Selçuk Demir*, Hamide Merve Çepni, Małgorzata Hołyńska and Muammer Kavanoz

A tetranuclear copper (II) complex with pyrazole-3,5-dicarboxylate ligands: synthesis, characterization and electrochemical properties

DOI 10.1515/znb-2015-0197
Received November 27, 2015; accepted December 19, 2015

Abstract: A tetranuclear copper (II) complex with pyrazole-3,5-dicarboxylate ligands (pdc^{3-}), $[Me_2NH_2]_4[Cu_4(pdc)_4]$, was synthesized using solvothermal and metal oxidation routes and characterized by elemental analysis, infrared, thermogravimetry/differential thermal analysis, and room-temperature magnetic measurements. The structure of the complex was determined by single-crystal X-ray diffraction. It comprises dimethylammonium cations and complex anions containing four Cu^{2+} cations. The crystal structure is stabilized by N–H···O hydrogen bonds. In addition, the electrochemical behavior was studied.

Keywords: copper; crystal structure; polynuclear; pyrazole-3,5-dicarboxylic acid; thermal analysis.

1 Introduction

Hydrothermal/solvothermal syntheses involving oxidation-reduction processes of elements are effective routes for producing new compounds in crystalline form. On the use of these approaches, new structural motifs can be observed that would not be obtained by conventional methods [1–3].

Pyrazole-3,5-dicarboxylic acid (H_3pdc) is known both as a multiple proton donor and as an acceptor ligand. The structures of the complexes of H_3pdc and its derivatives have been reviewed by Klingele et al. [4]. After deprotonation, the anion pdc^{3-} is a multifunctional ligand that can coordinate metal ions in monodentate, bidentate, or tetradentate mode and can bridge metal centers through different bridging modes generating coordination polymers with *M*–O and *M*–N bonds [4–7]. This ligand was used as building block to obtain oligomeric or polymeric structures of dimensionality 1 to 3 with different transition metals [5–16]. Particular interest in this ligand was raised because of its capacity to keep two metal ions in close proximity and to offer additional coordination sites through its carboxylate moieties [7, 17]. Thus, it should be possible to realize multinuclear complexes whose metal atoms might interact magnetically and electronically [7].

Herein we present the results of the synthesis and characterization of the complex $[Me_2NH_2]_4[Cu_4(pdc)_4]$. It was synthesized using solvothermal and metal oxidation routes and characterized by single crystal X-ray diffraction, elemental analysis, infrared (IR), magnetic measurements, as well as thermal analysis. In addition, the electrochemical behavior of the complex was studied.

2 Experimental section

2.1 Materials and methods

All reagents [CuI (Sigma-Aldrich, Steinheim, Germany) and $H_3pdc.H_2O$ (Alfa-Aesar, Karlsruhe, Germany)] and solvents [dimethylformamide (DMF), Merck, Darmstadt, Germany] used were of analytical grade. IR spectra were recorded on a Perkin-Elmer 100 FTIR spectrophotometer (PerkinElmer Inc., Buckinghamshire, UK) as ATR between 4000 and 650 cm^{-1}. The elemental analyses (C, H, and N) were determined with a LECO, CHNS-932 instrument (Leco Corp., St. Joseph, MI, USA). TG-DTA curves were obtained using a Seiko Exstar 6200 thermogravimetry/differential thermal analysis (TG/DTA) thermal analyzer (SII NanoTechnology Inc., Tokyo, Japan) under a dynamic air atmosphere. A sample size of 3–5 mg and a heating rate of 20 °C/min in the temperature range of 30–1000 °C were used. Room temperature magnetic susceptibility measurement was carried out using a Sherwood Scientific

---

***Corresponding author: Selçuk Demir,** Faculty of Arts and Sciences, Department of Chemistry, Recep Tayyip Erdoğan University, 53100, Rize, Turkey, Tel.: +90 464 223 6126, Fax: +90 464 223 5376, E-mail: selcuk.demir@erdogan.edu.tr
Hamide Merve Çepni and Muammer Kavanoz: Faculty of Arts and Sciences, Department of Chemistry, Recep Tayyip Erdoğan University, 53100, Rize, Turkey
Małgorzata Hołyńska: Department of Chemistry, Philipps University Marburg, 35043, Marburg, Germany

MKI model Gouy magnetic balance (Sherwood Scientific Ltd., Cambridge, UK). The electrochemical studies were performed using a CH Instruments system (model 1140B; CH Istruments Inc., Austin, TX, USA) with a Pt disc as working electrode, a Pt spiral as counter electrode, and Ag/AgCl as the reference electrode. Before the experiments, the working electrode was polished, rinsed with triply distilled water, cleaned in the ultrasonic bath, washed with DMF and dried.

