Inorganica Chimica Acta, *132* (1987) 207–212

An Electrochemical Study on the Oxidation of Tris(*N*,*N*-dimethyldithiocarbamato)ruthenium(III)

A. MONTREE, J. E. J. SCHMITZ, J. G. M. VAN DER LINDEN, J. J. STEGGERDA*
Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
L. H. PIGNOLET*
Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.
J. BOWMAN and S. H. WHEELER
Department of Chemistry, Bethel College, St. Paul, Minn. 55112, U.S.A.

(Received December 22, 1986)

Abstract

The electrochemical oxidation of $Ru(Me_2dtc)_3$ (where Me_2dtc = *N*,*N*-dimethyldithiocarbamate) in acetone or methylene chloride solution is a one-electron process followed by a dimerisation. This is concluded from cyclic voltammetric experiments at different scan rates, concentrations and temperatures with the use of Savéant's diagnostic criteria. NMR spectra taken at different temperatures confirm this conclusion. This behaviour is in contrast with that in coordinating solvents like acetonitrile where the one-electron oxidation is followed by addition of a solvent molecule to the coordination sphere, yielding $Ru(Me_2dtc)_3(CH_3CN)$.

Introduction

Several electrochemical studies have been reported which deal at least in part with the redox behaviour of the tris(*N*,*N*-disubstituted dithiocarbamato)-ruthenium(III) complexes, $Ru(R_2dtc)_3$ [1–5]. In various solvents, such as acetone, acetonitrile and dichloromethane, an electrochemically reversible one-electron reduction to $[Ru(R_2dtc)_3]^-$ has been observed [4, 5]. However, for the oxidation of $Ru(R_2dtc)_3$, an irreversible one-electron process has been observed with use of CH_3CN as solvent, and for R = ethyl the oxidation product was found to be the stable seven-coordinate complex of Ru(IV), $[(CH_3CN)Ru(Et_2dtc)_3]^+$ [4]. After exhaustive electrolysis, this diamagnetic complex has been isolated by column chromatography and identified by ^1H NMR and UV–Vis spectroscopy [4]. The analogous chloride complex, $ClRu(Et_2dtc)_3$, has been characterized by single crystal X-ray diffraction and has a pentagonal-bipyramidal geometry with the Cl^- in an axial position [3]. In this complex the chloride ion was found to dissociate in CH_3CN solution to give $[(CH_3CN)Ru(Et_2dtc)_3]Cl$ [3].

The R = methyl complex of Ru(III) shows the same general electrochemical behaviour in CH_3CN solution. With acetone and methylene chloride as solvent, however, a very different and striking dependence on the scan rate and temperature in cyclic voltammetry has been observed. This behaviour is unusual and has not been previously reported. An exhaustive electrochemical study on $Ru(Me_2dtc)_3$ has therefore been carried out with acetone and methylene chloride as solvents. In this study use is made of cyclic voltammetric and pulse polarographic (PP) techniques; variation of scan rate, concentration and temperature has led to a model which involves the rapid formation of a dimer, $[Ru_2(Me_2dtc)_6]^{2+}$, upon electrochemical (EC) oxidation. This study illustrates that the application of various electrochemical techniques and the diagnostic criteria of Savéant, when combined with the isolation and spectroscopic identification of redox intermediates, is a powerful and useful method for the elucidation of complex redox mechanisms.

Experimental

Measurements

Electrochemical measurements were made with a three-electrode PAR Polarographic Analyzer, model 174A, coupled with a Universal Programmer PAR, model 175. The working electrode was a platinum disc, the auxiliary electrode a platinum plate, and the reference electrode was dependent on the solvent used. For acetone as solvent the reference was Ag–AgCl (0.1 M LiCl in acetone), for acetonitrile SSCE (in acetonitrile) and for methylene chloride Ag–AgI

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*Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

