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Anion-directed structural diversity in the complexes of Cd(II)-arylazoimidazole: synthesis, spectral characterization and crystal structure

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Abstract

Cadmium(II) complexes of 1-alkyl-2-(arylazo)imidazoles [RaaiR′ (where R = H (**a**), Me (**b**); R′ = Me (**1/3/5/7**), Et (**2/4/6/8**)] are described in this work. Three representative complexes of the series, [Cd(HaaiMe)$_2$Cl$_2$] (**3a**), [Cd(HaaiEt)$_4$](ClO$_4$)$_2$ (**6a**) and [Cd(HaaiMe)$_4$](NO$_3$)$_2$ · 2H$_2$O (**7a**), have been characterized by single crystal X-ray diffraction measurements. In these complexes, cadmium is seated at the center of a tetrahedron. In [Cd(HaaiMe)$_2$Cl$_2$] (**3a**), the neutral metallo-organic compound consists of a central cadmium atom surrounded by two HaaiMe ligands and two chlorides. In [Cd(HaaiEt)$_4$] (ClO$_4$)$_2$ (**6a**), the cation consists of a central cadmium atom surrounded by four HaaiEt ligands. [Cd(HaaiMe)$_4$] (NO$_3$)$_2$ · 2H$_2$O (**7a**) is a tetragonal channel structure. Nitrate and interstitial water molecules assemble into a square-grid supramolecule (ca. 7 × 7 Å) and each grid is interlocked by chains parallel to the *Z*-axis passing through the middle of the square arms to form a layer in the *ac*- (or *bc*-) plane with a brick-wall topology (dimension 11.2 × 7 Å).

Keywords: Arylazoimidazoles; Cadmium (II) complexes; Square grid; X-ray structure

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1. Introduction

The work stems from our interest in the exploration of coordination chemistry of arylazoimidazoles [1–16]. The ligands act, in general, as a *N*,*N*′-bidentate chelator where *N* and *N*′ refer to imidazole-N (*N*) and azo-N (*N*′) donor centers, respectively. Major progress has been made in the area of transition metals [1–10]. Metal ions have preferential binding affinity towards *N* or *N*′. For example, Ru(II) [2–5] and Os(II) [6] prefer to coordinate with azo-N while Pd(II) [8] and Pt(II) [9,10] have a stronger affinity towards imidazole-N (*N*) in the M(*N*,*N*′)-chelated structures. These have been concluded on the basis of M–N(*N*′) bond length data of the complexes. Non-transition metal complexes of arylazoheterocycles have been studied recently [13–16]. We have reported Zn(II) [13,14] and Hg(II) [15,16] complexes of some of the members of the arylazoheterocycles. It is observed that the non-transition metals prefer heterocyclic-N during their interaction with *N*,*N*′ donor ligands. 2-(Arylazo)pyridines and 2-(arylazo)pyrimidines form distorted chelate complexes of Zn(II) [13] and Hg(II) [16]. 1-Alkyl-2-(arylazo)imidazoles (RaaiR′) act as monodentate imidazole-N donor ligands during their reaction with Zn(II) and Hg(II) metal ions [14,16].

In this paper we present an account on cadmium(II) complexes of RaaiR′, a member of the zinc triad. In

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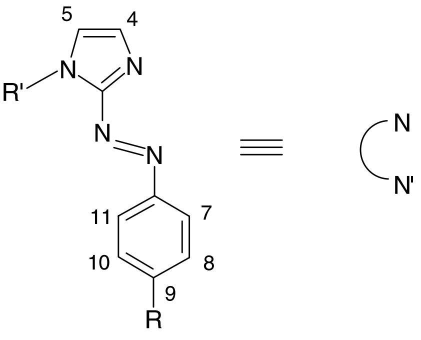
the cationic complexes of cadmium(II)-arylazoimidazoles the counterions are Cl^-, ClO_4^- and NO_3^-. The X-ray structure studies reveal the structural differences of the complexes which have originated from the nature of the anions. The anions do not only function as counterions to the molecule but are also a part of the structural integrity. Sometimes they play a key role to form bridge, helical structures and 1D, 2D, 3D networks. Anions are classified based on their charges, nature, denticity, periodic position, structures, etc. [17,18]. For example, Cl^- sometimes acts as a bridging ligand and can form 1D chains [19,20], CO_3^{2-}, NO_3^- are planar anions (D_{3h}) that contribute to 2D arrangements [21–24]; BF_4^-, ClO_4^- being tetrahedral (Td) symmetric are reasonable agents to generate 3D networks [25–29]; anions like $M(CN)_6^{n-}$, PF_6^-, SbF_6^-, etc. are used to generate superstructures [30]. Oxo-anions are able to synthesize a polymeric geometry via hydrogen bonding [30–34], N_3^- and SCN^- are special anions to construct varieties of networks and also participate in spin exchange processes in transition metal complexes [35–38]. In this paper we find out how the anions control the structure of cadmium(II) complexes of 1-alkyl-2-(arylazo)imidazoles (RaaiR′). Both spectral and X-ray crystallographic studies are detailed in each case.



RaaiR′

R = H (**a**), Me (**b**); R′ = Me (**1**), Et (**2**)

2. Experimental

2.1. Materials

Imidazole was purchased from Sisco Research Lab, India. $CdCl_2$ and $Cd(NO_3)_2 \cdot 6H_2O$ were obtained from Loba Chemicals, Bombay, India. $Cd(ClO_4)_2 \cdot 6H_2O$ was prepared by adding $CdCO_3$ to $HClO_4$ and crystallizing the product from warm water. All other chemicals and solvents were reagent grade and used as received. 1-Alkyl-2-(arylazo)imidazole (RaaiR′) was prepared by the reported procedure [1].

Warning: Cadmium and its compounds are toxic [39–41], and perchlorate salts are potential explosives. Only small amounts should be prepared.

2.2. Physical measurements

Microanalytical (C, H, N) data were obtained from a Perkin–Elmer 2400 CHNS/O elemental analyzer. Conductivity was measured with a Systronics model 304 conductivity meter. Spectroscopic data were obtained using the following instruments: UV–Vis, JASCO UV/Vis/NIR model V-570; IR (KBr, cm^{-1} disk, 4000–200 cm^{-1}), JASCO FT-IR model 420 spectrophotometers and ^1H NMR, Bruker 300 MHz FT-NMR spectrometer.

