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Synthesis, spectral, electrochemical, crystal structure studies of two novel di-μ-halo-*bis*[halo(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)cadmium(II)] dimer complexes and their thermolysis to nanometal oxides

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ABSTRACT

Two new neutral dimer Cadmium(II) complexes, $[Cd_2(dmdphphen)_2X_4]$ and where X = Cl (complex **1**), Br (complex **2**), and dmdphphen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, were synthesized and characterized by an elemental analysis, UV–Vis, IR, TG/DTA, CV and single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic system with the space group P-1 with unit cell parameters $a = 10.1124(8)$ Å, $b = 10.8875(8)$ Å, $c = 11.5730(9)$ Å, $\alpha = 108.323(3)°$, $\beta = 107.010(3)°$, $\gamma = 91.260(3)°$ $V = 1147.51(15)$ Å^3 and $Z = 1$. The Cd(II) ions are located in a slightly distorted square-pyramidal geometry. The complexes exhibit a quasi-reversible one electron response at −570 mV *vs.* Cp_2Fe/Cp_2Fe^+, which has been assigned Cd(II)/Cd(III) couples. TG/DTA result shows that these complexes are very stable and decomposed through one step reaction. Calcination of Complex **1**, revealed the formation of Cubic nanoparticle CdO.

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1. Introduction

1,10-Phenanthroline and its derivatives are well-established bidentate planar ligands and are used to prepare a large range of various metal ions complexes [1–8]. Their metal complexes have many applications and it is used frequently as catalysts [3–8]. Its complexing capability has been used to develop biomimetic models of metalloenzymes, to design analytical reagents and to prepare supramolecules for molecular recognition and self-assembling systems [1–3]. The binding of metal complexes with DNA base pairs has been a major focus in the study of bioinorganic chemistry [9]. Such metal-phen complexes owning their ability to bind DNA *via* both covalent and non-covalent interactions [10–12].

1,10-Phenanthroline as a versatile ligand was able to chelate Cadmium(II) to give mono-phen or bis–phen complexes [13–16]. Cadmium complexes have attracted more and more attentions because of their widely reported bioactivities, such as DNA binding affinity [17] and antibacterial activities [18]. Meanwhile, the antitumor activities of cadmium(II) complexes have been reported more frequently [19,20], despite the metal was regarded as a human carcinogen. Previous chemists reported that complexation of the cadmium ions could enhance their anticancer behaviors, and the cadmium complexes possessed the moderate cytotoxic activities [21].

Previously, a series of several mixed-ligand mononuclear and dinuclear metal complexes have a general formula $MX_2(dmphen)$ were prepared in our lab [13–16]. These complexes were found to

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be suitable precursors for spherical shape metal oxide nanoparticles [15]. Herein, two novel neutral dimer Cadmium(II) complexes of general formula [Cd_2(dmdphphen)X_4] (dmdphphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and X = Cl or Br), were synthesized and characterized by different spectroscopic methods. Complex **1** served as a precursor for preparation of CdO nanoparticles through direct open atmosphere calcination process.

2. Experimental section

2.1. Material and instrumentation

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand, $CdCl_2.2.5H_2O$ and $CdBr_2.2.5H_2O$ were purchased from Fluka. Elemental analyses were carried out on an Elementar Vario EL analyzer. The IR spectra for samples were recorded using (Perkin Elmer Spectrum 1000 FT-IR Spectrometer). The UV−vis spectra were measured by using a TU-1901double-beam UV−visible spectrophotometer. TG/DTA spectra were measured by using a TGA-7, Perkin−Elmer thermogravimetric analyzer. The cyclic voltammograms for the complexes were measured in CH_3CN and 0.1 M tetrabutyl ammonium hexaflurophasphate (TBAHF) using BAS 100 B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN, USA) and controlled by a standard 80486 personal computer (BAS control program version 2.0). All electrochemical experiments were carried out at room temperature under argon with a three-electrode cell. Voltalab 80 potentiostate PGZ402 with Pt-disk electrode (Metrohm, A = 0.0064 cm^2) was used as working electrode. Platinum wire (£ 1 mm) spiral with diameter 7 mm was used as a counter electrode. Haber−Luggin double reference electrode was used as a reference one.

2.2. General procedure for the preparation of the desired complexes

A mixture of CdX_2 salt (2 mmol) in distilled ethanol (15 mL) with free ligand dmdphphen (2.2 mmol) in CH_2Cl_2 (2 ml) was allowed to stir for around 20 min in an open atmosphere until the white precipitation appeared. The product was filtered and washed several times with ethanol. 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 couple of days.

