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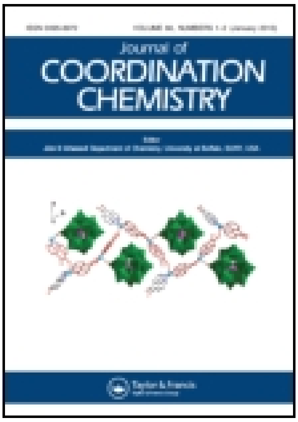

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Formation of a mixed valence copper(II)-copper(I) coordination polymer $\{[Cu(1,2\text{-}pn)_2(\mu_3\text{-}I)Cu_2(\mu_2\text{-}I)_3(CH_3CN)]\cdot CH_3CN\}_n$: in situ reduction of copper(II) at ambient condition

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Formation of a mixed valence copper(II)–copper(I) coordination polymer $\{[Cu(1,2\text{-}pn)_2(\mu_3\text{-}I)Cu_2(\mu_2\text{-}I)_3(CH_3CN)]\cdot CH_3CN\}_n$: *in situ* reduction of copper(II) at ambient condition

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A mixed valence copper(II)–copper(I) coordination polymer has been synthesized starting from a copper(II) salt at ambient condition and characterized by IR and Raman spectra and single crystal X-ray diffraction. The structure of the complex consists of a 1-D infinite chain with repeating unit $[Cu(1,2\text{-}pn)_2(\mu_3\text{-}I)Cu_2(\mu_2\text{-}I)_3(CH_3CN)]$ and a free CH_3CN, where 1,2-pn = 1,2-diamino-1-propene. The complex shows a very short copper(I)–copper(I) distance (2.412 Å).

Keywords: Copper(II); Copper(I); μ_3-I; Crystal structure; Coordination polymer

1. Introduction

Metal-organic frameworks (MOFs) have attracted attention due to its applications in electrical conductivity, magnetism, photochemistry, sorption, and catalysis [1]. Introduction of metal clusters into MOF systems to investigate structural versatility [2] and potential applications in biological systems, in catalysis, and in optical-electronic functional materials [3] are promising areas of research. There are some reports of MOFs which bear copper clusters as connecting nodes [4], but reports on polymers built by mixed-valence copper(I)–copper(II) clusters are limited [5]. Thus, synthesis of polymers with mixed-valence copper (I)–copper(II) clusters is still a challenge for inorganic chemists. Chemistry of mixed valence copper(I)–copper(II) complexes is also significant to understand the behavior of various multi-copper enzymes such as ascorbate oxidase [6]. Stereochemistry of copper(II) and copper(I) centers is different and both the oxidation states are labile. Thus, structural changes in metallo-enzymes occurring during electron transfer between mixed valence copper centers can be studied using multinuclear copper(I)–copper(II) model complexes.

The reaction of copper(I) halides with halides usually produces halogenocuprates(I) (e.g. $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_2X_3]^{2-}$, $[Cu_4X_6]^{2-}$, etc.) which may contain μ_2-, μ_3-, or μ_4-bridging X. These polynuclear copper(I) complexes have attracted considerable attention for diverse structures, photoluminescent properties, and potential applications in materials science [7].

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The ability of copper(I) to attain both trigonal planar and tetrahedral geometries is primarily responsible for the structural diversity of halogenocuprates(I), $[Cu_pX_q]^{(q-p)-}$. Face-sharing was long considered unlikely for MX_4 tetrahedra, since their centers would be very close. But, in addition to corner- and edge-sharing of tetrahedra, the face-sharing of tetrahedra is also possible for halogenocuprates(I) [8]. Iodocuprates(I) with face-sharing bi-tetrahedra are considered as a special, though not uncommon, feature of the structural chemistry of iodocuprates(I) [8]. Two, three, and five face-sharing CuI_4 tetrahedra are known, as well as endless chains of face-sharing tetrahedra [9]. The simplest of these is $[Cu_2(\mu_2\text{-}I)_3]^-$ which has already been characterized [10]. There is no report regarding the use of this unit to prepare mixed valence copper(II)–copper(I) complexes. Iodide usually acts as reducing agent and may cause reduction of copper(II) to copper(I), affording mixed valence copper(II)–copper (I) species [11]. Such *in situ* copper(II)→copper(I) reduction is common when copper(II) complexes along with I^- are subjected to solvothermal reactions at elevated temperature and pressure [12], but is unusual at ambient temperature and pressure.

