Polymeric Silver(I) Benzisothiazolinone Complex: Synthesis, Characterization and H_2 Gas Storage Capacity

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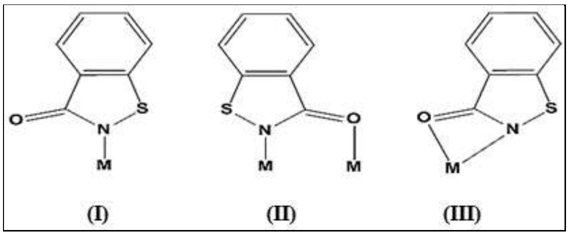
ABSTRACT

Treatment of silver(I) nitrate with sodium benzisothiazolinone (Nabit) affords $[Ag(bit)]_n$ complex. The produced silver coordination complex was characterized by infrared spectroscopy, elemental analysis, nuclear magnetic resonance (^{1}H-NMR and ^{13}C-{^{1}H}-NMR). These measurements showed that the bit anion behaves as a bidentate bridge linking two silver (I) ions through the oxygen and nitrogen atoms. The prepared $[Ag(bit)]_n$ has a high stability, didn't melt up to 320 °C and non-soluble in water in addition to a number of organic solvents except hot DMSO solvent. Therefore a polymeric structure was proposed, the polymeric structure has a high porosity showing thereby that an overall H_2 uptake of 5.5 mmol/g at 77 K and 10 bar.

1. Introduction

Silver metal or ion is the subject of interest owing to their rich and diverse coordination chemistry [1]. Silver metal has low toxicity and carcinogenic activities [2-4] compared to other transition metals, therefore, silver has been used extensively as anti-microbial agents, antitumor activities [3] and recently silver nanoparticles have been used as additives to promote the hydrogen storage properties of TiO_2 [5].

Within the a previous few years interests have been increased on the design of inorganic polymers or metal-organic frameworks (MOFs), due to fascinating diverse structures and numerous potential applications in the fields of magnetism [6], drug delivery [7], non-linear optic [8], gas storage [9], catalysis [10], luminescence [11], fluorescence [12], sensor [13], heavy metal elimination [14,15] and lithium storage [16]. Inorganic polymers have been extensively used as a hydrogen storage materials [17-22] whereby the hydrogen storage capacities of these polymers depend on their surface areas [23-25]. The structure of the ligand is the most important point in studying of the hydrogen storage capacity of the inorganic polymers. Thereby, the multicarboxylate, N-containing heterocyclic, and oxo-carbon ligands have been chosen in the studying gas storage because of N,O containing-ligands are coordinate to metal centers easily and have considerable coordination modes [26-30]. In the present article, we chose the potentially interesting benzisothiazolinone (Hbit) which is a heterocyclic ligand, similarly named as 1,2-benzisothiazol-3(2H)-one which is a poly-functional heterocyclic ligand, containing sulfur, nitrogen in addition to oxygen atoms and could coordinated to metal centers in various coordination modes; monodentate (I), bridging bidentate (II) and/or chelating bidentate (III) modes [31,32] as shown in Figure 1. Although Hbit or bit anion had many donor atoms (N, O, S), only a little information is available about its complexes in the literature [31-33] with no information on Ag-bit complex. Consequently, this complex was characterized to examine its gas storage ability.



(I) (II) (III)

Fig.1: A bonding modes of benzisothiazolinone anion to a metal cations.

2. Experimental

2.1. Chemicals

The benzisothiazolinone (Hbit) used as ligand, silver nitrate ($AgNO_3$) used as silver cation source, sodium hydroxide used as a deprotonating agent, ethanol and

DMSO used as a solvents. All these reagents purchased from Sigma-Aldrich and used without further purification.

