Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1296–1300

Synthesis and Characterization of Benzamide Metal Complexes

SABINA JHAUMEER-LAULLOO,* MINU G. BHOWON and KARUNA REDDI
Department of Chemistry, Faculty of Science, University of Mauritius, Reduit, Mauritius

A few metal complexes of 2,2′-dithiobisbenzamide (DTBA) were synthesized and characterised by analytical and spectroscopic techniques. The IR data suggest coordination through nitrogen rather than oxygen of the amide group. All these complexes were found to be more effective catalysts in the oxidation of benzyl alcohol to benzaldehyde compared to free ligands.

INTRODUCTION

The coordination chemistry of amide-containing ligands plays an important role in several areas of current research. Synthesis of transition metal amide $(RCONH_2)^{1,2}$ and amidato $(RCONH^-)^{1,3}$ complexes has received attention over the years and has recently been the focus of renewed interest following the confirmation that 'platinblau' and related compounds known as antitumour agents contain bridging $RCONH^-$ ligands.[4]

In view of these facts and as part of our interest in metal amide interactions we prepared metal amido complexes and studied their chemistry.

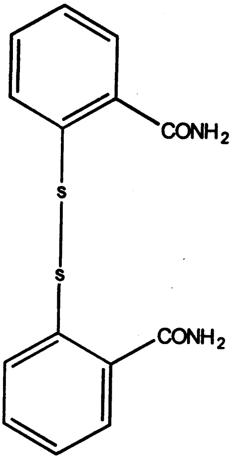

Fig. 1. Structure of dithiobisbenzamide, (DTBA)

EXPERIMENTAL

Most of the reagents were used without further purification, except for thionyl chloride, diethylether and toluene, which were distilled prior to use.

Melting point was determined on an electrothermal digital melting point apparatus. Infrared spectra were recorded on a Mattson 1000 FTIR spectrometer in the range 4000–400 cm^{-1}. Ultraviolet-visible spectra were recorded on a PU 8700 series UV/visible spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded at 250 MHz on a Bruker electrospin spectrometer and elemental analyses were obtained from a LECO CHNS-932 analyser.

Synthesis of 2,2′-dithiobisbenzamide (DTBA)

To 2,2′-dithiosalicylic acid (1.59 g, 5.20 mmol) an excess of thionyl chloride (50 mL) was added and refluxed for 1 h on a water bath. The excess of thionyl chloride was then distilled off under anhydrous conditions. The remaining traces of thionyl chloride were removed by co-distillation with dry toluene and the last traces of toluene were removed under *vacuo* to yield the bis-acid chloride as a reddish-brown solid. Concentrated ammonia (50 mL) was added to the resulting bis-acid chloride, which was then refluxed for a further 1 h. When dilute hydrochloric acid was added a yellow-brown solid precipitated out. The crude product was recrystallised from EtOH (95%), to yield the analytically pure ligand as a pale brown solid with percentage yield 86.2%.

Reaction of DTBA with ruthenium(III) chloride, hydrate and Palladium dichloride (1a–3a)

Ruthenium trichloride hydrate (0.199 g, 0.882 mmols) and DTBA (0.268 g, 0.880 mmols) were dissolved in 40 mL of EtOH (95%) and the resulting solution was refluxed for 3 h. A dark brown solid was obtained, which was filtered off, washed with EtOH (95%) and dried *in vacuo.*

Ruthenium trichloride hydrate (0.134 g, 0.594 mmol) with DTBA (0.400 g, 1.21 mmol) and palladium dichloride (0.224 g, 1.27 mmol) with DTBA (0.225 g, 0.740 mmol) were dissolved in 40 mL EtOH (95%) and the reaction mixtures were refluxed for 3 h. The resulting solutions were concentrated, and in both cases the addition of ether resulted in the formtion of a black solid which was filtered off. The solids obtained were washed with THF and petroleum ether and dried in *vacuo.*

Reaction of DTBA with ruthenium trichloride in the presence of L (L = triphenylphosphine, pyridine and 1,8-diaminooctane) (4a–6a)