2.3. Synthesis of [Cd(HaaiMe)$_2$Cl$_2$] (3a)

1-Methyl-2-(phenylazo)imidazole (0.08 g, 0.4 mmol) in MeOH (10 ml) was added in dropwise to a stirred methanolic solution (10 ml) of $CdCl_2$ (0.18 g, 0.1 mmol) at room temperature (298 K). The orange–yellow solution was left undisturbed for 2 weeks. Bright orange crystals were obtained. These were then washed with water and finally, dried in vacuo. The yield was 0.04 g (65%). Microanalytical data of the complex is given below: [Cd(HaaiMe)$_2$Cl$_2$] (**3a**): Found: C, 43.28; H, 3.5; N, 20.11. [$C_{20}H_{20}N_8Cl_2Cd$] requires C, 43.22; H, 3.6; N, 20.16%; IR (KBr, cm^{-1}) 1558m, 1508m, 1438m, 323w, 302w.

All other complexes in this series were prepared by the same procedure. The yield varied from 60% to 65% and microanalytical data of the complexes are as follows. [Cd(HaaiEt)$_2$Cl$_2$] (**4a**): Found: C, 45.18; H, 4.09; N, 19.10. [$C_{22}H_{24}N_8Cl_2Cd$] requires C, 45.26; H, 4.14; N, 19.19%; IR (KBr, cm^{-1}) 1559m, 1508m, 1443m, 324w, 294w. [Cd(MeaaiMe)$_2$Cl$_2$] (**3b**): Found: C, 45.12; H, 4.03; N, 19.26. [$C_{22}H_{24}N_8Cl_2Cd$] requires C, 45.26; H, 4.14; N, 19.19%; IR (KBr, cm^{-1}) 1559m, 1509m, 1425m, 326w, 296w. [Cd(MeaaiEt)$_2$Cl$_2$] (**4b**): Found: C, 47.05; H, 4.55; N, 18.22. [$C_{24}H_{28}N_8Cl_2Cd$] requires C, 47.11; H, 4.61; N, 18.31%; IR (KBr, cm^{-1}) 1558m, 1504m, 1428m, 324w, 294w.

2.4. Synthesis of [Cd(HaaiMe)$_4$](ClO$_4$)$_2$ (5a)

1-Methyl-2-(phenylazo)imidazole (0.09 g, 0.45 mmol) in MeOH (10 ml) was added in dropwise to a stirred methanolic solution (10 ml) of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.03 g, 0.1 mmol) at room temperature (298 K). The orange solution was left undisturbed for 2 weeks. Bright orange–red crystals were obtained. These were then washed with water and finally, dried in vacuo. The yield was 0.08 g (75%). Microanalytical data of the complex is given below: [Cd(HaaiMe)$_4$](ClO$_4$)$_2$ (**5a**): Found: C, 45.42; H, 3.76; N, 21.15. [$C_{40}H_{40}N_{16}Cl_2O_8Cd$] requires C, 45.48; H, 3.81; N, 21.21%; IR (KBr, cm^{-1}) 1581m, 1505s, 1440m, 1085vs, 625w.

All other complexes in this series were prepared by the same procedure. The yield varied from 70% to 75% and microanalytical data of the complexes are as follows. [Cd(HaaiEt)$_4$](ClO$_4$)$_2$ (**6a**): Found: C, 47.44; H, 4.27; N, 20.10. [$C_{44}H_{48}N_{16}Cl_2O_8Cd$] requires C, 47.51; H, 4.34; N, 20.1%; IR (KBr, cm^{-1}) 1558m, 1502s, 1444m, 1091vs, 627w. [Cd(MeaaiMe)$_4$](ClO$_4$)$_2$ (**5b**): Found: C, 47.42; H, 4.24; N, 20.09. [$C_{44}H_{44}N_{16}Cl_2O_8Cd$] requires C, 47.51; H, 4.34; N, 20.14%; IR (KBr, cm^{-1}) 1559m, 1508s, 1456m, 1089vs, 623w. [Cd(MeaaiEt)$_4$](ClO$_4$)$_2$ (**6b**): Found: C, 49.26; H, 4.78; N, 19.07. [$C_{48}H_{56}N_{16}Cl_2O_8Cd$] requires C, 49.34; H, 4.83; N, 19.18%; IR (KBr, cm^{-1}) 1558m, 1503s, 1447m, 1089vs, 623w.

*2.5. Synthesis of [Cd(HaaiMe)$_4$](NO$_3$)$_2$. 2H$_2$O (**7a**)*

The complex was synthesized by a similar procedure to **6a** with the use of 1-methyl-2-(phenylazo)imidazole (0.07 g, 0.4 mmol) in MeOH (10 ml) and a methanolic solution (10 ml) of Cd(NO$_3$)$_2$ · 6H$_2$O (0.03 g, 0.1 mmol) at room temperature (298 K). The orange solution was left undisturbed for 2 weeks. Bright orange–red crystals were obtained. They were then washed with water and finally, dried in vacuo. The yield was 0.07 g (70%). Microanalytical data of the complex is given below: [Cd(HaaiMe)$_4$](NO$_3$)$_2$ · 2H$_2$O (**7a**): Found: C, 47.04; H, 4.18; N, 24.95. [$C_{40}H_{44}N_{18}O_8Cd$] requires C, 47.22; H, 4.33; N, 24.79%; IR (KBr, cm^{-1}) 3448mb, 1559m, 1504m, 1436m, 1384s.

All other complexes in this series were prepared by the same procedure. The yield varied from 65% to 70% and microanalytical data of the complexes are as follows. [Cd(HaaiEt)$_4$](NO$_3$)$_2$ · 2H$_2$O (**8a**): Found: C, 49.54; H, 4.99; N, 23.66. [$C_{44}H_{52}N_{18}O_8Cd$] requires C, 49.24; H, 4.85; N, 23.50%; IR (KBr, cm^{-1}) 3438mb, 1558m, 1504m, 1439m, 1384s. [Cd(MeaaiMe)$_4$](NO$_3$)$_2$ · 2H$_2$O (**7b**): Found: C, 49.48; H, 5.01; N, 23.60. [$C_{44}H_{56}N_{18}O_{10}Cd$] requires C, 49.24; H, 4.85; N, 23.50%; IR (KBr, cm^{-1}) 3436mb, 1559m, 1508m, 1431m, 1383s. [Cd(MeaaiEt)$_4$](NO$_3$)$_2$ · 2H$_2$O (**8b**): Found: C, 50.91; H, 5.40; N, 22.56. [$C_{48}H_{60}N_{18}O_8Cd$] requires C, 51.04; H, 5.32; N, 22.33%; IR (KBr, cm^{-1}) 3428mb, 1559m, 1502m, 1436m, 1383s.

