FULL PAPER

Synthesis and Structural Characterization of Cadmium(II) and Mercury(II) Complexes Derived from 3-Aminoquinoline

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Two novel metal complexes derived from interactions of Cd^{2+} and Hg^{2+} ions with 3-aminoquinoline in the molar ratio 1:2 are reported. The synthesized and isolated metal complexes were characterized by UV/VIS, FT-IR, ^{1}H- and ^{13}C-NMR, and ESI-MS spectroscopic studies, and elemental analyses. FT-IR and NMR studies confirmed that the NH_2 group remains uncoordinated in both synthesized complexes. The molecular structure of the Cd^{II} complex was additionally determined by X-ray single-crystal analysis. The Cd complex crystallizes in the triclinic centrosymmetric $P\bar{1}$ space group. Moreover, the Cd^{II} complex exists as neutral discrete molecule and was found to show tetrahedral geometry.

Introduction. – Quinoline derivatives are a very important class of nitrogen-containing heterocycles and find extensive applications in the pharmaceutical industry as intermediates in the synthesis of antimalarial drugs [1][2]. In recent years, quinoline and its derivatives have received a lot of attention in coordination chemistry because of their structural, chemical, electrochemical, photophysical, photochemical, and catalytic properties [2][3]. Furthermore, it has been reported that complexes involving H-atom donors, such as N-containing heterocyclic and NH_2 groups, are of significant importance in various biological and photochemical processes [2][3]. Moreover, the use of the quinoline N-atom as coordinating atom has been an important target when coordination of Group XII metal ions is taken into consideration, since it combines two complementary and important features. Importantly, the marked coordinating capability of the N-atom, coupled with the chromophoric characteristics of the quinoline ring, induces the formation of stable metal complexes with potential photophysical properties [4–6]. Moreover, Group XII metal complexes containing a stable d^{10} electronic configuration find significant applications in the field of inorganic chemistry, biochemistry, and environmental chemistry, and also have been studied as potential luminescent materials [7–10]. Herein, we are exploring the coordination chemistry of 3-aminoquinoline with divalent metal ions, *viz.*, Cd^{2+} and Hg^{2+} ions. The new complexes have been characterized by UV/VIS, FT-IR, ^{1}H- and ^{13}C-NMR, and ESI-MS studies, and elemental analyses. In addition, the molecular structure of the Cd^{II} complex has been ascertained by X-ray single-crystal analysis.

Results and Discussion. – 3-Aminoquinoline (*Fig. 1*) acts as monodentate ligand and coordinates to the metal ions, Cd^{2+} and Hg^{2+}, *via* the quinoline N-atom in the molar ratio 2:1. The structures of the two synthesized complexes were ascertained on the basis of various studies, *viz.*, UV/VIS, FT-IR, NMR, ESI-MS, and elemental analyses. Additionally, the Cd^{II} complex was investigated by X-ray single-crystal analysis. Both complexes were colored diamagnetic solids, stable at room temperature, and obtained in excellent yields. Crystallographic data and refinement details for the structural analysis of complex **1** are summarized in *Table 1.*

Table 1. *Crystallographic Data and Structure Refinement for Complex* **1**

Identification code	epr259
Empirical formula	$C_{18}H_{16}CdI_2N_4$
M_r	654.55
Crystal size [mm]	$0.38 \times 0.21 \times 0.12$
T [K]	298
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
a [Å]	8.468(5)
b [Å]	8.473(5)
c [Å]	13.748(9)
α [°]	89.221(9)
β [°]	85.463(9)
γ [°]	89.901(9)
V [Å^3]	983.3(11)
D_x (calc.) [g cm^{-3}]	2.211
μ [mm^{-1}]	4.258
F(000)	612.0
2θ Range for data collection [°]	2.972–52.422
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-17 \le l \le 16$
Reflections collected	7682
Independent reflections	3868 [$R_{int} = 0.0217$, $R_{\sigma} = 0.0275$]
Data/restraints/parameters	3868/0/242
Goodness-of-fit on F^2	1.117
Final R indeces [$I \geq 2\sigma(I)$]	$R^1 = 0.0252$, $wR^2 = 0.0622$
Final R indeces (all data)	$R^1 = 0.0271$, $wR^2 = 0.0632$
Largest diff. peak/hole [e Å^{-3}]	0.37/−0.82

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Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *of Complex* **1**

