Reductive Nitrosylation of Tetraoxometallates. Part X [1]. Generation of $\{Re(NO)_2\}^7$ Moiety: Single Pot Double Step Synthesis of the Hitherto Unknown $[Re(NO)_2(NCS)_3]^-$ Anion and its 2,2'-Bipyridine and 1,10-phenanthroline Derivatives Directly from ReO_4^- in Aqueous–Aerobic Media

R. G. BHATTACHARYYA and P. S. ROY

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

Received October 18, 1983

Perrhenate anions, when treated with NH_2OH and NCS^- in aqueous–alkaline medium and then acidified and subsequently treated with NO_2^-, generate the $\{Re(NO)_2\}^7$ moiety. This is evident by synthesising the hitherto unknown pentacoordinated complexes of the type $R[Re(NO)_2(NCS)_3]$ ($R = Ph_4P$, Ph_4As, Me_4N and Et_4N). The structure of the complex anion is shown to depend on the nature of the counter-ions. Infrared and magnetic moment data of the isolated complexes indicate that the quaternary ammonium salts may have an SP structure, whereas their phosphonium and arsonium analogues may possess a TBP configuration. The electronic absorption spectra of the two sets of complexes also differ quite drastically. Instead of using the counter-ions, if neutral bidentate ligands, viz. *2,2'-bipyridine or 1,10-phenanthroline (L–L), are used then the hitherto unknown hexacoordinated species of the type $[Re(NO)_2(NCS)_2(L–L)]$ are produced, which possess slightly subnormal magnetic moments for a low spin $\{M(NO)_2\}^7$ moiety. The epr spectra of these neutral species are interesting: the perpendicular region constitutes a sextet possibly originating from the hyperfine interaction of the spin active ($I = 5/2$) rhenium isotopes while the parallel region gives broad peaks due to interaction of the unpaired electron with ^{14}N nucleus of NO. That is, for the first time a method has been developed whereby a direct conversion of ReO_4^- to a d^7 Re could be made facile, by a single pot and a two-step process in aqueous and aerobic media.*

Introduction

Reductive nitrosylation of ReO_4^- to the dinitrosyl rhenium moiety is still unknown. In fact, excepting unconfirmed reports [2, 3], the reductive nitrosylation of ReO_4^- even to rhenium mononitrosyl compounds using any of the known nitrosylating agents [4] was not known until we recently reported [5–7] a reaction scheme for furnishing the $\{Re(NO)\}^{2+}$ moiety directly from ReO_4^- using $NH_2OH \cdot HCl$ as the source of NO group. Moreover, only two compounds containing the $\{Re(NO)_2\}$ fragment have been reported so far; those are $[Re(NO)_2(PPh_3)_2(NO_3)_2]$ [8] and $[ReH(NO_2)(PPh_3)_2]$ [9] prepared by the reaction of HNO_3 on $[ReH_3(PPh_3)_4]$ in the case of the former and of N-methyl-N-nitrosotoluene-p-sulphonamide, PPh_3 and $NaBH_4$ on $[ReCl_4(PPh_3)_2]$ in the case of the latter.

However, before we established [5–7] that $NH_2OH \cdot HCl$ in an alkaline medium is a specific reagent for the facile conversion of ReO_4^- to the $\{Re(NO)\}^{2+}$ [*i.e.* $\{Re(NO)\}^6$] moiety, it was known [10] that NO_2^- in an acidic medium is capable of converting $[ReOCl_4(OH_2)]^-$ to $[Re(NO)Cl_5]^{2-}$ which obviously contains the $\{Re(NO)\}^{3+}$ moiety. It was, however, subsequently realised [11] that the latter reagent is inert towards ReO_4^- as well as even to $ReCl_6^{2-}$. The present paper shows that by harnessing the nitrosylating capability of these two sets of reagents in an organised manner, a double step conversion of ReO_4^- to $\{Re(NO)_2\}^{2+}$ [*i.e.* $\{Re(NO)_2\}^7$] can be achieved; firstly, by the reductive nitrosylation of ReO_4^- to $\{Re(NO)\}^{2+}$ species using NH_2OH and NCS^- in an alkaline medium and then allowing the above mono-nitrosyl species to react with NO_2^- in an acidic condition. This has been substantiated by synthesising the hitherto unknown compound $R[Re(NO)_2(NCS)_3]$ [$R = Ph_4P(1)$, $Ph_4As(2)$, $Me_4N(3)$ and $Et_4N(4)$; the Bu_4N salt could not be isolated pure], as well as its 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) derivatives, *viz.*, $[Re(NO)_2(NCS)_2(L–L)]$ [L–L = bipy(5) or phen(6)] directly from ReO_4^- in an aqueous and aerobic medium, using only a single pot. Our discovery of both the reaction schemes might meet a long standing demand of a suitable method of reduction of ReO_4^- to d^6 or d^7 rhenium, the examples of which, prepared otherwise, are rather scanty (represented by a very few carbonyl or substituted phosphine derivatives [12], obtained in an exclusively non-aerobic and

