Coordination Chemistry Reviews 266–267 (2014) 2–15

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Progress in molecular uranium-nitride chemistry

David M. King, Stephen T. Liddle*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Contents

ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 19 June 2013
Accepted 19 June 2013
Available online 29 June 2013

Keywords:
Uranium, nitride
Matrix isolation
Organometallic chemistry

ABSTRACT

The coordination, organometallic, and materials chemistry of uranium nitride has long been an important facet of actinide chemistry. Following matrix isolation experiments and computational characterisation, molecular, solution-based uranium chemistry has developed significantly in the last decade or so culminating most recently in the isolation of the first examples of long-sought terminal uranium nitride linkages. Herein, the field is reviewed with an emphasis on well-defined molecular species.

1. Introduction

Investigations into the chemical bonding and reactivity of actinide elements are vital for developing future nuclear applications, ameliorating existing legacy waste issues, as well as furthering our fundamental understanding of the f block elements [1]. In the past two decades, non-aqueous uranium chemistry has undergone a rapid expansion [2–4], in particular multiple bonds concerning U=O [5–14], U=N [6,9,15–41], and U=E (E = S, Se, Te) [12,42] have been investigated with great interest. Furthermore, recent developments into U=C multiple bonds means they now represent a burgeoning field of research [17,43–57]. However, due to the prominent paucity of reports of formal U≡N triple bonds in uranium nitrides significant attention focussed on the isolation of a terminal uranium-nitride linkage in order to address the lack of knowledge of its intrinsic physicochemical properties.

Uranium mononitride has long been considered a suitable material for Generation IV fast spectrum nuclear reactors such as the gas-cooled, lead-cooled and sodium-cooled fast reactors as well as new concepts for light-water reactors [58,59]. Binary UN is regarded a superior candidate over uranium oxide fuels due to its higher melting point (~2850 °C), higher thermal conductivity and advantageously increased density (14.32 g cm^{-3}) [60].

Uranium nitride exists in three stoichiometric ratios: UN, U_2N_3 and UN_2. U_2N_3 can be synthesised from uranium metal and N_2 at 850 °C, and subsequent decomposition to binary UN is achieved *via* further heating to 1150 °C [61]. A number of techniques have been developed to produce uranium nitride from UO_2. The most common of these is carbothermic reduction, which despite extensive research still requires expensive infrastructure and, due to relatively high carbon and oxygen content, often results in contamination by impurities [62–66]. Alternatively, sol–gel methods

* Corresponding author. Tel.: +44 1158467167.
E-mail address: stephen.liddle@nottingham.ac.uk (S.T. Liddle).

0010-8545/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ccr.2013.06.013

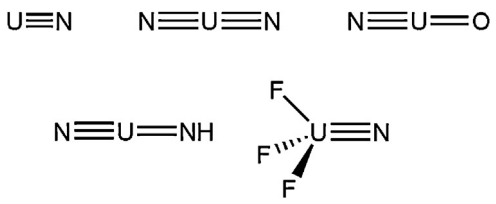

Fig. 1. Spectroscopically studied molecular nitrides.

have been utilised to synthesise UN. There have also been reports of these two techniques being applied in conjunction [59]. Less energetically demanding routes have been proposed by reacting UC or UF_4 with ammonia, however synthetic routes utilising UO_2 or uranium metal are more feasible on industrial scales due to the extent by which they are available, both commercially and naturally [67–69]. A relatively economical technique compared to carbothemic reduction has been developed, where UN is synthesised *via* ball-milling of uranium metal with N_2 to afford high purity UN [58]. However, despite the research conducted in this area the synthesis of UN and study of the bonding and reactivity of the U≡N fragment remains largely unexplored. As a result, significant attention has been focussed on utilising molecular precursors and matrix isolation experiments to probe the nature of uranium nitrides.

