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# Synthesis, Crystal Structure, and Fluorescence Property of a Thiocyanato-Bridged Polymeric Cadmium(II) Complex Derived from (1-Pyridin-2-ylethylidene)pyridin-2-ylmethylamine[1]

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**Abstract**—A new thiocyanato-bridged polymeric cadmium(II) complex with the Schiff base ligand (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine (L) derived from 2-acetylpyridine and 2-aminomethylpyridine has been prepared and characterized by elemental analyses, IR spectrum, and single crystal X-ray crystallographic determination. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a$ = 8.904(2), $b$ = 12.041(2), $c$ = 15.550(3) Å, β = 92.354(2)°, $V$ = 1665.7(5) Å$^3$, $Z$ = 4, $R_1$ = 0.0523, and $wR_2$ = 0.1274. The Schiff base ligand coordinates to the Cd atom through the three N atoms. The Cd atom of the complex is heptacoordinated by the Schiff base ligand in a tridentate fashion, one nitrate ligand in a bidentate fashion, and one N and one S atoms from two thiocyanate ligands. The overall coordination is pseudopentagonal bipyramidal geometry. The fluorescence property of the complex was investigated.

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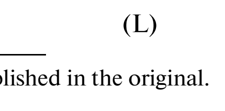
## INTRODUCTION

Considerable attention has been focused on the polymeric complexes containing bridging ligands because of their interesting molecular topologies, as well as the fact that they may be designed with specific functionalities [1–3]. Thiocyanate anions have been widely used in the construction of polymeric structures with either end-on or end-to-end bridging mode [4–6]. In addition, luminescent compounds are attracting much interest because of their versatile applications in medical and analytical chemistry [7, 8]. The cadmium complexes with Schiff bases have shown interesting fluorescence properties [4, 9, 10]. In this paper, a new thiocyanato-bridged polymeric cadmium(II) complex, $[CdL(NO_3)(\mu_{1,3}\text{-NCS})]_n$ (**I**), with the tridentate Schiff base (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine (**L**) has been prepared, characterized, and investigated for its fluorescence property.



(L)

## EXPERIMENTAL

**Material and methods.** 2-Acetylpyridine and 2-aminomethylpyridine were purchased from Fluka. The cadmium nitrate and other reagents were analytical grade and were used without further purification. The Schiff base L was prepared by the condensation of equimolar quantities of 2-acetylpyridine with 2-aminomethylpyridine in methanol according to the literature method [11]. Elemental (C, H, and N) analyses were made on a PerkinElmer Model 240B automatic analyser. Infrared spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD diffractometer. The luminescence spectrum was recorded on a JASCO FP-6500 spectrofluorimeter (solid) in the range of 300–550 nm.

**Synthesis of complex I.** The Schiff base L (0.105 g, 0.5 mmol) was diluted by methanol (20 mL), to which was added with stirring a methanol solution (10 mL) of cadmium nitrate tetrahydrate (0.154 g, 0.5 mmol), and an aqueous solution (1 mL) of ammonium thiocyanate (0.038 g, 0.5 mmol). The mixture was stirred for 1 h at ambient temperature to give a colorless solution. Colorless block-shaped single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution in air for a week. The crystals were fil-

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[1] The article is published in the original.

**Table 1.** Crystallographic data and structure refinement summary for complex I

| Parameter | Value |
|---|---|
| Habit, color | Block, colorless |
| Formula weight | 442.8 |
| Temperature, K | 298(2) |
| Crystal size, mm | 0.27 × 0.23 × 0.23 |
| Radiation ($\lambda$, Å) | Mo$K_\alpha$ (0.71073) |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions: | |
| $a$, Å | 8.904(2) |
| $b$, Å | 12.041(2) |
| $c$, Å | 15.550(3) |
| $\beta$, deg | 92.354(2) |
| $V$, Å$^3$ | 1665.7(5) |
| $Z$ | 4 |
| $\rho_{calcd}$, mg cm$^{-3}$ | 1.765 |
| Absorption coefficient, mm$^{-1}$ | 1.459 |
| $\theta$ Range for data collection, deg | 2.14–26.99 |
| Index ranges | $-11 \le h \le 11, -15 \le k \le 15, -19 \le l \le 17$ |
| Reflections collected | 13238 |
| Independent reflections | 3625 |
| Observed reflections ($I > 2\sigma(I)$) | 2356 |
| Parameters | 218 |
| Restraints | 6 |
| Final $R$ indices ($I \ge 2\sigma(I)$) | 0.0523 |
| $R$ indices (all data) | 0.0947 |
| Goodness-of-fit | 1.098 |
| Largest diff. peak and hole, $e$/A$^3$ | 1.282 and –0.568 |