2.2. Apparatus

^{1}H-,^{13}C-{^{1}H} NMR spectra were recorded on BRUKER BioSpin Gmbh (400MHz) and 100 MHz respectively, with a DMSO-d^{6} as a solvent. FT-IR spectra were recorded on JASCO FT/IR 430 spectrophotometer in the 400–4000 cm^{-1} range using KBr disk. Melting point measured on a Gallenkamp melting point apparatus. Elemental analysis was measured by EURO/EA 3000. Molar conductance of the complex was recorded using CONSORT C3030 analyzer at 26 °C.

2.3. Methods

2.3.1. Synthesis of the Nabit

Hbit (1.000 g, 6.613 mmol) in EtOH (15 cm^{3}) was added to a solution of sodium hydroxide (0.2645 g, 6.613 mmol) in hot EtOH (20 cm^{3}). The resulting solution was stirred at room temperature for 1 hour. The solution was reduced in volume by slow evaporation on a steam bath to give a white solid which was collected and dried under vacuum (yield: 1.09 g, 96%). IR (KBr disk, cm^{-1}): 3058m, 1685vw, 1642m, 1566w, 1506s, 1446m, 729s, 671m, 617m, m.p.: 312–315 °C [32].

2.3.2.Synthesis of [Ag(bit)]$_n$

Colorless solution of $AgNO_3$ (0.4903 g, 2.8862 mmol) in distilled water (15 cm^{3}) was added to a colorless solution of Nabit (0.5000 g, 2.8868 mmol) in hot ethanol (20 cm^{3}). A white precipitate was formed directly, the mixture was stirred for 15 minutes at room temperature and refluxed on a steam bath for a further 1 hour to give a white precipitate. The white solid was filtered, washed with distilled water and dried in a vacuum oven at 60 °C (yield: 0.764 g, 93 %).

2.3.3. Hydrogen storage

The H_2 storage capacity of [Ag(bit)]$_n$ in the range 0-10 bar was performed on Micromeritics ASAP 2050 hydrogen storage apparatus. The H_2 uptake was studied at 77 K (liquid nitrogen bath).

3. Results and discussion

Addition of one equivalent of silver nitrate to an ethanolic solution of sodium benzisothiazolate resulted in the formation of [Ag(bit)]$_n$ (Scheme 1). The elemental analysis supports the replacement of nitrate ion from silver nitrate as well as this assignment proved by the low molar conductivity of [Ag(bit)]$_n$ complex (Table 1) which demonstrated the non–ionic character of the prepared complex. IR spectrum (Figure 2), of [Ag(bit)]$_n$ complex indicates that the bit anion ligand coordinated as a bidentate ligand through the oxygen and the nitrogen atoms. This assignment has been concluded from the lower frequency shift of v(C=O) from 1642 cm^{-1} in the spectrum of bit anion ligand to 1567 cm^{-1} in the spectrum of [Ag(bit)]$_n$ (Table 2). The IR spectrum of the [Ag(bit)]$_n$ (Figure 2) shows absorption bands at 3068, 1491 and 1432 cm^{-1}, which are assigned to the stretching mode of the aromatic C-H groups, C-N and C=C, respectively. The C-H of *ortho*-substituted phenyl ring peaks were observed at 763 and 729 cm^{-1}. The bands appeared at 1351 and 869 cm^{-1} may be assigned to symmetrical and asymmetrical C-N-S stretching vibrations [32,33]. From the IR spectrum, the bit anion in its silver complex behaves as μ-bridge linking two silver(I) ions as a bidentate ligand through the oxygen and nitrogen atoms (Scheme 1).

