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Reductive Nitrosylation of Tetraoxometallates. Part VI [1]. Generation of $\{Os(NO)\}^{3+}$ Moiety: Single Step Synthesis of Azido Nitrosyl Complexes of the types $[Os(NO)(N_3)_5]^{2-}$ and $[Os(NO)(N_3)_3\text{-}phen]$ (phen = 1,10-phenanthroline) directly from OsO_4 in Aqueous and Aerobic Media

R. G. BHATTACHARYYA and A. M. SAHA

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

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Transition metal nitrosyls are becoming increasingly more important because of their interesting electron transfer properties [2] and catalytic uses in organic syntheses [3]. Though the reductive nitrosylation of tetraoxometallates using NH_2OH is known [4, 5], until our recent systematic work [1, 6–9], its synthetic potentialities had only been sporadically explored. Excepting a single attempt [10] such a reaction on OsO_4 substrate is unknown. In fact the osmium nitrosyl system is less well studied [11]. Moreover, azido nitrosyl complexes of any metal are extremely rare and literature records only two successful attempts for the isolation of such complexes [7, 12]. We describe in the present paper the reductive nitrosylation of OsO_4 using $NH_2OH{\cdot}HCl$ and N_3^- in a slightly acidic medium. The process generates the $\{Os(NO)\}^{3+}$ moiety, as confirmed by the isolation of the complexes of the types $R_2[Os(NO)(N_3)_5]$ (R = Ph_4P (1), Bu_4N (2), Et_4N (3) and $[Os(NO)(N_3)_3phen]$ (4)).

Experimental

Preparation and Characterisation of $[(C_6H_5)_4P]_2[Os(NO)(N_3)_5]$

To a solution of OsO_4 (0.1 g; 0.39 mmol) in 25 ml of water was added $NH_2OH{\cdot}HCl$ (0.4 g; 5.7 mmol) and NaN_3 (0.35 g; 5.38 mmol), and the resulting solution was stirred at 60–70 °C for 15 min. Another 0.35 g of NaN_3 was then added and the solution was heated at ~80 °C for 30 min when a clear deep red-brown solution was obtained. The solution (pH ≈ 6.8–7.0) was cooled to room temperature and the pH of the solution was adjusted to ~5 (Solution A) with 6 *M* HCl.

A hot solution of Ph_4PBr (0.4 g; 0.95 mmol) in 20 ml of water was added to the above solution with constant stirring at room temperature, when a chocolate brown precipitate was obtained. This was filtered off, washed with water, 60% isopropanol and ether, and dried over $CaCl_2$ *in vacuo*. The product was crystallised from nitromethane–ether mixture and the slightly sticky solid was worked up with n-pentane to get a chocolate-brown powder. This was further washed with water, isopropanol and ether, and recrystallised from the same solvent. Yield: 0.13 g, 30%. Found, C 51.6, H 3.5, N 20.0 and P 5.7; Calcd., C 52.0, H 3.6, N 20.2 and P 5.6%. IR: ν_{NN} 2040(s), ν_{NO} 1775(s), ν_{OsN}(NO) 620(w) and ν_{OsN}(N_3) 380(w) cm^{-1}. Λ_M (in CH_3NO_2) = 175 ohm^{-1} cm^2 mol^{-1}. UV–vis: λ_{max} (CH_3NO_2) 375 nm (ϵ = 14200 l mol^{-1} cm^{-1}).

Preparation and Characterisation of $[(C_4H_9)_4N]_2[Os(NO)(N_3)_5]$

A hot solution of Bu_4NI (0.35 g; 0.95 mmol) in 20 ml water was added to the solution A with constant stirring at room temperature, resulting in a brown precipitate which was filtered off, washed with water, 60% isopropanol and ether, and dried over $CaCl_2$ *in vacuo*. The product was crystallised from nitromethane–ether mixture and the crystallised product was worked up with n-pentane. The brown solid was again washed with water, isopropanol and ether and recrystallised from the same solvent. Yield: 0.035 g, 10%. Found, C 41.8, H 7.8, N 27.3; Calcd., C 42.0, H. 7.9 and N 27.6%. IR: ν_{NN} 2040(s), ν_{NO} 1780(s), ν_{OsN}(NO) 620(w) and ν_{OsN}(N_3) 378 (w) cm^{-1}. Λ_M (in CH_3NO_2) = 180 ohm^{-1} cm^2 mol^{-1}. UV–vis: λ_{max} (in CH_3NO_2) 380 nm (ϵ = 19400 nm).