0020-1693/84/$3.00

nonaqueous medium, apart from the two dinitrosyl compounds mentioned earlier). Their chemistry is yet to be enriched from the point of view of possible catalytic uses.

Experimental

All reagents required were of analytical grades and for physico-chemical measurements they were further purified by literature methods [13]. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 597 spectrophotometer and were calibrated with polystyrene. A Knauer Vapour Pressure Osmometer (Berlin) was used for the molecular weight determination using benzil solutions as calibrant. Electronic spectra were recorded on a Cary 17D recording spectrophotometer and the solution conductances were measured with a Wayne Kerr Autobalance Precision Bridge B 331. Thermoanalyses were made using a Shimadzu (Japan) Thermal Analyser DT-30 and the magnetic susceptibilities at room temperature were measured by using a vibrating sample Magnetometer Model 155 (U.S.A.). X-band EPR spectra of the polycrystalline samples of the compounds at 298 and 80 K were recorded on a Varian EPR-4 instrument.

Preparation of the Complexes

To an aqueous (40 ml) solution of $KReO_4$ (0.10 g; 0.35 mmol), NH_4SCN (0.40 g; 5.3 mmol) and $NH_2OH{\cdot}HCl$ (0.36 g; 5.3 mmol), 4 *M* NaOH was added to render the solution alkaline (pH ~ 10). The solution was stirred at 80 °C for 1.5 h, when a deep red solution with a greenish tinge was obtained. The hot solution was then cooled to 0 °C and the pH readjusted to ~2.5 using cold dil. HCl. An aqueous solution of $NaNO_2$ (0.70 g; 10 mmol) was added to the above acidic solution with stirring for 15 min, when a deep brown solution (A) was obtained.

$(Ph_4P)[Re(NO)_2(NCS)_3]$

Addition of an aqueous solution of Ph_4PCl (0.41 g; 1.1 mmol) to A, with stirring, gave a brown precipitate. The precipitate was filtered off, washed thoroughly with water, 95% ethanol and ether, and then crystallised from an acetonitrile–ether mixture. Chocolate-brown crystals were obtained, which were dried over $CaCl_2$ at a reduced pressure. Yield: 0.12 g (45%). Found, C 42.3, H 2.7, N 8.9, S 11.8, P. 3.9; Calcd. for $\{(C_6H_5)_4P\}[Re(NO)_2(NCS)_3]$ C 42.7, H 2.6, N 9.2, S 12.6, and P 4.1%. IR: ν_{CN} 2075(s), 2055(sh); ν_{NO} 1837(m), 1715(s); $\nu_{M-N(NO)}$ 615(w); δ_{NCS} 450(sh) cm^{-1}; λ_{max} (in CH_3CN) 690 nm (ϵ_{max} = 105 l mol^{-1} cm^{-1}); μ_{eff} = 4.7 B.M. at 298 K.

$(Ph_4As)[Re(NO)_2(NCS)_3]$

Instead of adding Ph_4PCl, Ph_4AsCl (0.46 g; 1.1 mmol) was added to A, when a brown precipitate was obtained. The precipitate was washed and crystallised in the similar manner as its tetraphenylphosphonium analogue; chocolate-brown crystals were obtained. Yield: 0.13 g (47%). Found, C 40.1, H 2.7, N 8.5, S 11.4; Calcd. for $\{(C_6H_5)_4As\}[Re(NO)_2(NCS)_3]$ C 40.3, H 2.5, N 8.7 and S 11.9%. IR: ν_{CN} 2075(s), 2060(sh); ν_{NO} 1845(m), 1720(s); $\nu_{M-N(NO)}$ 615(w); δ_{NCS} (masked by Ph_4As^+ absorptions); λ_{max} (CH_3CN) 680 nm (95); μ_{eff} = 4.7 B.M. at 298 K.