**Table 2.** Coordinate bond distances (Å) and angles (deg) for complex I*

| Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|
| Cd(1)–N(1) | 2.358(6) | Cd(1)–N(2) | 2.336(6) |
| Cd(1)–N(3) | 2.347(6) | Cd(1)–N(4)$^i$ | 2.298(7) |
| Cd(1)–O(1) | 2.526(7) | Cd(1)–O(2) | 2.400(7) |
| Cd(1)–S(1) | 2.809(2) | | |
| Angle | $\omega$, deg | Angle | $\omega$, deg |
| N(4)Cd(1)N(2)$^i$ | 97.2(2) | N(4)Cd(1)N(3)$^i$ | 93.2(3) |
| N(2)Cd(1)N(3) | 69.9(2) | N(4)Cd(1)N(1)$^i$ | 92.5(2) |
| N(2)Cd(1)N(1) | 69.9(3) | N(3)Cd(1)N(1) | 139.9(3) |
| N(4)Cd(1)O(2)$^i$ | 89.4(3) | N(2)Cd(1)O(2) | 153.8(2) |
| N(3)Cd(1)O(2) | 135.2(2) | N(1)Cd(1)O(2) | 84.5(3) |
| N(4)Cd(1)O(1)$^i$ | 82.0(2) | N(2)Cd(1)O(1) | 155.7(2) |
| N(3)Cd(1)O(1) | 85.8(2) | N(1)Cd(1)O(1) | 134.3(3) |
| O(2)Cd(1)O(1) | 50.3(2) | N(4)Cd(1)S(1)$^i$ | 172.66(19) |
| N(2)Cd(1)S(1) | 90.07(15) | N(3)Cd(1)S(1) | 88.61(16) |
| N(1)Cd(1)S(1) | 90.65(16) | O(2)Cd(1)S(1) | 84.32(19) |
| O(1)Cd(1)S(1) | 91.05(15) | | |

* Symmetry code for: $^i$ $1/2 - x, -1/2 + y, 1/2 - z$.

tered off, washed with cold methanol, and dried over silica gel. The yield was 63% (based on L).

For $C_{14}H_{12}N_5O_3SCd$

anal. calcd., %: C, 38.0; H, 2.7; N, 15.8.

Found, %: C, 37.8; H, 2.8; N, 15.7.

IR data ($\nu$, cm$^{-1}$): 3106 w, 3063 w, 2874 w, 2108 v.s, 1658 s, 1603 s, 1593 m, 1572 w, 1438 s, 1383 m, 1293 s, 1253 w, 1210 w, 1158 w, 1105 w, 1050 w, 1036 w, 1013 m, 817 w, 786 m, 770 m, 720 w, 668 w, 638 w, 605 w, 578 w, 456 w, 407 m.

**X-ray structure determination.** Data were collected from a selected well-shaped single crystal mounted on a glass fibre. The data for the complex was processed with SAINT [12] and corrected for absorption using SADABS [13]. Multiscan absorption correction was applied with $\psi$ scans [14]. The structure was solved by direct method using the program SHELXS-97 and was refined by full-matrix least-squares techniques on $F^2$ using anisotropic displacement parameters [15]. All hydrogen atoms were placed at the calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic $U$ values of the parent carbon atoms. The crystallographic data for the complex are listed in Table 1. Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 849708;

