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Voltammetric, EPR and UV-VIS-NIR spectroscopic studies associated with the characterisation of electrochemically generated tris(dithiocarbamato)cobalt(IV) complexes in dichloromethane †

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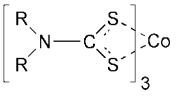
$Co^{III}(S_2CNR_2)_3$ (R = Et, cyclohexyl) complexes were electrochemically oxidised by one-electron in CH_2Cl_2 containing Bu_4NPF_6 as the supporting electrolyte. Voltammetric, EPR and UV-VIS-NIR spectroscopic data indicated that the cation complexes, $[Co^{IV}(S_2CNR_2)_3]^+$, formed by oxidation of the parent Co^{III} compounds were stable for at least several hours at low temperatures (T = 233 K), although instability was evident at higher temperatures and/or longer times. EPR spectroscopic data obtained by *in situ* electrogeneration of the oxidised species at low temperatures indicated that the unpaired electron largely resided on the metal centre, thereby confirming a formally Co^{IV} state. The UV-VIS-NIR spectra of the $[Co^{IV}(S_2CNR_2)_3]^+$ complexes showed a new set of low energy and moderate intensity series of bands at $\nu = 9600$, 13300 and 15500 cm^{-1} (ε = 700–1500 L cm^{-1} mol^{-1}) which were interpreted as ligand-to-metal charge transfer excitations to the unfilled t_{2g} orbital. The EPR spectra of $[Co^{IV}(S_2CNR_2)_3]^+$ ($g_{/\!/} \approx 2.65$ and $g_\perp \approx 1.90$) required low temperatures to be detected (T < *ca.* 50 K) and displayed a high degree of anisotropy consistent with a distorted octahedral structure.

1. Introduction

Stable and isolable compounds containing cobalt in the +4 oxidation state are rare, with well known examples being octahedral CoF_6^{2-} [1] and the tetrahedral low-spin alkyl complex, tetrakis(1-norbornyl)cobalt.[2] Two five-co-ordinate σ-bonded phenyl cobalt corroles[3] and an octahedral complex, *trans*-[η^4-1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene]bis(4-*tert*-butylpyridine)cobalt(IV),[4] were characterised by crystallography, electrochemistry, UV-VIS and EPR spectroscopies. Studies performed on a macrocyclic square planar complex containing tetraamido-*N* ligands[5] and five-co-ordinate 1,2-dithiolene complexes, $[Co(S_2C_2R_2)_2L]$,[6] were suggestive of cobalt(IV) complexes, although there remains difficulties in assigning the charge on the metal ion due to ambiguities in the ligand's oxidation state.

There exists a larger number of examples of reactive formally cobalt(IV) species generated by one-electron oxidation of their respective parent cobalt(III) complexes.[7–14] One important but contentious case that has been debated in the literature for over 25 years involves the one-electron oxidation of tris(dithiocarbamato)cobalt(III) complexes, $Co^{III}(S_2CNR_2)_3$.



Saleh and Straub[15] first attempted the oxidation of $Co(S_2CNR_2)_3$ in the presence of boron trifluoride, where R = ethyl or cyclohexyl (*c*-Hx), and reported obtaining paramagnetic compounds formulated as $[Co(S_2CNEt_2)_3]BF_4$ and $[Co(S_2CNc\text{-}Hx_2)_3]BF_4$. Gahan and O'Connor[16] using a similar procedure reported obtaining oligomeric cobalt(IV) complexes rendered diamagnetic by magnetic association. In contrast, Hendrickson *et al.*[17] using an identical reaction isolated and obtained the crystal structure of the dimeric diamagnetic pentakis(dithiocarbamato)dicobalt(III) complex, $[Co_2(S_2CNEt_2)_5]BF_4$. Furthermore, the UV-VIS spectrum of the claimed $[Co(S_2CNEt_2)_3]^+$ species[15] was indistinguishable from the dimeric species whose structure was verified by crystallography,[17] thereby casting doubt on the claimed isolation of a $[Co(S_2CNR_2)_3]^+$ monomer.[18]

To clarify the conflicting reports on the stability and identity of the products of oxidation of tris(dithiocarbamato)cobalt complexes, a succession of detailed voltammetric experiments were conducted which enabled the following conclusions to be reached.[14] (i) The one-electron electrochemical oxidation of $Co(S_2CNR_2)_3$ complexes does lead to semi-stable $[Co(S_2CNR_2)_3]^+$ species that are voltammetrically detectable in solution. (ii) Synthetic scale one-electron oxidation experiments (controlled potential electrolysis) eventually results in the formation of dimeric $[Co_2(S_2CNR_2)_5]^+$ species, most likely *via* subsequent reaction of the target $[Co(S_2CNR_2)_3]^+$ monomers. (iii) The lifetime of the $[Co(S_2CNR_2)_3]^+$ cations are dependent on the R groups, with the bulky cyclohexyl groups found to provide the greatest stability to date. (iv) The $[Co(S_2CNR_2)_3]^+$ and $[Co_2(S_2CNR_2)_5]^+$ species are very solvent sensitive, with non-co-ordinating solvents such as CH_2Cl_2 affording the greatest longevity of the monomeric and dimeric cations. Cyclic voltammetric experiments indicated that the $[Co(S_2CNR_2)_3]^+$ species were very unstable in acetone[14*a*,*b*] and that in acetonitrile the Co^{III} binuclear species cleave to form the starting material and $[Co(S_2CNR_2)_2(CH_3CN)_2]^+$.[14*d*]

However, despite the ready transformation of $[Co^{IV}(S_2CNR_2)_3]^+$ to $[Co_2^{III}(S_2CNR_2)_5]^+$ (R = Et and cyclohexyl) having been established,[14*a*,17] a later study by Barbier *et al.*[19] unexpectedly claimed to have isolated the Co^{IV} monomers by oxidising $Co(S_2CNR_2)_3$ with $Fe(ClO_4)_3$ in acetone. While the