$(Me_4N)[Re(NO)_2(NCS)_3]$

An aqueous solution of Me_4NCl (0.08 g; 0.7 mmol) was added to A with stirring in an ice-cold condition, when a dark coloured precipitate was obtained. The precipitate was filtered off, washed thoroughly with ice-cold water, and then vacuum dried. The product was then crystallised from acetonitrile–ether mixture when snuff-coloured crystals were obtained. Yield: 0.10 g (59%). Found, C 16.8, H 2.5, N 17.2, S 19.1; Calcd. for $\{(CH_3)_4N\}[Re(NO)_2(NCS)_3]$ C 17.0, H 2.4, N 17.0 and S 19.4%. IR: ν_{CN} 2165(sh), 2080(b, s), 2095(sh); ν_{NO} 1860(m), 1730(s); $\nu_{M-N(NO)}$ 620(w); δ_{NCS} 460(w); λ_{max} (CH_3CN) 624 (156), 408 (455), 340 (260) and 272 (7550) nm; μ_{eff} = 0.8 B.M. at 298 K.

$(Et_4N)[Re(NO)_2(NCS)_3]$

The snuff-coloured tetraethylammonium salt was prepared in a similar manner as its tetramethyl analogue. Yield: 0.11 g (58%). Found, C 23.9, H 3.5, N 14.9, S 17.1; Calcd. for $\{(C_2H_5)_4N\}[Re(NO)_2(NCS)_3]$ C 24.3, H 3.6, N 15.2 and S 17.4%. IR: ν_{CN} 2090(sh), 2080(s), 2075(s), 2055(sh); ν_{NO} 1855(m), 1745(s); $\nu_{M-N(NO)}$ 620(w); δ_{NCS} 430(w); λ_{max} (CH_3CN) 650 (20), 488 (70), 432 (105) and 288 (2410) nm; μ_{eff} = 0.9 B.M. at 298 K.

$[Re(NO)_2(NCS)_2(C_{10}H_8N_2)]$

An ethanolic solution (2 ml) of bipy (0.11 g; 0.7 mmol) was added with stirring to the Solution A, when a dark-coloured precipitate was obtained. The precipitate was washed with water, 95% ethanol and with ether, and then vacuum dried. The crude solid was then extracted with acetonitrile and the extract was treated with ether, when a black crystalline solid was obtained. Yield: 0.10 g (56%). Found, C 27.7, H 1.6, N 15.9, S 11.8, M.W. (CH_3CN) 488; Calcd. for $[Re(NO)_2(NCS)_2(C_{10}H_8N_2)]$ C 27.8, H 1.5, N 16.2 and S 12.4%, M.W. 518. IR: ν_{CN} 2075(s); ν_{NO} 1860(m), 1715(s); $\nu_{M-N(NO)}$ 612(w); δ_{NCS} 480(w, b); $\nu_{M-N(bipy)}$ 410(w), 430(w); λ_{max} (CH_3CN) 640 (335), 475 (450), 400 (775) and 315(sh) nm; μ_{eff} = 1.5 B.M. at 298 K.

$[Re(NO)_2(NCS)_2(C_{12}H_8N_2)]$

The phen derivative was prepared in a similar way as that described for its bipy analogue. The dark coloured crude product was crystallised from an acetonitrile–ether mixture, when a black crystalline solid was obtained. Yield: 0.10 g (53%). Found, C 30.7, H 1.4, N 14.9, S 11.2, M.W. (CH_3CN) 520; Calcd. for $[Re(NO)_2(NCS)_2(C_{12}H_8N_2)]$ C 31.0, H 1.5, N 15.5 and S 11.8%, M.W. 542. IR: ν_{CN} 2067(s); ν_{NO} 1845(m), 1720(s); $\nu_{M-N(NO)}$ 620(w); δ_{NCS} 458-(w); $\nu_{M-N(phen)}$ 410(w), 425(w, b); λ_{max} (CH_3CN) 660 (55), 400 (950) and 350 (360) nm; μ_{eff} = 1.5 B.M. at 298 K.

