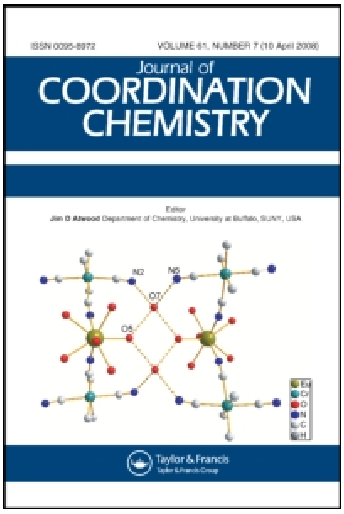

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Synthesis, crystal structure, and fluorescence properties of several schiff-base compounds

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Synthesis, crystal structure, and fluorescence properties of several schiff-base compounds

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Two new Schiff-base compounds, 1,6-bis(4-dimethylaminobenzyl)-2,5-diaza-1,5-hexadiene (bdh), 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene (bdb), and a silver complex of the latter ($[Ag_2(bdb)_3(NO_3)_2] \cdot H_2O$, **1**) have been synthesized and characterized. The crystal structure of complex **1** was determined. **1** is a dinuclear complex, with the silver ions lying in coordination tetrahedra formed by two nitrogen atoms from the bdb ligands and two oxygen atoms from the nitrate anions. The fluorescence properties of bdh and bdb were studied; the fluorescence of bdb was quenched by the addition of silver ions, indicating that it is a potential fluorescent reagent for the analysis of silver.

Keywords: Schiff-base; Crystal structure; Fluorescence

1. Introduction

Schiff-bases are a class of compounds formed by condensation between amino and carbonyl groups. In recent years Schiff-base compounds and their metal complexes have attracted research interest in bioorganic and medicinal chemistry. For example, Lumme *et al*. synthesized a series of amino acid Schiff-bases and their metal complexes, many of which have antibacterial or antitumor bioactivities, indicating that they may be used as chemotherapeutic agents against cancer [1]. Some copper complexes of the Schiff-base formed between benzaldehyde and alanine have shown the ability to suppress superoxide anion free radicals ($O_2^{-\bullet}$) [2], which may cause inflammation or cancer in humans. Some vanadium complexes of Schiff-bases may be efficient catalysts in the catalytic oxidation of thioethers to sulfoxides [3]. Many silver complexes containing Schiff-base ligands have been studied in recent years [4]. Ueda *et al*. studied the potentiometric performance of silver ion-selective electrodes based on tridentate

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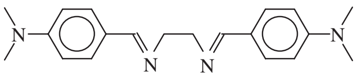
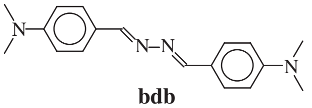
Schiff-base derivatives, and found some Schiff-bases exhibited excellent silver ion selectivity and were good ionophores for a silver-ion electrode [5]. Some Schiff-bases may also be used as fluorescent reagents for the determination of trace metal ions, because metal ions can either enhance or quench the fluorescence of the Schiff-base ligand [6]. Here we report the synthesis, characterization and fluorescence spectra of two Schiff-base compounds: 1,6-bis(4-dimethylaminobenzyl)-2,5-diaza-1,5-hexadiene (bdh), 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene (bdb), and a silver complex of bdb ($[Ag_2(bdb)_3(NO_3)_2] \cdot H_2O$, **1**). We found that silver ion can quench the fluorescence of bdb, indicating that bdb is a potential fluorescent reagent for the fluorophotometric determination of trace silver.



bdh



bdb

2. Experimental

2.1. *Materials and methods*

Silver nitrate, hydrazine, ethylenediamine and 4-(dimethylamino)benzaldehyde were purchased from ACROS. Infrared spectra were recorded on a Nicolet AVATAR 360 FT-IR spectrometer as KBr pellets. UV-vis spectra were obtained on a ShangHai Spectrum Instruments Inc. 756PC spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C instrument. Fluorescence measurements were made on a Perkin-Elmer LS-55 luminescence spectrophotometer equipped with a red sensitive photomultiplier tube (excitation slit, 10 nm; emission slit, 5 nm; scan speed, $1500\,nm\,min^{-1}$; 1-cm quartz cuvettes). The *FL WinLab* software [8d] was employed for instrument control and data processing. Stock solutions, 2.5×10^{-3} M, of 4-(dimethylamino)benzaldehyde, bdh or bdb were prepared in dichloromethane; $AgNO_3$ was prepared in dimethylformamide.

