

Synthesis and Crystal Structures of Cadmium(II) Complexes with 2-Acetylpyridine Schiff Bases of S-Methyldithiocarbamate or 4-Phenyl 3-thiosemicarbazide

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Metal complexes of the Schiff base ligand are of interest due to their unique physico-chemical properties^{1,2} and major biological activities.³⁻⁵ In this regard, we have reported metal (II, IV, and VI, where M(II) = Mn, Co, Ni, M(IV) = V(IV)O, M(VI) = Mo(VI)) complexes of mono- or bis-Schiff base ligands derived from the condensation of salicylaldehyde or 2-acetylpyridine with dithiocarbamate or thiosemicarbazide.⁶ Recently, dinuclear copper(II) complexes, $[\text{Cu}_2(\text{L})_2(\text{CH}_3\text{COO})](\text{ClO}_4)$ (L = 2-benzoylpyridine S-methyldithiocarbamate)⁷ and $[\text{Cu}_2\text{L}_2(\text{SO}_4)]$ (L = di-2-pyridyl ketone N(4), N(4)-(butane-1,4-diyl)thiosemicarbazone)⁸ were reported. In here, the sulfur atom from Schiff base ligand together with acetate or sulfate oxygen atoms as anion of starting material bridges the two copper(II) ions, respectively. Although many metal(II)-Schiff base complexes have been reported, there are few reports of dimeric Cd(II) complexes connected via a second ligand except the solvent molecule or the counter anion of the metal salt as starting material.⁹ In this work, we took the thiocyanate, azide, and dicyanoamide as the second ligands, respectively. For metal ions, the second ligands, especially thiocyanate can provide a variety of terminal and/or bridging coordination modes displayed by the linkage isomerism.¹⁰ As a part of the longstanding interest in the synthesis and dimension expansion of coordination compounds with mixed NNS donor system, we report herein a mono- and di-nuclear Cd(II) complexes of an acetylpyridine based dithiocarbamate or 4-phenyl-3-thio semicarbazide. Spectroscopic and thermal properties of the complexes are also discussed.

EXPERIMENTAL

Chemicals and Measurements

All chemicals are commercially available and were used as received without further purification. The ligand,

acpy-mdtcH was prepared as described in the literature.¹¹ Elemental analyses (CHNS) were performed on a FLASH 2000 Elementar Analyzer. Infrared spectra were recorded in the range from 4000 to 400 cm^{-1} on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. Thermogravimetric (TG) analysis were performed on a Shimadzu DTG-60 instrument with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$.

Preparation of $[\text{Cd}(\text{acpy-mdtc})_2](\mathbf{1})$: To a methanol solution (15 mL) of acpy-mdtcH ligand (0.225 g, 1.00 mmol) was added 5 mL methanol solution of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.463 g, 1.50 mmol). The solution turned to yellow and was stirred for 3 h to yield yellow solid. The solid was isolated by filtration and air-dried. The solid was recrystallized from the dmf solution to give yellow block crystals in good quality for X-ray crystallography. Yield: 70% (0.604 g) based on Cd. Elemental Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_6\text{S}_4\text{Cd}$: C, 38.53; H, 3.59; N, 14.98; S, 22.86. Found: C, 38.15; H, 3.20; N, 14.59; S, 23.13%. Selected IR bands (KBr pellet, cm^{-1}): 3069(w), 2920(w), 1650(w), 1588(w), 1558(w), 1480(w), 1403(s), 1368(m), 1290(m), 1137(w), 1063(w), 1001(m), 929(m), 803(w), 776(m), 742(w), 633(w).