Results and Discussion

Overall Reaction Pattern

From the experimental section it is apparent that the overall reaction pattern could be as shown in eqn. 1:

$$ReO_4^- \xrightarrow[\text{[ref. 5–7]}]{NH_2OH/OH^-/NCS^-} \underset{[\{Re(NO)\}^{2+} \textit{i.e.}\ \{Re(NO)\}^6]}{[Re(NO)(NCS)_3H_2O]^-} \xrightarrow{NO_2^-/H^+} \underset{[\{Re(NO)_2\}^{2+} \textit{i.e.}\ \{Re(NO)_2\}^7]}{[Re(NO)_2(NCS)_3]^-} \quad (1)$$

The observed facile conversion of $\{Re(NO)\}^6$ to $\{Re(NO)_2\}^7$ using NO_2^-/H^+ indicates that the nitrosylating agent in the second step is not NO^+ (the conventional belief [4]) and reflects a complex nature of nitrosylating behavior of NO_2^-/H^+ system [4]. The one-electron reduction of the metal ion in this step to generate formally Re(0) from a formal Re(I) ion suggests that here the nitrosylating agent is actually NO rather than NO^+. This observation also parallels the process of nitrosylation of $[Cr(H_2O)_6]^{2+}$ to $\{Cr(NO)\}^{2+}$ using NO_2^-/H^+ [14]. It is interesting to note that an attempt to introduce the second nitrosyl group in the compounds containing the $\{Re(NO)\}^{2+}$ moiety by the passage of pure NO gas, even in non-aqueous and non-aerobic media, met with no success. Instead of further nitrosylation the decomposition of the respective species via an oxidation of the metal centre (Re=O band observed in the i.r. spectra) took place, which may be due to the thermodynamic instability of gaseous NO [4].

It is also interesting to note that the thiocyanato dinitrosyl rhenate(0), as precipitated by using bulky cations, *viz.*, Ph_4P^+, Ph_4As^+, Me_4N^+ or Et_4N^+, is always five-coordinated (*i.e.* the composition of the species is independent of the type of cation used; also note the difference with the cyanonitrosyl chromates [15]) whereas its L–L derivatives $[Re(NO)_2(NCS)_2(L{-}L)]$ are always six-coordinated. It is apparent, that although the composition of the complex anionic species are independent of the cations used, their structural features differ. While the Me_4N^+ and Et_4N^+ salts have similar magnetic moment values (0.8–0.9 B.M.) and electronic absorption spectra, the bulkier and more polarizable cations (Ph_4P^+ and Ph_4As^+) give complexes with high magnetic moment values (4.7 B.M.) and their electronic absorption spectral features are also different from those of Et_4N^+ and Me_4N^+ complexes.

Neutral-6-Coordinate Complexes

The analytical, molecular weight, electrolytic conductance (non-electrolyte in CH_3CN), thermoanalytical and spectroscopic (IR, UV–Vis and EPR) data all indicate that the neutral L–L derivatives are six-coordinate complexes. The cis configuration of the two nitrosyl groups in the complexes is evident from the appearance of two well separated (~130 cm^{-1}) ν_{NO} i.r. bands (see the experimental section for the exact position of these bands in both bipy and phen derivatives). Also, by comparing the relatively small separation (~50 cm^{-1}) between the two ν_{NO} frequencies in the previously reported [8, 9] Re-dinitrosyl compounds, it seems that the arrangement of the two NO groups around the central metal ion in the present case may be quite different from that in the previous ones, and in the present case the two MNO angles may differ considerably [16]. The compounds, however, show only one $\nu_{M-N(NO)}$ stretching vibration. The appearance of ν_{CN} at ~2070 and δ_{NCS} at ~460 cm^{-1} indicates that the NCS^- ligand may be N-bonded [17]. Moreover, the broad and unsymmetrical nature of the ν_{CN} i.r. band in both cases indicates that the two NCS^- groups are in cis configuration with respect to each other.