2.6. X-ray diffraction study

Suitable single crystals of complexes **3a** (orange, 0.2 × 0.15 × 0.15 mm), **6a** (red, 0.50 × 0.40 × 0.38 mm) and **7a** (red, 0.36 × 0.29 × 0.16 mm) were mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo Kα ($\lambda = 0.711073$ Å) radiation. The crystallographic data, conditions for the intensity data collection and some features of the structure refinements of all the complexes are listed in Table 1. The unit cell parameters and crystal-orientation matrices were determined for the three complexes by least squares refinements of all reflections. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was also employed using the SAINT program for complexes **3a**, **6a** [42] and the SADABS program for complex **7a** [43]. A total of 13 450, 14 593 and 14 716 reflections were measured and 4002, 4325 and 2716 reflections were assumed applying the

Table 1
Summarized crystallographic data for [Cd(HaaiMe)$_2$Cl$_2$] (**3a**), [Cd(HaaiEt)$_2$](ClO$_4$)$_2$ (**6a**) and [Cd(HaaiMe)$_2$](NO$_3$)$_2$ · 2H$_2$O (**7a**)

	[Cd(HaaiMe)$_2$Cl$_2$] (**3a**)	[Cd(HaaiEt)$_2$](ClO$_4$)$_2$ (**6a**)	[Cd(HaaiMe)$_2$](NO$_3$)$_2$ · 2H$_2$O (**7a**)
Empirical formula	$C_{20}H_{20}CdCl_2N_8$	$C_{44}H_{48}CdCl_2N_{16}O_8$	$C_{40}H_{48}CdN_{18}O_{10}$
Formula weight	555.74	1112.28	1053.36
Temperature (K)	293(2)	293(2)	100(2)
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$P2_1/c$	$C2/c$	$I4_1/a$
Unit cell dimensions			
a (Å)	13.8422(10)	19.4733(15)	14.051(3)
b (Å)	13.5039(10)	13.1084(10)	14.051(3)
c (Å)	12.2983(9)	19.5613(15)	22.814(5)
β (°)	96.0530(10)	93.079(2)	90.00
V (Å^3)	2286.0(3)	4986.1(7)	4504.2(17)
Z	4	4	4
λ (Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	1.214	0.613	0.564
2θ range (°)	3.0–56.4	3.8–56.6	3.4–57.36
D_{calc} (Mg m^{-3})	1.615	1.482	1.553
Refine parameters	280	321	178
Reflection total	13450	14593	14716
Unique reflections	5138	5523	2716
$R_1[I > 2\sigma(I)]$	0.0300	0.0467	0.0549
wR_2	0.0752	0.1323	0.1374
Goodness of fit	1.027	1.019	1.135

condition $I > 2\sigma(I)$ for complexes **3a**, **6a** and **7a**, respectively. All these structures were solved by direct methods and followed by successive Fourier and difference Fourier syntheses. During refinement of **7a** the NO_3 anion was found to have symmetry imposed disorder. Full matrix least squares refinements on F_0^2 were carried out using SHELXL 97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. All calculations were carried out using SHELXS 97 [44], SHELXL 97 [44], PLATON 99 [45] and ORTEP-3 [46] programs.

3. Result and discussion

3.1. Synthesis and formulation

Ligands used are 1-alkyl-2-(arylazo)imidazole [RaaiR′, where R = H (**a**), Me (**b**); R′ = Me (**1**), Et (**2**)], they are unsymmetrical *N*,*N*′-bidentate chelator, where *N* and *N*′ refer to N(imidazole) and N(azo) donor centers, respectively. Methanolic solutions of $CdCl_2$ and RaaiR′ in 1:4.5 or higher mole proportion have isolated orange–yellow to orange crystalline products of composition $Cd(RaaiR')_2Cl_2$ (**3**, **4**). $[Cd(RaaiR')_4](ClO_4)_2$ (**5**, **6**) and $[Cd(RaaiR')_4](NO_3)_2 \cdot 2H_2O$ (**7**, **8**) complexes were synthesized on a reacting methanolic solution of the respective cadmium salts and RaaiR′ with the mole ratio 1:4.5. $[Cd(Meaaie)_2(H_2O)_2]X_2$ ($X = ClO_4^-$ (**9b**), NO_3^- (**10b**)) are also isolated immediately after mixing a methanolic solution of the cadmium(II) salts and RaaiR′ in the metal:ligand mole ratio of 1:2.5. However, on keeping the solution for a week to crystallize the complexes, only the tetrakis, cadmium(II) complexes, $[Cd(MeaaiMe)_4]X_2$ (**5b–8b**) were obtained. Microanalytical data support the composition of the complexes. Each class of complex has been structurally confirmed by the single crystal X-ray diffraction study. $Cd(RaaiR')_2Cl_2$ (**3**, **4**) are non-conducting ($\Lambda = 22–30\ \Omega^{-1}\ cm^{-1}\ mol^{-1}$) and complexes **5–8** show the usual 1:2 molar conductivity ($\Lambda = 180–210\ \Omega^{-1}\ cm^{-1}\ mol^{-1}$).

3.2. Molecular structures

3.2.1. $[Cd(HaaiMe)_2Cl_2]$ (**3a**)

An ORTEP view of $Cd(HaaiMe)_2Cl_2$ is shown in Fig. 1. The Cd center is tetrahedrally surrounded showing a CdN_2Cl_2 coordination sphere. Each HaaiMe acts as a monodentate-N(imidazole) donor ligand. Bond length data in Table 2 suggest unusually long Cd–N(azo) [Cd–N(4), 2.470(2); Cd–N(8), 3.006(2) Å] and very small chelate angle N(imidazole)–Cd–N(azo) [N(1)–Cd–N(4), 64.12(7); N(5)–Cd–N(8), 60.01(4)°] in a forced chelated CdN_4Cl_2 coordination sphere. The Cd–N(azo) distances are closer to the sum of the van der Waals radii of Cd(II) and N(azo) [47]. Hence, chelation is excluded and HaaiMe acts as a monodentate-N(imidazole) donor ligand. The ligand is planar. The two ligands make a dihedral angle of 71.87 (7)°. The azo group (–N=N–) binds to phenyl and imidazolyl groups. Bond length C(3)–N(3), 1.389(4) and C(4)–N(4), 1.416(4) Å suggest the azo group favors the imidazole ring more than the phenyl ring. The N=N bond lengths, N(3)–N(4), 1.261(3) and N(7)–N(8), 1.257(3) Å are closer to the free ligand value, 1.250(1) Å [48,49]. The Cd–N(imidazole) distance [Cd–N(1), 2.266(2); Cd–N(5), 2.282(2) Å] is comparable with reported data [50]. The Cd–Cl bond distances are 2.4883(8) and 2.4376(8) Å. The angles extended in tetrahedral CdN_2Cl_2 geometry are Cl(1)–Cd–Cl(2) 115.61(3), N(1)–Cd–N(5), 106.27(8)° and suggest a small distortion. All other angles are within the limits of distorted Td-geometry (Table 2).

