

Silver and copper-Supramolecular coordination polymers catalyzed alkyne–azide "Click" cycloadditions

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Abstract:Two3D-supramolecular coordination polymers (SCP); {[SnMe₃(bpe)] $[Ag(CN)_2].2H_2O\},$ 1 and [Cu^I(CN₂(phen)Cu^{II}(CN)₂(phen)].5H₂O],**2**have been synthesized and characterized by physicochemical andspectroscopic methods. The structure of 1 consists of cationic $\{-Sn(Me_3)-bpe_-\}$ chains that are neutralized by $[Ag(CN)_2]^$ anions. The dicyanoargentate anions present discrete uncoordinated fragments between the cationic chains. The water molecules bind the cationic chains and the anions forming 3D-supramolecular structure through hydrogen bonds. The most intriguing feature in the structure of 2 is the unusual supramolecular interactions, including hydrogen bonds which involve the terminal cyanide and the phenanthroline (phen) ligands and π - π stacking which generate a unique 3D-supramolecular architecture in the solid state. The SCP 1 and 2 exhibit good catalytic activity for the formation of substituted triazoles. In this case, the SCP 1 and 2-catalyzed alkyne-azidecycloaddition provide 1,4-disubstituted1,2,3-triazoles with such efficiency and scope that the transformation has been described as "click" chemistry.

Key words: click reaction, Cupper, Silver, supramolecular polymers, Catalysis.

Introduction:

The supramolecular coordination polymers are undergoing a renaissance due to their unique structural and electronic properties and potential use in creating new therapeutics and electronically tunable materials [1-6]. The design and crystal engineering of the supramolecular coordination polymers continue to be a quite active research field because of their intriguing structural motifs and their potential applications as functional materials in areas such as magnetism, molecular sieves, ion exchange, gas storage, sensors, luminescence, non-linear optics, corrosion inhibition, biological activity, chirality, electronics, catalysis and conductivity [1-6]. Phenanthroline (phen) and 1,2-bis(4-pyridyl)ethane (bpe) have been extensively used as chemically versatile modules exhibiting a fortunate combination of structural and chemical properties [7-9]. Rigidity and planar structure of phen makes it an entropically better chelating molecule while bpe acts as

angular bipodal spacer ligand creating diverse topologies. Thus, supramolecular self-assembly was used to design silver or copper cyanide SCP containing bpe or phen, which have been carried out at room temperature between [M(CN)₄]³⁻ (M=Ag or Cu) building blocks and bpe or phen in presence of Me₃SnCl to test their catalytic activity in click reactions. The concept of "click" chemical reactions was described by Sharpless, the copper(I)-catalyzed azide- alkyne cycloaddition (Cu-AAC: i.e., the copper-catalyzed Huisgencycloaddition) reaction has emerged as the most extensively investigated and applied [10]. This reaction permits the chemoselective, regiocontrolled conjugation of functionalized alkyne to a functionalized azide yielding 1,4- or 1,4,5-substituted 1,2,3-triazole and occasionally1,5regioisomer [11,13]. Applications in many areas ranging from functional materials, drug discovery, biological, and hybrid bioconjugate areas have increased exponentially over the last decade [14-16]. The silver and copper complexes have been shown to act as mild π acids, thus effectively promoting the cycloaddition of azides onto terminal alkynes [17-19].

The supramolecular catalysts are stable, well-defined nonsolvated materials, and soluble in most organic-aqueous solvents, thus making them attractive homogeneous alternatives to copper and silver salts for potentially promoting the formation of 1,2,3-triazole. То test this hypothesis,{[SnMe₃(bpe)][Ag(CN)₂].2H₂O}1,and{[Cu^I(CN)₁(phen)₂ $[Cu^{II}(CN)_2(phen)].5H_2O$ 2, were prepared and characterized, and their reactivity toward azide-alkyne cycloaddition reactions was evaluated, where, for the first time, superamolecular catalysts were used for 1,2,3-triazoles formation at room temperature

. 2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents used in this study were of analytical grade supplied by Aldrich or Merck and used as received. Microanalyses (C, H, N) were carried out with a Perkin Elmer 2400 automatic elemental analyzer. The IR spectra were recorded on Perkin Elmer 1430 Ratio Recording Infrared Spectrophotometer as KBr discs. The magnetic susceptibility was determined with Johnson-Matthey susceptometer.