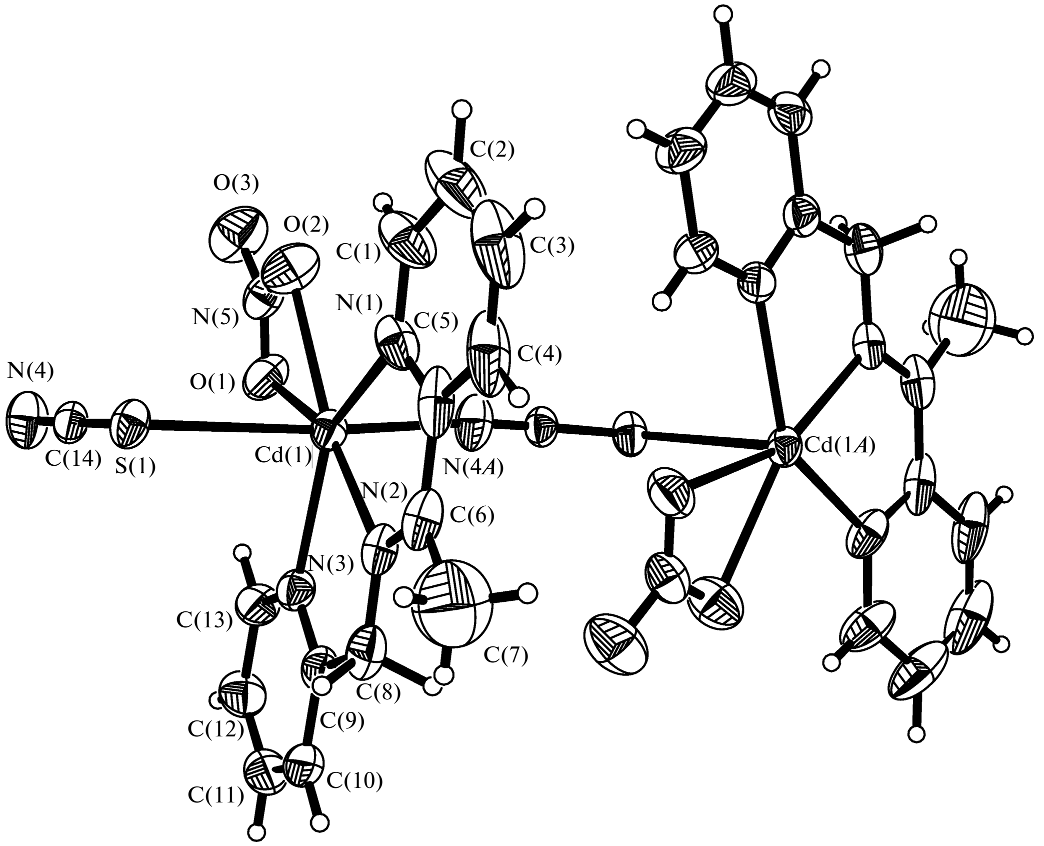

**Fig. 1.** Perspective view of complex **I** with 30% probability thermal ellipsoids. Unlabeled atoms and those labeled with the suffix *A* are related to the symmetry position $1/2 - x, -1/2 + y, 1/2 - z$.

deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The Schiff base ligand L was readily prepared by the condensation of equimolar quantities of 2–acetylpyridine and 2–aminomethylpyridine in methanol. The Schiff base prepared in this way is formed in nearly quantitative yield and is of high purity. There are one mononuclear Zn and one mononuclear Cd complexes with L and nitrate ligands have been reported [16]. As is well known, the thiocyanate ligands are easily coordinate to the Cd atoms, generating interesting polymeric structures [17–19]. In this paper, the thiocyanate ligand was introduced during the preparation. As expected, the thiocyanato-bridged polymeric complex with L and nitrate ligand was obtained. The complex is stable at room temperature in the solid state. The results of the elemental analyses are in accord with the composition suggested for complex **I**.

The molecular structure of complex **I** is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The complex is a thiocyanato-bridged polymeric Schiff base cadmium(II) compound. The smallest repeat unit of the complex is [CdL($NO_3$)(NCS)]. The Cd···Cd distance is 6.301(2) Å. Each Cd atom is hepta-coordinated by the Schiff base ligand L in a tridentate NNN fashion, one $NO_3^-$ in a bidentate fashion, and one S and one N atoms from two thiocyanate ligands. The overall coordination is pseudo-pentagonal bipyramidal geometry. As expected, the Cd–$N_{imine}$ is shorter than the Cd–$N_{pyridine}$. The coordinate bond lengths are comparable to those observed in similar cadmium(II) complexes with Schiff bases [16, 20, 21]. The chelate rings, Cd(1)–N(1)–C(5)–C(6)–N(2) and Cd(1)–N(2)–C(8)–C(9)–N(3) are nearly planar and form a dihedral angle of 0.1(2)°. The bidentate nitrate ligand occupies the pentagonal base and deviates from the plane formed by the two chelate rings by an angle of 9.5(2)°. The [CdL($NO_3$)] units are linked through end-to-end thiocyanate bridges, forming 1D chains running along the *y* axis, as shown by Fig. 2.

