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# Halide anion effects on coordination polymerization of cadmium(II) halide with 1: 1 mixed ligands

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## ABSTRACT

Insight into self-assembly of $CdX_2$ (X = Cl and Br) with a mixture of $L^1$ and $L^2$ ($L^1$ = diallylbis(3-pyridyl) silane; $L^2$ = diallylbis(4-pyridyl)silane) was carried out. The self-assembly of $CdCl_2$ with the 1: 1 mixture of $L^1$ and $L^2$ produces only 2D $[CdCl_2(L^1)(L^2)]$ with heteroleptic ligands, whereas that of $CdBr_2$ with the 1: 1 mixture of $L^1$ and $L^2$ gives rise to the statistical mixture of 2D sheet $[CdBr_2(L^1)_2]\cdot 2H_2O$, 1D loop-chain $[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$, and the 2D $[CdBr_2(L^1)(L^2)]$ with heteroleptic ligands.

## 1. Introduction

Self-assembly of desirable coordination polymers including topology and dimension has been an intriguing research issue for the last two decades, owing to their task-specific applications such as separation, toxic materials adsorption, molecular containment, ion exchange, molecular recognition, catalysis, luminescent sensing, and *etc* [1–7]. However, synthesis of advantageous coordination networks is both intricate and serendipitous, presumably due to the presence of numerous significant factors such as the flexibility of organic ligands, the coordination geometry of metal cations, counteranions, mole ratios, solvents, temperature, and unpredictable weak interactions, in addition to kinetic and thermodynamic control [8–13]. Some metal complexes with mixed ligands have been known to play a noteworthy role in biological processes and analytical chemistry [14–20], and their ligands been sensitive to metal ions [12,20–22]. In our laboratory, some interesting coordination polymers with heteroleptic ligands have been synthesized using silicon-containing bidentate *N*-donor ligands [8,12,23]. Main factors such as Lewis acidity and local geometry of central metal cations and Lewis basicity and planarity of ligands [24,25] are significant to decide the formation of mixed ligand complexes. Furthermore, the formation of coordination polymers with mixed ligands sometimes determines the mechanism including the sensitivity and selectivity of ligands, stability, and composition [26,27]. A research on formation of mixed ligand complex is of very interest to coordination chemists for the estimation of physical phenomena [28].

To date, a systematic insight into halide anion effect on coordination polymerization of metal halide with mixed ligands remains unexplored. Thus, in an effort to explore the direct results on coordination polymerization of metal cation with mixed bidentate ligands, slow diffusion of $CdX_2$ (X = Cl and Br) with a mixture of $L^1$ and $L^2$ ($L^1$ = diallylbis(3-pyridyl)silane; $L^2$ = diallylbis(4-pyridyl)silane) were attempted. The reactions give rise to quite significant results depending on halide anions of cadmium(II) halides. The cadmium(II) ion has been employed as an octahedral directional unit [29–32].

## 2. Experimental

### 2.1. Materials and physical measurements

Cadmium(II) halide, 3-bromopyridine, and 4-bromopyridine were purchased from Sigma-Aldrich, and diallyldichlorosilane was purchased from Gelest. They were used without further purification. Diallylbis(3-pyridyl)silane ($L^1$) and diallylbis(4-pyridyl)

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silane ($L^2$) were prepared by the literature methods [8,33]. Elemental microanalyses (C, H, N) were performed on crystalline samples at the KBSI Pusan Center using a Vario-EL III analyzer. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer using samples prepared as KBr pellets. $^1H$ (300 MHz) and $^{13}C$ (75 MHz) NMR spectra were recorded on a Varian Mercury Plus 300. Thermal analyses were performed under $N_2$ at a scan rate 10 °C/min using a Perkin Elmer-TGA-DSC 4000.

