Synthesis and structure and photochromism of DMF Co-ordinted Cd(II)-iodide complexes of 1-methyl-2-(*p*-nitro-phenylazo)imidazole

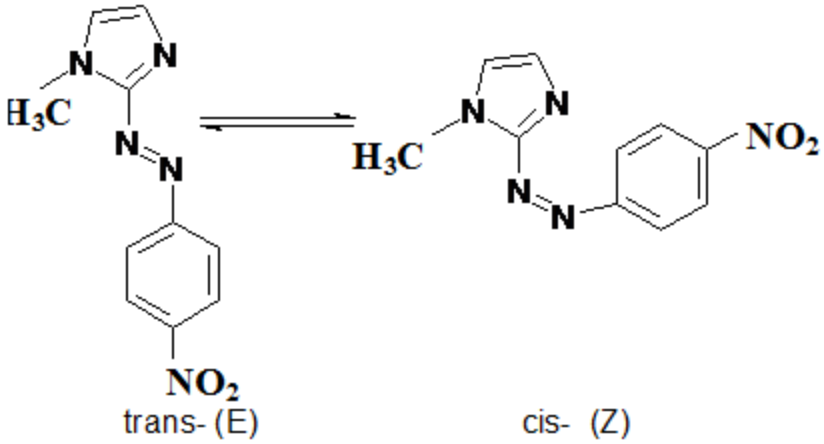
Dr. Gunomoni Saha, Assistant Professor, Department Of Chemistry, Barrackpore Rastraguru Surendranath College. Barrackpore, Kolkata-100120

ABSTRACT

Reaction between CdI_2 and 1-methyl-2-(*p*-nitro-phenylazo)imidazoles, [*p*-NO_2aaiCH_3] in DMF has isolated complexes having composition [Cd(p-NO_2aaiCH_3)I_2.DMF]. The structure has been established by spectral (UV-VIS, ^{1}H-NMR) data and confirmed by single crystal X-ray diffraction study. UV light irradiation in MeCN solution of [Cd(p-NO_2aaiCH_3)I_2.DMF] shows *trans*-to-*cis* isomerization of coordinated azoimidazole. Quantum yield ($\phi_{t\rightarrow c}$) of *trans*-to-*cis* isomerization is calculated and free ligand shows higher ϕ than their Cd(II)-iodo complexes.

1. Introduction

Contemporary chemical science research focuses on the various applications of organic-inorganic hybrid functional materials [1-7]. Divergent properties of various inorganic-organic hybrid materials may be regulated by varying the design of ligand types, the nature of substituents, different homo-cyclic and heterocyclic rings and incorporating different metal ions. Presently, we are engaged in exploring the photochromism of 1-Methyl-2-(*p*-nitro-phenylazo)imidazoles and their metal complexes. Photochromism is a reversible photo-induced transformation between two molecular states whose absorption spectra differ significantly [8-11]. Azo-conjugated metal complexes exhibit unique properties upon light irradiation in the area of photon-mode high-density information storage photoswitching devices [12-14]. The azoheterocycles have been extensively used as ligands for metal ions by us [15-17] and others [18, 19]. However, very few reports concerning the photochromic property (Scheme 1) of arylazoimidazole dyes are found in the literature [19–25]. The photochromism of 1-alkyl-2-(arylazo)imidazole [20, 21]and their Cu(I) [22], Cd(II) [23], Hg(II) [24] and Pd(II) [25] complexes are so far reported in literature. Here, we wish to report in the Cd(II) iodide complexes of 1-Methyl-2-(*p*-nitro-phenylazo)imidazole. The compounds are characterized by different spectroscopic studies and structural confirmation have been done by single crystal X-ray diffraction measurements.

