

Direct Electrochemical Synthesis and Characterization of Coordination Compounds of Copper(II) Chloride: Part - II

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Abstract: Coordination compounds of $\text{CuCl}_2 \cdot \text{L}$ (where $\text{L} = 1,10\text{-phenanthroline}$ or $2,2'\text{-bipyridyl}$) have been synthesized by electrolyzing the aqueous solution of hydrochloric acid and ligand at sacrificial copper anode and inert platinum cathode. The products isolated have been characterized by elemental analysis, infrared spectral data and x – ray crystallography. Current efficiencies of both these reactions are found to be quite high.

Keywords: Electrochemical synthesis, 1,10-Phenanthroline, 2,2'-Bipyridyl, Copper(II) chloride, Coordination compounds

Introduction

Electrochemical technique has been used as an integral tool for the synthesis of a variety of organic¹⁻⁶, inorganic⁷⁻¹⁰ and nanoparticles^{11,12}. The important advantages of this technique include single step reactions, direct route, high product yield and cheap starting material. In continuation to our interest in synthetic inorganic chemistry¹³⁻¹⁷, we report in this communication the electrochemical synthesis of the coordination compounds of the copper(II) chloride.

Experimental

Water was purified by adding potassium permanganate and a pellet of potassium hydroxide and then was fractionally distilled. Rectified spirit was fractionally distilled. 1:1 mixture of conductivity water and rectified spirit was used as solvent in both these reactions. Other organic compounds were used as procured.

Procedure and technique

Electrolysis of solution of conductivity water - rectified spirit mix solvent (1:1) containing 2 mL of hydrochloric acid and 0.5 g of ligand (1,10-phenanthroline or 2,2'-bipyridyl) have been conducted at sacrificial copper anode ($2.0 \times 10 \times 0.2 \text{ cm}^3$) and inert platinum ($1 \times 1 \text{ cm}^2$) cathode in H – type pyrex glass cell. Potential across the electrodes was adjusted so that a current of 15 mA passed through the solution. Potassium chloride was used as supporting electrolyte in both these reactions. The electrolytic solution was stirred efficiently using magnetic stirrer. The electrolytic cell can be represented as:



Where $\text{Cu}_{(+)}$ and $\text{Pt}_{(-)}$ represent sacrificial copper anode and platinum cathode respectively and L represents 1,10-phenanthroline or 2,2'-bipyridyl. After electrolysis for three hours, reaction mixture from anode compartment was concentrated and was kept for a day. The coloured crystals were isolated.

Elemental analysis of C, H and N were performed on elemental vario MICRO cube analyser. Copper contents in the products were determined volumetrically¹⁸. Infrared spectra were recorded as potassium bromide pellets on Perkin – Elmer spectrophotometer (RXI) in the region of 4000 - 450 cm^{-1} . The relevant analytical data are given in Table 1.

Table 1. Electrochemical characteristics, analytical data, current efficiencies and other related data of electrolytic products of hydrochloric acid + ligand systems at copper anode. [Potential : 30 V, current in coulombs : 162]

System	Product	Colour	Elemental analysis Found (Calcd.) %				Current efficiency (gram equivalent Faraday ⁻¹)
			Cu	C	H	N	
Hydrochloric acid +1,10-phenanthroline	CuCl_2 ($\text{C}_{12}\text{H}_8\text{N}_2$)	green	19.7 (20.1)	45.8 (45.8)	2.5 (2.5)	8.7 (8.8)	0.92
Hydrochloric acid +2,2'-bipyridyl	CuCl_2 ($\text{C}_{10}\text{H}_8\text{N}_2$)	blue	20.8 (21.8)	41.2 (41.3)	2.5 (2.7)	8.9 (9.6)	0.93