(0.05 M Bu_4NI and 0.4 M Bu_4NClO_4 in CH_2Cl_2). The reference electrode was separated from the test solution via a Luggin capillary containing the supporting electrolyte (0.1 M Bu_4NClO_4). The Luggin capillary was positioned as close as possible (within 0.5 mm) to the working electrode to minimize *iR* drop. No external *iR* compensation was employed. Normal pulse voltammograms were obtained at a scan rate of 5 mV s^{-1} with a pulse frequency of 2.0 pulses per second. Cyclic voltammograms (CVs) were taken with scan rates of 0.005–100 V s^{-1}. The recording device was a Kipp BD 30 recorder, while CVs with scan speeds larger than 200 mV s^{-1} were displayed on a Nicolet Explorer II Model 206. Controlled potential electrolyses were carried out with a Wenking LB 75M potentiostat and a Birtley electronic integrator at a potential 200 mV beyond the peak potential observed in the CV.

Complete electrolysis of about 15 mg of electroactive material generally required 50 min. The temperature of the electrochemical measurements was *ca.* 20 °C, *i.e.* room temperature. Several experiments were carried out at −78 °C by placing the cell in a solid CO_2–acetone solution and intermediate temperatures were maintained ±1 °C by use of a thermostatted cell. Complex concentrations were *ca.* 1.0 mM unless specifically stated otherwise. Concentrations were varied at least one order of magnitude in studies where a concentration dependence was determined. All measurements were carried out under a nitrogen atmosphere.

^1H NMR spectra were recorded at 300 MHz with use of a Nicolet NT-300 spectrometer. Chemical shifts are reported as δ values with positive shifts downfield.

Materials

All the reagents used were of reagent quality. Tris-(*N*,*N*-dimethyldithiocarbamato)ruthenium(III) was prepared according to a published procedure [6]. The supporting electrolyte tetrabutylammonium perchlorate was also prepared according to published procedures [7] and was crystallised twice from an ether–ethanol mixture. Acetone, methylene chloride and acetonitrile (Merck p.a.) were used without further purification.

Results and Discussion

The electrochemical redox behaviour of $Ru(Me_2dtc)_3$ in acetone solutions is very similar to that in methylene chloride. Results are presented mainly for acetone solutions; unless otherwise stated the methylene chloride solutions gave the same results. Results are summarized in Tables I and II and in Figs. 1–3.

TABLE I. Electrochemical Data for $Ru(Me_2dtc)_3$ at 20 and 78 °C

Solvent/process	Temperature (°C)	Normal pulse voltammetry			Cyclic voltammetry					
		$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_d/C (mA l mol^{-1})	ν (V s^{-1})	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)	i_b/i_f	$i_p/C\nu^{1/2}$ (mA l $s^{1/2}$ mol^{-1} $V^{-1/2}$)
Acetone[a]										
reduction	20	−0.62	59	47	0.2	−0.66	−0.60	61	0.99	62
reduction	−78	−0.59	44	26	0.2	−0.63	−0.59	41	0.90	34
oxidation	20	0.61	56	45	0.005	0.55	0.62	73	0.98	62
					0.2	0.47[b]	0.64			54
					10	0.58	0.66			54
						0.12				
oxidation	−78	0.56	37	15	0.2	−0.21	0.59			29
Methylene chloride[c]										
reduction	20				0.05	−0.59	−0.52	66	0.99	
oxidation	20				0.05	0.22[e]	0.65			
Acetonitrile[d]										
reduction	20	−0.52	60	48	0.2	−0.56	−0.48	70	0.96	48
oxidation	20	0.52	57	50	0.2	−0.30[e]	0.55			48

[a] Reference electrode Ag–AgCl (0.1 M LiCl in acetone); for comparison $E_{1/2}$ of ferrocene oxidation in acetone was measured to be 0.62 V. [b] Very broad peak. [c] Reference electrode Ag–AgI (0.05 M Bu_4NI, 0.4 M Bu_4NClO_4 in CH_2Cl_2); $E_{1/2}$ of ferrocene oxidation in CH_2Cl_2 was measured to be 0.66 V. [d] Reference electrode saturated sodium Calomel electrode (SSCE); $E_{1/2}$ of ferrocene oxidation in CH_3CN was measured to be 0.39 V. [e] Not observed in the first scan.