The thermoanalytical studies of the two compounds, in the temperature range 30–550 °C, reveal that any meaningful weight loss is not registered in the TGA curves corresponding to the endothermic peak at *ca.* 80 °C in the DTA curves of both (5) and (6). Also, neither do the compounds melt at this temperature. So, this endotherm may correspond to a change in the crystalline form of the compounds. However, the exotherm at *ca.* 160 °C shown in their DTA curves is reflected by a semi-stable region in their TGA curves between *ca.* 200–280 °C and the weight loss data calculated from the latter corroborate the loss of a NO molecule (exp. 5.7, calcd. 5.8 for (5) and exp. 5.4, calcd. 5.5% for (6)). Hence, the intermediate product may be formulated as $[Re(NO)(NCS)_2(L{-}L)]$.

Based on the M.O. energy level diagram [16] of $\{M(NO)_2\}^n$ systems in C_s field, the ground state electronic configuration in our $\{Re(NO)_2\}^7$ cases may be $(1a'')^2(1a')^2(1a')^2(1b_1)^1$ (another 2a′ M.O. between 1a′ and $1b_1$ is worked out [16] to be highly anti-bonding and as recommended [16] is not considered in the electron filling process). In bulk

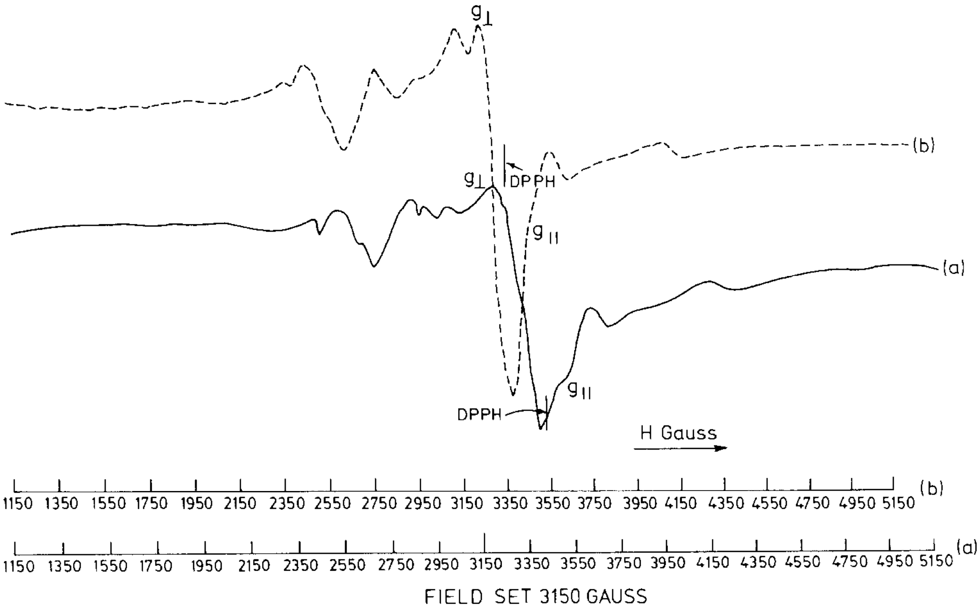

Fig. 1. X-band EPR spectra of polycrystalline sample of [$Re(NO)_2(NCS)_2(bipy)$] at (a) 298 K and (b) 80 K.