Preparation of solutions for comparison of fluorescence spectra between bdh, bdb and 4-(dimethylamino)benzaldehyde: 1 mL of bdh dichloromethane solution was added to a test tube and diluted to 25 mL with ethanol; test solutions of bdb and 4-(dimethylamino)benzaldehyde were prepared similarly. A reagent blank (1 mL of dichloromethane diluted to 25 mL with ethanol) was prepared for comparison.

Preparation of solutions for fluorescent quenching experiment: test solution of bdb: 1 mL of bdb dichloromethane solution and 1 mL of DMF were mixed and diluted to 25 mL with ethanol; test solution of bdb with $AgNO_3$: 1 mL of bdb dichloromethane solution and 1 mL of $AgNO_3$ DMF solution were mixed and diluted to 25 mL with ethanol. A reagent blank was prepared in a similar way but without bdb and $AgNO_3$. The fluorescence spectra of test solutions were measured against the reagent blank.

2.2. *Synthesis*

2.2.1. Preparation of bdh. 4-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) was dissolved in ethanol (50 mL), followed by addition of ethylenediamine

(0.36 g, 6 mmol). The mixture was stirred at room temperature for 24 h and then filtered, and the resultant white crystalline solid was washed with ethanol several times and dried in air. Yield 1.50 g, 93% (referenced to 4-(dimethylamino)benzaldehyde). IR (KBr, cm^{-1}): 2909, 2853, 2822, 1639, 1603, 1527, 1440, 1362, 1306, 1230, 1178, 948, 881, 799, 640, 523, 476. UV-vis (CH_2Cl_2–EtOH, 1 : 20) : 308(sh), 329 nm. Anal. Calcd for $C_{20}H_{26}N_4$ (%) : C, 74.50; H, 8.13; N, 17.38. Found : C, 74.81; H, 8.03; N, 17.65.

2.2.2. Preparation of bdb. The synthesis procedure for bdb was similar to bdh except for using hydrazine hydrate (0.30 g, 6 mmol) instead of ethylenediamine. The resultant product is a yellow crystalline solid. Yield 1.20 g, 82% (referenced to 4-(dimethylamino)benzaldehyde). IR (KBr, cm^{-1}): 2909, 2848, 1603, 1521, 1363, 1230, 1178, 809, 518. UV-vis (CH_2Cl_2–EtOH, 1 : 20) : 322(sh), 390 nm. Anal. Calcd for $C_{18}H_{22}N_4$ (%) : C, 73.44; H, 7.53; N, 19.03. Found: C, 73.16; H, 7.36; N, 19.43.

2.2.3. Preparation of $[Ag_2(bdb)_3(NO_3)_2]\cdot H_2O$ (1). Silver nitrate (0.017 g, 0.1 mmol) was dissolved in DMF (10 mL), then bdb (0.045 g, 0.15 mmol) was added to the solution and the mixture was stirred for 5 min. After addition of 10 mL of ethanol (95%), the mixture was filtered into a conical flask and sealed. Complex **1** was obtained as red needle crystals after one day. Yield 0.044 g, 71% (referenced to silver nitrate). IR (KBr, cm^{-1}): 3460, 2914, 2853, 1593, 1521, 1434, 1362, 1291, 1178, 810, 738, 518, 471. Anal. Calcd for $C_{54}H_{68}Ag_2N_{14}O_7$ (%) : C, 52.27; H, 5.52; N, 15.80. Found: C, 52.60; H, 5.81; N, 15.55.