2. Spectroscopic isolation of uranium nitrides

2.1. UN and NUN

In 1976 Green and Reedy first observed UN as part of an argon matrix isolation infra-red (IR) study (Fig. 1). At 14 K uranium atoms were produced by a hollow cathode sputtering device with argon (Ar) which was subsequently exposed to low concentrations of N_2 (0.05% in Ar) or NO_2. Upon annealing, an absorbance at 1001 cm^{-1} was observed which was attributed to UN. In addition, a tentative assignment of 1051 cm^{-1} was given to the ν_3 absorption of NUN [70]. In 1993 Andrews et al. examined the reactivity of laser ablated uranium atoms with molecular nitrogen in an Ar matrix at 12 K. The only product formed was determined to be linear NUN which was characterised through ν_3 absorption at 1051 cm^{-1} and this was confirmed by isotopic labelling which supported the previous observation by Green. Although IR inactive ν_1 modes are predicted to arise at 1008 cm^{-1}, the absence of such bands suggests linearity within these species. The NUN molecule is synthesised through uranium atom insertion into a single N_2 molecule and the reaction is enhanced by UV (ultraviolet) photolysis which helps overcome the activation energy for reaction. At high N_2 concentrations the nitrogen complexes UN_2—N_2 and UN_2—$(N_2)_2$ were identified by ν_3 absorbances at 1041 and 1032 cm^{-1}, respectively [71]. An extension of this work was reported in 1998 identifying two previously unreported uranium nitrides, U(μ-N)$_2$U and NU(μ-N)$_2$U (for IR absorbances see Table 1), which can be detected through laser ablation of uranium in condensing pure N_2 as minor products along with the major product of NUN. Quasirelativistic density functional theory (DFT) calculations revealed predicted ground states for UN and NUN of $^4\Sigma$ and $^1\Sigma_g$, respectively. Bond lengths for UN and NUN of 1.746 and 1.717 Å, respectively, were calculated wherein NUN exhibits a linear geometry in agreement with other theoretical results [72,73]. Viswanathan conducted a similar matrix isolation study and reported that increasing concentrations of N_2 yielded increasing amounts of UN. It was therefore suggested that at high N_2 concentrations new reaction channels are generated through the formation of $N^\bullet$ and N_3 radicals which can react with uranium atoms or NUN to yield UN [74].

Table 1
Experimentally observed IR U≡N absorbances and isotopomer shifts.

Compound	U≡N^{14} (cm^{-1})	U≡N^{15} (cm^{-1})
*U*N	1001	969
U*N*$_2$	1051	1019
U*N*$_2$(N)$_2$	1041	1010
U*N*$_2$(N$_2$)$_2$	1032	1001
U(μ-*N*)$_2$U	670	648
	580	562
*N*U(μ-N)$_2$U	968	938
NU(μ-*N*)$_2$U	844	817
*N*UO	984	953
[*N*UO]$^+$[NO]$^-$	1017	987
*N*UF$_3$	938	–
*N*UNH	967	937
22	955	930
23	936	900
27	914	883
31	856	827

2.2. NUO

In 1997 Andrews and co-workers investigated the reactivity of laser ablated uranium towards NO in argon matrices at 6–7 K, Fig. 1. This reaction predominantly formed the insertion product NUO which exhibits characteristic IR absorption bands at 984 (U—N) and 819 cm^{-1} (U—O). Quasirelativistic DFT calculations supported the assignment and predicted a linear geometry and a $^2\Phi$ electronic ground state. Also characterised in this report is the uranyl analogue $[NUO]^+[NO]^-$ [75]. NUO and $[NUO]^+$ have also been isolated in neon matrices whilst $[NUO]^+$ has been observed in the gas phase through mass spectrometry [76,77]. Collision-induced-dissociation experiments and ligand exchange reactions resulted in the identification of $[NUO]^+$ from the exothermic reaction of UN^+ (generated from $U^+ + NO_2$) with O_2, CO_2 SO_2 and COS. The study also deduced the heat of formation for $[NUO]^+$ to be $\Delta H_f^\circ = 145.6 \pm 29.2$ kcal mol^{-1} and theoretical calculations conducted by Pyykkö and Schwarz predicted the U—N bond distances to be shorter in comparison to the U—O bond lengths [76,78]. NUN and $[NUO]^+$ are isoelectronic analogues of the $[UO_2]^{2+}$ dication and thorough computational studies have been conducted on the species, deducing that the U—N bonding in NUN and $[NUO]^+$ is significantly more covalent than in the U—O bonding exhibited in $[UO_2]^{2+}$ and $[NUO]^+$ [79].

2.3. EUF_3 (E = N or P)

The terminal nitrido and phosphido molecules NUF_3 and PUF_3 have been observed using IR spectroscopy in the reaction of laser-ablated uranium atoms with EF_3 (E = N, P), Fig. 1. The U≡N vibrational absorbance was assigned to a band at 938 cm^{-1}, whilst U≡P was not observable. *Ab initio* studies support the assignment of the IR bands for these species with calculated bond lengths for U≡N and U≡P of 1.76 and 2.40 Å (CASPT2) and effective bond orders of 2.78 and 2.40, respectively. The studies also calculated the U≡N bonding in NUF_3 to be stronger and more covalent (460 kJ mol^{-1}) than the U≡P bonding in P≡UF_3 (176 kJ mol^{-1}) demonstrating that the U 5f orbitals achieve greater orbital overlap to N than P, therefore bonding more effectively with the smaller, harder nitrogen ligand [80].

A further study by Andrews reported the exposure of laser-ablated uranium atoms to N_2 and H_2 in an argon matrix at 5 K. Aside from the formation of NUN and UN, the new uranium(V) nitride imide molecule N≡U=NH was characterised through the identification of one N—H (3350 cm^{-1}), two U—N stretching modes (U≡N = 967 cm^{-1}, U=N = 752 cm^{-1}) and one UNH bending mode (433 cm^{-1}) in the IR spectrum of NUNH [81]. These assignments were fully supported by isotopic labelling studies. It is proposed