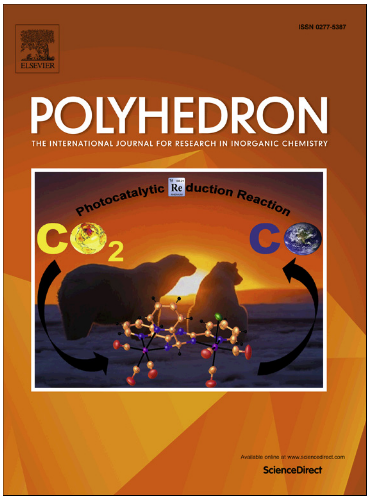

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Seven–Coordinated chiral uranyl(VI) salen complex as effective catalyst for C-H bond activation of dialkylanilines under visible light

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Abstract

A new chiral uranyl(VI) complex incorporating a tetradenate salen ligand is reported. The synthesized uranyl complex is studied by microanalyses, spectroscopic and X–ray diffraction studies. The structural studies reveal a slightly distorted pentagonal bipyramid coordination environment around uranyl ion. Interestingly, the uranyl complex was found to be potential visible light active catalyst for C–H bond functionalization of dialkylanilines, and afforded moderate to excellent yield of corresponding α–aminonitriles when exposed to visible light for 8 hours in the presence of NaCN and acetic acid as cyanide source, and H_2O_2 as oxidant.

Keywords: Chiral uranyl(VI) salen complex; C-H bond activation; Photocatalysis; Visible light; Dialkylanilines

Introduction

The chemistry of uranyl complexes, dominated by uranyl(VI) dication, has received remarkable attraction over the years, and has found a variety of applications as molecular receptors in the area of supramolecular chemistry, reactivity, coordination behavior and small molecule activation [1-3]. Furthermore, Uranyl(VI) dication UO_2^{2+} is a chemically robust species owing to strong covalent character of the axial U=O bond making its coordination chemistry quite exclusively limited in the equatorial plane. Moreover, uranyl(VI) dication is essentially a linear O=U=O species due to repulsion from its oxygen atoms forcing the coordinating ligand nearly into a plane perpendicular to the axis of the ion [4-12].

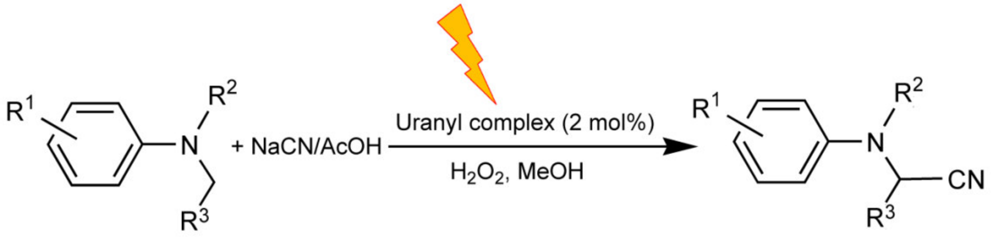
Uranyl(VI) dication is surrounded by 4-6 donor atoms at equatorial positions and exists in octahedral, pentagonal bipyramidal or hexagonal bipyramidal coordination environment [13].

Over the last few years, research on complexes featuring uranium is being explored in catalysis i.e. hydrogenation of alkenes, oligomerization, dimerization, hydrosilation, and hydroamination of terminal alkynes [14]. Interestingly, the large ionic radii and 5f valence orbitals provide actinides characteristic properties useful for catalysis [15].

In the recent decades, visible light assisted photochemical transformations have become a promising and useful tool in green organic synthesis as they use light which is an inexpensive, nonpolluting and endlessly renewable energy source, and can be carried out at room temperature under mild conditions [16].

Bakac and his co-workers reported that the uranyl(VI) dication (UO_2^{2+}) has strong property to photocatalytically oxidize organic substrates in air [17-19], and absorbs visible light to produce a strongly oxidizing excited state, $^*UO_2^{2+}$ (E^0 = 2.6 V), quenched by a variety of organic substrates [20]. The resulting U(V) species can then be oxidized back to UO_2^{2+} in the presence of oxygen [18]. Furthermore, studies have shown that $*UO_2^{2+}$ reacts with alcohol by H-atom abstraction to give UO_2H^+ and an organic radical [17]. In addition, low molecular weight alkanes and alkenes react with $*UO_2^{2+}$ by H-atom abstraction, electron transfer and oxygen atom transfer [18, 21, 22]. Recent work identified a U(V) species as a quenching product in the absence of oxygen, and suggested H-atom abstraction as the quenching mechanism [17].

We describe here the synthesis and structural study of a new chiral uranyl complex with a salen ligand, 2, 2'-((1E,1'E)-(cyclohexane-1,2-diylbis(azanyl-ylidene))bis(methanylylidene))diphenol, H_2L [Fig 1], and assessing its application as a photocatalyst for C-H bond activation of dialkylanilines to afford corresponding α-amino nitriles using NaCN/acetic acid as cyanide source and hydrogen peroxide as oxidant in the presence of visible light (Scheme 1).