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† Electronic supplementary information (ESI) available: figures containing additional voltammetric, UV-VIS-NIR and EPR spectroscopic data. See http://www.rsc.org/suppdata/dt/b1/b104636p/

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microanalysis data fitted the presence of $[Co^{IV}(S_2CNR_2)_3]ClO_4$ salts, the UV-VIS spectra of the claimed cations were identical to that of the dinuclear complexes, $[Co_2(S_2CNR_2)_5]ClO_4$. The authors[19] neglecting to account for the discrepancy in their optical data (simply stating that the UV-VIS data of the mononuclear and binuclear complexes were indistinguishable) and ignoring the voltammetric results from earlier studies that highlighted the instability of the Co^{IV} cations in acetone.[14a] Therefore, the magnetic susceptibility data[19] that were used to support the presence of low-spin Co^{IV} complexes must be treated with caution because of the inconsistencies in the spectroscopic and electrochemical data. Surprisingly, the claims of Barbier *et al.*[19] have been accepted uncritically as factually correct and reported in respected textbooks of Inorganic Chemistry.[20]

The aim of the present study is to provide an unambiguous characterisation of the Co^{IV} cations using voltammetry, UV-VIS-NIR and EPR spectroscopies in the non-co-ordinating solvent dichloromethane at low temperatures where the probability of indefinite stability is greatly enhanced. Co^{IV} is a d^5 ion and should therefore give rise to an EPR spectrum. The magnetic moment of $[Co(S_2CNc\text{-}Hx_2)_3]^+$ in CH_2Cl_2 at 253 K was previously estimated[14b] using the method of Evans[21] to be 1.7 μ_B, suggesting a low-spin cobalt(IV) complex. The UV-VIS-NIR spectrum of the Co^{IV} species, particularly in the low energy NIR region, would be expected to be substantially different than the parent and binuclear Co^{III} (t_{2g}^6) complexes since the removal of an electron allows electronic transitions to the unfilled t_{2g} orbital.

2. Experimental

2.1 Chemicals and reagents

$Co(S_2CNR_2)_3$ complexes where R = Et or *c*-Hx were prepared by first reacting stoichiometric amounts of NaOH, CS_2 and the appropriate amine (Et_2NH or $c\text{-}Hx_2NH$) in cold aqueous solution to produce the sodium dithiocarbamates.[22] Solid cobalt(II) nitrate was then added to the mixture in the presence of air to form $Co(S_2CNR_2)_3$ which were purified by Soxhlet extraction using dichloromethane (CH_2Cl_2) as the solvent followed by recrystallisation from hot CH_2Cl_2 to yield dark green solids.[18,22] Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) which was used as the supporting electrolyte was prepared and purified by standard methods and dried under vacuum at 393 K. HPLC grade CH_2Cl_2 used for electrochemical and spectroscopic experiments was dried by distillation over P_2O_5.

2.2 Electrochemical and spectroscopic instrumentation and procedures

Cyclic voltammetric and controlled potential electrolysis experiments were conducted with a PAR model 273A potentiostat/galvanostat controlled through a PC with standard PAR electrochemical software. Cyclic voltammograms were performed using either Pt or glassy carbon (GC) planar working electrodes in conjunction with a Pt auxiliary electrode and an Ag/Ag^+ (0.05 M $AgNO_3$ in MeCN) reference electrode connected to the test solution *via* a salt bridge containing CH_2Cl_2 and Bu_4NPF_6. Digital electrochemical simulations were performed using DigiSim 2.1[23] or ESP version 2.4,[24] with the capacitance = 0.2 μF, transfer coefficients (α) = 0.5 and the solution resistance variable depending on the temperature.

In situ UV-VIS-NIR spectra were obtained with a Varian Cary 5E spectrophotometer in an optically transparent thin layer electrochemical (OTTLE) cell[25] (pathlength = 0.05 cm) at 213 K using a Pt mesh working electrode. Typical exhaustive electrolysis time for the one-electron oxidation of 2 mM analyte in CH_2Cl_2 (0.5 M Bu_4NPF_6) was 1.5–2 hours.

Solutions of oxidised cobalt dithiocarbamates for the EPR experiments were prepared at 233 K in a divided controlled potential electrolysis cell that has been described previously,[26] and then transferred under vacuum into cylindrical 3 mm (id) EPR tubes that were immediately frozen in liquid N_2. EPR spectra were recorded on either a Bruker ER 200D (for temperatures between 233–133 K with liquid N_2 cooling) or Bruker ESP 300e (for temperatures between 50–5 K with liquid He cooling). Both spectrometers employed rectangular TE_{102} cavities with the modulation frequency set at 50–100 kHz and microwave power between 6 μW–20 mW. EPR simulations were performed using the Bruker computer software, WINEPR SimFonia version 1.2. (R. T. Weber, Bruker Instruments, Inc., Billerica, MA, USA, 1995).

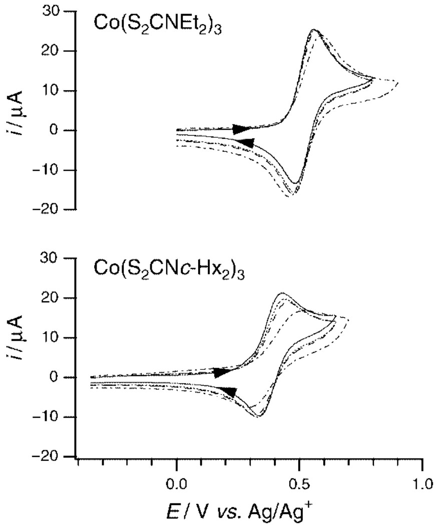

Fig. 1 Cyclic voltammograms recorded at 293 K at a 1.6 mm diameter Pt electrode in CH_2Cl_2 (0.5 M Bu_4NPF_6) for 2 mM solutions of analytes at scan rates of (——) 0.1, (• • •) 0.5, (---) 1 and (–•–) 5 V s^{-1}. Current scale has been normalised (see text).