2.3. *Crystal structure determination*

A single crystal with dimensions $0.10 \times 0.20 \times 0.20$ mm of **1** was mounted on a thin glass fiber and data were collected at 293 K on a Rigaku Mercury CCD X-ray diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 6623 independent reflections ($R_{int} = 0.0257$) were measured in the range of $3.23 \le \theta \le 27.49°$ ($h = -12 \rightarrow 12$, $k = -12 \rightarrow 15$, $l = -17 \rightarrow 17$), 4565 of which ($I > 2\sigma(I)$) were used in the refinement of the structure. An empirical absorption correction based on Multi-scan technique (*Sphere*, Rigaku CrystalClear) was applied [8b], which resulted in transmission factors ranging from 0.84 to 1.00. The structure was solved by direct methods and refined with full-matrix least-squares based on F^2 using the *SHELXL97* program [8a]. All non-H atoms were located directly from the difference Fourier maps and refined anisotropically. All H atoms of the ligands were placed in calculated positions and refined in the riding mode. The crystallographic data of complex **1** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

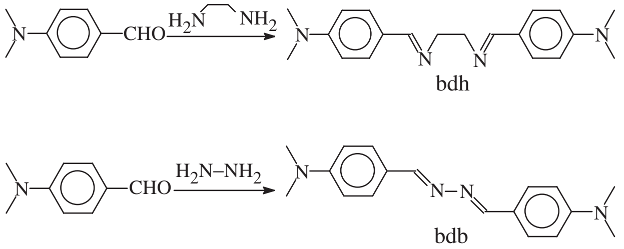
Compounds bdh and bdb were prepared by the Schiff-base condensation reaction (scheme 1) between 4-(dimethylamino)benzaldehyde and ethylenediamine (for bdh) or hydrazine (for bdb). Both bdh and bdb are readily soluble in CH_2Cl_2, but poorly soluble in polar solvents such as methanol, ethanol or water. It is difficult to obtain diffraction quality crystals of bdh. Complex **1** was formed by the coordination reaction

Table 1. Crystallographic data for complex **1**.

Formula	$C_{54}H_{66}Ag_2N_{14}O_6 \cdot H_2O$
Formula weight	1240.95
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.970(2)
b (Å)	11.860(2)
c (Å)	13.430(3)
α, β, γ (°)	71.45(3), 77.54(3), 79.57(3)
V (Å^3)	1459.2(6)
D_c (g cm^{-3})	1.410
Z	1
T (K)	293
μ (mm^{-1})	0.732
$F(000)$	638
θ range (°)	3.23–27.49
Reflections measured	11764
Independent reflections	6623
Observed reflection ($I > 2\sigma(I)$)	4565
Parameters	352
R (obs.)	$R_1{}^a = 0.060$, $wR_2{}^b = 0.154$
R (all)	$R_1 = 0.093$, $wR_2 = 0.176$
Goodness-of-fit	1.091

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

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0883P)^2 + 0.4585P]$ where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 1. The formation of bdh and bdb.

between silver nitrate and bdb in DMF–EtOH (1 : 1), and the reaction is not sensitive to the metal to ligand ratio. **1** was insoluble in water and common organic solvents. All of the compounds are very stable in air.

3.2. *Structure*

Selected bond lengths and angles for complex **1** are listed in table 2. Complex **1** is a dinuclear complex formed by two silver nitrate units and three bdb ligands (figure 1). Among the three bdb molecules, one is a bridging bidentate ligand to two silver ions, and the other two are monodentate. The coordination environment around the silver atom is a distorted tetrahedron formed by two N atoms from the bdb ligands (Ag–N12 = 2.254(4) Å, Ag–N23 = 2.223(4) Å) and two O atoms from the nitrate (Ag–O2 = 2.492(4) Å, Ag–O1 = 2.651(4) Å). In complex **1** the N atoms of the