Herein, we report synthesis and characterization of a mixed valence 1-D copper(II)–copper(I) complex, $\{[Cu(1,2\text{-pn})_2(\mu_3\text{-}I)Cu_2(\mu_2\text{-}I)_3(CH_3CN)]\cdot CH_3CN\}_n$ [1,2-pn = 1,2-diamino-1-propene], where I^- influences *in situ* partial copper(II)→copper(I) reduction to form $[Cu_2(\mu_2\text{-}I)_3I]^{2-}$ clusters, which are then used to bridge two $[Cu(1,2\text{-pn})_2]^{2+}$ units through a μ_3-I.

2. Experimental

Potassium iodide and 1,2-diaminopropane of reagent grade were purchased from Merck and used without purification.

2.1. *Preparation of $\{[Cu(1,2\text{-pn})_2(\mu_3\text{-}I)Cu_2(\mu_2\text{-}I)_3(CH_3CN)]\cdot CH_3CN\}_n$*

An acetonitrile solution (10 mL) of 1,2-diaminopropane (1 mM, 0.085 ml) was added to an acetonitrile solution (10 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mM, 0.370 g) and the solution was stirred for 10 min. A water solution (2 mL) of KI (2 mM, 0.332 g) was added and the mixture was stirred for an additional hour. Diffraction quality single crystals were obtained by slow diffusion of diethyl ether into the mother liquor for two days. The complex was characterized by elemental analysis and spectroscopic methods. Single crystal X–ray diffraction confirmed the structure of the complex. Yield: 0.38 g (41%). Anal. Calcd for $C_{10}H_{26}Cu_3I_4N_6$ (928.62): C, 12.93; H, 2.82; N, 9.05. Found: C, 13.1; H, 3.0; N, 8.9. IR (KBr, cm^{-1}): 3283 ($\upsilon_{N\text{–}H}$); magnetic moment: 1.72 BM.

2.2. *Physical measurements*

Elemental analyses (carbon, hydrogen, and nitrogen) were carried out using a Perkin–Elmer 2400II elemental analyzer. IR spectrum in KBr (4000–400 cm^{-1}) was recorded using a Perkin–Elmer RXI FTIR spectrophotometer. Electronic spectrum in acetonitrile (800–200 nm) was recorded in a Perkin–Elmer Lambda – 25 UV–Visible Spectrometer at 298 K. Raman spectrum was obtained using a Renishaw InVia Reflex micro-Raman spectrometer with excitation of argon ion (514 nm) lasers. The laser power was kept sufficiently low to avoid heating of the samples and spectra were collected with a resolution of 1 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB 250 high performance electron spectrometer using a monochromated Al Kα excitation source ($h\nu = 1486.6$ eV). The magnetic susceptibility measurement was done with an EG&PAR vibrating sample magnetometer, model 155, at room temperature; diamagnetic corrections were made using Pascal's constants.

2.3. *X-ray crystallography*

Single crystals having suitable dimensions were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 K. The molecular structures were solved by direct methods and refinement by full-matrix least-squares on F^2 using the SHELX-97 package [13]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed in their geometrically idealized positions and constrained to ride on their parent. Multi-scan empirical absorption corrections were applied to the data using SADABS [14]. A summary of the crystallographic data is given in table 1 (CCDC reference number 924090).

3. Results and discussion

3.1. *Synthesis*

Addition of 1 mM 1,2-diaminopropane to 1 mM copper(II) solution converts half of the copper(II) into [Cu(1,2-diaminopropane)$_2$]$^{2+}$. The reaction is carried out in air and at room temperature. It is very interesting to note that the 1,2-diaminopropane is oxidized to 1,2-diamino-1-propene (1,2-pn) in this stage of the reaction and this oxidative dehydrogenation is probably catalyzed by copper(II). Oxidative dehydrogenation of diamine ligands coordinated to several transition metals is reported in the literature [15]. The metal coordinated

Table 1. Crystal data and refinement details of complex.

