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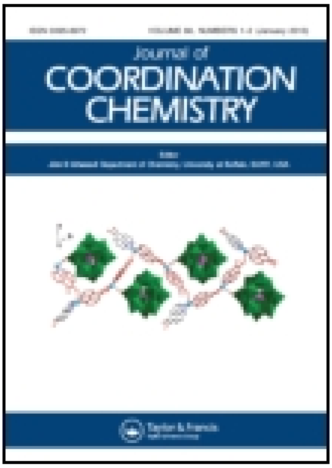

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Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Syntheses, molecular structure, and electrochemical investigations of cobalt(II), copper(II), palladium(II), and zinc(II) complexes with 3-methylpyrazole

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Accepted author version posted online: 23 Jun 2014.Published online: 18 Jul 2014.

To cite this article: Sher Ali Khan, Awal Noor, Rhett Kempe, Hanif Subhan, Afzal Shah & Ezzat Khan (2014) Syntheses, molecular structure, and electrochemical investigations of cobalt(II), copper(II), palladium(II), and zinc(II) complexes with 3-methylpyrazole, Journal of Coordination Chemistry, 67:14, 2425-2434, DOI: 10.1080/00958972.2014.938066

To link to this article: http://dx.doi.org/10.1080/00958972.2014.938066

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 14, 2425–2434, http://dx.doi.org/10.1080/00958972.2014.938066

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Syntheses, molecular structure, and electrochemical investigations of cobalt(II), copper(II), palladium(II), and zinc(II) complexes with 3-methylpyrazole

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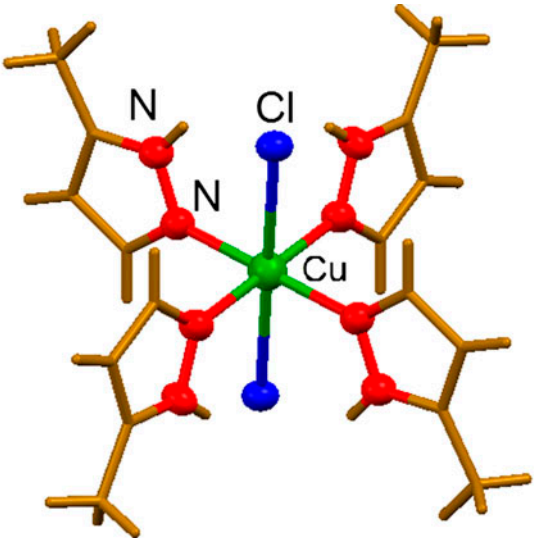
(*Received 28 February 2014; accepted 24 May 2014*)



Complexes of M(II) with 3-methylpyrazole as ligand were prepared at ambient temperature using MCl_2 metal salts (M = Cu, Co, Pd, and Zn). Reactions led to the formation of octahedral (Cu, Co), square-planar (Pd), and tetrahedral (Zn) mononuclear complexes. All reactions were straightforward and no appreciable amount of side products was detected. X-ray structures were determined for all the complexes. The cyclic voltammetric investigations indicate the involvement of proton during electron transfer reactions of these complexes.

Mononuclear complexes of 3-methylpyrazole with general formulas $(3\text{-Mepz})_4CuCl_2$ (**1**), $(3\text{-Mepz})_4CoCl_2$ (**2**), $(3\text{-Mepz})_2PdCl_2$ (**3**), and $(3\text{-Mepz})_2ZnCl_2$ (**4**) were prepared by reaction of the corresponding MCl_2 salt (M = Cu, Co, Pd, and Zn) with 3-methylpyrazole in appropriate amounts using acetonitrile as solvent at ambient temperature. The X-ray crystal structure determination reveals that

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1 and **2** possess octahedral geometry, while **3** and **4** are square planar and tetrahedral, respectively. All the synthesized compounds have the MCl_2 fragment, thus making the synthesized compounds attractive synthons for further transformation. The cyclic voltammograms of the synthesized complexes were obtained and the voltammetric signatures of **1**, **2**, and **4** showed a single irreversible pH-dependent cathodic peak, while **3** has two reversible cathodic peaks. Involvement of protons accompanying the electron transfer processes was ascertained from differential pulse voltammetric results, indicating peak potential shift as a function of pH.