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms are shown in Fig. 1 of 2 mM solutions of $Co(S_2CNR_2)_3$ that were obtained at several scan rates (0.1, 0.5, 1 and 5 V s^{-1}) at 293 K where the current response has been normalised by dividing by the square root of the scan rate ($v^{1/2}$). One-electron diffusion controlled processes uncomplicated by slow electron transfer and homogeneous chemical reactions are expected to display a $v^{1/2}$ relationship with the anodic peak current (i_p^{ox}).[27] For $Co(S_2CNEt_2)_3$, the normalised i_p^{ox}-values remained essentially constant up to a scan rate of 1 V s^{-1} whilst the cathodic peak current (i_p^{red}) values showed an incremental increase. The increase in the i_p^{red}/i_p^{ox} ratio towards unity with increasing scan rate for $Co(S_2CNEt_2)_3$ (Fig. 1) can partially be accounted for by an EC (electron transfer followed by a chemical step) mechanism, where the oxidised species is only moderately stable, hence faster scan rates are necessary to outrun the C step and obtain i_p^{red}/i_p^{ox} ratios approaching 1.[28] At 5 V s^{-1} the i_p^{ox}-value decreased slightly and there was an increase between the anodic peak potential (E_p^{ox}) and cathodic peak potential (E_p^{red}), which may be due to effects of solution resistance exacerbated at the higher scan rates in the relatively low dielectric constant (ε = 9.1)[29] CH_2Cl_2 medium. For $Co(S_2CNc\text{-}Hx_2)_3$ (Fig. 1), there occurs both a substantial decrease in the i_p^{ox}-value and a shift in the E_p^{ox} and E_p^{red} values as the scan rate is increased, considerably more than what can be accounted for by solution resistance effects. Instead the changes in current and potential peak-values with changing scan rate are likely to be due to a slow rate of heterogeneous electron transfer. Digital simulation of the electrochemical data (assuming a one-electron transfer) allowed the estimation of the temperature

Table 1 Diffusion coefficients (D) and heterogeneous rate constants (k_e) obtained by digital simulation of CV data. Voltammetric data recorded in CH_2Cl_2 (with 0.5 M n-Bu_4NPF_6) at a 1.6 mm diameter Pt electrode for concentrations of analytes between 0.5–10 mM, scan rates between 0.1–5 V s^{-1} and temperatures between 293–233 K

Compound	D/cm^2 s^{-1} × 10^{-6} (± 2 × 10^{-7}) 293/273/253/233 K	$E_{1/2}$/V (*vs.* Ag/Ag$^+$) (± 0.005) (293 K)	k_e/cm s^{-1} (293 K)
$Co(S_2CNEt_2)_3$	6.5/5.0/4.0/2.5	0.52	2 × 10^{-2}
$Co(S_2CNc\text{-}Hx_2)_3$	4.5/3.5/2.5/1.5	0.38	5 × 10^{-3}

dependant D-values and the maximum heterogeneous electron transfer (k_e) rates (Table 1). The estimated k_e-values are consistent with those reported for other dithiocarbamate complexes.[14a]

Previous experiments on $[Co(S_2CNR_2)_3]^+$ species with other R groups indicated increased stability in dilute solutions,[14b] and it was proposed that a reasonable mechanism to account for the instability of the $[Co(S_2CNR_2)_3]^+$ complexes was *via* an irreversible dimerization mechanism [eqns. (1)–(3)].

$$Co(S_2CNR_2)_3 \rightleftharpoons [Co(S_2CNR_2)_3]^+ + 1\,e^- \text{ heterogeneous} \quad (1)$$

$$2[Co(S_2CNR_2)_3]^+ \longrightarrow [Co_2(S_2CNR_2)_6]^{2+} \text{ homogeneous} \quad (2)$$

$$[Co_2(S_2CNR_2)_6]^{2+} \longrightarrow [Co_2(S_2CNR_2)_5]^+ + [\text{oxidised ligand}]^+ \text{ homogeneous} \quad (3)$$

The seven co-ordinate cobalt(IV) complex shown in eqns. (2) and (3) would be unusual, but there are transition metal precedents including the tris(dithiocarbamato)osmium analogue, $Os(S_2CNR_2)_3$ which undergoes a *reversible* dimerization reaction following one-electron oxidation to form $[Os_2(S_2CNR_2)_6]^{2+}$ [eqn. (4)],[30] where the diamagnetic dimer was isolated and characterised by crystallography.

$$2[Os(S_2CNR_2)_3]^+ \rightleftharpoons [Os_2(S_2CNR_2)_6]^{2+} \text{ homogeneous} \quad (4)$$

In the present study no temperature, concentration or scan rate dependent responses typical of dimerization reactions were evident during the voltammetric experiments on $Co(S_2CNEt_2)_3$ or $Co(S_2CNc\text{-}Hx)_3$ in CH_2Cl_2 (see ESI). Even at high analyte concentrations (10 mM) and low temperatures (T = 203 K), situations where electrogenerated dimers have been reported to be favoured,[31–33] there was no observable change in the i_p^{red}/i_p^{ox} ratio associated with the oxidation process, nor any voltammetric evidence of dimer species that are frequently reduced at potentials several hundred mV more negative than the initiating oxidation process.[31–34]

Consequently, for these particular R groups, solvent and temperature combinations, complete stability of the one-electron oxidised cation is indicated on the voltammetric time-scale which is clearly a necessary precursor for stability to be achievable in comparable media on the synthetic time-scale.

