Asian Journal of Chemistry Vol. 14, Nos. 3–4 (2002), 1251–1256

Synthesis and Characterization of Some C_2-Symmetric Copper(II), Ruthenium(II) and Chromium(0) Complexes with Quadridentate Ligands having 2-Quinolinyl Auxiliary Groups

ADNAN S. ABU-SURRAH
Department of Chemistry, Hashemite University, P.O. Box 150 459, Zarqa 13115, Jordan

Some new octahedral transition metal carbonyl and dichloro complexes (**2–7**) of the tetrapodal, stereorigid amine ligands (N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)-1,2-ethylenediamine (DBQED) (**1a**) and N,N′-dimethyl-N,N′-di(quinoline-2-methyl)-1,2-ethylene diamine (DMQED) (**1b**) have been prepared and characterized. The reaction of the ligands with $CuCl_2 \cdot 2H_2O$ afforded the corresponding Cu(II) dichloride complexes [(DBQED)$CuCl_2$] (**2**) and [(DMQED)$CuCl_2$] (**3**), respectively..Ru(II) complexes of the types [(DBQED)$RuCl_2$] (**4**) and [(DBQED)$Ru(CO)_2Cl_2$] (**5**) were prepared by the treatment of $RuCl_3 \cdot 3H_2O$ or $[Ru(CO)_2Cl_2]_n$ with the ligand DBQED. The chromium(0) carbonyl complexes [(DMQED)$Cr(CO)_2$] (**6**) and [(DBQED)$Cr(CO)_4$] (**7**) were prepared by refluxing the corresponding ligand with $Cr(CO)_6$ in xylene. In the complexes (**2, 3, 4** and **6**) the ligands act as a tetradentate chelate. While in **1** and **7** the ligand coordinates in a bidentate fashion.

Key Words: Synthesis, C_2-symmetric, Cu(II), Ru(II), Cr(0), Complexes, Quadridentate, Ligand.

INTRODUCTION

The coordination behaviour of the new tetradentate, stereorigid amine ligand system containing terminal 2-quinaldinyl-N-donor groups with late transition metals, like iron(II) and cobalt(II), has been investigated[1]. The results of X-ray structure analysis carried out on the octahedral complex [(DBQED)$FeCl_2$] showed that the quinoline units open a chiral cage around the metal centre, which resembles that of the two indenyl fragments in C_2-symmetric *ansa*-metallocene dichloride catalysts[2].

The reactions of these ligands with transition metals, that typically form square-planar geometry, such as palladium(II), has also been investigated[3]. The results confirmed that these ligands, bearing sterically demanding 2-quinolinyl moieties, coordinate in a tetradentate fashion and adopt a C_2-symmetric arrangement around the metal centre. The dichloro palladium(II) complexes show a dynamic behaviour by exchange of the terminal quinolinyl donor groups. A fluxional coordination behaviour was suggested for these quinoline moieties, which enables this new family of complexes to act as catalysts for cyclic olefin polymerization, even when chloride is present as counter ion. This fluctuation phenomenon, which is common in the coordination chemistry of kinetically labile palladium(II) complexes, is explained as a result of preliminary ligand dissociation enabling a variety of processes to occur[4].

As an extension of our studies upon both the coordination chemistry of heteroatom-containing ligands and the catalytic application of their metal complexes[5, 6], we report here on the synthesis of new copper(II), ruthenium(II) and chromium(0) complexes of the tetradentate amine ligands N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)-1,2-ethylene diamine (DBQED) and N,N′-dimethyl-N,N′-di(quinoline-2-methyl)-1,2-ethylene diamine (DMQED). The isolated complexes were characterized by their physical properties, elemental analysis, mass spectroscopy, and infrared spectroscopy.

EXPERIMENTAL

All reactions were carried out under dry nitrogen or argon by using standard Schlenk tube techniques. $[Ru(CO)_2Cl_2]_n$[7] and $[Ru(DMSO)_4Cl_2]$[8] [N,N′-dibenzyl-N,N′-di(quinoline-2-methyl]-2-ethylenediamine (DBQED) **(1a)**[1] and [N,N′-dimethyl-N,N′-di(quinoline-2-methyl]-1,2-ethylenediamine (DMQED) **(1b)**[1], were prepared according to literature procedures. The hydrocarbon and ether solvents were purified by distillation over $LiAlH_4$. $CHCl_3$ was purified by distillation over CaH_2. Ethanol was treated with sodium ethoxide/diethyl terphthalate and subsequently distilled. Elemental analysis was performed by Carlo Erba, Model 1106. Infrared spectra (KBr or CsI pellet) were measured on Bruker model IFS66V spectrometer or Bruker IFS 48 spectrometer. Mass spectra were acquire with Finnigan instrument Finnigan TSQ 70 (FAB, nitrobenzylalcohol matrix 70 eV). Melting points were determined with Philip-Harris melting point apparatus and are uncorrected.