Keywords: 3-Methylpyrazole; M(II) complexes; X-ray structures; Electrochemistry

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1. Introduction

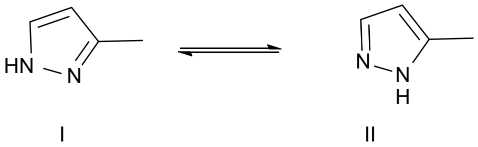
Pyrazole and its derivatives are useful ligands in a variety of inorganic and organometallic compounds [1]. They have a long history of development due to their wide range of applications, i.e. in electroluminescent materials [2, 3], metal extraction [4, 5], and polymerization catalysis [6–9]. Pyrazole derivatives have been applied because of structural variations in their complexes which offer a high degree of diversity that is useful for the development of new therapeutic agents with improved potency and low toxicity [10]. Compounds containing the pyrazole moiety exhibit several biological activities [11]. Recently, these derivatives have been reported as COX-2 inhibitors as well as potential antitumor agents, increasing the importance of such heterocyclic ligands in medicinal chemistry [12–14]. The pyrazole derivatives usually are monodentate ligands, coordinating to the metal center through unsubstituted nitrogen, but in some cases they also coordinate through both nitrogens [15]. The geometry around the metal center of the resultant complexes depends upon the steric bulk of the pyrazole derivatives and on the nature of the metal itself [16]. The number of pyrazole ligands coordinated to a metal and nuclearity of the respective complex is also determined by their bulk [17]. Additionally, structural changes arise from the binding mode (scheme 1). One pyrazole derivative used extensively in coordination chemistry is 3-methylpyrazole. Although its complexes with M(II) (M = Cu, Pd, Co, and Zn) have been reported [6, 18], to the best of our knowledge, their crystal structures have not yet been reported.

Starting from commercially available 3-methylpyrazole, we were interested to study the ligand behavior on the nuclearity of the metals. Here, we report the straightforward syntheses of mononuclear complexes of 3-methylpyrazole containing the MCl_2 fragment (M = Cu (II), Co(II), Pd(II), and Zn(II)). Structures of all these complexes were determined by X-ray diffraction (**1**–**4**) and NMR data were collected for Pd and Zn complexes.

2. Experimental section

2.1. *General considerations*

Solvents were dried by distillation using sodium wire/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled



Scheme 1. The two isomeric forms of 3-methylpyrazole.

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prior to use. NMR spectra were recorded on a Varian 300 MHz at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. $CuCl_2$, $CoCl_2$, $PdCl_2$, $ZnCl_2$, and 3-methylpyrazole were purchased from Aldrich and used without further purification. Elemental analyses (CHN) were performed on a Vario EL III instrument. The X-ray crystal structure analyses were carried out using a STOE-IPDS II machine equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97 [19], SHELXL97 [20], and WinGX [21].

2.2. *Synthesis of 1*

3-Methylpyrazole (0.33 mL, 0.33 g, and 4 mM) in acetonitrile (5 mL) was added to $CuCl_2$ (0.134 g, 1 mM) in acetonitrile (10 mL) at room temperature with vigorous stirring, resulting in sudden precipitation and the stirring was continued for 1 h. The blue crystalline precipitate was separated from the mother liquor by filtration and washed with copious amounts of diethylether. The solid was dissolved in acetonitrile, crystals suitable for X-ray analysis were obtained and the structure was determined. $C_{16}H_{24}N_8CuCl_2$; Yield: 92%.

2.3. *Synthesis of 2*

3-Methylpyrazole (0.33 mL, 0.33 g, and 4 mM) in acetonitrile (5 mL) was added to $CoCl_2$ (0.128 g, 1 mM) in the same solvent (10 mL) at room temperature. It resulted in a sudden pink precipitate and the reaction mixture was further stirred for 1 h. The precipitates were filtered and dissolved in dichloromethane to obtain analytically pure pink crystals after one day. $C_{16}H_{24}N_4CoCl_2$; Yield: 97%; ^{1}H NMR ($CDCl_3$) $\delta = 47.2$ (br, 4H, NH), 31.6 (br, 4H, pyz), 14.6 (br, 4H, pyz), 2.2 (s, 12H, Me) ppm.

2.4. *Synthesis of 3*

3-Methylpyrazole (0.16 mL, 0.16 g, and 2 mM) in acetonitrile (5 mL) was added to a stirred solution of $PdCl_2$ (0.177 g, 1 mM) in acetonitrile (10 mL). The stirring was continued overnight. Solvent was evaporated under vacuum. The residues were dissolved in dichloromethane to obtain analytically pure dark yellow crystals after one day. $C_8H_{10}N_4PdCl_2$; Yield: 96%; ^{1}H NMR ($CDCl_3$) $\delta = 11.29$ (br, 2H, NH), 7.8 (br, 2H, CH), 6.1 (br, 2H, CH), 2.3 (s, 6H, 3-Me) ppm. ^{13}C NMR $\delta = 142.6$ (C-3), 141.2 (C-5), 106.0 (C-4), 11.1 (Me) ppm. The NMR data are comparable with previously reported data [6(a)].

2.5. *Synthesis of 4*

3-Methylpyrazole (0.16 mL, 0.16 g, and 2 mM) and $ZnCl_2$ (0.136 g, 1 mM) were mixed in acetonitrile following the same procedure as for **1**–**3**. The reaction mixture was stirred overnight and all volatiles were evaporated under vacuum. The residue was dissolved in dichloromethane to obtain analytically pure colorless crystals. ^{1}H NMR ($CDCl_3$) $\delta = 10.3$ (br, 2H, NH), 7.7 (br, 2H, pyz), 6.1 (br, 2H, pyz), 2.3 (s, 6H, 3-Me) ppm. ^{13}C NMR $\delta = 144.5$ (C-3), 137.8 (C-5), 106.2 (C-4), 11.4 (Me) ppm.

