Niobium(V) and Tantalum(V) Hexaisothiocyanates

Sir:

Thiocyanato complexes of molybdenum and tungsten, *e.g.*, $\mathrm{Mo(NCS)_6}^{3-}$[1] and $\mathrm{W(NCS)_6\cdot 2(CH_3)_2CO}$,[2] are well known. However, conspicuous by their absence among the known thiocyanates are those of other elements in the first half of the second and third transition series. Furthermore, molybdenum and tungsten appear to form isothiocyanato complexes (N-bonded) while the elements of the latter half of the second and third transition series tend to form thiocyanates (S-bonded). For this reason it was of interest to examine other elements in the vicinity of molybdenum and tungsten in order to further ascertain that the formation of isothiocyanato rather than thiocyanato complexes is preferred. We wish to report the preparation of thiocyanato complexes of niobium and tantalum which appear to be N-bonded.

Because of the high affinity of niobium and tantalum for oxygen, the isothiocyanato complexes of these elements cannot be obtained from aqueous solution by the usual laboratory methods. Therefore, the compounds $\mathrm{KNb(NCS)_6}$ and $\mathrm{KTa(NCS)_6}$ were prepared according to reactions 1 and 2 by extraction of the

$$\mathrm{MCl_5 + CH_3CN \longrightarrow MCl_5\cdot CH_3CN\ (M = Nb, Ta)} \tag{1}$$

$$\mathrm{MCl_5\cdot CH_3CN + 6KCNS \longrightarrow KM(NCS)_6(CH_3CN)_{\mathit{x}} + 5KCl} \tag{2}$$

respective transition metal pentachloride with acetonitrile into a solution containing a stoichiometric quantity of potassium thiocyanate in acetonitrile using apparatus and techniques similar to those previously described.[3] The resulting metal complexes were highly soluble in acetonitrile and were removed from the insoluble potassium chloride formed during the course of the reaction by filtration. Complete removal of acetonitrile from the product was achieved by heating the compounds *in vacuo* at 80° for 24–36 hr. The compounds were slightly soluble in 1,2-dichloroethane and were further purified by extraction and recrystallization from this solvent. Chemical analyses[4] of the products indicated the formation of the potassium salts of the hexaisothiocyanates of niobium and tantalum. *Anal.* Calcd for $\mathrm{KNb(NCS)_6}$: K, 8.1; Nb, 19.3; S, 40.0; C, 15.0; N, 17.5. Found: K, 8.4; Nb, 19.1; S, 39.8; C, 15.1; N, 17.3; color, deep blue. Calcd for $\mathrm{KTa(NCS)_6}$: K, 6.9; Ta, 31.8; S, 33.8; C, 12.7; N, 14.8. Found: K, 7.2; Ta, 32.1; S, 33.6; C, 12.5; N, 14.6; color, orange. In a similar fashion the pentabromides and pentaiodides of niobium and tantalum react with KCNS to yield the hexaisothiocyanates. This is less convenient, however, because of the slower rate of extraction of these halides with acetonitrile. The method of preparation outlined above appears to be a rather unique way of preparing thiocyanate complexes of various elements in different oxidation states. Thus we have also prepared $\mathrm{K_2Nb(NCS)_6}$ and $\mathrm{K_2Mo(NCS)_6}$ starting with the respective tetrachlorides. By appropriate use of different solvents one may also carry out reactions with halides such as $\mathrm{MoCl_5}$ and $\mathrm{WCl_5}$ which are not stable in acetonitrile. These reactions are presently under investigation and the results will be reported at a later date.

As in the case of the hexahalo complexes,[5] the hexaisothiocyanates of niobium and tantalum are not stable in water. The potassium salts undergo hydrolysis with the evolution of $\mathrm{H_2S}$ to oxo and hydroxo species within a matter of minutes, and complete conversion to the oxide is observed after about 1 hr. Similar observations are obtained with alcohols and other oxygen-containing solvents. The solubility of these compounds without reaction in acetonitrile has allowed us to prepare analogous compounds containing different cations such as tetraphenylarsonium and tetrabutylammonium. Again taking advantage of the low solubility of potassium chloride in acetonitrile, the potassium hexaisothiocyanatoniobate(V) and potassium hexaisothiocyanatotantalate(V) compounds were added to acetonitrile solutions of tetraphenylarsonium chloride and tetrabutylammonium chloride, respectively, the KCl being removed by filtration. Analysis of the resulting compounds verified the formation of the tetraphenylarsonium and tetrabutylammonium salts.

The X-ray diffraction powder patterns of the potassium salts show them to be isomorphous. Conductivity studies in acetonitrile and 1,2-dichloroethane show the presence of 1:1 electrolytes, thus indicating monomeric structures. These conclusions are further substantiated by the infrared data presented below.