R^1= H, $-CH_3$, $-OCH_3$, Cl, Br, R^2 = $-CH_3$, R^3= H, $-CH_3$

Scheme 1. C-H bond functionalization of dialkylanilines by uranyl(VI) complex in the presence of visible light

Experimental

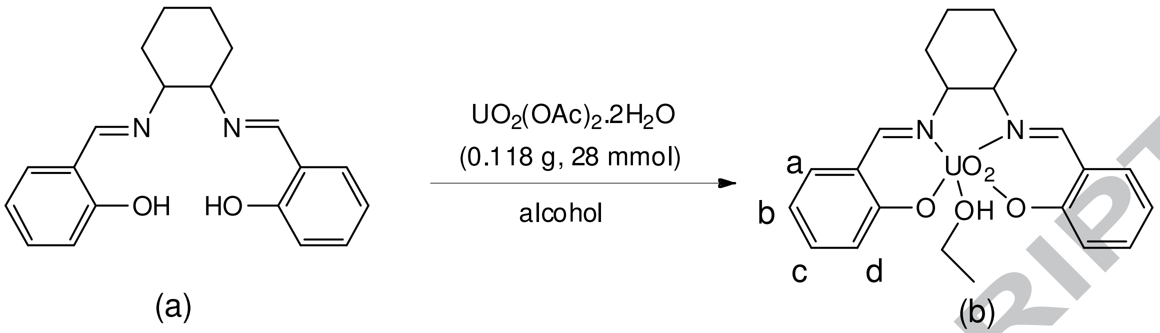
Materials and instrumentation

Dialkylanilines, *n-tert*-butyl amine $(n\text{-Bu})_3N$ (90 %), sodium cyanide (99.98%), acetic acid (≥99.7%), hydrogen peroxide (30 wt%), methanol HPLC grade (≥99.9%) were purchased from Sigma-Aldrich and used as received without further purification. Ethanol, N,N-dimethyl formamide, acetonitrile were obtained from various commercial sources and dried prior use by standard methods and stored over 4 A^o molecular sieves. *tert.*-butyl-hydroperoxide was bought from Sigma-Aldrich. Uranyl acetate was procured from commercial source, BDH chemical company, England and used as received. Chiral salen ligand, H2L [Scheme 2] was prepared following method reported in literature [23]. The microanalyses were performed on Elementar Varrio elemental analyzer. ^{1}H- and ^{13}C-NMR spectra were collected from Jeol spectrometer at 400 MHz (^{1}H-NMR) and 100 MHz (^{13}C-NMR), respectively in $CDCl_3$. FT-IR spectra were collected using Perkin Elmer 621 spectrophotometer at 400-4000 cm^{-1} at pressed KBr discs.

Synthesis of chiral uranyl(VI) complex

To a stirred solution of chiral salen ligand (0.09 g, 28 mmol) in 15 ml ethanol, uranylacetate dihydrate (0.118 g, 28 mmol) was added in equimolar ratio at room temperature in air. The obtained resulting solution was left for stirring for 5 h. An orange color solution was obtained, which was clarified by filtration to remove any turbidity. The orange colored filtrate solution was kept for few days at room temperature. Good quality crystals were produced within few days [Scheme 2].

Molecular Formula, $C_{22}H_{26}N_2O_5U$, Molecular Weight, 636.48, Color, Orange; Yield: 80 %, Anal. Cal: C, 41.52; H,4.12; N, 4.40: Found: C, 41.50; H,4.07; N,4.38 % IR (KBr): 1629 ν(C=N), 1344 ν(C_{arom}–O) , 908 asy(UO_2), 850 sym(UO_2), ^{1}HNMR ($CDCl_3$): δ (ppm) 7.24 (t, 2H, J = 7.32 Hz, Ph-H_b), 7.13 (d, 2H, J = 7.32 Hz, Ph-H_a), 6.92 (d, 2H, J = 8.04, Ph-H_d), 6.78 (t, 2H, J = 8.04 Hz, Ph-H_c), 3.18-3.28 (m, 2H, -N-C**H**-C**H**-N-), 1.73-1.89 (m, 4H, -C$\mathbf{H_2}$-CH_2-CH_2-C$\mathbf{H_2}$-), 1.31-1.43 (m, 4H, -CH_2-C$\mathbf{H_2}$-C$\mathbf{H_2}$-CH_2-), ^{13}CNMR ($CDCl_3$): δ (ppm) 161.1 (-CH=N), 164.7 (-C-O), 116.8-132.2 (Ar-C), 72.6 (N-**C**H-**C**H-N), 33.1 (-**C**H2-CHN-CHN-**C**H2-), 29.7 (-CH_2-**C**H_2-**C**H_2-CH_2-)