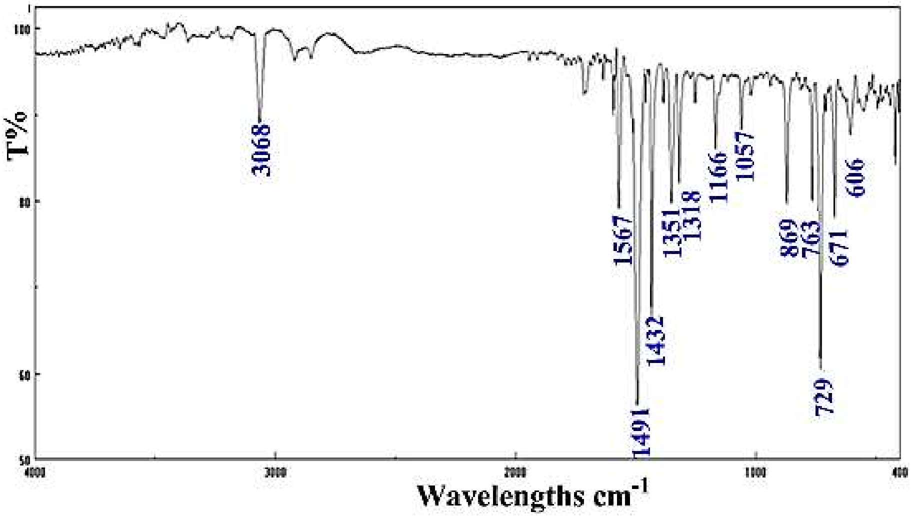


Fig.2: IR spectrum of [Ag(bit)]$_n$ complex.

Furthermore, the ^{1}H-NMR spectrum of [Ag(bit)]$_n$ in d^{6}-DMSO (Figure 3, Table 2) shows two doublets for H6 and H9 protons at 7.97 and 7.88 ppm with coupling constant $^{3}J_{H6\text{-}H7}$=7.8 and $^{3}J_{H9\text{-}H8}$=8.2 Hz, respectively. In addition to two virtual triplets for the other two protons H7 and H8 of the aromatic ring at 7.62 and 7.43 ppm with coupling constant $^{3}J_{HH}$=8.0 and 8.2 Hz, respectively. The low solubility in a number of organic solvents include DMSO, suggests a polymeric structure of [Ag(bit)]$_n$. Numberings of protons are given in Scheme1.

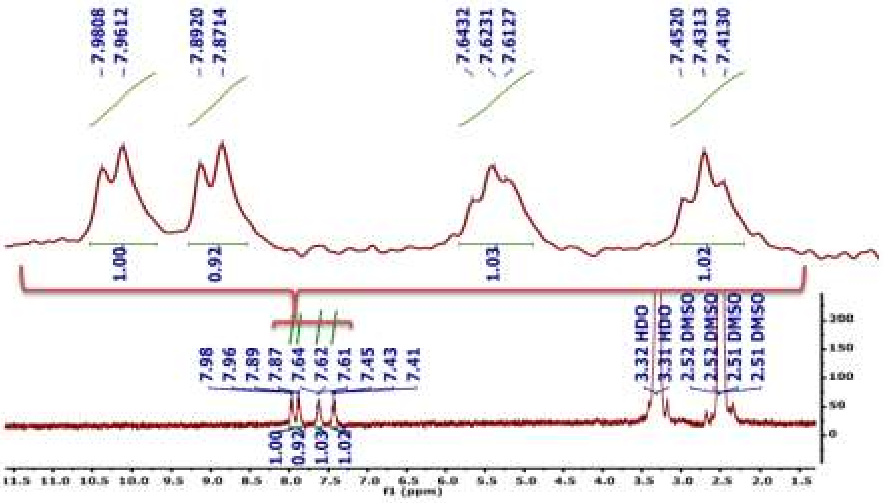


Fig.3: ^{1}H-NMR spectrum of [Ag(bit)]$_n$ complex in DMSO-d^6

The ^{13}C-{^{1}H}NMR spectrum (Figure 4) of [Ag(bit)]$_n$ complex in d^6-DMSO shows six signals of the aromatic carbon at 133.98, 131.79, 128.23, 125.77, 124.68, and 120.30 ppm, in addition, the quaternary carbon atom which appeared at 160.23 ppm attributed to C2(C=O) group. Numberings of protons are given in Scheme1.

