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A Mini Review on Monodentate Coordination Behavior of Dicyanoargentate Anion towards 3d Transition-Metal Ion, Blocked by Different Blocking Ligands

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Abstract

Synthesis of coordination compounds using dicyanoargentate, $[Ag(CN)₂]$ as inorganic ligand is an interesting topic in the research area of supramolecular chemistry. Again cyano bridged compound is especially significant due to their remarkable structural diversity. As cyanometalate anions has strong affinity towards transition metal ions and it has been widely used as building blocks for the creation of coordination polymer. Dicyanoargentate anion, $[\mathsf{Ag(CN)}_2]^-$ can behaves as bridging ligandas well as monodentate ligand and discrete anion. This review article mostly highlights the monodentate coordination behavior of dicyanoargentate anion towards 3d-transition metal ion in which the transition metal ion is blocked by different blocking ligands. This review also reveals the formation of different dimensionality complexes through Ag**Ag interactions when dicyanoargentate anion act as monodentate ligand.

> **Keywords:** Dicyanoargantate, Monodentate behavior, 3d-transition metal, Blocking ligand, Coordination compounds.

Introduction

It has been well-known that among the cyanometalates $^{\text{1-47}}$ like [Fe(CN) $_{\text{6}}$] $^{\text{2-}},$ hexacyan nidoferrate(II);[Fe(CN)₆]3-, hexacyanidoferrate (III);[Cr(CN)₆]³⁻, hexacyanidochromate(III);[Co $\left(\textsf{CN}\right)_{6}]^{3-}$, hexacyanidocobaltate(III),[Ni $\left(\textsf{CN}\right)_{4}]^{2}$, tetracyanonickelate(II) etc. Omot abain dicyanoargentate ion, $[Ag(CN)]$ is one of the potential inorganic bridging ligand^{1,5,16-25} to form coordination polymer due to the ambidentate

behavior of CN⁻ ion. Silver(I) has been prefer two fold linear coordination geometry, $6,7$ however higher coordination numbers with diverse geometries like trigonal,⁸ tetrahedral,⁹⁻¹¹ squareplanar,¹² trigonal pyramidal¹³ T-shaped,¹⁴ or octahedral¹⁵ coordination geometry are also possible. In addition to bridging behaviour^{1,5,16-25} dicyanoargentate anion, $[Ag(CN)_2]$ ⁻ can also behave as noncoordinating anions,²⁶⁻³⁰ polymeric anion^{20,31-33} and monodentate ligands.³⁴⁻⁴³ Several coordination compounds have been reported with

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this anionic/terminal/bridging dicyanoargentate moieties.1,5,16-43 The derived systems are either discrete mono, di or trinuclear syatems or polynuclear systems with one, two or threedimensional (1D, 2D, 3D) structures.¹⁶⁻⁴³ Again in the anionic form all the nitrogen atoms and in the monodentate or bridging [Ag(CN) $_{\textrm{\scriptsize{2}}}$]⁻ anion the non-coordinating nitrogen atoms can potentially form hydrogen bonds with suitable hydrogen bond donors to generate supramolecular self-assemblies. Thus these ligands have potential to make supramolecules through coordinate bonds, $1,1625,27-29$ and/or through hydrogen bonds.36-39,42,43 In spite of extensive developments, it is difficult to control the nature of the final product containing ${\sf [Ag(CN)}_2{\sf]}$ ligand. The uncertainty is mostly due to their different modes of coordination.