TABLE II. Diagnostic Criteria According to Savéant [11]

Solvent	Temperature (°C)	Process	dE_p/dlog ν[a] (mV)	dE_p/dlog C[b] (mV)
Acetone	20	reduction	2	2
		oxidation	13	−24
Acetone	−78	reduction	5	0
		oxidation	30	6
Methylene chloride	20	reduction		2
		oxidation		−28
Acetonitrile	20	reduction	3	−2
		oxidation	36	3

[a] At a $Ru(Me_2dtc)_3$ concentration (C) of 1.0 mM and scan rates (ν) in the range 0.005–10 V s^{-1}. The limited accuracy in the determination of E_p and the small range in the logarithms of C and ν cause an uncertainty in the differentials of about 5 mV. [b] At a scan rate of 50 mV s^{-1} and concentrations of $Ru(Me_2dtc)_3$ in the range 0.1–1.0 mM. Estimated inaccuracy 5 mV.

Reduction of $Ru(Me_2dtc)_3$

The electrochemical reduction of $Ru(Me_2dtc)_3$ in acetone has firmly been established to be a reversible one-electron process [5]: $Ru(Me_2dtc)_3 + e \rightleftarrows Ru(Me_2dtc)_3^-$. It is an uncomplicated electron transfer process without any subsequent reaction in acetonitrile, acetone or methylene chloride in the temperature range from −78 °C to room temperature. This is confirmed (*vide infra*) by our data of dE_p/dlog ν and dE_p/dlog C (Table II).

Oxidation of $Ru(Me_2dtc)_3$

EC_{dim} reaction mechanism

The electrochemical oxidation of $Ru(Me_2dtc)_3$, occurring at about +0.60 V is a one-electron process also, as evidenced by the measured current functions (Table I, $i_p/C\nu^{1/2}$ in CV; i_l/C in PP). At room temperature and a scan rate of 5 mV s^{-1}, ΔE_p in the CV was 73 mV and i_b/i_f was 0.98, indicating a fast electron transfer (*vide infra*: $k \geqslant 0.05$ cm s^{-1}) and chemical reversibility.

The remarkable influence of the scan rate, ν, on the shape of the cyclic voltammograms is illustrated in Fig. 1. The shape of the forward oxidation wave had little dependence on ν and the anodic peak potential E_{pa} was shifted slightly to higher values at increasing ν (Table I). However, the shape of the backward reduction wave changed considerably when the scan rate was varied. At low scan rates the oxidation reaction looks quasi-reversible with a peak separation $E_{pa} - E_{pc} = 73$ mV and $i_b/i_f = 0.98$. At high scan rates two reduction peaks appeared, one at about the same potential as before (0.58 V) and another at much lower potential (0.12 V). At intermediate scan rates (between 0.2 and 2 V s^{-1}) a gradual broadening was observed which eventually leads to a separation into two peaks.

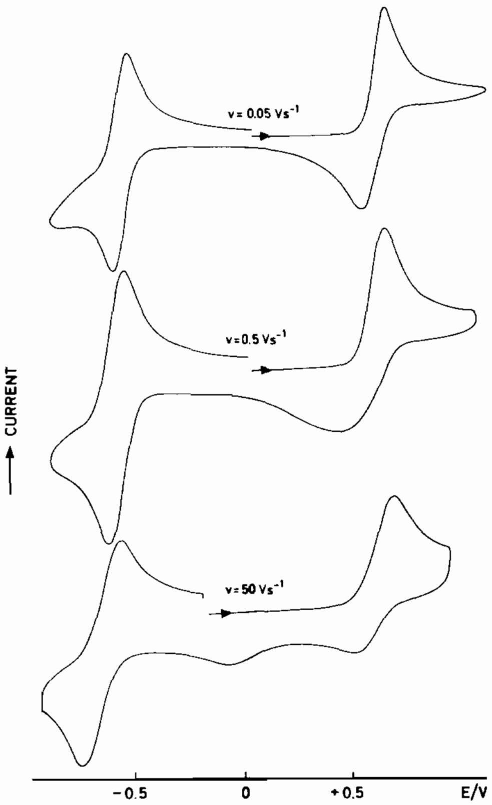

Fig. 1. Cyclic voltammograms of $Ru(Me_2dtc)_3$ in acetone at 20 °C and at scan rates of 0.05, 0.5 and 50 V s^{-1}.