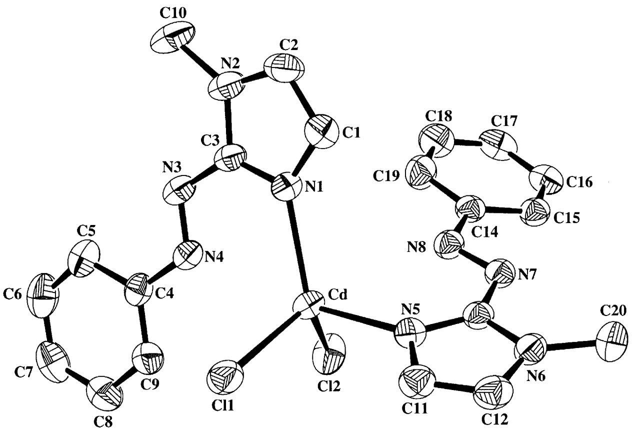


Fig. 1. X-ray structure of $Cd(HaaiMe)_2Cl_2$ (**3a**).

Table 2
Selected bond distances (Å) and angles (°) for $[Cd(HaaiMe)_2Cl_2]$ (**3a**)

Bond distances		Bond angles	
Cd–Cl(1)	2.488238)	Cl(1)–Cd–Cl(2)	115.61(3)
Cd–Cl(2)	2.4376(8)	Cl(1)–Cd–N(1)	107.91(6)
Cd–N(1)	2.266(2)	Cl(1)–Cd–N(4)	84.6(5)
Cd–N(5)	2.282(2)	Cl(1)–Cd–N(5)	92.18(6)
Cd–N(4)	2.470(2)	Cl(2)–Cd–N(1)	123.76(6)
Cd–N(8)	3.006(2)	Cl(2)–Cd–N(4)	85.89(5)
N(3)–N(4)	1.261(3)	Cl(2)–Cd–N(5)	105.85(6)
N(7)–N(8)	1.257(3)	N(1)–Cd–N(4)	64.12(7)
		N(1)–Cd–N(5)	106.27(8)
		N(4)–Cd–(N5)	168.03(7)
		N(5)–Cd–N(8)	60.01(4)
		Cd–N(1)–C(3)	121.04(18)
		Cd–N(5)–C(13)	126.49(18)

3.2.2. $[Cd(HaaiEt)_4](ClO_4)_2$ (**6a**)

The cationic complex $[Cd(HaaiEt)_4]^{2+}$ (Fig. 2) consists of a central cadmium atom surrounded by four

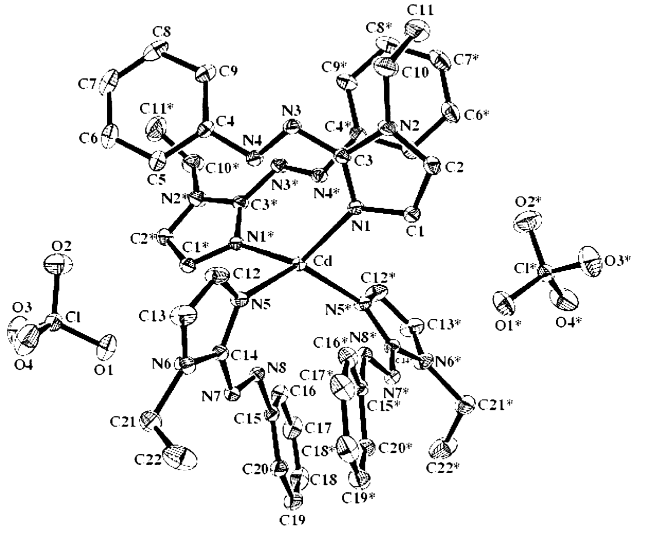


Fig. 2. X-Ray structure of $[\mathrm{Cd(HaaiEt)_4}](\mathrm{ClO_4})_2$ (**6a**).

Table 3
Selected bond distances (Å) and angles (°) for $[\mathrm{Cd(HaaiEt)_4}](\mathrm{ClO_4})_2$ (**6a**)

Bond distances		Bond angles	
Cd–N(1)	2.261(3)	N(1)–Cd–N(1)*	130.85(13)
Cd–N(5)	2.260(3)	N(1)–Cd–N(5)*	97.86(11)
Cl–O(1)	1.412(4)	N(1)*–Cd–N(5)	97.86(11)
Cl–O(4)	1.360(4)	N(5)–Cd–N(5)*	131.15(14)
Cl–O(2)	1.378(5)	N(1)*–Cd–N(5)*	101.96(11)
Cl–O(3)	1.400(5)	N(1)–Cd–N(5)	101.96(11)
N(3)–N(4)	1.254(4)	O(3)–Cl–O(4)	111.0(4)
N(3)–C(3)	1.385(5)	O(2)–Cl–O(1)	111.8(4)
N(4)–C(4)	1.412(4)	O(1)–Cl–O(3)	109.8(3)
N(5)–C(14)	1.328(4)	O(1)–Cl–O(4)	111.9(3)
N(7)–N(8)	1.256(4)	O(2)–Cl–O(3)	102.4(4)
N(7)–C(14)	1.378(5)	O(2)–Cl–O(4)	109.7(4)
N(8)–C(15)	1.419	Cd–(N1)–C(1)	129.8(2)
		N(4)–N(3)–C(3)	112.8(3)
		N(3)–N(4)–C(4)	114.2(3)
		Cd–N(5)–C(12)	130.2(3)
		Cd–N(5)–C(14)	124.4(2)
		N(8)–N(7)–C(14)	112.8(3)
		N(7)–N(8)–C(15)	114.4(3)
		Cd–N(1)–C(3)	124.1(1)