3.2. UV-VIS-NIR spectroscopy

Fig. 2 shows UV-VIS-NIR spectra obtained during the one-electron *in situ* oxidation of $Co(S_2CNEt_2)_3$ at the low temperature of 213 K in CH_2Cl_2 (0.5 M Bu_4NPF_6) (see Experimental section). The dashed line (---) is the initial spectrum of $Co(S_2CNEt_2)_3$ whilst the solid dark line (——) is the final spectrum of the one-electron oxidised product, $[Co(S_2CNEt_2)_3]^+$. The UV-VIS-NIR spectra obtained during the oxidation of $Co(S_2CNc\text{-}Hx_2)_3$ (data not shown) were completely reversible, that is, applying a potential sufficiently negative to cause the reduction of $[Co(S_2CNc\text{-}Hx)_3]^+$ resulted in the regeneration of the spectrum with the same appearance and signal intensity as the starting material, $Co(S_2CNc\text{-}Hx)_3$, indicating that the oxidised form was fully stable on the time frame of the experiment (2–3 hours). For $[Co(S_2CNEt_2)_3]^+$ a small amount of irreversible decomposition was evident at long times, indicated by a 10% decrease in the signal intensity of the $Co(S_2CNEt_2)_3$ that was regenerated by reduction of $[Co(S_2CNEt_2)_3]^+$. However, the appearance of several well defined isosbestic points (such as shown in Fig. 2) in the spectral progression for both compounds were a further indication of the efficiency of conversion and the stability of the oxidised forms of the compounds (at least during the forward generation stage for $[Co(S_2CNEt_2)_3]^+$).

Isosbestic points observed during progressive optical experiments are not necessarily an indication of the formation of one unique product since the occurrence of an equilibrium reaction (such as a reversible dimerization) where more than one stable product was produced would also give the appearance of a straightforward reversible transformation from starting material to final product(s). Second-order processes can be made apparent by varying the substrate concentration, as has been observed optically during the oxidation of methyl viologen[35] where the relative intensities of the absorption bands changed according to initial concentration. However, varying the concentration of $Co(S_2CNR_2)_3$ (and hence $[Co(S_2CNR_2)_3]^+$ *via* electrochemical oxidation) between 0.01–10 mM resulted in no detectable difference in the relative intensities of the absorption bands, other than the expected linear increase in intensity with increasing concentration due to Beer's law. Therefore, the cyclic voltammetric data obtained over short time-frames (seconds) and the UV-VIS-NIR spectroscopic data obtained during intermediate time-scales (2–3 hours) are consistent with the straightforward oxidative transition of $Co(S_2CNR_2)_3$ into $[Co(S_2CNR_2)_3]^+$, uncomplicated by second-order dimerization (reversible or irreversible) processes.

Fig. 3 show the UV-VIS-NIR spectra obtained in an OTTLE cell of the starting materials, $[Co^{III}(S_2CNR_2)_3]$, and final products of the one-electron exhaustive oxidation, ($[Co^{IV}(S_2CNR_2)_3]^+$). The energies of the d–d transitions mapped on the abscissa axis in Fig. 3 were calculated by standard computational methods using ligand fields parameterised within an angular-overlap model for low-spin $d^6(t_{2g}^{\,6})$ ($^1A_{1g}$ ground state) and $d^5(t_{2g}^{\,5})$ ($^2T_{2g}$ ground state) $Co^{III/IV}$ ions.[36,37] (The terms t_{2g} and e_g are used cautiously here since strict octahedral geometry for the Co^{III} and Co^{IV} species are unlikely.) For $Co^{III}(S_2CNR_2)_3$ the first two spin-allowed d–d transitions are observable in the UV-VIS spectra (at *ca.* 16000 and 21000 cm^{-1}) thereby allowing a reasonable estimate of the values of the crystal field splitting parameter (Dq) and Racah interelectronic repulsion parameter (B) (1660 cm^{-1} and 375 cm^{-1} respectively).[37] However, for the $[Co^{IV}(S_2CNR_2)_3]^+$ species, relatively low energy ligand-to-metal charge transfer (LMCT) transitions to the partially filled metal t_{2g} orbital are feasible (which are not possible in the closed shell low-spin Co^{III} complexes), so that one must consider whether the lower energy bands originate from d–d or LMCT transitions. Increased metal–ligand interaction upon oxidation makes it certain that Dq will increase while increased covalency (delocalisation) between Co^{4+} and the dithiocarbamate ligand support B decreasing.[38] The bands present in the UV-VIS spectra of the Co^{IV} species at *ca.* 13500 cm^{-1} and 15500 cm^{-1} could be matched to theoretical d–d transitions using appropriately altered values (from those of the Co^{III} compounds) for Dq and B of 2030 cm^{-1} and 330 cm^{-1} respectively (for a d^5 ion with octahedral co-ordination). However, the quintet terms

Table 2 Summary of the wavenumber (ν) and approximate molar absorptivities (ε) of the principal absorption bands obtained by *in situ* electrochemical UV-VIS-NIR spectroscopy (compare Figs. 2 and 3)[a]

$Co^{III}(S_2CNEt_2)_3$			$Co^{III}(S_2CNc\text{-}Hx_2)_3$		$[Co^{IV}(S_2CNEt_2)_3]^+$			$[Co^{IV}(S_2CNc\text{-}Hx_2)_3]^+$	
ν/cm^{-1}	ε/L cm^{-1} mol^{-1}	Transition	ν/cm^{-1}	ε/L cm^{-1} mol^{-1}	ν/cm^{-1}	ε/L cm^{-1} mol^{-1}	Transition	ν/cm^{-1}	ε/L cm^{-1} mol^{-1}
15540	480	d–d	15890	560	9550	700	LMCT (t_{2g})	9860	700
20650	720	d–d	20920	1160	13390	910	LMCT (t_{2g})	13210	1100
25570	9000	LMCT	25440	10000	15540	1400	LMCT (t_{2g})	15890	1500
27790	13000	LMCT	27060	17000	19140	4100	LMCT	18880	4100
30950	21000	LMCT	31270	20000	20650	5100	LMCT	20920	5300
37050	32000	π–π*	36000	33000	24780	8500	LMCT	24650	10000
40520	30000	π–π*	40000	27000	31140	20000	LMCT	31270	23000
44000	25000	LMCT	43270	25000	34610	21000	LMCT	34010	24000
					38090	27000	π–π*	36780	27000
					40310	28000	π–π*	39660	28000

[a] ν measured to nearest 10 cm^{-1}. ε-values calculated from $A = \varepsilon bc$ (A = absorbance, c = concentration, b = cell pathlength) and calibrated to 293 K. LMCT = charge transfer and π–π* = ligand only absorption bands.

