Res Chem Intermed (2013) 39:2451–2461
DOI 10.1007/s11164-012-0771-y

Novel di-μ-chloro-bis[chloro(4,7-dimethyl-1,10-phenanthroline)cadmium(II)] dimer complex: synthesis, spectral, thermal, and crystal structure studies

Ismail Warad · Maha Al-Ali · Belkheir Hammouti · Taibi Ben Hadda · Rami Shareiah · Mohamed Rzaigui

Received: 21 July 2012 / Accepted: 16 August 2012 / Published online: 1 September 2012

Abstract A novel di-μ-chloro-bis[chloro(4,7-dimethyl-1,10-phenanthroline)cadmium(II)] dimer complex has been prepared by reacting $CdCl_2{\cdot}2.5H_2O$ with 4,7-dimethyl-1,10-phenanthroline (dmphen) ligand. The complex was characterized on the basis of elemental analysis, FAB-MS, IR, UV–visible, ^{1}H, and ^{13}C NMR spectroscopy, TG/DTA, and X-ray single-crystal diffraction studies. The Cd(II) ions in $[CdCl_2(C_{14}H_{12}N_2)]_2$ are coordinated to three Cl atoms with the centrosymmetric dimer bridged through the Cl atoms and two N atoms in a slightly distorted square-pyramidal disposition. Several hydrogen bonds formed between the terminal Cl atoms and H-Me/H-Ph groups may stabilize the structure in the dimer form.

I. Warad (✉)
Department of Chemistry, Science College, King Saud University,
P. O. Box 2455, Riyadh 11451, Saudi Arabia
e-mail: warad@ksu.edu.sa

M. Al-Ali
Department of Chemistry, College of Science, University of Hail,
P. O. Box 2440, Hail, Saudi Arabia

B. Hammouti
LCAE-URAC18, Faculté des Sciences, Université Mohammed Ier, 60000 Oujda, Morocco

T. B. Hadda
Laboratoire Chimie Matériaux, FSO, Université Mohammed Ier, 60000 Oujda, Morocco

R. Shareiah
Department of Basic Science, Allied Medical Science College,
Applied Science Private University, P. O. Box 166, Amman 11931, Jordan

M. Rzaigui
Laboratoire de Chimie des Matériaux, Facultédes Sciences de Bizerte,
7021 Zarzouna Bizerte, Tunisia

Keywords Cadmium(II) dimer complex · 2,9-Dimethyl-1,10-phenanthroline · Single crystal structure

Introduction

There has been particular emphasis on developing new metal complexes with extended planar aromatic ligands to enhance noncovalent binding to transition metal ions. Ligands such as 2,2-bipyridine (bpy), 2,2-bipyridylamine (bpa), and 1,10-phenanthroline (phen) and their derivatives have been found very suitable in this respect [1–5]. As a result of rotational flexibility around the carbon–carbon single bond bridging the two pyridine rings of bpy, and the central amine bridging the two pyridine rings of bpa, the two pyridine planes adopt either a coplanar or tilted conformation in coordination with the metal centers [6, 7]. However, such rotational flexibility is not possible for phen ligands, which remain coplanar even after metal-coordination.

Cadmium(II) ions have been found to induce a variety of pathological conditions, for example cardiovascular diseases, hypertension, and cancer [8, 9]. Cadmium can replace the zinc of superoxide dismutase (SOD) and this results in a drop in the biological activity of SOD [10].

As a part of our ongoing studies on the synthesis of new ligands and their coordination transition metal complexes, and use of these for studies of structural, medicinal, and catalytic application [11–21], we report here the synthesis and crystal structure of the novel di-μ-chloro-bis[chloro(4,7-dimethyl-1,10-phenanthroline)cadmium(II)] dimer complex for the first time. Elemental analysis, FAB-MS (mass spectrometry), FT-IR, electronic absorption, thermal, and NMR studies are also reported.