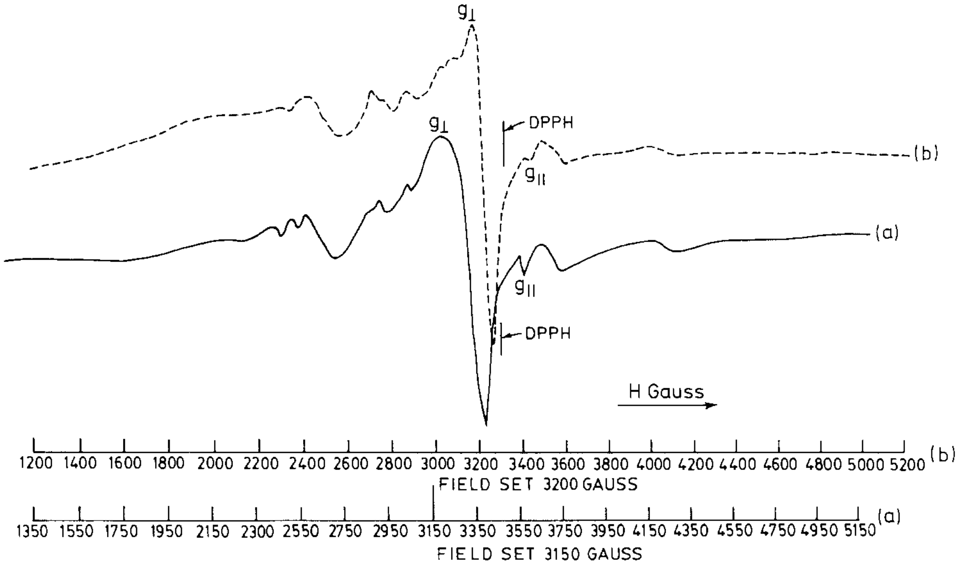

Fig. 2. X-band EPR spectra of polycrystalline sample of [$Re(NO)_2(NCS)_2(phen)$] at (a) 298 K and (b) 80 K.

magnetic susceptibility measurements the compounds show a moment value of 1.5 B.M. at 298 K—a subnormal value so far as the $\mu_{s.o.}$ for magnetically dilute compounds containing one unpaired electron is concerned. As per NO^+ formalism [16], the formal oxidation state of rhenium in these compounds should be zero and hence (5) and (6) contain d^7 rhenium. Since the complexes were found to be monomeric, the subnormal moment values may be due to inter-molecular magnetic exchange coupling.

The X-band electron spin resonance spectra of polycrystalline samples of both (5) and (6) at 298 and 80 K (Figs. 1 and 2) show certain features which are not atypical for the presence of a pronounced magnetic exchange [18]. The absorptions were observed at resonance fields well above and well below the region ($g_{eff} \approx 2$) where signals are normally found for S = 1/2 (Doublet) ground state. The different g values from the signals obtained for the complexes both at ambient and at the liquid nitrogen temperatures are shown in Table I. The g values, both at RT and LNT, are not very much isotropic (as is evidenced by their departure from the spin only value of 2.00). Such anisotropic g values indicate the presence of a

TABLE I. Electron Spin Resonance Data of the Isolated Re(0) Dinitrosyl Complexes.

	$[Re(NO)_2(NCS)_2(bipy)]$		$[Re(NO)_2(NCS)_2(phen)]$	
	298 K	80 K	298 K	80 K
g_s	2.05	2.04	2.06	2.07
$g_\perp$	2.15	2.10	2.14	2.12
$g_\parallel$	1.92	1.93	1.91	1.94

low symmetry ligand field component which is quite obvious in the present cases [19]. The profile of the epr curves in both cases (Figs. 1 and 2) indicate that the nuclear hyperfine splitting is of a complicated nature, though in the perpendicular components of the spectra of both the compounds at RT and LNT it is possible to detect the sextet which obviously arises from the hyperfine coupling with the spin-active ^{185}Re and ^{187}Re nuclei (both have I values = 5/2; see ref. [20]). Interestingly, the parallel component consists of a triplet composed of rather broad peaks (Figs. 1 and 2) arising from the interaction of the unpaired electron with the ^{14}N nucleus of NO [21].

In the C_s symmetry, the four closely-spaced orbitals (LUMO) will be 2a′, 3a′, 2a″ and $2b_1$ [16]. Hence, the observed electronic absorption maxima in both the compounds can be tentatively assigned to $1b_1 \rightarrow 2a'$, $1b_1 \rightarrow 3a'$ and $1b_1 \rightarrow 2a''$ transitions, respectively, in order of increasing energy. In the scan range 800–280 nm the bipy complex shows another absorption maxima. The shoulder at 315 nm, otherwise absent in the free bipy [22], may be due to the fourth transition, namely, $1b_1 \rightarrow 2b_1$.