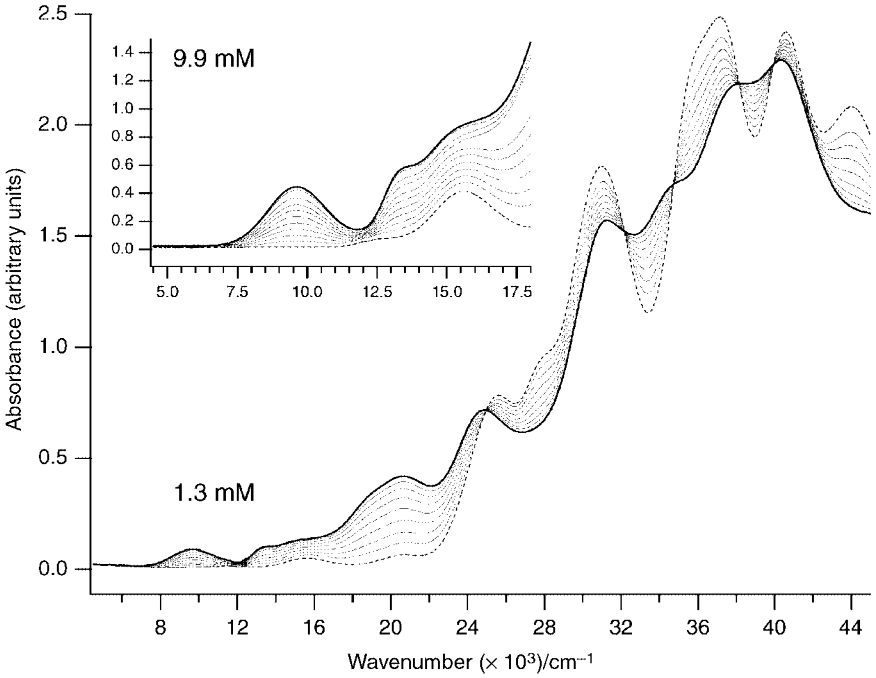

Fig. 2 UV-VIS-NIR spectra obtained during the one-electron *in situ* electrochemical oxidation of $Co(S_2CNEt_2)_3$ (1.3 and 9.9 mM) at 213 K in CH_2Cl_2 (0.5 M Bu_4NPF_6) in an OTTLE cell. (---) First scan = $Co(S_2CNEt_2)_3$, (——) final scan = $[Co(S_2CNEt_2)_3]^+$, (——) = sequential intermediate scans.

estimated at 13500 cm^{-1} and 15500 cm^{-1} (Fig. 3) are spin forbidden and are likely to be much less intense than the experimentally observed bands. Furthermore, the band in the Co^{IV} spectra at *ca.* 10000 cm^{-1} in both examples (Figs. 2 and 3 and Table 2) is much lower in energy (and higher in intensity) than can be accounted for by reasonable estimates of values of *Dq* and *B* and is more likely to be LMCT based. Therefore, it is probable that all bands in the spectra of the Co^{IV} complexes below 35000 cm^{-1} originate from CT transitions that inevitably obscure (or at least overlap with) the weaker expected d–d transitions.

The UV-VIS-NIR spectra of NaS_2CNEt_2 and $Zn(S_2CNEt_2)_2$ were recorded as a means of distinguishing the characteristic position and intensity of the π–π* dithiocarbamate ligand absorptions from the CT bands in the spectra of the $Co^{III/IV}$ dithiocarbamate complexes. For NaS_2CNEt_2, π–π* absorption bands are solely possible, whilst Zn^{2+} is a d^{10} ion therefore, no d–d or LMCT bands are feasible. The dithiocarbamate spectra were similar to one another (see ESI) showing two bands between 34000 and 42000 cm^{-1} which would be expected to occur at similar wavenumber in the spectra of the corresponding tris(dithiocarbamato)cobalt complexes.

In order to pursue the rearrangement chemistry of the cations, solutions of $Co(S_2CNR_2)_3$ were bulk electrochemically oxidised by one-electron in a controlled potential electrolysis cell (see Experimental section) at room temperature in CH_2Cl_2. The so formed $[Co(S_2CNR_2)_3]^+$ complexes were observed to decompose to the $[Co_2(S_2CNR_2)_5]^+$ binuclear complexes consistent with eqns. (1)–(3). There is no definitive evidence of the formation of the dimer dication indicated in eqn. (2), hence other less direct mechanisms are possible for the formation of $[Co_2^{III}(S_2CNR_2)_5]^+$.[14a] A cyclic voltammogram and UV-VIS-NIR spectrum of $[Co_2(S_2CNEt_2)_5]^+$ is shown in Fig. 4 (the UV-VIS-NIR spectrum of $[Co_2(S_2CNc\text{-}Hx_2)_5]^+$ was very similar). In contrast to the claims of Barbier *et al.*[19] who reported that the $Co(S_2CNR_2)_3$ and $[Co_2(S_2CNR_2)_5]^+$ complexes were oxidised at almost the same potential, we found that $[Co_2(S_2CNR_2)_5]^+$ are more difficult to oxidise than $Co(S_2CNR_2)_3$ by approximately 0.4 V [Fig. 4(a)] (which is in agreement with earlier studies[14a,b]). Furthermore, the UV-VIS-NIR spectrum of $[Co_2(S_2CNEt_2)_5]^+$ was substantially different from $[Co(S_2CNEt_2)_3]^+$ (compare Figs. 3 and 4) with bands at 12500 cm^{-1} (ε = 250 L cm^{-1} mol^{-1}), 16000 cm^{-1}, (ε = 900 L cm^{-1} mol^{-1}), 24200 cm^{-1} (ε = 7000 L cm^{-1} mol^{-1}), 31800 cm^{-1} (ε = 23000 L cm^{-1} mol^{-1}) and 40100