Formula	$C_{10}H_{22}Cu_3I_4N_6$
Formula weight	924.59
Temperature (K)	150
Crystal system	Triclinic
Space group	*P-1*
a (Å)	8.9022(2)
b (Å)	11.1739(3)
c (Å)	12.4595(4)
α (°)	99.462(1)
β (°)	90.443(1)
γ (°)	93.112(2)
Z	2
d_{Calcd} (g cm^{-3})	2.516
μ (mm^{-1})	7.653
F (0 0 0)	846
Total reflections	18,549
Unique reflections	5058
Observed data [$I > 2\sigma(I)$]	4157
No. of parameters	213
R (int)	0.0332
$R1$, w$R2$ (all data)	0.0441, 0.0743
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.0332, 0.0664

amine (or diamine) is oxidized by O_2 to form α-imine (or α-di-imine) [15]. However, use of copper(II) in oxidative dehydrogenation was not reported before the present work. In our case, 1,2-diaminopropane coordinated to copper(II) is oxidized by oxygen to an α-imine. The methyl group probably restricts the formation of an α-di-imine. This α-imine may easily then be rearranged to form the 1,2-diamino-1-propene. Addition of excess KI then reduces the remaining free copper(II) in solution into copper(I) in the form of face sharing bi-tetrahedral $Cu_2I_4^{2-}$, which is used to bridge to two $[Cu(1,2\text{-pn})_2]^{2+}$ using a μ_3-I to form a 1-D chain.

3.2. *Description of structure*

The complex crystallizes in triclinic space group *P-1*. The crystal structure of the complex is shown in figure 1. The asymmetric unit contains one $[Cu(1,2\text{-pn})_2(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]$ and a solvent acetonitrile. The structure of the complex consists of a 1-D infinite chain system with the repeating unit $[Cu(1,2\text{-pn})_2(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]$. In $[(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]^{2-}$, both copper(I) centers have face-sharing tetrahedral geometry (figure 2) with two copper(I) centers bridged by three μ_2-I ions. One copper(I) in this dimeric unit, Cu(4), is terminally coordinated by nitrogen of solvent acetonitrile, whereas

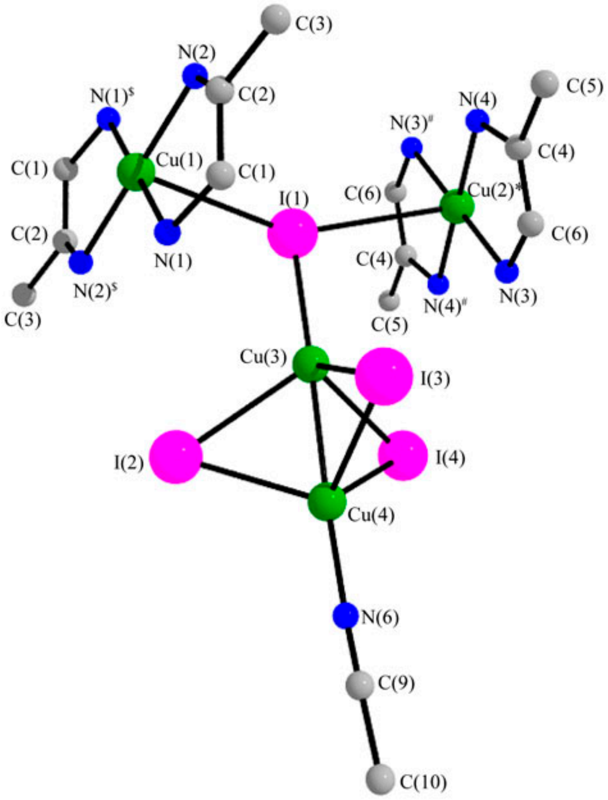

Figure 1. Perspective view of the complex. Hydrogen atoms and lattice solvent molecule are not shown for clarity.

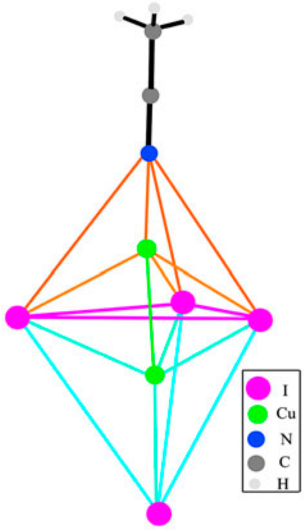

Figure 2. Perspective view of $[(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]^{2-}$.

