = 0.1407 ($w = 1/[\sigma^2(F_o)^2 + (0.1044P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), S = 1.001, $(\Delta/\sigma)_{max} = 0.001$, $(\Delta/\rho)_{max} = 0.964$ and $(\Delta/\rho)_{min} = -0.985$ e/Å^3.

REFERENCES

1. J.M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **27**, 89 (1988).
2. X.H. Bu, H. Liu, M. Du, L. Zhang, Y.M. Guo, M. Shionoya and J. Ribas, *Inorg. Chem.*, **41**, 1855 (2002).
3. H. Liu, X.H. Bu, M. Du, K.M.C. Wong, V.W.W. Yam and M. Shionoya, *Inorg. Chem.*, **40**, 4143 (2001).
4. H. Liu, B.H. Zhong, L.P. Liu and S.T. Han, *J. Chem. Crystal*, **34**, 289 (2004).
5. H. Liu, X.H. Bu and M. Du, *Acta Crystallogr.*, **E57**, o372 (2001).
6. G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution; Gottingen University: Germany (1997); G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement; Gottingen University: Germany (1997).

(*Received*: 9 December 2005; *Accepted*: 1 September 2006) AJC-5074