2.2.1. Complex **1**

Yield: (92%). Anal. Calc. for $C_{52}H_{40}Cd_2Cl_4N_4$: C, 57.43; H, 3.71; N, 5.15%. Found. C, 57.43; H, 3.51; N, 5.28%. MS m/z = 1087.0 [theoretical = 1087.5 M]. UV−Vis bands in dichloromethane 225, 235 and 270 nm. M.p 310 °C. Conductivity in CH_3CN: 8.3 (μS/cm). ^{1}H NMR ($CDCl_3$): d (ppm) 2.21 (br, 12H, CH_3), 7.40−8.20 (4 m, 22H, Ph, Py), ^{13}C{^{1}H} NMR ($CDCl_3$):d (ppm) 25.2 (s, 4C, CH_3), 125.0−165.0 (9s, 36C, Ph, Py).

2.2.2. Complex **2**

Yield: (90%). Anal. Calc. for $C_{52}H_{40}Cd_2Br_4N_4$: C, 49.36; H, 3.19; N, 4.43%. Found. C, 49.22; H, 3.21; N, 4.48%. MS m/z = 1265.0 [theoretical = 1265.4 M]. UV−Vis bands in dichloromethane 230, 245 and 280 nm. M.p 330 °C. Conductivity in CH_3CN: 10.5 (μS/cm). ^{1}H NMR ($CDCl_3$): d (ppm) 2.05 (br, 12H, CH_3), 7.00−8.50 (4 m, 22H, Ph, Py), ^{13}C{^{1}H} NMR ($CDCl_3$):d (ppm) 25.2 (s, 4C, CH_3), 125.0−165.0 (9s, 36C, Ph, Py).

2.3. Crystallography

A colorless rectangle shaped single crystal of dimensions 0.3 × 0.27 × 0.25 mm of the title compound was chosen for an X-ray diffraction study. The X-ray intensity data were collected at a
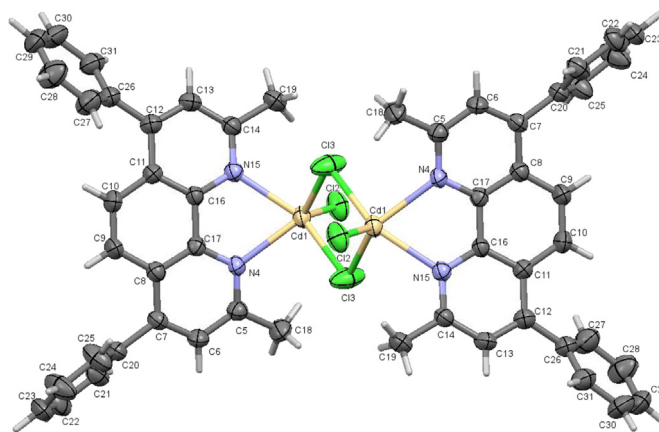

Fig. 1. ORTEP of the complex **1** with atoms libeled. Thermal ellipsoids are drawn at the 50% probability level.

temperature of 296 K on a Bruker Proteum2 CCD diffractometer equipped with an X-ray generator operating at 45 kV and 10 mA, using CuK_α radiation of wavelength 1.54178 Å. Data were collected for 24 frames per set with different settings of φ (0° and 90°), keeping the scan width of 0.5°, exposure time of 2 s, the sample to detector distance of 45.10 mm and 2θ value at 46.6°. A complete data set was processed using *SAINT PLUS* [22]. The structure was solved by direct methods and refined by full-matrix least squares method on F^2 using *SHELXS* and *SHELXL* programs [23]. All the non-hydrogen atoms were revealed in the first difference Fourier map itself. All the hydrogen atoms were positioned geometrically and refined using a riding model. After ten cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residuals saturated to 0.0434. The geometrical calculations were carried out using the program *PLATON* [24]. The molecular and packing diagrams were generated using the software *MERCURY* [25]. The details of the crystal structure and data refinement are given in Table 1. The list of bond lengths and bond angles of the non-hydrogen atoms are given in Table 2. Fig. 6 represents the ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.

3. Results and discussion

3.1. Synthesis of the desired complexes

Mixing of dmdphphen with equivalent amount of CdX_2 salt in EtOH−CH_2Cl_2 mixture solvents and open atmosphere revealed the formation of novel dimer Cd(II) complexes **1** and **2** in very fast reaction. The desired dimer complexes were isolated in a good yield without side product as seen in Scheme 1.