Single crystal of $[\text{CuCl}_2\text{C}_{10}\text{H}_8\text{N}_2]$ with approximate dimensions of 0.18 x 0.09 x 0.06 mm^3 was mounted on a glass fiber and data were collected at 100(2) K on a “Bruker SMART APEX” CCD diffractometer using graphite monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography¹⁹. The data integration and reduction were carried out with SAINT²⁰ software. Empirical absorption correction was applied to the collected reflections with SADABS²¹ and the space group was determined using XPREP²². The structure was solved by the direct methods using SHELXL-97²³ and refined on F^2 by full-matrix least-squares using the SHELXL-97 program package²⁴. All non-hydrogen atoms were refined anisotropically. In order to refine H atoms, these atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. A summary of crystal data, experimental details and refinement result are listed in Table 2. Atomic coordinates of non-hydrogen atoms are given in Table 3. Efforts have done to collect the single crystal x- ray data of $[\text{CuCl}_2\text{C}_{12}\text{H}_8\text{N}_2]$, but these crystals do not diffract.

Results and Discussion

The selected bond lengths and angles are listed in Table 4. The x-ray data analysis reveals that $[\text{Cu}(\text{bipy})\text{Cl}_2]$ unit exist as polymer (Figure 1) in which central copper ion is coordinated to both nitrogen donors from bidentate 2,2'-bipyridine ligand forming five membered chelating ring and Cu – N bond length are 2.026(7) and 2.032(6) \AA . Each copper ion is covalently bonded to two chlorine anions and the central copper ion forms two four membered rings through chlorine bridging thus can be described as distorted octahedral. The bond lengths of Cu – Cl are 2.273(2) and 2.65(2) \AA . The important bond lengths and bond angles are listed in Table 4.

Table 2. Crystal data and structure refinement for CuCl₂.C₁₀H₈N₂

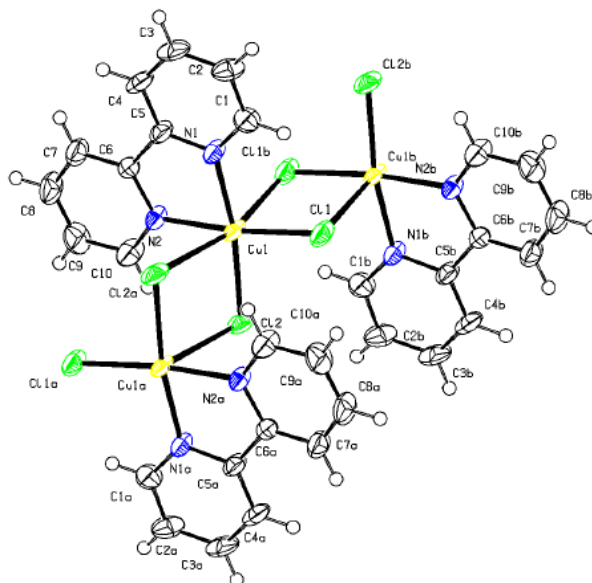
Formula weight	290.62	
Temperature	100(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.255(4) Å b = 8.992(3) Å c = 9.530(5) Å	$\alpha = 115.719(2)^\circ$ $\beta = 108.199(3)^\circ$ $\gamma = 94.142(5)^\circ$
Volume	516.2(5) Å ³	
Z	2	
Density (calculated)	1.870 g/cm ³	
Absorption coefficient	2.594 mm ⁻¹	
F(000)	290	
Crystal size	0.18 x 0.09 x 0.06 mm ³	
Theta range for data collection	2.57 to 26.00°	
Index ranges	-8<= <i>h</i> <=8, -11<= <i>k</i> <=10, -10<= <i>l</i> <=11	
Reflections collected	2731	
Independent reflections	1950 [R(int) = 0.0607]	
Completeness to theta = 26.00°	96.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8599 and 0.6524	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1950 / 0 / 136	
Goodness-of-fit on F ²	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.1040, wR2 = 0.2508	
R indices (all data)	R1 = 0.1189, wR2 = 0.2835	
Largest diff. peak and hole	1.701 and -2.308 e.Å ⁻³	

