Transition Met. Chem. 8, 255–256 (1983)

Reductive Nitrosylation of Tetraoxometallates. Part VII(1). Generation of the $\{Mo(NO)_2\}^{2+}$ Moiety: Single Step Synthesis of $[Mo(NO)_2(CN)_4]^{2-}$ and $[Mo(NO)_2(CN)_2(1,10\text{-phenanthroline})]$

Ramgopal Bhattacharyya*, Gobinda Prashad Bhattacharjee and Alok Mohan Saha

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

Introduction

Reductive nitrosylation of $[MoO_4]^{2-}$ using NH_2OH and CN^- in an alkaline medium and the generation of $\{Mo(NO)\}^+$ moiety has been known for many years(2, 3), but such a reaction converting $[MoO_4]^{2-}$ to $\{Mo(NO)_2\}^{2+}$ is still unknown. The conversion of $[MoO_4]^{2-}$ to a dinitrosyl moiety in a neutral or a slightly acidic medium was also poorly understood(4) until our recent work on the disproportionation of the $\{Mo(NO)(NH_2O)\}^{2+}$ moiety to $\{Mo(NO)_2\}^{2+}$ and $\{Mo_2O_4\}^{2+}$ in a near neutral medium(5). Herein is described for the first time the single-step conversion of $[MoO_4]^{2-}$ to $\{Mo(NO)_2\}^{2+}$ using an excess of NH_2OH and KCN in an alkaline medium, as confirmed by synthesis of $[Ph_4P]_2[Mo(NO)_2(CN)_4]$ and $[Mo(NO)_2(CN)_2(phen)]$ (phen = 1,10-phenanthroline) in moderate yields in an aqueous aerobic medium.

Experimental

Materials and methods

All reagents were of reagent grade and used without further purification. For physicochemical measurements, the solvents were further purified using literature methods(6). Infrared spectra were recorded as KBr discs in a Perkin Elmer 597 spectrophotometer calibrated with polystyrene. Solution conductances were measured with a Wayne-Kerr Autobalance Precision Bridge B 331 and the electronic spectra (800–280 nm) were taken in MeCN using a Pye Unicam SP 8-150 u.v.-vis. spectrophotometer. Magnetic susceptibilities were measured with a Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. TGA curves were recorded in a Shimadzu (Japan) DT – 30 Thermoanalyser.

Preparation of the complexes

A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.5 g, 2.0 mmol) and NaOH (0.5 g, 12.5 mmol) in water (25 cm^3) was stirred at 80 °C for 10 min. To the resulting solution, first KCN (2.4 g, 37 mmol) and then $NH_2OH \cdot HCl$ (3.8 g, 55 mmol) were added with stirring at 80 °C when an orange red solution was obtained. To this solution, 5–6 drops of 12 M HCl were added and stirred for 5 min when the colour of the solution became red. The solution was stirred for another 5 min and then cooled. The pH of the solution (~7.5) was reduced to ~5.5 (Solution A).

$[Ph_4P]_2[Mo(NO)_2(CN)_4] \cdot 2H_2O$

A hot aqueous (40 cm^3) solution of $[(C_6H_5)_4P]Br$ (2.4 g, 5.7 mmol) was added to Solution A with stirring at 50 °C when a greenish yellow solid separated. It was filtered off, washed with H_2O, 90% EtOH, and Et_2O and dried over fused $CaCl_2$ at reduced pressure. The compound was crystallised from acetonitrile-ether as greenish yellow needles. Anal. Calcd. $C_{52}H_{40}N_6O_2P_2Mo \cdot 2H_2O$: C, 64.1; H, 4.1; N, 8.6; P, 6.4; Mo, 9.8; H_2O, 3.7. Found: C, 63.8; H, 4.0; N, 8.4; P, 6.1; Mo, 10.0 and H_2O, 3.9%. Yield, 1.0 g (50%). I.r.: 1658(s), 1792(s), $\nu(NO)$; 2140(sh), 2110(s), $\nu(CN)$; 610(w), $\nu(MoN^{NO})$ and 345(w), $\nu(MoC)$ cm^{-1}. ν_{max}, 22800 cm^{-1} (ε_{max} = 945 l mol^{-1} cm^{-1}).

$[Mo(NO)_2(CN)_2phen] \cdot 2H_2O$

An aqueous solution of 1,10-phenanthroline monohydrate (0.7 g, 3.5 mmol) was added to Solution A with stirring at 50 °C. The separated yellow solid was filtered off, washed with H_2O, 90% EtOH, Et_2O and dried over fused $CaCl_2$ at reduced pressure. The compound was recrystallised from acetonitrile-ether as golden yellow needles. Anal. Calcd. $C_{14}H_8N_6O_2Mo \cdot 2H_2O$: C, 39.6; H, 1.9; N, 19.8; Mo, 22.6; H_2O, 8.5; M.W., 424; Found: C, 39.5; H, 1.7; N, 19.5; Mo, 22.4; H_2O, 9.0%. M.W. (CH_3CN, osmometric) 400; Yield 0.35 g (40%). I.r.: 1665(s), 1780(s), $\nu(NO)$; 2150(sh), 2130(s), $\nu(CN)$; 620(w), $\nu(MoN^{NO})$; 400(w), $\nu(MoN^{phen})$ and 350(w), $\nu(MoC)$ cm^{-1}. ν_{max}, 23000 cm^{-1} (2960).

