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Structural diversity of silver (I) azine complexes – Effect of substituents and counter anions

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ABSTRACT

Three new Ag(I) complexes, **1**, **2**, and **3** of two azine ligands diacetyl dihydrazone (**L1**) and benzil dihydrazone (**L2**) have been synthesized and characterized by single crystal X-ray diffraction studies (for **2** and **3**), X-ray powder diffraction studies(**1** and **2**), elemental analyses, IR and UV–VIS spectroscopy and TGA analysis. They represent one-dimensional polymeric assemblies and discrete dinuclear Ag(I) complex depending on functionality of the ligands and the counter anions. Tetrahedral as well as square pyramidal coordination motifs of the silver (I) ions have been observed in the supramolecular designing of such hybrid organic–inorganic materials.

1. Introduction

Construction of inorganic–organic hybrid materials received considerable attention because of their unusual topologies [1–8] and relevance in wide range of applications in superconductors [9,10], magnetic materials [11–13], gas adsorption [14–17], molecular sensing [18–20], catalyst [21–23], non linear optics [24–26] and luminescent materials [27–30]. In those hybrid systems, the factors by which the self assemblies are mainly influenced include coordination properties of the metal ions, functionality and denticity of the ligands, solvent, ratio of ligands to metal ions and size and nature of the counter ions [31–39]. This study is a part of our ongoing project to design and characterize an extensive series of coordination polymers and oligomers consisting of polydentate imino-pyridyl ligands and Ag(I) building blocks [40–42]. Silver (I) complexes are very important in the area of self-assembled coordination chemistry [40–43]. As soft acids silver (I) ions facilitate stable coordination to the soft bases containing unsaturated nitrogen atoms [44]. Though the azine ligands, diacetyl dihydrazone and benzil dihydrazone are known since 1956, recently we have published the Ag(I) helical coordination polymer of benzil dihydrazone [40] but the Ag(I) complex of diacetyl dihydrazone is hitherto unknown. Herein we have described the syntheses, structures and properties of two coordination polymers (**1**, and **2**) along with another one dimer of silver (I) (**3**) with the two different azine ligands, diacetyl dihydrazone (**L1)** and benzil dihydrazone(**L2**) and compared these structures with a previously reported [40] silver (I) helical coordination polymer (**4**).

The anions not only balance the charges of the cationic complexes but also impart their influence on the structures of the supramolecular systems [45,46]. One can to some extent tune the structures of some supramolecules by simply changing the anions [47,48]. Moreover the nuclearities of the supramolecules can also be influenced by minor structural change of the ligand moieties [49,50]. In this article we have demonstrated the effect of counter anion and substitution change in ligands on the structural diversity of the silver (I) complexes.

2. Experimental

2.1. General procedures

Diacetyl dihydrazone (2,3-butane dihydrazone) and benzil dihydrazone (1,2-diphenyl dihydrazone) were synthesized by a reported procedure [51]. All other reagents were procured commercially and used without further purification. Microanalyses were carried out using a Perkin–Elmer 2400II elemental analyzer. Infrared (IR) spectra and electronic spectra were recorded on Nicolet Magna-IR (Series II) and Shimadzu UV-160A spectrophotometers, respectively. Fluorescence spectra were recorded on a Perkin Elmer LS50B spectrophotometer. TGA analyses were done on a Universal

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V4.2E TA Instruments. X-ray powder patterns were collected on a Philips PW-1710 automated diffractometer.

2.3. Synthesis of [Ag(**L1**)]$_n$ (NO$_3$)$_n$ (**1**)

2,3-butane dihydrazone (0.114 g, 1 mmol) was dissolved in methanol (40 mL). To this solution, 0.170 g (1 mmol) of solid $AgNO_3$ was added and dissolved with stirring. Stirring was continued for another 1 h. Then the colorless reaction mixture was kept in the refrigerator for 36 h. White microcrystalline solid precipitated out. It was filtered off washed with few drops of methanol and dried in *vacuo* over fused $CaCl_2$. Yield, 0.17 g (60%). *Anal.* Calcd. for $C_4H_{10}N_5O_3Ag$: C, 16.91; H, 3.55; N, 24.66. Found C, 16.95; H, 3.51; N, 24.68% (for powder sample). FTIR/cm^{-1} (KBr): 510s, 565m, 650m, 760m, 890m, 1328vs (NO$_3$), 1647vs (C=N), 3353wb. UV–VIS λ_{max}/nm: 290; 238.

2.5. Synthesis of [Ag(**L1**)]$_n$ (ClO$_4$)$_n$ (**2**)

2, 3-butane dihydrazone (0.114 g, 1 mmol) was dissolved in methanol (40 mL). To this solution, 0.21 g (1 mmol) of solid $AgClO_4$ was added and dissolved with stirring. Stirring was continued for 1 h. Then the reaction mixture was kept in the refrigerator for about 24 h. White crystalline solid, which were suitable for X-ray analysis, precipitated out. It was filtered off washed with few drops of methanol and dried in *vacuo* over fused $CaCl_2$. Yield, 0.21 g (65%). *Anal.* Calcd. for $C_4H_{10}N_4O_4ClAg$: C, 14.95; H, 3.14; N, 17.43. Found C, 15.01; H, 3.17; N, 17.48%. FTIR/cm^{-1} (KBr): 520m, 570s, 636s, 880m, 948m, 1091vs (ClO$_4$), 1650vs (C=N). UV–VIS λ_{max}/nm: 295; 238.

