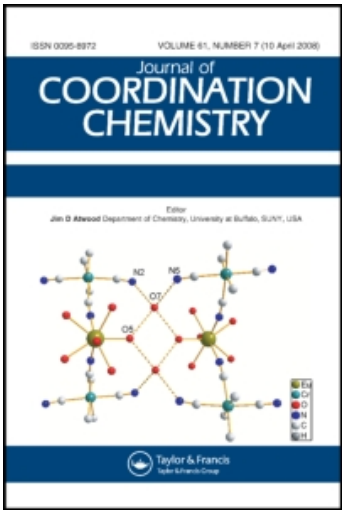

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Reactivity and improved synthesis of aquotris(dimethylsulfoxide)bis-(trifluoroacetato)ruthenium(II)

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Reactivity and improved synthesis of aquotris(dimethylsulfoxide)bis-(trifluoroacetato)ruthenium(II)

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Reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ with triphenylphosphine and triphenylarsine gives complexes of the type $[Ru(Me_2SO)(O_2CCF_3)_2(EPh_3)_2]$ (where E = P or As) in which there is a partial substitution of dimethylsulfoxide. Reaction with unidentate N donors resulted in $[Ru(O_2CCF_3)_2L_4]$ (where L = pyridine, imidazole, benzimidazole); reaction with diimines yielded $[Ru(L–L)_3](O_2CCF_3)_2$ (where L–L = 2,2′-bipyridyl, 1,10-phenanthroline). All complexes have been characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectroscopy.

Keywords: Ruthenium(II); Trifluoroacetate; Dimethylsulfoxide; Synthesis; Reactivity

1. Introduction

The chemistry of dimethylsulfoxide complexes of ruthenium containing halides has been extensively studied [1–9] and several derivatives are reported to be good catalysts for various homogenous reactions [7, 10–12]. Ruthenium sulfoxide complexes find applications due to their anti-tumor activities [13–16]. Ruthenium dimethylsulfoxide complexes also find use in the field of medicinal chemistry as radiosensitizers [17]. Despite interest in ruthenium dimethylsulfoxide complexes, very few reports on ruthenium dimethylsulfoxide complexes containing trifluoroacetato groups as anionic ligand are available in the literature [18]. Here an improved synthesis of aquotris (dimethylsulfoxide)bis(trifluoroacetato)ruthenium(II) and its reactivity towards various mono and bidentate ligands are reported.

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2. Experimental

All chemicals used were of AR or chemically pure grade. Solvents were purified prior to use by standard methods. $RuCl_3 \cdot nH_2O$ was used as received from Arora–Mathey Ltd., Calcutta. Molar conductivity measurements in chloroform (mM concentrations) were made using a Wayne–Kerr B905 conductometer. IR spectra were recorded (KBr pellets) using a Perkin–Elmer 983 and Nicolet 410 spectrophotometers. C, H and N analysis were carried out at RSIC, NEHU, Shillong; satisfactory analyses were obtained for all complexes. ^{1}H NMR spectra were recorded on a Brucker ACF 300 spectrometer. Silver trifluoroacetate was prepared by metathesis of silver carbonate with trifluoroacetic acid in water.

2.1. *[Ru(Me$_2$SO)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)]*

To a solution of *cis*-[$Ru(Me_2SO)_4Cl_2$] (1.00 g, 2.1 mmol) in methanol (50 cm^3), solid $Ag(O_2CCF_3)$ (0.95 g, 4.3 mmol) was added. The mixture was stirred at room temperature for 6 h. AgCl precipitated out and was filtered off. The filtrate was allowed to concentrate at room temperature by slow evaporation for several days, when the resulting pale yellow crystalline solid was collected, washed with acetone and dry ether and dried *in vacuo*. Yield: 0.95 g (80%), m.p.: 158°C, $\Lambda_M(CHCl_3) = 18\,\Omega^{-1}\,cm^2\,mol^{-1}$, IR (cm^{-1}): 3300, 1680, 1625, 1442, 1426, 1193, 1148, 1116.

2.2. *[Ru(Me$_2$SO)(O$_2$CCF$_3$)$_2$(PPh$_3$)$_2$]*

A methanolic solution (25 cm^3) of [$Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)$] (0.25 g, 0.43 mmol) was added to a solution of triphenylphosphine (0.47 g, 1.8 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 6 h, when a light yellow compound separated. The compound was isolated by centrifugation, washed with dry ether and dried *in vacuo*. Yield: 0.24 g (60%), m.p.: 169°C, $\Lambda_M(CHCl_3) = 15\,\Omega^{-1}\,cm^2\,mol^{-1}$, IR (cm^{-1}): 1678, 1484, 1435, 1193, 1148, 1110, 1085, 1025.

