Reductive Nitrosylation of Tetraoxometalates. Single-pot and a Virtually Single-step Synthesis of $[Os(NO)(NCS)_5]^{2-}$ and its 1,10-Phenanthroline and 2,2′-Bipyridine Derivatives directly from OsO_4 in Aqueous Aerobic Media

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The complexes $R_2[Os(NO)(NCS)_5]$ ($R = AsPh_4$, PPh_4, NMe_4, or NEt_4) and $[Os(NO)(NCS)_3(L-L)]$ [L–L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)] have been synthesised directly from OsO_4 *via* reductive nitrosylation using $NH_2OH{\cdot}HCl$ and NCS^- in an acidic medium in a single step and using a single pot. The complexes have been characterised by analytical, molecular weight, molar conductance, magnetic susceptibility, i.r. and electronic spectral data.

In view of the growing interest in the catalytic activities,[1,2] capacity for pollution control,[2] and electron-transfer properties [3] of transition-metal nitrosyl derivatives, a detailed and systematic study of the reductive nitrosylation of various tetraoxometalates has recently been carried out in this laboratory.[4] However, very little attention has so far been paid to the reductive nitrosylation of OsO_4 and, in fact, osmium-nitrosyl systems are quite rare and less well studied [5] not withstanding the catalytic properties and ability for pollution control exhibited in general by complexes of the platinum metals. In a recent communication [4e] we described the reductive nitrosylation of OsO_4 using hydroxylamine and azide ion and reported the synthesis of some novel azido-nitrosyl complexes of osmium. Sarkar and Müller,[6] however, carried out such a reaction using an excess of thiocyanate ion but a limited amount of hydroxylamine hydrochloride and obtained a 50% conversion of OsO_4 into $[Os(NO)(NCS)_5]^{2-}$, precipitated as its tetraphenylphosphonium salt. As in our previous work,[4] in this particular case also we find that the use of excess of hydroxylamine hydrochloride facilitates the nitrosylation reaction.

Here we describe a single-pot and a virtually single-step synthesis of $[Os(NO)(NCS)_5]^{2-}$, precipitated with various counter ions, *viz.* $AsPh_4^+$ (1), PPh_4^+ (2), NMe_4^+ (3), and NEt_4^+ (4), in very good yield, as well as of its hitherto unknown derivatives $[Os(NO)(NCS)_3(L-L)]$ [L–L = 1,10-phenanthroline (phen) or 2,2-bipyridyl (bipy)].

Experimental

Materials and Methods.—All reagents required for compound preparation were of analytical grade. The analytical grade solvents used for physicochemical studies were further purified by literature methods.[7] Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 597 spectrophotometer and were calibrated with polystyrene. The electronic spectra were obtained on a Pye-Unicam SP8-150 UV-VIS spectrophotometer (800—200 nm). A Knauer vapour-pressure osmometer was used for the molecular weight determination. The magnetic susceptibilities were measured with the help of a EG and G Princeton Applied Research Model 155 vibrating-sample magnetometer. The elements C, H, and N were analyzed microanalytically and S and P by a standard method.[8] All the complexes were dried at reduced pressure over P_4O_{10}.

Preparations and Characterisations.—$[AsPh_4]_2[Os(NO)(NCS)_5]$ (1). To a solution of OsO_4 (0.1 g, 0.39 mmol) in water (20 cm^3) was added $NH_2OH{\cdot}HCl$ (0.5 g, 7.2 mmol) and NH_4NCS (0.5 g, 6.58 mmol), and the resulting solution was stirred at *ca.* 80 °C for 45 min. More $NH_2OH{\cdot}HCl$ (0.4 g, 5.75 mmol) and NH_4NCS (0.2 g, 2.6 mmol) were added, while stirring at the same temperature for another 30 min when a clear deep red solution (A) (pH *ca.* 2.6) was obtained. The solution was cooled to 0—5 °C.