The structures of the desired dimer complexes were confirmed by using elemental analysis, IR, UV−vis, TG/DTA, CV and X-ray single crystal measurement for complex **1**. The isolated complexes were stable in air, insoluble in water, ethanol, *n*-hexane and ethers, but was also soluble in CH_2Cl_2. The solubility and molar conductance showed that the two complexes are non-electrolytic in their nature. The analytical data of the complexes show the formation of [1:1:2] [M:dmdphphen:2×] ratio in a good agreement with the suggested formula [CdX_2(dmdphphen)]$_2$ of the isolated complexes.

3.2. X-ray crystal structure

Crystal structure data and selected bonds length for Complex **1** are compiled in Tables 1 and 2 respectively. ORTEP drawing of the
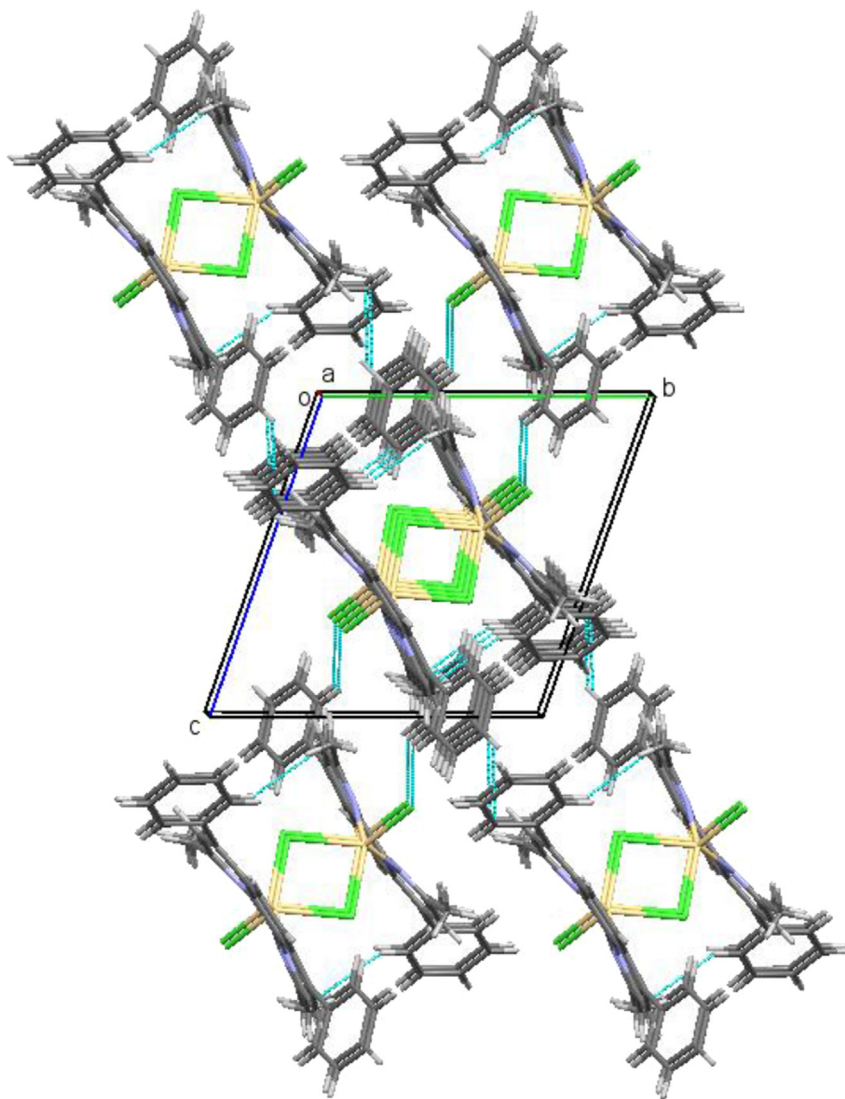
Fig. 2. A crystal packing of complex **1** exhibiting layered stacking when viewed (perspective) along the crystallographic *a* axis.
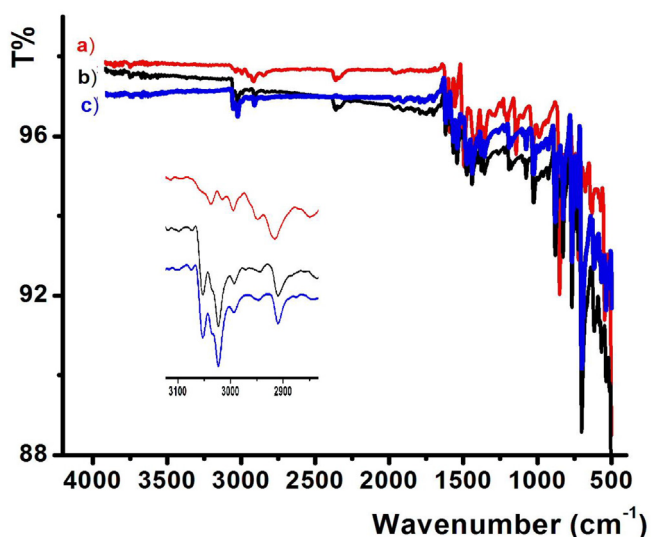