5-Coordinate Complexes

The molar conductance values [(1)120, (2)110, (3)95 and (4)100 ohm^{-1} cm^2 mol^{-1}] indicate that the compounds, as expected, behave as 1:1 electrolytes [23] in CH_3CN solvent (concentration *ca.* 10^{-3} *M*). The positions of ν_{NO} bands in these monoanionic complexes fall in two distinctly different regions (see experimental). The complexes containing quaternary ammonium salts absorb at a considerably higher wave number region (~1860, ~1720) than their quaternary phosphonium and arsonium counterparts (~1840, ~1720). This might imply that the $[Re(NO)_2(NCS)_3]^-$ species precipitated as Ph_4A (A = P, As) salts have TBP geometry where the NCS^- group trans to NO facilitates the Re–NO back π-bonding, while the isomeric species precipitated as quaternary ammonium salts possibly possess SP configuration. This hypothesis is further supported by the ν_{CN} band positions (see Experimental) of the N-bonded thiocyanato groups. The σ–π synergic mechanism as prevails in the TBP complexes, also in turn facilitates the σ electron transfer from NCS nitrogen to the metal ion which weakens the CN π-bonding and hence lowers the force constant of the said bond. Some components of the ν_{CN} bands, however, have comparable positions in both the TBP and SP series. This is quite realistic, insofar as in TBP geometry both (assuming fluxionality via Berry mechanism in TBP cases [12]) and in SP one of the NO groups have NCS^- as a trans ligand.

It is even more interesting to note that the magnetic moments of these two sets of complexes differ significantly. This $\{M(NO)_2\}^7$ moiety in TBP configuration may have comparatively closely-spaced d orbitals $[(d_{xz}, d_{yz}), (d_{x^2-y^2}, d_{xy})$ and $d_{z^2}]$, and this may be the reason why the complexes (1) and (2) have magnetic moments as high as 4.7 B.M., in spite of the fact that these are 5d metal ion complexes with ligands of quite high fields. On the contrary, the complexes (3) and (4) have their magnetic moment values almost half the spin only value for one unpaired electron. In SP configuration one unpaired electron (residing at d_{z^2} orbital) for a $\{M(NO)_2\}^7$ moiety should be the expected situation and a *little lower* than the spin only value is quite common for 5d systems. However, in the present case a pronounced intermolecular magnetic exchange coupling might be a reasonable attribute for such *drastically low* magnetic moment values. However, it is also known that Re(0) complexes sometimes differ quite widely amongst themselves with respect to their magnetic susceptibility values [24].

While the compounds (3) and (4) do not give any meaningful EPR spectra, possibly due to their very high magnetic exchange coupling, the compounds (1) and (2), which possess rather high magnetic moments (~4.7 B.M.), show an extremely complex pattern of EPR signals both at RT and LNT (for representative spectra see Fig. 3).

Another prominent difference that exists between these two series of complexes is that while the supposed TBP complexes show up only one UV–Vis spectral band (range 800–280 nm), the SP species show four such bands. Absence of any working model of five-coordinate $\{M(NO)_2\}^7$ system in the appropriate symmetry conditions does not permit any designation of the origin of these transitions.

Similar to the six-coordinate L–L derivatives, here also it has been found that the complexes undergo a change in the crystalline form when heated under N_2 at 135 °C, the process being endothermic. The exothermic peak around 200 °C shows a weight loss [Exp. 3.6, calcd. 3.9 for (1); exp. 3.4, calcd. 3.7 for (2); exp. 5.8, calcd. 6.1 for (3) and exp. 5.3, calcd. 5.4% for (4)] in the TGA (near horizontal region in the range 290–340 °C) which accounts for the loss of a nitrosyl ligand forming otherwise air-sensitive diamagnetic $R[Re(NO)(NCS)_3]$ (R = Ph_4P, Ph_4As, Me_4N, Et_4N) complexes.