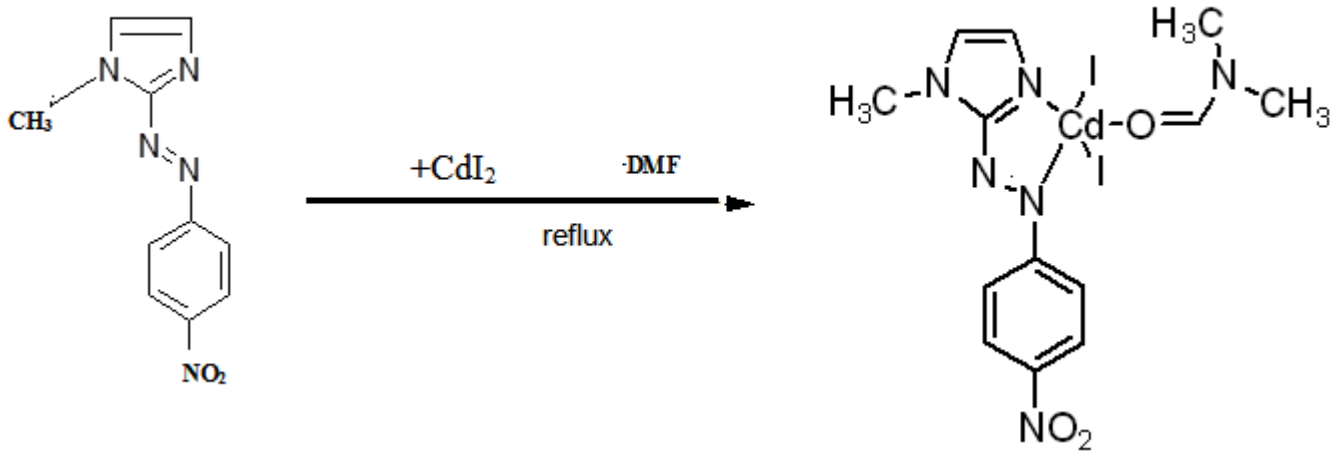


Scheme 1. Isomerization of 1-Methyl-2-(*p*-nitro-phenylazo)imidazole [*p*-NO_2aaiMe]

2. Results and discussion:

2.1. Synthesis and formulation of compounds

1-Methyl-2-(p-nitro-phenylazo)imidazole (*p*-NO_2aaiCH_3) is used in this work to prepare cadmium(II) complex. The reaction between CdI_2 and ligand (1:1, v/v) in DMF has afforded coordination complexes of composition [Cd(*P*-NO_2aaiCH_3)I_2.DMF]. The compound is non-conducting, and its composition has been supported by microanalytical data.



Scheme 2. Preparation of Cd(II)-iodide complex

2.2. Molecular structure of [Cd(*p*-NO_2aaiMe)I_2. DMF] (2)

The crystal structure of the complex is shown in Fig.1 and the bond parameters are listed in Table.1. The structure shows a distorted trigonal bipyramidal (TBP) geometry around Cd(II).The atomic arrangements Cd(1), I (1), I (2), N(5) constitute a trigonal plane and chelate angle is 65.96^0 and is comparable with reported results in the series of chelated arylazoimidazole complexes of d^{10} metal complexes. [15, 16, 20, 21] The small chelate angle may be the cause for distortion from symmetric TBP geometry. The Cd-N(2) [Cd-N(azo)] is the longest (2.663 Å) one in the family of M-N(azo) bond length so far known in the literature. [15, 16, 19-23] The elongation may be due to axial coordination of N(2) with reference to the trigonal plane described by $CdNI_2$ and from the small chelate bite angle. Although Cd–N(azo) bond length is very long but it is less than the sum of van der Waals radii of Cd(II) (1.58 Å) and N(sp^2) (1.53 Å). This implies significant bonding interaction between these components. Strong coordination of imidazole-N to Cd(II) has significant biochemical implication and explains strong toxicity of Cd(II).[24] Weak and flexible bonds are very effective to induce some functional property in the molecules. The weak bonding interaction between Mn(II) and N(azo) center in $[Mn(N_3)_2(TaiEt)]_n$ (TaiEt = 1-ethyl-2-(*p*-tolylazo)imidazole) is responsible for structural distortion and hence the canting phenomenon and remnant magnetism at low temperature.[22] Because of long Cd(II)–N(azo) distance, the molecule may exhibit photophysical activation *via* cleavage of this bond followed by rotation to introduce photoisomerisation. In fact, we have examined photochromism of these molecules (*vide infra*). Imidazole and *p*-NO_2-phenyl rings are joined by azo group. The N=N bond length is 1.275 Å and is slightly elongated than that of free ligand value (1.250(1)Å). [14, 23] The stability of chelated azoimine $\overline{\text{Cd-(N=C-N=N-)}}$ owes to the metal-to-ligand π-back bonding and azo group is directly involved in this process.[17, 19] This reduces M-N(azo) bond length and subsequently increases N=N bond length from that of free ligand values. The acute chelate angle may develop a strain that is relieved partially by structural distortion and bond length elongation. The Cd-I distances are comparable with published results.[25]