Scheme 2. Preparation of chiral uranyl(VI) complex; (a) Chiral salen ligand; (b) Chiral salen uranyl(VI) complex

Crystal structure determination

The crystallographic data for the orange prsim crystal of chiral uranyl(V) complex were collected using KM-4-CCD automatic diffractometer with graphite-monochromated CuK_α (λ = 1.54178 Å) radiation with ω scan mode. Crystallographic details and refinement are given in Table 1. Lorentz, polarization and numerical absorption [24] corrections were applied during the data reduction [24]. All the non-hydrogen atoms were refined anisotropically on F^2 using full-matrix, least-squares methods. The SHELXS, SHELXL and SHELXTL [25] programs were applied for all calculations. Selected bond lengths and angles are given in Table 2 and intermolecular interactions are listed in Table 3.

Photocatalytic C–H bond activation of dialkylanilines

The reaction mixture of dialkylaniline (1 mmol), sodium cyanide (1.0 mmol, 49.0 mg), acetic acid (1 mL), hydrogen peroxide (30 wt %; 1.5 mL) and uranyl(VI) complex (2 mol%, 12.7 mg) were stirred continuously together in methanol (5 mL) in round bottom flask under the irradiation visible light (20 Watt LED) having intensity at vessel 75 W m^{-2} at room temperature. The progress of the reaction was monitored by running TLC on silica gel plate. After completion of the reaction, the mixture was diluted with sodium bicarbonate ($NaHCO_3$) solution and extracted with ethyl acetate. The organic layer, so formed, was washed with brine water followed by drying over anhydrous Na_2SO_4 under reduced pressure. The crude product so obtained was purified with column chromatography over silica gel using ethyl acetate and hexane as eluent to afford corresponding α–aminonitriles. The identification and quantitative determination of product was done with GC–MS and obtained spectral data was matched with authentic samples in GCMS library.

Results and Discussions

A perspective view of uranyl complex structure is shown in Fig 1. The asymmetric part of the unit cell contains the two complex molecules and all atoms, except these ones belonging to bridging part of the cyclohexane moiety are related by non-crystallographic pseudosymmetry centre. Two pairs of carbon atoms (C8:C58, C13:C63) and neighbouring hydrogen atoms are not interrelated by symmetry centre, due to chiral centres located at these C atoms. The other parts of the complex molecules are mutually symmetry deepened. This affects the reflections statistics, which show rather the centrosymmetric behaviour than the non-centrosymmetric one. This situation is similar to those observed in crystal structure of triethylammonium bis(μ-2,2'-(cyclohexane-1,2-diylbis(nitrilomethylylidene)) diphenolato)-trichloro-di-zinc [23], in which two pairs of complex cations are related by pseudosymmetry. The all chiral centres (located at C8, C13, C58 and C63 atoms) of the dominant crystal phase have the S configuration. The symmetry independent complex molecules possess almost identical conformations (Supplementary Information S1), and the root mean squares deviation of superimposed molecules is 0.146(17) Å, respectively (the most distant equivalent atoms C17:C67 are separated at 0.282(8) Å, respectively).