Such a scan rate dependent behaviour is indicative [8] of a subsequent dimerization reaction (eqn. 1), evidence for which will be given later.

$$Ru(Me_2dtc)_3 \overset{k}{\rightleftharpoons} Ru(Me_2dtc)_3^+ \underset{k_m}{\overset{k_d}{\rightleftharpoons}} \tfrac{1}{2}Ru_2(Medtc)_6^{2+} \qquad (1)$$

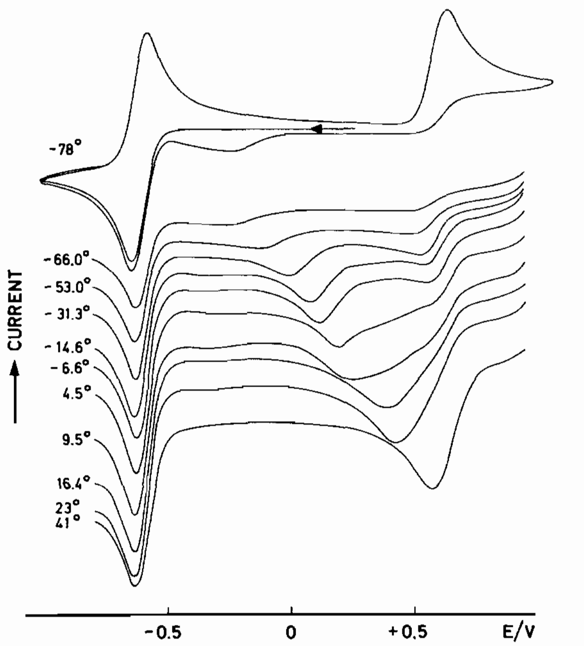

Fig. 2. Cyclic voltammogram of $Ru(Me_2dtc)_3$ in acetone at -78 °C, the 1st and the 2nd scans are shown. For higher temperatures up to 40 °C only the 2nd backward scans are shown. The scan rate is 1 V s^{-1}.

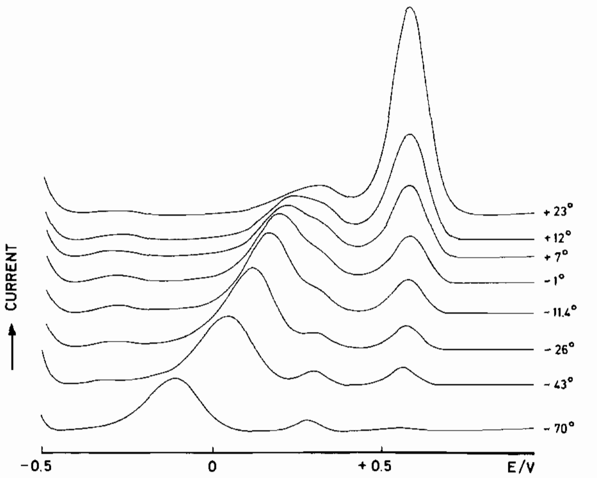

Fig. 3. Differential pulse voltammograms of acetonic solutions of $Ru(Me_2dtc)_3$ previously oxidized by exhaustive electrolysis at +0.8 V at room temperature. The temperature at which the DPPs were taken are indicated in the Fig. The potential range from +0.95 to -0.55 V is such that the reduction to $Ru(Me_2dtc)_3$ is not seen.

The influence of the scan rate on the shape of the CVs (Fig. 1) is caused by the limited rate of the splitting of the dimer, $Ru_2(Me_2dtc)_6{}^{2+}$, into the monomer $Ru(Me_2dtc)_3{}^+$. The NMR study (*vide infra*) shows that the equilibrium is far to the dimer side so that $k_m \ll k_d$. At small scan rates there is enough time for a decomposition of the dimer into $Ru(Me_2dtc)_3{}^+$, so in the backward scan only the reduction of the monomer was detected at 0.55 V. But at scan rates above *ca.* 1 V s^{-1} the reduction of the dimer was observed as a separate peak in the backward scan at 0.12 V.

