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Reductive Nitrosylation of Tetraoxometallates.
Part I. Generation of $\{Cr(NO)\}^{2+}$ Moiety: Single Step Synthesis of Complexes of the Type $[Cr(NO)(NCS)_2\text{-}LL]$ (LL = 2,2′-bipyridine or 1,10-phenanthroline) and $[Cr(NO)(dtc)_2]$ (dtc = N,N′-diethyldithiocarbamate) directly from Chromate(VI) in Aqueous and Aerobic Media

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Reductive nitrosylation of tetraoxometallates using hydroxylamine in strong alkaline medium is classically known [1–3] but very sparsely exploited [3]. Recently it has also been shown that this reaction occurs in neutral and in slightly acidic media [4]. However, those synthetic works succeeded only in a partial conversion (specially CrO_4^{2-} and VO_4^{3-}) of the oxoanions to the lower valent metal–nitrosyl derivatives as is evident from the low yield of the products isolated so far [1–5] and from the failure to isolate pure 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) derivatives from the reaction mixture [5, 6] even in the molybdenum case. Moreover, the reductive nitrosylation of CrO_4^{2-}, described so far, both in alkaline [2] as well as in acidic [4a] medium gives a major amount of unconverted residue at several steps [6]. In the present communication we describe a method leading to a smooth and almost quantitative and single step conversion of CrO_4^{2-} to the $\{Cr(NO)\}^{2+}$ moiety in aqueous aerobic condition (pH ≈ 5) as evidenced by synthesising its pure and hitherto unknown bipy, phen and dtc derivatives in 95% yield.

Results and Discussion

While the mechanisms of reductive nitrosylation reaction are not yet known properly and the synthetic methods so far gave limited yields of the nitrosyl derivatives, affording a variety of other reaction products precipitable with bipy or phen [5], the comments regarding the details of the mol requirements of NH_2OH with respect to the optimum yield of the products and the steric course of the reactions [5] seem to be unwarranted. The previous authors [1–5] always used 3 or 4 mol of nitrosylating agent (NH_2OH) per mol of tetraoxometallates. For CrO_4^{2-} and VO_4^{3-} [2–4] this meagre amount of NH_2OH used makes the nitrosylation reaction extremely sluggish and ultimately apart from a very poor yield of the metal–nitrosyl derivatives, the procedures become rather cumbersome. But we notice that a dramatic improvement of the efficiency of the nitrosylation process in a slightly acidic medium (pH ≈ 5) can be observed if an excess of $NH_2OH\cdot HCl$ (10–15 mol per mol of the oxoanion) is used in the presence of excess of NCS^- ion. The mononitrosylation of MoO_4^{2-} to $\{Mo(NO)\}^{3+}$ moiety is achieved in quantities within 5 minutes and then proceeds towards the dinitrosylation stage [6] (infrared probing) whereas in the present case of CrO_4^{2-}, the $\{Cr(NO)\}^{2+}$ moiety is quantitatively generated within 15–20 min and even after prolonged heating (2–4 hr), dinitrosylation is almost negligible. So, this method can be regarded as specific for the generation of pure $\{Cr(NO)\}^5$ [*i.e.* $\{Cr(NO)\}^{2+}$] moiety from CrO_4^{2-}. The reaction mixture on addition of Ph_4PCl affords a quantitative yield of $(Ph_4P)_3$ $[Cr(NO)(NCS)_5]$ (otherwise obtained at a low yield [4a] in a rather cumbersome way [6]), and on addition of bipy, phen or dtc, the so far unreported compounds $[Cr(NO)(NCS)_2(bipy)]$ (I) [ν_{CN} 2080; ν(NO) 1705; ν_{CrN}(NO) 590; ν_{NCrN}(bipy) 328, 362; λ_{max} 645, 490(sh) and 350 nm], $[Cr(NO)(NCS)_2(phen)]$ (II) [the ir and uv–vis characteristics are almost identical with those of (I)] and $[Cr(NO)(dtc)_2]$ (III) [$\nu_{(NO)}$ 1700; ν_{CrN}(NO) 620; ν_{CrS}(dtc) 368; the dtc bands are, as expected from a bidentate group; λ_{max} 635, 500 and 320 nm] (for the assignments of the ir bands, see refs. [7, 8]) are obtained. None of these complexes could at all be isolated in the pure state using conventional amount (3–4 or even 5 mol per mol of CrO_4^{2-}) of $NH_2OH\cdot HCl$.

Considering NO^+ formalism, the formal oxidation state of chromium becomes +1 which is further substantiated by the magnetic susceptibility [2.0 B.M. for (I) and (II) and 1.8 B.M. for (III)] and esr data [g_{av} = 1.98 for all the three cases; data are comparable with the analogous Cr(I) compounds. See ref. 9].

Experimental

Preparation of $[(C_6H_5)_4P]_3[Cr(NO)(NCS)_5]$

A solution of 0.5 g (2.5 mmol) of K_2CrO_4 and 1.9 g NH_4SCN (25.0 mmol) in 25 ml H_2O, to which 2.7 g (37.5 mmol) $NH_2OH\cdot HCl$ was added with stirring, was heated at 80° for about 40 min when a clear greenish violet solution was obtained. An aqueous solution (25 ml) of 2.8 g (7.5 mmol) $[(C_6H_5)_4P]Cl$ was added. The yellowish-green precipitate was stirred for 2.5 hr and then filtered, washed with water, 80% ethanol (to wash out Ph_4PSCN) and ether and dried over $CaCl_2$ at reduced pressure. The dry product was crystallised from acetone–ether mixture. Yield: 3.3 g; 92%. Found, C 66.2, H 4.4, N 5.9, S 11.7, P 6.5, Cr 3.2; Calcd. C 66.6, H 4.3, N 6.1, S 11.5, P 6.5 and Cr 3.8%.

Preparation of [Cr(NO)(NCS)$_2$(bipy)]

To the greenish violet solution obtained above an aqueous solution (hot, 25 ml) of bipy (0.6 g, 3.8 mmol) was added with stirring and the same was continued for 1 hr. The yellowish-brown precipitate was filtered, washed with water, ethanol and ether and dried over $CaCl_2$ under reduced pressure. The product was further crystallised from acetone–ether mixture. Yield: 0.85, 95%. Found, C 41.0, H 2.6, N 19.6, S 18.5 and Cr 14.5; Calcd. for $[Cr(NO)(NCS)_2(C_{10}H_8N_2)]$ C 40.7, H 2.3, N 19.8, S 18.1 and Cr 14.7%.

Preparation of [Cr(NO)(NCS)$_2$(phen)]

Same as described under the bipy complex. Yield: 0.88 g, 94%. Found, C, 44.0, H 2.5, N 18.1, S 17.1, Cr 13.4; Calcd. for $[Cr(NO)(NCS)_2C_{12}H_8N_2]$, C 44.4, H 2.1, N 18.5, S 16.9 and Cr 13.8%.

Preparation of [Cr(NO)(dtc)$_2$]

To the greenish violet solution obtained above an aqueous solution (25 ml) of $NaEt_2dtc \cdot 3H_2O$ (1.5 g, 6.6 mmol) was added with constant stirring and the same was continued for another 30 min. The brown precipitate was filtered, washed with water, ethanol and light petroleum, dried, and finally crystallised from acetone. Yield: 0.9 g, 90%. Found; C 31.4, H 5.6, N 10.8, S 33.7, Cr 13.3; Calcd. for $[Cr(NO)(S_2CN(C_2H_5)_2)_2]$, C 31.7, H 5.3, N 11.1, S 33.9 and Cr 13.8%.

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