2.2 Synthesis of $[Me_2NH_2]_4[Cu_4(pdc)_4]$

A 5-mL DMF suspension of CuI (0.19 g, 1 mmol) was mixed with a 5-mL DMF solution of 0.087 g (0.5 mmol) $H_3pdc{\cdot}H_2O$. The stock mixture distributed in five glass vials was placed in an oven at 100 °C. Block-shaped deep-blue single crystals of the complex were obtained within 4 days (0.021 g, yield 16%, based on $H_3pdc{\cdot}H_2O$). $C_{28}H_{36}Cu_4N_{12}O_{16}$ (1050.839): calcd. C 32.00, H 3.45. N 15.99; found C 31.64, H 3.90, N 16.18. IR (ATR) (cm^{-1}): ν = 3098m, 3047m (C–H$_{arom}$); 2935w (CH_3); 2789, 2484 [ν(N^+–H)]; 1619vs, 1602vs, 1573vs (ν_{as} C=O); 1384s (ν_s C=O).

2.3 Crystal structure determination

Single-crystal data collection was carried out on a STOE IPDS2 diffractometer. The structure was solved by Direct Methods with SHELXS and refined with SHELXL [18]. Where possible, H atom positions were calculated, and a riding model was applied with U_{eq} = 1.2/1.5 U_{eq} (parent atom). The highest peak on the final difference Fourier map of 0.41 e/Å^3 was located on the C4–C5 bond. The basic crystallographic data are collected in Table 1.

CCDC 1058512 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

As part of our efforts to prepare metal polycarboxylate frameworks, we obtained the title complex $[Me_2NH_2]_4[Cu_4(pdc)_4]$ in a reaction of CuI with $H_3pdc{\cdot}H_2O$ in DMF. The complex comprises dimethylammonium cations and complex anions containing four Cu^{2+} cations (see below). The dimethylammonium cations are most probably the result of DMF decomposition and reduction (see below) under solvothermal conditions [19].

Table 1: Crystal structure data for $[Me_2NH_2]_4[Cu_4(pdc)_4]$.

Formula	$C_{20}H_4Cu_4N_8O_{16}{\cdot}4(C_2H_8N)$
Formula weight	1050.85
Crystal size, mm^3	0.47 × 0.24 × 0.1
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	6.355(3)
b, Å	18.123(4)
c, Å	16.084(4)
β, deg	106.17(3)
V, Å^3	1779.1(10)
Z	2
D, g/cm^3	1.96
μ(MoK_α), mm^{-1}	2.5
F(000), e	1064
Radiation (λ), Å	MoK_α; 0.71073
θ range, deg	1.73–24.99
Refl. total/unique/R_{int}	22 032/3137/0.073
Absorption correction	numerical
Transmission factors (min/max)	0.507/0.806
Data/restraints/ref. param.	3137/0/271
$R1$ [$I > 2\,\sigma(I)$]	0.028
$wR2$ (all data)	0.062
GOF (F^2)	1.00
$\Delta\rho$ (max/min), e/Å^3	0.41/−0.46

If in our experiments the metal-to-ligand ratio is 2:0.5 in DMF at 70 or 80 °C, the reaction produces the extended metal-organic framework reported by Barman et al. [3], which was originally prepared using $Cu(NO_3)_2{\cdot}2.5H_2O$ as a metal source in DMF at 100 °C for 20 h [3]. According to X-ray powder diffraction results, we obtained this material as a second product. Additionally, a silver test (formation of a yellowish precipitate, AgI) is an indication of I^- anions in the reaction medium that did not participate in any oxidation reaction. Furthermore, we did not observe any orange-brown precipitate formation as indication of Cu^0 in the vials, which confirms that only the oxidation of copper(I) occurred in the solution. We assume that during the reaction, Cu^+ is oxidized to Cu^{2+}, while some of the ligand and potentially part of DMF are reduced. In addition, the poor solubility of CuI in DMF probably favors the formation of good-quality single crystals of $[Me_2NH_2]_4[Cu_4(pdc)_4]$ *via* slow oxidation. The block-shaped crystals were separated manually from solution.