Diagnostic criteria for an electrochemically generated dimerization reaction have been developed independently by Savéant *et al.* [9] and Nicholson *et al.* [10]. The shift of the peak potential of an oxidation reaction with changing concentrations and scan rates, $dE_p/d\log C$ and $dE_p/d\log \nu$ should be -19.7 and 19.7 mV, respectively, for an EC_{dim} mechanism. The experimental data (Table II) for acetone and methylene dichloride solutions are reasonable close to these theoretical values, so an EC_{dim} mechanism is operating.

For an EC_{dim} mechanism to give $dE_p/d\log C = -19.7$ mV it should be controlled by the kinetics of the dimerization reaction (KP zone according to Nadjo and Savéant [11]). Therefore $\Lambda = k(RT/D\nu F)^{1/2} > 10$, where D is the diffusion constant estimated to be 10^{-5} cm^2 s^{-1} and ν is the scan rate for these experiments taken at 50 mV s^{-1}. At room temperature $RT/F = 25.2$ mV and k, the electron transfer rate constant, must be greater than 0.05 cm s^{-1}, which is a reasonable assumption. Further $\lambda = RTk_dC/\nu F > 1.35$, where k_d is the second-order reaction rate constant for the dimerization reaction (eqn. (1)). Therefore, $k_d > 2.7 \times 10^3$ l mol^{-1} s^{-1}, which indicates that the dimerization is a fast reaction.

In acetonitrile solution the oxidation of $Ru(Et_2dtc)_3$ is followed by a chemical reaction with the solvent to produce $Ru(Et_2dtc)_3(CH_3CN)^+$ [4]. For $Ru(Me_2dtc)_3$ we found for this process $dE_p/d\log C = +3$ mV and $dE_p/d\log \nu = 36$ mV; this is in accord with Nadjo and Savéant's predictions [11] which give for the KP zone (where the EC process is controlled by the rate of the subsequent reaction) $dE/d\log C = 0$ and $dE/d\log \nu = 29.6$ mV.

The influence of the temperature on the dimer–monomer equilibrium

A set of cyclic voltammograms (Fig. 2) taken at various temperatures show clearly the influence of the temperature on the rate constants of the dimer–monomer equilibrium. The peaks of the reduction process to $Ru(Me_2dtc)_3{}^-$ and the forward wave of the oxidation were nearly unaffected, but the backward wave of the oxidation changed considerably when the temperature was varied. At about room temperature a single reduction dominated, but at about 0 °C there were two reduction peaks visible, one with a peak potential which shifted in negative direction when the temperature was lowered further, the other which stayed at about +0.5 V.

The peak currents of both reduction peaks decreased when the temperature was lowered. The explanation of this phenomenon goes along similar lines to those given above for the scan rate dependent behaviour. At room temperature the decomposition rate of the dimer is fast enough to keep up with the reduction of the monomer, so in the backward scan only a single reduction peak was seen, at 0.58 V, corresponding to the reduction of the monomer. But at low temperatures, where the dimerization is still fast, the reverse reaction is so slow that the reduction of the dimer could be detected in a separate reduction peak at a potential which was strongly dependent on the temperature. For the oxidation process in acetone solutions at −78 °C, $dE_p/d\log C$ is +6 mV, which is not significantly different from zero and $dE_p/d\log \nu$ has grown to 30 mV. This is indicative of Savéant's zone KI where the process is controlled by the chemical reaction as well as by the electron transfer [11], Λ should be smaller than about 1 so $k < 0.005$ cm s^{-1}. By lowering the temperature from +20 °C to −78 °C k has decreased by a factor of at least 10, which means that the activation energy for the electron transfer should be at least 2 kcal mol^{-1}, which is a realistic value. The temperature dependent redox behaviour of $Ru_2(Me_2dtc)_6^{2+}$ and $Ru(Me_2dtc)_3^+$ was studied in some more detail in a more concentrated solution of $Ru_2(Me_2dtc)_6^{2+}$ using differential pulse voltammetry. When at room temperature an acetone solution of $Ru(Me_2dtc)_3$ is oxidized at 0.80 V by exhaustive electrolysis $Ru_2(Me_2dtc)_6^{2+}$ will be the dominant product. The temperature dependent redox behaviour of $Ru_2(Me_2dtc)_6^{2+}$ and $Ru(Me_2dtc)_3^+$ is followed by taking differential pulse voltammograms of this solution at various temperatures (Fig. 3). At room temperature only the reduction of the monomer at 0.58 V occurs: $Ru(Me_2dtc)_3^+ + e \rightarrow Ru(Me_2dtc)_3$, because the monomerization reaction is fast enough.