2.2 Synthesis of

{[SnMe₃(bpe)] [Ag(CN)₂].2H₂O}, 1

A solution of 82 mg (0.25 mmol) of $K_3[Ag(CN)_4]$ in 5 mL H₂O was added, with gentle stirring, to a mixture of solutions containing 150 mg (0.75 mmol) of Me₃SnCl in 5 mL MeCN and of 46 mg (0.25 mmol) of bpe in 5 mL MeCN. After about 2-3 weeks, colorless prismatic crystals of **1** started growing from initially clear solution. After filtration, washing with small, quantities of cold H₂O and MeCN and overnight drying, 107 mg of **1** were obtained. Anal. Calc. for 1 (C₁₇H₂₅N₄O₂AgSn): C, 37.53; H, 4.63; N, 10.30%. Found: C, 37.65; H, 4.17; N, 10.07%.

2.3 Synthesis of{[Cu^I(CN)(phen)₂][Cu^{II}(CN)₂(phen)].5H₂O}, 2

At room temperature, a solution of 99 mg (0.33 mmol) of $K_3[Cu(CN)_4]$ in 30 mL H₂O was added, under gentle stirring to a solution of 60 mg (0.334 mmol) of 1,10-

phenanthroline (phen) in 20 mL acetonitrile. After 1 week green needle crystals were resulted from yellow solution, after filtration, subsequent washing with water and overnight drying, about 70 mg (51% referred to $K_3[Cu(CN)_4]$ of green crystals were obtained. leff. = 1.95 BM, Anal. Calc. for 1 (C₃₉H₃₄N₉O₅Cu₂): C, 56.0; H, 2.8; N, 15.0%. Found: C, 55.96; H, 2.7; N, 14.9%.

2.2.3 Synthesis of benzyl azide

Sodium azide (1.4gm, 2.5equiv.) and Benzyl bromide(1mL, 1.5equiv.) are dissolved in mixture of acetone and water (1:1, 20mL) by stirring in 100mL round – bottom flask under close system over night at room temperature,then leaving the mixture to evaporate acetone.The benzyl azide was extracted with water $(1\times10$ mL) and diethyl ether $(2\times10 \text{ mL})$.



2.2.4Synthesis of 1-benzyl- 4-bromomethyl triazole

Propargyl bromide (1equiv,0.09gm) and (2equiv,0.19gm)), benzyl azide ((1equiv. 0.12mL) and(2equiv. 0.25mL)) and the catalyst(0.025 ,0.05 ,0.1 ,0.15equiv.) were mixed in presence of acetonitrile and water mixture(1:1,20mL). The mixture was stirred at room temperature or with heating to deliver exclusively the corresponding 1,4-triazole.



2.2.5 Synthesis of 1-benzyl-4-phenyl triazole

Phenyl acetylene (1equiv.0.1 mL) and (2 equiv. 0.22 mL)), benzyl azide (1equiv. 0.12 mL) and (2 equiv. 0.25 mL)) and catalyst (0.025 ,0.05 ,0.1 ,0.15 equiv.) in

presence of acetonitrile and water mixture (1:1, 20 mL) and stirring the mixture at room temperature or with heating to deliver exclusively the corresponding 1,4-triazole.