Ruthenium trichloride (1.17 mmols), DTBA (1.65 mmols) and L(3.90 mmols) were dissolved in 50 mL of EtOH (95%) and the resulting mixture was refluxed for 3 h. The solution obtained was concentrated and precipitated with ether to obtain a solid. It was filtered and washed with EtOH, THF and petroleum ether, and dried in *vacuo.*

Oxidation of benzyl alcohol

To a solution of benzyl alcohol (0.125 g, 1.15 mmol) in DCM, N-methylmorpholine N-oxide, (NMO) (3 mmol) was added followed by the metal complexes (1.37×10^{-2}–2.13×10^{-2} mmol). The solution was stirrred for 3 h in the presence of 3 Å molecular sieves (0.5 g). The mixture was filtered and then evaporated to dryness and extracted with diethylether (2×25 cm^3). The combined ethereal extracts were then filtered and evaporated to give benzaldehyde, which was quantified as the 2,4-dinitrophenylhydrazone derivative.

RESULTS AND DISCUSSION

2,2′-Dithiosalicylic acid was refluxed with excess $SOCl_2$ to yield the bis acid chloride. Refluxing the bis acid chloride in concentrated NH_3 yielded a brown solid DTBA. When DTBA and $RuCl_3\cdot 3H_2O$ were refluxed in molar ratio 1 : 1, a brown paramagnetic solid **1a** was obtained while 2 : 1 molar ratio yielded a diamagnetic compound **2a**. A red soid was isolated from the reaction of DTBA and palladium(II) chloride (1 : 2). Refluxing DTBA and $RuCl_3\cdot 3H_2O$ (1 : 1) with two-fold excess of ligand L (L = triphenylphosphine, pyridine and 1,8-diamino-octane) three compounds **4a–6a** were isolated.

Repeated attempts to react with other metal salts such as zinc(II) chloride, copper(II) chloride, manganese(II) chloride, ferric(III) chloride, cobalt(II) chloride, nickel(II) chloride and lanthanide salts such as Sm(III) nitrate, Nd(III) nitrate and Ce(III) nitrate failed even though the reaction mixtures were refluxed for 3 days. It led to the precipitation of the ligand DTBA, which was confirmed by analytical and spectroscopic data.

The IR spectrum of DTBA showed a sharp intense peak at 1641 cm^{-1} and small peaks at 1616 and 1562 cm^{-1} due to amide bands I and II respectively. Amide band I consists mainly of ν(C=O) frequency and the amide band II arises from ν(C=N) as well as from ν(N—H) frequency.[1, 5] The peak at 3384 cm^{-1} showed N—H stretching frequency, confirming the presence of the amide group in DTBA. In the metal complexes **1a–6a**, amide band I (1646–1633 cm^{-1}) showed a slight shift to lower frequency or no shift at all compared to DTBA indicateing the non-coordination of the carbonyl oxygen to the metal. The N—H stretching band in metal complexes **1a–6a** at 3384–3318 cm^{-1} and amide band II 1587–1573 cm^{-1} and 1538–1517 cm^{-1} (downfield compared to DTBA, 1616 and 1562 cm^{-1}) suggested the coordination of nitrogen to the metal. The additional intense peak of ν(C=N) at 1606 cm^{-1} confirmed the presence of pyridine moiety in metal complex **5a**.

In the ^{1}H NMR, a broad mulitplet in all the complexes, was observed at δ 6.8–8.3 ppm due to aromatic protons. Peaks at δ 7.9–9.4 ppm were indicative of NH_2 protons which are shifted downfield compared to DTBA (δ 8.1 ppm).