However, when the temperature was lowered the decomposition rate of the dimer into monomer became so slow that at −78 °C only the dimer reduction was observed at −0.2 V: $Ru_2(Me_2dtc)_6^{2+} + 2\ e \rightarrow 2\ Ru(Me_2dtc)_3$. The reaction mechanism of this irreversible two-electron reduction was not studied in detail, but the ultimate product must be $Ru(Me_2dtc)_3$ as its normal reduction peak was seen at −0.6 V and there were no further indications of other electrochemically active species. The large shift with the temperature (about 400 mV) of the reduction potentials of $Ru_2(Me_2dtc)_6^{2+}$ is as yet not understood.

The very small peaks at 0.3 V and −0.3 V in the DPPs are assigned to side products of the oxidation. The peak at −0.3 V was sometimes seen in DPPs of $Ru(Me_2dtc)_3$, which was incompletely purified. It was probably due to the reduction of $Ru_2(Me_2dtc)_5^+$, which has been reported to be in this range [5]. The origin of the small wave at +0.3 V is unknown. The DPP of pure $Ru(Me_2dtc)_3$ in acetone solution at 20 °C showed only two peaks at +0.50 V and −0.55 V, which correspond to the oxidation and reduction reactions to $Ru(Me_2dtc)_3^+$ and $Ru(Me_2dtc)_3^-$, respectively.

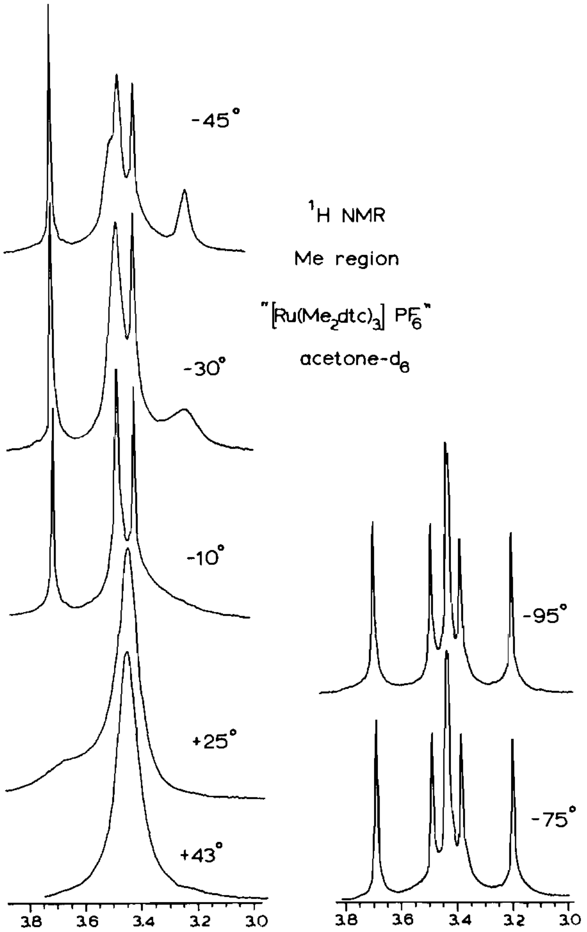

Fig. 4. NMR spectra in the CH_3 region of an acetone solution of oxidized $Ru(Me_2dtc)_3$ (see text) at various temperatures.