### 2.2. *$[CdCl_2(L^1)(L^2)]$*

A methanol solution (2 mL) of cadmium(II) chloride (1.8 mg, 0.01 mmol) was carefully layered on to an ethanol solution (2 mL) of a mixture of $L^1$ (2.6 mg, 0.01 mmol) and $L^2$ (2.6 mg, 0.01 mmol) at room temperature. After four days, colorless crystals suitable for X-ray crystallography were obtained. Yield, 4.4 mg (61%). m.p. 210 °C (dec.). Anal. Calcd. For $C_{32}H_{36}N_4Si_2CdCl_2$: C, 53.67; H, 5.07; N, 7.82%. Found: C, 53.60; H, 5.19; N, 7.72%. IR (KBr pellet, $cm^{-1}$): 3077(w), 3058(w), 1631(m), 1585(m), 1407(s), 1326(m), 1195(m), 1160(m), 1126(s), 1037(s), 1029(s), 991(m), 902(m), 813(w), 790(m), 771(m), 709(m), 640(m), 613(m), 582(m), 501(m), 447(w).

### 2.3. *$[CdCl_2(L^1)_2]\cdot 2H_2O$*

A methanol solution (1.0 mL) of cadmium(II) chloride (1.8 mg, 0.01 mmol) was carefully layered onto an ethanol solution (1.0 mL) of $L^1$ (2.6 mg, 0.01 mmol) at room temperature. After two days, colorless crystals suitable for X-ray crystallography were obtained. Yield, 2.5 mg (67%). m.p. 215 °C (dec.). Anal. Calcd. For $C_{32}H_{40}O_2N_4Si_2CdCl_2$: C, 51.10; H, 5.36; N, 7.45%. Found: C, 51.60; H, 5.29; N, 7.42%. IR (KBr pellet, $cm^{-1}$): 3536(s, O—H), 3446(m, O—H), 3077(w), 3056(w), 3000(w), 2971(w), 2917(w), 2362(w), 1629(m), 1583(s), 1473(m), 1403(s), 1336(m), 1191(m), 1162(m), 1128(m), 1041(m), 1027(m), 985(w), 927(m), 902(s), 790(s), 748(s), 711(s), 644(m), 611(m), 580(w), 485(m), 424(m).

### 2.4. *Mixture crystals of $[CdBr_2(L^1)(L^2)]$, $[CdBr_2(L^1)_2]\cdot 2H_2O$ and $[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$*

A methanol solution (1.5 mL) of cadmium(II) bromide (3.4 mg, 0.01 mmol) was carefully layered onto a dichloromethane solution (1.5 mL) of $L^1$ (2.6 mg, 0.01 mmol) and $L^2$ (2.6 mg, 0.01 mmol) at room temperature. After seven days, statistical mixture crystals of $[CdBr_2(L^1)(L^2)]$, $[CdBr_2(L^1)_2]\cdot 2H_2O$, and$[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$ suitable for X-ray crystallography were obtained. Total yield (80%). IR (KBr pellet, $cm^{-1}$) for the mixture crystals: 3058(w), 2996(w), 2969(w), 2360(w), 2341(w), 1631(m), 1585(m), 1527(w), 1473(w), 1407(s), 1326(m), 1226(w), 1199(m), 1160(m), 1126(s), 1041(m), 991(w), 902(m), 809(m), 790(m), 771(m), 709(m), 640(w), 613(m), 582(m), 489(w), 451(w).

### 2.5. *$[CdBr_2(L^1)_2]\cdot 2H_2O$*

A methanol solution (5.0 mL) of cadmium(II) bromide (13.6 mg, 0.05 mmol) was carefully layered onto an ethanol solution (5.0 mL) of $L^1$ (13.3 mg, 0.05 mmol) at room temperature. After two days, colorless crystals suitable for X-ray crystallography were obtained. Yield, 13.7 mg (65%). m.p. 191 °C (dec.). Anal. Calcd. For $C_{32}H_{40}O_2N_4Si_2CdBr_2$: C, 45.70; H, 4.79; N, 6.66%. Found: C, 45.20; H, 4.68; N, 6.59%. IR (KBr pellet, $cm^{-1}$): 3515(m, O—H), 3440(m, O—H), 3077(w), 3056(w), 2998(w), 2973(w), 2915(w), 2885(w), 1629(m), 1581(s), 1473(m), 1403(s, 1336(m), 1189(m), 1159(m), 1126(m), 1026(s), 985(w), 900(s),790(s), 748(s), 709(s), 642(s), 611(m), 485(m).