3.Results and Discussion 3.1 Crystal structure of

{[SnMe₃(bpe)] [Ag(CN)₂].2H₂O}n, 1

The asymmetric unit of 1contains one 1,2-bis(4pyridyl)ethane (bpe) molecule, one Me₃Sn cation, one Ag atom, two cyanide ligands and two water molecules, Fig. 1. The structure of 1 constructed of repeating asymmetric units with one distinct type of both silver and tin. The tin atom is penta-coordinated and has trigonalbipyramidal configuration (TBPY-5) with two nitrogen atomsof bpe ligands axially anchored to it forming cationic chain;N3-Sn1-N4 angle is 175.5°. The silver (I) ion is coordinated to twocyanide groups to form the discrete linear [Ag(CN)2]⁻ anion;C-Ag-C=177.6°. The structure of 1 consists of cationic {-(Me₃)Sn-bpe-}⁺ chains thatare neutralized by $[Ag(CN)_2]^$ anions. The dicyanoargentate(I) anions present discrete uncoordinatedfragments between the cationic chains. The cationic chains form parallel sets oflayers which contain infinite chains with separation distances excluding any packing interaction, Fig. 2. The dicyanoargentate anionsand the water molecules thread in the cationiclayers. space between the Thewatermolecules exist as pairs that aremutually interactedby hydrogen bonds; O10--H7 = 1.92 Å, O7--H10 = 1.943 Å and oxygen--oxygencontacts, 2.879. At the same time, thedimeric water molecules connect two $[Ag(CN)_2]^-$ anions throughhydrogen bonds; N5--H10i = 2.077 Å, N24--H7 = 2.058 Å, forming octagonal rings which connected together by H-bonds are atwatermolecules, 3.009 Å, and short contacts; 2.786 Å, forming ribbonlikestructure. The anionic ribbons connect the cationic layers by extensive hydrogen bonds; 2.715--2.958 Å, and π - π stacking and short contacts creating unique supramolecular 3D-network structure [20].

3.2 Spectral characteristics of 1

The IR spectrum of the SCP 1 displays strong band at 2138 cm⁻¹ corresponding to v_{CN} . The presence of this band at lower wavenumber than those of thebridging cyanides and higher value than those of the terminal cyanides is a good evidence of the presence of the hydrogen bondsbetween the [Ag(CN)2]⁻ anions and the water molecules. Also, the IR spectrum of 1 shows the band of $v_{(Ag-C)}$ at about 468 cm⁻¹; the presence of this band confirms the presence of Ag-CN moiety. Water molecules in 1 give rise to the appearance of a broad band at3425 cm⁻¹. Methylene groups of the bpe ligand as well as the methyl groups of the Me₃Sn fragment are characterized in the IRspectrum of 1 by C-H stretching vibrations at 2925 and 2871 cm-1 and by C-H deformation band at 1461 cm⁻¹. ¹H NMR spectrum of the SCP 1, displays three distinct bands for the bipodal ligand, bpe. The doublet at 8.42 and 8.43 ppm isassigned to $H_{2.6}$ & $H_{2\backslash 6\backslash}$ while the doublet at 7.24 and 7.25 ppm is assigned to $H_{3,5}$ & $H_{3\backslash,5\backslash}$. The ethylenic group gives rise to one singletband at 2.93 ppm. The protons of the Me₃Sn group gave rise to band at 0.53 ppm with its characteristics satellite bands that result fromspin-spin coupling with the tin atom. The singlet band at 3.38 ppm is due to the protons of the water molecules. On the other hand, there are four bands for bpe, in the ¹³C-spectrum; at 123.4 ppm for β carbon nuclei, at 148.9 ppm for γ carbon nuclei, at 149.3 ppm for α carbon nuclei and at 33.4 ppm for the ethylenic carbons. The cyanide groups display singlet band in the ¹³C-spectrum; at 142.5 ppm and the Me₃Sn units give rise to a triplet band at 0.21 ppm with its characteristic satellite bands. Thus, the NMRspectra confirm the presence of the cyanide ligand, the bipodal ligands, water molecules as well as the Me₃Sn units as bridging groups. The ratio between the peaks' areas of all types in the ¹H NMR spectrum of **1** support the composition elucidated by X-ray diffraction and elemental analysis.

3.3Crystal Structure of the SCP {[Cu^I(CN) (phen)₂][Cu^{II}(CN)₂(phen)].5H₂O}, 2

The asymmetric unit of the SCP 2 contains two discrete molecular structures and consists of two crystallography different Cu(I/II) atoms, three ordered cyanide groups, three phen molecules and five clathrated water molecules, Fig. 3. The structure of the SCP 2 contains [Cu^I(CN)₂(phen)],[Cu^{II}(CN)₂(phen)] fragments and five water molecules which are connected with each other by hydrogen bonds. In [Cu^I(CN)₂(phen)] fragment, the copper center is coordinated by two phen ligands and one cyanide ligand in a distorted trigonalbipyramid (TBPY-5) geometry. On the other hand, the copper atom, in the [Cu^{II}(CN)₂(phen)] fragment, is coordinated to one phen ligand and two cyanide groups, forming slightly distorted tetrahedral (T-4) geometry. There are five clathrated water molecules per $\{[Cu^{I}(CN)_{2}(phen)][Cu^{II}(CN)_{2}(phen)]\}\$ fragments which form hydrogen bonds. The oxygenatoms of the water molecules are close packed by short contacts in the range of 2.75-2.87 A°, forming a unique 1D-tape. This 1Dtape consists of fused two four- and one six-oxygen member rings creating water cluster. The water molecules spread between the layers of the [Cu^I(CN) (phen)₂] and[Cu^{II}(CN)₂(phen)] fragments forming Hbonds with the terminal cyanide groups and the hydrogen atoms of the phen ligand to extend the structure of 2 to 3D-network^[21]. So, these water tapes play a complementary role via hydrogenbonds for stabilizing the network structure of the SCP 2 inaddition to the π - π stacking, Fig. 4.