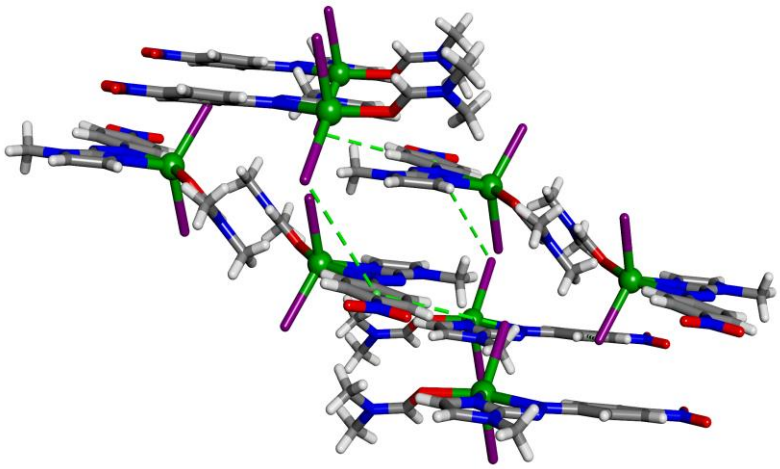


Fig.1. Crystal structure of [Cd(*p*-NO_2)aaiCH_3)I_2.DMF]

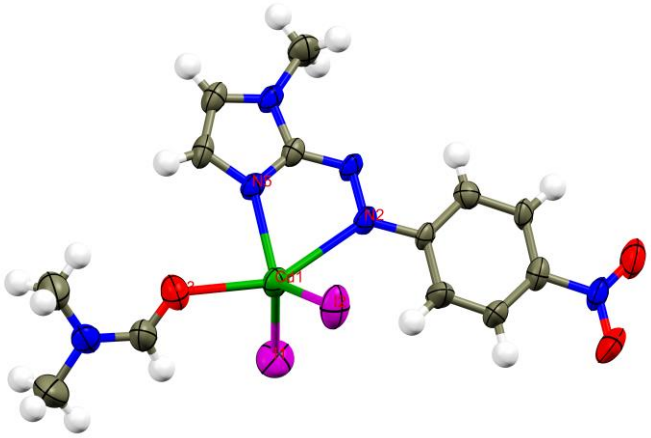


Fig.2. ORTEP view of [Cd(*p*-NO_2)aaiCH_3)I_2.DMF]