Preparation of $[\text{Cd}(\text{acpy-phTsc})_2](\mathbf{2})$: To a methanol solution (15 mL) of 2-acetylpyridine (0.121 g, 1.00 mmol) and 4-phenyl-3-thiosemicarbazide (0.167 g, 1.00 mmol) was added a drop of conc-HCl. The solution was heated to reflux for 2 h. After cooling to room temperature, 5 mL methanol solution of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.463 g, 1.50 mmol) was added with stirring. The resulting solution was stirred further for 3 h to yield a pink crystalline solid. The solid was recrystallized from dmf solution. Yield: 65% (0.631 g) based on Cd. Elemental Anal. Calcd. for $\text{C}_{28}\text{H}_{26}\text{N}_8\text{S}_2\text{Cd}$: C, 51.65; H, 1.55; N, 17.21; S, 9.85. Found: C, 51.93; H, 1.59; N, 17.03; S, 10.14%. Selected IR bands (KBr pellet, cm^{-1}): 3289(m), 3126(w), 3065(w), 1592(m), 1537(m), 1489(m), 1451(m), 1415(s), 1312(m), 1234(m), 1177(m),

1080(m), 821(w), 744(w), 692(w).

Preparation of [Cd(acpy-mdtc)(NCS)]₂(3): To a methanol solution (20 mL) of acpy-mdtcH (0.225 g, 1.00 mmol) was added Cd(NO₃)₂·4H₂O (0.463 g, 1.50 mmol). The reaction solution was stirred for 3 h at room temperature. To the resulting solution was added a methanol solution (5 mL) of KNCS (0.243 g, 2.5 mmol). The solution was stirred further for 2 h at room temperature. The solid was filtered and the filtrate was kept at room temperature to yield yellow block crystals in good quality for X-ray crystallography. Yield: 58% (0.344 g) based on Cd. Elemental Anal. Calcd. for C₂₀H₂₀N₈S₆Cd₂: C, 30.42; H, 2.55; N, 14.19; S, 24.36. Found: C, 30.28; H, 2.34; N, 14.48; S, 23.84%. Selected IR bands (KBr pellet, cm⁻¹): 2924(w), 2396(w), 2115(m), 1762(w), 1369(s), 1045(w), 1010(w), 929(w), 828(m), 774(w).

Preparation of [Cd(acpy-phTsc)(NCS)]₂(4): To a methanol solution (15 mL) of 2-acetylpyridine (0.121 g, 1.00 mmol), 4-phenyl-3-thiosemicarbazide (0.167 g, 1.00 mmol) was added a drop of conc-HCl. The solution was heated to reflux for 2 h. After cooling to room temperature, 5 mL methanol solution of Cd(NO₃)₂·4H₂O (0.463 g, 1.50 mmol) was added with stirring. The reaction solution was further stirred for 3 h at room temperature. To the resulting solution was added a methanol solution (5 mL) of KNCS (0.243 g, 2.5 mmol). The solution was stirred further for 2 h at room temperature. The solid was filtered and the filtrate was kept at room temperature to yield yellow block crystals in good quality for X-ray crystallography. Yield: 53% (0.395 g) based on Cd. Elemental Anal. Calcd. for C₃₂H₂₆N₁₂S₆Cd₂: C, 38.60; H, 2.63; N, 16.88; S, 19.32. Found: C, 38.82; H, 2.93; N, 15.98; S, 15.35%. Selected IR bands (KBr pellet, cm⁻¹): 3292(w), 3036(m), 2107(s), 2072(s), 1620(w), 1550(s), 1485(m), 1370(m), 1331(m), 1234(m), 1226(m), 1172(w), 761(m), 691(w).

X-ray Structure Determination

Single crystals of 1-4 were obtained by the method described in the above procedures. Structural measurement for the complexes were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at the Korea Basic Science Institute. The structures were solved by direct method and refined on F₂ by fullmatrix least-squares procedures using the SHELXTL programs.¹² All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the DIAMOND

program.¹³ The crystallographic data for complexes 1-4 are listed in Table S1-S4.