Table 3. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for CuCl₂.C₁₀H₈N₂. (U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor)

Atom	x	y	z	U(eq)
Cu(1)	7623(1)	688(1)	10(1)	30(1)
Cu(2)	5441(3)	-1897(3)	-1699(3)	40(1)
Cu(1)	9529(3)	-213(3)	1735(3)	40(1)
N(1)	9156(11)	3155(9)	1522(8)	30(2)
N(2)	6189(10)	1708(8)	1424(8)	27(1)
C(4)	9212(14)	5968(11)	1964(12)	44(2)
C(6)	6829(11)	3440(10)	-708(10)	28(2)
C(2)	11524(14)	5519(12)	4069(11)	43(2)
C(7)	6058(14)	4303(13)	-1529(13)	40(2)
C(8)	4571(14)	3430(13)	-3107(11)	46(2)
C(10)	4736(15)	884(12)	-2940(11)	41(2)
C(9)	3890(15)	1727(15)	-3829(12)	50(2)
C(5)	8454(13)	4241(10)	976(11)	32(2)
C(1)	10686(13)	3809(12)	3042(11)	40(2)
C(3)	10769(15)	6627(12)	3545(13)	47(2)

Table 4. Bond lengths [\AA] and angles [$^\circ$] for $\text{CuCl}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$

Cu(1)-N(1)	2.026(7)	Cu(1)-Cl(2)	2.265(2)
Cu(1)-N(2)	2.032(6)	Cu(1)-Cl(1)	2.273(2)
N(1)-Cu(1)-N(2)	80.4(3)	N(2)-Cu(1)-Cl(2)	93.3(2)
N(1)-Cu(1)-Cl(2)	170.3(2)	N(1)-Cu(1)-Cl(1)	93.9(2)
N(2)-Cu(1)-Cl(1)	173.6(2)	Cl(2)-Cu(1)-Cl(1)	92.71(9)

**Figure 1.** A perspective view of structure of $\text{CuCl}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$

Both these products were soluble in acetonitrile, *N,N*-dimethyl formamide, dimethyl sulphoxide and acetone. Melting point determination of both the products shows that these products do not melt up to 300°C , but decompose in temperature range of $150 - 250^\circ\text{C}$. The decomposition of these products is indicated from the change in colour of the compounds in this temperature range. Elemental analysis data (Table 1) of both these products corresponds to 1:2:1 stoichiometry of copper, chlorine and ligand.

Infrared spectra of both these products have been recorded in the region of $4000 - 450\text{ cm}^{-1}$. Examination of infrared data shows that the electrochemical products exhibit multiple bands in the regions of $1653 - 1057\text{ cm}^{-1}$ and $854 - 720\text{ cm}^{-1}$. Literature reveals that bands due to $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ bands and $\delta(\text{C}-\text{H})$, ring deformation bands of 1,10-phenanthroline and 2,2'-bipyridyl^{25,26} are present in the region of $1620 - 1217\text{ cm}^{-1}$, $849 - 733\text{ cm}^{-1}$ and $1665 - 1065\text{ cm}^{-1}$, $755 - 740\text{ cm}^{-1}$ respectively. Multiple bands appearing in the region of $1653 - 1057\text{ cm}^{-1}$ in the present products thus can be assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ stretching vibrations and also $\delta(\text{C}-\text{H})$ mode and those in the region of $854 - 720\text{ cm}^{-1}$ can be assigned to ring deforming vibrations of the ligand molecules.

The infrared data thus supports the analytical data and confirm the attachment of ligand molecules to the electrochemical products of the present systems. Current efficiencies of both the systems have been determined, which was found to be very high. High current efficiencies of these systems indicate that reactions leading to the formation of coordination compounds of copper(II) chlorides are the predominant reactions of these systems.