Table I. Thiocyanate Infrared Frequencies ($\mathrm{cm^{-1}}$)

Complex	Medium[a]	ν(C≡N)	ν-(C—S)	δ(N≡C—S)
$\mathrm{KNb(NCS)_6}$	B	2027 w, 1981 vs	...[b]	511 m
$\mathrm{[(C_6H_5)_4As]Nb(NCS)_6}$	A	1954 vs, 1911 w	922 m	...[c]
$\mathrm{[(C_6H_5)_4As]Nb(NCS)_6}$	C	1984 vs, 1929 w	...[b]	506 m
$\mathrm{KTa(NCS)_6}$	B	2058 w, 1994 vs	...[b]	508 m
$\mathrm{[(C_6H_5)_4As]Ta(NCS)_6}$	A	1981 vs, 1922 m	929 m	...[c]
$\mathrm{[(C_6H_5)_4As]Ta(NCS)_6}$	C	1987 vs, 1945 sh	...[b]	506 m

[a] A = Nujol mull; B = acetonitrile; C = 1,2-dichloroethane. [b] Obscured by cation or solvent absorptions. [c] Not examined in this region.

The infrared spectra of the complex anions $\mathrm{Nb(NCS)_6^-}$ and $\mathrm{Ta(NCS)_6^-}$ (Table I) indicate the presence of N-bonded thiocyanates. The C≡N stretching,[6] C—S stretching,[1] and N≡C—S bending[7] vibrations at 2150–2050, 880–690, and 500–400 $\mathrm{cm^{-1}}$, respectively, have been used to differentiate between thiocyanato and isothiocyanato complexes. It has been shown that a change from a C≡N bond to one having more double-bond character will result in a corresponding increase in the double-bond character of the C—S bond.[1] Thus, for an N-bonded complex, an increase in the covalent character of the coordinate bond results in a decrease of the C≡N stretching frequency and an increase of both the C—S stretching and N≡C—S bending frequencies from those observed for the free thiocyanate ion. Furthermore, this type of bonding suggested for

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(1) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(2) H. Funk and H. Böhland, *Z. Anorg. Allgem. Chem.*, 324, 168 (1963).

(3) T. M. Brown and B. Ruble, *Inorg. Chem.*, 6, 1335 (1967).

(4) The C, N, and S analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The metal was determined by conversion to the oxide. K was determined with sodium tetraphenylborate (III).

(5) T. S. Shemyakina, E. K. Smirnova, T. I. Popova, and V. M. Kuptsova, *Zh. Neorgan. Khim.*, 10, 2387 (1964).

(6) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(7) A. Sabatini and I. Bertini, *Inorg. Chem.*, 4, 959, 1665 (1965).

the thiocyanate ligand allows for the M–N–C bond to be angular rather than linear. This feature would explain the presence of more than one absorption band in the C≡N region of the niobium and tantalum complexes. The infrared data imply that the C≡N and C—S bonds are weaker and stronger, respectively, than those observed in any previously reported thiocyanato complex. A preliminary examination of the niobium(IV) complex, $[(C_6H_5)_4As]_2Nb(NCS)_6$, has shown the C≡N stretching absorption to occur at 2030 cm^{-1}. This leads us to believe that the bonding in the thiocyanate ligand is dependent upon the oxidation state of the central atom, especially for those elements containing few if any available d electrons. In order to examine the effect of oxidation state on the C≡N and C—S bonds in isothiocyanato complexes, we are presently preparing and studying similar complexes with molybdenum and tungsten, as these elements are capable of exhibiting an even wider range of oxidation states.[8]

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T. M. Brown, G. F. Knox
Department of Chemistry, Arizona State University
Tempe, Arizona 85281
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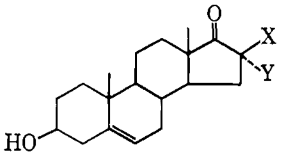
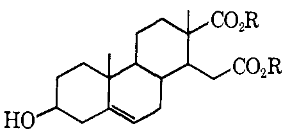
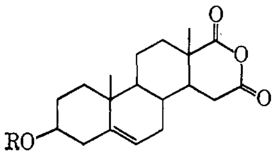
On the Mechanism of Oxidation of Enolizable Nonmethyl Ketones by Base and Iodine. The Role of Atmospheric Oxygen

Sir:

In contrast to the well-studied iodoform reaction of methyl ketones,[1] the reaction of enolizable nonmethyl ketones with alkaline solutions of iodine has received little attention. Cullis and Hashmi[2] subjected 3-pentanone and 3-heptanone to these conditions and isolated a mixture of acids, but only a small amount of organically bound iodine was found among the products. Similarly, cyclic ketones have yielded dibasic acids on treatment with alkaline solutions of iodine.[3]


