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A copper–cyclen coordination complex associated with a polyoxometalate anion: Synthesis, crystal structure and electrochemistry of $[Cu(cyclen)(MeCN)][W_6O_{19}]$

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ABSTRACT

The reaction between $Cu(NO_3)_2 \cdot 3H_2O$ and a tetra-aza macrocycle, more specifically, cyclen in 1:1 MeCN-MeOH solvent mixture forms a Cu^{2+} -cyclen coordination complex *in situ*, that has been reacted with an isopolyanion $[W_6O_{19}]^{2-}$ in a slow diffusion technique, resulting in the isolation of an ion-pair solid [Cu (cyclen)(MeCN)][W₆O₁₉] (1). Single crystal structural investigation on 1 shows a square pyramidal geometry around the metal centre (copper ion) with an axially bound MeCN solvent molecule. The title compound 1 is the first crystallographically characterized ion-pair compound, in which a transition metal coordination complex of a tetra-aza-crown ether (cyclen) has been associated with a polyoxometalate cluster anion. This communication deals with synthesis, spectroscopic, structural and electrochemical analyses of compound 1. © 2010 Elsevier B.V. All rights reserved.

1,4,7,10-tetraazacyclododecane (commonly known as cyclen) is a well known aza-crown ether in the area of coordination chemistry owing to its affinity to form coordination complexes with transition metals [1]. Coordination complexes of cyclen have versatile applications, for example, in the areas of medical science [2-4], biology [5-7], photochemistry and sensor materials [8-11] etc. Till date, several transition metal complexes of simple or functionalized cyclen have been reported [1-11]. Interestingly, aza-crown macrocycles have the potential to reduce the toxicity of toxic metal environment/surrounding through their strong coordination with concerned metal ions. However, such supramolecular complex species are generally soluble in common laboratory solvents, as a result of which, separation of the concerned metal ions from solution becomes difficult. In this context, polyoxometalate (POM) cluster anions can play an important role in the sense that, they can easily be associated with such soluble supramolecular complex cations (ion-pair association/adduct formation) which are generally insoluble in common solvents. In other words, combination of the azacrown-ethers with POM anions can be used to separate specific metal ions (depending on cavity size of the aza-crown ethers) from an aqueous solution by precipitation method. Usage of the POM cluster anions in combination with the crown ethers has been described in the separation of radioactive wastes [12-14]. Structural, topological and electronic diversities are the key aspects of the chemistry associated with POM anions [15-18]. Inorganic solids, based on POM counter anions and supramolecular and/or coordination complexes of crown ethers [19–28] or porphyrins [29] as cations, have drawn considerable interest in contemporary research as new functional materials, in addition to the separation aspect. However, no structurally characterized coordination complexes of the aza-crown ethers associated with a POM counter anion have been demonstrated yet in literature [30]. The major difficulty in isolating such crystalline materials lies in the fact that, very often the physical mixture of the components ends up with an immediate formation of precipitate that inhibits complete characterization of such synthesized materials. Our preliminary investigation on coordination complexes of tetra-aza-crown ethers associated with POM anions has prompted us to synthesize an ion-pair compound [Cu (cyclen)(CH₃CN)][W₆O₁₉] (1) through a slow diffusion technique.

Various synthetic routes/strategies have been developed, so far, to obtain cyclen in small to bulk quantities [31–34]. We have taken up one of them. First, diethanolamine and diethylenetriamine have undergone base mediated tosylation reaction to yield the tosylated derivatives **2a** and **2b** respectively.

The next step involves the base mediated cyclization between –OTs and –NHTs groups of the tri-tosylated diethanolamine (**2a**) and tritosylated diethylenetriamine (**2b**) under "high dilution condition" to obtain the cyclic product cyclen tetratosylate (**2c**). It has been then protonated with conc. H_2SO_4 (see Scheme 1). Direct mixing of a solution (MeCN, MeOH etc.) containing a Cu²⁺ salt and cyclen (i.e. Cucyclen coordination complex) with $[Bu_4N]_2[W_6O_{19}]$ results in the immediate formation of a blue precipitate, which cannot be characterized unambiguously. Thus, single crystals of the compound [Cu (cyclen)(CH₃CN)][W₆O₁₉] (**1**), suitable for X-ray crystallography, have been grown by a slow diffusion technique [**35**], more specifically, in a U-tube set-up as shown in Fig. 1. In this technique, two different solutions containing the reacting substances are allowed to diffuse