HaaiEt ligands. The Cd is sitting at the center of a tetrahedron. The four Cd–N bond lengths are almost equal and the length is 2.260(3) Å. HaaiEt acts as a monodentate ligand and binds via the N(imidazole) donor center. The coordination environment about Cd is compressed along the crystallographic **c**-axis in such a way that two of the N–Cd–N angles are higher than the tetrahedral angle with a value of N1–Cd–N1*, 130.85(13)° and N5–Cd–N5*, 131.15(14)°. Two other N–Cd–N angles show a lower value, each of them, N1–Cd–N5* and N1*–Cd–N5, being 97.86(11)°. The remaining N–Cd–N angles (N1*–Cd–N5* or N5*–Cd–N1*) are 101.96(11)° (Table 3). The angular distortion from a regular tetrahedron may be due to steric crowding among the pendant azophenyl groups. The 1-ethyl-imidazole and phenyl group at the two sides of the azo (N=N) group are planar. The N=N bond length is av. 1.255(4) Å and is near to the free ligand value (1.250(1) Å) [48,49].

3.2.3. *$[\mathrm{Cd(HaaiMe)_4}](\mathrm{NO_3})_2 \cdot 2\mathrm{H_2O}$ (7**a**)*

The cationic complex (Fig. 3) consists of a central cadmium atom surrounded by four HaaiMe ligands with the cadmium center sitting on a site of crystallographic symmetry ($\bar{4}$). The coordination environment about the cadmium is compressed like **6a** along the crystallographic **c**-axis, in such a way that two of the N–Cd–N angles are splayed open, with a value 139.49(16)°, while the other angles about the cadmium atom have a common value of 96.89(5)°. The Cd–N distance of 2.283(3) Å differs only slightly from the average value of 2.30 Å reported for Cd–N (imidazolate) distances in a compilation of average structural parameters [50], in which it is also reported that the range of these Cd–N values is quite broad (the lower and upper quartile values are 2.26 and 2.35 Å). Along the backbone of the HaaiMe ligand, the N=N distance of the azo moiety, 1.263(5) Å, is near the upper limit of the average of all values found for this unit (1.240 Å) and is quite similar to the average value found for $\mathrm{C_{ar}}$–N=N– motifs (1.255 Å) [51] (cf. Table 4).

It is interesting to note that the solvent water molecules interact with anion $\mathrm{NO_3}^-$ through –NO$_3$–water–NO$_3$–water–hydrogen bonding interactions to form a chain along the ***a***-direction and these chains interact with a chain along the ***b***-direction via the sequence –NO$_3$–water–water–NO$_3$–water–water–NO$_3$–running along the ***c***-direction (Table 5, Fig. 4). The 1D chains line up in the *ab*-plane and by virtue of 4-fold symmetry, assemble into a square-grid supramolecule with grid

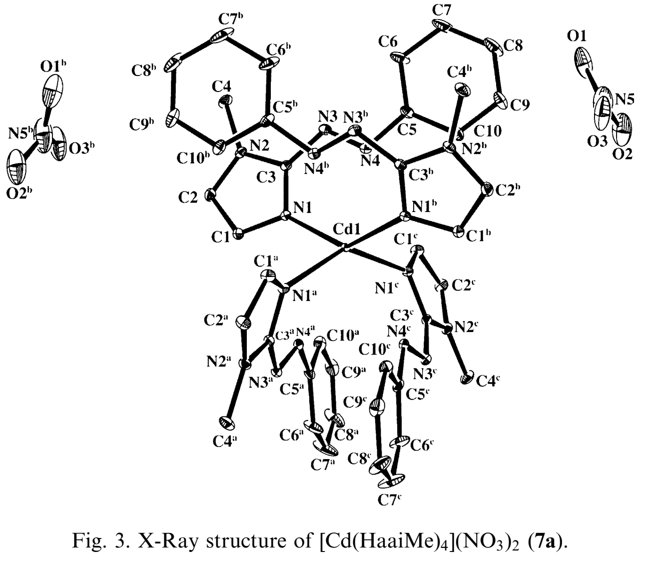


Fig. 3. X-Ray structure of $[\mathrm{Cd(HaaiMe)_4}](\mathrm{NO_3})_2$ (**7a**).

Table 4
Selected bond distances (Å) and angles (°) for $[Cd(HaaiMe)_4](NO_3)_2 \cdot 2H_2O$ (**7a**)

Bond distances		Bond angles	
Cd–N(1)[A]	2.283(3)	N(1)^a–Cd(1)–N(1)^b	96.89(5)
N(1)–C(3)	1.326(5)	N(1)^a–Cd(1)–N(1)	139.49(16)
N(1)–C(1)	1.356(5)	N(1)^b–Cd(1)–N(1)	96.88(5)
N(3)–N(4)	1.263(5)	N(1)^a–Cd(1)–N(1)^c	96.88(5)
N(3)–C(3)	1.374(5)	N(1)^b–Cd(1)–N(1)^c	139.49(16)
N(4)–C(5)	1.412(5)	N(1)–Cd(1)–N(1)^c	96.88(5)
N(5)–O(2)	1.195(15)	C(1)–N(1)–Cd(1)	130.4(3)
N(5)–O(3)	1.228(18)	N(4)–N(3)–C(3)	112.3 (3)
N(5)–O(1)	1.275(18)	N(1)–C(3)–N(3)	128.1(4)
		N(3)–N(4)–C(5)	115.7(3)
		Cd–(N1)–C(3)	120.9(3)
		O(2)–N(5)–O(3)	126.0(19)
		O(2)–N(5)–O(1)	107.9(17)
		O(3)–N(5)–O(1)	126(2)

[A] Cd–N(1)/N(1)$^{a/b/c}$ distances are the same.

Table 5
Contact distances in the anion framework of $[Cd(HaaiMe)_4](NO_3)_2 \cdot 2H_2O$ (**7a**)

Contact	Distance (Å)	Contact	Distance (Å)
O(1)···O(1)W^i	2.97(3)	O(1)···O(2)W	3.03(2)
O(2)···O(1)W^i	2.81(4)	O(3)···O(2)W	1.97(3)
O(3)···O(1)W	2.74(4)	O(3)···O(2)W^{ii}	2.82(4)
O(1)W···O(2)W^{ii}	2.72(3)	O(1)W···O(2)W	2.97(3)
O(2)W···O(2)W	2.60(3)^{iii}		

Symmetry code: (i) $x, 1/2+y, -z$; (ii) $-1-x, 1/2-y, z$; (iii) $1/4-y, 3/4+x, -1/4-z$.