The deep blue color of the compound confirms the oxidation state +2 of the metal centers. The magnetic susceptibility measurement at room temperature showed that the complex is paramagnetic. However, the value of $\chi_M T$ at 298 K is 2.38 μ_B, which is lower than the expected value for a tetranuclear Cu(II) complex (4.90 μ_B). The close proximity of the copper ions probably leads to a significant coupling both through space and through the π system of the pyrazole rings [17]. The coupling is stronger than in $[Cu_2(Hpdc)_2][dpdo]$ (dpdo = 4,4′-dipyridyl-*N*,*N*′-dioxide hydrate) [12].

3.1 Description of the crystal and molecular structure

Each complex anion consists of two nearly planar dinuclear $[Cu^{II}_2(pdc)_2]$ units, where pdc is the triply deprotonated pyrazole-3,5-dicarboxylate (pdc^{3-}) anion (Fig. 1). The dinuclear $[Cu^{II}_2(pdc)_2]$ units are stacked together to form a tetranuclear complex. The stacking of the $[Cu^{II}_2(pdc)_2]$ units occurs with a small offset with respect to each other, resulting in additional axial Cu–N and Cu–O bonds and expansion of the coordination sphere of the Cu^{2+} ions from four to five in a square-pyramidal arrangement. The entire tetranuclear aggregate has crystallographic inversion symmetry.

Interestingly, two dinuclear Cu^{2+} complexes containing solely the planar $[Cu^{II}_2(pdc)_2]$ unit have been synthesized and structurally characterized before ($[Et_3NH]_2[Cu_2(pdc)_2(H_2O)_2]$ [6] and $[Me_2NH_2]_2[Cu_2(pdc)_2(H_2O)_2]\cdot H_2O$ [20]). In these dinuclear complexes, additional water molecules are coordinated to the axial position of the square-pyramidal Cu^{2+} ions, thus preventing the formation of the tetranuclear complex that we obtained in our project. $[Me_2NH_2]_2[Cu_2(pdc)_2(H_2O)_2]\cdot H_2O$ [20] was synthesized using copper(II) chloride as metal source in aqueous dimethylamine and DMF solutions after a month. $[Et_3NH]_2[Cu_2(pdc)_2(H_2O)_2]$ [6] was synthesized starting from $Cu(NO_3)_2\cdot 3H_2O$ under hydrothermal conditions at 165 °C for 16 h.

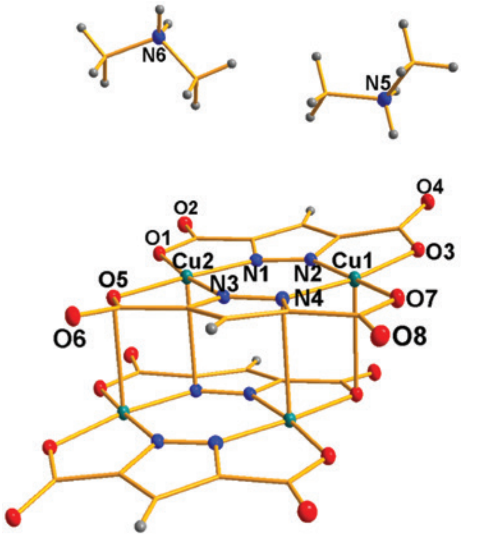

Fig. 1: Molecular structure of the complex $[Me_2NH_2]_4[Cu_4(pdc)_4]$. Symmetry-independent non-hydrogen and non-carbon atoms are labeled. Displacement ellipsoids are drawn at the 30% probability level.

Although no temperature was reported for the synthesis of $[Me_2NH_2]_2[Cu_2(pdc)_2(H_2O)_2]\cdot H_2O$ [20], regarding the long crystallization time, we assume that reaction conditions probably milder than ours yield the dinuclear complex. Meanwhile, in the case of $[Et_3NH]_2[Cu_2(pdc)_2(H_2O)_2]$ [6], much harsher reaction conditions likewise yielded only a dinuclear species. Thus, it is not clear what exactly caused the formation of $[Me_2NH_2]_4[Cu_4(pdc)_4]$, but it is reasonable to assume that the complex redox reactions leading to the tetranuclear complex also played a role.

