

Reactivity of the Re–NO centre: Proton induced oxidation of $\text{Re}(\text{NO})^{2+}$ to $\text{Re}(\text{NO})^{3+}$. Synthesis and characterisation of some Re(II) thiocyanato-halogenonitrosyl complexes

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Abstract. The $\text{Re}(\text{NO})^{2+}$ moiety as $[\text{Re}(\text{NO})(\text{NCS})_3\text{H}_2\text{O}]^-$ or $[\text{Re}(\text{NO})(\text{NCS})_2(\text{L}-\text{L})\text{H}_2\text{O}]$ [$\text{L}-\text{L}$ = phen (1,10-phenanthroline) or bipy (2,2'-bipyridine)] undergoes proton-induced oxidation reaction with HX ($\text{X} = \text{Cl}, \text{Br}$) to produce a $\text{Re}(\text{NO})^{3+}$ moiety. The spectral and physico-chemical data suggest that the anionic complex is 5 coordinate and the neutral one is 6 coordinate with axial NO group and two NCS ligands in *trans*-equatorial positions. The complex, $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Br}]\cdot\text{H}_2\text{O}$ shows complicated magnetic behaviour which is discussed in the paper. The ESR spectrum of this compound shows typical rhenium hyperfines and $\langle g \rangle$ -tensor anisotropy compatible with the loss of axial symmetry. However, the spectrum of $[\text{Re}(\text{NO})(\text{NCS})_2\text{Br}_2]^-$ quite reasonably shows axial symmetry, other features being grossly comparable to the $\text{L}-\text{L}$ compounds. The anionic species and the neutral $\text{L}-\text{L}$ complex show irreversible one-electron oxidation waves at different voltages. This may correspond to a conversion of $\text{Re}(\text{NO})^{3+}$ to $\text{Re}(\text{NO})^{4+}$ in both the cases. Interestingly enough, only the neutral complexes exhibit an irreversible reduction wave due probably to a conversion of $\text{Re}(\text{NO})^{3+}$ to $\text{Re}(\text{NO})^{2+}$.

Keywords. Reductive nitrosylation; proton induced oxidation; temperature-independent paramagnetism; exchange inversion; thiocyanato-halogenonitrosyls of rhenium.

1. Introduction

Reactivity of coordinated NO has created a recent upsurge due mainly to an understanding of the mode of bonding of NO to metal (Enemark and Feltham 1974; Hoffmann *et al* 1974) and the catalytic application of metal nitrosyls in organic syntheses (Pandey 1983; Seidler and Bergman 1984) and pollution control (Johnson and Bhaduri 1973). We have recently shown (Bhattacharyya and Roy 1983) that ReO_4^- undergoes reductive nitrosylation in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NCS^- in alkaline media furnishing the $\text{Re}(\text{NO})^{2+}$ species, for example, $[\text{Re}(\text{NO})(\text{NCS})_3\text{H}_2\text{O}]^-$ (1) or $[\text{Re}(\text{NO})(\text{NCS})_2(\text{L}-\text{L})\text{H}_2\text{O}]$ (2) [$\text{L}-\text{L}$ = phen (1, 10-phenanthroline) (2a) or bipy(2, 2'-bipyridine) (2b)]. But the same reaction in the absence of NCS^- generates (Bhattacharyya *et al* 1988) the $\text{Re}(\text{NO})^{3+}$ moiety trapped as $[\text{Ph}_4\text{P}][\text{Re}(\text{NO})(\text{OH})_4]$ or $[\text{Re}(\text{NO})(\text{OH})_3(\text{L}-\text{L})]$. The hydroxo compounds undergo X^- -assisted ($\text{X} = \text{Cl}, \text{Br}$) electrophilic attack by H^+ leading to an interesting