RESULTS AND DISCUSSION

The reactions of Cd(NO₃)₂·4H₂O with the appropriate Schiff base ligand derived from 2-acetylpyridine and *s*-methylthiocarbamate/4-phenylthiosemicarbazate acting as tridentate ligand in methanol solution gave a monomeric cadmium(II) complexes, **1** and **2** of M(II)L₂ type, respectively. In addition, to here by introducing the second ligands like thiocyanate, azide, and dicyanoamide anions, dimeric complexes **3** and **4** were isolated. The formulations were in accordance with the results of elemental analysis, IR, and single crystal X-ray diffractometer measurements. Our aim in this work was to prepare the higher dimensional coordination polymers which metal centers are bridged by the anion ligands as spacer. Unfortunately, despite many attempts to obtain a high-dimensional network of complexes by changing reaction conditions, such as stoichiometry, metal salts and other reaction parameters, this effort eventually proved to be a failure.

Description of the Structures

The structures of complexes **1** and **2** with atomic notation are shown in Figs. 1 and 2, respectively. The structure of **1** consists of two trifunctional Schiff base ligands, in which the Cd(II) ion located on the twofold symmetry axis. Two Schiff base ligands are coordinated to the Cd(II) ion in the meridional form of thiolate sulfur, pyridine nitrogen atom (cis) and azomethine nitrogen atoms which are trans to each other.

Similar meridional configurations have also been found

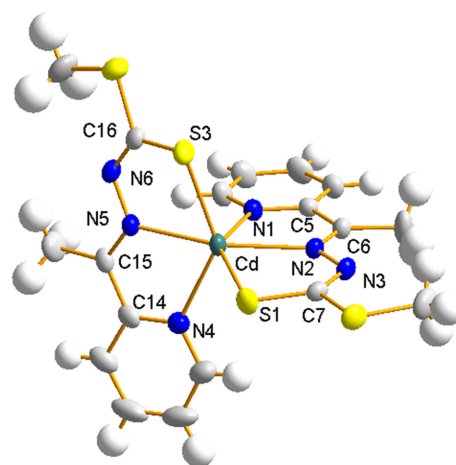


Figure 1. Molecular structure of complex [Cd(acpy-mdtc)]₂ (**1**). The thermal ellipsoids are at 50% probability level.

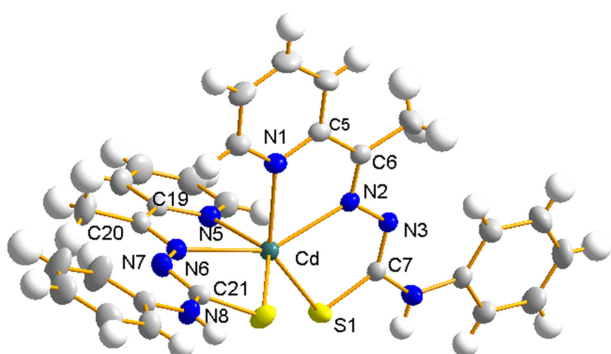


Figure 2. Molecular structure of $[\text{Cd}(\text{acpy-phTsc})_2]$ (**2**). The thermal ellipsoids are at 50% probability level.

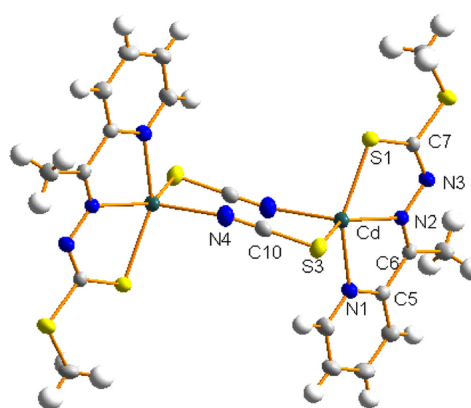


Figure 3. Molecular structure of complex $[\text{Cd}(\text{acpy-mdtc})(\text{NCS})]_2$ (**3**). The thermal ellipsoids are at 50% probability level.