Fig. 3. IR-KBr disk spectra of free ligand a), complexes **1** b) and complexes **1** c).

complex is shown in Fig. 1.

The structure of the title compound (Fig. 1) consists of a centrosymmetric dimeric unit, [Cd$_2$Cl$_4$(dmdphphen)$_2$], in which two chlorine atoms bridge to Cd(II) ion, forming a four-membered ring; a terminal chlorine atom and a bidentate chelating Ph$_2$phen complete a five coordination. The coordination environment of the Cd(II) ion in the binuclear desired complex and crystallizes in the triclinic crystal system with the *P-1* 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 3.909 Å. The phenanthroline ring in the structure is essentially planar with an rms deviation of 0.1214 Å. The phenyl rings (C20–C25 and C26–C31) are twisted out of the plane of the phenanthroline ring as indicated by the dihedral angle values of 68.0(2)° and 59.0(3)° respectively. X-ray single-crystal diffraction analysis shows that complex [Cd$_2$(dmdphphen)$_2$X$_4$], is a centrosymmetric dimer bridged through the Cl atoms. The bridging Cd$_2$Cl$_2$ 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. No classic hydrogen bonds were observed in
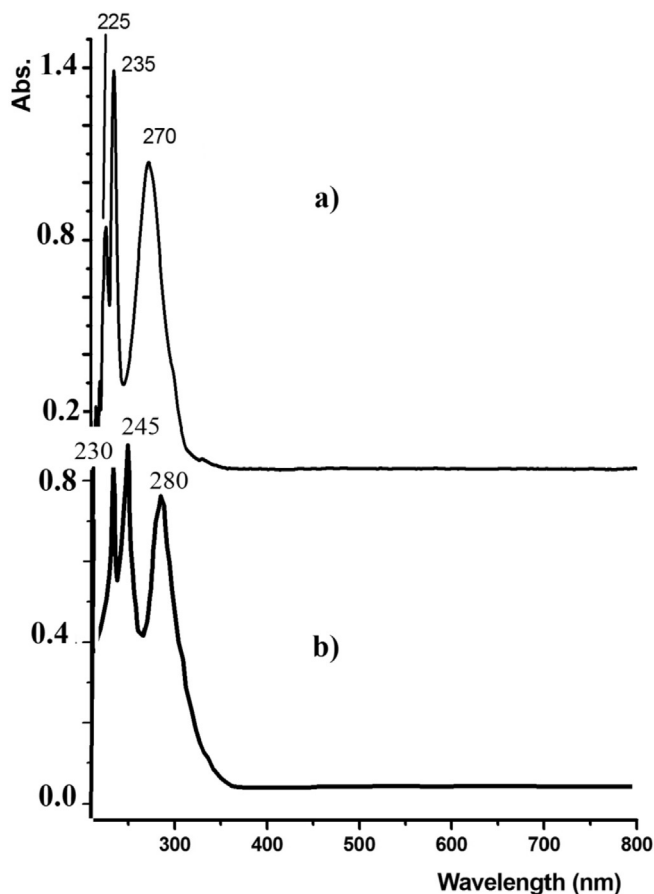
Fig. 4. UV−Vis spectrum of the desired complexes **1** a) and complexes **2** b) dissolved in dichloromethane at RT.

Fig. 5. ^{1}H NMR spectra of complex **1** a) and complex **2** c) in $CDCl_3$ at RT.

the structure. The packing of the molecules as shown in Fig. 2 when viewed down along the *a* axis indicates that the molecules are stacked in pairs.