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disproportionation reaction, generating, besides nitrosyl products, a metal-metal multiple-bonded non-nitrosyl compound also (Bhattacharyya *et al* 1988). Here it is shown that $\text{Re}(\text{NO})_2^{2+}$ present in the complexes **1** and **2** reacts with HX (X = Cl, Br) via oxidation of the former to the $\text{Re}(\text{NO})_3^{3+}$ moiety, furnishing hitherto unknown $[\text{Re}(\text{NO})(\text{NCS})_2\text{X}_2]^-$ [isolated as Ph_3MeP salts (**3**)] or as neutral L-L derivatives viz. $[\text{Re}(\text{NO})(\text{NCS})_2(\text{L-L})\text{X}]$ (**4**) with the evolution of H_2 . It may be mentioned that previous authors (Biswas *et al* 1985) isolated a thiocyanatohalogenonitrosyl, $[\text{Re}(\text{NO})(\text{NCS})_3\text{Cl}_2]^{2-}$, which incidentally also contains the $\text{Re}(\text{NO})_3^{3+}$ moiety. The compound, however, was obtained by ligand substitution of the chloro products (viz. $\text{K}_2[\text{Re}(\text{NO})\text{Cl}_5]$ or hydrated $\text{Re}(\text{NO})\text{Cl}_3$), also possessing the same $\text{Re}(\text{NO})_3^{3+}$ core.

2. Materials and methods

2.1 Materials

The starting material, KReO_4 , was of extra pure quality and obtained from Johnson and Mathey. All reagents required for compound preparation were of analytical grade. Analytical grade solvents used for physicochemical studies were further purified by the literature methods (Perrin *et al* 1966) before use. Water of high purity was obtained by distilling deionised water over KMnO_4 . Sodium perchlorate for electrochemical work was recrystallized from water and the supporting electrolyte $[\text{Et}_4\text{N}]\text{ClO}_4$ was prepared using literature method (Goswami *et al* 1982). Dinitrogen was purified by bubbling it through an alkaline dithionite solution. Benzil was further crystallized from ethanol. Infrared spectra as CsI pellets ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Model 597 Perkin-Elmer IR spectrophotometer. Electronic spectra were recorded on a Pye-Unicam SP8-150 UV-VIS spectrophotometer. All pH measurements were made with an E.C. (India) digital pH meter (Model 5651). A Knauer vapour pressure osmometer was used for the molecular weight determination using benzil as calibrant and the solution conductances were measured with a Wayne Kerr B 331 autobalance precision bridge. Magnetic susceptibilities at room temperature were obtained by the Guoy method with the help of a Model 155 PAR vibrating sample magnetometer and those at varied temperatures were measured by the Faraday method using a Satorius microbalance in conjunction with a Bruker B-E 10C8 research magnet equipped with a B-VT 1000 automatic temperature control. Diamagnetic corrections were applied with the use of Pascal's constants (O'Connor 1982). X-band ESR spectra were obtained using a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K. The spectra were calibrated with diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$). Thermoanalyses were made on a Shimadzu Model DT 30 thermoanalyser. Voltammetric measurements were made using a Model 370-4 PAR electrochemistry system [Model 174A polarographic analyser, Model 175 universal programmer, Model Re 0089 XY recorder, Model 173 potentiostat, and Model 179 digital coulometer]. All experiments were performed under a dinitrogen atmosphere in a three-electrode cell using a stout platinum wire as working electrode, a platinum foil as auxiliary electrode, and a saturated calomel reference electrode (SCE). All results were collected at 298 K and the reported potentials are uncorrected for junction contribution. Elemental analyses were carried out on a Perkin Elmer Model 240C elemental analyser. The H_2 gas evolved was

toeplerized at -196°C and collected in an inverted tube fitted with a septum. A gas syringe was then used for sampling it for gas chromatographic analysis. A Shimadzu (Japan) gas chromatograph Model G.C. RIA equipped with T.C. detector (detector temperature 80°C) was used for the detection of H_2 using He as the carrier gas.

2.2 Preparation of the complexes

2.2a *Triphenylmethylphosphonium di-bromo/chlorodithiocyanatonitrosylrhodium(II) monohydrate* (**3**) (**3a**, chloro; **3b**, bromo): If solution I (Bhattacharyya and Roy 1983) or compound **1** (Bhattacharyya and Roy 1983) (0.10 g, 0.15 mmol) is boiled with concentrated HX (30 ml, X = Cl, Br) for 30 min, there occurs a sharp colour change (from green to reddish brown). The solution is then cooled and filtered if necessary. The filtrate, on addition of an aqueous solution of Ph_3MePI (0.28 g; 0.70 mmol), yields a reddish brown solid which is removed by filtration, washed with water, 1:1 ethanol and finally with ether and dried in vacuo over P_4O_{10} . The solid is then crystallized from a 2:1 acetone-*n*-hexane solvent mixture (**3a**; 0.17 g, 70%; **3b**; 0.17 g, 62% when prepared from solution I and **3a**; 0.08 g, 78%; **3b**; 0.09 g, 78% when prepared from compound **1**).