### 2.6. *$[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$*

An ethanol solution (1.0 mL) of cadmium(II) bromide (5.4 mg, 0.02 mmol) was carefully layered onto an dichloromethane solution (1.0 mL) of $L^2$ (5.3 mg, 0.02 mmol) at room temperature. After three days, colorless crystals suitable for X-ray crystallography were obtained. Yield, 6.0 mg (62%). m.p. 320 °C (dec.). Anal. Calcd. For $C_{34}H_{40}N_4Si_2CdCl_4Br_2$: C, 41.89; H, 4.14; N, 5.75%. Found: C, 41.20; H, 4.21; N, 5.71%. IR (KBr pellet, $cm^{-1}$): 3058(w), 3035(w), 2993(w), 2969(w), 2877(w), 1631(s), 1596(s), 1527(w), 1407(s), 1315(m), 1226(m), 1160(s), 1122(s), 1037(m), 335(m), 910(s), 786(m), 763(s), 728(w), 705(w), 605(m), 582(m), 485(m), 458(m).

### 2.7. *X-ray crystallography*

All X-ray crystallographic data collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo Kα

**Table 1**

Crystal data and structural refinements for $[CdCl_2(L^1)(L^2)]$, $[CdCl_2(L^1)_2]\cdot 2H_2O$, $[CdBr_2(L^1)(L^2)]$, $[CdBr_2(L^1)_2]\cdot 2H_2O$, and $[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$.

| | $[CdCl_2(L^1)(L^2)]$ | $[CdCl_2(L^1)_2]\cdot 2H_2O$ | $[CdBr_2(L^1)(L^2)]$ | $[CdBr_2(L^1)_2]\cdot 2H_2O$ | $[CdBr_2(L^2)_2]\cdot 2CH_2Cl_2$ |
|---|---|---|---|---|---|
| Formula | $C_{128}H_{144}N_{16}Cd_4Cl_8\ Si_8$ | $C_{32}H_{40}O_2N_4Si_2CdCl_2$ | $C_{128}H_{144}N_{16}Si_8Cd_4Br_8$ | $C_{32}H_{40}O_2N_4Si_2CdBr_2$ | $C_{34}H_{40}N_4Si_2CdCl_4Br_2$ |
| $M_w$ (g $mol^{-1}$) | 2864.50 | 752.16 | 3220.18 | 841.08 | 974.90 |
| Cryst. system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | C*c* | C2/*c* | C*c* | C2/*c* | P-*1* |
| *a* (Å) | 22.2153(4) | 17.5640(3) | 22.795(1) | 18.2600(4) | 8.6825(1) |
| *b* (Å) | 22.2168(4) | 13.3531(3) | 22.780(1) | 12.4538(3) | 10.5733(1) |
| *c* (Å) | 28.0505(7) | 15.6320(3) | 27.728(1) | 15.3525(3) | 12.7062(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 76.079(1) |
| $\beta$ (°) | 101.414(1) | 105.163(1) | 101.943(3) | 102.782(1) | 88.599(1) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 67.760(1) |
| $V$ ($Å^3$) | 13570.6(5) | 3538.7(1) | 14086(1) | 3404.8(1) | 1045.06(2) |
| $Z$ | 4 | 4 | 4 | 4 | 1 |
| $\rho$ (g $cm^{-3}$) | 1.402 | 1.412 | 1.518 | 1.641 | 1.549 |
| $\mu$ ($mm^{-1}$) | 0.899 | 0.870 | 2.984 | 3.094 | 2.776 |
| $F(000)$ | 5856 | 1544 | 6432 | 1688 | 486 |
| $R_{int}$ | 0.0859 | 0.0213 | 0.0740 | 0.0237 | 0.0207 |
| GoF on $F^2$ | 1.012 | 1.063 | 1.042 | 1.087 | 1.081 |
| $R_1$ $[I > 2\sigma(I)]$[a] | 0.0963 | 0.0193 | 0.0740 | 0.0333 | 0.0352 |
| $wR_2$ (all data)[b] | 0.2908 | 0.0517 | 0.2332 | 0.0925 | 0.0931 |
| Completeness (%) | 100.0% ($\theta = 25.2°$) | 100% ($\theta = 25.2°$) | 100.0%($\theta = 25.2°$) | 100.0%($\theta = 25.2°$) | 99.9%($\theta = 25.2°$) |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.