Preparation of complexes

[(DBQED)CuCl$_2$·3H$_2$O] (2) and [(DMQED)CuCl$_2$·3H$_2$O] (3): To a filtered solution of $CuCl_2·2H_2O$ (0.5 g, 2.9 mmol) in EtOH (40 mL) was added a solution of the ligand (2. 9 mmol) in $CHCl_3$ (50 mL). Upon addition a green precipitate started to form. Stirring was continued for 12 h, then the product was isolated, washed with petroleum ether (b.p. 30–50°C) and dried in vacuum. The yield was 25 and 68% for 2 and 3, respectively.

[(DBQED)RuCl$_2$·H$_2$O] (4): A mixture of $RuCl_3·3H_2O$ (0.87 g, 3.33 mmol) and the ligand (2.0 g, 3.83 mmol) in EtOH (100 mL) was refluxed for 24 h, after which the solution was filtered and the solvent was evaporated to dryness. Extraction with benzene (100 mL) and evaporation of the solvent gave the product which was then washed with Et_2O and dried in vaccum (yield *ca.* 90%).

[(DBQED)Ru(CO)$_2$Cl$_2$] (5): To a suspension of $[Ru(CO)_2Cl_2]_n$ (0.67 g, 2.94 mmol) in EtOH (50 mL) was added the ligand (1.69 g, 3.23 mmol) in the same solvent (50 mL). The mixture was refluxed for 48 h, then the solution was filtered and the solvent was evaporated to dryness. The isolated orange solid which was washed with petroleum ether (30–50 b.p.) (30 mL × 2) and dried in vacuum (yield *ca.* 27%).

[(DMQED)Cr(CO)$_2$] (6): A filtered solution of Cr(CO)$_6$ (0.89 g, 4.04 mmol) in toluene (50 mL) was added to a filtered solution of the ligand (1.50 g, 4.05 mmol) in the same solvent (50 mL). The mixture was refluxed for 24 h, during which a red precipitate was formed, which was then filtered, washed with toluene (20 mL× 3) and Et$_2$O (30 mL × 3) and dried in vacuum (yield *ca.* 67%).

[(DBQED)Cr(CO)$_4$·2H$_2$O] (7): A mixture of Cr(CO)$_6$ (0.25 g, 1.14 mmol) and the ligand (0.60 g, 1.15 mmol) in xylene (50 mL) was refluxed for 6 h, during which the milky suspension became a colourless solution. Evaporation of the solvent gave the product which was isolated after washing with Et$_2$O (30 mL × 2) (yield *ca.* 32%).

RESULTS AND DISCUSSION

For octahedal complexes bearing two bidentate or one tetradentate ligand like **1a, b,** three isomers are possible (Fig. 1). Based on a molecular model study and the X-ray structure analysis of the dichloro iron(II) complex [(DBQED)FeCl$_2$]^1 and the complex [(bipy)$_2$FeEt$_2$]^9, we expect also that the octahedral complexes prepared in the present study exist in the chiral and C$_2$-symmetric geometry of the *cis* isomer **A** (Fig. 1).