3.3. IR spectrum

The IR spectrum of complex **1** and **2** and the free dmdphphen ligand is shown in Fig. 3. The complexes revealed five main characteristic absorptions peaks in range 3060, 2950, 1060, 550 and 350 cm^{-1}, which was assigned to C−H$_{aromatic}$, C−H$_{CH3}$, C=N, Cd−N and Cd−Cl stretching vibrations, respectively.

3.4. Electronic absorption spectral study

The experimental absorption spectra (UV−Vis) of the dimer complexes in dichloromethane solution showed three dominant bands in the region 200−800 nm. All the bands were centered at UV area: for complex **1**, 225, 235 and 270 nm (Fig. 4a)and for complex **2**, 230, 245 and 280 nm (Fig. 4b), which assigned to ligand-centered π−π^* transitions, no other bands were detected elsewhere.

3.5. NMR investigation

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes were recorded in $CDCl_3$ solvent to confirm the binding of the dmdphphen ligand to the cadmium(II). The ^{1}H and ^{13}C{^{1}H} NMR spectra

Table 1
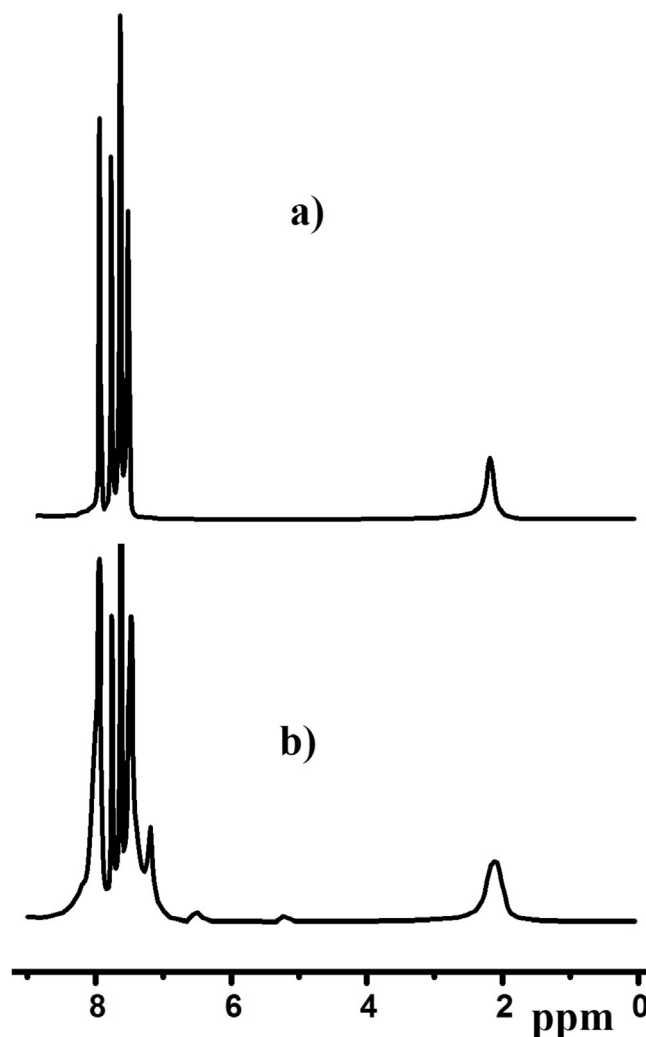Crystal data and structure refinement for Ligand and complex **1**.