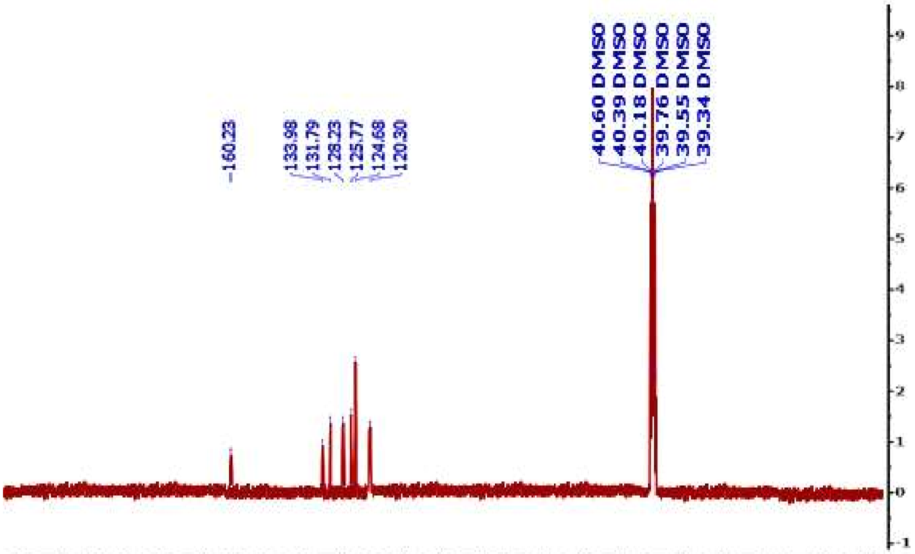
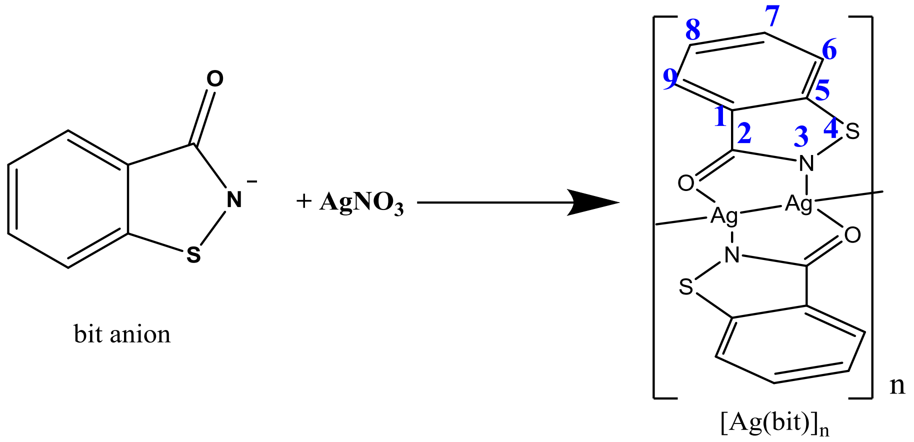


Fig.4: ^{13}C-{^{1}H}NMR spectrum of [Ag(bit)]$_n$ complex DMSO-d^6

Table 1: Color, yield (%), m.p., elemental analysis and molar conductivity of [Ag(bit)]$_n$.

Color	Yield (%)	Decomposition (°C)	Elemental analysis (%) Found (Calc.)				Molar Cond. (Ω^{-1} cm^{-1} mol^{-1})
			C	H	N	S	4
white	93	300-320	32.59 (32.58)	1.57 (1.65)	5.45 (5.43)	12.44 (12.42)	



Scheme 1: Schematic illustration for the synthesis of [Ag(bit)]$_n$

Table 2 IR data of Nabit ligand and [Ag(bit)]$_n$ with ^{1}H-NMR data of [Ag(bit)]$_n$.