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Scheme 1. Synthetic route used to obtain the macrocycle, cyclen.

slowly into each other through a Grade-4 silica crucible in a U- or Hshaped shell. The slow mixing of the reacting components results in lower molecular concentration of the resulting product (which is less soluble) that helped us to isolate good crystalline materials of **1**, suitable for facile crystallographic characterization. The title compound **1** has been isolated as a deep blue crystalline solid and its structure has been determined through spectroscopic analyses and unambiguously by single crystal X-ray structure determination [36].

The infrared spectrum of compound **1** (KBr disc) shows the characteristic features for the tetra-aza-crown ether and the POM anion. Strong IR band at 3250 cm⁻¹ is assigned to the asymmetric and symmetric N–H stretching vibrations of cyclen whereas, the band for –C (sp³)–H stretching at 2949 cm⁻¹ is weakly intense. The medium intensity and sharp IR band at 2310 cm⁻¹ might be attributed to Cu coordinated MeCN molecule (see crystallographic discussions, *vide infra*).

Characteristic IR absorptions of the hexatungstate POM anion appear as strong bands centred at 983 cm⁻¹ and 808 cm⁻¹ that correspond to the W=0 stretching and W-O_b-W bending motions of the cluster anion respectively. A broad band in the visible region, centred at 610 nm in the electronic absorption spectrum of **1** (DMSO, ca. 10^{-4} M), is assigned to the d-d transition in a Cu^{2+} (d⁹) system (see Supplementary material). The four-component hyperfine ESR spectrum of 1 (frozen DMSO, -140 °C) with g_{II} = 2.28 (A_{II} = 179–198G) and g[⊥] = 2.07 suggests the tetragonally elongated environment around Cu^{2+} (d⁹) ion with $g_{\parallel} > g^{\perp}$ [37-39] (see Fig. 2). Furthermore, the diffuse reflectance spectrum of compound **1** shows a very weak absorption at 1458 nm that might be assigned to the characteristic peak for a square pyramidal Cu²⁺ complex [40]. Based on the above spectroscopic observations, it can be inferred that the inorganic-solid **1** comprises of a square pyramidal Cu^{II}-cyclen as the cation which might be axially coordinated to an acetonitrile molecule and the cation is associated with a POM anion $[W_6O_{19}]^{2-}$.

Single crystal X-ray structure determination on a dark blue crystal of compound $[Cu(cyclen)(CH_3CN)][W_6O_{19}]$ (1), indeed, illustrates good convergence with the spectroscopic structure prediction. The crystal structure of compound **1** is elucidated by the assembly of the molecules obeying C2/c space symmetry with half of the [Cu(cyclen) (MeCN)]²⁺ cation and half of the $[W_6O_{19}]^{2-}$ isopolyanion in its asymmetric unit $(Z' = \frac{1}{2})$. The crystal structure of the compound **1** has been shown in Fig. 3. As shown in Fig. 3, the coordination geometry around copper is square pyramidal in which the four nitrogen atoms of cyclen provide the basal coordination and a solvent acetonitrile molecule defines the axial coordination of the square pyramid. The POM anion is positioned at the centre of the crystallographic [100] axis. O(10) i.e. the central oxygen atom of the hexatungstate anion is located at the crystallographic inversion centre (0.5, 0.0, 0.0) with half occupancy in the asymmetric unit. Cu(1)-N(3)-C(5)-C(6) axis of the square pyramid projects parallel to the two-fold rotational axis of a monoclinic crystal system, as a result of which, these atoms are found to have half occupancies in the asymmetric unit of the concerned crystal structure. The methyl protons of the MeCN molecule are symmetrically disordered over two positions with respect to the twofold rotational symmetry passing through the Cu-MeCN bond. Thus, these atoms have been refined after fixing their occupancies to 0.5 (AFIX 133). The cavity size of the tetra-aza-crown ether cyclen is not large enough for complete encapsulation of Cu²⁺ due to the larger size of the cation. Thus, in the crystal structure of compound 1, the Cu^{2+} ion is located 0.564(8)Å away from the basal {N4} plane of the macrocycle (Fig. 3) and the macrocycle is found to be bent outwards from Cu²⁺ ion for facile Cu–N coordination. In the relevant crystal



Fig. 1. Slow diffusion between two components in a U-shaped cell for the growth of good quality crystals suitable for single crystal XRD analysis.



