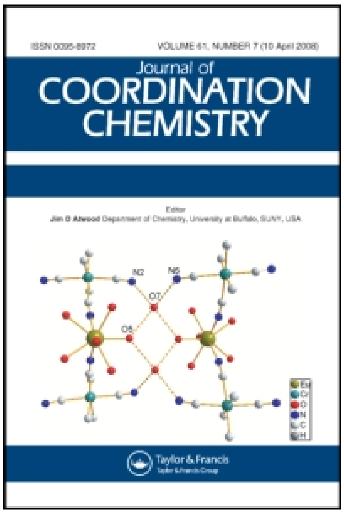

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Synthesis, crystal structure and spectroscopic characterization of silver(I), cadmium(II) complexes with the Schiff base derived from pyridine-2-carboxaldehyde and 4-[(*E*)-2-phenyldiazenyl]aniline

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Synthesis, crystal structure and spectroscopic characterization of silver(I), cadmium(II) complexes with the Schiff base derived from pyridine-2-carboxaldehyde and 4-[(*E*)-2-phenyldiazenyl]aniline

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The bidentate Schiff-base L is synthesized by condensation of pyridine-2-carboxaldehyde with 4-[(*E*)-2-phenyldiazenyl]aniline. Hydrothermal reaction of L with $AgNO_3$ and $Cd(ClO_4)_2 \cdot 6H_2O$ afforded complexes $AgLNO_3$ (**1**) and $[CdL_2(H_2O)ClO_4]ClO_4$ (**2**), respectively, which are characterized by elemental analysis and IR spectroscopy. The single crystal X-ray diffraction analyses reveal that both **1** and **2** are mononuclear. In **1**, Ag(I) is coordinated by two N atoms from the Schiff-base ligand and one O atom from NO_3^- group in a distorted trigonal geometry. In **2**, the cadmium(II) is coordinated in a distorted octahedral geometry, with an equatorial plane composed of four nitrogen atoms from two bidentate Schiff-base ligands, and the apical position occupied by one O atom from aqua ligand and one O atom from perchlorate.

Keywords: Silver(I); Cadmium(II); Crystal structure; Schiff base; Pyridine-2-carboxaldehyde; 4-[(*E*)-2-phenyldiazenyl]aniline

1. Introduction

Schiff-base ligands have played an integral and important role in the development of coordination chemistry since the late 19th century. That metal complexes of these ligands are ubiquitous is a reflection of their facile synthesis, wide application and the accessibility of diverse structural modifications [1]. Research of Schiff-base metal complexes has expanded enormously, and embraces very wide and diversified

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subjects comprising vast areas of organometallic compounds and various aspects of bioinorganic chemistry [2]. In the last decades, coordination chemistry of Schiff bases derived from 2-pyridinecarboxaldehyde has received much attention [3–7]. Recently we reported a series of transition metal complexes with such ligands, such as Ni(II) [8], Co(II) [9], and Co(III) [10] complexes. Recently, photoswitchable units have been incorporated in a variety of supramolecular systems as a new strategy to effect photochemical control over molecular self-assembly, by using photoresponsive azobenzene units as supramolecular building blocks [11]. Therefore, it is important to investigate Schiff-base complexes containing a diazo group. Although complexes with Schiff bases derived from phenylenediamines have been widely investigated [12], thus far, complexes with the Schiff base derived from 4-[(*E*)-2-phenyldiazenyl]aniline have not been reported. In this paper we report the synthesis, spectroscopic characterization and X-ray crystal structure of complexes of Ag(I), and Cd(II) with Schiff-base ligands derived from 2-pyridine-carboxaldehyde and 4-[(*E*)-2-phenyldiazenyl]aniline.

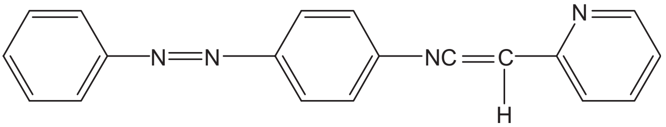
2. Experimental

2.1. *Physical measurements*

All reagents used were of analytical grade. C, H, N elemental analyses were carried out with a Perkin–Elmer analyser model 240II. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (0.1 mol dm^{-3}) at 20°C with a Bruker AVANCE AV 500 MHz spectrometer using Me_4Si as internal standard. IR spectra were recorded as KBr discs on a Perkin–Elmer Spectrum One FT-IR spectrophotometer in the 4000–400 cm^{-1} region.