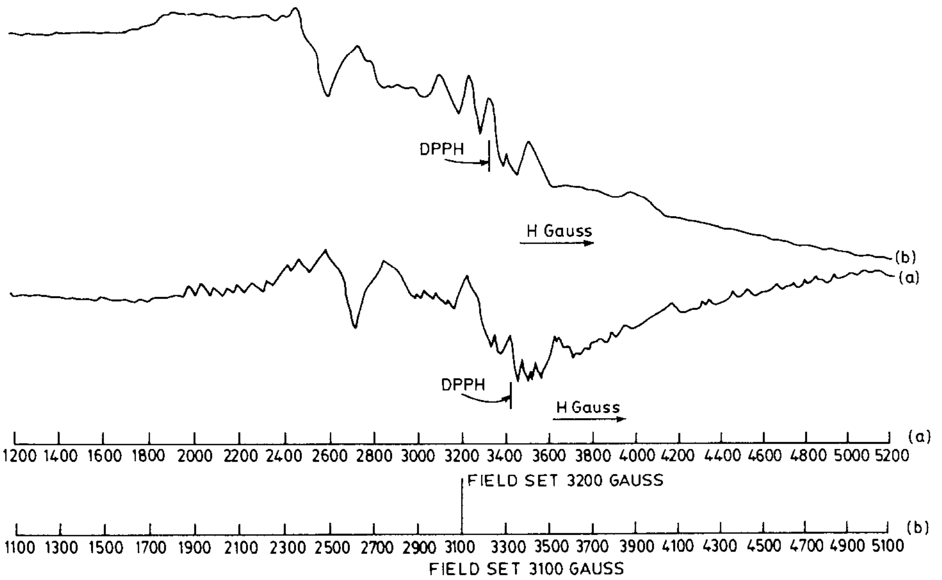

Fig. 3. X-band EPR spectra of polycrystalline sample of $(Ph_4P)[Re(NO)_2(NCS)_3]$ at (a) 298 K and (b) 80 K.

Acknowledgements

Our grateful thanks are due to the Alexander Von Humboldt Foundation for donating the IR spectrophotometer used in this work and to the UGC (New Delhi) for financial support. We also thank RSIC of IIT Madras, for the EPR measurements.

References

1 Part IX. R. G. Bhattacharyya and G. P. Bhattacharjee (Communicated).
2 A. Sergeeva, A. V. Mazera and A. Mazuroki, *Koord. Khim.*, *1*, 1681 (1975).
3 W. P. Griffith, P. M. Kiernan and J. M. Bregeanlt, *J. Chem. Soc. Dalton*, 1411 (1978).
4 K. G. Caulton, *Coord. Chem. Rev.*, *14*, 317 (1975).
5 R. G. Bhattacharyya and P. S. Roy, *Transition Met. Chem.*, *7*, 285 (1982).
6 R. G. Bhattacharyya and P. S. Roy, *J. Coord. Chem.*, *12*, 129 (1982).
7 R. G. Bhattacharyya and P. S. Roy, *Indian J. Chem.*, *22A*, 111 (1983).
8 M. Freni, D. Giusto and V. Valenti, *Gazz. Chim. Ital.*, *94*, 797 (1964).
9 G. LaMonica, M. Freni and S. Cenini, *J. Organomet. Chem.*, *71*, 57 (1974).
10 J. A. Casey and R. K. Murmann, *J. Am. Chem. Soc.*, *92*, 78 (1970).
11 R. G. Bhattacharyya and P. S. Roy (unpublished work).
12 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley–Interscience (New York), 1980.
13 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon Press (New York), 1966.
14 A. Takenata, Y. Sasada, T. Omura, H. Ogoshi and Z. Yoshida, *Bull. Chem. Soc. Jap.*, *47*, 308 (1974).
15 R. G. Bhattacharyya, G. P. Bhattacharjee and N. Ghosh, *Polyhedron*, *2*, 543 (1983).
16 J. H. Enermark and R. D. Feltham, *Coord. Chem. Rev.*, *13*, 339 (1974).
17 K. Nakamoto, 'Infrared and Raman spectra of Inorganic and Coordination Compounds', Wiley–Interscience (New York), 1978.
18 D. M. L. Goodgame and K. A. Price, *Nature*, *220*, 783 (1968).
19 B. N. Figgis, 'Introduction to Ligand Fields', Wiley Eastern Limited (New Delhi), 1976.
20 B. A. Goodman and J. B. Raynor, 'Electron Spin Resonance of Transition Metal Complexes', *Adv. Inorg. Chem. Radiochem.*, *13*, 135 (1970).
21 B. A. Goodman, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc.*, 1973 (1968).
22 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, *12*, 135 (1969).
23 W. F. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).
24 M. Freni, D. Giusto and P. Romiti, *J. Inorg. Nucl. Chem.*, *29*, 761 (1967).