IR			^{1}H-NMR		
Wavelength of Nabit (cm^{-1})	Wavelength of [Ag(bit)]$_n$ (cm^{-1})	Bands	Chemical shifts (ppm)	Splitting	$^3J_{HH}$,(Hz) Assignment
3058vw	3067m	ν(C-H)	7.97	Doublet	7.8, 1H, (H6)
1642m	1567m	ν(C=O)			
1506vs	1491vs	ν(C-N)	7.88	Doublet	8.2, 1H, (H9)
1446m	1432s	ν(C=C)			
1348m	1351m	ν$_{sym.}$(C-N-S)	7.62	Triplet	8.0, 1H, (H7)
1317w	1313m	ω(C-H)			
873w	869m	ν$_{asym.}$(C-N-S)	7.43	Triplet	8.2, 1H, (H8)
769w,729s	763m, 729s	ν(C-H) ring			

vw= very weak; w=weak; m=medium; s= strong; vs= very strong.

4. Application of hydrogen adsorption

To examine the H_2 uptake of [Ag(bit)]$_n$ within the pressure range (0-10 bar), dry air was passed through the [Ag(bit)]$_n$ sample to be analyzed under a certain temperature (77 K). Then argon gas as adsorbent was passed through the [Ag(bit)]$_n$ sample. Thereafter, H_2 gas was passed through the sample and the volume of the adsorbed H_2 gas by the [Ag(bit)]$_n$ was measured .This process continues within the pressure 0-10 bar range and ends at the highest preselected pressure. Results of the measurements made at 77 K, are presented in the isotherm as the hydrogen adsorption against increasing pressure which is given in Figure 5. According to this isotherm, it could clearly notice that the H_2 storage capacity increases with increasing pressure. The total hydrogen storage capacity for [Ag(bit)]$_n$ complex was 5.5 mmol/g at low pressure. The good H_2 storage of [Ag(bit)]$_n$ may attribute to good porosity and high surface area, according to its proposed structure, which includes a polymeric structure that can easily catch hydrogen (Scheme 2).

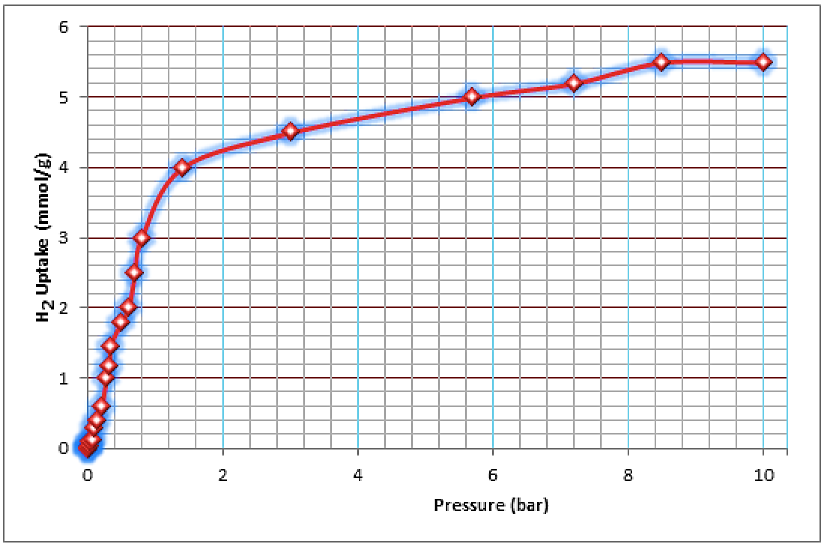
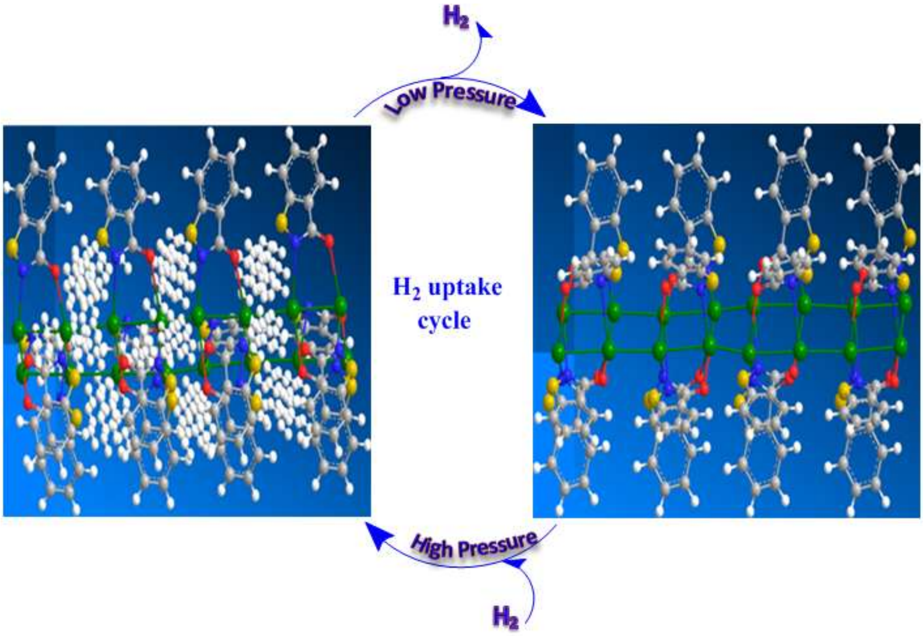