1a, X = Y = H
b, X = H; Y = I
c, X = Y = I

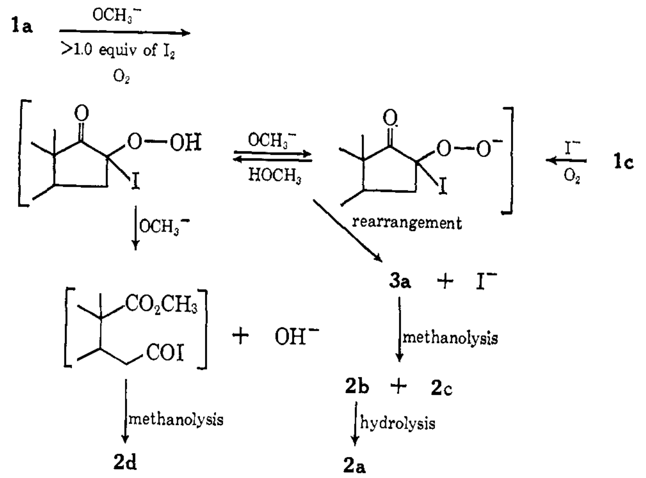

2a, R = R¹ = H
b, R = H; R¹ = CH₃
c, R = CH₃; R¹ = H
d, R = R¹ = CH₃


3a, R = H
b, R = Ac

For example, in aqueous methanol 5-androsten-3β-ol-17-one (**1a**) has been reported[3a,e-g] to yield varying amounts of **2a–d** depending on the reaction conditions and method of work-up.

The present work shows that, in methanolic iodine and base, oxidation of **1a** proceeds *via* a novel mechanism requiring the incorporation of molecular oxygen. Furthermore, the accumulated data on stoichiometry, detectable intermediates, and observed products define a probable reaction pathway, as shown in Chart I.

Chart I



The participation of molecular oxygen is demonstrated by the contrasting results obtained on reaction of **1a** in nitrogen-purged and air-saturated solutions. Thus, treating methanolic sodium methoxide (or methanolic potassium hydroxide) solutions of **1a** at 0° *under nitrogen* with 1 equiv of iodine gives the monoiodo ketone **1b** in 58% yield; mp 142–143° dec; $[\alpha]^{24}\text{D}$ +17° ($CHCl_3$) (*Anal.* Calcd for $C_{19}H_{27}O_2I$: I, 30.63. Found: I, 30.32);[4] carbonyl band in the infrared ($CHCl_3$) at 1741 cm^{-1}; ultraviolet ($CHCl_3$) λ_{max} 285 mμ (ϵ 485), λ_{sh} 330 mμ (ϵ 290); nmr peaks ($CDCl_3$) at δ 0.91 (3 H, singlet, C-13 angular methyl) and 4.86 (1 H, multiplet, C-16 β proton).[5,6] Similar treatment of **1a** with 2 equiv of iodine under nitrogen yields the diiodo ketone **1c** (85%) which crystallizes from the solution as pale yellow needles; mp 131–133° dec; $[\alpha]^{24}\text{D}$ −11° ($CHCl_3$) (*Anal.* Calcd for $C_{19}H_{26}O_2I_2$: I, 47.00. Found: I, 46.78); carbonyl band in the infrared ($CHCl_3$) at 1741 cm^{-1}; ultraviolet ($CHCl_3$) λ_{max} 305 mμ (ϵ 1470); nmr peak ($CDCl_3$) at δ 1.13 (3 H, singlet, C-13 angular methyl). Both **1b** and **1c** are stable for several hours under these reaction conditions. However, rapid and complete oxidation of **1a** occurs in *air-saturated* solutions using only 1.25 equiv of iodine. Moreover, a suspension of **1c**, prepared *in situ* under nitrogen, rapidly (10–15 min) produces a reddish brown solution (due to liberated iodine as I_3^-) after saturation with air giving **2a–d** in over 90% yield. Quantitative measure-

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(1) For the most recent review see M. H. Hashmi, *Pakistan J. Sci.*, **10**, 159 (1958).

(2) C. F. Cullis and M. H. Hashmi, *J. Chem. Soc.*, 1548 (1957).

(3) (a) A. Wettstein, H. Fritzsche, F. Hunziker, and K. Miescher, *Helv. Chim. Acta*, **24**, 332 E (1941); (b) C. Djerassi, H. Bendas, and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955); (c) J. Heer and K. Miescher, *Helv. Chim. Acta*, **28**, 156 (1945); (d) J. Heer, J. R. Billeter, and K. Miescher, *ibid.*, **28**, 991 (1945); (e) J. Heer and K. Miescher, *ibid.*, **30**, 786 (1947); (f) C. von Seemann and G. A. Grant, *J. Am. Chem. Soc.*, **72**, 4073 (1950); (g) E. B. Hershberg, E. Schwenk, and E. Stahl, *Arch. Biochem.*, **19**, 300 (1948); (h) L. Mamlok, A. Horeau, and J. Jacques, *Bull. Soc. Chim. France*, 2359 (1965).

(4) Satisfactory carbon and hydrogen analyses were obtained for all new compounds.

(5) The chemical shifts are downfield from TMS as internal standard.

(6) The assignment of the 16α-iodo configuration is based on the ultraviolet and pmr spectral data by analogy with the work of R. E. Counsell and G. W. Adelstein, *J. Pharm. Sci.*, **55**, 947 (1966).