Experimental

Materials and instrumentation

4,7-Dimethyl-1,10-phenanthroline (dmphen) ligand and cadmium chloride hemipentahydrate $CdCl_2 \cdot 2.5H_2O$ were purchase from Across and used as received. Elemental analysis was performed on an Elementar Vario EL analyzer. High-resolution liquid ^{1}H, ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies were: ^{1}H NMR: 250.12 MHz, ^{13}C{^{1}H} NMR: chemical shifts in the ^{1}H and ^{13}C{^{1}H} NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Mass spectra were obtained by FAB-MS with a Finnigan 711A (8 kV), modified by AMD and are reported as mass-to-charge ratio (*m*/*z*).

General procedure for preparation of the dimer complex

A solution of dmphen (0.08 g, 3.51 mmol) in CH_2Cl_2 (5 ml) was added to a solution of $CdCl_2 \cdot 2.5H_2O$ (0.07 g, 3.51 mmol) in dry ethanol (10 ml) and the mixture was then stirred for 3 h at room temperature in an open atmosphere. The solution obtained was concentrated to approximately 1 ml under reduced pressure and mixed with 40 ml diethyl ether (yield; 0.12 g, 78 %). Suitable crystals for X-ray diffraction experiments were obtained by diethyl ether diffusion to a solution in CH_2Cl_2. Colorless prisms were isolated after two days.

$CdCl_2 \cdot 2.5H_2O$ was treated with dmphen ligand to produce the dimer complex of formula $[CdCl_2(C_{14}H_{12}N_2)]_2$ as a white powder, mp = 208 °C. ^1H NMR ($CDCl_3$): δ (ppm) 2.91 (br, 12H, CH_3), 7.40–8.20 (3m, 12H, Ph, Py), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 25.78 (s, 4C, CH_3), 122.23–160.22 (6s, 24C, Ph, Py). MS $m/z = 783$ [M^+] for $C_{28}H_{24}Cl_3N_4Cd_2$. Calculated: C, 42.94; H, 3.09; N, 7.15; Cl, 18.11 %. Found: C, 42.58; H, 3.22; N, 7.01; Cl, 18.07 %.

X-ray structural analysis of the dimer complex

Crystallographic details obtained from determination of the structure of the complex are summarized in Table 1.

The X-ray data for the crystal of the dimer complex were collected with graphite-monochromated Ag $K\alpha$ radiation ($\lambda = 0.56087$ Å) which was used for measurement of intensity data in the ω-scan mode at a temperature of 298 K. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic temperature factor, for the non-hydrogen atoms. The hydrogen atoms

Table 1 Crystal data and structure refinement for the dimer complex

Empirical formula	$C_{28}H_{24}Cd_2Cl_4N_4$
Formula weight	783.13
Temperature	293 K
Wavelength	0.56087 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 9.973(3)$ Å, $\alpha = 90°$
	$b = 15.645(2)$ Å, $\beta = 107.93\ (3)°$
	$c = 9.706(4)$ Å, $\gamma = 90°$
Volume	1440.9(8) Å^3
Z	4
Density (calculated)	1.805 mg/m^3
Absorption coefficient	0.985 mm^{-1}
$F(000)$	768
Crystal size	0.33 × 0.27 × 0.19 mm
θ Range for data collection	2–28°
Reflections collected	10200
Independent reflections	7036 [$R_{(int)} = 0.061$]
Completeness to $\theta = 27.51°$	99.8 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Ag $K\alpha$ radiation	$\lambda = 0.56087$ Å

were located on the difference Fourier map and adjusted to 0.97 Å for bonded atoms. Cell parameters were determined from 35 to 50 automatically centered reflections. The intensity data were corrected for polarization and Lorentz effects. Structure solution and refinement of the structure were realized by use of crystallography software [22].

Results and discussion

Synthesis of the dimer complex

The title complex, which has a dimer structure, was prepared by use of a modification of our literature method [13, 14]. The complex was isolated in good yield from a simple, 3 h, RT reaction of one equivalent of dmphen ligand with $CdCl_2{\cdot}2.5H_2O$ under gentle, stirred, open atmosphere conditions, using mixture of dichloromethane and ethanol as solvent (Scheme 1). The white powder complex product is soluble in chlorinated solvents, for example chloroform and dichloromethane, and insoluble in alcohols, water, ethers, and *n*-hexane.