Cd1–I1	2.7123(14)	C11–N4	1.355(5)
Cd1–I2	2.7092(13)	C2–N3	1.353(5)
Cd1–N1	2.299(3)	C18–N2	1.364(4)
Cd1–N2	2.269(3)	C9–N1	1.355(4)
C1–N1	1.322(4)	C10–N2	1.306(4)
I2–Cd1–I1	112.30(4)	N3–C2–C1	119.2(3)
N1–Cd1–I2	104.80(8)	N3–C2–C3	123.4(3)
N1–Cd1–I1	113.83(8)	N1–C9–C4	120.4(3)
N2–Cd1–I2	118.21(7)	N1–C9–C8	120.2(3)
N2–Cd1–I1	108.49(7)	C1–N1–C9	118.8(3)
N2–Cd1–N1	98.55(10)	C10–N2–C18	119.1(3)
C1–N1–Cd1	116.2(2)	N2–C10–C11	124.8(3)
C9–N1–Cd1	123.9(2)	N4–C11–C10	120.0(3)
C10–N2–Cd1	118.7(2)	N4–C11–C12	123.1(4)
C18–N2–Cd1	121.9(2)	N2–C18–C13	119.3(3)
N1–C1–C2	124.0(3)	N2–C18–C17	120.3(3)

Table 3. *H-Bonding Parameters of Complex* **1**

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	∢DHA [°]	Symmetry code
N3–H3A···I1	0.90	2.86	3.742	167	*x*, −1+*y*, *z*
N4–H4B···I2	0.75	2.96	3.687	165	1+*x*, *y*, *z*

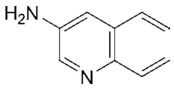

Fig. 1. *Structure of 3-aminoquinoline used in the synthesis of Cd^{II} and Hg^{II} complexes*

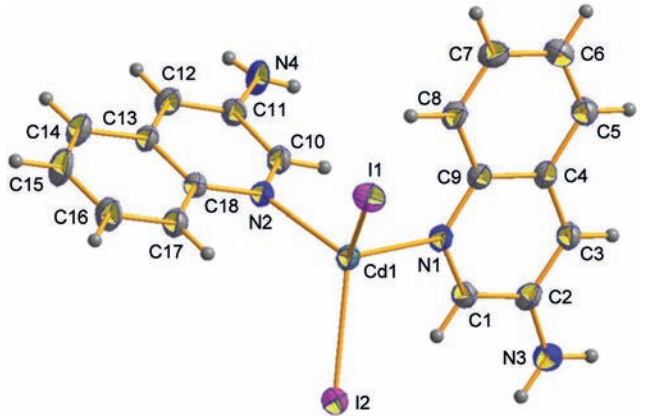

Fig. 2. *Crystal structure of complex* **1**. Thermal ellipsoids are drawn at 30% probability level except for H-atoms, which are shown as circles of arbitrary radius.

Selected bond lengths and bond angles with their estimated standard deviations are presented in *Table 2*, while selected parameters for weak interactions are listed in *Table 3*. Thermal ellipsoidal plots of complex **1** are shown in *Fig. 2*. X-Ray single-crystal analysis revealed that complex **1** crystallizes in the triclinic centrosymmetric P$\bar{1}$ space group. The whole complex exists as a neutral discrete molecule in each asymmetric unit, and there are two such molecules in the unit cell. In the crystal structure, each Cd^{2+} ion is coordinated with two N-atoms of the 3-aminoquinolone rings and two I^{-} ions in a tetrahedral geometry (*Fig. 3, a*). Each Cd^{II} complex is linked to the next one *via* N–H···I H-bonds along the crystallographic *b* axis, and two such chains are stabilized by $\pi \cdots \pi$ stacking interactions between two 3-aminoquinoline moieties at a distance of 3.52 Å resulting in a 2D sheet-like supramolecular structure along the crystallographic *b* axis (*Fig. 3, b*). IR Data obtained for both complexes, as well as for 3-aminoquinoline, are listed in the *Exper. Part*. The stretching bands at 3000–3450 cm^{-1} due to the NH$_2$ group in both complexes indicate that the NH$_2$ group remains unaffected during complexation. Moreover, the bands at 1350–1375 cm^{-1} are attributed to C–NH$_2$ stretching vibrations [11]. Furthermore, stretching bands observed at 1450–1608 cm^{-1} are associated with C=C (quinoline) bands due to π-electronic redistribution in the heterocyclic ligand caused by metalllation of the quinoline N-atom [12][13]. The ^{1}H-NMR spectra of Cd^{II} and Hg^{II} complexes showed a certain high-frequency shift with respect to the free 3-aminoquinoline ligand. The decrease in the electron density in the heterocyclic aromatic ring caused by the coordination of the quinoline N-atom to the metal atom brings about deshielding of the atoms adjacent to the ligation sites. Thus, significant downfield shifts were observed for 3-aminoquinoline H-atoms in both complexes (Figs. 1S and 2S in the *Supporting Information* (SI)[1])). Furthermore, ^{13}C-NMR spectra of the complexes showed the largest downfield shifts for C–N and C–NH$_2$ C-atoms (Figs. 3S and 4S in the SI). The UV/VIS spectra of the complexes, recorded in MeOH, exhibited an intense band at 350–400 nm due to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [14][15]. Furthermore, absorption bands

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[1]) Supporting material is available upon request from the authors.