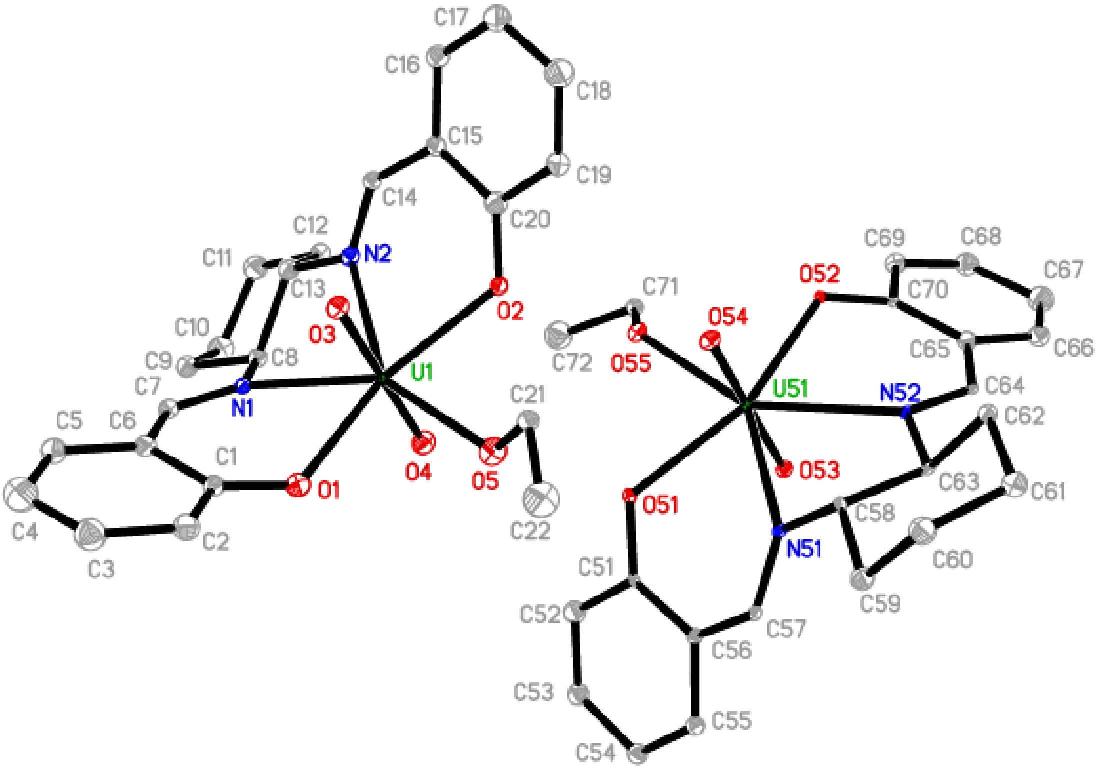


Fig 1. X-ray structure of uranyl complex plotted with 50% probability of displacement ellipsoids. The hydrogen atoms were omitted for clarity.

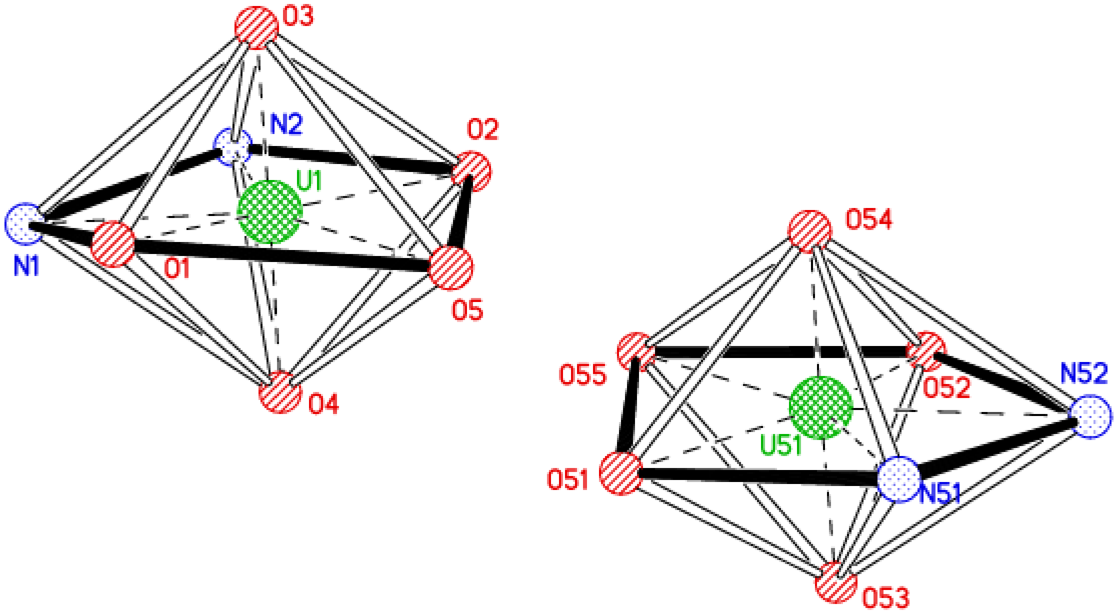


Fig 2. The coordination polyhedral of uranyl complex

Uranium atom is seven-coordinated and form a pentagonal plane with two imine nitrogen atoms, two alkoxide oxygen atoms and one hydroxyl oxygen atom from coordinated ethanol lying in the equatorial plane, whereas two oxide oxygen atoms are located at axial position resulting a slightly distorted pentagonal bipyramid coordination sphere [26] with the oxide oxygen atoms positioned at the polyhedron apexes [Fig 2]

The 2-hydroxidebenzylideneamino moieties of both molecules of uranyl complex are slightly distorted from planarity (the largest deviations from the respect weighted least squares planes are 0.147(78), 0.185(7), 0.155(7) and 0.146(6) Å, respectively for N1, N2, C57 and N 52 atoms). The cyclohexane rings show slightly distorted chair conformation, with the C_s asymmetry parameters [27] (placed on opposite ring atoms) in range 0.44-6.00, and C_2 asymmetry parameters [27] (placed on opposite ring bonds) in range 1.35-8.08. The asymmetric unit molecules are assembled to the dimer *via* O—H•••O intermolecular hydrogen bonds [Table 3, Fig. 3]. Additionally the dimer is internally linked by C—H•••O interaction, which can be classified as weak hydrogen bond [28] [Table 3]. The neighbouring dimers are well separated and they are not connected by any classical or non-classical interactions. The stacking interactions are not observed within the crystal structure of uranyl complex (the aromatic rings are surrounded by aliphatic moieties).