2.7. Synthesis of [Ag(**L2**)]$_2$(NO$_3$)$_2$ (**3**)

1,2-diphenyl dihydrazone (0.24 g, 1 mmol) was dissolved in methanol (50 mL). To this light yellow colored solution, 0.170 g (1 mmol) of solid $AgNO_3$ was added and dissolved with stirring. Stirring was continued for 1 h. Then the reaction mixture was kept in the refrigerator for 36 h. White crystalline solid, suitable for X-ray analysis, precipitated out. It was filtered off washed with few drops of methanol and dried in *vacuo* over fused $CaCl_2$. Yield 0.24 g (70%). *Anal.* Calcd. for $C_{28}H_{28}N_9O_3Ag$: C, 52.02; H, 4.37; N, 19.50. Found C, 52.16; H, 4.39; N, 19.53%. FTIR/cm^{-1} (KBr): 530m, 626s, 850m, 1280m, 1320vs (NO$_3$), 1412s, 1556m, 1638vs (C=N), 3353vb. UV–VIS λ_{max}/nm: 390; 270.

2.7.1. Caution!

Though we have not met with any incident while working with the perchlorate compounds described here, care should be taken in handling them as the perchlorates are potentially explosive. They should not be prepared and stored in large amounts.

2.8. X-ray crystallography

X-ray single crystal data were collected using Mo Kα (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX [52]. The structures were solved by direct methods (*SHELXS-97*) and standard Fourier techniques, and refined on F^2 using full matrix least squares procedures (*SHELXL-97*) using the *SHELX-97* package [53] incorporated in *WinGX* [54]. In most of the cases, non-hydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. The crystallographic details of **2** and **3** are summarized in Table 1, selected bond lengths and angles of **2** and **3** are listed in Table 2 and selected hydrogen bonding parameters of **2** and **3** are shown in Table 3.

3. Results and discussion

3.1. Synthesis and IR spectroscopy of the complexes

The azine ligands **L1** and **L2**, are the 2 + 1 condensates of diacetyl/benzil and hydrazine, were prepared by following a reported procedure [51]. Their silver (I) complexes **1**, **2**, and **3** were synthesized in good yields by reacting silver (I) salts with the corresponding ligands at room temperature in methanol in equimolar proportion. The syntheses of the complexes **1**, **2** and **3** are summarized in Scheme 2. We have recently published the synthesis and structure of the silver (I) complex **4** [40]. The silver (I) complexes are stable in solid state for about 2–3 weeks in air and in solution for at least 4–8 h. On prolonged exposure to light the complexes turned black.

The complexes **1–4** under study show characteristic peaks due to the ligation of the ligands **L1** and **L2** to the metal center in the KBr-phase IR spectra. In the IR spectrum of the ligands **L1** and **L2**, characteristic band at 1639 cm^{-1} and 1622 cm^{-1} were assigned to the imine (C=N) stretching frequencies [55]. These bands due to C=N stretching are shifted to lower energy and appear at around 1647 cm^{-1}, 1649 cm^{-1}, 1638 cm^{-1} and 1632 cm^{-1} in the complexes **1, 2, 3** and **4** respectively. The typical strong bands due to the stretching vibrations of the non-coordinated ClO_4^- ions in **2** and **4** appear at the expected regions; 1091 and 636 cm^{-1} (for **2**); 1088 and 626 cm^{-1} (for **4**). The bands due to NO_3^- ions appear at 1328 cm^{-1} and 1320 cm^{-1} for **1** and **3** respectively.

3.2. UV–VIS, photophysical and TGA data

The Ag(I) complexes **1** and **2** display broad unstructured band around 290–295 nm and 235–240 nm, while in case of the complexes **3** and **4** these bands appear around 395–400 nm and 270–275 nm. The complexes **1–4** are non luminescent at room temperature within the charge transfer envelope. In TGA of **1**, a weight loss of 10.76% was observed with in the temperature range

Table 1
Crystallographic data and refinement parameters for **2** and **3.**

Crystal parameters	2	3
CCDC No.	760011	760012
Empirical formula	$C_4H_{10}AgClN_4O_4$	$C_{56}H_{56}Ag_2N_{18}O_6$
Formula weight	321.48	1292.93
Crystal size/mm	0.24 × 0.18 × 0.08	0.30 × 0.20 × 0.06
Crystal system	Tetragonal	Triclinic
Space group	*P4*(3)	*P-1*
a/Å	9.456(2)	9.976(6)
b/Å	9.456(2)	12.268(8)
c/Å	14.230(7)	25.472(16)
α/°	90.00	78.132(8)
β/°	90.00	80.052(9)
γ/°	90.00	69.171(8)
Volume/Å^3	1272.5(7)	2835(3)
Z	4	2
D_{calc}/g cm^{-3}	1.678	1.515
μ Mo Kα/mm^{-1}	1.791	0.758
R_{int}	0.0484	0.0954
θmin/max/°	2.15/22.12	0.82/25.00
Reflections collected/unique/ observed [I>2σ(I)]	9076/1448/1207	26467/9906/5490
Goodness of fit on F^2	1.097	1.021
Final R indices [I>2σ(I)]	R_1 = 0.0586 wR_2 = 0.1552	R_1 = 0.1088 wR_2 = 0.2839
R indices (all data)	R_1 = 0.0699 wR_2 = 0.1636	R_1 = 0.1693 wR_2 = 0.3263