Fig. 2. ESR spectrum of 1 recorded at -140 °C (frozen DMSO).



Fig. 3. Top: thermal ellipsoidal plot of compound **1** in 20% probability level. Only the asymmetric unit has been labeled. Only some of hydrogen atoms have been shown for clarity. Middle: hydrogen bonding environment around the Cu–cyclen coordination complex. Bottom: perspective view of the crystal packing viewed down the crystallographic c-axis. Geometrical parameters for hydrogen bonding interactions: C (1)–H(1A)–O(5) 0.97, 2.68 and 3.601(15) Å, 159.4° (-x + 0.5, y + 0.5); C(2)–H(2A)–O (3) 0.97, 2.50 and 3.315 (14) Å, 141.4° (-x + 1, y, -z + 0.5); N(1)–H(1 N)–O(7) 0.88 (11), 2.44(11) and 3.301(13) Å, 169(10)° (x, -y, z + 0.5); N(2)–H(2 N)–O(4) 0.79(11), 2.46(12) and 3.175(14) Å, 151(11)°. Selected bond lengths: C(1) N(1) 1.432(17), C (2) N(1) 1.503(16), C(2) C(3) 1.511(17), C(3) N(2) 1.432(18), C(4) N(2) 1.508(18), C (5) N(3) 1.11(2), C(5) C(6) 1.44(2), Cu(1) N(2) 2.004(12), Cu(1) N(1) 2.035(11), Cu (1) N(3) 2.070(14).

structure, the bond lengths of cyclen are observed as an average C-C 1.512(20) Å and average C–N 1.431–1.507(19) Å. The average Cu–N bond length for the $[Cu(cyclen)(MeCN)]^{2+}$ complex cation is found to be 2.019(12) Å for cyclen coordination whereas, the apical MeCN molecule is located at a distance of 2.071(14)Å from Cu(1) (see caption of Fig. 3 for the relevant bond distances). Extensive C-H-O and N-H-O supramolecular hydrogen bonding interactions between $[Cu(cyclen)(MeCN)]^{2+}$ counter cation and the POM anion have been observed in the crystal lattice of compound **1** (see Fig. 3). Along with the coulombic interactions between the cationic and anionic counter parts of compound 1, the supramolecular C-H-O and N-H-O hydrogen bonding interactions between them assemble six POM cluster anions around the cationic complex (see Fig. 3 and caption of Fig. 3 for the geometrical parameters for the relevant supramolecular interactions). The Cu-cyclen complexes pack in such a way that a channel-like arrangement is formed in the crystal lattice of 1 (Fig. 3, bottom) in which the POM cluster anions occupy the voids through coulombic and H-bonding interactions. The isopolyanion $[W_6O_{19}]^{2-1}$ (also known as Lindqvist type isopolyanion) comprises of six edge shared $\{WO_6\}$ octahedra. All the W atoms in the isopolyanion reside in a distorted octahedral geometry bonded to one terminal (O_t), four bridging (O_b) and one central (O_c) oxygen atoms. Thus, the W–O bonds in the isopolyanion can be grouped into three categories and these bond lengths are observed as $W-O_t 1.686(9)-1.700(9)$ Å, $W-O_b$ 1.916(7)–1.948(9) Å and W–O_c 2.317(1)–2.339(4) Å in the crystal structure of compound **1**.