2.2. *Synthesis of the ligand and its complexes*

2.2.1. Synthesis of the ligand. *N*-{4-[(*E*)-2-phenyldiazenyl]phenyl}-*N*-[(*E*)-2-pyridinylmethylidene]amine (L) (scheme 1) was prepared as previously reported [13]. Pyridine-2-carbaldehyde (1.08 g, 0.01 mol) was directly added to an ethanolic suspension (50 mL) of 4-[(*E*)-2-phenyldiazenyl]aniline (1.97 g, 0.01 mol). After 2 hours of heating at 80°C, the deep brown solid was obtained by evaporation *in vacuo*, washed with ethanol and dried in vacuum over $CaCl_2$. Yield 2.32 g (80%), mp 119°C. Anal. Calcd. for $C_{18}H_{14}N_4$(%): C, 75.50; H, 4.93; N, 19.57. Found: C, 75.41; H, 4.87; N, 19.62. ^{1}H NMR(500 MHz, $CDCl_3$, ppm): 6.77(d, 1H, $J = 9$ Hz, –N=C–CH= of pyridine), 7.41–7.57(m, 5H), 7.82–8.05(m, 5H), 8.25(d, 1H, $J = 8$ Hz), 8.69(s, 1H, –N=CH–), 8.77(d, 1H, $J = 4.5$ Hz, –N=CH– of pyridine); ^{13}C NMR(500 MHz, $CDCl_3$, ppm): 161.4(–N=CH–), 154.3, 153.3, 152.7, 151.2, 149.8, 136.8, 131.0, 129.1, 129.0, 125.5, 125.1, 124.1, 122.9, 122.3, 122.2, 121.9, 114.6. IR (KBr, cm^{-1}): 3430(s),



Scheme 1. *N*-{4-[(*E*)-2-phenyldiazenyl]phenyl}-*N*-[(*E*)-2-pyridinylmethylidene]amine (L).

3060(w), 2921(w), 1957(w), 1599(s, ν(C=N)), 1506(m), 1489(w), 1461(w), 1411(m), 1331(w), 1307(w), 1236(w), 1139(s), 1089(w), 1070(w), 1048(w), 1020(w), 996(w), 922(w), 882(w), 852(m), 883(m), 768(s), 745(w), 723(w), 687(s), 612(w), 563(m), 545(m), 492(w).

2.2.2. Synthesis of [AgLNO$_3$] (1). A methanolic mixture (15 mL) containing L (0.568 g, 2 mmol), $AgNO_3$ (0.34 g, 2 mmol) and dichloromethane (3 mL) was placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), and the vessel was sealed and heated to 45°C for 6 days. Orange block-like crystals were obtained. Yield 0.73 g (80.0%). Anal. Calcd. for $C_{18}H_{14}AgN_5O_3$ (%): C, 47.39; H, 3.09; N, 15.35. Found: C, 47.47; H, 3.15; N, 15.43. IR (KBr, cm^{-1}): 34178(s), 3059(w), 1623(w), 1597(s), 1493(w), 1460(w), 1422(s), 1384(s), 1362(s), 1298(s), 1221(w), 1188(w), 1152(m), 1100(w), 1070(w), 1053(w), 1034(w), 1007(w), 974(w), 928(w), 905(w), 846(s), 814(w), 768(s), 742(w), 723(w), 689(s), 619(m), 559(m), 500(w), 413(w).

2.2.3. Synthesis of [CdL$_2$(H$_2$O)ClO$_4$]ClO$_4$ (2). Complex **2** was prepared by using the same procedure as for complex **1**. Orange block-like crystals were obtained. Yield 0.77 g (85%). Anal. Calcd. for $C_{36}H_{30}CdCl_2N_8O_9$ (%): C, 47.94; H, 3.35; N, 12.42. Found: C, 47.82; H, 3.27; N, 12.35. IR (KBr, cm^{-1}): 3498(s), 3068(w), 1680(w), 1641(w), 1601(s), 1490(w), 1450(w), 1419(w), 1373(w), 1321(w), 1278(w), 1230(w), 1205(w), 1117(s), 1060(w), 1025(w), 990(w), 922(w), 850(w), 779(m), 746(w), 737(s), 698(w), 637(m), 600(w), 576(w), 550(w), 521(w), 470(w), 420(w), 413(w).