2.3. *[Ru(Me$_2$SO)(O$_2$CCF$_3$)$_2$(AsPh$_3$)$_2$]*

A solution of [$Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)$] (0.25 g, 0.43 mmol) in methanol (20 cm^3) was added to a methanolic solution (20 cm^3) of triphenylarsine (0.55 g, 1.8 mmol). The mixture was refluxed on a water bath for 6 h, when a light yellow compound separated out. This was isolated by centrifugation, washed with dry ether and dried *in vacuo*. Yield: 0.24 g (55%), m.p.: 195°C, $\Lambda_M(CHCl_3) = 12\,\Omega^{-1}\,cm^2\,mol^{-1}$, IR (cm^{-1}): 1677, 1483, 1438, 1196, 1142, 1110, 1080, 1020.

2.4. *[Ru(O$_2$CCF$_3$)$_2$(L)$_4$] (where L = imidazole, benzimidazole)*

To a solution of [$Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)$] (0.25 g, 0.43 mmol) in methanol (20 cm^3), imidazole or benzimidazole (L) was added in a complex : L mol ratio of 1 : 4. The mixture was refluxed on a water bath for 3 h and concentrated to 5 cm^3. The solution was then evaporated to dryness at room temperature. The green product was washed with diethylether several times and dried *in vacuo*. Yield of imidazole complex: 0.16 g (67%), m.p.: 279°C, $\Lambda_M(CHCl_3) = 10\,\Omega^{-1}\,cm^2\,mol^{-1}$, IR (cm^{-1}): 3450,

3095, 1679, 1555, 1471, 1408, 1324, 1196, 1139, 1091, 740, 690; yield of benzimidazole complex: 0.22 g (64%), m.p.: 256°C, $\Lambda_M(CHCl_3) = 20\,\Omega^{-1}\,cm^2\,mol^{-1}$, IR($cm^{-1}$): 3450, 3010, 1682, 1545, 1482, 1405, 1332, 1200, 1145, 1094, 850, 740, 728, 695.

3. Results and discussion

$[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ has been prepared with improved yield as compared with the method reported earlier [18] by metathesis of *cis*-$[Ru(Me_2SO)_4Cl_2]$ with $Ag(O_2CCF_3)$ at room temperature. The compound is diamagnetic and non-electrolytic in nature. IR spectra of the compound show strong, sharp bands at 1680 and 1425 cm^{-1}, which are assigned to $\nu_{(OCO)asym}$ and $\nu_{(OCO)sym}$, respectively, of trifluoroacetate. The large $\Delta\nu$ value (253 cm^{-1}) clearly indicates unidentate bonding [19, 20]. Moreover, the spectrum shows a strong, sharp band at 1116 cm^{-1}, characteristic of $\nu_{(SO)}$ of *S*-bonded dimethylsulfoxide [2]. No band in the region 1000 to 900 cm^{-1} was observed, thereby confirming the absence of any *O*-bonded dimethylsulfoxide. A broad band around 3300 cm^{-1} and a medium sharp band at 1625 cm^{-1} are assigned to $\nu_{(OH)}$ and $\delta_{(HOH)}$, respectively, of the coordinated water molecule. ^1H NMR in $CDCl_3$ showed three sharp singlets of equal intensity at 3.29, 3.31 and 3.33 ppm, assignable to the methyl protons of the dimethylsulfoxide molecules. Signals due to methyl protons of *S*-bonded dimethylsulfoxide are observed between 3.0 to 3.4 ppm, whereas *O*-bonded dimethylsulfoxide gives signals lower than 3.0 ppm [2].

3.1. *Reactivity of $[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ towards triphenylphosphine and triphenylarsine*

$[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ is fairly soluble in most organic solvents, thereby making reactivity studies convenient. Reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ with triphenylphosphine and triphenylarsine at room temperature and at under reflux caused part or complete substitution of the dimethylsulfoxide groups. When $[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ was reacted with triphenylphosphine with $Ru : PPh_3 = 1 : 2$ or $1 : 4$ in boiling methanol, complete substitution of dimethylsulfoxide took place and the resultant complex was $[Ru(PPh_3)_2(O_2CCF_3)_2]$, similar to that reported in the literature [21]. IR spectra showed a strong, sharp band at 1620 cm^{-1} characteristic of $\nu_{(OCO)asym}$ of chelated trifluoroacetate [19, 20]. Characteristic $\nu_{(SO)}$ bands due to coordinated dimethylsulfoxide were absent.