the second one, Cu(3), is coordinated by a μ_3-I^- to complete the tetrahedral structure. This μ_3-I^- actually bridges the anionic $[Cu_2(\mu_2\text{-I})_3(CH_3CN)]^-$ unit with two cationic $[Cu(1,2\text{-pn})_2]^{2+}$ units to form the 1-D polymer, $\{[Cu(1,2\text{-pn})_2(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]\}_n$ (figure 3). The coordination polyhedron around copper(II) is best described as a distorted octahedron. Four nitrogen atoms from two 1,2-pn groups equatorially coordinate to copper(II) and two iodides, I(1) and I(1)*, coordinate axially at rather long distances to form a tetragonally distorted octahedron, a direct consequence of the Jahn–Teller effect for six-coordinate copper(II). Copper(II) does not deviate from the equatorial plane formed by amine nitrogen atoms. Details about the bond lengths and angles are given in table 2.

Cu(I)–Cu(I) bond distance in the $[(\mu_3\text{-I})Cu_2(\mu_2\text{-I})_3(CH_3CN)]^{2-}$ unit is 2.412 Å, much smaller than the sum of the van der Waals radii (2.80 Å), indicating copper–copper bond formation [16]. The attractive interactions between closed-shell d^{10} metal ions have already received great attention because they play an important role in the structural, optical, and electronic properties of poly-nuclear complexes [17]. This behavior has been frequently observed in Au, with the term “aurophilicity” being coined to describe Au(I)–Au(I) interactions [18]. The occurrence of analogous metallophilic effects has been found even in lighter Cu. Cu(I)–Cu(I) interaction, viz. cuprophilicity is associated with structure-controlling factors, such as ligand bridging, hydrogen bonding, electrostatic interaction, etc. [19]. Cuprophilicity has been the subject of a long debate due to the intramolecular character of the reported interactions [20]. Thus, the present work may or may not be an example of cuprophilicity, but it is obvious that the Cu(I)–Cu(I) bond observed in the title complex is among the shortest known. We have compared it to other very short Cu(I)–Cu(I) distances in other face-sharing Cu_2I_3 moieties (table 3).

3.3. *IR, Raman, electronic and XPS spectra*

The infrared spectrum of the complex shows absorption bands at 3444 and 3278 cm^{-1} assigned to NH_2 stretching (figure 4(a)). The band corresponding to C–H stretching occurs

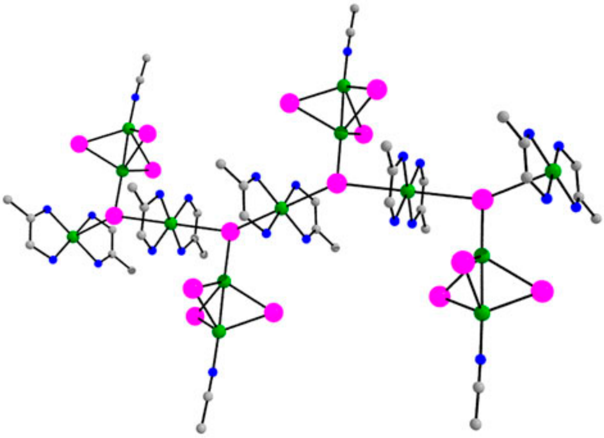

Figure 3. Perspective view of one-dimensional chain of the complex.

Table 2. Selected bond lengths (Å) and angles (°) of the complex.