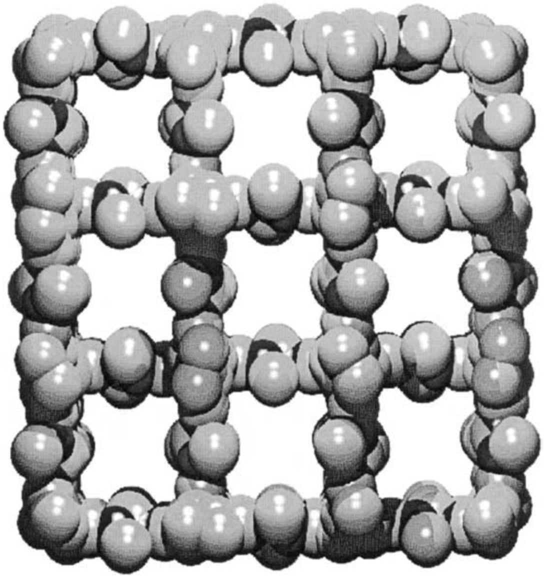


Fig. 5. Interlocked anion framework of the square-grid supramolecule in the *ab*-plane (grid dimension ca. 7 × 7 Å).

dimension ca. 7 × 7 Å as shown in Fig. 5. Every square grid is interlocked by chains parallel to the *Z*-axis passing through the middle of the square arms to form a layer in the *ac*- (or *bc*-) plane with brick-wall topology (dimension 11.2 × 7 Å) (Fig. 6). These interactions facilitate the generation of an infinite 3D supramolecular anion network. The channels parallel to the *Y*-axis are filled with cationic species, $Cd(HaaiEt)_4^{2+}$, of whose the pendant arm, coordinated HaaiEt, penetrates into the square grid voids (looking like two antenna of a cockroach). It should be mentioned that though the anion network formation is evident from figures, Figs. 4–6, due to the symmetry-imposed disorder of NO_3^- (vide supra) it is really impossible to segregate the two-disorder parts of the network.

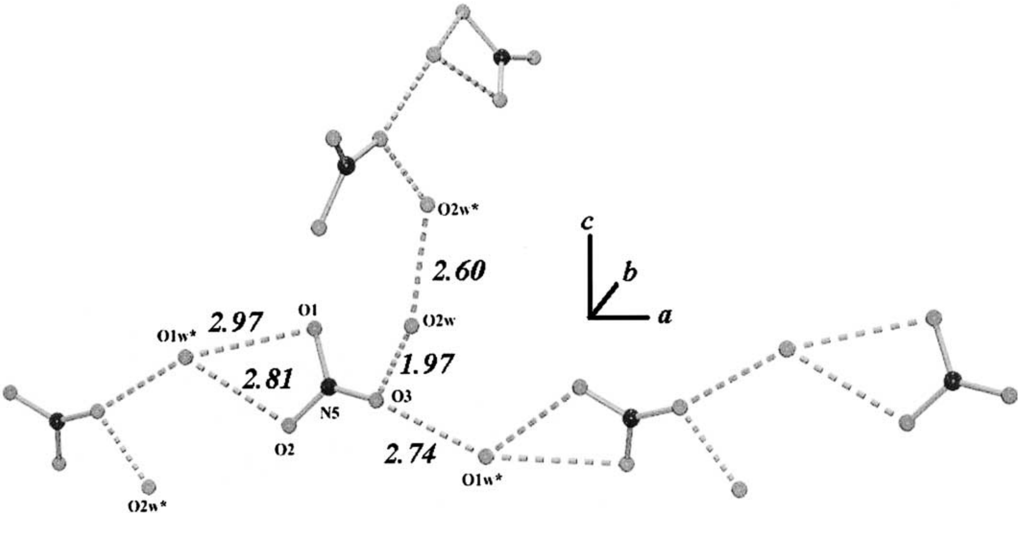


Fig. 4. A perspective view of a part of the anion framework showing the $-NO_3^-$–O(water)– interactions (doted line) in the structure of **7a**.

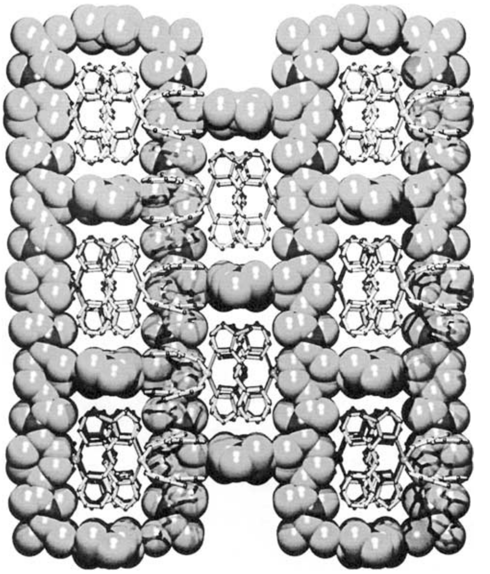


Fig. 6. A view of the brick-walled channel (dimension 11.2 × 7 Å) filled with cations in the *ac*-/*bc*-plane.

3.3. Spectral studies

The IR stretching frequencies of the complexes are assigned by comparing with the free ligand values [52]. Not all the bands have been assigned and some significant stretching frequencies are set out. The $\nu(N=N)$ is shifted to a lower frequency by 20–30 cm^{-1} compared to the free ligand value. $Cd(RaaiR')_2Cl_2$ show two $\nu(Cd–Cl)$ at ca. 324 and ca. 298 cm^{-1}. The $\nu(ClO_4)$ of $[Cd(RaaiR')_4](ClO_4)_2$ appears at 1082–1091cm^{-1} with a weak stretch at 624–627 cm^{-1}. The $\nu(NO_3)$ of $[Cd(RaaiR')_4](NO_3)_2$ appear at ca. 1382–1384 cm^{-1}.

The reflectance spectra of the complexes show intense bands at 470–490 and 360–380 nm along with a weak transition at 500–510 nm. These intense transitions correspond to intra-ligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions [52].