Different types coordination compounds with dicyanoargentate, [Ag(CN)₂]⁻ anion

It has been found that blocking ligands like 1,3 diamino propane, 2,2'-bipyridine, 1,10-phenanthroline, Schiff base ligand etc. plays a crucial role to govern the dimensionality and topology of cyanid-linked coordination compounds. A large number of compounds¹⁶⁻²⁵ with 1D,¹⁶⁻²⁰ 2D²¹⁻²³ and 3D^{24,25} topology have been reported by introducing different types of blocking ligands and $[\mathsf{Ag(CN)}_2]^-$ as anionic moiey. Again silver atom has strong affinity to form metal^{***}metal bond, so dicyanoargentate, $[Ag(CN)_2]$ ⁻ ion can also form Ag"Ag bond (argentophilic interaction) and due to such type of interaction $[Ag(CN)_2]$ ⁻ can form polymeric anion $^{20,31-33}$. of types $[Ag_{n}(CN)_{n}]^{-}$, $[Ag(CN)_{2}]_{n}^{-}$, [Ag(CN) $_{2}$] $_{5}^{-}$, [Ag $_{3}$ (CN) $_{5}$] $^{2-}$ anions etc. $^{20,31-33}$ So the structural dimensionality can also be increased efficiently through such weak argentophilic interactions in addition to the metal–ligand coordinate bond formation. 17,36,39-49 Large no of compounds of different dimensionality and topology have been reported by using $[Ag(CN)_{2}]$ anion as ligand where Ag"Ag interaction playes the key role for dimensionality and topology.17,36,39-49 Table 1 represents the Chemical name and abbreviations of blocking ligands considered in this context.

Table 1: The Chemical name and abbreviations of blocking ligands considered in this review article

$\textsf{Dicyano}$ argentate [Ag(CN)₂]⁻ ion as monodentate **ligand**

As already mentioned that due to ambidentate behavior of CN− ion, dicyanoargntate, $[\text{Ag(CN)}_{2}]$ ⁻ ion is a potential inorganic bridging ligand. However inspite of the bridging behavior it can also act as a good monodentate ligand. A number of compounds have been reported in which dicyanoargenate, [Ag(CN) $_{\rm 2}$] $\overline{}$ ion act as monodentate ligand.34[−]45 The 3d-transition metal-silver(I) compounds that are reported and structurally characterized using blocking ligands in which [Ag(CN) $_{2}$]⁻ ion act as monodentate ligand are summarized in Table 2.

Among reported compounds most of the compounds (Table 2) form supramolecular polymeric structure,³⁶⁻⁴⁵ due to weak interactions like hydrogen bonding interactions, Ag^{**}Ag interactions, $\pi^{\bullet\bullet}\pi$ stacking interactions etc.^{36–45} On the other hand only in case of two compounds^{34,35} {*cis-*[Cr(en)₂][Ag(CN)₂]₂}CIO₄ H₂O and {[Cu₂(dmpzpo)₂] $[\mathsf{Ag}(\mathsf{CN})_2]_2$ } no supramolecular polymerization have been observed due to such type of weak interactions. Therefore these two compounds are solely discrete systems of which the first one is a trinuclear system and the latter one is a tetranuclear system. The reported dinuclear systems^{36-38,40,44} include Cu"Ag' and Mn"Ag', Mn"'Ag', Ni"Ag', trinuclear systems $^{34,39,41-43,45}$ include Cu_{II}Ag₂', Ni"Ag₂', and Cr $^{\shortparallel\textsf{A}}$ g $_2^{\shortparallel\textsf{,}}$ and only tetranuclear system 35 include Cu $_2$ "Ag $_2$ '.

Table 2: A summary of reported 3d-transition metal-silver(I) compounds in which dicyanoargenate [Ag(CN)2]- **ion act as momodented ligand and**

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For the complex 34 {cis-[Cr(en) $_2$][Ag(CN) $_2\mathrm{l}_2$ } $\text{ClO}_4\text{H}_2\text{O}$ the two cis-positions are coordinated to two cyanide nitrogens of monodentate dycyanoargentateion and four other positions are coordinated to four nitrogens of two ethylenediamine ligands to adopts a distorted octahedral shape around the central chromium(III) ion. Whereas the complex³⁵ {[Cu₂(dmpzpo)₂][Ag(CN)₂]₂} (Fig. 1) consists of two monodentate $[Ag(CN)₂]$ ions and one dicopper(II) dication, $\text{[Cu}_{2}\text{(dmpzpo)}_{2}\text{]}^{2+}$ moiety. The two monodentate dictanoargentate anions are coordinated with two different Cu(II) centre of the dinuclear [Cu₂(dmpzpo)₂]²⁺ unit in *trans* configuration. Each of the two copper(II) centre is penta-coordinated to two propanoxo-oxygens, two nitrogen atoms of pyrazole loigand (one from each ligand) and one nitrogen from the monodentate $[Ag(CN)₂]$ ⁻ anion. So the shape of the complex is an transitional between the best square-pyramidal geometry and trigonal-bipyramidal geometry.