An aqueous solution (25 cm^3) of $AsPh_4Cl{\cdot}H_2O$ (0.4 g, 0.92 mmol) was added to the above solution at *ca.* 10 °C. The orange-red precipitate obtained was stirred for 30 min and then filtered off, washed thoroughly with water, 90% cold ethanol (to wash out $AsPh_4NCS$), and diethyl ether, and dried as described. The product was dissolved in dry acetone (in which $AsPh_4NCS$ is insoluble). The solution was filtered and a deep orange-red crystalline solid was precipitated with light petroleum (b.p. 40—60 °C). Yield: 0.43 g, 86% (Found: C, 49.3; H, 3.1; N, 6.3; S, 12.3. Calc. for $C_{53}H_{40}As_2N_6OOsS_5$: C, 49.8; H, 3.1; N, 6.5; S, 12.5%). I.r.: ν(CN) at 2 080s, ν(NO) 1 822s, and ν(OsN)(NO) 610w cm^{-1}. Λ (in CH_3CN) = 230 ohm^{-1} cm^2 mol^{-1}. U.v.–visible: $\nu_{max.}$ (in CH_3CN) at 22 300 (1 395) and 34 500 cm^{-1} (ε = 6 620 dm^3 mol^{-1} cm^{-1}).

$[PPh_4]_2[Os(NO)(NCS)_5]$ (2). A solution of PPh_4Br (0.4 g, 0.96 mmol) in water (20 cm^3) was added to solution (A) at 5—10 °C with constant stirring for 30 min when a brick-red precipitate appeared. This was filtered off, washed thoroughly with water, 90% cold ethanol, and diethyl ether, and dried as usual. The solid was then extracted with dry acetone and to the red extract was added light petroleum (b.p. 40—60 °C) yielding a deep brick-red microcrystalline solid. Yield: 0.39 g, 83% (Found: C, 53.1; H, 3.3; N, 6.9; P, 5.1; S, 13.2. Calc. for $C_{53}H_{40}N_6OOsP_2S_5$: C, 53.5; H, 3.4; N, 7.1; P, 5.2; S, 13.5%). I.r.: ν(CN) at 2 078s, ν(NO) 1 825s, ν(OsN)(NO) 610w, and δ(NCS) 448w cm^{-1}. Λ (in CH_3CN) = 220 ohm^{-1} cm^2 mol^{-1}. U.v.–visible: $\nu_{max.}$ (in CH_3CN) at 21 900 (1 840) and 34 500 cm^{-1} (ε = 17 823 dm^3 mol^{-1} cm^{-1}).

$[NMe_4]_2[Os(NO)(NCS)_5]$ (3). To the deep red solution (A) (10 cm^3) was added an aqueous solution (cold, 5 cm^3) of NMe_4Cl (0.4 g, 3.65 mmol) with constant stirring when a deep brown-red precipitate was obtained. This was filtered off, washed with the minimum volume of cold water, and dried. The product was crystallised from nitromethane–diethyl ether (1 : 3), the slightly sticky solid was worked up with n-pentane, and recrystallised from the same solvent mixture. Yield:

0.18 g, 70%. The mother-liquor on further concentration deposited another 10% of the product which was crystallised as before (Found: C, 23.5; H, 3.6; N, 16.9; S, 24.1. Calc. for $C_{13}H_{24}N_8OOsS_5$: C, 23.7; H, 3.7; N, 17.0; S, 24.3%). I.r.: ν(CN) at 2 080s, ν(NO) 1 830s, ν(OsN)(NO) 615vw, and δ(NCS) 442w cm^{-1}. Λ (in CH_3CN) = 240 ohm^{-1} cm^2 mol^{-1}. U.v.-visible: $\nu_{max.}$ (in CH_3CN) at 22 200 (2 890) and 34 000 cm^{-1} (ε = 7 110 dm^3 mol^{-1} cm^{-1}).

$[NEt_4]_2[Os(NO)(NCS)_5]$ (4). As described for the tetramethylammonium salt, except that the deep brown compound, which was more sticky, was solidified by suddenly freezing the acetone solution of the product after adding a few drops of light petroleum, under liquid nitrogen. The almost colourless liquid was decanted off and the solid was vacuum dried. Yield: 0.18 g, 60% (Found: C, 32.9; H, 5.1; N, 14.2; S, 20.5. Calc. for $C_{21}H_{40}N_8OOsS_5$: C, 32.7; H, 5.2; N, 14.6; S, 20.8%). I.r.: ν(CN) at 2 082s, ν(NO) 1 830s, ν(OsN)(NO) 610vw, and δ(NCS) 450w, br cm^{-1}. Λ (in CH_3CN) = 225 ohm^{-1} cm^2 mol^{-1}. U.v.-visible: $\nu_{max.}$ (in CH_3CN) at 22 100 (1 970) and 35 700 cm^{-1} (ε = 2 650 dm^3 mol^{-1} cm^{-1}).