3.4 Spectral characteristics of 2

The IR spectrum of the SCP **2** exhibits a strong broad band at 3397 cm⁻¹ corresponding tothe stretching vibrations of the water molecules. The IR spectrum of the SCP **2** exhibits bands characteristic of the(CuCN)_n fragment and the phen ligand. The spectrum displays the bands of the phen ligand at 3059, 2926 cm⁻¹($v_{CH(arom)}$), (1421 cm⁻¹ (δ_{CH}) and at 770, 724 cm-1 (γ_{CH}). These bands are shifted to lower wave numbers from thevibration frequencies of the free phen ligand due to the formation of hydrogen bonds between the hydrogen atoms of the ligand and the donor sites of the (CuCN)_n fragment. In contrast, the band at 1617 cm⁻¹ corresponds to $\upsilon_{C=N}$ while those at 1586, 1507 and 1459 $cm^{\text{-1}}$ are attributed to $v_{C=C}$ of the phen ligand in theSCP1. These bands exhibit small shifts to lower wave numbers from those of the phen ligand supporting coordination of phen to Cu centers. The presence of two v_{CN} IR absorption bands in the spectrum of the SCP 2 at 2129 and 2086 cm⁻ ¹ supports the presence of two different cyanide groups. The first type of the cyanide groups is bonded to CuI while the other is coordinated to CuII center, supporting the presence of mixed valence copper cyanide coordination polymer. It is noteworthy that the v_{CN} bands (2129, 2086 cm⁻¹) of the SCP $\mathbf{2}$ are different from that of $K_3[Cu(CN)_4]$ (2081 cm⁻¹), which also supports the presence of two types of cyanide groups. In addition, the v_{Cu-C} bands at 429 and 435 cm⁻¹ confirm the presence of two (CuCN)_n fragments.

3.5 Click reactions

The advantageous properties of Huisgencyclo-addition, together with the most useful modular nature of the click chemistry approach, make it well-suited for use in the synthesis of new molecules, especially conjugatescomposed of two quite different subunits. Examples are bioorganic- inorganic conjugates such as the organic azides and the boron clusters [22].A preliminary screening study using phenyl acetylene, benzyl azide and catalysts 1 and 2, which differ in the nature ligands, geometry and metals, was undertaken (Figures 1 and 2). For initial studies, reactions wereperformed in acetonitrile and water (1:1). This ratio was found to be suitable solvent because of the high solubility of both alkyne and azides to give corresponding triazoles(1-benzyl-4-bromomethyl triazole and 1-benzyl-4-phenyl triazole) in 100% yield. The different factors affecting the yield of triazoles such as concentration of azide and alkyne, catalyst amount, time and temperature, have been investigated to apply the best conditions to obtain 98-100% yield triazoles. The results are shown in Tables 1-8. It is observed that the azide/alkyne ratio as well as the amount of catalyst (0.05-0.15 mol%) affects the time required to obtain the best yield of triazole. Using 0.15 mol% of SCP 1 as a catalyst with the ratio 2:1 azide/ alkyne (propargyl bromide) affords the full conversion (yield 98%) of azide/alkyne to triazole after 25 min at room temperature, Table1, entry7. On the other hand, full conversion [yield100%]of azide/alkyne (propargyl bromide) [1:2] to triazole required the use of 0.15 mol% of the catalyst SCP 2 within 30 min at room temperatureTable 2, entry4. Above reactions represent the best conditions for the formation of 100% yield triazole within shortest time. Also, in case of the alkyne phenyl acetylene, using 0.10 mol% of the SCP 1 as a catalyst with the ratio 1:1 azide/ alkyne affords the full conversion (yield 100%) of azide/alkyne to triazoleafter 30 min at room temperature, Table 3, entry7.In tha case full conversion [yield100%]of of the SCP 2. azide/alkyne [1:1] to triazole required the use of 0.15 mol% of the catalyst 2 within 35 min at room temperatureTable 4, entry4. Above reactions represent the best conditions for the formation of 100% yield triazole within shortest time. Varying the nature of the catalyst between the silver 1 and copper 2 metals had little impact on the yield. A key advantage of using **1**is that there was no evidence that the catalyst and alkyne reacted vigorously, including when reactions are done at a larger scale. For instance, when a 10-fold increase in reaction scale was run using phenyl acetylene and SCP 1, the desired triazole was readily isolated in 100% yield after 30 mintes at room temperature. One additional advantage of using the homogeneous catalyst as opposed to AgNO₃ is that at the completion of a reaction there was no evidence of silver metal deposition, owing to the robust nature of the metal complex [17-19]. The general utility of the catalyst under the most promising conditions was evaluated subsequently using SCP 1 and 2 and two of different alkynes in direct comparison to reactions performed in the presence of catalysts Cu(OAc)₂ and AgNO₃ as shown in Tables 5-8. In all cases