2.2b *Bromo/chlorodithiocyanato unis{1,10-phenanthroline} nitrosylrhodium(II) monohydrate* (**4a**, chloro; **4b**, bromo): When solution I or compound **2a** (Bhattacharyya and Roy 1983) (0.10 g, 0.19 mmol) is boiled with concentrated HX (30 ml, X = Cl, Br) and an aqueous solution of phen (0.12 g; 0.70 mmol) is added to the resulting red-brown solution, a red-brown solid separates. The solid is filtered off, washed with water, ethanol and ether and then vacuum dried. The crude product is then crystallized from 2:1 acetone-*n*-hexane mixture (**4a**; 0.14 g, 71%; **4b**; 0.14 g, 66% when prepared from solution I and **4a**; 0.08 g, 75%; **4b**; 0.09 g, 75% when prepared from compound **2a**).

2.2c *Bromo/chlorodithiocyanato unis{2,2'-bipyridine} nitrosylrhodium(II) monohydrate* (**4c**, chloro; **4d**, bromo): Exactly the same procedure is followed as in the case of the phen-derivative using either solution I or compound **2b** (Bhattacharyya and Roy 1983) and using an aqueous solution of bipy (0.11 g; 0.07 mmol) instead of phen (**4c**; 0.12 g, 64%; **4d**; 0.12 g, 60% when prepared from solution I and **4c**; 0.08 g, 75%; **4d**; 0.08 g, 73% when prepared from compound **2b**).

3. Results and discussions

3.1 Overall reaction pattern - generation of $\text{Re}(\text{NO})^{3+}$ moiety

When solution I (see §2) or compound **1** or **2** is boiled with a concentrated solution of HX (X = Cl, Br) there occurs a sharp colour change, and the resulting solution, in each case, on employment of the counterion (PMePh_3^+) or neutral L-L ligands (phen or bipy) gives two different species i.e. $[\text{Re}(\text{NO})(\text{NCS})_2\text{X}_2]^-$ (**3**) [X = Cl (**3a**); X = Br (**3b**)] or $[\text{Re}(\text{NO})(\text{NCS})_2(\text{L-L})\text{X}]$ (**4**) [L-L = phen, X = Cl (**4a**); X = Br (**4b**); L-L = bipy, X = Cl (**4c**); X = Br (**4d**)]. It is interesting to note that the reaction is accompanied by evolution of dihydrogen which was toeplerized at -196°C and was identified by gas-

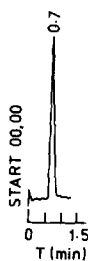
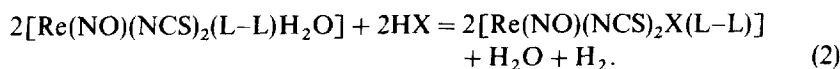
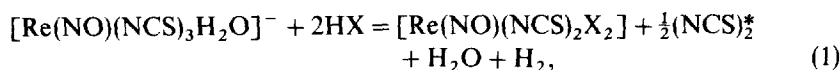


Figure 1. Gas chromatogram of H_2 . Molecular sieve 5A 60/80 ss, column temp. 55°C , flow rate He 40 ml min^{-1} , TCD 150 mA, speed 10 mm min^{-1} .

chromatography (figure 1) using He as carrier gas. Thus, the overall reaction scheme can be represented as



The reaction is essentially an electrophilic attack on Re-NO centre whereby the proton captures an electron from the diamagnetic $\{\text{Re}(\text{NO})\}^6$ [i.e. $\text{Re}(\text{NO})^{2+}$] substrate[†] converting it to paramagnetic and ESR sensitive $\{\text{Re}(\text{NO})\}^5$ [i.e. $\text{Re}(\text{NO})^{3+}$] species.

3.2 General characterisation, IR data, and structural aspects

The compound **3** is a 1:1 electrolyte in CH_3CN while **4** is monomeric and non-electrolyte in this solvent (Geary 1971) (table 1). The thermoanalytical (TGA and DTA) studies of the compounds reveal that neither compound **3** nor **4** shows any meaningful weight loss in its TGA curve corresponding to the endothermic peak at $\approx 70^\circ\text{C}$ in the DTA diagram. Interestingly, this is a phase transition temperature (here, the Néel temperature, T_N), as confirmed in the case of **4b** (*vide infra*). The TGA, however, records weight loss corresponding to one water molecule at a temperature close to 100°C for both **3** and **4** indicating that the water molecules in the respective compounds are held in the lattice. However, after $\approx 150^\circ\text{C}$, more serious decomposition starts in both the cases.