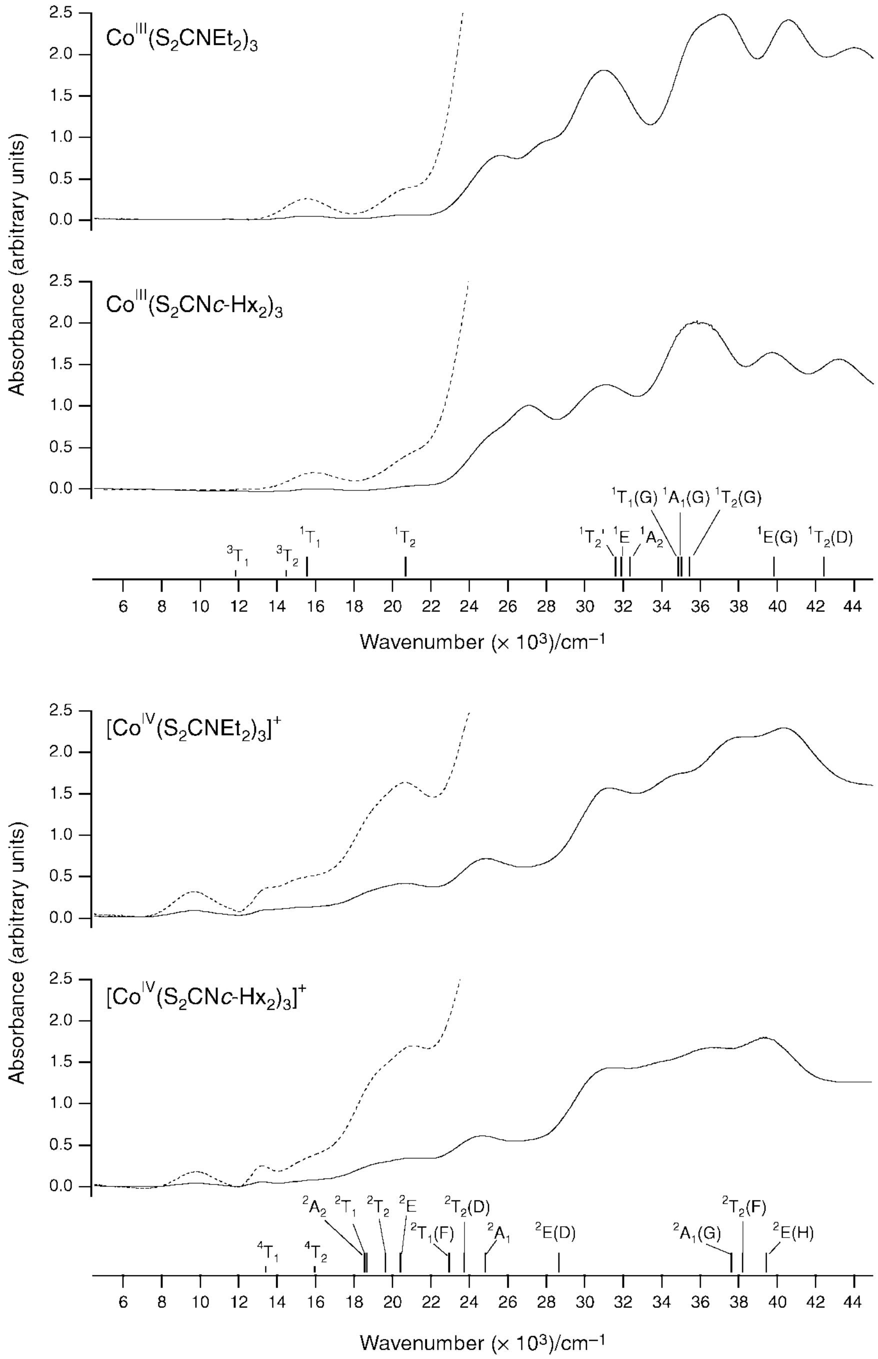

Fig. 3 (——) UV-VIS-NIR spectra obtained at 213 K in an OTTLE cell prior to and at the completion of the exhaustive one-electron *in situ* electrochemical oxidation of Co(S$_2$CNR$_2$)$_3$ in CH$_2$Cl$_2$ (0.5 M Bu$_4$NPF$_6$). The concentration of Co(S$_2$CNEt$_2$)$_3$ and [Co(S$_2$CNEt$_2$)$_3$]$^+$ = 1.3 mM, and the concentration of Co(S$_2$CN*c*-Hx$_2$)$_3$ and [Co(S$_2$CN*c*-Hx$_2$)$_3$]$^+$ = 1.0 mM. (---) Vertical expansion of spectra between 4000–24000 cm^{-1}. The plotted theoretical d–d transitions are for reference only and are experimentally obscured in most cases by much stronger CT bands (see text).

cm^{-1} (ε = 30000 L cm^{-1} mol^{-1}). We also repeated the experiments of Barbier *et al.*[19] by oxidising Co(S$_2$CNR$_2$)$_3$ with Fe(ClO$_4$)$_3$ in acetone (see Introduction section) [a mixture of FeCl$_3$ and NaClO$_4$ was used due to Fe(ClO$_4$)$_3$ being unavailable]. As expected, the UV-VIS-NIR spectrum of the species obtained in the present study by oxidation of Co(S$_2$CNEt$_2$)$_3$ with Fe^{III} was identical to that reported for the Co^{III} dimer[14b,17] (Fig. 4) with no evidence of the characteristic Co^{IV} monomer absorption band at ≈10000 cm^{-1} displayed in Figs. 2 and 3. Therefore, the UV-VIS data obtained in the present study conclusively shows that the solid compounds obtained first by Saleh and Straub[15] and later by Barbier *et al.*[19] by chemical oxidation of Co(S$_2$CNR$_2$)$_3$ cannot be the pure [Co(S$_2$CNR$_2$)$_3$]$^+$ monomers (but are supportive of the formation of the [Co$_2$(S$_2$CNR$_2$)$_5$]$^+$ complexes instead).