isolated yields are reported.

Under identical conditions for the AgNO₃ orCu(OAc)₂ and sodium ascorabate-catalyzed reaction, it was found that Propargyl bromide and phenyl acetylene were converted to the corresponding triazole in 100% yield in both cases after only 25-28 and 5-12 hours, respectively, at room temperature, Tables 5-8. The reactions progress were monitored by TLC and the products were purified by preparative TLC using CH₂Cl₂ (1:1) as a mobile phase to generate the desired tris-triazoles in quantitative high yields. The SCP 2 was successful in producing 1,2,3triazoles in 100 % in 50 minutes without using sodium ascorbate. During the course of our studies, as previously reported by Sharpless [14], the use of the SCP 2 reduced by sodium ascorbate gave generally higher yields than a direct source of Cu owing to the high degree of efficiency, the reaction could be conducted with a stoichiometric amount (4.5 equiv.) of azides. Purification was greatly simplified by the absence of side products. When experiments are repeated at high temperatures (40-60 $^{\circ}\text{C})$, the yields of the catalyzed reactions were below 80% for all the compounds tested after 20 minutes. However after 30 minutes two of the alkynes tested generated triazole in greater than 90.% yield. When the control reactions were run in the absence of the catalyst, yields of the products at room temperature were negligible (< 1%).

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Table1 Optimization with silver polymer catalyst in the Ag-AAC reaction for entries 1-9 propargyl bromide ,benzyl azide, entry 10 recovery reaction

Entry	Azide	Alkyne	Catalyst ratio	Time	Temperature	Yield
1	2	1	0.15	80	r.t	98%
2	2	1	0.1	30	r.t	98%
3	2	1	0.05	25	r.t	100%
4	1	2	0.15	90	r.t	97%
5	1	2	0.1	70	r.t	100%
6	1	2	0.05	95	r.t	98%
7	1	1	0.15	110	r.t	100%
8	1	1	0.1	130	r.t	100%
9	1	1	0.05	145	r.t	100%
10	2	1	0.15	50	r.t	100%
11	2	1	0.15	12	60c	98%
12	2	1	0.15	20	40c	100%

Entry	Azide	Alkyne	Catalyst ratio	Time/min	Temperature	Yield
1	2	1	0.15	90	r.t	100%
2	2	1	0.1	105	r.t	100%
3	2	1	0.05	120	r.t	95%
4	1	2	0.15	30	r.t	100%
5	1	2	0.1	70	r.t	98%
6	1	2	0.05	60	r.t	98%
7	1	1	0.15	60	r.t	95%
8	1	1	0.1	80	r.t	100%
9	1	1	0.05	95	r.t	100%
10	1	2	0.15	50	r.t	100%

Table 20ptimization with copper polymer catalyst in the Cu-AAC reaction for entries 1-9 propargylbromide ,benzylazide, entry 10 recovery reaction

table 3 Optimization with silver polymer catalyst in the Ag-AAC reaction for entries 1-9 phenyl acetylene , benzyl bromideEntry 10 reaction recovery.

