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The correct formulation of the sulfur transfer reagent benzyltriethylammonium tetracosathioheptamolybdate ☆

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Dedicated to Dr. J. K. Kirtany on the occasion of his 60th birthday

Abstract—The recently reported sulfur transfer reagent benzyltriethylammonium tetracosathioheptamolybdate $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$ [*Tetrahedron Lett.* **2003**, *44*, 887] is correctly formulated as benzyltriethylammonium tetrathiomolybdate $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$. The correct formulation explains the unusual sulfur transfer properties of $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$ observed in the earlier work.

The use of Mo–S complexes like diammonium bis(μ-disulfido)tetrakis(disulfido)dimolybdate(V) $(NH_4)_2[Mo_2S_{12}]$,[1] piperidinium tetrathiomolybdate[2] $(C_5H_{12}N)_2[MoS_4]$, benzyltriethylammonium tetrathiomolybdate $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$,[3,4] and ammonium tetrathiomolybdate[5,6] $(NH_4)_2[MoS_4]$ as sulfur transfer reagents in organic syntheses for the preparation of organo-sulfur compounds, has added an extra dimension to the known chemistry of Mo–S compounds. All the above mentioned compounds have been reported to convert alkyl halides to the corresponding disulfides. Chandrasekaran and co-workers[7] have pioneered the use of $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$ in organic syntheses and have demonstrated this complex to be a versatile sulfur transfer reagent for the convenient synthesis of a variety of organo sulfur compounds under mild reaction conditions. In a recent paper, Kaushik and co-workers[8] have reported that benzyltriethylammonium tetracosathioheptamolybdate $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$ is a superior sulfur transfer agent for the synthesis of disulfides, as compared to the tetrathiomolybdate reagents reported earlier. However, the preparation of the sulfur transfer reagent $[Mo_7S_{24}]^{6-}$ mentioned therein, appears very unlikely under the reported reaction conditions, in view of the known stability of tetrahedral $[MoS_4]^{2-}$ anions in alkaline media.[9] The existence of oxochromates, oxo or thiomolybdates, oxo and thiotungstates as the tetrahedral $[MX_4]^{2-}$ ($M = Cr$ and $X = O$; $M = Mo$ or W and $X = O$ or S) compounds in alkaline media is well documented.[9,10] In our recent work, we have isolated and structurally characterised tetrahedral organic diammonium salts of oxochromates,[11,12] tetrathiomolybdates[13] and tetrathiotungstates[14] from alkaline media.

When MoO_3 is dissolved in aqueous alkali or amine the resulting solution contains tetrahedral $[MoO_4]^{2-}$ ions and simple or normal molybdates can be crystallised from this solution.[10,15] If this solution is made strongly acidic a precipitate of yellow molybdic acid $MoO_3{\cdot}2H_2O$ is obtained. At pH values between these two extremes, however, polymeric anions (polyoxometalates) made up almost invariably of MoO_6 octahedra are formed and their salts can be crystallised. The first major polyanion formed when the pH of an aqueous molybdate solution is acidified to a pH below 6 is the heptamolybdate[16] $[Mo_7O_{24}]^{6-}$, which is made up of MoO_6 octahedra exclusively in which all the metals are in the +6 state as shown below.[10]

$$7[MoO_4]^{2-} + 8H^+ \rightarrow [Mo_7O_{24}]^{6-} + 4H_2O$$

When aqueous ammonia is added to a solution of heptamolybdate, the reverse reaction takes place and the $[Mo_7O_{24}]^{6-}$ is converted to the simple tetrahedral $[MoO_4]^{2-}$.

Keywords: Tetracosathioheptamolybdate; Tetrathiomolybdate; Sulfur transfer reagent; Correct formulation.

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Mo–S compounds behave similarly. Thus the tetrahedral $(NH_4)_2[MoS_4]$ complex is isolated from aqueous ammonia solutions.[17] Acidification of $[MoS_4]^{2-}$ results in the formation of the insoluble MoS_3 as the ultimate product.[18,19] Condensation of the $[MoS_4]^{2-}$ units to form complexes like $[Mo_2OS_7]^{2-}$, $[Mo_2O_2S_9]^{2-}$, $[Mo_2S_{11}]^{2-}$ etc. has been described under controlled acidification conditions.[20,21] It is pertinent to note that no di-, tri- or polynuclear Mo–S complexes other than $[Mo_2S_{11}]^{2-}$ and $[Mo_2O_2S_9]^{2-}$ are reported in the literature[22] in which all the Mo atoms retain their +6 oxidation state. The formation of $[Mo_2S_7]^{2-}$ species[23] (the Mo–S analogue of dichromate) has been shown to be a key intermediate in the acidification of $[MoS_4]^{2-}$. Based on the above considerations, it is expected that the product formed by passing H_2S gas into an ammoniacal solution of heptamolybdate, which essentially contains tetrahedral $[MoO_4]^{2-}$ ions, should be the tetrahedral complex $(NH_4)_2[MoS_4]$ **III** and not the heptanuclear complex $(NH_4)_6[Mo_7S_{24}]$ hereinafter referred to as compound **I**. In addition, the reported[8] electronic spectral data in DMF (268, 323 and 477 nm) of the complex $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$ hereinafter referred to as compound **II** are in good agreement with those (274, 320 and 472 nm) of the previously reported[3] $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$ **IV** in the same solvent. Hence we have reinvestigated the earlier work[8] and the results are presented here.