The IR spectra of both **3** and **4** exhibit a sharp and symmetrical ν_{CN} band which indicates that the two NCS groups may occupy the equatorial position *trans*- to each other. The appearance of ν_{CN} , ν_{CS} and δ_{NCS} vibrations for all complexes at ≈ 2075 , 750 and 480 cm^{-1} , respectively, indicate that the NCS ligand may be N-bonded (Nakamoto 1978). Also, the complexes exhibit a single split (separation $25\text{--}40\text{ cm}^{-1}$) ν_{NO} vibrational band at $\approx 1740\text{ cm}^{-1}$. This type of splitting in mononitrosyl halogenometallates [as against well-separated ($50\text{--}100\text{ cm}^{-1}$) bands in the case of dinitrosyls] is attributable (Gans *et al* 1966) to the fact that there may be an

* This is supposed to be trapped within the liquid nitrogen dewar, but was not identified, however.

[†] The numerical superscripts indicate the total number of valence electrons in the metal and NO orbitals (Enemark and Feltham 1974).

Table 1. Analytical^a and physical data of the complexes.

Complex	Analysis (%)					Λ_M^b ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Selected IR data (cm^{-1})						μ_{eff} (B.M.)
	C	H	N	S	X		ν_{CN}	ν_{NO}	$\nu_{\text{Re(NO)}}$	$\nu_{\text{Re-N(L-L)}}$	$\nu_{\text{Re-X}}$		
(3a) $[\text{Ph}_3\text{MeP}][\text{Re}(\text{NO})(\text{NCS})_2\text{Cl}_2] \cdot \text{H}_2\text{O}^c$	36.0 (36.1)	3.1 (2.9)	5.8 (6.0)	9.0 (9.2)	10.0 (10.2)	125	2075 s 1740 s ^e	1780 s ^e 1740 s ^e	610 w	—	295 m	1.3	
(4a) $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Cl}] \cdot \text{H}_2\text{O}$	29.5 (29.7)	2.1 (1.8)	12.3 (12.4)	11.0 (11.3)	6.1 (6.2)	^d	2070 s 1740 s ^e	1775 s ^e 1740 s ^e	615 w	450 w	280 m	1.2	
(4c) $[\text{Re}(\text{NO})(\text{NCS})_2(\text{bipy})\text{Cl}] \cdot \text{H}_2\text{O}$	26.5 (26.6)	2.0 (1.8)	12.6 (12.9)	11.6 (11.8)	6.4 (6.5)	^d	2075 s 1740 s ^e	1780 s ^e 1740 s ^e	610 w	450 w	280 m	1.2	
(3b) $[\text{Ph}_3\text{MeP}][\text{Re}(\text{NO})(\text{NCS})_2\text{Br}_2] \cdot \text{H}_2\text{O}^c$	31.8 (32.0)	2.6 (2.5)	5.3 (5.3)	8.0 (8.1)	20.1 (20.3)	120	2075 s 1740 s ^e	1780 s ^e 1740 s ^e	610 w	—	230 m	1.3	
(4b) $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Br}] \cdot \text{H}_2\text{O}$	27.5 (27.5)	1.7 (1.6)	11.3 (11.5)	10.3 (10.5)	13.0 (13.1)	^d	2075 s 1755 s ^e	1780 s ^e 1755 s ^e	615 w	450 w	240 m	1.4	
(4d) $[\text{Re}(\text{NO})(\text{NCS})_2(\text{bipy})\text{Br}] \cdot \text{H}_2\text{O}$	24.5 (24.6)	1.9 (1.7)	11.7 (11.9)	10.8 (10.9)	13.3 (13.6)	^d	2075 s 1755 s ^e	1780 s ^e 1755 s ^e	615 w	450 w	240 m	1.4	

^aCalculated values in parentheses. ^bIn CH_3CN . ^c% P = 4.3(4.4) (3a); 3.7(3.9) (3b) respectively. ^dNon-electrolyte. ^eThe pair comprises a single split band.