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

Ag–N(23)	2.223(4)	N(21)–C(203)	1.364(6)
Ag–N(12)	2.254(4)	N(21)–C(201)	1.441(7)
Ag–O(2)	2.492(4)	N(21)–C(202)	1.448(7)
Ag–O(1)	2.651(4)	N(22)–C(209)	1.259(6)
N(11)–C(103)	1.365(5)	N(22)–N(23)	1.413(5)
N(11)–C(101)	1.452(8)	N(23)–C(210)	1.298(6)
N(11)–C(102)	1.463(7)	N(24)–C(214)	1.358(6)
N(12)–C(109)	1.286(6)	N(24)–C(217)	1.448(7)
N(12)–N(12)#1	1.423(6)	N(24)–C(218)	1.458(6)
N(23)–Ag–N(12)	136.01(14)	N(12)–Ag–O(2)	110.07(15)
N(23)–Ag–O(2)	109.76(15)	C(109)–N(12)–N(12)#1	113.6(4)
C(209)–N(22)–N(23)	113.0(4)	C(210)–N(23)–N(22)	113.1(4)

Symmetry transformations used to generate equivalent atoms: $\#1 -x+1, -y+2, -z$.

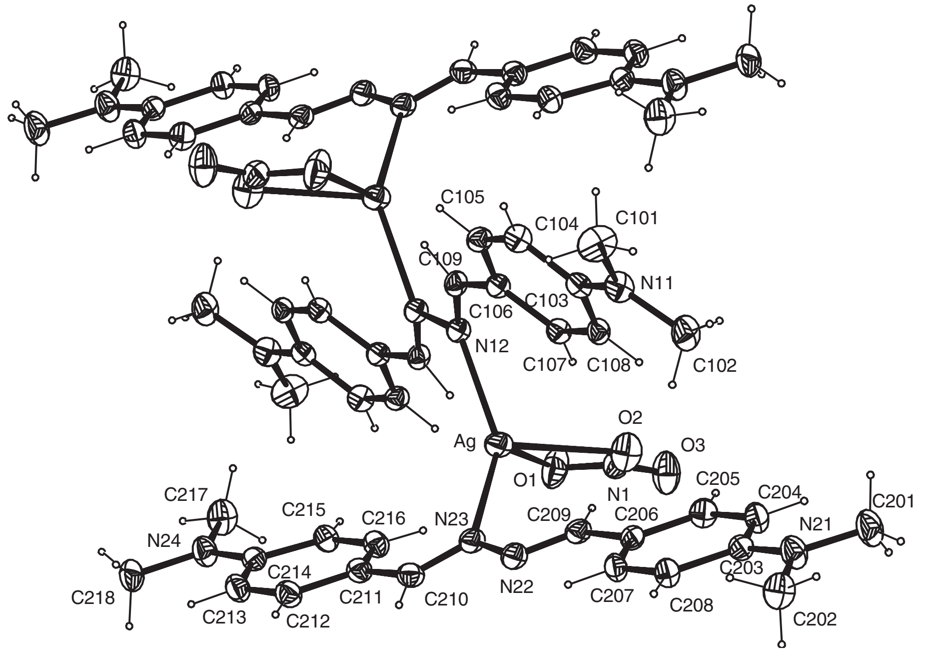
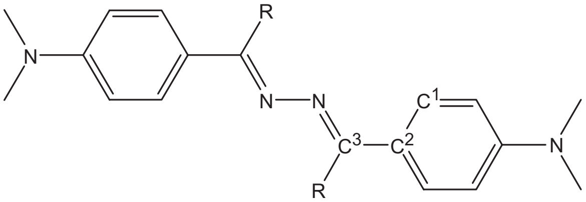


Figure 1. Molecule structure for complex **1**. Displacement ellipsoids are drawn at 20% probability level and H atoms are represented by small spheres of arbitrary radii. The disordered water molecule has been omitted for clarity.

dimethylamino groups did not coordinate, the imine N atoms coordinated instead, suggesting that imine is a stronger electron donor than dimethylamine. However, in the cobalt and cadmium complexes of 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene [7], the imine N atoms did not coordinate, pyridyl N atoms coordinated instead, suggesting that pyridyl is a stronger electron donor than imine.