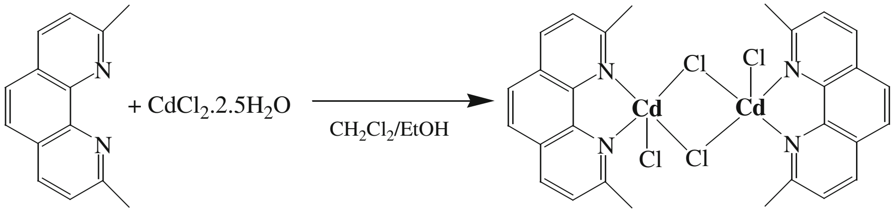
The structure of the complex was deduced from elemental analysis, infrared spectroscopy, electron-impact FAB-MS, TG/DTA, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray single-crystal structure measurements.

Elemental analyses and FAB-MS

The elemental analysis of the complex was in a good agreement with the proposed composition which is further confirmed by the molecular ion peak at $m/z = 783$ ("Experimental" section). The FAB-MS spectrum confirms the presence of the toxic Cd(II) ion in the complex. The spectrum contains eight peaks assigned to the formula $[Cd_2Cl_4(C_{14}H_{12}N_2)_2]^+$ (at $m/z = 783$, 100 % $[M]^+$; $m/z = 781$, 83.3 %; $m/z = 782$, 66.7 %; $m/z = 780$, 60.5 %; $m/z = 779$, 45.2 %; $m/z = 784$, 48.4 %; $m/z = 785$, 33.9 %; $m/z = 786$, 16.7 %) as seen in Fig. 1.

IR spectral investigation

IR analysis of the dimer complex revealed no water or solvent of coordination or adsorbed on the complex lattice. The IR spectra of the complexes were compared



Scheme 1 Synthesis of the dimer complex

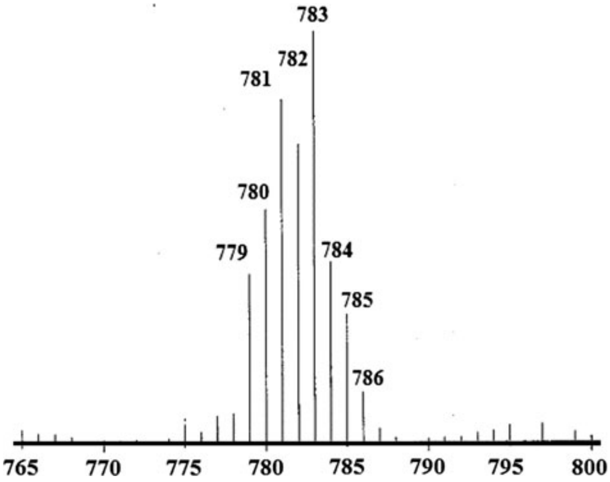


Fig. 1 FAB-MS spectrum of the dimer complex

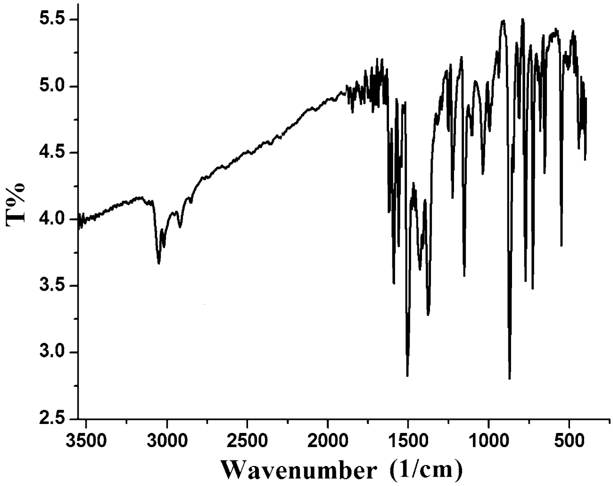


Fig. 2 IR spectrum of the dimer complex (KBr disk)

with of the spectra of the dmphen free ligand. IR spectra of the complex contained four characteristic absorption peaks at 3090, 2890, 820, and 290 cm^{-1}, which can be assigned to, Ph–CH, Me–CH, Cd–N, and Cd–Cl stretching vibrations, respectively. All other functional group vibrations appeared at their expected positions (Fig. 2).