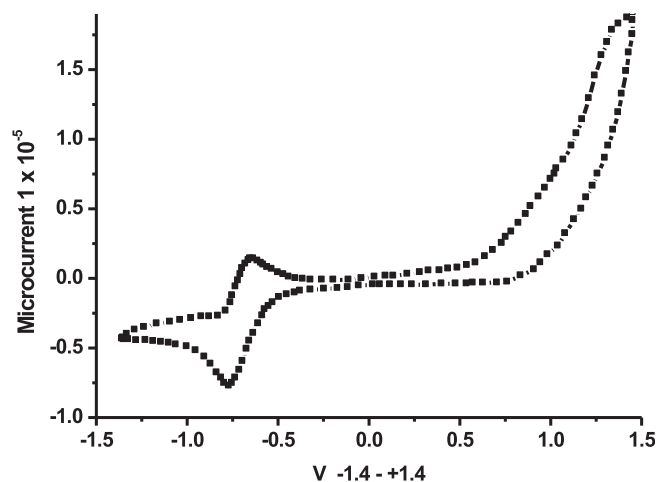|	
CCDC number	1403575
Empirical formula	$C_{52}H_{40}Cd_2Cl_4N_4$
Formula weight	1087.48
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, *P-1*
Unit cell dimensions	$a = 10.1124(8)$ Å
	$b = 10.8875(8)$ Å
	$c = 11.5730(9)$ Å
	$\alpha = 108.323(3)°$
	$\beta = 107.010(3)°$
	$\gamma = 91.260(3)°$
Volume	1147.51(15) Å^3
Z, Calculated density	1, 1.574 Mg/m^3
Absorption coefficient	9.878 mm^{-1}
$F_{(000)}$	544
Crystal size	0.25 × 0.24 × 0.23 mm
Theta range for data collection	4.24° to 64.44°
Limiting indices	$-11 \leq h \leq 11, -12 \leq k \leq 12, -13 \leq l \leq 13$
Reflections collected/unique	13701/3760 [R(int) = 0.0458]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3760/0/282
Goodness-of-fit on F^2	1.091
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0434, wR2 = 0.1361$
R indices (all data)	$R1 = 0.0474, wR2 = 0.1447$
Largest diff. peak and hole	0.977 and -1.066 e. Å^{-3}

Table 2
Selected bond distances (Å) and bond angles (°) of the complex **1**.

Atoms	Length	Atoms	Length
Cd1–N4	2.355(4)	C12–C13	1.375(7)
Cd1–N15	2.357(4)	C12–C26	1.477(7)
Cd1–Cl2	2.4115(13)	C13–C14	1.400(7)
Cd1–Cl3	2.5692(14)	C14–N15	1.330(6)
Cd1–Cl3	2.5791(15)	C14–C19	1.510(6)
Cl3–Cd1	2.5791(15)	N15–C16	1.357(6)
N4–C5	1.334(6)	C16–C17	1.457(6)
N4–C17	1.355(6)	C20–C25	1.375(8)
C5–C6	1.401(7)	C20–C21	1.395(8)
C5–C18	1.488(7)	C21–C22	1.385(8)
C6–C7	1.367(8)	C22–C23	1.395(10)
C7–C8	1.430(6)	C23–C24	1.345(10)
C7–C20	1.488(6)	C24–C25	1.379(8)
C8–C17	1.396(6)	C26–C27	1.372(9)
C8–C9	1.432(7)	C26–C31	1.394(7)
C9–C10	1.352(7)	C27–C28	1.375(9)
C10–C11	1.427(7)	C28–C29	1.356(9)
C11–C16	1.411(6)	C29–C30	1.380(10)
C11–C12	1.428(7)	C30–C31	1.394(8)
Atoms	**Angle**	**Atoms**	**Angle**
N4–Cd1–N15	70.16(12)	C11–C12–C26	123.2(4)
N4–Cd1–Cl2	109.83(10)	C12–C13–C14	121.7(4)
N15–Cd1–Cl2	105.41(10)	N15–C14–C13	121.2(4)
N4–Cd1–Cl3	92.68(10)	N15–C14–C19	117.9(4)
N15–Cd1–Cl3	144.21(11)	C13–C14–C19	120.9(4)
Cl2–Cd1–Cl3	109.98(6)	C14–N15–C16	119.1(4)
N4–Cd1–Cl3	130.46(11)	C14–N15–Cd1	126.3(3)
N15–Cd1–Cl3	86.67(10)	C16–N15–Cd1	113.8(3)
Cl2–Cd1–Cl3	118.49(6)	N15–C16–C11	122.7(4)
Cl3–Cd1–Cl3	81.20(5)	N15–C16–C17	117.9(4)
Cd1–Cl3–Cd1	98.80(5)	C11–C16–C17	119.2(4)
C5–N4–C17	119.1(4)	N4–C17–C8	123.4(4)
C5–N4–Cd1	125.9(3)	N4–C17–C16	117.0(4)
C17–N4–Cd1	114.3(3)	C8–C17–C16	119.4(4)
N4–C5–C6	120.5(4)	C25–C20–C21	117.9(5)
N4–C5–C18	118.5(4)	C25–C20–C7	122.2(5)
C6–C5–C18	121.0(4)	C21–C20–C7	119.9(5)
C7–C6–C5	121.7(4)	C22–C21–C20	120.4(6)
C6–C7–C8	118.0(4)	C21–C22–C23	119.6(6)
C6–C7–C20	120.3(4)	C24–C23–C22	120.0(5)
C8–C7–C20	121.6(4)	C23–C24–C25	120.3(6)
C17–C8–C7	117.0(4)	C20–C25–C24	121.7(6)
C17–C8–C9	120.1(4)	C27–C26–C31	118.6(5)
C7–C8–C9	122.6(4)	C27–C26–C12	121.5(5)
C10–C9–C8	120.4(4)	C31–C26–C12	119.9(5)
C9–C10–C11	121.8(4)	C26–C27–C28	121.2(6)
C16–C11–C10	119.1(4)	C29–C28–C27	121.2(6)
C16–C11–C12	117.7(4)	C28–C29–C30	118.7(5)
C10–C11–C12	123.0(4)	C29–C30–C31	121.1(6)
C13–C12–C11	117.2(4)	C30–C31–C2	119.2(6)
C13–C12–C26	119.6(4)		