in 6-coordinate Cd(II) octahedral complexes of NNS-donor thiosemicarbazones^{14,15} and dithiocarbazates.^{16–18} In the complex **1** and **2**, this CdN4S2 coordination spheres are considerably distorted, which is probably due to the ligand rigidity.⁶ The angles at the Cd center show large deviations (*Table S1*) from the ideal octahedral values of 90 and 180°. In **1**, the mean deviation of plane N1N4S1S3 from the least-square plane is 0.158(1) Å, in contrary to the planes, N1N2S1N5 and N2N4N5S3 with mean deviation 0.080(1) and 0.120(1) Å, respectively. The tridentate ligands in the complex is almost planar. The three individual rings, namely the acetylpyridine (N1C1–C5) and the two five-membered chelate rings (CdN1C5C6N2 and CdN2N3C7S1), are individually nearly planar with small dihedral angles (3.85(5)–10.7(5)°) between them. The pair of coordinating Schiff base ligands are nearly orthogonal to each other with the dihedral angle 87.59(2)°.

When coordinating in the form of an iminothiolate, the negative charges generated by deprotonation are delocalized in the –C–N–N–C system as shown by the intermediate C15–N5 [1.282(2) Å], N5–N6 [1.388(2) Å] and N6–C16 [1.301(2) Å] bond distances. In thiosemicarbazone and dithiocarbamate complexes, the bonds that are expected to be most affected by coordination are the imine C–N and the thiolate C–S bonds. Enethiolization of thiosemicarbazone or dithiocarbamate ligands is expected to lengthen the C–S bond, but the length of the C16–S3 bond, [1.728(2) Å] in the present complex is intermediate between a C–S single and C=S double bond indicating that electron delocalization in the dithiocarbamate side chain extends to the C–S bond. For **1**, bond distances, Cd–N_{py}, Cd–N_{azomethine}, and Cd–S_{thiolate} are 2.427(1) and 2.405(2) Å, 2.580(1) and 2.622(1) Å, and 2.580(1) and 2.622(1) Å, respectively, which are in accordance with the similar Cd(II) complexes reported previously.¹⁹ In the complex, **1** and **2**, the Cd–N_{azomethine} bonds are also shorter than the Cd–N_{py} bonds, complex **2**

shows the essentially similar to the structure of complex **1**.

Structure of the complex **3** is shown in *Fig. 3* and bond lengths and bond angles are shown in *Table S3*. The crystal structure is a centrosymmetric dimer in which each of the cadmium(II) ions adopts a five-coordinate square-pyramidal geometry ($\tau = 0.034$, the geometric parameter $\tau = |\beta - \alpha|/60$, where β and α are the two largest angles around the central atom; $\tau = 0$ and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively.²⁰) with a N3S2 donor. The basal plane of the square-pyramid consists of the pyridine nitrogen (N1), the azomethine nitrogen atom (N2) and the thiolate sulfur atom (S1) together with the thiocyanate sulfur atom (S3) whereas the apical positions are occupied by nitrogen atom (N4) of another thiocyanate ligand. In the complex the C7–S1 bond distance (1.721(2) Å) finds to be longer than those known free thiosemicarbazones, such as 1.678(2) Å in 4-formyl pyridinethio-semicarbazone²¹ and 1.684(4) Å in 2-keto-3-ethoxybutyl aldehyde-bis(thiosemicarbazone).²² The C6–N2 (1.290(2) Å) and C7–N3 (1.309(2) Å) bond distances show partial double bond character due to delocalization of π -electrons throughout the whole molecule²³ where the ligand molecules exist in the deprotonated thiol form. The Cd–S distance, 2.553(1) Å is in accordance with that found in the related five-coordinate cadmium(II) complex of di-2-pyridylketone Schiff base of S-benzylidithiocarbamate (dpksbz), which the Schiff base is bonded to the cadmium(II) via the thiolate sulfur atom.²⁴ The Cd–N_{py} and Cd–N_{azomethine} bond distances, 2.349(2) and 2.303(1) Å, respectively, compare well with those in $[\text{Cd}(\text{fptsc})\text{Cl}_2]$.²⁴ Also, the Cd–N4 and Cd–S3 bond distances, 2.282(2) and 2.571(1) Å, respectively, compare well with 2.287(4) for Cd–N_b and 2.576(1) Å for Cd–S in complex $[\text{Cd}_2(\text{SCN})_4(\text{py})_2\text{C}(\text{OCH}_3)(\text{OH})_2]$.¹⁰