The non-H atoms of bdb ligands in **1** are nearly coplanar, forming a large conjugated system. The N–N bond distances are 1.423(6) and 1.413(5) Å for bridging and terminal bdb, respectively, slightly longer than the corresponding bond length (1.410(3) Å)



Scheme 2. The labelling scheme for the torsion angle.

Table 3. Torsion angles (°) in bdb and similar compounds.

Compounds	−R	C^1–C^2–C^3–N torsion angle (°)	Reference
Free bdb	−H	−4.8(3)	[9]
bdb ligand in complex **1**	−H	−4.7(8), 14.4(7), 17.1(8)	This work
(E,E)-p-N,N-Dimethylaminoacetophenone azine	$-CH_3$	−14.2(2)	[10a]
4,4′-bis(Dimethylamino)benzophenone azine	$-Ph-N(CH_3)_2$	−18.1(3)	[10b]

in free bdb [9]. The C209–N22 and C210–N23 bond distances are 1.259(6) and 1.298(6) Å, respectively, indicating that the coordination of N23 to silver weakened the C=N bond. The C^1–C^2–C^3–N torsion angle (scheme 2) in bdb ligands and similar compounds were summarized in table 3. The torsion angles for C207–C206–C209–N22, C216–C211–C210–N23 and C107–C106–C109–N12 in complex **1** were −4.7(8), 17.1(8) and 14.4(7)°, respectively. The corresponding torsion angle in free bdb [9] was −4.8(3)°, in (E,E)-p-N,N-dimethylaminoacetophenone azine [10a] was −14.2(2)° and in 4,4′-bis(-dimethylamino)benzophenone azine [10b] was −18.1(3)°. The above data indicate that coordinating N or substitution of H by a bulkier group in the –CH=N– unit increases the torsion angle and twists the molecular backbone. Like many other compounds with $Ph-N(CH_3)_2$ units [10, 11], the non-H atoms of the $N(CH_3)_2$ moiety and phenyl ring in complex **1** are nearly coplanar. However, in compounds with protonated $Ph-NH^+(CH_3)_2$ [12], the $N(CH_3)_2$ moietiy deviated from the plane defined by the phenyl ring, indicating that the hybridization mode of N atom has changed from sp^2 to sp^3.

Each unit cell of **1** also contains one disordered water molecule, which is disordered over two centrosymmetrically related sites with 50% occupancy. As the O atom of water involves high disorder the positions of the associated H atoms cannot be located.

3.3. *Fluorescence properties*

3.3.1. Molecular structure and fluorescence intensity. The fluorescence spectra of 4-(dimethylamino)benzaldehyde, bdh and bdb were measured and the results shown in figure 2 revealed that 4-(dimethylamino)benzaldehyde and bdh are weakly fluorescent, with fluorescence intensity (I_f) of 14.5 and 59.4, respectively. The reason for the weak fluorescence intensity of 4-(dimethylamino)benzaldehyde can be ascribed to its small conjugated system; for bdh the reason may be that it is not a coplanar conjugated molecule. However, bdb has an intense fluorescence emission at 468 nm, due to its extended conjugated plane.