Fig. 6. Voltammogram diagram of complex **2** (c = 1 × 10^{-4} M, in acetonitrile solution, 0.1 M TBAHF, Scan rate: 100 mV/s at RT).

3.7. Thermal decomposition analysis of complex **1**

The thermal analysis of complex **1** was investigated in the range of 0–800 °C and at a heating rate of 10 °C/min. The typical thermal TG/DTA curves are given in Fig. 7. Fig. 7 shows there is no uncoordinated or coordinated water in the range 0–150 °C and 150–180 °C respectively. Also, both Cl and dmdphphen ligands were de-structured away from the Cd metal center with one broad step decomposition in range 330–520 °C with weight loss ~82% and an exothermic DTA signal at ~405 °C. The final residue was confirmed by IR to be CdO.

3.8. CdO nanoparticle formed by direct calcination of complex **1**

The composition and phase information of the TG/DTA final residue produced through thermolysis of complex **1** was investigated by X-ray powder diffraction (XRD). As seen in Fig. 8, CdO nanoparticles were collected by simple open atmosphere TG/DTA calcination process. Comparison XRD pattern of CdO prepared with JCPDS file No. 05–0640, confirmed CdO cubic crystal with the space group of Fm3m (225) formation. No impurities are detected, since there is no unknown peak in XRD pattern or IR spectrum. The morphology and size of these particles were investigated by Scanning Electron Microscopy (SEM) (Fig. 9). According to this micrograph, nanoparticles with less than 200 nm in diameter were recorded.

corroborate the structure of the dimer complexes; only two functional group (complex **1**, CH$_3$ ~ 2.2 ppm and aromatic ~ 7.4–8.2 ppm, (complex **2**, CH$_3$ ~ 2.0 ppm and aromatic ~ 7.0–8.5 ppm)) signals belonging to the dmdphphen ligand coordinated with CdCl$_2$ were recorded as seen in Fig. 5.

3.6. Electrochemistry of complex **2**

The electron-transfer behavior of the complex **2** in acetonitrile solution was examined by cyclic voltammetry. As a representative example, the cyclic voltammogram for complex **2** is shown in Fig. 6. Complex **2** exhibited on single electron reversible oxidative response at −750 vs. Cp$_2$Fe/Cp$_2$Fe$^+$, which has been assigned to Cd(II)/Cd(III) couples, The dmdphphen ligand is electro-inactive over the studied range of +1.4 to −1.4 V.

4. Conclusions

Two novel Cd(II) dimer complexes of general formula [Cd$_2$(dmdphphen)$_2$X$_4$] were prepared through a fast, simple and efficient synthetic procedure. These complexes were characterized by elemental analysis, UV–vis, FT-IR, TG/DTA, CV and finally confirmed by X-ray diffraction studies. XRD of complex **1** revealed that the Cd(II) ions are located in a slightly distorted square-pyramidal environment. The desired dimer complexes exhibited a quasi-reversible one electron transfer and high degree of thermal stability. The TG/DTA residue of complex **1** were found to be regular CdO nanoparticles.
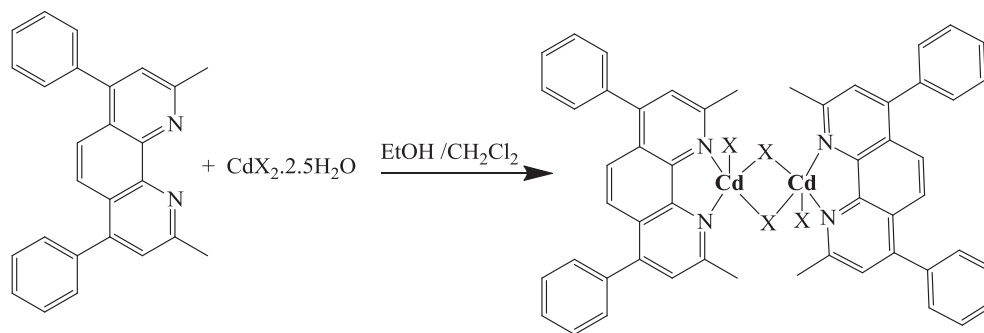
X = Cl   complex **1** or Br complex **2**