The ^1H NMR spectra of $Cd(RaaiR')_2Cl_2$ and $Cd(RaaiR')_4X_2$ ($X = NO_3$, ClO_4) are recorded in $CDCl_3$. The spectral data are set out in Table 6. Data reveal that the signal in the spectra of $Cd(RaaiR')_4X_2$ are shifted to higher δ values compared to $Cd(RaaiR')_2Cl_2$. Imidazole protons 4- and 5-H appear at lower δ values, in general, relative to aryl protons 7-H to 11-H. On comparison with free ligand data the imidazole protons (4- and 5-H) suffer significant shifting to higher δ values by ~0.5 and 0.4 ppm, respectively. The aryl protons are also shifted by 0.1–0.4 ppm. This is in support with the bonding of imidazole-N → Cd(II) in the complexes and overall charge drifting from the ligand. Aryl signals shift to the lower field side on Me-substitution to the aryl ring. This may be due to the electron donating effect of the Me-group.

3.3.1. Thermal studies

Effect of temperature on the complexes has been carried out on representative compounds. Because of the explosive nature of ClO_4^- and NO_3^- salts, the thermal program of **5b** and **7b** are restricted to the temperature range 300–450 K while the thermogram of **3b** has been observed up to 800 K. In the case of $Cd(MeaaiMe)_2Cl_2$ (**3b**) mass loss has been observed in the temperature range 480–540 K and corresponds to loss of coordinated MeaaiMe groups. The final residue is observed at 750 K which corresponds to CdO. $Cd(MeaaiMe)_4(ClO_4)_2$ does not show any thermal loss up to 480 K. We did not proceed further to prevent any damage to equipment due to a possible explosion. This observation supports that there is no coordinated or crystallized water or methanol (since preparation has been done from water–methanol, see Section 2) to the molecule. $Cd(MeaaiMe)_4(NO_3)_2$ (**5b**) shows two overlapped thermal loss

Table 6
^1H NMR spectral data in $CDCl_3$

Compounds	4-H[a]	5-H[a]	7-H[b]	11-H[b]	8,10-H	9-H	$1-CH_3/–CH_2–CH_3$	Me
$Cd(HaaiMe)_2Cl_2$ (**3a**)	7.44	7.22	8.05 (8.0)	8.05 (8.0)	7.52[c]	7.52[c]	4.13	
$Cd(MeaaiMe)_2Cl_2$ (**3b**)	7.40	7.20	7.91 (8.5)	7.91[b] (8.5)	7.31[b] (8.5)		4.13	2.42
$Cd(HaaiEt)_2Cl_2$[d] (**4a**)	7.45	7.25	8.08 (9.0)	8.08 (9.0)	7.55[c]		4.84[e] (15.0)	
$Cd(MeaaiEt)_2Cl_2$[d] (**4b**)	7.42	7.20	7.94 (8.0)	7.44 (8.0)	7.34[b] (8.0)		4.80[e]	2.44
$[Cd(HaaiMe)_4](ClO_4)_2$ (**5a**)	7.48	7.34	7.90 (10.0)	7.90 (10.0)	7.52[c]		3.99	
$[Cd(MeaaiMe)_4](ClO_4)_2$ (**5b**)	7.55	7.39	7.94 (10.0)	7.94 (10.0)	7.58[b] (8.0)		4.04	2.46
$[Cd(HaaiEt)_4](ClO_4)_2$[d] (**6a**)	7.60	7.44	8.05 (9.0)	8.05 (9.0)	7.68[c]		4.94[e] (20.0)	
$[Cd(MeaaiEt)_4](ClO_4)_2$[d] (**6b**)	7.55	7.40	7.92 (9.0)	7.92 (9.0)	7.24[b] (8.0)		4.55[e] (20.0)	2.44
$[Cd(HaaiMe)_4](NO_3)_2$ (**7a**)	7.50	7.36	7.85 (9.0)	7.85 (9.0)	7.45[c]		4.11	
$[Cd(MeaaiMe)_4](NO_3)_2$ (**7b**)	7.56	7.38	7.94 (8.0)	7.94 (8.0)	7.29[b] (8.0)		4.18	2.45
$[Cd(HaaiEt)_4](NO_3)_2$[d] (**8a**)	7.43	7.35	7.86 (8.0)	7.86 (8.00	7.50[c]		4.45[e] (20.0)	
$[Cd(MeaaiEt)_4](NO_3)_2$[d] (**8b**)	7.62	7.36	7.91 (10.0)	7.91 (10.0)	7.23 (8.0)		4.52[e] (22.0)	2.44

[a] Broad singlet.

[b] Doublet.

[c] Multiplet.

[d] $\delta[(1-CH_2)–CH_3]$, 1.52 (7.5) (**4a**), 1.49 (7.5) (**4b**), 1.52 (**6a**), 1.55 (**6b**), 1.57 (**8a**), 1.55 (**8b**).

[e] Quintet.

steps within the temperature range 350–380 and 415–440 K and the overall loss corresponds to two moles of H_2O. This is revealed from the X-ray crystal structure study of the complex.

4. Conclusion

In this paper we have accounted for the effect of the anion on the structure of molecules being formed from cadmium(II) and 1-alkyl-2-(arylazo)imidazoles (RaaiR′). Chloride (Cl^-) has a stronger affinity to Cd(II) and thus forms $Cd(RaaiR')_2Cl_2$. The oxo anions, perchlorate (ClO_4^-) and nitrate (NO_3^-), prefer to synthesize tetrakis derivatives $Cd(RaaiR')_4^{2+}$. In solution at lower M:L ratio (1:2.5) precipitated compounds are $[Cd(RaaiR')_2(H_2O)_2]_2^{2+}$; however, in an equilibriated solution on crystallization $Cd(RaaiR')_4^{2+}$ are precipitated. Single crystal structure determination helps us to identify the compounds. $Cd(HaaiMe)_4(NO_3)_2 \cdot 2H_2O$ provides a square-grid supramolecule interacting through a NO_3^-–HOH hydrogen bonded network and cation is grooved into the channel.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 209310 for $[Cd(HaaiEt)_4](ClO_4)_2$; CCDC No. 209311 for $[Cd(HaaiMe)_4](NO_3)_2 \cdot 2H_2O$ and CCDC No. 209312 for $[Cd(HaaiMe)_2Cl_2]$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J. Dinda, U.S. Ray, G. Mostafa, T.-H. Lu, A. Usman, I.A. Razak, S. Chantrapromma, H.K. Fun, C. Sinha, Polyhedron 22 (2003) 247.

[2] T.K. Misra, D. Das, C. Sinha, P.K. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672.

[3] S. Pal, D. Das, P. Chattopadhyay, C. Sinha, K. Panneerselvam, T.H. Lu, Polyhedron 19 (2000) 1263.