 $\left[\mathsf{Fig.~1.~Crystal~structure~of~compound~[Cu_{2} (dmpzpo)_{2}]\right]$ [Ag(CN)₂]₂. The hydrogen atoms are not shown for clarity³⁵

The Mn(II) centre in the dinuclear Compound, $36 \{ Mn(H₂O)(bipy)₂[Ag(CN)₂]\}$ $[Ag(CN)]$ and the Cu(II) centre in the dinuclear Cu"Ag' compound, $^{\rm 38}$ {[Cu(saldmen)(H $_{\rm 2}$ O) $[Ag(CN)]$ made up of a dinuclear monocation, ${Mn(H₂O)(bipy)₂[Ag(CN)₂]}$ ⁺ and a mononuclear monocation, $[(H, O)(saldmen)Cu]^{+}$ respectively and a monodentate [Ag(CN) $_{\textrm{\tiny{2}}}$] $\overline{}$ anion, whereas The MN(III) centre in the dinuclear $Mn^{\text{III}}Ag^{\text{II}}$ compound 37 {(H₂O)(valen)Mn[Ag(CN)₂]} H₂O, contains neutral dinuclear units, $\{[(H, O)]\}$ $(valen)Mn][Ag(CN),]$ and a water molecule of crystalization. The Mn(III) centre in Mn^{III}Ag¹ compound37 is penta-coordinated in which the equatorial planes are coordinated to two nitrogens and two phenoxo oxygens of Valen Schiff base ligand and the apical positions

are coordinated to one oxygen atom of water molecule which is coordinated to the Mn(III) centre and one cyanide nitrogen of monodentate $[\mathsf{Ag}(\mathsf{CN})_2]$ ⁻ ligand. Whereas the Cu(III) centre in CuⁱⁱAgⁱ compound³⁸ is penta-coordinated in which the equatorial planes are coordinated to two nitrogens and one phenoxo oxygen of saldmen Schiff base ligand and the axial positions are coordinated to the one cyanide nitrogen atom of monodentate [Ag(CN) $_{\textrm{\scriptsize{2}}}$]⁻ ligand and oxygen atom of the water molecule which is coordinated to the the Cu(III) centre. Again in both the compounds^{37,38} the hydrogen atom/s of the coordinated water molecules from one dinuclear unit form hydrogen bonds with O4 compartment of another dinuclear unit to form a supramolecular Mn(III)/Cu(II) dimer. The supramolecular dimer in compound³⁸ Cu¹¹Ag¹ generates a one-dimensional double chain through another hydrogen bonding interaction form between nitrogen atom of noncoordinated cyano group and hydrogen atom of the coordinated water molecule. Whereas The supramolecular dimer in compound³⁷ the Mn^{ill}Agⁱ dimers are further linked through argentophilic interaction with Ag**Ag distance 3.092 Å to build a infinite supramolecular chains. The packing of the chains in the crystal creates a channel in which the cocrystallized water molecules are grouped in almost planar hexamers and hosted in the channels of the chains. Each of the hydrogen atoms of water molecules coordinated to Cu(II)/Mn(III) centres are also hydrogen bonded to terminal nitrogens of the dicyanoargentate ligands. The dinuclear compound³⁶ MnⁱAgⁱ, forms a infinite 2D layers due to intermolecular hydrogen bonding interactions and it forms a 3D network through weake $\pi^{\bullet\bullet}\pi$ stacking interactions.

The compound⁴⁰ $\{[Ni(pn)₂][Ag₂(CN)₄]\}$ and ${[Cu(pn)_2][Ag(CN)_2]}[Ag(CN)_2]$ (Fig. 2) forms a chainlike structure, whereas the compound⁴¹ ${[Cu(1-Meen)][Ag(CN)]}$ forms 2D sheet (Fig. 3) through Ag"Ag interactions and The compound⁴² $\{[[Ni (2-teta)][Ag(CN)]_2\}$ forms a ladder like structure through argentophilic interactions and weak hydrogen bonded interactions. The compound⁴⁰ ${[Cu(pn)]}$ $[Ag(CN),]$ [Ag(CN)₂] consists of a dinuclear dication, $\left[\mathsf{Cu(pn)}_{2}\mathsf{Ag(CN)}_{2}\right]$ and two free crystallographically independent [Ag(CN),]⁻ ions. Here the Ag1 atom forms two Ag"Ag

interactions, one with Ag2 atom and another with Ag3 atom. So there are Ag1"Ag2"Ag1 triads by shorter argentophilic interactions with Ag"Ag distances of 3.2270 Å and these triads are linked to Ag3 atom by longer argentophilic interactions with Ag"Ag distance of 3.4166 Å. So a chain-like structure of silver (Ag"Ag"Ag) is form with alternating argentophilic interactions of distances 3.2270 Å and 3.4166 Å (Ag"Ag) which is extended along the x axis (Figure 2).

