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Synthesis and crystal structure of $[Cu(dpq)_2(ClO_4)](ClO_4)\cdot 1.5CHCl_3$ (dpq =2,3-di-2- pyridylquinoxaline)

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The title complex $[Cu(dpq)_2(ClO_4)](ClO_4)\cdot 1.5CHCl_3$ (dpq =2,3-di-2- pyridylquinoxaline) was prepared by the ligand dpq with $Cu(ClO_4)_2\cdot 6H_2O$ and its structure was first elucidated by X-ray analysis.

Keywords: crystal structure, 2,3-di-2-pyridylquinoxaline

The research on the coordination chemistry of transition metal complexes with polypyridyl bridging ligands has progressed rapidly in recent years.[1] They are of considerable interest because of their potential as building blocks for supramolecular assemblies directed by either metal coordination or other intermolecular electronic interactions.[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 complex have been a particular focus.[3,4] In our effort to develop new functionalised complexes with such ligands, we report herein the complex $[Cu(dpq)_2(ClO_4)](ClO_4)\cdot 1.5CHCl_3$.

2,3-Di-2-pyridylquinoxaline and its derivatives are the potential tetradentate ligands and can adopt different coordinated modes. The dpq bonded to the metal centre in five-membered bidentate mode (N donors of pyridine and quinoxaline rings), a bridged tridentate mode (N donors of two pyridine and quinoxaline rings) and a seven-membered bidentate mode (N donors of two pyridine rings), respectively.[5,6] In the title complex, the Cu(II) centre is five coordinated by four nitrogen atoms of the two ligands which adopts a seven-membered bidentate mode. The molecular structures of five coordinate copper(II) complexes show an extensive range from regular trigonal bipyramidal to regular square based pyramidal structure of the majority of $[Cu(chelate)_2X]Y$ complexes.[7] In the title complex the Cu(II) centre is adopted in a distorted square based pyramidal geometry. The ORTEP view of the title complex with atom labelling is shown in Fig. 1. It consists of a discrete $[Cu(II)(dpq)(ClO_4)]^+$ cation, the uncoordinated ClO_4^- anion and $CHCl_3$ molecules. The Cu(II) centre is five coordinated by four nitrogen atoms of the two ligands which thus binds the metal centre in a bidentate fashion, and a ClO_4^- anion. The four Cu–N bonds of the two ligands are nearly equal with the values being 1.989(8) and 2.002(9) Å. The Cu–O distances are 2.397(9)Å. The coordination geometry around Cu(II) can be described as a distorted square based pyramidal geometry with Cu–O band occupying the axial positions. The Cu(II) centre deviates by 0.1024 Å from the plane defined by N(1), N(2), N(1A) and N(2A). The sum of the bond angles [$\angle$ N(1)–Cu(1)–N(1A) = 93.6(7)°, $\angle$ N(1)–Cu(1)–N(2) = 86.8(2)°, $\angle$ N(2)–Cu(1)–N(2A) = 92.2(6)° and $\angle$ N(1A)–Cu(1)–N(2A) = 86.8(2)°] is 359.4°, being very close to 360° . In this complex, the Cu(II) centre 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 49.6 and 60.8°, respectively, and between the two pyridine rings is 94.5°. The quinoxaline rings of two ligands in the complex are nearly parallel, the neighboring aromatic rings separated by approximately 3.5 Å, indicating the presence of significant face-to-face π–π stacking interactions.

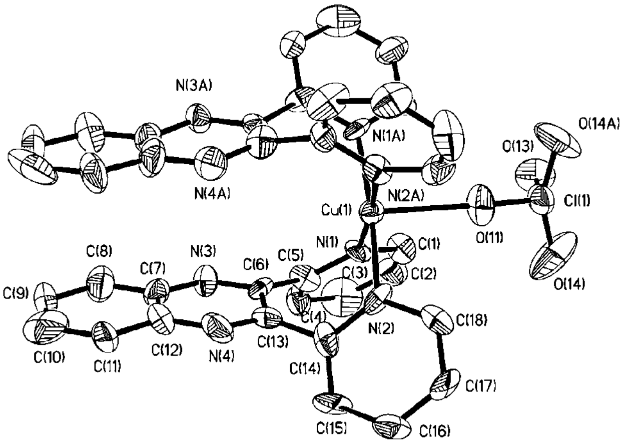

Fig. 1 The ORTEP structure of the title compound with atom labelling.

