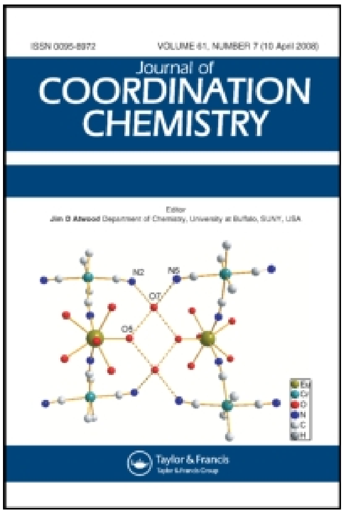

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SHORT COMMUNICATION

Reductive Nitrosylation of ReO_4^- and Synthesis of an Azido Nitrosyl Complex of Rhenium and its 1,10-Phenanthroline and 2,2′-Bipyridine Derivatives Directly from ReO_4^-

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INTRODUCTION

Reductive nitrosylation of ReO_4^- by any of the known nitrosylating agents[1] and subsequent synthesis of rhenium nitrosyl derivatives have not yet been reported. The known nitrosyl compounds of this metal are very few and were prepared from low valent rhenium compounds (cyano, chloro or carbonyl complexes) by the treatment with HNO_3[2,3] or NO[4,5] or NOX.[6] We have recently reported[7] the reduction and subsequent nitrosylation of ReO_4^- using NH_2OHHCl and NCS^- in alkaline medium. Herein is described the direct reductive nitrosylation of ReO_4^- using NH_2OHHCl and N_3^- as evidenced by synthesing the complex ion $[Re(NO)(N_3)_3H_2O]^-$ and its 1,10-phenanthroline and 2,2′-bipyridine derivatives from an aqueous-aerobic medium. It may be mentioned that azido nitrosyl complexes of any metal are extremely rare (only one is known).[8]

EXPERIMENTAL

Materials and Methods

All reagents required for compound preparation were of analytical grades or were purified by literature methods.[9] Infrared spectra were recorded as KBr pellets in a Perkin-Elmer 597 IR-spectrophotometer and were calibrated with polystyrene. A Knauer vapour pressure osmometer (Berlin) was used for the molecular weight determination. Electronic spectra were taken in a Pye-Unicam model SP 8-150 recording spectrophotometer and the solution conductances were measured with a Wayne Kerr Autobalance Precision Bridge B331. Thermoanalyses were made using a Shimadzu thermal analyser DT-30 and the magnetic susceptibilities at varied temperatures were measured by the Faraday method with the help of a vibrating sample Magnetometer Model 155 using liquid nitrogen in the cryostat.

Preparation of the complexes

A mixture of 0.1 g (0.35 mmol) $KReO_4$, 0.33 g (5.25 mmol) NaN_3 and 0.36 g (5.25 mmol) of NH_2OHHCl were taken together in 40 ml water and stirred at 70°C for 1.5 h. The pH of the solution was then raised to ~10 with NaOH solution after addition of another 0.33 g NaN_3 when a deep red solution was obtained, which was then cooled to 0°C and the pH of the solution re-adjusted to ~5 with cold dil. HCl keeping the temperature of the solution below 10°C.

For (Ph_4P) $[Re(NO)(N_3)_3H_2O]$: A cold aqueous solution of Ph_4PCl (0.26 g; 0.7 mmol)

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was added to the above solution with gentle stirring when a dirty green precipitate was obtained, which was filtered off, washed thoroughly with water and then dried over fused $CaCl_2$ in vacuo. Anal. Calcd. for $C_{24}H_{22}N_{10}O_2PRe$: C, 41.2; H, 3.2; N, 20.0; P, 4.4 and H_2O, 2.6. Found: C, 42.0; H, 3.4; N, 19.2; P, 4.5 and H_2O (TGA and DTA) 2.8%. Yield 0.13 g (~55%). IR (ν_{NN}): 2060(s) (sharp and symmetrical); (ν_{NO}): 1675(s); (ν_{ReN}(NO)): 625(w) cm^{-1}. $\bar{\nu}_{max}$ (in CH_3CN) of the anion: 14.6 ($\varepsilon_{max}^{298°K} = 570$), 22.2 (380) and 29.4 (490) kK. Crystallised product from CH_3CN shows a lower intensity ratio of ν_{NN} to ν_{NO} in the infrared spectrum and the nitrogen content of the substance becomes also low (17.5%).