The anions chelate each of the Cu^{2+} cations through one of the pyrazole N atoms and two carboxylate O atoms (Fig. 1). Within each planar unit, the Cu–N and Cu–O bond lengths are at 1.908(2)–1.924(2) and 1.961(2)–1.988(2) Å, respectively (Table 2). The units comprising two Cu^{2+} ions and the organic pdc^{3-} anion are essentially planar, especially the unit with the N3–N4 ligand. The uncoordinated carboxylate atoms O4 and O8 are displaced from these planes by 0.40(1) and 0.12(1) Å, respectively. The two units are stacked through Cu–O/N bonds (Cu2–N4 at $-x, -y, 1 - z$ of 2.850(3) Å; Cu1–O5 at $-x, -y, 1 - z$ of 2.876(3) Å). Similar planar units arranged in stacks were reported for the related compounds of various transition metals [6, 17].

The Cu1···Cu2 distance within each planar dinuclear complex unit is 3.957(1) Å, which is similar to the distance previously observed in the complex $[Et_3NH]_2[Cu_2(pdc)_2(H_2O)_2]$ (3.962 Å [6]). The shortest Cu···Cu distance between the two stacked dinuclear units is 3.458(2) Å (Cu1···Cu2 at $-x, -y, 1 - z$). Between the pairs of stacked dinuclear units,

Table 2: Selected geometric parameters (distances in Å and angles in deg) for $[Me_2NH_2]_4[Cu_4(pdc)_4]$.

Cu1–N2	1.910(2)	Cu2–N3	1.909(2)
Cu1–N4	1.924(2)	Cu2–O1	1.961(2)
Cu1–O7	1.967(2)	Cu2–O5	1.988(2)
Cu1–O3	1.979(2)	N1–N2	1.331(3)
Cu2–N1	1.908(2)	N3–N4	1.335(3)
N2–Cu1–N4	93.03(10)	N1–Cu2–N3	93.65(10)
N2–Cu1–O7	173.31(9)	N1–Cu2–O1	81.11(9)
N4–Cu1–O7	81.24(9)	N3–Cu2–O1	173.97(9)
N2–Cu1–O3	81.29(9)	N1–Cu2–O5	174.15(9)
N4–Cu1–O3	171.72(9)	N3–Cu2–O5	80.51(9)
O7–Cu1–O3	104.02(8)	O1–Cu2–O5	104.74(8)

the shortest Cu⋯Cu distance is 4.716(3) Å (Cu1⋯Cu2 at 1 − *x*, −*y*, 1 − *z*).

The anions form columns in the crystal structure, extending along [100] (Fig. 2). In the voids between these columns, the organic cations are located. Dimethylammonium cations act as donors in N–H⋯O hydrogen bonds with carboxylate O atoms as acceptors to create a three-dimensional hydrogen-bonded network (Table 3 and Fig. 2).

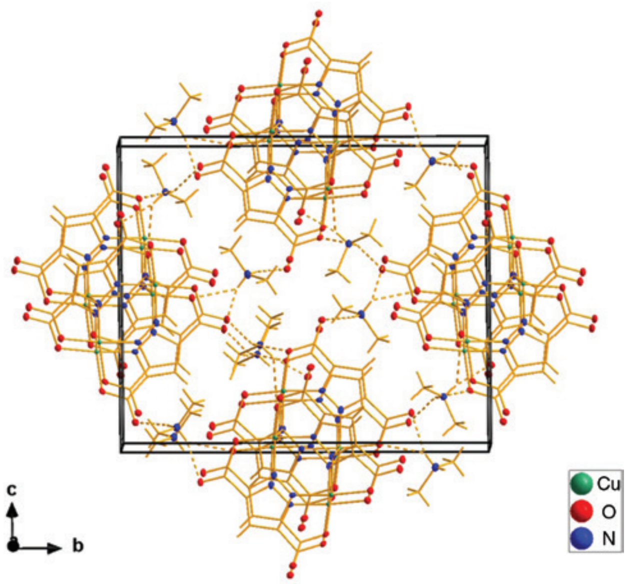

Fig. 2: Columns of the complex anions extending along [100] in the crystal structure of $[Me_2NH_2]_4[Cu_4(pdc)_4]$. H atoms are omitted and C atoms are shown as sticks for clarity.