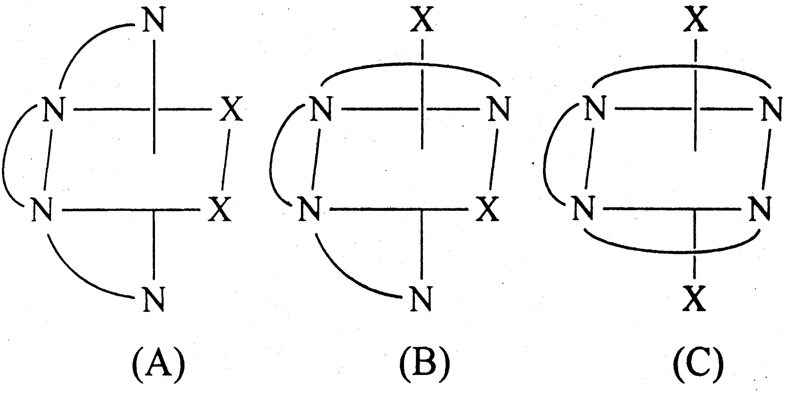
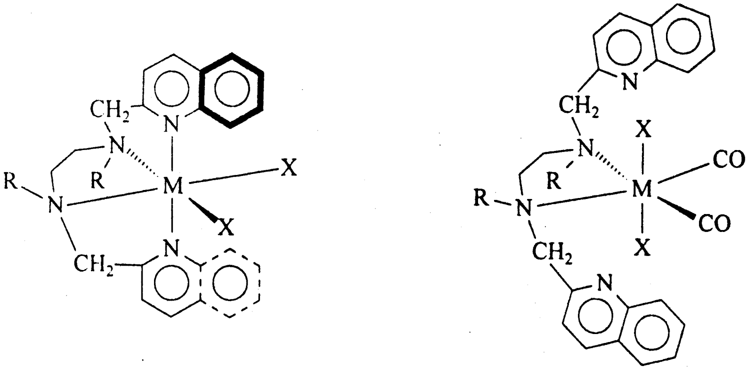


Fig. 1 Conformational isomers of tetradentate ligands in an octahedral coordination geometry: A, chiral, C2-symmetric; B, chiral asymmetric; C, chiral.

The copper(II) complexes **2** and **3** were prepared by stirring the ligands **1a, b,** respectively, with CuCl$_2$.2H$_2$O in ethanol or chloroform (Fig. 2). The suggested formula was elucidated based on IR-spectra, MS (FAB) and elemental analysis.

An effective route to synthesize ruthenium complexes with the tetradentate ligands **1a** and **1b**, is the applying of RuCl$_3$ as starting material. Reaction of **1a** with RuCl$_3$·3H$_2$O in EtOH under reflux conditions afforded the corresponding dichloride complex **(4)** in 90% yield (Fig. 2). IR-analysis of the complex indicates the presence of the respective ligand in it. Elemental analysis showed also that the ruthenium to ligand in the complex is 1 : 1. Moreover, the complex solubility behaviour in organic solvents further supports its non-ionic nature.

Using the halogenocarbonyl complex $[Ru(CO)_2Cl_2]_n$ as starting material provides also a simple method of preparing halogenocarbonyl amine complexes[10]. Treatment of the ligand **1b** with $[Ru(CO)_2Cl_2]_n$ in ethanol under reflux conditions afforded the complex $[(DBQED)Ru(CO)_2Cl_2]$ **(5)** as an orange solid. According to IR-and mass spectroscopic analysis, the ligand was found to behave as a bidentate chelate in the complex (Fig. 2). Such a coordination behaviour for the ligand has been also observed in its palladium(II) complexes when relatively stronger coordinating ligands are present[3].



(2 , 3 , 4 , 6)

2 : M = Cu ; R = CH_2Ph ; X = Cl
3 : M = Cu ; R = CH_3 ; X = Cl
4 : M = Ru ; R = CH_2Ph ; X = Cl
6 : M = Cr ; R = CH_3 ; X = CO

(5 , 7)

5 : M = Ru ; R = CH_2Ph ; X = Cl
7 : M = Cr ; R = CH_2Ph ; X = CO

Fig. 2. Proposed structures of the complexes prepared in the present study.

The IR-spectrum shows two strong bands at 2062 and 1999 cm^{-1} which indicate that the terminal Ru-CO are in *cis*-arrangement[4]. The decrease in the M—CO stretching frequency can be due to the M-ligand complexation.

Octahedral metal carbonyls and derivatives can offer an opportunity for fundamental mechanistic studies of transition metal complexes[11, 12]. Although a large number of chromium carbonyl compounds with phosphorus ligands have been described[13], complexes of Cr(0) with amine chelate systems are rare[14]. A convenient synthetic route to carbonyl amine chromium complexes is to reflux a solution of $Cr(CO)_6$ in toluene or xylene with the presence of a slight excess of the ligands[7]. Refluxing of the quadridentate ligand DMQED with the chromium carbonyl for 24 h afforded the complex $[(DMQED)Cr(CO)_2]$ **(6)** (Fig. 2). The IR-spectrum of the air-stable isolated product shows only two strong bands at 1887 and 1760 cm^{-1} which can be assigned to two terminal carbonyl groups in *cis*-arrangement[4, 15] and thus indicating the presence of the ligand as a tetradentate chelate. However, under shorter reflux time, this type of ligands showed a different coordination behaviour. Based on IR-, MS (FAB) and elemental analysis, the reaction of the ligand DBQED with Cr(CO)$_6$ under reflux conditions for 6 h, afforded the mononuclear complex (7) which contains four terminal carbonyl groups and a bidentate amine chelate in the molecule (Fig. 2).

