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Synthesis, structure, and redox states of homoleptic d-block metal complexes with bis-1,2,4-triazin-3-yl-pyridine and 1,2,4-triazin-3-yl-bipyridine extractants

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Dedicated to Professor Mike Hursthouse on the happy occasion of his 65th birthday.

Abstract

It has been established that triazinyl bipyridines (*hemi*-BTPs) and bis-triazinyl pyridines (BTPs), ligands which are currently being investigated as possible ligands for the separation of actinides from lanthanides in nuclear waste, are able to form homoleptic complexes with first row transition metals such as cobalt(II), copper(II), iron(II), manganese(II), nickel(II) and zinc(II). The metal complexes exhibit six-co-ordinate octahedral structures and redox states largely analogous to those of the related terpyridine complexes. The reactivity of the different redox states of cobalt bis-*hemi*-BTP complex in aqueous environments has been studied with two-phase electrochemistry by immobilisation of the essentially water-insoluble metal complexes on graphite electrodes and the immersion of this modified electrode in an aqueous electrolyte.

It was found that redox potentials for the metal-centred reactions were pH-independent whereas the potentials for the ligand-centred reactions were strongly pH-dependent. The reductive degradation of these complexes has been investigated by computational methods. Solvent extraction experiments have been carried out for a range of metals and these show that cobalt(II) and nickel(II) as well as palladium(II), cadmium(II) and lead(II) were all extracted with the ligands **1e** and **2c** with higher distribution ratios that was observed for americium(III) under the same conditions. The implications of this result for the use of these ligands to separate actinides from nuclear waste are discussed.

Keywords: Redox potentials; Crystal structures; Transition metals; Bis-1,2,4-triazine-3-yl-pyridines

1. Introduction

The aqueous solution (PUREX first cycle raffinate) remaining after the extraction of uranium and plutonium from dissolved used nuclear fuel by the PUREX process is a complex mixture of fission products and corrosion products [1] that also contains the transplutonium actinides, americium and curium. These actinides, together with the residual plutonium, are responsible for the majority of the radiotoxicity that will be present between 300 and 20000 years in the future [2]. If these metals were removed from the PUREX raffinate then the majority of the radiotoxicity will decay during the likely lifetime of a stainless steel drum [3]. After removal from the PUREX raffinate, the actinides could be disposed of separately, or transmutated by nuclear means or employed in medical [4] or industrial applications. The lanthanides have similar properties to the trivalent

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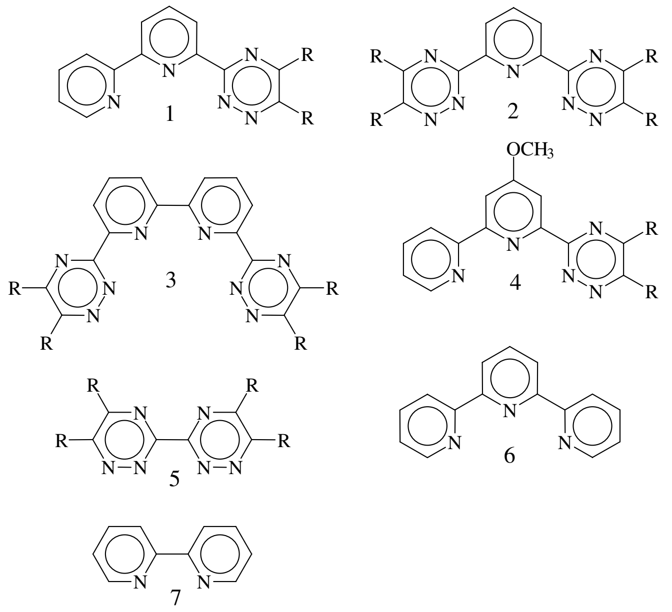

Fig. 1. Key to parent structures. *Hemi*-BTP (**1**), BTP (**2**), BTBP (**3**), methoxy-*hemi*-BTP (**4**), 3,3′-bi-1,2,4-triazinyl (**5**), terpyridine (**6**), 2,2′-bipyridine (**7**). Key to ancillary groups, hydrogen (**a**), methyl (**b**), ethyl (**c**), *n*-propyl (**d**) and *n*-pentyl (**e**).