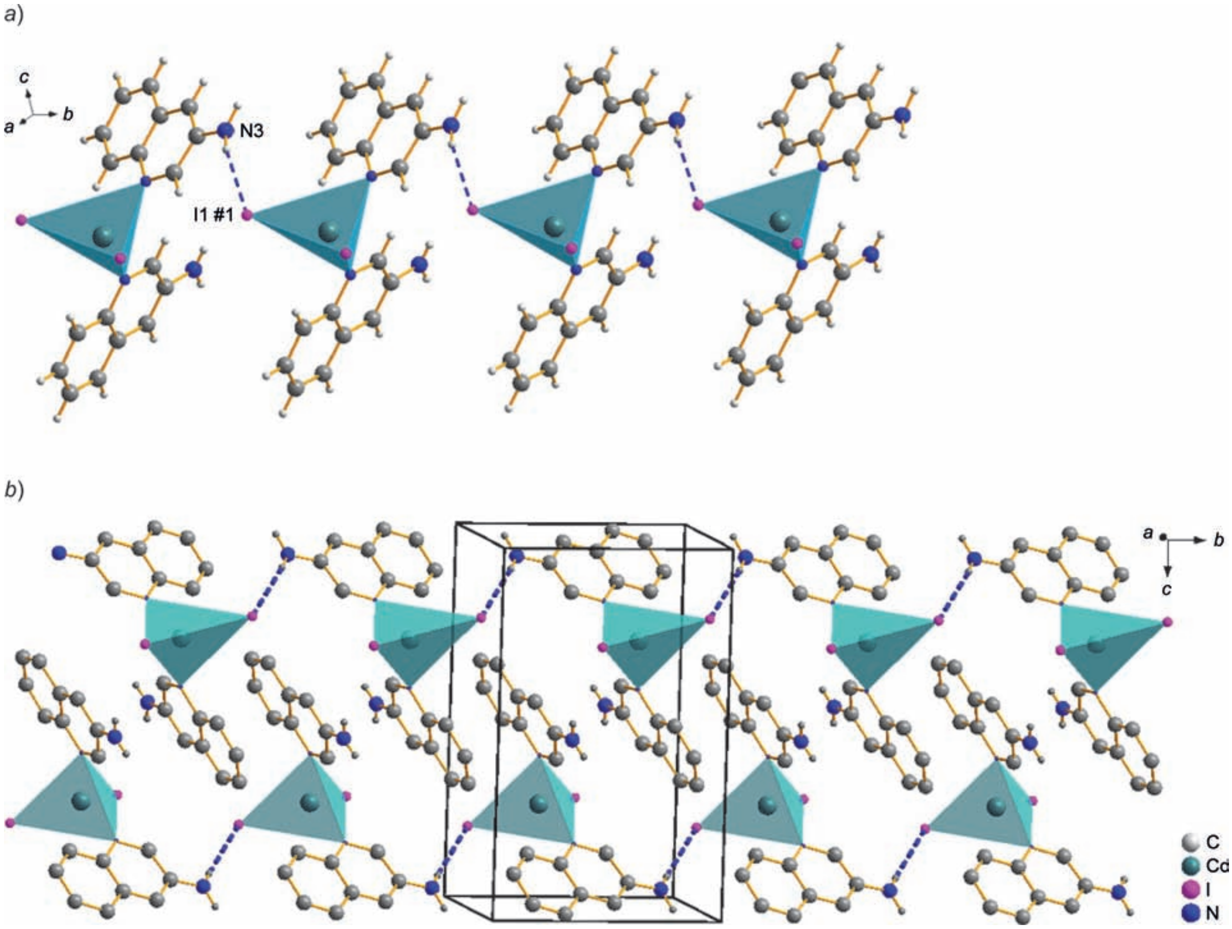

Fig. 3. a) *1D Chine formed by N–H···I H-bonds.* b) *2D Sheet-like supramolecular structure along the crystallographic* b *axis.*

observed at 270 nm may be assigned to metal charge transfers for their d^{10} electronic configuration. A weak transition in the visible region (440–500 nm) is assigned to a MLCT band [14][15]. ESI-MS Spectra of Cd^{II} and Hg^{II} complexes exhibited molecular-ion peaks ($[M+H]^+$) at *m/z* 655.56 (calc. 655.85) and 561.05 (calc. 561.05) corresponding to their molecular formulae, $C_{18}H_{16}CdI_2N_4$ and $C_{18}H_{16}Cl_2HgN_4$, respectively.