Fig. 5: H_2 isotherm of [Ag(bit)]$_n$ at 77 K.



Scheme 2: Schematic illustration for 3D view in H_2 uptake cycle

5. Conclusion

In this work, we proved that a new polymeric complex could be prepared with benzisothiazoli-none ligand. This complex has three main characteristic features: non-melting ability, high thermal stability and non-solubility in water and number of common organic solvents except the DMSO solvent, which showed very low solubility during heating. These properties encourage us to use it in the eco-friend applications of hydrogen storage. The results of hydrogen storage showed good storage capacity at low pressures not exceeding 10 bar with storage potential within the normal atmospheric pressure (approx. 1 bar), while the storage was observed to be 5.5 mmol/g with 10 bar only. This assignment can be a strong evidence for the porosity and high surface area of this inorganic polymer which is suitable for storage of hydrogen within its composition or between particles.

Acknowledgement

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معقد ايون الفضة الاحادي مع البنزايزوثايازولينون: تحضير وتشخيص وسعة خزن غاز الهيدروجين

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الملخص

نتج عن معاملة نترات الفضة احادية التكافؤ مع بنزايزوثايازولينون الصوديوم المعقد $[Ag(bit)]_n$ وان معقد الفضة التناسقي الناتج تم تشخيصه بواسطة تحليل مطيافية الاشعة تحت الحمراء والتحليل الدقيق للعناصر وطيف الرنين النووي المغناطيسي للبروتون و الكربون. اظهرت هذه القياسات ان ايون البنزايزوثايا– زولينون سلك كليكاند ثنائي السن جسري يربط ايوني الفضة الاحادية عبر ذرتي الاوكسجين والنيتروجين ووجد ان المعقد $[Ag(bit)]_n$ المحضر يمتلك استقرارية عالية ولم ينصهر حتى عند درجات حرارة اعلى من 320 درجو مئوية وايضا عدم ذوبانه في الماء وكذلك في عدد من المذيبات العضوية ماعدا مذيب ثنائي مثيل سلفوكسيد الساخن ولذلك تم اقتراح البنية البوليمرية لهذا المعقد وكذلك وجد انه يمتلك مسامية عالية والتي بالتالي اظهرت قابلية لخزن الهيدروجين بحوالي 5ونصف ملمول لكل غرام عند 77 كلفن و 10 بار.