Preparation and Characterisation of $[(C_2H_5)_4N]_2[Os(NO)(N_3)_5]$

A solution of Et_4NCl (0.2 g; 1.2 mmol) in 10 ml water was added to the solution A at room temperature. The resulting solution was then concentrated on a steam bath to about 5 ml and kept in a cold condition (~10 °C) for 3–4 h, when a reddish brown solid was precipitated. This was filtered off, washed with water, 90% ethanol and ether and dried over $CaCl_2$ at reduced pressure. The substance was then crystallised from DMF–ether mixture. Yield: 0.05 g, 20%. Found, C 27.5, H 6.1, N 36.1; Calcd., C 27.8, H 5.8, and N 36.5%. IR: ν_{NN} 2055(s), ν_{NO} 1785(s), ν_{OsN}(NO) 620 (w), ν_{OsN}(N_3) 372 (w). Λ_M (in DMF) = 150 ohm^{-1} cm^2 mol^{-1}. UV–vis: λ_{max} (DMF:CH_3CN = 2:8) 496 (ϵ = 1200) and 360 (ϵ = 800) nm.

Preparation and Characterisation of $[Os(NO)(N_3)_3phen]$

To the solution A, a hot aqueous (25 ml) solution of phen (0.16 g; 0.88 mmol) was added with constant stirring at room temperature and the stirring was continued for another 20 min. The separated

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solid was filtered off, washed with water, 60% ethanol and ether, and dried over $CaCl_2$ under reduced pressure. The product was crystallised from acetone–ether mixture and the solid was worked up with n-pentane when a deep brown solid was obtained. This was further washed with water, 70% ethanol and ether, and recrystallised from the acetone–ether mixture. Yield: 0.11 g, 50%. Found, C 27.0, H 1.7, N 31.5, M.W. 514 (osmometric, DMF); Calcd. for $[Os(NO)(N_3)_3C_{12}H_8N_2]$, C 27.4, H 1.5, N 31.9%, M.W. 526. IR: ν_{NN} 2050(s), ν_{NO} 1790(s), $\nu_{OsN}(NO)$ 615(w), $\nu_{OsN}(N_3)$ 385(w). UV–vis: λ_{max} ($DMF{:}CH_3CN = 2{:}8$) 388 nm ($\epsilon = 900$).

Results and Discussion

While in the case of rhenium the azido nitrosyl complexes are quite unstable in solution and their purification by crystallisation in a suitable solvent is almost impossible [7], in the case of osmium these could be crystallised quite pure and complexes could be obtained in a solid condition much more easily than their thiocyanato analogues where it is extremely difficult to solidify the gummy products [13]. The rarity of the known azido nitrosyl compounds of metals can be traced to the mechanistic study of Feltham and Douglas [14] according to which 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 breaking the metal–nitrosyl or metal–azido bonds. The successful isolation of the azido nitrosyl complex of osmium in the pure state may imply that the reductive nitrosylation in the present case proceeds via a concerted mechanism. The lower yield in compound 2 is due to the fact that after one crop of the crystals were separated, the mother liquor subsequently deposits shining crystals of a compound containing no azido nor NO groups (IR evidence). However, after the isolation of all the desired osmium complexes described here, the mother liquors can be collected together, boiled with alkaline hydrogen peroxide and from the $[Os_4(OH)_2]^{2-}$ solution thus obtained OsO_4 can be recovered by distillation with HNO_3 [11(a)].

As expected, the phen compound is a non-electrolyte and monomeric, while the anionic complexes behave as 2:1 electrolytes [15]. The position of ν_{NO} in the IR (for the assignment of the IR bands see ref. 16) is in the lowest wavenumber region when one compares their position in the isoelectronic $\{M(NO)\}^6$ series (M = Fe, Ru, Os) and this is obviously due to the highest M → NO π bonding in the case of Os, considering that series. According to the NO^+ formalism, the formal oxidation state of osmium in the $\{Os(NO)\}^6$ moiety should be +2, confirmed by the observed diamagnetism of the isolated complexes. The symmetry species in these $[OsNN_5]$ or $[OsNN_3N_2]$ chromophores may be approximated to C_{4v} and the two electronic absorption bands observed in the compound 3 may be due to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions (in order of increasing energy), respectively [17]. Other compounds however recorded only a single absorption band around 380 nm (the range studied being 800–300 nm), which in the compounds 1 and 2 has comparable intensities, whereas compound 4 possesses a much reduced intensity. This band may be originated from a $b_2 \rightarrow b_1$ transition, the $b_2 \rightarrow e$ one being missing.

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