Table 3: Hydrogen bond parameters (distances in Å and angles in deg) for $[Me_2NH_2]_4[Cu_4(pdc)_4]$.[a]

D–H⋯A	*d*(D–H)	*d*(H⋯A)	*d*(D⋯A)	∠(D–H⋯A)
N5–H5A⋯O4	0.86	2.04	2.876(3)	164
N5–H5B⋯O1^{i}	0.86	2.36	3.028(3)	134
N5–H5B⋯O2^{i}	0.86	2.12	2.930(3)	158
N6–H6A⋯O5^{i}	0.86	2.65	3.296(3)	133
N6–H6A⋯O6^{i}	0.86	1.98	2.824(3)	167
N6–H6B⋯O2^{ii}	0.86	2.07	2.775(3)	139
N6–H6B⋯O3^{iii}	0.86	2.65	3.076(3)	112
C3–H3⋯O8^{iv}	0.95	2.66	3.549(4)	157
C1N–H1ND⋯O7^{iv}	0.98	2.62	3.576(4)	164
C1N–H1NE⋯O8^{iii}	0.98	2.66	3.547(4)	151
C2N–H2ND⋯O4^{v}	0.98	2.64	3.580(4)	161
C2N–H2NF⋯O8^{iii}	0.98	2.65	3.548(4)	152
C4N–H4NE⋯O3^{iv}	0.98	2.59	3.521(5)	158

[a] Symmetry codes: (i) *x*, −*y* + 1/2, *z* − 1/2; (ii) *x* + 1, *y*, *z*; (iii) −*x* + 1, *y* + 1/2, −*z* + 1/2; (iv) −*x*, *y* + 1/2, −*z* + 1/2; (v) −*x*, −*y*, −*z*.

3.2 Infrared spectra

The IR spectra of H_3pdc and of the $[Cu_4]$ complex are given in Figs. S1 and S2, respectively, in the Supplementary Information available online (see note at the end of the paper for availability). As expected, characteristic changes are observed. The C–H stretching modes of the aromatic ring and of the CH_3 group of the cations are observed in the region around 3000 cm^{-1}. The medium-weak bands at 2789 and 2484 cm^{-1} are attributed to the NH_2^+ stretching band of dimethylammonium cations [21]. The strong and sharp bands centered at 1602 cm^{-1} with two shoulders at 1384 cm^{-1} are assigned as the asymmetric (ν_{as}) and the symmetric (ν_s) stretching modes of the COO groups. The value of $\Delta\nu$ ($\nu_{as}-\nu_s$) is 216 cm^{-1}, indicating a monodentate coordination mode of the carboxylate groups [22]. Other characteristic peaks are at 1474 and 1285 cm^{-1}, which can be attributed to C=N and C=C stretching vibrations of the pyrazole linker. The parent acid spectrum shows a strong absorption band at 1700 cm^{-1}, which is due to the stretching vibration of the COOH groups. The absence of this peak confirms the deprotonation of the ligand in the $[Cu_4]$ complex.

3.3 Thermal analysis

The thermal behavior of the complex was studied by TG-DTA under dynamic air atmosphere. The TG-DTA curves are illustrated in Fig. 3. The mass loss at the first stage, between 30 and 100 °C, is attributed to the loss of one dimethylamine molecule. The experimental mass loss of 4.3 % is consistent with the calculated value of 4.4 %. The exothermic elimination of the remaining dimethylamine molecules and of the ligands occurs in the range of 231–563 °C, with mass loss of 66.9 % (calcd. 65.4 %). The final decomposition product is CuO (exp. 28.8 %, calcd. 30.3 %).

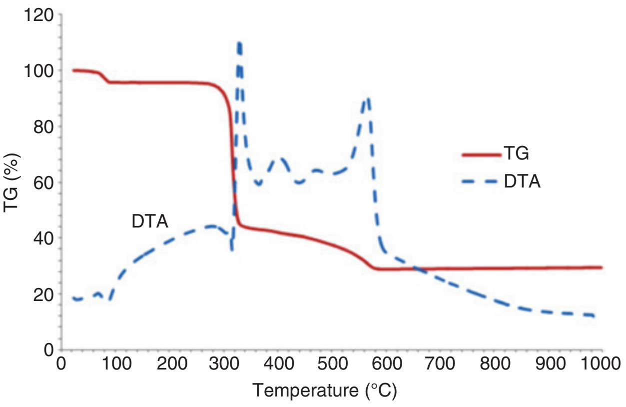

Fig. 3: TG/DTA curves of $[Me_2NH_2]_4[Cu_4(pdc)_4]$.