The U(1)-O(3) = 1.773 (8) A° and U(1)-O(4) = 1.816 (9) A° bond distances in the studied uranyl complex are typical values reported for such type of uranyl complexes [29-31]. Furthermore, O=U=O angle (177.6(4)^{o}) indicate that uranyl moiety is slightly bent [1]. The U-O$_{phen}$ [U(1)-O(1) = 2.231(7)A° and U(1)-O(2): mean 2.315(6) A°] and U-N$_{imi}$ U(1)-N(1) = 2.528(9) A° and U(1)-N(2) = 2.564(9) A° bond distances are in close agreement reported for such type of uranyl complexes [29-34]. Furthermore, the U–O$_{phen}$ distance, [(U(1)–O(1) and U(1)–O(2)], is relatively greater than the axial oxygens [(U(1) –O(3) and U(1)–O(4)] due to overlap between the 6d and 5f orbitals of the uranium atom and the three p orbitals (or two p and one hybrid sp orbitals) of each axial oxygen giving the linear structure [29]. U-O$_{alc}$ bond length [U(1)-O(5) = 2.429 (9) A°] is comparable to U-O$_{solvent}$ distances reported for mononuclear uranyl(VI) salen complexes [1]. Interestingly, U-O$_{alc}$ bond distance is significantly lengthier than that of U-O$_{phe}$ distances due to the formation of centrosymmetric dimeric species, and steric overcrowding of equatorial coordination spheres with solvent in the uranyl complex [29].

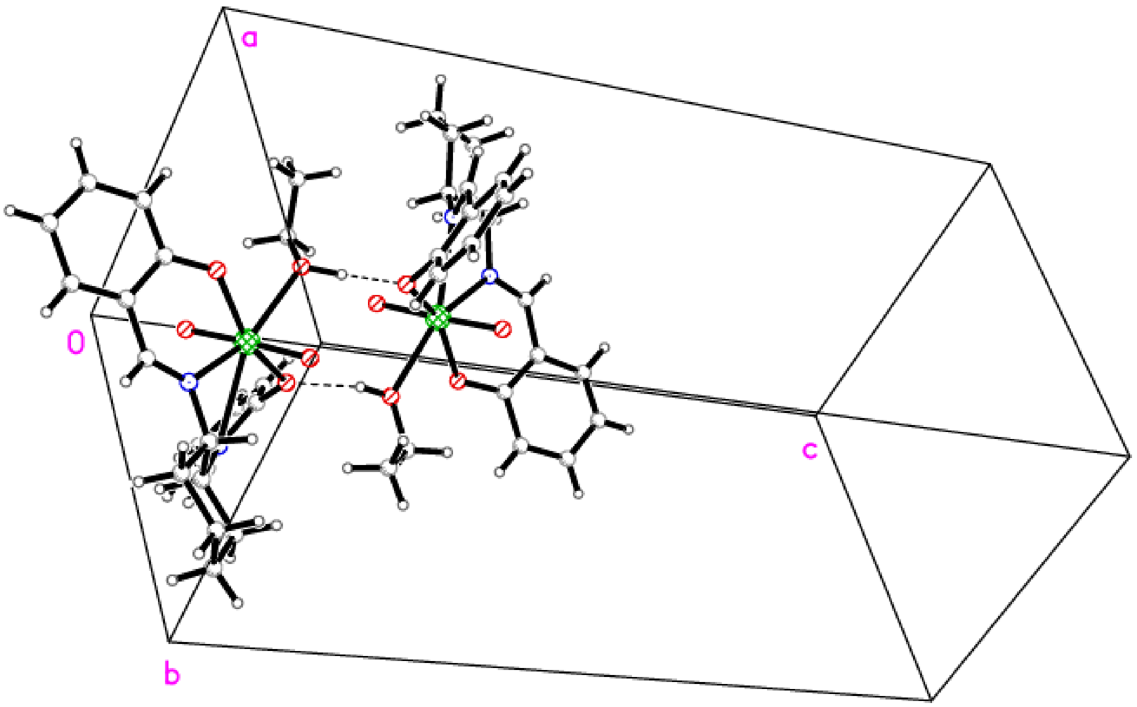


Fig 3. The part of molecular packing showing the hydrogen bonded dimer. The atoms are drawn as spheres of arbitrary radii. The O—H•••O hydrogen bonds are indicated by dashed lines