Compound **I** was prepared[†] by passing H_2S gas into an ammoniacal solution of heptamolybdate for 5 h as described.[8] The pH of the reaction mixture (10.1) was then found to be alkaline. Compound **II** was prepared by the cation exchange method as described.[8] $(NH_4)_2[MoS_4]$ **III**[17] was prepared by passing H_2S gas into an ammoniacal solution of heptamolybdate for 30 min while $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$ **IV** was prepared by the literature procedure.[4] The IR and UV–vis spectra of **I** are identical[24] with those of ammonium tetrathiomolybdate **III**. If complex **I** is the $(NH_4)_6[Mo_7S_{24}]$ complex as claimed, then its IR spectrum should have been different from that of **III**, which is not observed. Both compounds exhibited identical Mo–S stretching vibrations at 478 cm^{-1}. Furthermore the ammonium content of **I** (13.84%) corresponds to the formula of **III** (expected 13.87%) and not **I** (expected 6.98%) clearly indicating that compound **I** is ammonium tetrathiomolybdate **III**. These observations reinforce our earlier prediction that no $[Mo_7S_{24}]^{6-}$ complex can be isolated from an alkaline medium. The IR and UV–vis spectra of **II** are identical[25] with those of **IV** and both have the same melting point. DSC data add credence to the melting points. The elemental analysis of compound **II** as well as the MoO_3 residue formed on heating in air correspond to the formulation of **IV** and not **II**. The UV–vis spectra of all the four compounds **I**–**IV** exhibit characteristic charge transfer bands of the $[MoS_4]^{2-}$ moiety as reported.[9,17] The identical nature of all the spectra indicates that the chromophore present in **I** to **IV** is one and the same. It seems that the authors have formulated compounds **I** and **II** as heptanuclear complexes based on mp, UV–vis data and an incorrect assumption that the $(NH_4)_6[Mo_7S_{24}]$ **I** complex can be isolated by passing H_2S for extended periods into heptamolybdate. It is to be noted that no analytical data were reported in the earlier work[8] for the S-transfer reagents.

In the earlier work it was reported that complex **II** is a superior S-transfer reagent as 1.8 mol of **II** can convert 10 mol of alkyl halide to disulfide unlike compound **IV**, which reacts with alkyl halide in an equimolar ratio. The correct formulation of **II** as **IV** by us in this work can also clarify the earlier observed S-transfer characteristics. 1.8 mol of **II** (mol wt 2595.42) actually correspond to 7.67 mol of **IV** (mol wt 608.94). To prove conclusively that **II** is nothing but **IV** we have investigated the reaction of benzyl bromide in $CHCl_3$ with the S-transfer reagent **IV** in a 1:0.8 mole ratio as described earlier.[3] The same amount by weight of **II** was reacted with benzyl bromide under identical conditions. In both the cases, the yield (~75%) of dibenzyl disulfide was nearly the same. This reaction proves conclusively that the complex $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$ **II** described earlier[8] is the well-known S-transfer reagent benzyltriethylammonium tetrathiomolybdate **IV**.

In summary, we have shown that no $(NH_4)_6[Mo_7S_{24}]$ complex but only $(NH_4)_2[MoS_4]$ can be isolated from an alkaline medium, as predicted. The method described earlier[8] for the preparation of the S-transfer reagent involves the passing of H_2S gas for 5 h instead of 30 min. The recently reported benzyltriethylammonium tetracosathioheptamolybdate **II** is the well-known complex benzyltriethylammonium tetrathiomolybdate **IV**. The conversion of alkyl halides to disulfides using **IV** as a S-transfer reagent is a well-known reaction.[3] The use of **IV** as a versatile S-transfer reagent in organic syntheses has been recently reviewed.[7]

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References and notes

1. MacDonald, J. G.; Harpp, D. N. *Tetrahedron Lett.* **1984**, *25*, 703–706.
2. Dhar, P.; Chandrasekaran, S. *J. Org. Chem.* **1989**, *54*, 2998–3000.

[†] See Supplementary material.