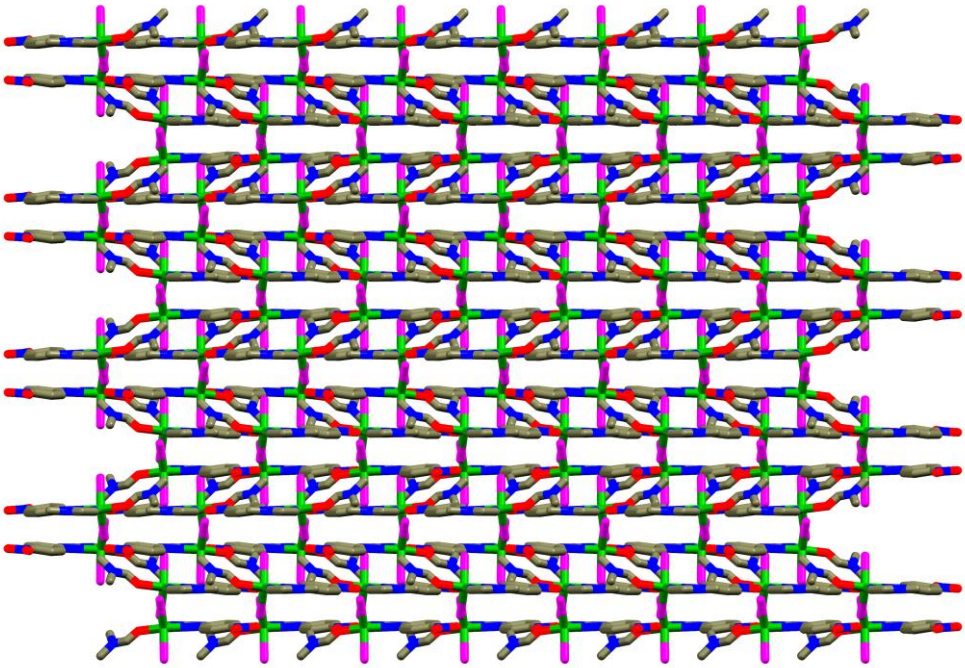


Fig.3. Crystal packing in [Cd(p-NO_2)aaiCH_3)I_2.DMF

Table.1. Selected bond distances (Å) and angles (°) for [Cd(*p*-NO_2)aaiCH_3)I_2.DMF]

Bond distances (Å)		Bond angles (°)	
[Cd(*P*-NO_2)aaiCH_3)I_2.DMF]			
Cd-I(1)	2.722	I(1)-Cd-I(2)	122.04
Cd-I(2)	2.710	I(2)-Cd-N(5)	118.73
Cd-N(2)	2.663	N(2)-Cd-O(3)	150.95
Cd-N(5)	2.251	N(2)-Cd-N(5)	65.96
Cd–O(3)	2.333	N(5)-Cd-O(3)	85.57
N(2)-N(3)	1.275	I(1)-Cd-O(3)	96.53
O(1)-C(14)	1.229	I(2)-Cd-O(3)	105.03
N(3)-C(3)	1.384	N(3)-N(2)-Cd	113.74
N(2)–C(5)	1.420	Cd-O(3)-C(13)	125.88
N(5)–C(3)	1.320	N(3)-N(2)-C(5)	114.7
O(1)-N(1)-O(2)	122.7	N(3)-N(2)-Cd(1)	113.7
O(1)-N(1)-C(8)	119.1	C(5)-N(2)-Cd(1)	131.6
O(2)-N(1)-C(8)	118.2	N(2)-N(3)-C(3)	113.5
C(2)-N(4)-C(3)	107.4	C(3)-N(5)-C(1)	104.7
C(4)-N(4)-C(3)	124.8	C(3)-N(5)-Cd(1)	119.4
C(2)-N(4)-C(4)	127.8	C(1)-N(5)-Cd(1)	135.5
C(13)-N(6)-C(11)	121.8	C(13)-N(5)-C(12)	121.8

2.3. Spectral studies

2.3(a) IR Spectra

The bands in the FT-IR spectra of the ligand (1) and the complexe are assigned based on comparing with reported work [22, 26, 27, 28]. The point of interest is the band due to the azo (–N=N–) and imine (–C=N–) groups in compounds. Free ligand, 1, values appear at frequency, around 1367 and 1604 cm^{-1} respectively and the complex, 2-3, shows moderately intense stretching at around 1375 and 1597 cm^{-1} in case of (2) and 1361 and 1584 cm^{-1} in case of (3) for ν(N=N) andν(C=N) respectively. In the complex, stretching frequency are shifted to lower frequency region which are in support of coordination of azo -N and imine -N to Cd(II). The spectral data are shown in Table .2.

2.3(b) UV-Vis Spectra

The absorption spectra were recorded in MeOH solution for the ligand and in DMF solution (because of sparing solubility of the complexes in MeOH) for the complex, in the wavelength range 200-700 nm. The spectra of the ligands show absorption band at 360–390 nm with a molar absorption coefficient in the order of 10^4 M^{-1} cm^2 and a weak band at around 455 nm. The intense absorption band is assigned to π-π* transitions, while the tail corresponds to n-π* transition. The π-π* band exhibits bathochromic shifts by ~30 nm compared with azobenzene [28], while the n-π* band shows little shift. As a consequence, the energy separation between the π-π* and n-π* transitions in arylazoimidazoles is narrower than that of azobenzene. The spectral data are shown in the Table. 2.