3.4 Electrochemical studies

Cyclic voltammograms of H_3pdc, Cu(II) nitrate and of the [Cu_4] complex (Fig. 4) were obtained at room temperature in 100 mM tetrabutylammonium perchlorate (TBAP) solutions in DMF, at the potential range of 1.5 to –1.5 V using Pt disc electrode *versus* an Ag/AgCl reference electrode.

The Cu(II) nitrate solution displays two reduction peaks at −0.298 V (reduction of Cu^{2+} to Cu^{+}) and −0.759 V (reduction of Cu^{+} to Cu^{0}) and two oxidation peaks at 0.723 V (oxidation of Cu^{0} to Cu^{+}) and 1.027 V (oxidation of Cu^{+} to Cu^{2+}). The complex displays two reduction peaks at −0.508 and –1.251 V, as well as one oxidation peak at 1.227 V. As a result of complexation, one oxidation peak disappeared. This may be caused by the chemical oxidation of copper during the complex formation (i.e. in complexation reaction the Cu(I) species is transformed to Cu^{2+} and the ligand is reduced). Voltammograms of the ligand solution show one reduction peak at –1.081 V and one oxidation peak at 0.827 V. The complex shows a lower current than observed for the Cu(II) salt solutions. This may lead to the following conclusions: (a) the diffusion coefficient of the complex is lower than that of the Cu(II) nitrate solution (i.e. the mass transfer rate for Cu^{2+} is higher than the mass transfer rate of the complex) and (b) the conductivity of the copper film and the rate of charge transfer on the electrode surface formed in Cu(II) nitrate solution is higher than that for the solution containing the [Cu_4] complex.

When the scan direction of potential was changed, we obtained similar results, which means that the initial oxidation state of the species present in the electrochemical cell does not affect the electrochemical behavior.

Cyclic voltammograms of the [Cu_4] compound at different scan rates are shown in Fig. S3 (Supplementary Information). The peak currents of all reduction and oxidation processes change linearly with the square root of the scan rate, indicating the diffusion characteristics of the electrochemical reactions. Furthermore, the logarithm of the peak current changes linearly with the logarithm of the scan rate by a slope value very close to 0.5, supporting the diffusion effect on the electrochemical mechanism [23]. In cyclic voltammogram studies, successive cycles were measured, and each cycle displays nearly the same peak current, indicating the diffusion control in the mechanism (Figs. S4–S6; Supplementary Information).

4 Conclusion

A new anionic tetranuclear copper complex with pyrazole-3,5-dicarboxylate ligands with dimethylammonium cations as counterions was synthesized and characterized. Each complex anion comprises two planar [$Cu^{II}_2(pdc)_2$] units and a triply deprotonated 3,5-pyrazoledicarboxylate anion. Dimethylammonium cations are located in the voids between the columns participating in N–H···O hydrogen bonds. Cyclic voltammetric studies indicate that the complex exhibits a metal-centered and diffusion-controlled one-electron reduction process.

5 Supplementary information

The IR spectra of H_3pdc and the complex $[Me_2NH_2]_4[Cu_4(pdc)_4]$, cyclic voltammograms at different scan rates, and the related plots of I_{c1} and I_{c2} are available online (DOI: 10.1515/znb-2015-0197).

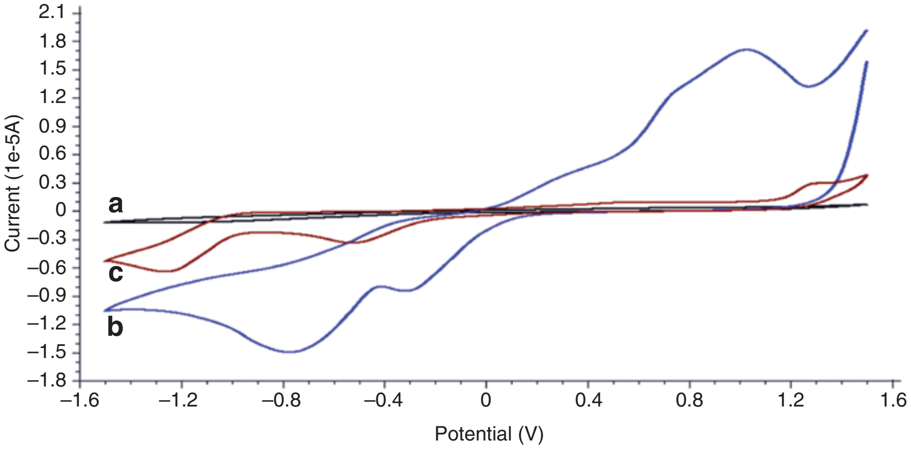

Fig. 4: Cyclic voltammograms of (a) H_3pdc and (b) Cu(II) nitrate solution. (c) The complex (0.50 mM) in DMF containing 100 mM TBAP at a scan rate of 100 mV/s.