I(1)–Cu(1)[b]	3.231(4)	I(1)–Cu(3)	2.515(1)
I(1)–Cu(2)[b]	3.221(4)	I(2)–Cu(3)	2.734(1)
I(2)–Cu(4)	2.709(1)	I(3)–Cu(3)	2.771(1)
I(3)–Cu(4)	2.671(1)	I(4)–Cu(3)	2.748(1)
I(4)–Cu(4)	2.818(1)	Cu(1)–N(4)	2.007(5)
Cu(1)–N(5)	2.016(4)	Cu(1)–N(4)[c]	2.007(5)
Cu(1)–N(5)[c]	2.016(4)	Cu(2)–N(2)	2.016(4)
Cu(2)–N(3)	2.001(5)	Cu(2)–N(2)[d]	2.016(4)
Cu(2)–N(3)[d]	2.001(5)	Cu(4)–N(1)	1.913(6)
Cu(1)[b]–I(1)–Cu(3)	99.16(3)	N(2)–Cu(2)–N(3)[d]	95.8(2)
Cu(1)[b]–I(1)–Cu(2)[b]	149.83(2)	I(1)[f]–Cu(2)–N(2)	88.50(14)
Cu(2)[b]–I(1)–Cu(3)	99.67(3)	I(1)[a]–Cu(2)–N(3)	89.00(14)
Cu(3)–I(2)–Cu(4)	52.64(3)	N(2)[d]–Cu(2)–N(3)	95.8(2)
Cu(3)–I(3)–Cu(4)	52.63(3)	I(1)[f]–Cu(2)–N(3)	91.00(14)
Cu(3)–I(4)–Cu(4)	51.39(3)	I(1)[a]–Cu(2)–N(2)[d]	88.50(14)
N(4)–Cu(1)–N(5)	95.70(18)	I(1)[a]–Cu(2)–N(3)[d]	90.00(14)
I(1)[a]–Cu(1)–N(4)	89.83(14)	N(2)[d]–Cu(2)–N(3)[d]	84.2(2)
N(4)–Cu(1)–N(5)[c]	84.30(18)	I(1)[f]–Cu(2)–N(2)[d]	91.50(14)
I(1)[e]–Cu(1)–N(4)	90.17(14)	I(1)[f]–Cu(2)–N(3)[d]	89.00(14)
I(1)[a]–Cu(1)–N(5)	90.92(14)	I(1)–Cu(3)–I(2)	116.00(4)
N(4)[c]–Cu(1)–N(5)	84.30(18)	I(1)–Cu(3)–I(3)	117.06(4)
I(1)[e]–Cu(1)–N(5)	89.08(14)	I(1)–Cu(3)–I(4)	116.53(4)
I(1)[a]–Cu(1)–N(4)[c]	90.17(14)	I(2)–Cu(3)–I(3)	102.82(4)
I(1)[a]–Cu(1)–N(5)[c]	89.08(14)	I(2)–Cu(3)–I(4)	101.03(3)
N(4)[c]–Cu(1)–N(5)[c]	95.70(18)	I(3)–Cu(3)–I(4)	100.88(3)
I(1)[e]–Cu(1)–N(4)[c]	89.83(14)	I(2)–Cu(4)–I(3)	106.23(4)
I(1)[e]–Cu(1)–N(5)[c]	90.92(14)	I(2)–Cu(4)–I(4)	99.86(4)
N(2)–Cu(2)–N(3)	84.2(2)	I(2)–Cu(4)–N(1)	116.78(19)
I(1)[a]–Cu(2)–N(2)	91.50(14)	I(3)–Cu(4)–I(4)	101.61(4)
I(4)–Cu(4)–N(1)	113.22(18)	I(3)–Cu(4)–N(1)	116.81(19)

[a] $x, -1 + y, z$.
[b] $x, 1 + y, z$.
[c] $1 - x, -y, -z$.
[d] $1 - x, -y, 1 - z$.
[e] $1 - x, 1 - y, -z$.
[f] $1 - x, 1 - y, 1 - z$.

Table 3. Selected Cu(I)–Cu(I) distances (Å) in Cu_2I_3 moieties in some reported complexes.

Complexes	Shortest Cu(I)–Cu(I) distance	Ref.
$\{[Cu(1,2\text{-}pn)_2(\mu_3\text{-}I)Cu_2I_3(CH_3CN)]\}_n$	2.414(1)	This work
$[{}^iPr_2EtNH]_n[Cu_2I_3]_n$ (${}^iPr$ = diisopropylethylamine)	2.490(3)	[21]
$[Na(C_{10}H_{20}O_5)]_2$ $[Na(C_{10}H_{20}O_5)$ $(H_2O)]_2$ $[Cu_2I_4]$ $[Cu_4I_6]$	2.472(4)	[22]
$(C_8H_{20}N)[Cu_2I_3]$	2.467(3)	[23]
$[Cs(C_{10}H_{20}O_5)][Cu_2I_3]$	2.430(9)	[24]
$[K(C_{10}H_{20}O_5)][Cu_2I_3]$	2.448(7)	[24]
$[N(CH_3)_4][Cu_2I_3]$	2.458	[25]

at 2923 cm^{-1}. Raman spectrum of the complex shows a band at 3073 cm^{-1} due to NH_2 stretching. The bands corresponding to C–H stretching and bending occur at 2923 and 1539 cm^{-1}, respectively (figure 4(b)). The UV–Vis spectrum of the complex in acetonitrile shows two absorptions at 292 and 362 nm and these are assigned as metal to ligand charge transfer. The tail of the band at 362 nm falls in the visible region and is responsible for the pale yellow color of the complex in acetonitrile solution. The complex does not show any fluorescence on exciting at 292 and 362 nm. The presence of mixed copper oxidation states may lead to non-radiative relaxation and no fluorescence observed.