Table.2. IR and UV-Vis spectral data

Compounds	IR in KBr disc(cm^{-1})		UV-VIS spectral data
	$\nu_{(N=N)}$	$\nu_{(C=N)}$	λ_{max}(nm) ($10^{-4}\in$ (dm^3 $mol^{-1}cm^{-1}$)
[*p*-NO_2aaiCH_3]	1367	1604	273(0.61),380(2.2),392(1.8),455(0.76)
[Cd(p-NO_2)aaiCH_3)I_2.DMF]	1375	1597	270(0.9), 382(2.1), 404(2.2)

The characteristics common to the complexes are a structured absorption band around 350-400 nm with a molar absorption coefficient on the order of 10^4 M^{-1} cm^2 . From the analogy with the absorption spectra of ligands (1) it is likely that the large absorption band around 360-380 nm corresponds to π-π* transitions, while the tail corresponds to n-π* transition. The transitions are shifted to longer wavelength by *av*. 10 nm. This may due to the overlapping of MLCT transition from Cd(II) → π^*(azoimine). The π-π* absorption peaks (λ_{max}) for derivatives of (2-phenylazo)imidazole are within a range of 365-385 nm, which is between the π-π* absorption bands of azobenzene (313 nm) and 4-*N*,*N*-dimethylaminoazobenzene (390 nm) [29, 30, 31].

2.3(c) ^{1}H NMR Spectra

The ^{1}H NMR spectra of ligand (1) are recorded in $CDCl_3$ and those of complex, [Cd(*P*-NO_2)aaiCH_3)I_2.DMF] (2) in dmso-d^6 (Table.3) because of solubility problem in former solvent. The alkylation of imidazole is supported by the disappearance of δ(N–H) at ~10.30 ppm and the appearance of N(1)- alkyl signal at 4.03 ppm. Imidazole 4- and 5-H appears as broad singlet at 7.33-7.93 and 7.08-7.33 ppm, respectively. Broadening may be due to rapid proton exchange between these imidazole protons. Data (Table.4) reveal that the signals in the spectra of the complexes are shifted to downfield side relative to free ligand values[23]. Important features of the spectra are the shifting of imidazole protons 4-H and 5-H to lower δ-values, in general, relative to perturbation of aryl protons (7-H – 11-H)[23]. Imidazole protons suffer downfield shifting by 0.2-0.5 ppm compared to the free ligand signal position[23]. This supports the strong preference for binding of imidazole-N to Cd(II).

Compound	4-H^s	5-H^s	7,11- H^d	8,10- H^d	1-CH_3
[Cd(p-NO_2)aaiCH_3)I_2.DMF]	7.93	7.33	8.15(6.6)	8.43(6.3)	4.04

Table. 3. ^{1}H NMR spectral data
^{s}Singlet; ^{d}Doublet

2.4. Photochromism

Up on repetitive UV-light irradiation at fixed time interval at λ_{max} to a MeOH solution of the ligand [*p*-NO_2aaiCH_3] (1) shows the changes of absorption spectrum that is corresponding to the structural change of the ligand from *trans*-(*E*-isomer) to *cis*- (*Z*-isomer) (Fig.4). The intense peak at λ_{max} decreases, which is accompanied by a slight increase at the tail portion of the spectrum until a stationary state is reached. Subsequent irradiation at the newly appeared longer wavelength peak reverses the course of the reaction and the original spectrum is recovered up to a point, which is another photostationary state under irradiation at the longer. The *E*-to-*Z* isomerisation of [Cd(p-NO_2)aaiCH_3)I_2.DMF] is carried out in DMF solution because of sparing solubility in MeOH. It is observed that upon irradiation with UV light *E*-to-*Z* change proceeds and the *Z* molar ratio is reached to ~ 70%. The absorption spectra of the coordinated *p*-NO_2aaiMe (1) in E-form have changed with isosbestic points upon excitation (Fig. 4) into the *Z*-isomer. The ligands and the complexes show little sign of degradation upon repeated irradiation at least upto 15 cycles in each case. The quantum yields were measured for the *E*-to-*Z* ($\phi_{E\rightarrow Z}$) photoisomerisation of these ligands in MeOH and that of the complexes in DMF on irradiation of UV wavelength (Table.4). The photoisomerisation rate and quantum yields of coordinated ligand are decreased compared to free ligand and in general, increase in mass of the molecule reduces the rate and quantum yield of isomerisation. The lowering of $\phi_{E\rightarrow Z}$ in the complexes may be due to the presence of coordinated CdI_2 that increases molecular weight and severely interferes the motion of the –N=N-Ar moiety and photo bleaching

efficiency of halide [31] may snatch out energy from π-π* excited state. These may cause very fast deactivation other than photochromic route. Both rotor mass and volume are increased upon coordination of ligand to CdI_2. These two factors have significant influence on the isomerisation rate and quantum yields.