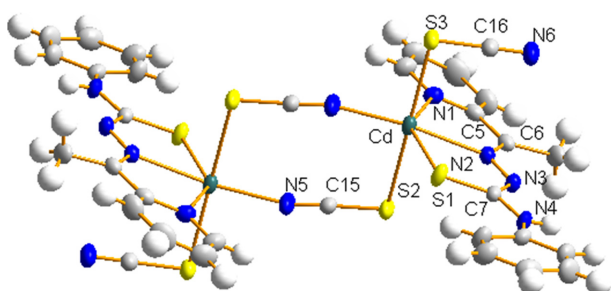


Figure 4. Molecular structure of complex $[\text{Cd}(\text{acpy-phTsc})(\text{NCS})_2]_2$ (**4**). The thermal ellipsoids are at 50% probability level.

The structure of **4** consists of the dinuclear $[\text{Cd}_2(\text{acpy-phTsc})_2(\text{SCN})_4]$ units as suggested in *Fig. 4*. The dimer results from the pairing of the two mononuclear units $[\text{Cd}(\text{acpy-phTsc})(\text{SCN})_2]$, related by a crystallographic center of inversion. Like **3**, the Cd(II) ions are doubly bridged by thiocyanate anions in an end-to-end coordination mode. The double NCS^- bridge forms an essentially planar (mean deviation 0.013(1) Å), rectangular eight-membered $\text{Cd}(\mu_{1,3}\text{-SCN})_2\text{Cd}$ ring with an intradimeric Cd...Cd separation of 6.033(1) Å, slightly longer in comparison with the related dinuclear cadmium(II) coordination compounds based on a double thiocyanate bridge and incorporating tridentate terminal co-ligand: 5.889 Å in $[\text{Cd}_2(\text{C}_{11}\text{H}_{14}\text{N}_3\text{O}_3)_2(\mu_{1,3}\text{-SCN})_2(\text{CH}_4\text{O})_2]$,²⁵ and 5.791 Å in $[\text{Cd}(\text{L1})(\text{NCS})(\mu_{1,3}\text{-SCN})_2]$ (L1 = N-(4,6-dimethyl-pyrimidin-2-yl)-N'-ylidin-2-ylmethylene-hydrazine).²⁶ Each cadmium(II) ion is six-coordinated in a highly distorted $\{\text{N}_3\text{S}_3\}$ octahedral geometry