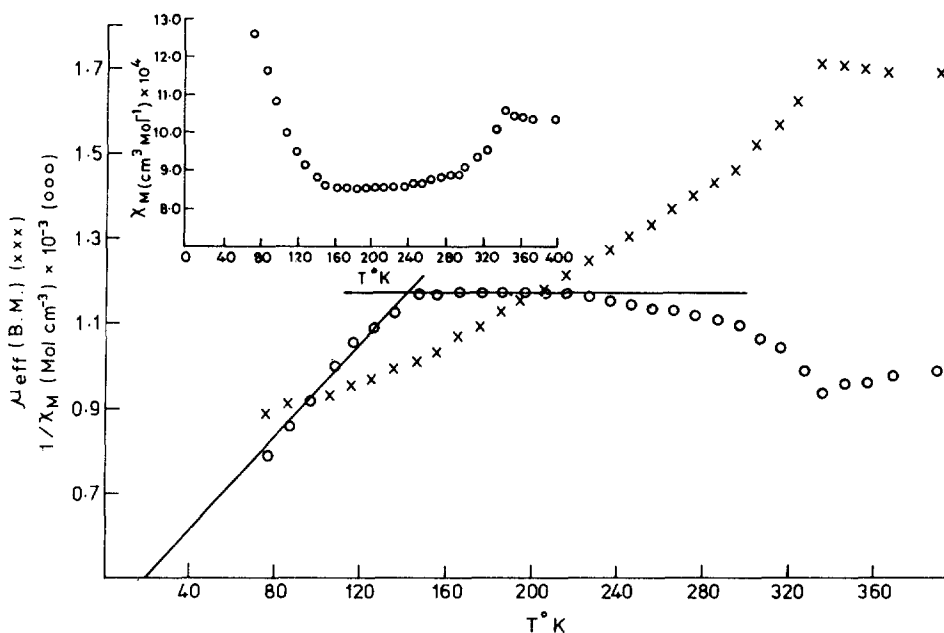


Figure 2. The magnetic behaviour with temperature of $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Br}] \cdot \text{H}_2\text{O}$ ($1/\chi_M$ (—○—○—) μ_{eff} (—×—×—). The inset shows the variation of χ_M (—○—○—) with temperature.

contribution, caused by a strong spin-orbit coupling effect in this $5d$ system to the susceptibility. Magnetic moment also increases with the increase in temperature and interestingly, the slope of the μ_{eff} vs T curve corresponding to the apparent TIP region is somewhat greater (figure 2) than that of the ferromagnetic region. When the Néel temperature is attained, a practically steady state is reached. It may be assumed, from their identical room temperature moments as well as a DTA peak at 70°C corresponding to a phase transition (here, T_N) in both **3b** and **4b**, that similar magnetic properties prevail in the **4** series also. Hence, this class of nitrosyl compounds should be regarded as materials exhibiting interesting solid state properties. The X-band ESR profiles (figure 3a and b) of **4b** in its polycrystalline state are almost identical at 298 and 77 K. The profile at 77 K may be assumed to be representing the spectrum of the weakly ferromagnetic and that at 298 K of the antiferromagnetic phase. In both the cases a well defined sextet due to rhenium hyperfine [^{185}Re and ^{187}Re , both with $I = 5/2$ (Goodman *et al* 1968; Goodman and Raynor 1970)] structure is observed (it is noteworthy that the exchange effects are too weak to impair Re hyperfines) but the middle Kramer derivative line is hardly clear (figure 3a and b) (may be due to the complicated magnetic behaviour) and three extractable $\langle g \rangle$ -tensors are obviously due to the lack of axial symmetry in the molecule. The data for both the temperatures are shown in table 2. The $\langle A \rangle_{\text{Re}}$ -tensor values of **4b** at 77 and 298 K are comparable.

The compound **3b** with *trans* configuration of the two NCS and two Br ligands, should possess an axial symmetry and, as expected, its ESR spectrum (figure 3c) in acetonitrile glass shows axial symmetry insofar as $\langle g_{\perp} \rangle$ and $\langle g_{\parallel} \rangle$ components are clearly recognisable. The rhenium hyperfines are also quite prominent here (figure 3c).