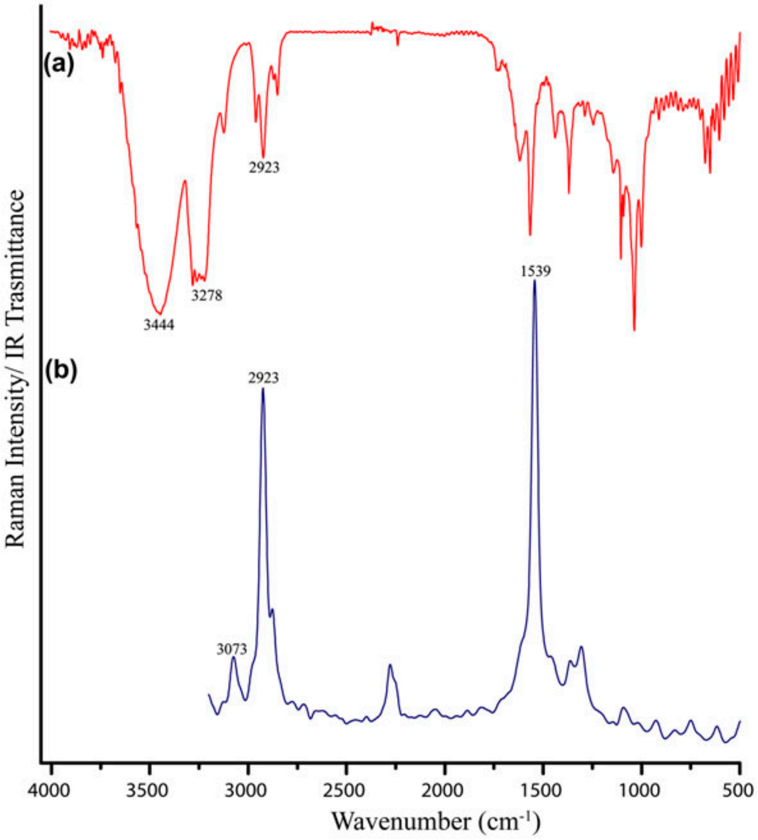

Figure 4. (a) IR and (b) Raman spectra of the complex.

The oxidation states of copper ions are confirmed by XPS. The XPS spectrum of the bulk sample shows the peaks of copper $^2P_{3/2}$ and $^2P_{1/2}$ at 932.7 and 952.6 eV, respectively, which supports the presence of copper(I) in the complex. The middle intense satellite peaks at 944.5 and 963.4 eV indicate the presence of copper(II) [26–28].

4. Conclusion

An unusual mixed-valent 1-D copper(II)–copper(I) complex containing tetraiododicuprate(I) dianion as a bridging ligand have been synthesized using $Cu(ClO_4)_2$ and 1,2-diaminopropane and potassium iodide at room temperature. The copper(I) of $Cu_2I_4^{2-}$ is the *in situ* reduction product of copper(II) assisted by I^-. Oxidative dehydrogenation of 1,2-diaminopropane coordinated to copper(II) into 1,2-diamino-1-propene is also observed for the first time. $Cu_2I_4^{2-}$ is a bridging ligand between two copper(II) centers generating the very rare 1-D mixed valence complex $\{[Cu(1,2\text{-pn})_2(\mu_3\text{-I})Cu_2I_3(CH_3CN)]\cdot CH_3CN\}_n$. There is no example of using CuI_4^{2-} to bridge between two copper(II) centers to prepare a mixed valence copper(II)–copper(I) complex. Thus, the method opens up the possibilities of forming this type of mixed valence complexes.

Thiocyanato-bridged mixed valence copper(II)–copper(I) coordination polymer is already reported in literature [29]. So, the iodide can be replaced by several pseudo-halides to prepare mixed valence copper(II)–copper(I) complexes.

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