For $[Re(NO)(N_3)_2(LL)(H_2O)]$ (LL = phen or bipy): An alcoholic solution of ~0.12 g (0.7 mmol) of phen or bipy was added to the above solution in the cold with gentle stirring, when the phen compound separated as a brown black solid. The solid was filtered off, washed with water, then with 1:1 water-ethanol mixture and vacuum dried. Anal. Calcd. for $C_{12}H_{10}N_9O_2Re$: C, 28.9; H, 2.0; N, 25.3 and H_2O, 3.6; M.W., 498. Found: C, 29.2; H, 2.4; N, 24.8 and H_2O, 3.7%; M.W (in CH_3CN, osmometric), 470. Yield 0.07 g (~40%). The compound loses nitrogen when further purification is attempted by recrystallisation. IR (ν_{NN}): 2060(s) (broad and unsymmetrical); (ν_{NO}): 1693(s); (ν_{ReN}(NO)): 620(w) and (ν_{ReN}(LL)): 410(w) cm^{-1}. $\bar{\nu}_{max}$(CH_3CN): 15.1 (275), 24.3 (1000), 37.0 (29,880) kK. The bipy compound separated as a reddish brown solid, washed and dried as its phen analogue. Here the intensity ratio of ν_{NN} and ν_{NO} in the IR spectrum is rather low and nitrogen content is also not quite satisfactory. Yield, 0.06 g (~36%). Anal. Calcd. for $C_{10}H_{10}N_9O_2Re$: C, 25.3; H, 2.1; N, 26.5 and H_2O, 3.8; M.W., 474. Found: C, 25.0; H, 2.5; N, 24.6 and H_2O, 4.2%; M.W., 425. IR (ν_{NN}): 2070(s); (ν_{NO}): 1680(s) and (ν_{ReN}(NO)): 625(w) and (ν_{ReN}(LL)): 415(w) cm^{-1}. ν_{max}(CH_3CN): 14.4 (220); 24.4 (880) and 35.0 (18,900) kK. (For the assignment of IR bands, see Ref. 10).

RESULTS AND DISCUSSION

While in the cases of CrO_4^{2-},[11,12] MoO_4^{2-} [12] and OsO_4,[12] reductive nitrosylation using NH_2OH and NCS^- occurs at a neutral or a slightly acidic medium, the key step in the case of ReO_4^- and NCS^-[7] as well as in the present case of ReO_4^- and N_3^- is to render the medium strongly alkaline after a long preheating period. The rarity of the known azido nitrosyl compounds of metals can be traced to the mechanistic study of Feltham and Douglas[13] that an incoming azide ion attacks preferentially the NO group already coordinated to the metal ion (with the evolution of N_2 and N_2O) and an incoming NO ligand preferentially attacks the azido group bound to the metal ion (to produce a dinitrogen complex after the evolution of N_2O), thereby rupturing metal-nitrosyl or metal-azido bonds. The successful isolation of the azido nitrosyl complexes of rhenium in the pure state (in the solid state the compounds are stable at least for a week at the ambient temperature and they do not explode on heating) may imply that the reductive nitrosylation in the present case proceeds *via* a concerted mechanism.

The compounds are soluble in acetonitrile, acetone and dimethylformamide and in the former solvent the bipy and phen complexes are non-electrolytes and monomeric while the tetraphenylphosphonium salt behaves as a 1:1 electrolyte (Λ_M = 124 ohm^{-1} cm^2 mol^{-1}).[14] However, the compounds are not stable in solution as is evident from the reduced IR intensity of the ν_{NN} band, and the lowering of the nitrogen content of the crude substances, after recrystallising them.

A single, sharp and symmetrical ν_{NN} vibration in the phosphonium salt (as against a broad and unsymmetrical band in the cases of bipy and phen complexes which may imply a *cis*-configuration of the N_3 groups) at good resolution (±2 cm^{-1}) indicates that the anion may have a TBP configuration (NO assumed to be linear) with the three N_3 groups in the equatorial plane (C_{3v}). That the water molecules are coordinated to the metal ion in each of the complexes, is proved by the TGA and DTA studies. Like the corresponding thiocyanato complex[7], the anionic complex of the tetraphenylphosphonium salt is, again, 5-coordinated (compare also: $(Ph_4As)[ReOCl_4]$[15] and $(Ph_4P)[Mo(NO)Cl_4]$[16] as against $Cs_2[ReOCl_5]$ and $Cs_2[Mo(NO)Cl_5]$).

Considering the NO^+ formalism[17,18], the formal oxidation state of rhenium should be $+I(5d^6)$ which is further confirmed by the magnetic susceptibility data ($\chi_A \approx +140 \times 10^{-6}$ cgs units at the room temperature for all the complexes and remains fairly constant down to 80°K). The data are not atypical for a TIP term arising out of a group $(e)^4(b_2)^2$ configuration[18] of the $\{Re(NO)\}^6$ moiety (conditions being suitable for a second order spin-orbit interaction due to the lower symmetry of the molecule and a higher spin-orbit coupling constant of rhenium[19]) in the TBP anion, $[Re(NO)(N_3)_3H_2O]^-$. In that case, the three electronic spectral bands can be assigned[18] to: $b_2 \rightarrow a_1$; $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions respectively. The hexacoordinated phen and bipy complexes may also have the identical ground state M.O. configuration[18] (local symmetry of $[ReNN_4O]$ chromophore is expected to generate the M.O. energy levels, not much different from that worked out[18] for C_{4v} cases), but in these cases the first two observed electronic spectral bands (the rest is for an intraligand (bipy or phen) transition[20]) may be due to $b_2 \rightarrow e$ and $b_2 \rightarrow a_1$ transitions (compare, ref. 18). The expected band due to $b_2 \rightarrow b_1$ is unobserved in both the cases.

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