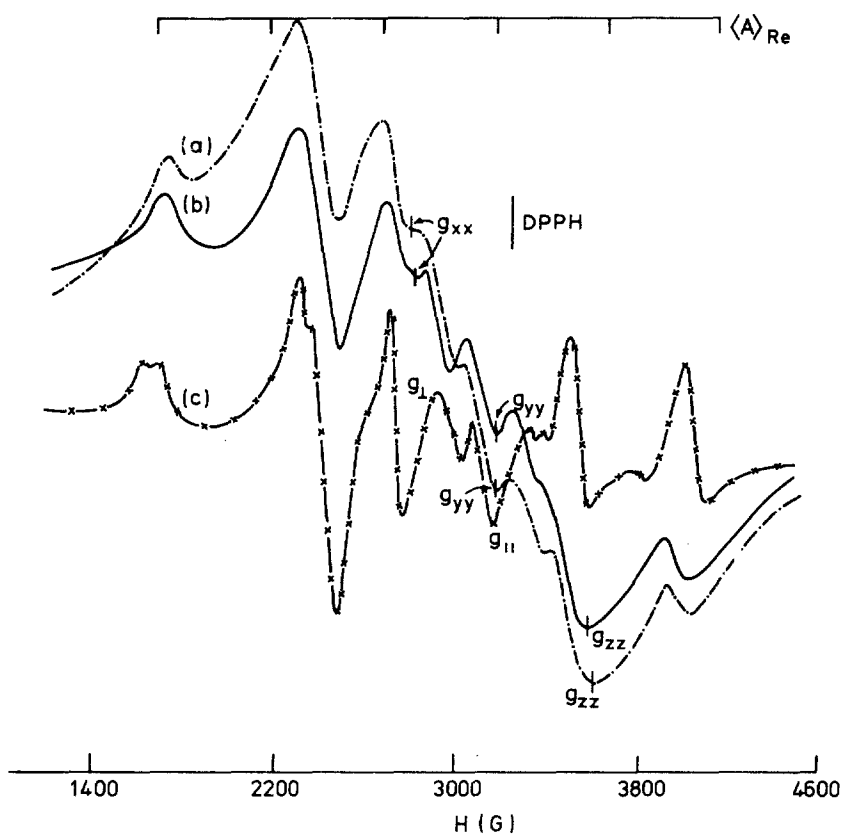


Figure 3. X-band ESR spectra of $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Br}] \cdot \text{H}_2\text{O}$, (a) polycrystalline at 298 K (—○—○—); (b) 77 K (—); and (c) $[\text{Ph}_3\text{MeP}][\text{Re}(\text{NO})(\text{NCS})_2\text{Br}_2] \cdot \text{H}_2\text{O}$ in frozen acetonitrile (—x—x—).

Table 2. ESR parameters of complexes containing the $\text{Re}(\text{NO})^{3+}$ moiety.

Complex	Temperature (K)	g_{xx}	g_{\perp}	g_{yy}	g_{\parallel}	g_{zz}	$\langle A \rangle_{\text{Re}}/\text{G}^c$
3b ^a	77		2.29		2.11		360–620
4b ^b	77	2.34		2.06		1.84	380–580
4b ^b	298	2.35		2.06		1.81	320–660

^a In acetonitrile glass. ^b Polycrystalline. ^c The available data so far obtained do not permit an unequivocal assessment of $\langle A_{\parallel} \rangle_{\text{Re}}$, $\langle A_{\perp} \rangle_{\text{Re}}$, and $\langle A_0 \rangle_{\text{Re}}$.

It is noteworthy that in its spectrum the two outermost peaks in the perpendicular region and the rather feeble innermost peak in the parallel region are again split to doublets possibly due to the field-dependent $\langle A \rangle$ -tensor anisotropy (s.h.f., on the contrary, should show much more lines). However, only average $\langle A \rangle$ values could be given in the table (table 2) since the spectrum does not clearly and regularly reveal parallel and perpendicular features of the $\langle A \rangle$ -tensor. It may be noted that the EPR spectrum of $[\text{Re}(\text{NO})\text{Cl}_5]^{2-}$ reported by Mercati *et al* (1978) is grossly comparable with that of our *trans*- compound, 4b.

3.4 Electronic spectral data

The dihalogeno species (**3**) is assumed to possess C_{2v} symmetry (**1**) and hence has $(b_1)^2(b_2)^2(a_2)^1$ ground state configuration (Enemark and Feltham 1974). The occurrence of two electronic spectral bands in **3** may be designated as $a_2 \rightarrow a_1$ and $a_2 \rightarrow b_1$ in order of increasing energy (table 3), quite in agreement with a 5-coordinate

Table 3. Electronic spectral data of the complexes in CH_3CN .