actinides since they have high neutron cross-sections and they are abundant among the fission products of ^{235}U (the atom yield for the lanthanides is ca. 28%). Recently, we have investigated the lanthanide coordination chemistry of triazinyl pyridines such as the triazinyl bipyridines (*hemi*-BTPs, **1**) [5], the bis-triazinyl pyridines (BTPs, **2**) [6] and the bis-triazinyl bipyridines (BTBPs, **3**) [7]. However, when compared with the oligopyridines, little is known about the coordination chemistry of the 1,2,4-triazines with the first row transition metals [8–10]. It has been shown during an actinide extraction test using tetrapropyl-BTP (**2d**) that much of the iron, ruthenium and palladium present in the acid aqueous feed solution enters the organic phase [11] so that a transition metal could inhibit the extraction of the desired metals by sequestering the extractant. Also the transition metal could enter a product or waste stream where it could cause undesirable reactions such an exothermic reactions during the bituminisation of waste [12]. It is therefore appropriate to carry out a systematic investigation of the first row transition metal coordination chemistry of tridentate triazinyl-pyridines. In this paper, we report the synthesis and the spectroscopic, crystallographic and electrochemical characterisation of a series of transition metal complexes with a variety of 1,2,4-triazinyl pyridine ligands shown in Fig. 1.

2. Experimental

2.1. Synthesis

All organic reagents were purchased from Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich. 6-(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl (diethyl-*hemi*-BTP, **1c**) and 6-(5,6-di methyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl (dimethyl-*hemi*-BTP, **1b**) were prepared as previously described [5] while 6-(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl (dipentyl-*hemi*-BTP, **1e**) was prepared by an analogous procedure. 4-Methoxy-2,2′-bipyridine-*N*-oxide was obtained by the nitration and subsequent methanolysis of 2,2′-bipyridine-*N*-oxide [13]. Oxalodihydrazonic acid diamide was formed by the reaction of dithiooxamide (rubeanic acid) and hydrazine in ethanol (*WARNING*: The reaction forms a large volume of toxic gas [hydrogen sulfide]) [14]. ^{1}H, ^{13}C-{^{1}H} and ^{13}C NMR spectra were recorded using either a Bruker AMX400 or an Avance DPX250 instrument. Chemical shifts are reported in ppm downfield from tetramethylsilane. Magnetic moments were determined in dichloromethane also using the Avance DPX250 by the Evans' NMR method. Carbon, hydrogen and nitrogen microanalysis was performed by Medac Limited.

2.1.1. 2,6-Bis-(5,6-diethyl-[1,2,4]triazin-3-yl)-pyridine (tetramethyl BTP, 2b) [15]

Pyridine-2,6-dihydrazonic acid diamide (3.19 g) was combined with THF (100 mL), triethyl amine (3 mL) and butane-2,3-dione (6 mL) and heated under reflux (3 h). After cooling toluene was added to the reaction flask, and the mixture heated briefly under reflux. After allowing the mixture to cool, the orange solid was isolated by filtration. After washing with ethanol and diethyl ether the solid (2.66 g; 55%) was allowed to dry in air. δ_H 8.81 (2H, d, 7.9 Hz), 8.14 (1H, t, 7.9 Hz), 2.80 (3H, s) and 2.74 (3H, s) ppm.

2.1.2. 2,6-Bis-(5,6-diethyl-[1,2,4]triazin-3-yl)-pyridine (tetraethyl BTP, 2c)

Pyridine-2,6-dihydrazonic acid diamide (5.47 g) was combined with THF (175 mL), triethyl amine (10 mL) and hexane-3,4-dione (10 mL). The resulting mixture was heated under reflux (2 h). After allowing the mixture to cool, the first crop (4.61 g; 47%) was obtained by filtration and washing with a small volume of ethanol. By concentration of the mother liquor a second crop (2.18 g; 22%) was obtained giving an overall yield of 69%. *Anal*. Calc. for $C_{19}H_{23}N_7 \cdot 0.5EtOH$: C, 62.0; H, 6.7; N, 25.3. Found: C, 62.0; H, 6.9; N, 26.7%. δ_H 8.77 (2H, d, 7.9 Hz), 8.12 (1H, t, 7.9Hz), 3.06 (8H, m) and 1.47 (12 H, m). δ_C 163.36 (quat), 161.41 (quat), 161.00 (quat), 154.00 (quat), 138.62, 125.70, 27.67 (CH_2), 26.15 (CH_2), 12.82 and 12.13. MS (CI) 350 $(MH)^+$ and 240 amu. Molecular ion found at 350.2104 amu, $^{12}C_{19}{}^{1}H_{24}{}^{14}N_7$ requires 350.2093 amu (error of 3.2 ppm).

2.1.3. 6-(5,6-Dimethyl-[1,2,4]triazin-3-yl)-4-methoxy-[2,2′]bipyridinyl (dimethyl methoxy hemi BTP, 4b)

To a solution of 4-methoxy-2,2′-bipyridine-*N*-oxide (6.67 g) in dichloromethane (100 mL) was added trimethylsilyl cyanide (5 mL) and dimethyl carbomyl chloride (3.5 mL). After allowing the mixture to stand for 3 days,