2.3. *X-ray structure determination*

The diffraction intensity data for **1** were collected on a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using $\omega/2\theta$ scan mode at 295(2) K. Lp and empirical absorption corrections were applied. The diffraction experiments for **2** were carried out on a Siemens Smart CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 231(2) K. In the latter case, using the program SAINT [14] reduced the collected data and SADABS [15] did empirical absorption correction. Both structures were solved by direct methods and refined on F^2 using SHELXTL97 [16]. All non-hydrogen atoms were refined by full-matrix least-squares methods. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms. The crystal data and structure parameters are summarized in table 1. It must be pointed out that the three largest peaks from the difference map for **2** are located very near to the Cd1 heavy atom due to Fourier series termination errors.

3. Results and discussion

The molecular structures with atomic numbering schemes and packing views of **1** and **2** are shown in figures 1–4, respectively. Selected bond lengths (Å) and bond angles (°) for **1** and **2** are listed in table 2.

Table 1. Crystal data and refinement parameters of **1** and **2**.

Complex	$AgLNO_3$ (**1**)	$[CdL_2(H_2O)ClO_4]ClO_4$ (**2**)
Empirical formula	$C_{18}H_{14}AgN_5O_3$	$C_{36}H_{30}CdCl_2N_8O_9$
Formula weight	456.21	901.98
Temperature (K)	295(2)	213(2)
Wavelength (Mo-Kα) (Å)	0.71073	0.71073
Crystal size (mm)	0.44 × 0.44 × 0.26	0.46 × 0.28 × 0.12
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.766(1)	7.7276(2)
b (Å)	9.827(1)	11.9899(3)
c (Å)	11.000(2)	21.0842(5)
α (°)	79.36(1)	100.323(1)
β (°)	83.06(1)	90.400(1)
γ (°)	68.22(1)	105.805(1)
V (Å^3)	863.4(2)	1846.0(1)
Z	2	2
D_c (mg m^{-3})	1.755	1.623
μ (mm^{-1})	1.198	0.804
$F(000)$	456	912
θ range (°)	1.89 to 25.50	2.83 to 28.36
Limiting indices	$0 \le h \le 10$, $-10 \le k \le 11$, $-13 \le l \le 13$	$-10 \le h \le 10$, $-15 \le k \le 15$, $-27 \le l \le 27$
Reflections collected	3537	11424
Unique reflections	3202 (R(int) = 0.0102)	8580 (R(int) = 0.0806)
Data/restraints/parameters	3202/0/245	8580/0/506
Goodness-of-fit on F^2	0.896	0.965
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0284$, $wR2 = 0.0612$	$R1 = 0.0761$, $wR2 = 0.1882$
All data	$R1 = 0.0466$, $wR2 = 0.0645$	$R1 = 0.0877$, $wR2 = 0.1974$
Largest diff. peak and hole (e Å^{-3})	0.338, −0.357	3.638, −1.590

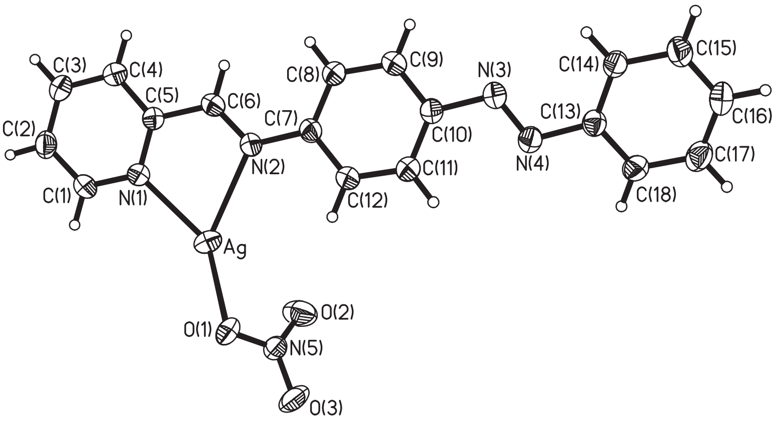


Figure 1. Crystal structure of $AgLNO_3$ (**1**) showing the atom numbering scheme with the thermal ellipsoids drawn at the 30% probability level.

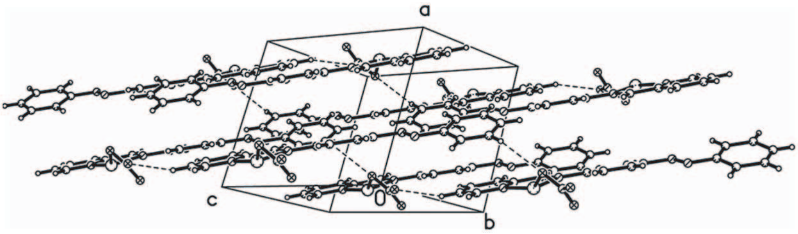


Figure 2. Packing view of $AgLNO_3$ (**1**).