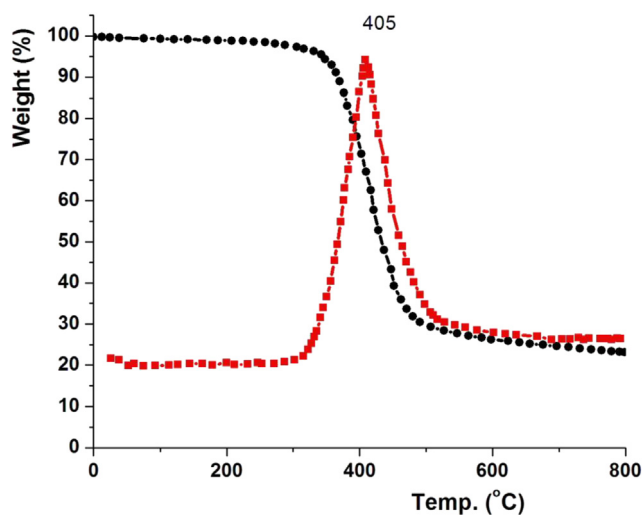**Scheme 1.** Synthesis of the complexes **1** and **2**.

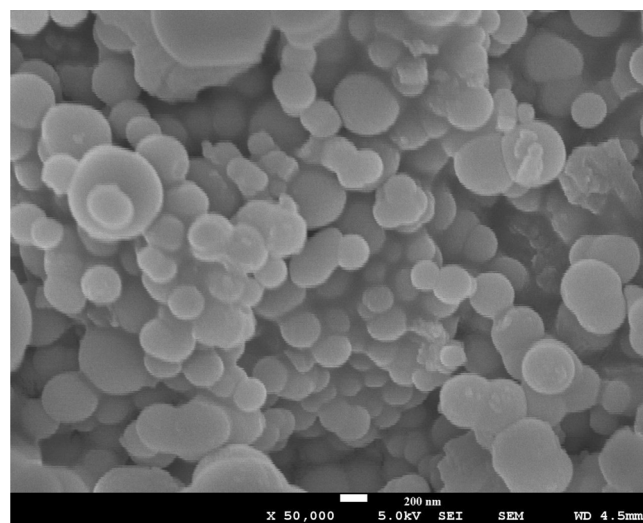**Fig. 7.** TG/DTA thermal curves of the complex **1**.

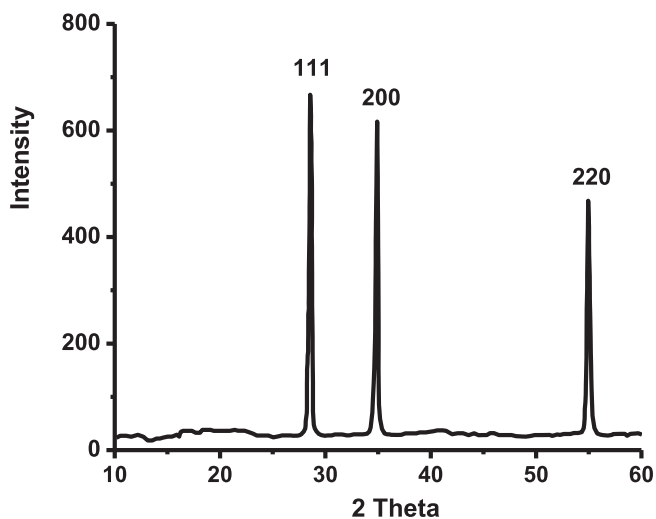**Fig. 9.** The SEM image and the of CdO nanoparticles prepared by direct calcination complex **1**.

Fig. 8. Powder XRD pattern of CdO prepared by direct calcination of complex **1**.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2015.06.043.

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