Fig. 2. Crystal structure of compound $\{[\mathsf{Cu}(\mathsf{pn})_2][\mathsf{Ag}(\mathsf{CN})_2]\}$ **[Ag(CN)2]. The dotted line represents the Ag•••Ag interactions40**

Fig. 3. Two-dimensional sheets of compound {[Cu (1-Meen)2][Ag2 (CN)4]}which is formed due to Ag•••Ag interactions. The hydrogen atoms of diamine ligand and less populated carbon atoms of diamine ligand are not shown for clearity. Dotted lines represent the argentophilic interactions40

The compound³⁹ $\{[Ni(Me2en)]\}$ $\mathsf{[Ag(CN)}_2\text{]}_2\mathsf{)}\mathsf{0.5H}_2\mathsf{O}$ made up of two independent centrosymmetric trinuclear molecules consist of a mononuclear dication [Ni(Me2en) $_2$]*² connected to two monodentate [Ag(CN)₂]⁻ ions in trans arrangement. But the compound⁴³ ${[Cu(imH)_4]}$ [Ag(CN) $_{2}$] $_{2}$ } composed of a asymmetric trinuclear centrosymmetric unit consists of a [Cu(imH) $_2$]*² dication and two monodentate [Ag(CN) $_{\textrm{\scriptsize{2}}}$] $\overline{}$ ions linked through cyanide in trans arrangement. The

trinuclear moities in compound³⁹ are connected through hydrogen bonded interactions involving cyanide nitrogen atoms and hydrogen atoms of water of crystallization to form a irregular chains. Whereas in compound⁴³ the trinuclear units are connected to each other by strong hydrogen bonded interactions involving the cyanide nitrogen atoms and imidazole (N–H) hydrogen atoms. Besides these comparatively strong hydrogen bonded interactions there also exist a number of weak C-H"N hydrogen bonding interactions and the presence of such weak hydrogen bonding interactions built a polymeric chain like structure.

The compound⁴⁴ $[{Cu(bipy)(sal)}]$ ${Ag(CN)}_2$] is a dinuclear system in which the copper(II) centre adopts a square 2-pyramidal shape in which the besal planes are coordinated to the two nitrogens of bipy ligand and one hydroxo and one phenoxo oxygen atoms of salicyaldehyde ligand and the axial positions are coordinated to one nitrogen of the monodentate ${\sf [Ag(CN)}_2]^{\sf -}$ ion. It forms a 1D supramolecular zig-zag chain through argentophilic interactions and $\pi^{\bullet\bullet}\pi$ stacking interactions. But the compound⁴⁵ {[Ni(3tet)][Ag(CN) $_{\mathrm{2}}$] $_{\mathrm{2}}$ is a discrete trinuclear octahedral system in which the nickel(II) centre is coordinated by four nitrogens of the 3-teta amine ligand in besal plane and two nitrogen atoms of the two monodentate [Ag(CN) $_{\textrm{\scriptsize{2}}}$] $\overline{}$ ligands coordinated to at axial positions. It forms a 2D polymeric sheet due to weak Ag"Ag interactions.

Simultaneous existence of both bridging and terminal [Ag(CN)₂]⁻ ions in a single compound

Simultaneous existence of both bridging and non-coordinated anion is common phenomenon.27−29 But it is a unusual phenomenon that [Ag(CN) $_{\textrm{\tiny{2}}}$][–] anions can act as both monodentate as well as bridging ligand in a single compound. However very few compounds were reported where simultaneous existence of both bridging and monodentate [Ag(CN) $_{\textrm{\scriptsize{2}}}$] $\overline{}$ ions are found in a single compound.17,46−48 The reported 3d-transition metal-silver compounds in which dicyanoargenate $[\mathsf{Ag}(\mathsf{CN})_2]^\text{-}$ act as both monodentate and bridging ligand in a single compound are summarized in Table 3.