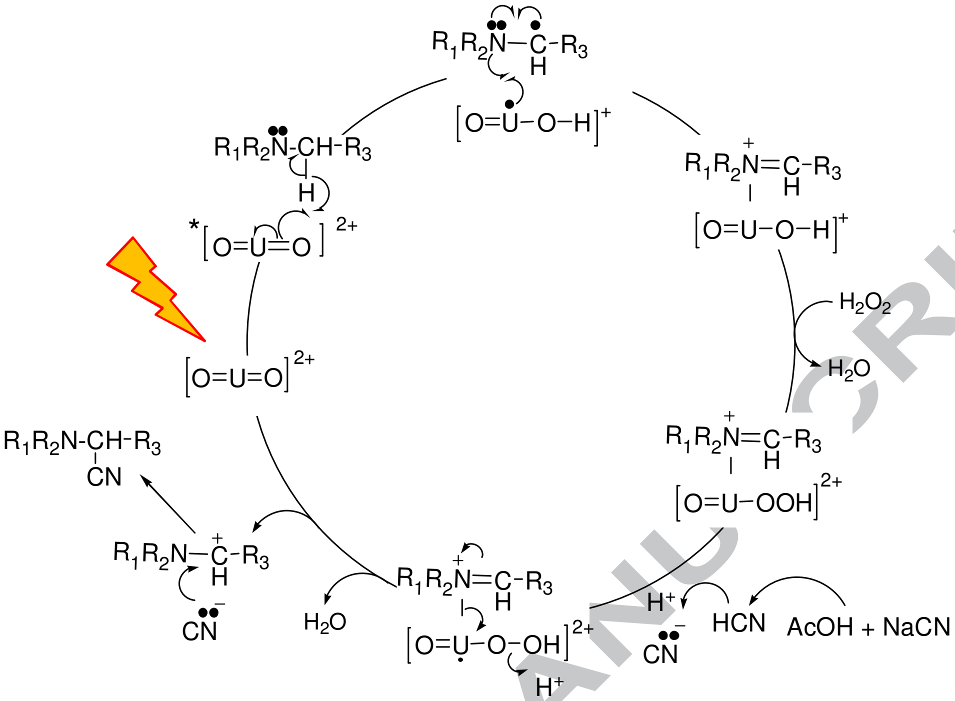
IR spectra of uranyl complex (Supplementary Information S2) show various vibrations at 500–4000 cm^{-1} consistent with the geometry revealed from X-ray analyses. A strong band due to ν(C=N) vibrations is observed at 1629 cm^{-1} in uranyl complex [29]. The vibration due to coordinated phenolic hydroxyl group at 1344 cm^{-1} is ascribed to ν(C_{arom}–O) vibrations [31]. Bands at 908 cm^{-1} and 850 cm^{-1}, attributed to the asymmetric and symmetric stretching vibration of (O=U=O) group, respectively, indicate that the uranyl moiety is linear in the studied complex, and these values assigned for the vibrations are in close agreement with the values already reported in literature [1, 35]. Furthermore, there is no significant effect of coordinated ethanol on asymmetric vibrations of uranyl moiety. However, low intensity vibrations of uranyl moiety due to either asymmetric transition or symmetric vibrations which are in centosymetric structure are IR inactive [36].

^{1}H-NMR spectrum of uranyl complex shows (Supplementary Information S3) two sets of signals corresponding to aliphatic and aromatic protons. A singlet for azomethine proton appears at 8.21 ppm. The cyclohexane bridge protons appear as multiplets at 3.18-3.28 (m, 2H, -N-C$\underline{H}$-C$\underline{H}$-N-) in the complex due to the diastereotopic coupling, while the chemical shifts for cyclohexane ring protons were observed at 1.39-1.87 ppm (m, 8H, cyclohexane). Further support for ^{1}H-NMR spectrum comes from ^{13}C-NMR spectral findings showing a sharp signal due to azomethine carbon at 161. 1 ppm, whereas the rest of signals were found at their positions expected. (Supplementary Information S4).

C–H Bond Activation

The synthesized uranyl complex was tested for C–H bond activation of dialkylanilines using in situ generated HCN from NaCN/AcOH as cyanide source and hydrogen peroxide as oxidant under visible light irradiation in methanol. The pKa values for AcOH/ACO$^-$ and for HCN/CN$^-$ is 4.75 and 9.21 respectively; hence the reaction between NaCN and AcOH will provide HCN in situ during the reaction. The source of visible light was 20 Watt LED light which has most of the emission in visible region (λ >400 nm). At first, N,N–dimethylaniline was chosen as representative substrate for optimization studies by changing the reaction parameters. The reaction did not occur in the absence of uranyl complex photocatalyst even after prolonged irradiation time under identical conditions (Table 4, entry 1). However, in the presence of uranyl photocatalyst under similar conditions, the reaction was completed in 8h and afforded 97% isolated yield of the corresponding α–aminonitrile (Table 4, entry 2). In order to confirm the superiority of the uranyl complex, the reaction was carried out using uranium acetate as photocatalyst under otherwise identical conditions (Table 4, entry 3). The reaction was found to be very slow and yielded only trace amount of the desired product. To confirm the effect of visible light, the reaction was performed using uranyl complex as photocatalyst in dark, after 24 h, only trace of α-aminonitrile could be isolated which confirmed that visible light irradiation is essential to provide activation energy for the reaction (Table 4, entry 4). Similarly, the presence of acetic acid was found to be essential and in its absence, no reaction occurred (Table 4, entry 5). Furthermore, among the various solvents such as ethanol, water, dimethylformamide, acetonitrile and methanol studied, methanol was found to be promising and afforded highest product yield under described reaction conditions (Table 4, entry 2, 6–8). Similarly, no reaction was occurred in the absence of hydrogen peroxide (Table 4, entry 9), however the use of other oxidants such as molecular oxygen and *tert*-butyl hydroperoxide (TBHP) afforded poor product yield (Table 4, entry 10–11). Further, we generalized the reaction to a number of substituted dialkylanilines under described optimized reaction conditions [Table 5]. In all cases, the reaction products were identified by comparing their GC–MS with authentic ones. The dialkylanilines bearing electron donating groups were found to be more active in comparison to those having electrons withdrawing groups. For example, $–CH_3$, $–OCH_3$ groups substituted dialkylanilines afforded higher product yield in the range of 94-98% (Table 5, entry 2–4), whereas substrates having –Cl, –Br groups afforded only 82, 84% yield, respectively (Table 5, entry 5-8). Similarly, the substrates containing electron donating groups at *p*–position of aromatic ring were found to be more reactive (Table 5, entry 2,4) than *m*–substituted substrates (Table 5, entry 3). Aliphatic tertiary amines such as *n*-*tert*-butyl amine $(n–Bu)_3N$ did not give any product under the described reaction conditions (Table 5, entry 9).