Experimental

All the reagents for synthis were commercially available and used without further purification or purified by standard methods prior to use. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a FT-IR 170SX (Nicolet) spectrometer with KBr pellets and electronic spectra on a Hitachi UV-3010 spectrometer.

Synthis of the Cu(II) complex: A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1 mmol) in CH_3CN (10 ml) were laid upon a solution of dpq (0.1 mmol) in $CHCl_3$ (10 ml) in a tube with very careful and subsequent diffusion. After several days, blue cubic crystals of the complex suitable for X-ray analysis were adhering to the wall of the tube. Yield: 45%. IR (KBr pellet, cm^{-1}): 3438w, 1638s, 1586s, 1479m, 1353m, 1095s, 786w, 746w, 625w. Anal. Calcd for $C_{37.5}H_{25.5}Cl_{6.5}CuN_8O_8$: C, 44.59; H, 2.54; N, 11.09%. Found: C, 44.48; H, 2.56; N, 11.02 %.

Crystal data: $C_{37.5}H_{25.5}Cl_{6.5}CuN_8O_8$, Mr = 1010.12, orthorhombic, $Pma2_1$, a = 11.819(4) Å, b = 20.014(7) Å, c=10.547(3) Å. V = 2494.9(14) Å^3, D_x = 1.345 g cm^{-3}, Z = 2, μ = 0.838 cm^{-}1, T = 293(2)K. A blue cube crystal with dimensions of 0.20 mm × 0.30 mm × 0.35 mm was mounted on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite monochromator for data collection. The determination of unit cell parameters and data collections were performed with Mo$K\alpha$ radiation (λ = 0.71073 Å). A total of 9863 reflections with 3699 independent ones with R_{int} = 0.1303 and 1393 observed reflections with $I > 2\sigma(I)$ were collected in the range of 2.18 < θ < 25.02° by an ω/θ scan mode at 293(2) K. All data were corrected by using SADABS method. The structure was solved by direct methods with SHELXL-97 program.[8] The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. Cu(II) atom in the complex was located from E-maps. The hydrogen atoms were added theoretically, riding on the concerned atoms and being refined with fixed thermal factors. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0800P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to the final R = 0.0696 and wR = 0.1512. S = 0.957. Molecular graphics were drawn with the program package XP. Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition number CCDC-228694.

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References

1 A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.
2 S. Leininger, B. Olenyuk and P.J. Stang, *Chem. Rev*., 2000, **100**, 853.
3 R.R. Ruminski, P.T. Deere, M. Oliver and D. Serveiss, *Inorg. Chim. Acta*, 1998, **281**, 1.
4 M.R. Waterland, T.J. Simpson, K.C. Gordon and A.K. Burrell, *J. Chem. Soc., Dalton Trans.* 1998, 185.
5 O-S. Jung, S.H. Park, Y.J. Kim, Y-A. Lee, H.J. Jang and U. Lee, *Inorg. Chim. Acta.*, 2001, **312**, 93.
6 X-H. Bu, H. Liu, M. Du, K. M-C. Wong and V. W-W. Yam, *Inorg. Chim. Acta.*, 2002, **333**, 32.
7 M. Brophy, G. Murphy, C. O’Sullivan, B. Hathaway and B. Murphy, *Polyhedron*, 1999, **18,** 611.
8 G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, Göttingen University: Germany, 1997; Sheldrick, G.M. SHELXL-97, Program for X-ray Crystal Structure Refinement; Göttingen University: Germany, 1997.