3.3. EPR spectroscopy

Fig. 5(a) shows X-band EPR spectra obtained at 5.6 K of frozen solutions of [Co(S$_2$CN*c*-Hx$_2$)$_3$]$^+$ that were prepared by one-electron electrochemical oxidation of Co(S$_2$CN*c*-Hx$_2$)$_3$ at 233 K in CH$_2$Cl$_2$ (0.5 M Bu$_4$NPF$_6$) (see Experimental section). The spectra indicate the presence of at least two signals representative of at least two paramagnetic species; a sharp signal (ΔH_{pp} = 1 mT) centred at g = 2.004, and a much broader (ΔH_{pp} = 12.5–35 mT) anisotropic signal that occurs over approximately 0.2 T. Digital integration of the spectra in Fig. 5 suggest that the sharp signal is present in low abundance (<1%) in relation to the broad signal (assuming similar relaxation times at the lowest temperature). The EPR spectrum of [Co(S$_2$CNEt$_2$)$_3$]$^+$ that was prepared electrochemically using the same

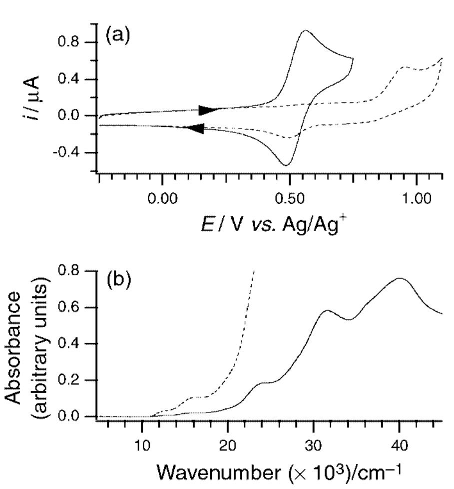

Fig. 4 (a) Cyclic voltammograms recorded at 100 mV s^{-1} at a 1.0 mm diameter GC electrode in CH_2Cl_2 (0.2 M Bu_4NPF_6) at room temperature. (——) 1 mM $Co(S_2CNEt_2)_3$. (---) After the one-electron oxidative electrolysis of 1 mM $Co(S_2CNEt_2)_3$ to form 0.5 mM $[Co_2(S_2CNR_2)_5]^+$. See eqns. (1)–(3) in text. (b) (——) UV-VIS-NIR spectrum of 0.5 mM $[Co_2(S_2CNR_2)_5]^+$ in CH_2Cl_2. (---) Vertical expansion of spectrum between 5000–24000 cm^{-1}.

procedure and conditions as for the *c*-Hx derivative showed the same temperature and microwave power variations and also contained a small amount of a narrow line width signal at $g = 2.004$ (see ESI).

The broad line width EPR signal showed no detectable difference in shape as the power levels were varied from 20 μW to 20 mW, other than the expected increase in intensity as the power was increased [Fig. 5(a)]. In contrast, the sharp signal showed signs of saturation at higher microwave powers indicated by a decrease in intensity relative to the broad signal with increasing power level [compare Fig. 5(a) 20 μW and 20 mW]. The broad line width signal was difficult to detect at temperatures above approximately 50 K [Fig. 5(b)], whilst the narrow line width signal could still be detected at the highest temperature measured (233 K). In frozen solutions (T < *ca.* 200 K), the shape of the narrow line width signal was typical of that obtained for species with rhombic symmetry. As the temperature of the solution was raised above the freezing point of the solvent/electrolyte mixture the narrow line width signal showed additional hyperfine structure, similar to that observed for an organic free radical undergoing molecular tumbling (see ESI).

The broad line width signal showed a linear relationship between concentration and EPR signal intensity, whilst the sharp signal displayed a considerable variation in intensity, even between electrolysed solutions of very similar concentrations. It was found that the most important parameters in determining the intensity of the sharp signal were the length of time of the electrolysis, the delay between electrolysing and placing the sample in the EPR cavity, and brief temperature fluctuations during the transfer of the electrolysed solution from the electrochemical to the EPR cell. The high abundance and appearance of the broad line width EPR signals suggest that they are due to the primary one-electron oxidised products, $[Co(S_2CNR_2)_3]^+$, with the sharp signals most likely due to an intermediate decomposition product of $[Co(S_2CNR_2)_3]$,$^+$ such as an organic based radical resulting from oxidation of the ligand [eqn. (3)].