¹H NMR study

A concentrated acetone solution (0.15 M) of $Ru(Me_2dtc)_3$ was oxidized by controlled potential electrolysis with use of tetraethylammonium hexafluorophosphate as supporting electrolyte. A solid dark brown product precipitated out of this solution during oxidation. This product was recrystallized several times from acetone yielding dark red–brown microcrystals. These crystals were not suitable for X-ray diffraction analysis. A variable temperature ¹H NMR study was carried out on these microcrystals dissolved in acetone-d_6. Selected spectra recorded in the methyl region are shown in Fig. 4. At temperatures above *ca.* +40 °C a single broad resonance was observed. This resonance broadened unsymmetrically as the temperature was lowered and eventually split into six resolved peaks at temperatures below *ca.*

-90 °C. The complexity at low temperature suggests the presence of a compound which is dimeric in nature, and the variable temperature behaviour shown in Fig. 4 suggests that this spectrum is due to a single compound, although the presence of several compounds which undergo fast Me_2dtc ligand exchange cannot be ruled out.

It was not possible to determine the formulation of the stereochemistry of this dimeric compound as analytically pure samples could not be isolated, but the six line NMR pattern is consistent with a $Ru_2(dtc)_6^{2+}$ formulation. The solid state structure of the osmium analogue $Os_2(Et_2dtc)_6^{2+}$, has been determined [12] by X-ray crystallography and this complex has six non-equivalent ethyl groups. However, $Os_2(Et_2dtc)_6^{2+}$ is non-rigid on the ^1H NMR timescale even at -90 °C and only a single ethyl pattern was observed [1]. The addition of CH_3CN to this acetone solution of oxidized $Ru(Me_2dtc)_3$ resulted in the immediate appearance of a single Me resonance in the ^1H NMR ($\delta = 3.25$ ppm). This resonance remained a sharp singlet at low temperature and is due to the Me analogue of the known compound $(CH_3CN)Ru(Et_2dtc)_3^+$ [4]. No peaks due to the $Ru_2(Me_2dtc)_6^{2+}$ species were observed with CH_3CN present.

Several bimetallic cationic compounds of ruthenium(III) are known: e.g. $[\alpha\text{-}Ru_2(Me_2dtc)_5]^+$ and $[\beta\text{-}Ru_2(Me_2dtc)_5]^+$ [4]. Both of these complexes show five singlet Me resonances in their ^1H NMR spectra at room temperature, consistent with the 5-dtc formulation. At higher temperatures these lines begin to coalesce. This observation lends some support for the presence of $Ru_2(Me_2dtc)_6^{2+}$ in the acetone solution of oxidized $Ru(Me_2dtc)_3$, because in this case six singlet Me resonances were observed. It should be emphasized that the compound studied by NMR was isolated as a solid from the electrochemical cell after oxidation of a concentrated solution. It may or may not reflect the composition of the solution during normal cyclic voltammetry, which is carried out at much lower complex concentrations. In any case, the NMR analyses show that the formation of a dimeric species is thermodynamically favourable and that such species must be considered likely during cyclic voltammetry.

Conclusions

Application of various diagnostic criteria on the electrochemical one-electron oxidation process of $Ru(Me_2dtc)_3$ gave evidence of a fast subsequent dimerization process according to eqn. (1). At low temperatures (-70 °C) the oxidation process is controlled by the dimerization and the electron transfer process. The monomer–dimer equilibrium is at all temperatures far on the dimer side.

The expansion of the coordination sphere of $Ru(Me_2dtc)_3^+$ from 6 to 7 can be accomplished by the coordination of a solvent molecule (such as CH_3CN) or any coordinating anion (like Cl^-) in the solution [3, 4]. But in the case of acetone or methylene chloride as solvents and NBu_4ClO_4 as supporting electrolyte, 7-coordination can only be reached by dimerization, involving S-bridges. The corresponding Os dimer, $Os_2(Et_2dtc)_6^{2+}$, seems to be less stable because in CH_2Cl_2 solution monomers and dimers are in equilibrium as detected by NMR [9] and the monomer $Os(dtc)_3^+$ can be oxidized in a reversible step to $Os(dtc)_3^{2+}$ [13].

Acknowledgements

The authors gratefully acknowledge the Netherlands Foundation for Chemical Research (SON), and NATO for a travel grant. Prof. L. H. Pignolet acknowledges support from the National Science Foundation (NSF CHE-81-08490).

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