Although the exact mechanism of the reaction is known at this stage, however the mechanism for ruthenium catalyzed oxidative cyanation of tertiary amines is very well explained by Murahashi et al in the literature [37]. In analogy to the Murahashi mechanism and existing photocatalytic oxidation with uranyl complexes report [38], a plausible mechanism for the photocatalytic C–H activation of dialkylanilines with uranyl complex is shown in Scheme 3. After absorption of visible light, uranyl complex gets excited and reacts with dialkylaniline to abstract H–atom from α–carbon of dialkylanilines to give a radical intermediate coordinated with complex [17]. This radical undergoes one electron transfer from amine to uranium complex to form $UO_2(V)^{+1}$ cation intermediate, which subsequently reacts with hydrogen peroxide to give an intermediate having $UO_2(VI)^{+2}$ cation. Finally, hydrogen cyanide (HCN) generated in situ from the reaction of NaCN/acetic acid interacts with uranyl peroxo intermediate and provide cyanide ion which undergoes nucleophilic attack on the iminium ion intermediate gives the corresponding α–aminonitrile, water, and the uranyl complex completing the catalytic cycle (Scheme 3).



Scheme 2: Plausible mechanism of visible light driven C–H bond functionalization of dialkylanilines by chiral uranyl complex.

Supplementary Data: Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non–hydrogen atoms, H–atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. CCDC1442015.

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Table 1. Crystal and structure refinement data of uranyl complex

Compound	Uranyl complex
Empirical formula	$C_{22}H_{26}N_2O_5U$
Formula weight	636.48
Crystal system, space group	monoclinic, $P2_1$ (No. 4)
Unit cell dimensions [Å, °]	a = 10.373(2)
	b = 9.6822(19)
	c = 22.267(5)
	β = 96.73(3)
Volume [$Å^3$]	2221.0(8)
Z, Calculated density [Mg/m^3]	4, 1.903
Absorption coefficient [mm^{-1}]	20.866
F(000)	1216
Crystal size [mm]	0.108, 0.106, 0.101
θ range for data collection [°]	4.00 to 72.42
Index ranges	$-12 \le h \le 12$, $-11 \le k \le 11$, $-27 \le l \le 27$
Reflections collected / unique	22348 / 7956 [$R_{(int)}$ = 0.0460]
Completeness [%]	99.6 (to θ = 67°)
Min. and max. transmission	0.116, 0.172
Data / restraints / parameters	7956 / $1^{\$}$ / 544
Goodness-of-fit on F^2	1.066
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0498, $wR2$ = 0.1304
R indices (all data)	$R1$ = 0.0499, $wR2$ = 0.1306
Largest diff. peak and hole [$e{\bullet}Å^{-3}$]	5.095, -5.060

Table 2. Selected structural data of uranyl complex [Å, °].