TABLE-1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES[a]:

No.	Complex (Colour)	m.p. (°C)	%Analysis: Found (Calcd.)			ν(C=O) cm^{-1}	MS (FAB) m/e (rel. int.)
			C	H	N		
2.	(DBQED)CuCl$_2$ (green)	155	60.80 (60.79)	5.66 (5.66)	7.87 (7.88)	—	620.2 (85%, M$^+$–Cl) 585.3 (35%, M$^+$–2Cl)
3.	(DMQED)CuCl$_2$ (green)	183	51.56 (51.60)	5.77 (5.77)	10.0 (10.0)	—	468.0 (75%, M$^+$–Cl 433.0 (40%, M$^+$–2Cl)
4.	(DBQED)RuCl$_2$ (yellow)	177	60.86 (60.67)	5.37 (5.09)	8.35 (7.86)	—	694.5 (60%, M$^+$) 659.4 (40%, M$^+$–Cl)
5.	(DBQED)Ru(CO)$_2$Cl$_2$ (orange)	160	60.52 (60.80)	4.43 (4.56)	7.83 (7.46)	2062s, 1999s, sh	686.5 (40%, M$^+$–COCl)
6.	(DMQED)Cr(CO)$_2$ (red)	265	64.73 (65.26)	5.21 (5.48)	11.6 (11.7)	1887s, 1747s	478.5 (15%, M$^+$) 422.5 (100%, M$^+$–2CO)
7.	(DBQED)Cr(CO)$_4$ (colourless)	145	66.63 (69.47)	5.49 (5.29)	7.14 (7.15)	1957s, 1899s, 1762s	686.7 (6%, M$^+$) 630.7 (15%, M$^+$–2CO) 537.9 (40%, M$^+$–4CO)

[a] Complexes (2) and (3) crystallize with 3 moles of H$_2$O and complexes (4) and (7) and with one and two moles of H$_2$O, respectively.

The above observation about the coordination behaviour of the tetradentate amine ligands DMQED and DBQED indicates that these ligands can, under certain reaction conditions, behave in a hemilabile fashion.

REFERENCES

1. B. Rieger, A.S. Abu-Surrah, R. Fawzi and M. Steiman, J. *Organomet. Chem.*, **497,** 73 (1995).
2. H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34,** 1143 (1995).
3. A.S. Abu-Surrah, U. Thewalt and B. Rieger, *J. Organomet. Chem.*, **587,** 58 (1999).
4. J.A. Casares, S. Coco, P. Espinet and Y.S. Lin, *Organometallics,* **14,** 3058 (1995) and references therein.
5. A.S. Abu-Surrah, K. Lappalainen, T. Repo, M. Klinga, M. Leskelä and H.A. Hodali, *polyhedron,* **19,** 1601 (2000).
6. A.S. Abu-Surrah and B. Rieger, *J. Mol, Catal. A*, **128,** 239 (1998).
7. M.J. Cleare and W.P. Griffith, *J. Chem. Soc.*, A, 372 (1969).
8. I.P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans., 204 (1973).*

9. E.H. Witten, W.M. Reiff, K. Lázár, B.W. Sullivan and B.N. Foxman, *Inorg. Chem.*, **24,** 4585 (1985).
10. A.S. Abu-Surrah, H.A. Samha, H.A. Hodali and A.M. Seyam, *Synth. React. Inorg. Met-Org. Chem.*, **22,** 805 (1992).
11. J.R. Graham and R.J. Angelici, *Inorg. Chem.*, **6,** 992 (1967).
12. D.J. Darensbourg and R.L. Kump, *Inorg. Chem.*, **17,** 2680 (1978).
13. A.O. Baghlaf, M. Ishq, S.A. Rahman, A.B. Al-Tahir, A. Zaidan and R.A. Kabli, *Polyhedron,* **7,** 219 (1988).
14. T. Daniel, N. Suzaki, K. Tanak, A. Nakamura, *J. Organomet. Chem.*, **505,** 109 (1995).
15. J.P. Collman and L.S. Hegedus, in: *Principles and Applications of Organotransition Metal Chemistry,* University Science Books, California, p. 85. (1980)

(*Received*: 15 February 2002; *Accepted:* 1 May 2002) AJC-2676