Results and Discussion

The key step in the generation of the $\{Mo(NO)_2\}^{2+}$ moiety is to render the reaction mixture containing $]MoO_4]^{2-}$, OH^-, CN^- and an excess of $NH_2OH \cdot HCl$ slightly acidic (pH ~5) after a short preheating at pH ~8. The analogous reaction using NCS^- in this pH is extremely pH sensitive and various nitrosyl species can be generated depending on the actual pH of the reaction medium(5). The complex $[Mo(NO)_2(CN)_4]^{2-}$ was, however, alleged to be obtained by the treatment of $[MoCl_2(NO)_2(py)_2]$ with KCN/MeOH, but no details regarding the preparation and characterization were reported(7). The phen compound is a non-electrolyte and monomeric in acetonitrile while the tetraphenylphosphonium salt, as expected, behaves as a 2 : 1 electrolyte (Λ_M = 232 ohm^{-1} cm^2 $mole^{-1}$) in the same solvent(8). The *cis*-dinitrosyl compounds as expected have two $\nu(NO)$ bands in the i.r. Accepting the NO^+ formalism, the oxidation state of Mo in these $\{Mo(NO)\}^6$ moieties be zero, which is further confirmed by the diamagnetism of the isolated compounds. If the symmetry species of the molecules are approximated as C_{2v}, then their M.O. configuration may be $(a_2)^2$ $(a_1)^2$ $(b_2)^2$ and accordingly three electronic transitions ($b_2 \rightarrow a_1$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow b_2$) should be observed(9). However, only the very intense(5) $b_2 \rightarrow b_1$ transition is observed in both cases. Others are possibly concealed by absorptions due to the organic moieties. The lattice water molecules are rather strongly held and the TGA and DTA curves indicate that they are lost stepwise, one at

---

* Author to whom all correspondence should be addressed.

0340–4285/83/0408–0255$02.50/0

90 °C and the other at 120 °C. These are possibly strongly hydrogen bonded to the NO^+ and CN^- ligands, as structurally characterised in some other cyanonitrosyl species(10, 11).

Acknowledgements

Our grateful thanks are due to the U.G.C., New Delhi, for financial support for the project and to the Alexander Von Humboldt Foundation for the donation of the i.r. spectrophotometer used in this work. AMS thanks the U.G.C. for a research Fellowship.

References

(1) R. G. Bhattacharyya and A. M. Saha, *Inorg. Chim. Acta, in press.* – (2) W. Hieber, R. Nast and G. Gehring, *Z. Anorg. Allg. Chem., 256,* 169 (1948). – (3) K. G. Caulton, *Coord. Chem. Rev., 14,* 317 (1975) and refs. cited therein. – (4) S. Sarkar and P. Subramaniam, *Inorg. Chim. Acta, 35,* L357 (1979). – (5) R. G. Bhattacharyya and G. P. Bhattacharjee, *J. Chem. Soc., Dalton Trans.,* (in press). – (6) D. D. Perin, W. L. F. Armarego and D. R. Perin, *Purification of Laboratory Chemicals,* Pergamon Press, New York (1966). – (7) S. Sarkar and P. Subramaniam, *J. Inorg. Nucl. Chem., 43,* 202 (1981). – (8) W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971). – (9) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev., 13,* 339 (1974). – (10) A. Tullberg and N. Vannerberg, *Acta. Chem. Scand., 21,* 1462 (1967).

(11) S. Jagner and N. Vannerberg, *Acta. Chem. Scand., 22,* 3330 (1968).

(Received March 7th, 1983) TMC 936(C)

– Printed in the Federal Republic of Germany by Schwetzinger Verlagsdruckerei GmbH, D-6830 Schwetzingen. Subscription Price: Volume *8* (1983) DM 478.– (plus postage); Single copies: DM 95,–; Editor-in-Chief: Dr. D. R. M. Walton, Univ. of Sussex, School of Molecular Sciences, Brighton BN1 9QJ, England; Advertising Manager: R. J. Roth, D-6940 Weinheim; Published by Verlag Chemie GmbH, (Managing Directors: Prof. Dr. Helmut Grünewald and Hans Dirk Köhler), Pappelallee 3, P. O. Box 1260/1280, D-6940 Weinheim, Federal Republic of Germany. Telephone Weinheim (06201) 602-0; Telex 465516 vchwh d; Telefax (06201) 602328.
Transition Metal Chemistry does not publish book reviews; books submitted for review will not be returned.