Electronic absorption spectral study

The electronic absorption spectrum of the complex was acquired in chloroform at room temperature. Intense transitions were observed for the complex in the

UV–visible region. Bands at the high-energy end at 200–290 nm were assigned to intra-ligand electron transfer; no other bands were detected elsewhere (Fig. 3).

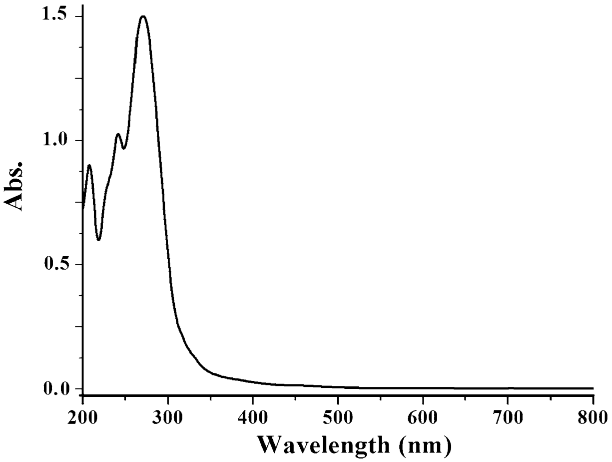


Fig. 3 UV–visible spectrum of dimer complex dissolved in $CHCl_3$ at RT

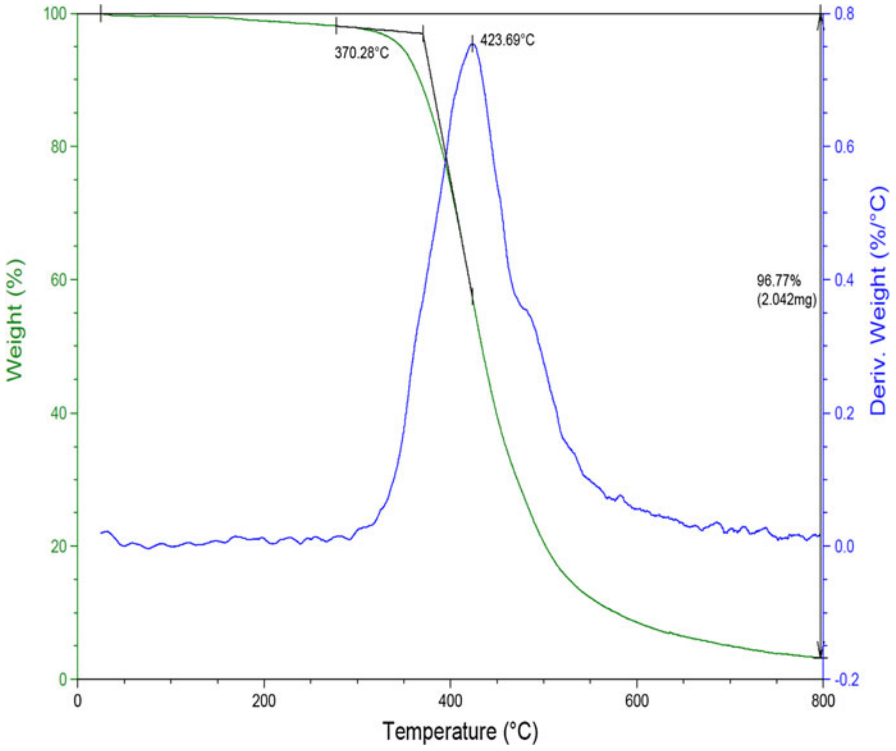


Fig. 4 TG and DTA thermal curves of the complex

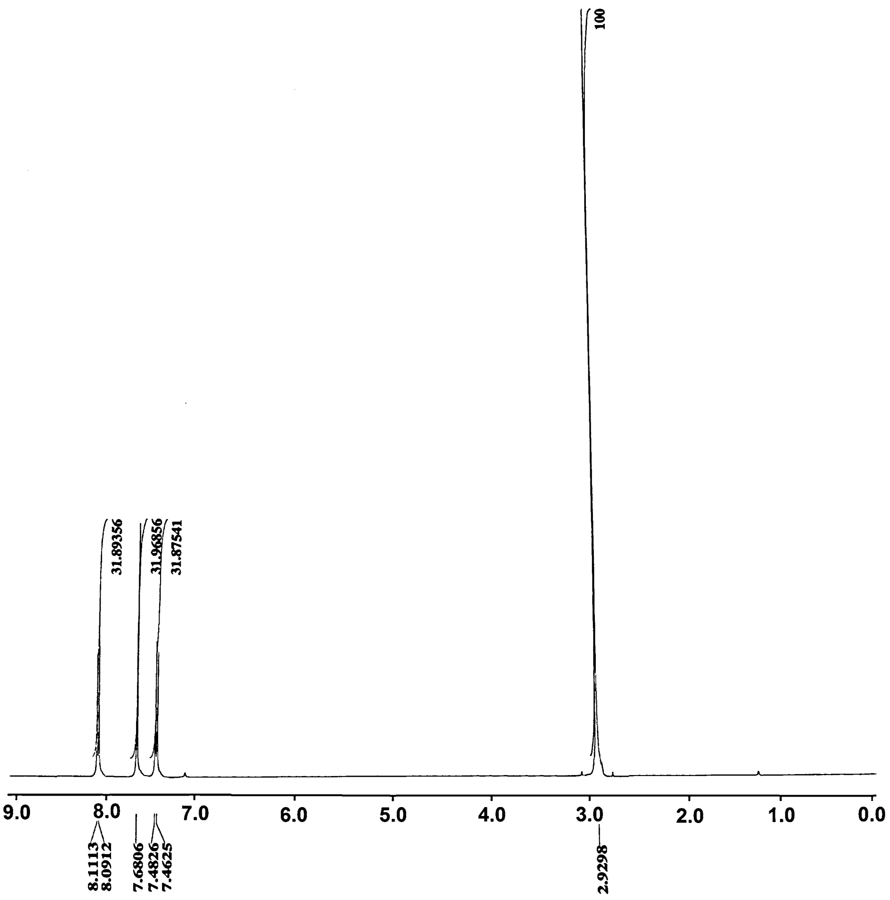


Fig. 5 ^{1}H NMR spectrum in $CDCl_3$ at RT corroborates the structure of the dimer complex

Thermal analysis

The thermal properties of the dimer complex were investigated in the 0–800 °C temperature range under an open atmosphere at a heating rate of 10 °/min. Typical thermal TG/DTA curves of the dimer complex are given in Fig. 4.

No coordinated or uncoordinated water molecules were detected, because no weight loss was recorded in the range 25–200 °C; this confirmed IR and XRD results. This complex undergoes simple one-step decomposition with weight loss experimentally 96 %. The coordinated chloride and dmphen ligands were lost from the complex structure between 370 and 600 °C, with a major exothermic DTA peak at 423.7 °C.

NMR investigation

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the complex were recorded in $CDCl_3$ solution to confirm the binding of the dmphen ligand to the cadmium(II); the assignments are