Cyclic voltammetric experiment on compound 1 has been performed in DMSO (c.a. 10^{-3} M) at 298 K. The relevant experiment includes three electrode assembly consisting of Pt as the working electrode, Ag/AgCl as the reference electrode, a Pt gauze as the counter electrode and tetrabutylammonium perchlorate (TBAP) as the reference electrolyte. The relevant cyclic voltammogram has been shown in Fig. 4. In order to comprehend any variation in red-ox properties of the metal macrocyclic complex in presence of a POM anion in solution, we have also performed cyclic voltammetry on the starting precursors, Cu(cyclen)(NO₃)₂ and [Bu₄N]₂[W₆O₁₉] (see Supplementary material for the relevant voltammograms). The Cu (cyclen)(NO₃)₂ complex shows an almost irreversible reductive response at -0.75 V vs Ag/AgCl, which has been assigned to the red-ox couple $[Cu(cyclen)]^{2+}/[Cu(cyclen)]^+$. But, in the cyclic voltammogram of compound 1 (Fig. 4) two important phenomena have been observed: (i) the almost reversible nature of the [Cu



Fig. 4. Cyclic voltammogram of **1** in DMSO at $25^{\circ}(\pm 2)$ with a scan rate of 0.1 V s⁻¹.

(cyclen)]²⁺/[Cu(cyclen)]⁺ couple and (ii) considerable shift of the red-ox potential of the $[Cu(cyclen)]^{2+}/[Cu(cyclen)]^{+}$ couple (from -0.75 V to -0.45 V vs Ag/AgCl), while the red-ox response corresponding to the POM cluster anion $(W_6O_{19}^{2-})$ remains almost constant. Previously reported electrochemical studies on Cu-cyclen complexes have shown that voltammograms for the $[Cu(cyclen)]^{2+}$ [Cu(cyclen)]⁺ couple were mostly irreversible [41–43]. Because of some conformational change/change of geometry around copper ion in the Cu-cyclen complex (e.g., from square planar to tetrahedral), the cyclen cavity cannot bind and/or stabilize the Cu¹⁺ oxidation state [44-46]. It has been observed in some cases that solvent effects can overcome this problem of irreversibility by its coordination to Cu¹⁺ centre when the chemical processes associated with these structural changes are fast enough on the electrochemical scale thereby showing reversibility [46]. But in the case of compound 1, probable reason for the reversible nature of the concerned couple in presence of a POM anion in solution is not so clear to us.

In conclusion, we have shown, for the first time, a crystallographic evidence for the co-existence of a transition metal aza-crown ether complex with a polyoxoanion in compound $[Cu(cyclen)(CH_3CN)]$ $[W_6O_{19}]$ (1). We have demonstrated that the red-ox potential of the couple $[Cu(cyclen)]^{2+}/[Cu(cyclen)]^+$ has been altered (as compared to that of same couple in bare Cu–cyclen complex) in presence of an isopolyanion. This study clearly suggests that the title complex is a better oxidizing agent when it is supramolecularly associated with a POM anion. Rigorous investigations on electrochemical and catalytic behaviours of transition metal aza-crown ether complexes containing POMs as the counteranions are in progress in our laboratory.

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Appendix A. Supplementary material

Text and figures depicting spectroscopic studies (IR, UV–visible, ESR) and elemental analysis, figures and tables related to the crystal structure of **1**. X-ray crystallographic data for **1** (CIF format) may be obtained free of charge via www.ccdc.cam.ac.uk using the CCDC depository number CCDC 771216. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. inoche.2010.06.013.

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- [35] To a 10 ml (1:1 mixture of CH₃CN and CH₃OH) solution of cyclen (51.6 mg, 0.3 mmol) was added Cu(NO₃)₂ (69.8 mg, 0.3 mmol) and the reaction mixture was stirred overnight at room temperature. A solution of [Bu₄N]₂[W₆O₁₉] (567 mg, 0.3 mmol) in CH₃CN was prepared separately. These two solutions were then charged onto two different arms of an U-tube setup (see Fig. 1) and allowed to mix slowly through a G4 frit that joins two arms of the U-tube. Deep blue needles of 1 were isolated after few days. IR (KBr, cm⁻¹): 3250.35 (s, NH), 2949.43 (w, aliphatic CH), 2883.84 (w), 2310.93 (m, M–N=C), 983.78 (s, W O), 808.25 (W–O_b–W). Anal. Calcd. For C₁₀H₂₃CuN₅O₁₉W₆ (1683.97): C, 7.12; H, 1.37; N, 4.16. Found: C, 7.21; H, 1.31; N, 4.32.
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