 $\frac{6}{2}$ 47 $\overline{1}$ ge meppersies in Districted trigonal distorted trigonal distorted trigonal chain 30.2322 2.2322 2.2322 2.2322 2.33 1 (Lu2)ng(halin-distorted trigonal Distorted trigonal 2.040 1.997−2.622 3.222.022 3.1152 Unique compination of one-dimensional distorted trigonal distorted trigonal 47 [(cupied αποτοποιημα Unique combination of one-dimensional chain with two-dimensional plane atanidal Ricconsiders (Ricconsiders). 2H O2 by Paramidal chain with two-dimensional advantages of two-dimensional plane plane plane plane and all chain with two-dimensional plane and all chain with two-dimensional plane an Terminal Bridging Throuch bridging cyanide Through Ag••••Ag interaction Through Ag""Ag interaction 1D chain Ω Throuch bridging cyanide 1D zigzag chain 3.2322 3.0563 3.1152 1.997-2.622 1.975, 1.967 Bridging 2.0827 Terminal 2.040 2.290 1.985 Distorted trigonal Square-pyramidal Distorted trigonal bypyramidal bipyramid geometry ${\rm (Cyc)}$ [Cu(applicate) and the contract of ${\rm (Cyc)}$ {Cu(app)MeOH)}(µ-Ag(CN),]} $[Cu(mepy)₂{Ag(CN)₂}]_n$ [(Cu(app)[Ag(CN)], $\operatorname{Cu}_2(\mathsf{bn})_2\{\mathsf{Ag(CN)}_2\}_4$ **O^{CH}S** [CHN]

The structure of the complex⁴⁶ [Cu(mepy) $_2$ {Ag(CN) $_2$ } $_2$] $_{{\rm n}}$ consist of a neutral zigzag chains, which are connected by weak Ag"Ag interactions (3.2322 Å).The Cu(II) centre is pentacoordinated in which the equatorial positions are coordinated to one nitrogen of terminal ${\sf [Ag(CN)}_2{\sf]}^{\!\scriptscriptstyle{\top}}$ ion, two nitrogens of two bridging $[\mathsf{Ag}(\mathsf{CN})_2]^-$ ion and two nitrogens of Mepy ligands are coordinated at the two axial positions to adopts a deformed trigonal bipyramidal geometry. The nitrogen atoms of terminal $[\mathsf{Ag(CN)}_2]^-$ ions are connected from the peaks of zig-zag chains of one layer to the `valleys' between two chains in the layers above and below. Therefore, each Ag1 (from the bridging [Ag(CN) $_2$]⁻ ion) is surrounded by two adjacent Ag2 (from terminal [Ag(CN) 2] – ions), and each Ag2 is conjujated by two Ag1 from two different chains in adjacent layers by argentophilic interactions (Ag1"Ag2 distance of 3.2322 Å). These Ag^{**}Ag interactions join the chains to form 3D infinite network. The $\mathsf{compound^{47}\left[Cu_{2}(bn)_{2}\{Ag(CN)_{2}\}_{4}{(NH_{3})}\right]}$ 2H $_{2}$ O, contains two crystallographically different copper atoms, Cu1 and Cu2 in which copper atom (Cu1) is penta-coordinated with distorted trigonal bypyramidal geometry and another copper atom (Cu2) is hexacoordinated with elongated tetragonal bypyramidal geometry and both the copper atoms (Cu1 and Cu2) are coordinated to three dicyanoargentate anions. The Cu1 atom is coordinated with two monodentate dicyanoargentate anions and one bridging dycyanoargentate anion in equatorial plane and the axitial positions are coordinated to two bridging 1,4-diaminobutane ligands which connect the adjacent Cu1 atoms to generate infinite chain parallel to [100] and the bridging dycyanoargentate anion in equatorial plane connect the atom Cu2. Where as in case of Cu2 atom all the three dycyanoargentate anions and two diaminobutane ligands are bridging. The equitorial plane of Cu2 atom is occupied by two bridging dycyanoargentate anions and two bridging diaminobutane ligands and two axial positions are occupied by ammonia ligand and another bridging dicyanoargentate ligand which link adjacent Cu1 atom. Again the two bridging 1,4-diaminobutane ligands connect the adjacent Cu2 atoms which is parallel to Cu1 chain containing. The Cu2 atoms of two adjacent chains are linked through two bridging dicyanoargentate ions to generate a chain in a plane parallel to [001]. As one bridging dicyanoargentate anions links Cu1 and Cu2 atoms.