Conclusion

The electrochemical technique thus provides a direct route for the synthesis of anhydrous coordination compounds of copper(II) chloride, which otherwise involve multi-step process when prepared through traditional synthetic methods. In addition, the present method is single – pot, single step to carry out synthesis by using routine laboratory chemicals, apparatus and metals as reagent at room temperature.

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References

1. Kim Tae-Hun and Park Su Moon, *Electrochimica Acta*, 2005, **50**, 1461-1467.
2. Rehan H A, *Polym Int.*, 2003, **52**, 218 - 224.
3. Tsuchiya Youichi and Fujihara Hisashi, *Electrochem.*, 2002, **70**, 584 - 586.
4. Wadhawan Jay D, Marken Frank, Compton Richard G, Bull Steve D and Devis Stephen G, *Chem Commun.*, 2001, 87- 88.
5. Lyalin B V and Petrosyan V A, *Russian J Electrochem.*, 2013, **49(6)**, 497-529.
6. Senboku H, Takahasi M, Fukuhara T and Hara S, *Chem Lett.*, 2007, **36**, 228-229.
7. Padraes Antonio Sousa, Romero J, Garcia Vazquez Jose A, Duran M L, Casanova I and Sousa A, *Dalton Trans.*, 2003, 1379-1388.
8. Tripathi V S, Bairwa K K, Mal D and Naik D B, *J Electrochem Soc.*, 2014, **161(3)**, E34-E39.
9. Yuan Y, Yao J, Lin C, Zhang Y and Gu R, *Synth React Inorg Met Org Nanometal Chem.*, 2005, **35**, 385-390.
10. Yakhvarov D G, Ganushevich YU, Dobrynin A B, Kryvolapov D B, Litvinov I A and Sinyashin D G, *Russ J Electrochem.*, 2009, **45(2)**, 139-144.
11. Ledesma-Garcia J, Arriaga L G, Chapman T W, Velazquez-Castillo R and Godinez L A, *J Electrochem Soc.*, 2010, **157**, E1-E5.
12. Singh Dinesh Pratap and Srivastava Onkar Nath, *J Nanoscience Nanotech.*, 2009, **9**, 5515-5522.
13. Banait J S, Singh Baljit and Kaur Harpreet, *J Indian Chem Soc.*, 2011, **88**, 641-646.
14. Banait J S, Singh Baljit and Kaur Harpreet, *J Indian Chem Soc.*, 2010, **87**, 261-264.
15. Kaur Harpreet, Banait J S and Singh Baljit, *Asian J Chem.*, 2010, **3**, 1073-1076.
16. Banait J S, Singh Baljit and Kaur Harpreet, *Port Electrochim Acta*, 2007, **25**, 435-442.
17. Kaur Harpreet and Kaur Amandeep, *J Indian Chem Soc.*, 2013, **90**, 685.
18. Vogel's "Text Book of Quantitative Chemical Analysis", 5th Edition, Longman group UK, Ltd., 1989, 393-394.
19. International Tables for X-Ray Crystallography, Kynoch Press, Vol. III, Birmingham, England, 1952.
20. SAINT, version 6.02, Bruker AXS, Madison, WI, 1999.
21. Sheldrick, GM SADABS: Empirical Absorption Correction Program, University of Gottingen, Gottingen, Germany, 1997.
22. XPREP, version 5.1; Siemens Industrial Automation Inc., Madison, WI, 1995.
23. Sheldrick, GM SHELXTL Reference Manual, version 5.1; Bruker AXS, Madison, WI, 1997.

24. Sheldrick, GM SHELXL-97: Program for Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1997.
25. Campos Vallette M M, Clavijo R E, Mendizabal F, Zamudio W, Baraona R and Diaz G, *Vib Spect.*, 1996, **12**, 37 - 44.
26. Lucile Arnaudet, Roland Bougon, Buu Ban, Pierrette Charpin, Jacques Isabey, Monique Lance, Martine Nierlich and Julien Vigner, *Can J Chem.*, 1990, **68**, 507-512