defined by two nitrogen and one sulfur atoms of the tridentate chelating molecule, sulfur and nitrogen atoms from the bridging thiocyanate ligands and a sulfur atom from the terminally bound thiocyanate ion. The bridging and terminal thiocyanate units are quasi-linear, as reflected in their bond angles of 177.9(2) and 179.3(2)°, respectively. Cd-S(2)br bond distances, 2.838(1) Å is longer than Cd-S(3)t 2.721(1) Å. However, unlike complex **1-3**, Schiff base ligand is coordinated to the cadmium(II) ion as thione form. The key difference in geometric parameters as a result of thione bond is the contraction of the thiolate-S and the elongation of an adjacent imine bond. In the complex **4**, bond distances; C7-S1 = 1.683(2) and C7-N3 = 1.363(2) Å (Table S4) are consistent with those (C=S, 1.672(2) and C-N, 1.334(3) Å) in free ligand S-4-methylbenzyl-β-N-(2-furylmethylene) dithiocarbamate (S4MFuH) as thione form.²⁷ Also, in the complex $\text{Cd}(\text{S4MFu})_2$, which S4MFu acts as thiol form, the bond distance C=S (1.737(4) Å) is longer than that in **4** and C-N distance 1.306(5) Å is shorter than that in it, respectively. These values are also well consistent with those of complex **1-3**. Complex **4** is also further stabilized through inter-molecular H-bonds and it constructs 1D chains along c-axis by H-bonds between phenyl amine nitrogen atoms and terminal phTsc nitrogen atoms (N(4)-(H4N)...N(6)#2 d(D-H) = 0.85(2) d(H...A) = 2.11(2) d(D...A) = 2.940(3) <(DHA) = 166(2) #2 -x+1,-y,-z (*Fig. 5*). Bond length and angles are listed in *Table S4*.

A comparison of the IR spectrum of the ligand with those of its complexes is useful in ascertaining the mode

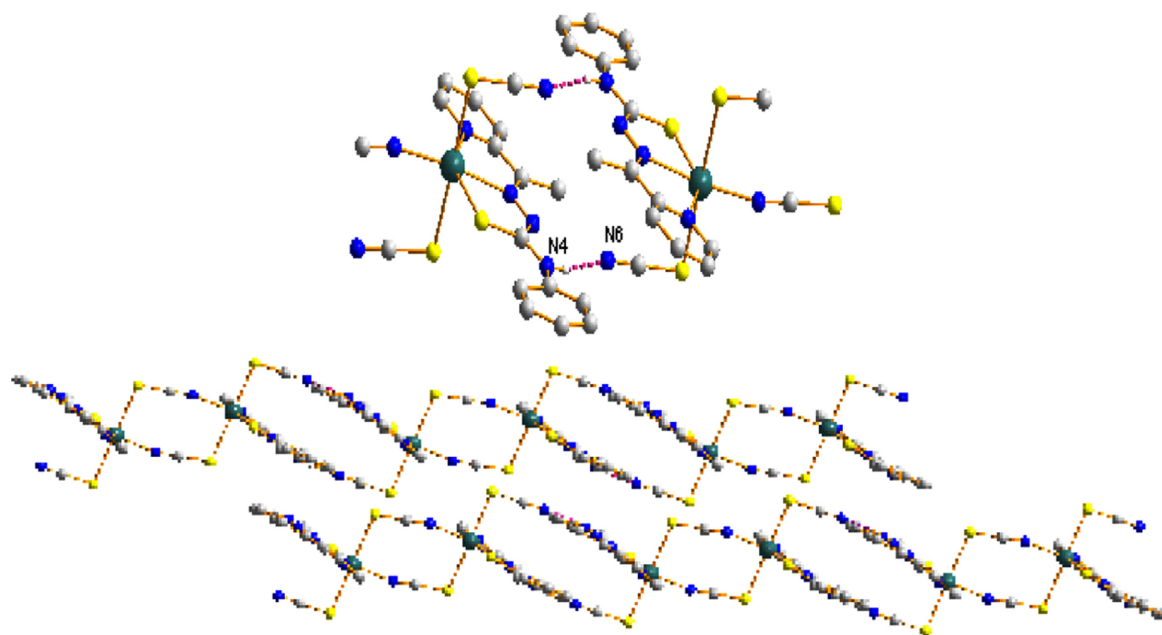


Figure 5. 1D network of $[\text{Cd}(\text{acpy-mdte})(\text{NCS})_2]_2$ (**4**) by H-bonds. All hydrogen atoms except H4N are omitted for clarity.