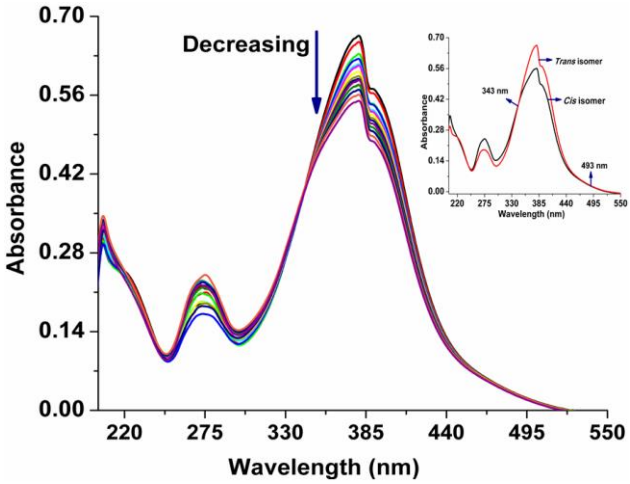


Fig.4. Spectral changes of [Cd(p-NO_2)aaiCH_3)I_2.DMF] in DMF upon repeated irradiation at 368 nm at 5 min interval at 25^0C.

3. Experimental

3.1 Materials

CdI_2 was prepared by adding KI solution to $CdCl_2$ solution, filtered and washed with a profuse amount of water and dried in a $CaCl_2$ desiccator, [*p*-NO_2aaiCH_3] was synthesized by reported procedure [29]. All other chemicals and solvents were reagent grade as received.

Table.4. Results of photochromism, rate of conversion and quantum yields upon UV light irradiation.

Compounds	λ_{π,π^*} (nm)	Isosbestic point (nm)	Rate of E→Z conversion x 10^8 (s^{-1})	$\phi_{E\rightarrow Z}$ conversion
[*p*-NO_2aaiCH_3]	380	343,493	4.90	0.215
[Cd(p-NO_2)aaiCH_3)I_2.DMF]	398	357	3.01	0.149

3.2. Physical measurements

Spectroscopic data were obtained using the following instruments: UV-Vis spectra from a Perkin Elmer Lambda 25 spectrophotometer; IR spectra (KBr disk, 4000-400 cm^{-1}) from a Perkin Elmer RX-1 FTIR spectrophotometer; photo excitation has been carried out using a Perkin Elmer LS-55 spectrofluorimeter and ^{1}H NMR spectra were recorded from a Bruker (AC) 300 MHz FTNMR spectrometer.

3.3. Preparation of compounds

3.3.1. Synthesis of p-NO_2aaiMe

To dry THF solution (75 ml) of 2-(*p*-NO_2 phenylazo)imidazole (2.0 g, 9.9 mmol), NaH (50% paraffin) (0.56 g) was added in small portion and stirred at cold condition on ice bath for 0.5h. CH_3I (0.62 ml 9.9 mmol) was added slowly through pressure equalizing system under stirring condition for a period of 1 hr and then warm for another 1 hr on steam bath.The solution was evaporated to dryness,extracted with CH_2Cl_2, washed with NaOH solutin (10%, 10 ml x 3) and finally by distilled water (20 ml x 3). The CH_2Cl_2 extract was chromatographed over silica gel column (45 x 1 ml) prepared in benzene. The elution was performed by 1:10 benzene-acetonitrile mixture. On slow evaporation in air orange crystalline product was obtained and was then dried over P_4O_{10} under vacuum. Other compounds were prepared under identical conditions. The yield varied in the range 70%.