Complex	$\lambda_{\text{max}}/\text{nm} (\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$
3a	450(1400), 320(1510)
4a	460(1445)
4c	460(1425)
3b	450(1540), 324(1660)
4b	460(1500)
4d	460(1470)

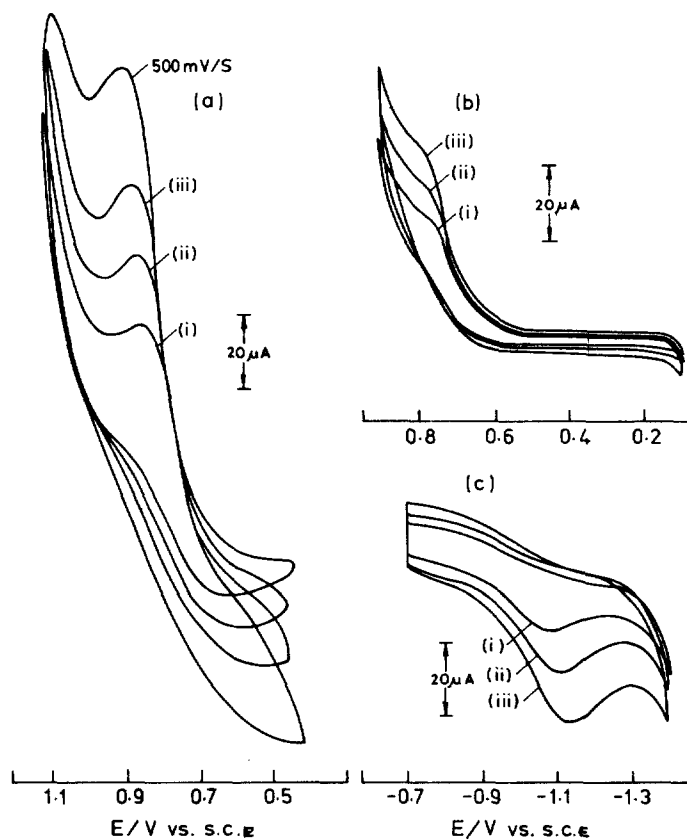


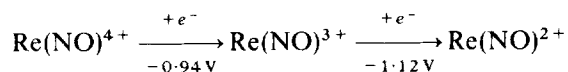
Figure 4. Segmented cyclic voltammograms of (a) $[\text{Ph}_3\text{MeP}][\text{Re}(\text{NO})(\text{NCS})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$, (b) and (c) $[\text{Re}(\text{NO})(\text{NCS})_2(\text{phen})\text{Br}] \cdot \text{H}_2\text{O}$ in acetonitrile at scan rates (i) 50, (ii) 100, and (iii) 200 mV s^{-1} .

model. The symmetry of **4** being lower (II), only one electronic spectral band with enhanced intensity occurs in this case. The other possible bands may be missing or may probably be embedded within the intraligand (phen or bipy) transitions.

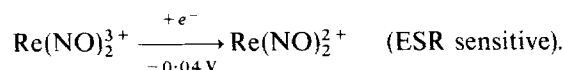
3.5 Electrochemistry

Voltammetry was carried out in acetonitrile solution at a platinum working electrode. All potentials are with reference to the saturated calomel electrode (SCE). Tetraethylammonium perchlorate (TEAP) was added as an inert electrolyte.

The anionic species **3a** displays an irreversible one-electron oxidation wave (figure 4a) at +0.86 V vs SCE which corresponds to a conversion of $\text{Re}(\text{NO})^{3+}$ to $\text{Re}(\text{NO})^{4+}$ (assessed by constant potential coulometry and ESR silence of the oxidised product). For neutral species (i.e. **4b** and **4d***) also, the irreversible oxidation peak appears but at a slightly lower positive potential (at +0.78 V) (figure 4b). Moreover, these complexes show an irreversible reduction peak (figure 4c) at -1.10 V, characteristic of the $\text{Re}(\text{NO})^{3+}$ to $\text{Re}(\text{NO})^{2+}$ conversion (Bhattacharyya *et al* 1988). To include a comparative account of other rhenium nitrosyls, it is quite pertinent to mention here that $\text{Re}(\text{NO})^{4+}$ species, as already mentioned in a previous communication (Bhattacharyya *et al* 1988), shows a CV reaction pattern



all the peaks being irreversible, whereas the $\text{Re}(\text{NO})_2^{3+}$ moiety shows a reversible redox couple



Acknowledgements

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* The cyclic voltammograms of **4b** and **4d** are identical.

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