In the UV-visible spectra the intense peak at 216–397 nm was assigned to

TABLE-1
SPECTRAL AND ANALYTICAL DATA OF DTBA AND ITS COMPLEXES

	Compound	Colour, yield (%), m.p. (°C)	Elemental analysis, calcd. (found)				IR (cm^{-1})	^{1}H NMR^a ppm	UV^b nm
			C	H	N	S			
	DTBA $C_{14}H_{12}N_2O_2S_2$	Brown, 86, 243	55.3 (54.8)	4.0 (4.2)	9.2 (9.2)	21.1 (20.8)	1641, 3384	7.3–7.7, 8.1	302
1a	$C_{14}H_{18}N_2O_5S_2Cl_3Ru$	Brown 30, >300	29.7 (29.4)	3.1 (3.1)	4.9 (5.2)	11.4 (13.8)	1639, 3318		257, 306, 588
2a	$C_{14}H_{16}N_2O_4S_2Cl_2Ru$	Black 62, >300	32.8 (34.6)	3.1 (3.2)	5.5 (5.8)	12.5 (13.1)	1641, 3324	6.8–8.1, 8.7–9.1	295, 428
3a	$C_{14}H_{16}N_2O_4S_2Cl_2Pd$	Red 55, 287	32.5 (32.9)	3.1 (3.1)	5.4 (5.4)	12.3 (12.2)	1639, 3330	6.9–7.5, 7.9–8.0	296, 368, 548
4a	$C_{32}H_{37}N_2O_7S_2Cl_2PRu$	Green 49, >300	46.3 (42.0)	4.5 (4.0)	3.4 (4.5)	7.7 (10.7)	1637, 3349	7.0–7.7, 9.0–9.4	297, 604
5a	$C_{19}H_{27}N_3O_7S_2Cl_2Ru$	Green 43, >300	35.3 (35.3)	4.1 (4.3)	6.5 (6.7)	9.9 (10.0)	1633, 3378	6.8–8.3, 8.6–8.9	297, 397, 596
6a	$C_{22}H_{42}N_4O_7S_2Cl_2Ru$	Black 93, >300	37.2 (37.2)	5.9 (5.2)	7.9 (8.2)	9.0 (9.1)	1646, 3372		

[a] DMSO-d_6
[b] Ethanol

π–π^* and n–π^* transition of the aromatic rings, whereas the peak at 428–604 nm could be due to ligand (π^*) to metal (d) charge transfer.

Repeated attempts to obtain the analytically pure compound **4a** were unsuccessful. Compound **6a** was found to be insoluble in all solvents. It could be due to the formation of a polymeric complex because of the long aliphatic chain present in 1,8-diaminooctane.

The catalytic activity of the ruthenium metal complexes was studied in the presence of N-methylmorpholine-N-oxide (NMO) for selective oxidation of primary alcohol such as benzylalcohol to benzaldehyde.[6] The results for the catalytic oxidation are summarised in Table-2. The benzaldehyde formed was quantified as its 2,4-dinitrophenylhydrazone derivative. No catalytic activity was observed while using only the ligand, DTBA. There was also no detectable oxidation of benzyl alcohol in the presence of NMO alone in the absence of the ruthenium complex. All the synthesised ruthenium complexes of DTBA were found to catalyse the oxidation of benzyl alcohol to benzaldehyde but the yields and turnover were found to vary as indicated in Table-2. Compound **2a** was found to be the most effective catalyst.

TABLE-2
CATALYTIC OXIDATION OF BENZYL ALCOHOL IN THE PRESENCE OF NMO

Ruthenium complex	No. of moles of complex used/mmol	Yield[a] (%)	Turnover[b]
1a	1.95×10^{-2}	34.8	19.8
2a	1.95×10^{-2}	100.0	57.5
3a	2.13×10^{-2}	28.3	15.5
4a	1.37×10^{-2}	45.6	46.9
5a	1.60×10^{-2}	29.3	23.0
6a	1.69×10^{-2}	43.3	31.8

[a] Yield based on alcohol
[b] Mole of product per mole of catalyst

REFERENCES

1. H. Sigel and R.B. Martin, *Chem. Rev.*, **82,** 385 (1982).
2. T.C. Woon and D.P. Fairlie, *Inorg. Chem.*, **31,** 4069 (1992).
3. T. Ito, S. Kurishima, M. Tanaka and Osakada, *Organometallics*, **11,** 2333 (1992).
4. F.D. Rochon, P.C. Kong and R. Melanson, *Inorg. Chem.*, **29,** 1352 (1990).
5. T. Satyanarayana and K.V. Reddy, *Trans. Met. Chem.*, **19,** 283 (1994).
6. M.G. Bhowon, H. Li Kam Wah and R. Narain, *Polyhedron*, **18,** 341 (1999).

(*Received:* 26 June 2000; *Accepted:* 26 July 2000) AJC-2090