[4] P. Byabartta, Sk. Jasimuddin, B.K. Ghosh, C. Sinha, A.M.Z. Slawin, J.D. Woollins, New J. Chem. 26 (2002) 1415.

[5] P. Byabartta, J. Dinda, P.K. Santra, C. Sinha, K. Panneerselvam, F.-L. Liao, T.-H. Lu, J. Chem. Soc., Dalton Trans (2001) 2825.

[6] P. Byabartta, S. Pal, C. Sinha, F.-L. Liao, K. Paneerselvam, T.-H. Lu, J. Coord. Chem. 55 (2002) 479.

[7] D. Das, T.K. Misra, C. Sinha, Transition Met. Chem. 23 (1998) 233.

[8] J. Dinda, P.K. Santra, C. Sinha, L.R. Falvello, J. Organomet. Chem. 629 (2001) 28.

[9] S. Pal, D. Das, P. Chattopadhyay, C. Sinha, K. Panneerselvam, T.-H. Lu, Polyhedron 19 (2000) 1263.

[10] S. Pal, D. Das, C. Sinha, C.H.L. Kennard, Inorg. Chim. Acta 313 (2001) 21.

[11] P.K. Santra, T.K. Misra, C. Sinha, Indian J. Chem. A 38 (1999) 82.

[12] D. Das, A.K. Das, C. Sinha, Talanta 48 (1999) 1013.

[13] J.K. Nag, P.K. Santra, C. Sinha, F.-L. Liao, T.H. Lu, Polyhedron 20 (2001) 2253.

[14] B.G. Chand, U.S. Ray, J. Cheng, T.-H. Lu, C. Sinha, Polyhedron 22 (2003) 1213.

[15] K. Bag, T.K. Misra, C. Sinha, J. Indian Chem. Soc. 75 (1998) 421.

[16] B. Chand, U. Ray, P.K. Santra, G. Mostafa, T.-H. Lu, C. Sinha, Polyhedron 22 (2003) 1205.

[17] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley, New York, 1988.

[18] J.E. Huheey, Inorganic Chemistry, 3rd ed., Harper International SI ed., New York, 1983.

[19] Y.-C. Liang, M.-C. Hong, R. Cao, W.-P. Su, Y.-J. Zhao, J.B. Weng, Polyhedron 20 (2001) 2477.

[20] L.C. Tabares, J.A.R. Navarro, J.M. Salas, J. Am. Chem. Soc. 123 (2001) 383.

[21] Y.-J. Zhao, M.-C. Hong, Y.-C. Liang, W.-P. Su, R. Cao, Z.-Y. Zhou, A.S.C. Chan, Polyhedron 20 (2001) 2619.

[22] R.S. Rarig, J. Zubieta, Inorg. Chim. Acta 319 (2001) 235.

[23] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. 116 (1994) 1151.

[24] B. Sui, J. Fan, T.A. Okamura, W.Y. Sun, N. Ueyama, New J. Chem. 25 (2001) 1379.

[25] P.S. Mukherjee, T.K. Maji, G. Mostafa, W. Hibbs, N.R. Chaudhuri, New J. Chem. 25 (2001) 760.

[26] A.J. Blake, N.R. Champness, S.S.M. Chung, W.-S. Li, M. Schröder, Chem. Commun. (1997) 1675.

[27] C.-Y. Su, Y.-P. Cai, C.-L. Chen, F. Lissner, B.-S. Kang, W. Kaim, Angew. Chem., Int. Ed. 41 (2002) 3371.

[28] K. Jin, X. Huang, L. Pang, J. Li, A. Appel, S. Wherland, Chem. Commun. (2002) 2872.

[29] M. Rivas, J.C. Brammer, Coord. Chem. Rev. 183 (1999) 43.

[30] A. Datta, G.M. Golzar Hossain, N.K. Karan, K.M. Abdul Malik, S. Mitra, Inorg. Chem. Commun. 6 (2003) 658.

[31] D. Braga, F. Grepioni, J.J. Novoa, Chem. Commun. (1998) 1959.

[32] J.J. Novoa, I. Nobeli, F. Grepioni, D. Braga, New J. Chem. 24 (2000) 5.

[33] D. Braga, F. Grepioni, E. Tangliavini, J.J. Novoa, F. Mota, Chem. Eur. J. 6 (2000) 4536.

[34] P. Mukhopadhyay, P.K. Bharadwaj, G. Savitha, A. Krishnan, P.K. Das, Chem. Commun. (2000) 1815.

[35] H. Zhang, X. Wang, K. Zhang, B.K. Teo, Coord. Chem. Rev. 183 (1999) 157.

[36] A.M. Golub, H. Kohler, V.V. Skepenko, Chemistry of Pseudohalides, Elsevier, Amsterdam, 1986.

[37] J. Ribas, M. Monfort, B.K. Ghosh, X. Solans, M. Font-Bardia, J. Chem. Soc., Chem. Commun. 1986 (1995) 2375.

[38] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.

[39] Cadmium in the environment and its significance to man, Pollution paper No. 17, Her Majesty's Stationery Office, London, 1980.

[40] Sax's Dangerous Properties of Industrial Materials, ninth ed., 617 pp.

[41] R.M. Izatt, J.J. Christensen, J.H. Rytting, Chem. Rev. 71 (1971) 439.

[42] Bruker (1998). SMART and SAINT. Bruker AXS Inc., Madison, WI, USA.

[43] SADABS: Area-Detector Absorption Correction, Siemens Industrial Automation Inc., Madison, WI, 1996.

[44] G.M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.

[45] A.L. Spek, PLATON, Molecular Geometry Program, University of Utrecht, The Netherlands, 1999.

[46] L.J. Farrugia, ORTEP-3 for Windows, J. Appl. Cryst. 30 (1997) 565.

[47] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) SI.

[48] D. Das, Ph.D. Thesis, Burdwan University, Burdwan, India, 1998.

[49] A. Saha, C. Das, S. Goswami, S.-M. Peng, Indian J. Chem. A 40 (2001) 198.

[50] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C: Mathematical, Physical and Chemical Tables, Kluwer Academic Publishers, Dordrecht, 1995, Table 9.6.3.3.

[51] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C: Mathematical, Physical and Chemical Tables, Kluwer Academic Publishers, Dordrecht, 1995, Table 9.5.1.1.

[52] T.K. Misra, Ph.D. Thesis, Burdwan University, Burdwan, India, 1999.