of coordination of the Schiff base to the metal ion. The IR spectra of the free ligand have prominent bands appearing at ca. 3148, 1060, and 951 cm^{-1} due to ν_{NH} , $\nu_{\text{N-N}}$, and $\nu_{\text{C=S}}$ for acpy-mdtcH ligand (Fig. S1). Since the acpy-phTscH ligand was synthesized in solution by the direct reaction of metal salt and the reagents for ligand formation, its spectrum could not be obtained. On complexation these all bands for the Schiff base disappeared indicating that the ligand is coordinated in its deprotonated thiol form. The $\nu_{\text{N-H}}$ bands for phenyl amine of complex **2** and **4** appeared at 3289 and 3036 cm^{-1} , respectively. The $\nu_{\text{N-N}}$ band of the free ligand shift to higher wave numbers, [1063 (1), 1080(2), 1098(3), and 1103 cm^{-1} (4), respectively] supporting coordination via the azomethine nitrogen atom. Intense absorptions associated with the stretching modes of SCN^- ions occur at 2115 cm^{-1} for **3**, at 2107 and 2072 cm^{-1} for **4**, respectively (Fig. S2, S3). The presence of two strong C-N bands in its IR spectrum for **4** is in agreement with the two different coordination modes of the thiocyanate groups in these complexes.^{10,28} This mode of bonding of the NCS^- ion in the complexes has also been confirmed by X-ray crystallography.

Thermogravimetric analyses (TGA) of complexes **1-4** were performed on crystalline samples under a nitrogen atmosphere. The TGA results show that all of these have similar thermal behaviors. The complexes were stable up to 200, 260, 193, and 210 $^{\circ}\text{C}$ for **1-4**, respectively. The most significant weight losses occurred from 200 to 550 $^{\circ}\text{C}$ for **1** (55.37%), from 260 to 550 $^{\circ}\text{C}$ for **2** (65.72%), from 193 to 550 $^{\circ}\text{C}$ for **3** (39.48%) and from 210 to 550 $^{\circ}\text{C}$ for **4** (50.90%). Then the mass was gradually reduced to 800 $^{\circ}\text{C}$, which are associated with the simultaneous decomposition of the Schiff base and the thiocyanate (for **3** and **4**) in a continuous fashion. Considering the formation of stoichiometric amounts of CdS as a final product, the weight % by 33.19(1), 29.99(2), 47.11(3) and 49.09%(4) of the residues for **1-4**, respectively, which are greater than the expected values (25.75% for **1**, 22.19% for **2**, 36.59% for **3**, and 29.02% for **4**) were attributed to the incomplete decomposition of the complexes to form CdS as a final product (Fig. S4-S7).

In conclusion, by the reactions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and appropriate Schiff base ligands with NNS donor system in methanol solution, monomeric Cd(II) complexes, $[\text{Cd}(\text{acpy-mdtc})_2](\mathbf{1})$ and $[\text{Cd}(\text{acpy-phTsc})_2](\mathbf{2})$ are synthesized, respectively. Also, by introducing thiocyanate as spacer, dimeric Cd(II), complexes, $[\text{Cd}(\text{acpy-mdtc})\text{NCS}]_2(\mathbf{3})$, and $[\text{Cd}(\text{acpy-phTsc})\text{NCS}]_2(\mathbf{4})$ are synthesized. In complexes **1-3**, the Schiff base ligand coordinated to metal center as thiol form, which is identified by IR and X-ray diffractometer mea-

surement. In the case of complex **4**, it is interesting that the Schiff base ligand acts as neutral tridentate thione fashion. Also, unlike complex **3**, it is uncommon for the thiocyanate to be bridged and terminally bonded to the metal, respectively. All complexes were stable up to ca. 200 $^{\circ}\text{C}$ and decomposed continuously up to 800 $^{\circ}\text{C}$.

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Supporting Information. Crystallographic data in CIF format have been deposited with the Cambridge Structural Database CCDC 1939081~1939084 for **1-4**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk). Table S1~S4, Fig. S1~7.

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