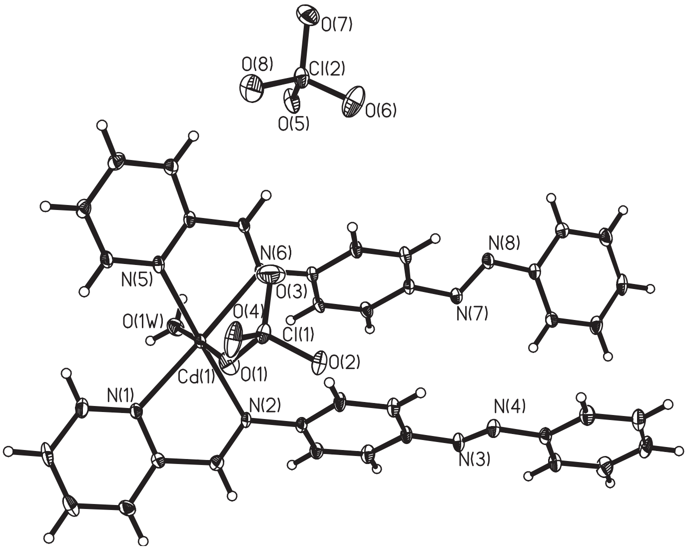


Figure 3. Crystal structure of $[CdL_2(H_2O)ClO_4]ClO_4$ (**2**) showing the atom numbering scheme with the thermal ellipsoids drawn at the 30% probability level.

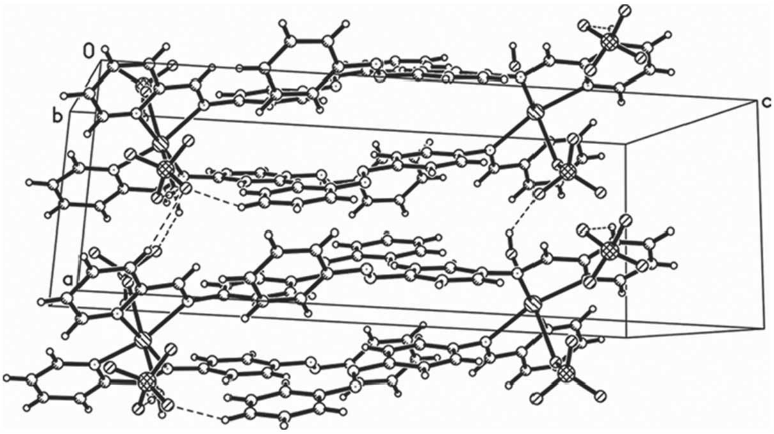


Figure 4. Packing view of $[CdL_2(H_2O)ClO_4]ClO_4$ (**2**).

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

*$AgLNO_3$ (**1**)*			
Ag–N(1)	2.254(2)	N(1)–Ag–O(1)	145.14(7)
Ag–O(1)	2.2767(19)	N(1)–Ag–N(2)	72.30(7)
Ag–N(2)	2.437(2)	O(1)–Ag–N(2)	128.77(8)
*$[CdL_2(H_2O)ClO_4]ClO_4$ (**2**)*			
Cd(1)–N(1)	2.325(4)	Cd(1)–N(6)	2.319(4)
Cd(1)–N(2)	2.304(4)	Cd(1)–N(5)	2.3000(4)
Cd(1)–O(1W)	2.317(4)	Cd(1)–O(1)	2.511(4)
N(5)–Cd(1)–N(2)	165.01(14)	N(5)–Cd(1)–N(1)	106.03(14)
N(5)–Cd(1)–O(1W)	97.72(14)	N(2)–Cd(1)–N(1)	73.24(14)
N(2)–Cd(1)–O(1W)	97.24(13)	O(1W)–Cd(1)–N(1)	89.08(14)
N(5)–Cd(1)–N(6)	73.71(13)	N(6)–Cd(1)–N(1)	176.32(13)
N(2)–Cd(1)–N(6)	89.08(14)	N(5)–Cd(1)–O(1)	84.70(14)
O(1W)–Cd(1)–N(6)	87.33(13)	N(2)–Cd(1)–O(1)	80.32(14)
O(1W)–Cd(1)–O(1)	176.99(13)	N(6)–Cd(1)–O(1)	95.10(13)
N(1)–Cd(1)–O(1)	88.52(14)	N(5)–Cd(1)–N(2)	165.01(14)