Conclusions. – We have reported two complexes of Cd^{2+} and Hg^2 ions derived from 3-aminoquinoline. The Cd^{II} complex has been studied by X-ray crystallography which revealed that this complex shows tetrahedral geometry formed by two N-atoms of the 3-aminoquinoline ligands and two I^- ions.

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Experimental Part

General. All chemicals and solvents, *viz.*, MeOH, 3-aminoquinoline, CdI_2, and $HgCl_2$, were purchased from *Sigma–Aldrich*. UV/VIS Spectra: *Pharmacia LKB-Biochem* UV/VIS spectrophotometer; in MeOH; at r.t.; λ_{max} in nm. FT-IR Spectra: *PerkinElmer 621* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *JEOL-400* spectrometer (400 and 100 MHz, resp.); in (D_6)DMSO; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS (pos.): *Ion Trap LC/MS 6320* mass spectrometer (*Agilent Technologies*); in *m/z*. Elemental analyses: *Elementar Vario EL* analyzer; in %.

X-Ray Single-Crystal Analysis of Complex **1**[2]). Single crystals of complex **1**, $C_{18}H_{16}CdI_2N_4$, grew in the form of plate from MeOH/H_2O 3:1. Intensity data for complex **1** were recorded on a *Bruker Smart Apex* diffractometer equipped with a CCD detector, using monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at r.t. The structures were solved by direct methods and the refinements were carried out against F^2 using SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically; H-atoms were included using a riding model. H-Atoms attached to the N-atom were located from difference *Fourier* maps and refined isotropically in both cases. The relevant crystallographic data and structure refinement details of complex **1** are listed in *Table 1.*

Synthesis of Complex **1***, [Cd(Aquin)$_2$I$_2$].* To a MeOH soln. of 10 ml of CdI_2 (0.5 mmol), a soln. of 3-aminoquinoline (1 mmol, 144 mg) dissolved in minimum quantity of MeOH was added dropwise resulting in a colored soln. The resulting mixture was dried under air at r.t., washed with Et_2O and hexane, and recrystallized from MeOH/H_2O 3:1. Yellow crystals, suitable for X-ray single-crystal analysis, were obtained by slow evaporation of the solvent.

Synthesis of Complex **2***, [Hg(Aquin)$_2$Cl$_2$].* The Hg^{II} complex was synthesized in an analogous way using $HgCl_2$.

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[2]) CCDC-1033788 contains the supplementary crystallographic data for $[Cd(Aquin)_2I_2]$. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

[Cd(Aquin)$_2$I$_2$] (**1**). Yield: 80%. IR: 3400 (NH_2), 1350 (C–NH_2). ^{1}H-NMR: 8.43 (*s*, N=CH–C); 7.60 – 7.29 (*m*, Ar–H); 7.12 (*s*, –CH=C–N); 5.65 (*s*, NH_2). ^{13}C-NMR: 144.0; 142.9; 141.5; 130.0; 129.0; 126.9; 126.9; 124.0; 111.9. ESI-MS: 655.56 ([M + H]$^+$). Anal. calc. for $C_{18}H_{16}CdI_2N_4$ (654.57): C 33.03, H 2.46, N 8.56; found: C 32.95, H 2.41, N 8.51.

[Hg(Aquin)$_2$Cl$_2$] (**2**). Yield: 85%. Yellow crystals. IR: 3370 (NH_2), 1375 (C–NH_2). ^{1}H-NMR: 8.48 (*s*, N=CH–C–); 7.89 – 7.34 (*m*, Ar–H); 7.21 (*s*, –CH=C–N); 5.84 (*s*, NH_2). ^{13}C-NMR: 143.9; 143.1; 140.7; 130.2; 128.4; 128.4; 127.2; 124.8; 113.1. ESI-MS: 561.05 ([M + H]$^+$). Anal calc. for $C_{18}H_{16}Cl_2HgN_4$ (559.84): C 38.62, H 2.88, N 10.01; found: C 38.55, H 2.81, N 9.93.

Unfortunately, we couldn't obtain crystals suitable for X-ray single-crystal analysis for complex **2**.

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