So Cu2 atoms lie down in a plane parallel to [010] which is created by a chain parallel to [100] and [001] plane and the bridging dicyanoargentate ions which connect the two Cu atoms (Cu1 and Cu2) are hang from the [010] plane. Therefore the structure is a unique combination of 1D chain with 2D plane where both the one- and two-dimensional structure form one layer. Again it forms a three-dimensional network through Ag"Ag interaction (3.1152 Å). The argentophilic interactions connect the upper layer which is a Cu1-containing chain with the neighbouring lower layer which is Cu2–containing plane and thereby forming a three-dimensional network (Fig. 4). In compound¹⁷ [{Cu(app)MeOH)} (μ-[Ag(CN)₂]}{(Cu(app)[Ag(CN)]₂}], each copper(II) atom is pentacoordinated with square-pyramidal shape and two {Cu(app)} units are connected by cyanide groups of bridgind $[\text{Ag(CN)}_2]^-$ ligand in equitotial position. It forms a 1D chain through argentophilic interaction (Ag"Ag distance is 3.0563 Å) with monocoordinated [Ag(CN) $_2$]⁻ ligand in equatorial position to the next unit (Figure 5).

Fig. 4. Three-dimensional structure of complex $\left[\mathsf{Cu}_{\text{2}}\text{(bn)}_{\text{2}}\right\{\mathsf{Ag}(\mathsf{CN})_{\text{2}}\}_{\text{4}}\text{(NH}_{\text{3}}\right]\cdot\mathsf{2H}_{\text{2}}\mathsf{O}$ through Ag \cdots Ag **interactions. It is a combination of one dimensional chain and two dimensional layer47**

Fig. 5. One-dimensional structure of complex {[Cu(app) (MeOH)][Cu(app)][Ag(CN)₂]₂} through argrntophilic interactions¹⁷

Conclusion

This review presented a brief structural features of 3d-transition metal coordination compounds blocked by some blocking ligands like 1,2 diaminoethane, 1,3 diaminopropane, 2,2'-bipyridine, imidazole, Schiff base etc. in which dicyanoargentate anion acts as monodentate ligand. The main aim of this survey is to converse the different types of structural aspect of 3d-transition metal coordination compounds blocked by some blocking ligands where dicyanoargentate anion acts as monodentate ligand. Another aim of this review is to demonstrate the formation of different dimensionality complexes through Ag"Ag interactions when dicyanoargentate anion act as monodentate ligand. Different types of 3d-transition metal coordination compounds in which dicyanoargentate anions act as monodentatelig and that have been reported and structurally characterized, reviewed in this context. As already mentioned that the nitrogen atom of dicyanoargentite ion can form hydrogen bond with suitable hydrogen donor atom and it can also form Ag**Ag bond (argentophilic interactions) and structural dimensionality can also be increased effectively through hydrogen bonded and Ag"Ag interactions. Herein the increased structural dimensionality through hydrogen bonding and argentophilic interactions and the coexistence of both bridging and monodentate behaviour of dicyanoargentate ligand have also been reviewed. It has to be mentioned that a number of review article have been published on different coordination mode of cyanometallates^{1−5} but monodentate behavior of dicyanocyanoargentate ligand has not been reviewed yet. This Current wide effort dedicated to the structural characterization of monodentate dicyanoargentate-3d transition metal coordination compounds in which the transition metal ion is blocked by different blocking ligands, confirms that the chemistry of monodentate dicyanoargentate-3d transition metal compounds represents a rising field of attention in crystal engineering and supramolicular chemistry. Therefore it has been expected that with a lucid designe, more atypical monodentate dicyanoargentate-3d transition metal coordination compounds of different structural designs with different blocking ligands will be possible that can also have potential applications.

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Conflict of Interest

The author declares that no conflict of interest to disclose.

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