3. Ramesha, A. R.; Chandrasekaran, S. *Synth. Commun.* **1992**, *22*, 3277–3284.
4. Sinha, S.; Ilankumaran, P.; Chandrasekaran, S. *Tetrahedron* **1999**, *65*, 14769–14776.
5. Ilankumaran, P.; Prabhu, K. R.; Chandrasekaran, S. *Synth. Commun.* **1997**, *27*, 4031–4034.
6. Devan, N.; Sureshkumar, D.; Beadham, I.; Prabhu, K. R.; Chandrasekaran, S. *Indian J. Chem.* **2002**, *41B*, 2112–2115.
7. Prabhu, K. R.; Devan, N.; Chandrasekaran, S. *Synlett* **2002**, 1762–1778, and references therein.
8. Polshettiwar, V.; Nivsarkar, M.; Acharya, J.; Kaushik, M. P. *Tetrahedron Lett.* **2003**, *44*, 887–889.
9. Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955.
10. Greenwood, N. N.; Earnshaw, A. *Chemistry of The Elements*. 1st ed.; Pergamon: Oxford, 1984; pp 1171–1183.
11. Srinivasan, B. R.; Näther, C.; Bensch, W. *Acta Crystallogr.* **2003**, *59E*, m639–m641.
12. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. *Indian J. Chem.* **2003**, *42A*, 2735–2741.
13. Srinivasan, B. R.; Vernekar, B. K.; Nagarajan, K. *Indian J. Chem.* **2001**, *40A*, 563–567.
14. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. *Acta Crystallogr.* **2002**, *58E*, m622–m624; *Acta Crystallogr.* **2003**, *59C*, m124–m127; *Acta Crystallogr.* **2003**, *59E*, m681–m683.
15. Bensch, W.; Hug, P.; Emmenegger, R.; Reller, A.; Oswald, H. R. *Mater. Res. Bull.* **1987**, *22*, 447–454.
16. The pH of a 5% aqueous solution of heptamolybdate is 5.0 to 5.5:*Merck Index*. 9th ed.; Merck: Rahway, NJ, USA, 1976; pp 73–74.
17. MacDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205–210.
18. Svehla, G. *Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis*. 5th ed.; Orient Longman: New Delhi, 1982; pp 512–513.
19. Wang, H. W.; Skeldon, P. W.; Thompson, G. E.; Wood, G. C. *J. Mater. Sci.* **1997**, *32*, 497–502.
20. Xin, X.; Morris, N. L.; Jameson, G. B.; Pope, M. T. *Inorg. Chem.* **1985**, *24*, 3482–3485.
21. Chandrasekaran, J.; Ansari, M. A.; Sarkar, S. *Inorg. Chem.* **1988**, *27*, 3663–3665.
22. Coucouvanis, D. *Adv. Inorg. Chem.* **1998**, *45*, 1–73.
23. Saxena, R. S.; Jain, M. C.; Mittal, M. L. *Aust. J. Chem.* **1968**, *21*, 91–96.
24. Compound **I**: IR (KBr): 3100, 1381, 478 ($v_{(\mathrm{Mo–S})}$) cm^{-1}; UV–vis (dil NH_4OH): λ_{max} in nm ($\varepsilon_{\mathrm{max}}$) 469 (10,060), 317 (13,700), 242 (20,400). Anal. Found (Calcd) for $(NH_4)_6[Mo_7S_{24}]$: (NH_4) 13.84 (6.98), Mo 36.70 (43.34) S 49.08 (49.68)%. Compound **III**: IR (KBr): 3100, 1381, 478 ($v_{(\mathrm{Mo–S})}$) cm^{-1} ; UV–vis (dil NH_4OH): λ_{max} in nm ($\varepsilon_{\mathrm{max}}$) 469 (11,160), 317 (15,050), 242 (22,990). Anal. Found (Calcd) for $(NH_4)_2[MoS_4]$: (NH_4) 13.85 (13.87), Mo 36.70 (36.85) S 49.11 (49.28)%.
25. Compound **II**: IR (KBr): 3036, 2969, 1508, 1473, 1450, 1392, 1373, 1153, 1010, 941, 788, 750, 704, 468 ($v_{(\mathrm{Mo–S})}$) cm^{-1}. UV–vis (dil NH_4OH): λ_{max} in nm ($\varepsilon_{\mathrm{max}}$) 469 (10,560), 317 (14,340), 242 (20,970). Anal. Found (Calcd) for $C_{78}H_{132}N_{12}Mo_7S_{24}$: C, 51.06 (36.09); H, 7.29 (5.14); N 4.60 (3.24); S 20.92 (29.66); Mo 15.64 (25.87) MoO_3 residue 22.5 (38.76)%. Mp 130 °C (dec). DSC onset temperature 133 °C. Compound **IV**: IR (KBr): 3036, 2969, 1508, 1473, 1450, 1392, 1373, 1153, 1010, 941, 788, 750, 704, 468 ($v_{(\mathrm{Mo–S})}$) cm^{-1}. UV–vis (dil NH_4OH): λ_{max} in nm ($\varepsilon_{\mathrm{max}}$) 468 (9920), 317 (13,450), 242 (19,720). Anal. Found (Calcd) for $C_{26}H_{44}N_2MoS_4$: C, 51.08 (51.28) H, 7.27 (7.30) N 4.58 (4.60) S 20.95 (21.06), Mo 15.67 (15.75) MoO_3 residue 22.23 (23.64) %. Mp 130 °C (dec). DSC onset temperature 130 °C.