3.1. *Crystal structure of $AgLNO_3$ (1)*

Compound **1** is similar to nitrato-2-pyridylleneanilline-silver(I) [17]. The central silver atom is surrounded by two N atoms from pyridyl ring and imine of the Schiff-base ligand L and one O atom from monodentate NO_3^-. The pyridyl N and imine N coordinate to silver atom to form a stable five-membered ring with a bite angle of 72.30(7)°. The molecule is essentially planar three-coordinate trigonal geometry (figure 1) with Ag-(N, O) distances ranging from 2.254(2) to 2.437(2) Å, and the O atom deviates from the AgN_2 plane by 0.9399 Å. The bond distances and angles are comparable to those of Ag(dmp)NO_3 [18]. The two-dimensional network is formed through weak intermolecular hydrogen bonding interactions (C–H···O 3.252(4) to 3.352(4) Å) involving C–H and NO_3^- groups (figure 2).

3.2. *Crystal structure of $[CdL_2(H_2O)ClO_4]ClO_4$ (2)*

As shown in figure 3, compound **2** consists of discrete $[CdL_2(H_2O)ClO_4]^+$ cations and ClO_4^- counterions. The $[CdL_2(H_2O)ClO_4]^+$ cation has a distorted octahedral geometry with two bidentate Ls in the equatorial plane and one water molecule and one perchlorate ion in the axial position. Similar to **1**, the Schiff-base chelates cadmium(II) through the pyridyl N and imine N atoms to form a stable five-membered ring with bite angles of N(2)–Cd(1)–N(1) (73.24(13)°) and N(5)–Cd(1)–N(6) (73.71(13)°), which are larger than found in aqua-perchlorate-(bis(o-phenylene)-bis (pyridine-2,6-dialdimino))-cadmium(II) perchlorate methanol solvate [18]. In **2**, the bond distances of $Cd–N_{py} = 2.3000(4)–2.325(4)$ and $Cd–N_{imine} = 2.304(4)–2.319(4)$ Å are shorter than corresponding bonds found in the literature [19], while the $Cd–O_{H_2O}$(2.317(4) Å) and $Cd–O_{ClO_4^-}$ (2.511(4) Å) are longer than the values of 2.241(2) and 2.328(26) Å found in the literature [19]. A two-dimensional network is constructed through strong intermolecular hydrogen bonding interactions involving aqua ligand and perchlorate group (O_W–H···O 2.8079–2.8327 Å), C–H and perchlorate group (C–H···O 3.1875–3.4390 Å) (figure 4).

3.3. *IR spectroscopic characterization*

The IR band attributable to ν(C=N) shifts to lower frequencies in complex **1** (ν(C=N) = 1597 $\mathrm{cm^{-1}}$), but to higher frequencies in complex **2** (ν(C=N) = 1601 $\mathrm{cm^{-1}}$) compared to those of the ligands (ν(C=N) = 1599 $\mathrm{cm^{-1}}$), indicating coordination through the imine nitrogen [20, 21]. On the other hand, the pyridine ring stretching band observed between 1600 and 1400 $\mathrm{cm^{-1}}$ and the ring deformation bands which appear at about 600 and 400 $\mathrm{cm^{-1}}$ are shifted to higher frequencies in the complexes. Three strong bands due to coordinated nitrato groups in **1**, $\nu_{\mathrm{asym}}(\mathrm{NO_3}) = 1384$, $\nu_{\mathrm{sym}}(\mathrm{NO_3}) = 1298$ and $\nu(\mathrm{NO}) = 974\ \mathrm{cm^{-1}}$ are assignable to monodentate nitrate [22, 23]. Anti-symmetric and symmetric O–H stretching modes were observed in the range of 3498–3060 $\mathrm{cm^{-1}}$. The absence of the bending mode H–O–H at 1630 $\mathrm{cm^{-1}}$ for **2** may be explained by coordination of the water molecules and involvement in the system of hydrogen bonds [20]. Vibrations of perchlorate groups are relatively broad in **2** ($\nu(\mathrm{ClO_4}) = 1117\ \mathrm{cm^{-1}}$) indicating that these groups are either coordinated or involved in the system of hydrogen bonds [20]. Therefore, these results are in agreement with the structures of **1** and **2** elucidated by X-ray diffraction.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 247066, 247067 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

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