The weak absorptions at 3106 and 3063 $cm^{-1}$ in the spectrum of complex **I** are assigned to the aromatic C–H vibrations. The intense absorption band at 2108 $cm^{-1}$ is assigned to the stretching vibrations of the thiocyan-

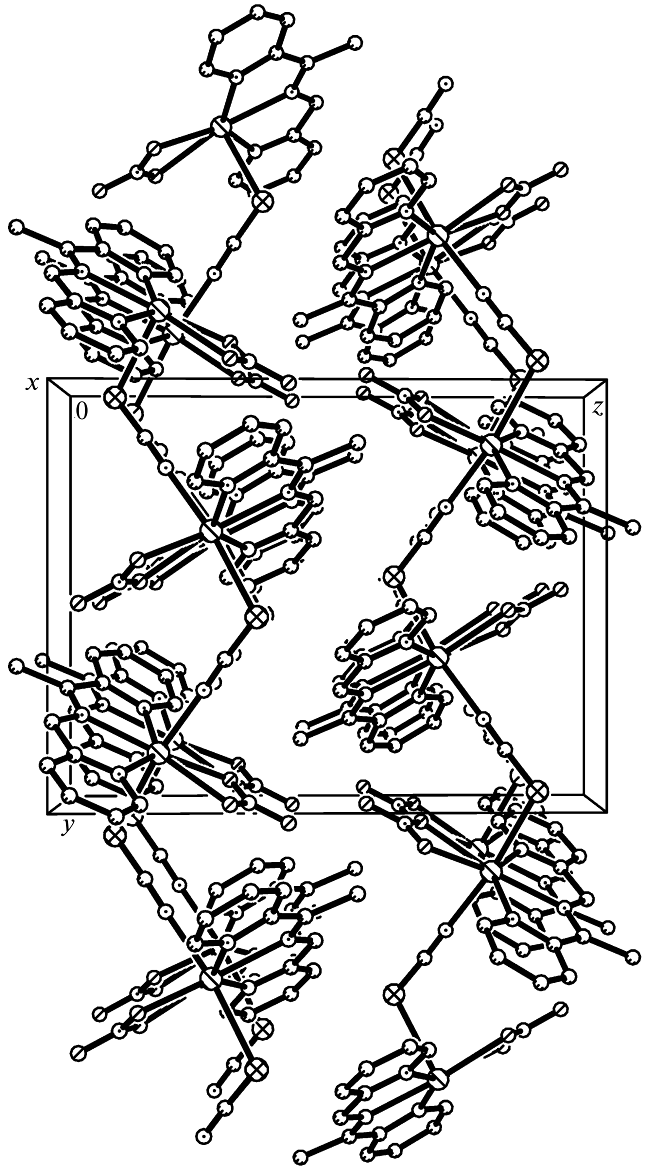

**Fig. 2.** Molecular packing of complex **I**, viewed along the *x* axis.

ate groups. The strong absorption band centered at 1658 $cm^{-1}$ is assigned to the azomethine group, $\nu(C{=}N_{imine})$, and that centered at 1603 $cm^{-1}$ is attributed to the vibration of the $\nu(C{=}N_{pyridine})$. The vibrations of the Cd–O, Cd–N, and Cd–S bonds are located in the low wave numbers 400–700 $cm^{-1}$.

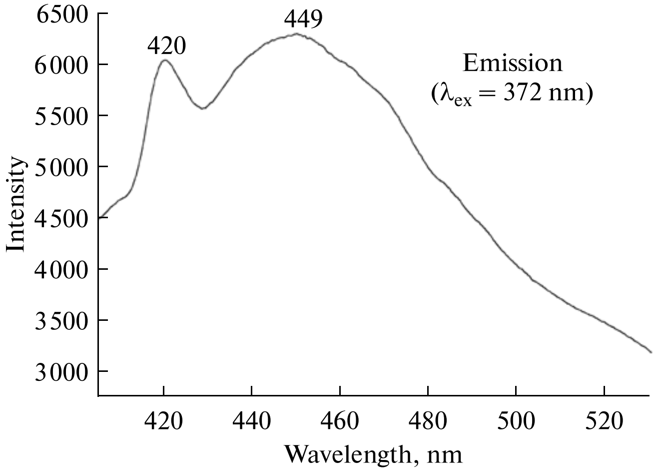

**Fig. 3.** Emission spectra of complex **I**.

The fluorescence property of complex **I** was studied at room temperature (298 K) in the solid state. Figure 3 is the emission spectrum of the complex. There are two emission bands for the complex, centered at 420 and 449 nm ($\lambda_{ex}$ = 372 nm), respectively. This may be caused by the ligand-to-metal charge transfer (LMCT) [22]. Such luminescent behavior suggests that the emission bands of the complex are mainly due to a ligand-to-metal charge transfer emission state as reported for Cd(II) or other $d^{10}$ metal compounds [23, 24].

## ACKNOWLEDGMENTS

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