Acknowledgments: This work was financially supported by The Scientific and Technological Research Council of Turkey (Project Number 112T956). We thank Dr. İbrahim Hüdai Taşdemir from Amasya University for the useful discussions on electrochemical studies, Prof. Dr. Stefanie Dehnen and Prof. Dr. Florian Kraus for their generous support, and Michael Marsch for his support in the X-ray diffraction studies.

References

[1] J. Y. Lu, *Coord. Chem. Rev.* **2003**, *246*, 327.
[2] R. Peng, M. Li, D. Li, *Coord. Chem. Rev.* **2010**, *254*, 1.
[3] S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O. M. Yaghi, G. X. Jin, H. Berke, *Chem. Commun.* **2011**, *47*, 11882.
[4] J. Klingele, S. Dechert, F. Meyer, *Coord. Chem. Rev.* **2009**, *253*, 2698.
[5] X. Feng, L. Y. Wang, J. S. Zhao, B. Liu, J. G. Wang, X. G. Shi, *Inorg. Chim. Acta* **2009**, *362*, 5127.
[6] P. King, R. Clérac, C. E. Anson, A. K. Powell, *Dalton Trans.* **2004**, *6*, 852.
[7] S. S. Massoud, F. R. Louka, L. T. Nguyen, M. Mikuriya, J. H. Albering, F. A. Mautner, *Inorg. Chim. Acta* **2011**, *366*, 394.
[8] C. An, Y. Lu, Z. Shang, Z. Zhang, *Inorg. Chim. Acta* **2008**, *361*, 2721.
[9] W. L. Driessen, L. Chang, C. Finazzo, S. Gorter, D. Rehorst, J. Reedijk, M. Lutz, A. L. Spek, *Inorg. Chim. Acta* **2003**, *350*, 25.
[10] P. King, R. Clerac, C. E. Anson, C. Coulon, A. K. Powell, *Inorg. Chem.* **2003**, *42*, 3492.
[11] F. M. Nie, Z. Y. Dong, F. Lu, G. X. Li, *J. Coord. Chem.* **2010**, *63*, 4259.
[12] J. L. Tian, S. P. Yan, D. Z. Liao, Z. H. Jiang, P. Cheng, *Inorg. Chem. Commun.* **2003**, *6*, 1025.
[13] C. Z. Xie, R. F. Li, L. Y. Wang, Q. Q. Zhang, *Z. Anorg. Allg. Chem.* **2010**, *636*, 657.
[14] X. H. Zhou, Y. H. Peng, X. D. Du, C. F. Wang, J. L. Zuo, X. Z. You, *Cryst. Growth Des.* **2009**, *9*, 1028.
[15] K. L. Ziegelgruber, K. E. Knope, M. Frisch, C. L. Cahill, *J. Solid State Chem.* **2008**, *181*, 373.
[16] X. H. Zhou, Y. H. Peng, Z. G. Gu, J. L. Zuo, X. Z. You, *Inorg. Chim. Acta* **2009**, *362*, 3447.
[17] J. C. Bayon, P. Esteban, G. Net, P. G. Rasmussen, K. N. Baker, C. W. Hahn, M. M. Gumz, *Inorg. Chem.* **1991**, *30*, 2572.
[18] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
[19] J. Juillard, *Pure Appl. Chem.* **1977**, *49*, 885.
[20] X. H. Li, *Acta Crystallogr.* **2005**, *E61*, m2405.
[21] H. Ilkimen, C. Yenikaya, M. Sari, M. Bulbul, E. Tunca, Y. Suzen, *Polyhedron* **2013**, *61*, 56.
[22] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley-Interscience, New York, **1997**.
[23] M. Iqbal, I. Ahmad, S. Ali, N. Muhammad, S. Ahmed, M. Sohail, *Polyhedron*, **2013**, *50*, 524.

Supplemental Material: The online version of this article (DOI: 10.1515/znb-2015-0197) offers supplementary material, available to authorized users.