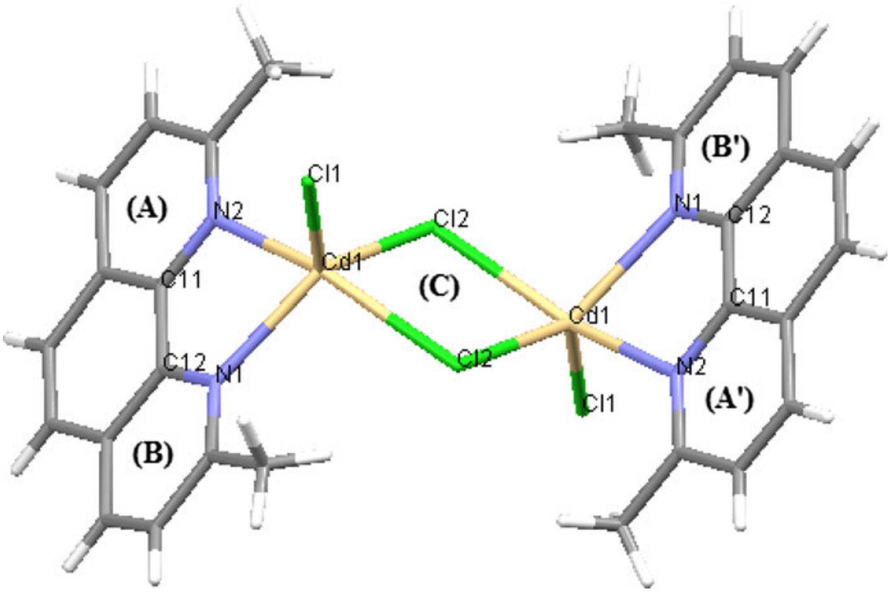


Fig. 6 Molecular structure of the dimer complex, with atom labeling. Thermal *ellipsoids* are drawn at the 50 % probability level

given in the "Experimental" section. The ^1H and $^{13}C\{^1H\}$ NMR spectra corroborate the structure of the dimer complex; only two functional group (CH_3 and phenyl) signals belonging to the dmphen ligand coordinated with $CdCl_2$ were recorded, No water was recorded in the composition of the complex by ^1H NMR (Fig. 5).

X-ray structural determination of the complex

Solvent-free crystals suitable for X-ray structural analysis were prepared from the complex. The molecular structure and packing view are shown in Figs. 6 and 7, respectively, selected bond distances and angles are given in Tables 2 and 3, respectively.

The coordination environment of the Cd(II) ion in the binuclear desired complex crystallizes in the monoclinic system with the $P2_1/c$ space group. Each Cd(II) ion is five-coordinated by three Cl and two N atoms, Cd···Cd metal ions are separated by a distance of 3.978 Å. X-ray single-crystal diffraction analysis shows that complex $[CdCl_2(C_{14}H_{12}N_2)]_2$, is a centrosymmetric dimer bridged through the Cl atoms. The bridging Cd_2Cl_2 unit is planar and each Cd(II) ion has two different distances to the bridging and terminal Cl atoms. The overall geometry around the cadmium atoms is in a slightly distorted square-pyramidal disposition. Several hydrogen bonds are formed by the terminal Cl atoms and H-Me/H-Ph groups, which may stabilize the structure.