U1—O3	1.773(8)	U51—O54	1.770(8)
U1—O4	1.816(9)	U51—O53	1.799(7)
U1—O1	2.231(7)	U51—O52	2.238(6)
U1—O2	2.315(6)	U51—O51	2.299(6)
U1—O5	2.429(9)	U51—O55	2.464(8)
U1—N1	2.528(9)	U51—N51	2.536(8)
U1—N2	2.564(9)	U51—N52	2.571(8)
O3—U1—O4	177.6(4)	O54—U51—O53	177.4(4)
O3—U1—O1	86.4(3)	O54—U51—O52	92.5(3)
O4—U1—O1	94.9(3)	O53—U51—O52	88.6(3)
O3—U1—O2	88.6(3)	O54—U51—O51	92.2(3)
O4—U1—O2	91.0(3)	O53—U51—O51	87.8(3)
O1—U1—O2	157.1(3)	O52—U51—O51	154.7(3)
O3—U1—O5	96.2(3)	O54—U51—O55	86.0(3)
O4—U1—O5	86.0(3)	O53—U51—O55	96.5(3)
O1—U1—O5	80.5(3)	O52—U51—O55	79.0(2)
O2—U1—O5	77.8(3)	O51—U51—O55	76.5(2)
O3—U1—N1	92.7(3)	O54—U51—N51	87.4(3)
O4—U1—N1	85.8(3)	O53—U51—N51	90.1(3)
O1—U1—N1	70.2(3)	O52—U51—N51	135.3(2)
O2—U1—N1	132.5(3)	O51—U51—N51	69.8(2)
O5—U1—N1	148.7(3)	O55—U51—N51	145.3(2)
O3—U1—N2	85.0(3)	O54—U51—N52	91.4(3)
O4—U1—N2	92.6(3)	O53—U51—N52	86.7(3)
O1—U1—N2	132.7(3)	O52—U51—N52	71.7(3)
O2—U1—N2	69.0(3)	O51—U51—N52	133.0(2)
O5—U1—N2	146.8(3)	O55—U51—N52	150.5(2)
N1—U1—N2	63.9(3)	N51—U51—N52	63.7(3)

Table 3. Hydrogen bonds geometry of uranyl complex [Å, °].

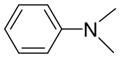
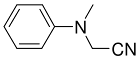
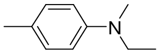
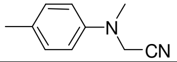
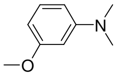
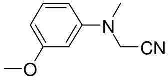
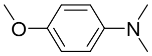
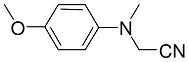
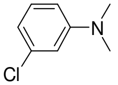
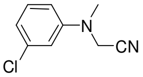
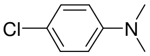
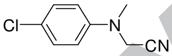
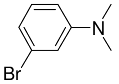
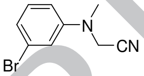
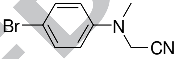
D—H•••A	d(D-H)	d(H•••A)	d(D•••A)	<(DHA)
O5—H5O•••O51	0.99	1.59	2.577(10)	172.3
O55—H55O•••O2	0.84	1.81	2.594(10)	155.6
C21—H21A•••O54	0.99	2.33	3.261(17)	155.7

Table 4. Results of optimization experiments.[a]

Entry	Solvent	Oxidant	Time (h)	Yield (%)[b]	TOF (h^{-1})
1[c]	CH_3OH	H_2O_2	24	-	-
2	CH_3OH	H_2O_2	8	97	12.1
3	CH_3OH	H_2O_2	8	trace	-
4[d]	CH_3OH	H_2O_2	24	-	-
5[e]	CH_3OH	H_2O_2	8	-	-
6	C_2H_5OH	H_2O_2	8	92	11.5
7	H_2O	H_2O_2	8	65	8.1
8	CH_3CN	H_2O_2	8	55	6.8
9	DMF	H_2O_2	8	72	9
10	CH_3OH	-	18	12	0.6
11[f]	CH_3OH	O_2	12	48	4.0
12	CH_3OH	TBHP[g]	12	84	7.0

[a]Reaction conditions: N,N-dimethylaniline (1 mmol, 121.19 mg), photocatalyst (2 mol%, 12.7 mg), NaCN (1.0 mmol, 49.0 mg), acetic acid (1.0 mL), oxidant (1.5 mL), solvent (5 mL); [b]Isolated yield; [c]without Uranium catalyst, [d]In dark, [e]In the absence of acetic acid; [f]using oxygen balloon; [g]TBHP: *tert*-Butyl hydroperoxide.

Table 5. Uranyl complex catalyzed photochemical C-H activation of tertiary amines.[a]

Entry	Reactant	Product	Time (h)	Yield (%)[b]	TOF (h^{-1})
1			8.0	97	12.1
2			7.5	98	13.0
3			7.0	93	13.3
4			7.0	94	13.4
5			8.0	82	10.2
6			8.0	85	10.6
7			8.0	84	10.5
8			8.0	88	11.0
9	$(n\text{-Bu})_3N$	-	24.0	-	-

[a] Reaction conditions: Dialkylaniline substarte (1 mmol), uranyl complex (2 mol%, 12.7 mg), NaCN (1.0 mmol, 49.0 mg), acetic acid (1.0 mL), H_2O_2 (1.5 mL), methanol (5 mL), [b] Isolated yield.

A new chiral uranyl(VI) salen complex reported. The complex is seven-coordinated with slightly distorted pentagonal bipyramid coordination environment. The uranyl complex proved to be potential visible light active catalyst for C-H bond functionalization of tertiary amines.