The shape of the broad line width signal is not surprising when compared to the EPR spectra reported for other $S = ½$ complexes containing the dithiocarbamate ligand [including $Fe(S_2CNR_2)_3$[39,40] and $Ru(S_2CNR_2)_3$[40]] and other six co-ordinate complexes containing sulfur ligands such as dithioacetylacetonato.[40,41] DeSimone[40] observed that octahedral complexes containing bidentate sulfur ligands that have a moderate degree of geometric distortion from octahedral co-ordination [as has been shown for $Co(S_2CNEt_2)_3$ by crystallography[42]] and with a high degree of covalency, have anisotropic EPR spectra which are not observed in the less covalently bonded analogous complexes containing oxygen or nitrogen donor atoms. A computer simulation for a species with axial symmetry ($g_{//} = 2.65$ and $g_\perp = 1.90$ and line width of 12–30 mT) provided an approximate match to the experimental data (see ESI). Simulations based on rhombic symmetry did not substantially improve the match between experimental and theoretical spectra. It is possible that the experimental spectra represent a large number of species with slightly differing geometry, which could account for the large line width (especially in the $g_\perp$ portion of the spectrum) and which makes accurately simulating the spectra very difficult. The feature at *ca.* 2800 G in Fig. 5 may be due to coupling to the ^{59}Co nucleus ($I = {}^7/_2$) with hyperfine splitting in the order of 3–4 mT. Reported values of hyperfine splitting on the ^{59}Co nucleus of other cobalt(IV) complexes are between 1.5–8 mT,[3,4,5,8d,9c] smaller than predicted for the free Co^{IV} ion (10–20 mT).[8d,9c] The temperature dependent behaviour, broad line width and evidence of hyperfine coupling to ^{59}Co are

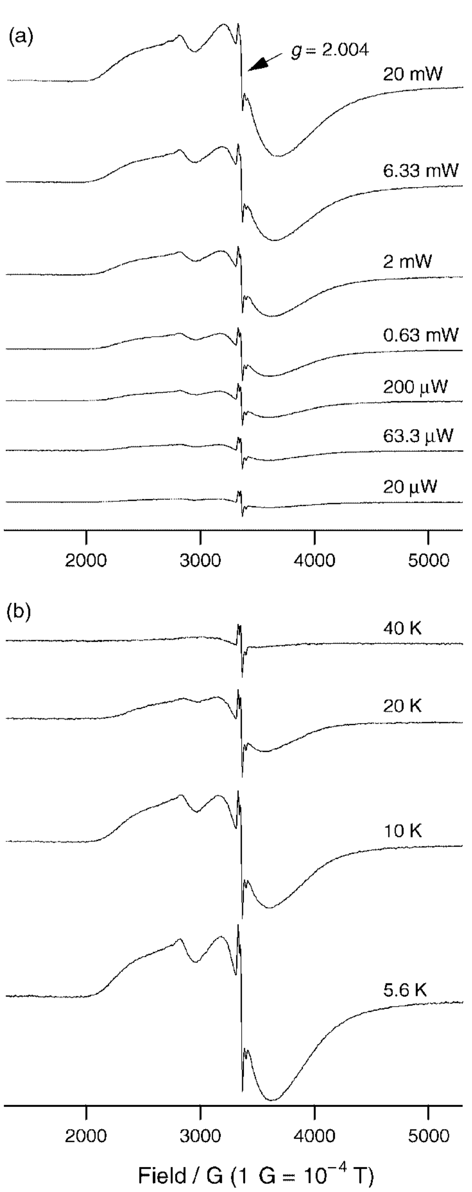

Fig. 5 First derivative X-band EPR spectra of 2.5 mM $[Co(S_2CN\textit{c}\text{-}Hx_2)_3]^+$ that were obtained by one-electron bulk electrochemical oxidation of $Co(S_2CN\textit{c}\text{-}Hx_2)_3$ in CH_2Cl_2 (0.5 M Bu_4NPF_6). (a) Effect of varying microwave power at T = 5.6 K. (b) Effect of varying temperature at a constant microwave power of 2 mW. The EPR modulation amplitude = 0.5 mT, time constant = 0.33 s, sweep width = 0.4 T and sweep time = 330 s.

suggestive of the unpaired electron largely residing on the metal ion, *i.e.* confirming a formally $\mathrm{Co^{IV}}$ state. A purely organic thioradical would be expected to show a much narrower line width spectrum with characteristic differences in hyperfine coupling in the EPR spectra of Et and *c*-Hx derivatives.

4. Conclusions

Electrochemical, EPR and UV-VIS-NIR spectroscopic studies have confirmed that the one-electron oxidation of the ethyl and cyclohexyl substituted tris(dithiocarbamato)cobalt(III) complexes in CH_2Cl_2 produces the tris(dithiocarbamato)cobalt(IV) species ($[\mathrm{Co^{IV}(S_2CNR_2)_3}]^+$). Although the $[\mathrm{Co^{IV}(S_2CNR_2)_3}]^+$ cations are known to react under some conditions *via* a bimolecular self-reaction involving loss of a ligand to form $[\mathrm{Co_2^{III}(S_2CNR_2)_5}]^+$, the electrochemical and spectroscopic data of the $\mathrm{Co^{III}}$ and $\mathrm{Co^{IV}}$ complexes obtained in the present study were free from any detectable concentration dependent behaviour and are therefore, entirely representative of the $\mathrm{Co(S_2CNR_2)_3}/[\mathrm{Co(S_2CNR_2)_3}]^+$ redox couple [with the exception of the generation of a very low abundance narrow line width signal detected in the EPR spectra of oxidised $\mathrm{Co(S_2CNR_2)_3}$ attributable to an organic radical product]. The spectroscopic and electrochemical data indicate that the R = Et and *c*-Hx $[\mathrm{Co(S_2CNR_2)_3}]^+$ derivatives are stable for at least 1 hour (possibly much longer for *c*-Hx) at 233 K in CH_2Cl_2 with 0.5 M $\mathrm{Bu_4NPF_6}$ electrolyte. The approximately axial EPR spectra obtained at low temperatures for the $[\mathrm{Co(S_2CNR_2)_3}]^+$ cations suggest a distorted octahedral structure whilst the UV-VIS-NIR data are consistent with low-spin d^5 ($t_{2g}{}^5$) complexes displaying a series of LMCT transitions to t_{2g} and e_g levels. The definitive UV-VIS-NIR spectra obtained for the true $\mathrm{Co^{IV}}$ compounds in the present study disproves previous claims[15,16,19] for isolation of pure solid $[\mathrm{Co(S_2CNR_2)_3}]^+$ complexes and invalidates the interpretation of the reported magnetic susceptibility data for these complexes.[19,20]

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