Entry	Azide	Alkyne	Catalyst ratio	Time	Temperature	Yield
1	2	1	0.15	90	r.t	100%
2	2	1	0.1	103	r.t	95%
3	2	1	0.05	105	r.t	98%
4	1	2	0.15	130	r.t	98%
5	1	2	0.1	135	r.t	100%
6	1	2	0.05	90	r.t	97%
7	1	1	0.15	100	r.t	98%
8	1	1	0.1	30	r.t	100%
9	1	1	0.05	90	r.t	97%
10	1	1	0.1	70	r.t	100%
11	1	1	0.1	20	40c	100%

12	1	1	0.1	10	
	4	-	10	10	

Table4 Optimization with copper polymer catalyst in the Cu-AAC reaction for entries 1-9 phenyl acetylene ,benzyl bromide. Entry 10 reaction recovery

Entry	Azide	Alkyne	Catalyst ratio/equiv	Time	Temperature	Yield
1	2	1	0.15	50	r.t	100%
2	2	1	0.1	80	r.t	98%
3	2	1	0.05	50	r.t	98%
4	1	2	0.15	60	r.t	95%
5	1	2	0.1	90	r.t	100%
6	1	2	0.05	75	r.t	98%
7	1	1	0.15	35	r.t	100%
8	1	1	0.1	50	r.t	98%
9	1	1	0.05	65	r.t	100%
10	1	1	0.15	55	r.t	100%
11	1	1	0.15	10	40	98%
12	1	1	0.15	7	60	100%

Table5 comparison between SCP1 and AgNO₃ as catalysis for Ag-AAC reaction in the case of propargyl bromide and benzyl azide

Compound	Catalyst ratio	Alkyne	Azide	yield	Time
SCP1	0.15	1	2	100%	30 min
AgNO ₃	0.15	1	2	100%	28 hour

Table 6 comparison between SCP2 and $Cu(OAc)_2$ as catalysis for Ag-AAC reaction in the case of propargyl bromide and benzyl azide

Compound	Catalyst ratio	Alkyne	Azide	Yield	Time
Scp2	0.15	1	2	100%	30 min
Cu(OAc) ₂	0.15	1	2	100%	12Hour

Table7 comparison between SCP1 and AgNO₃ as catalysis for Ag-AAC reaction in the case of phenyl acetylene and benzyl azide

Compound	Catalyst ratio	alkyne	azide	yield	Time
Scp1	0.15	1	1	100%	30 min
AgNO₃	0.15	1	1	100%	25 hour

Table 8 comparison between SCP2 and Cu(OAc) $_2$ as catalysis for Ag-AAC reaction in the case of phenyl acetylene and benzyl azide

compound	Catalyst ratio	Alkyne	azide	yield	Time
Scp2	0.15	1	1	100%	35min
Cu(OAc) ₂	0.15	1	1	98%	12 hour



Figure 1 An ORTEP plot of the asymmetric unit of the SCP 1 with atom labeling scheme



Figure 2 View of the overall 3D-structure of 1 showing the alternating cationic and anionic layers.



Figure 3 An ORTEP plot of the asymmetric unit of the SCP 2 with atom labeling scheme



Figure 4 3D-network structure showing hydrogen bonds in the SCP 2 along the a-axis

الملخص العربي

إمكانية إستخدام بعض البوليمرات التناسقية الجديدة فائقة الجزيئية متعددة الابعاد المحتوية على النحاس أحادى التكافؤ والفضة أحادية التكافؤ كمحفزات لبعض التفاعلات الكيميائية. وهذا النوع من البوليمرات التناسقية فائقة الجزيئية قد تم تحضيره عن تفاعلات التجمع باستخدم التجمع الذاتي بين املاح النحاس الاحادى والثنائى التكافوء والمعطيات الأحادية لقواعد البيريدين أوعن طريق المعطيات الثنائية الحلقية غير المتجانسة. استخدام النحاس الأحادى والفضة الأحاديه كعوامل حفازة فى التفاعلات النقريه للحصول على 1.4 ــثنائى الاستبدال للتراي زول ويتم در اسة هذا المركب عن طريق الاشعة تحت الحمراء وقياس الرنين المغناطيسى للهيدروجين.