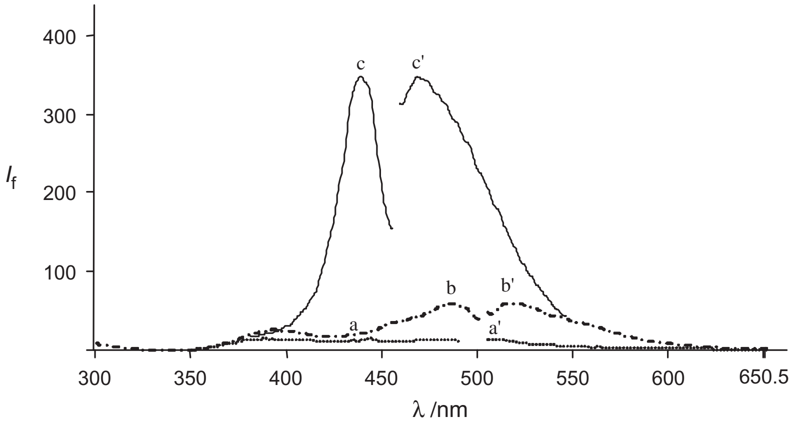


Figure 2. The fluorescence spectra of 4-(dimethylamino)benzaldehyde, bdh and bdb (10^{-4} M in CH_2Cl_2–EtOH. Left, excitation spectra; right, emission spectra) a,a′ 4-(dimethylamino)benzaldehyde, $\lambda_{ex}/\lambda_{em} = 443/509$ nm, $I_f = 14.5$; b,b′ bdh, $\lambda_{ex}/\lambda_{em} = 486/519$ nm, $I_f = 59.4$; c,c′ bdb, $\lambda_{ex}/\lambda_{em} = 438/468$ nm, $I_f = 347.0$.

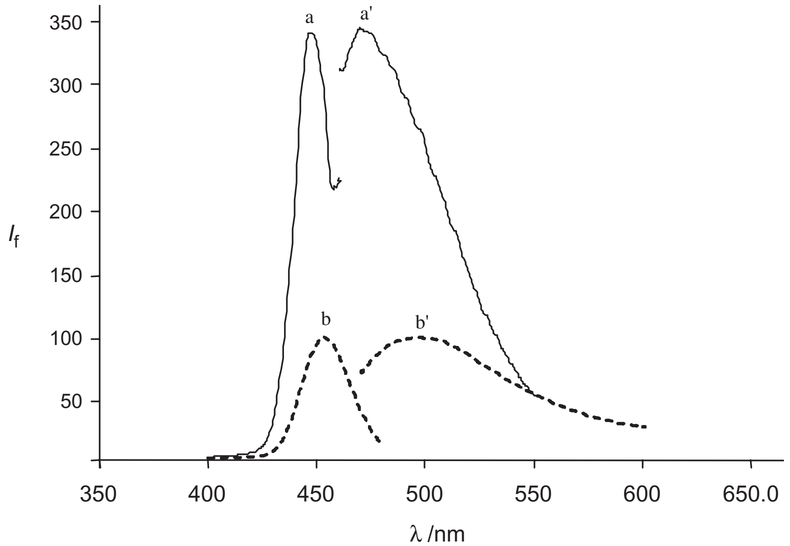


Figure 3. The fluorescence spectra of bdb and bdb with silver nitrate in CH_2Cl_2–DMF–EtOH (Left, excitation spectra; right, emission spectra). a,a′ bdb (10^{-4} M), $\lambda_{ex}/\lambda_{em} = 447/469$ nm, $I_f = 345.1$; b,b′ bdb (10^{-4} M) + Ag^+ (10^{-4} M), $\lambda_{ex}/\lambda_{em} = 453/494$ nm, $I_f = 103.2$.

3.3.2. Fluorescence quenching reaction with silver ions. The fluorescence spectra of bdb and bdb with silver nitrate are shown in figure 3. The results indicated that bdb has a strong fluorescence emission at 469 nm. The addition of silver ions to the system changed both the peak position and intensity of the fluorescence spectra. There is a red-shift with maximum excitation and emission wavelengths (λ_{ex}: 447 → 453 nm;

λ_{em}: 469 → 494 nm), and the fluorescence intensity decreased. Silver ions added to the system will combine with bdb and reduce electron density on the conjugated plane of bdb, thus decreasing the fluorescence intensity. A test of effect on the fluorescence intensity of bdb by addition of other metal ions was conducted, and the result showed that K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+} did not change the fluorescence intensity. Thus bdb is a potential fluorescent reagent for the analysis of silver by fluorescence quenching photometry.

Supplementary material

CCDC 256605 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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