$[Os(NO)(NCS)_3(phen)]$ (5). To solution (A) was added a hot (50—60 °C) aqueous solution (20 cm^3) of phen (0.15 g, 0.76 mmol) with constant stirring at 10—15 °C and the stirring was continued for 10 min. The product was filtered off, washed with water, 50% ethanol and diethyl ether, and dried. The product was crystallised from *NN*-dimethylformamide (dmf)–diethyl ether (1 : 4) and washed further with water, 50% ethanol, chloroform, and ether. The slightly gummy product thus obtained was worked up with n-pentane to yield a deep red-brown powder. Yield: 0.18 g, 79% [Found: C, 31.6; H, 1.3; N, 14.4; S, 16.5%; *M*, 556 (osmometric, dmf). Calc. for $C_{15}H_8N_6OOsS_3$: C, 31.4; H, 1.4; N, 14.6; S, 16.7%; *M*, 574]. I.r.: ν(CN) at 2 082s, ν(NO) 1 825s, ν(OsN)(NO) 612w, ν(OsN)(phen) 402, 382w, and δ(NCS) 450m cm^{-1}. U.v.-visible: $\nu_{max.}$ (dmf-CH_3CN 2 : 8) at 22 100 (2 420) and 34 500 cm^{-1} (ε = 7 820 dm^3 mol^{-1} cm^{-1}).

$[Os(NO)(NCS)_3(bipy)]$ (6). The method described above was repeated using bipy instead of phen. The product remained as a semi-solid even after freezing the analogous solution under liquid nitrogen. I.r.: ν(CN) at 2 080s, ν(NO) 1 825s, ν(OsN)(NO) 615w, ν(OsN)(bipy) 395w, and δ(NCS) 460w,br cm^{-1}. U.v.-visible: $\nu_{max.}$ (in CH_3CN) at 22 100 and 33 600 cm^{-1}.

Results and Discussion

Synthesis of the thiocyanato-derivatives described requires cold conditions during the precipitation with the counter ions or L–L ligands, and the isolation of the pure solid complexes is more difficult than of the azido–nitrosyl complexes.[4e] In fact, the bipy derivative of the thiocyanate series (characterised by i.r. and u.v.-visible spectroscopy) could only be obtained as a semi-solid and all attempts to solidify it have failed.

Also noteworthy is that whereas N-bonded thiocyanate and azide ligands are essentially σ donors and the former possesses a higher field factor (1.02) than the latter (0.83),[9] the ν(NO) vibrations (*ca.* 1825 cm^{-1}) of the isolated osmium thiocyanatonitrosyl derivatives are at a higher wavenumber than those observed (*ca.* 1 780 cm^{-1}) in the cases of the corresponding azido-derivatives. Interestingly, this is also the case in the appropriate nitrosyl derivatives[4] of Cr, Mo, and Re. Under the circumstances it is reasonable to conclude that, in the cases of the low valent metal nitrosyl derivatives, an azide ligand can effect a better electron transfer to the central metal ion than that achieved by the isothiocyanate ligand. [As in other *thiocyanato-nitrosyl complexes, the position of the* ν(CN) and δ(NCS) bands in all the osmium complexes studied here suggest that the NCS group is N-bonded.[10]]

The anionic complexes behave as 2 : 1 electrolytes[11] and the phen complex is monomeric and as expected behaves as a non-electrolyte. Assuming the NO^+ formalism,[12] the oxidation state of Os in the complexes containing a $\{Os(NO)\}^6$ moiety should be +2, which is corroborated by the observed diamagnetism of the complexes. The symmetry species in these $OsNN'_5$ or $OsNN'_3N''_2$ chromophores may be approximated to C_{4v} and the two bands observed in the electronic absorption spectra of complexes (3)—(6) may be assigned to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions (in order of increasing energy) respectively. For compounds (1) and (2) the band due to the latter transition may be mixed with the cation (PPh_4^+ and $AsPh_4^+$) bands.

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