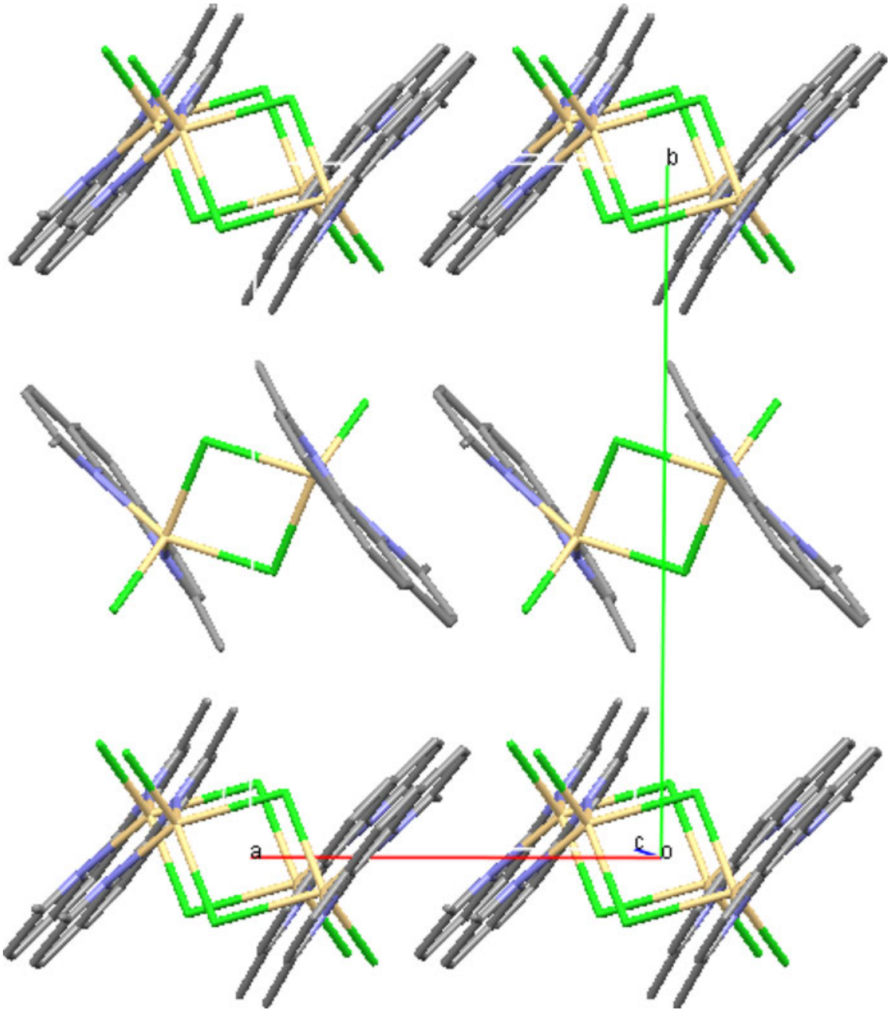


Fig. 7 View of packing the complex chains extending along the *a* axis. The H-atoms not involved in H-bonding have been omitted

Conclusion

A binuclear cadmium(II) complex has been prepared, and its crystal and molecular structure have been determined by X-ray diffraction. The crystal is monoclinic, space group $P2_1/c$, overall distorted square-pyramidal. The structure of the dimer complex was characterized on the basis of elemental analysis, FAB-MS, IR, UV–visible, ^{1}H and ^{13}C NMR spectroscopy, and TG/DTA.

Table 2 Selected bond distances (Å) of the dimer complex

Atoms	Distance	Atoms	Distance
Cd(1A)–Cl(1A)	2.410(5)	Cd(1B)–Cl(1B)	2.410(5)
Cd(1)–Cl(2A)	2.627(3)	Cd(1B)–Cl(2B)	2.580(6)
Cd(1A)–N(1A)	2.330(1)	Cd(1B)–N(1B)	2.330(1)
Cd(1A)–N(2A)	2.360(1)	Cd(1B)–N(2B)	2.360(1)
N(1A)–C(12A)	1.370(2)	N(1B)–C(12B)	1.370(2)
N(2A)–C(11A)	1.370(2)	N(2B)–C(11B)	1.370(2)
C(11A)–C(12A)	1.430(3)	C(11B)–C(12B)	1.430(3)
N(1A)–C(1A)	1.300(3)	N(1B)–C(1B)	1.300(3)
N(2A)–C(10A)	1.280(2)	N(2B)–C(10B)	1.280(2)

Table 3 Selected bond angles (°) of the dimer complex

Atoms	Angle	Atoms	Angle
N1A–Cd1A–N2	72.9(4)	N1B–Cd1B–N2B	72.9(4)
N1A–Cd1A–Cl1A	115.3(3)	N1B–Cd1B–Cl1B	115.3(3)
N2A–Cd1A–Cl1A	108.3(3)	N2B–Cd1B–Cl1B	108.3(3)
Cl1A–Cd1A–Cl2A	120.7(2)	Cl1B–Cd1B–Cl2B	120.7(2)
Cd1A–Cl2A–Cd1A	99.6(2)	Cd1B–Cl2B–Cd1B	99.6(2)
Cl2A–Cd1A–Cl2A	80.4(1)	Cl2B–Cd1B–Cl2B	80.4(1)

Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 892180. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments The project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

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