3.3.2 Synthesis of [Cd(p-NO_2)aaiCH_3)I_2.DMF]

1-Methyl-2-(*p*-NO_2-phenylazo)imidazole (54 mg, 0.25 mmol) in MeOH (20 ml) was added dropwise to a MeOH-AN mixtures solution (5 ml) of CdI_2 (92 mg., 0.25 mmol), which was refluxed for 2h. Orange-yellow precipitate appeared. The precipitate was collected by filtration, washed with cold MeOH and dissolved in DMF-MeOH mixture and kept for crystallization. After few days red colour with fine shape crystal was collected dried. The yield was 64 %.

3.4. X-Ray diffraction study

The crystallographic data are shown in Table .6. Suitable single crystal of 2 and 3 were mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation. The unit cell parameters and crystal-orientation matrices were determined for two complexes by least squares refinements of all reflections. The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed using the SAINT program. Data were collected by applying the condition $I>2\sigma(I)$. All these structures were solved by direct methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 [32] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. Complex neutral atom scattering factors were used throughout for all cases. All calculations were carried out using SHELXS 97 [33], SHELXL97 [32], PLATON 99 [34] program.

Table.6 Summarized crystallographic data.

Compound	[Cd(p-NO_2)aaiCH_3)I_2.DMF]
Empirical formula	'C_{13} H_{16} Cd I_2 N_6 O_3'
Formula weight	670.53
Temperature (K)	273 K
Crystal system	Monoclinic
Space group	'C 2/c'
Crystal size $(mm)^3$	
a(Å)	21.549(3)
b(Å)	15.8676(16)
c(Å)	14.8833(16)
$\alpha/^0$	90
β/°	123.755(3)
$\gamma/^0$	90
$V(Å)^3$	4231.2(9)
Z	8
μ (MoK_α) (mm^{-1})	3.973
θ range	2.27-27.06
hkl range	-25<h<25; -18<k<18. -17<l<17
D_{calc} ($mg\ m^{-3}$)	2.105
Refine parameters	229
Total reflections	22664
Unique reflections	3241
R_1[a] [I > 2σ (I)]	0.0779
wR_2[b]	0.2329
Goodness of fit	1.077

[a] $R=\Sigma\,||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$,

$w = 1/[\sigma^2(F_0)^2+ (0.0482P)^2+ (4.8416P)]$ for 5b; where $P = ((F_0^2 + 2F_c^2) / 3$

3.5. Photometric measurements

Absorption spectra were taken with a PerkinElmer Lambda 25 UV/VIS Spectrophotometer in a 1x1 cm quartz optical cell maintained at 25°C with a Peltier thermostat. The light source of a PerkinElmer LS 55 spectrofluorimeter was used as an excitation light, with a slit width of 10 nm. An optical filter was used to cut off overtones when necessary. The absorption spectra of the *cis* isomers were obtained by extrapolation of the absorption spectra of a *cis*- rich mixture for which the composition is known from ^{1}H NMR integration. Quantum yields (ϕ) were obtained by measuring initial *trans*-to-*cis* isomerization rates (ν) in a well-stirred solution within the above instrument using the equation, $\nu = (\phi\ I_0 /V)\ (1- 10^{-Abs})$ where I_0 is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial absorbance at the irradiation wavelength. The value of I_0 was obtained by using azobenzene ($\phi = 0.11$ for π-π* excitation [28] under the same irradiation conditions.

4. Conclusion

1-Methyl-2-(*p*-nitro-phenylazo)imidazole, [*p*-NO_2aaiMe] (1) is used in this study. Cadmium(II) complex with the formula [Cd(*P*-NO_2 aaiMe)I_2. DMF] (2) and [Cd(*P*-NO_2 aaiMe)I_2. DMF] (2) of this ligand were synthesized. The complexes are characterized by spectroscopic techniques and in one case the structures are confirmed by single crystal X-ray diffraction study. Photochromism of the complexes are examined by repeatitive UV light irradiation in methanol solution for the ligand and the DMF solution is used for the complexes. The rate and quantum yield of E-to-Z isomerisation of the complexes are less than that of free ligand data. The rotor mass and volume may be the regulating agents for these data. The higher rotor volume and mass of the complxes may support the slow rate of isomerisation than that of free ligand.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; the CCDC Nos. for the complex [Cd(p-NO_2)aaiCH_3)I_2.DMF] is 2267124. Copy of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.com.ac.uk or www.
ccdc.cam.ac.uk).

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