Reaction of $[Ru(Me_2SO)_3(O_2CCF_3)_2(H_2O)]$ with triphenylphosphine or triphenylarsine in methanol at room temperature or with triphenylarsine in boiling methanol resulted in the substitution of two molecules of dimethylsulfoxide and one molecule of water to form $[Ru(Me_2SO)(EPh_3)_2(O_2CCF_3)_2]$ (E = P or As). Low molar conductance values indicate that these species are non-electrolytes. IR spectra showed a strong band at ~1680 cm^{-1} and a medium sharp band at ~1435 cm^{-1}. The former is assignable to $\nu_{(OCO)asym}$ whereas the latter is due to a combination of $\nu_{(OCO)sym}$ of trifluoroacetate and characteristic absorption of triphenylphosphine or triphenylarsine. Large $\Delta\nu$ (245 cm^{-1}) values indicate that trifluoroacetato groups remain bonded as unidentates. A medium intensity band at ~1110 cm^{-1} is attributable to $\nu_{(SO)}$ of *S*-bonded dimethylsulfoxide. Other bands due to triphenylphosphine or triphenylarsine were also observed. ^1H NMR spectra in $CDCl_3$ showed a sharp singlet at 3.0 ppm and

multiplets in the region 7.1 to 7.6 ppm. The singlet is assigned to methyl protons of dimethylsulfoxide and the multiplets between 7.1 to 7.6 ppm are due to protons of phenyl groups in triphenylphosphine or triphenylarsine [2].

3.2. *Reactivity of [Ru(Me$_2$SO)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)] towards monodentate nitrogen donors*

Reaction of [Ru(Me$_2$SO)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)] with monodentate nitrogen donors (pyridine, imidazole and benzimidazole) resulted in complexes [Ru(O$_2$CCF$_3$)$_2$L$_4$] (L = pyridine, imidazole and benzimdazole). The complexes with L = imidazole and benzimdazole are new, while [Ru(O$_2$CCF$_3$)$_2$(py)$_4$] has been prepared previously [19] by reaction of [Ru(μ–O$_2$CCF$_3$)$_4$] with pyridine. The complexes are non-electrolytes and diamagnetic, as expected. IR spectra show characteristic bands due to pyridine, imidazole and benzimdazole. Absence of any strong absorption around 1100 cm^{-1} indicates all dimethylsulfoxide ligands are substituted. The presence of unidentate trifuoroacetato groups is confirmed by the appearance of strong, sharp bands at ~1680 and ~1405 cm^{-1} due to $\nu_{(OCO)asym}$ and $\nu_{(OCO)sym}$ vibrations, respectively. ^{1}H NMR of [Ru(O$_2$CCF$_3$)$_2$(py)$_4$] complex is in conformity with data in the literature [22]. The spectrum of [Ru(O$_2$CCF$_3$)$_2$(Im)$_4$] shows singlets at 7.06, 7.32 and 8.10 ppm, attributed to the C–H protons of imidazole groups. [Ru(O$_2$CCF$_3$)$_2$(BenzIm)$_4$] shows signals at 7.04(q), 7.24(m), 7.34(m) 7.69(m) and 8.30(s) ppm for C–H protons of the benzimidazole groups. Broad singlets at 12.75 ppm for [Ru(O$_2$CCF$_3$)$_2$(Im)$_4$] and at 12.58 ppm for [Ru(O$_2$CCF$_3$)$_2$(BenzIm)$_4$] were observed and are assigned to N–H protons of imidazole and benzimidazole, respectively. The N–H signals indicate that coordination of imidazole/benzimidazole is through the tertiary N atom. Absence of methyl signals confirms complete substitution of dimethylsulfoxide.

3.3. *Reactivity of [Ru(Me$_2$SO)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)] towards bidentate nitrogen donors*

Reactions of [Ru(Me$_2$SO)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)] with 2,2′-bipyridine and 1,10-phenanthroline yielded [Ru(L–L)$_3$](O$_2$CCF$_3$)$_2$ [22]. IR spectra showed a very strong band around 1670 cm^{-1} due to $\nu_{(OCO)asym}$ of ionic trifluroacetate, but $\nu_{(OCO)sym}$ could not be assigned unambiguously due to the presence of diimine bands in the region 1400–1500 cm^{-1}. Conductivity measurements gave $\Lambda_M = 210$–$230\ \Omega^{-1}\,cm^2\,mol^{-1}$ in acetonitrile solution, confirming the ionic nature of the trifluoroacetate groups.

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