3. Electrochemistry

Stock solutions (4 mM) of the synthesized compounds were prepared in ethanol and stored at 4 °C. Fresh working solutions of 2 mM concentration were prepared in 50% ethanol and

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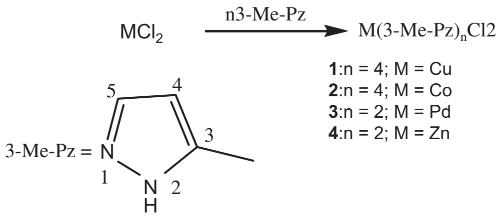
50% supporting electrolyte [the Britton Robinson (BR) buffer]. Electrochemical experiments were performed at 25 ± 1 °C using μAuto-lab running with GPES 4.9 software, Eco-Chemie, Utrecht, The Netherlands. Glassy Carbon, Pt wire, and Ag/AgCl were employed as working, counter, and reference electrodes, respectively. Cyclic voltammetry (CV) was carried out at 100 mVs^{-1}. Differential pulse voltammetry (DPV) was performed at a scan rate of 5 $mV\,s^{-1}$. All the voltammetric experiments were conducted in a high-purity nitrogen atmosphere. The working electrode was polished by diamond spray (particle size 1 mm) followed by thorough rinsing with distilled water and then placed in the desired buffer electrolyte, and various DP voltammograms were recorded until the achievement of a steady state baseline voltammogram. This procedure ensured reproducible experimental results. Microvolumes were measured using EP-10 and EP-100 Plus Motorized Microliter Pipettes (Rainin Instrument Co. Inc., Woburn, MA, USA). The pH measurements were carried out with a Crison micro pH 2001 pH-meter with an Ingold combined glass electrode.

4. Results and discussion

The steric bulk of pyrazole derivatives as ligand plays an important role in defining coordination number around a metal center, and therefore, greatly affects its chemistry [22]. 3-Methylpyrazole was selected as a ligand in this study for the purpose to get solid-state structures and more insight into the coordination behavior of this particular ligand with different M(II) ions. The corresponding 3-methypyrazole complexes (**1**–**4**) were prepared by reacting appropriate amounts of 3-methypyrazole with the corresponding MCl_2 salts (M = Cu (**1**), Co (**2**), Pd (**3**), and Zn (**4**)) in acetonitrile at ambient temperature (scheme 2). All complexes were reasonably pure and excellent yields were obtained (see section 2). Crystals of **1** suitable for X-ray analysis were obtained from acetonitrile and of **2**–**4** were grown in dichloromethane solution.

The data related to crystal structure determination of **1**–**4** are summarized in table 1 and the relevant bond angles and bond lengths are summarized in table 2. The molecular structures of **1**–**4** are shown in figures 1–3.

Complexes **1** and **2** are isostructural in which four pyrazole ligands are coordinated to the central metal (figure 1) and two chlorides, possessing an octahedral environment. The metal is a quasi-symmetry center with a two-fold axis. Pyrazole prefers the second isomeric form of coordination (scheme 1) due to steric stability and could now instead be assigned as 5-methylpyrazole rather than 3-methylpyrazole [23, 24]. The coordinating nitrogens are



Scheme 2. Syntheses of metal complexes (**1**–**4**) with 3-methylpyrazole ligand.

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Table 1. Crystal data and structure refinement for **1–4**.

Empirical formula	$C_{16}H_{24}N_8Cl_2Cu$ (**1**)	$C_{16}H_{24}N_8Cl_2Co$ (**2**)	$C_8H_{12}N_4Cl_2Pd$ (**3**)	$C_8H_{12}Cl_2N_4Zn$ (**4**)
Formula weight	462.88	458.26	341.52	300.49
Temperature	133 K	133 K	133 K	133 K
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*
Unit cell dimensions	*a* = 7.48(5) Å *b* = 8.31(5) Å *c* = 9.42(6) Å α = 93.17(5)° *β* = 105.13(5)° *λ* = 113.02(5)°	*a* = 7.12(5) Å *b* = 8.54(6) Å *c* = 8.91(6) Å α = 88.44(6)° *β* = 74.31(5)° *λ* = 79.42(6)°	*a* = 7.85(5) Å *b* = 8.48(6) Å *c* = 9.16(6) Å α = 92.12(5)° *β* = 93.40(5)° *λ* = 102.97(5)°	*a* = 7.44(1) Å *b* = 8.42(12) Å *c* = 10.95(14) Å α = 83.08(11)° *β* = 72.93(10)° *λ* = 71.35(11)°
Volume ($Å^3$)	512.09(6)	513.18(6)	592.55(7)	621.05(15)
Z	1	1	2	2
Density ($Mg\,m^{-3}$)	1.501	1.483	1.914	1.607
Absorption coefficient (mm^{-1})	0.35	1.12	1.99	2.38
F (0 0 0)	239	237	336	304
Crystal size (mm)	0.25 × 0.18 × 0.16	0.16 × 0.15 × 0.15	0.20 × 0.15 × 0.12	0.14 × 0.13 × 0.12
θ range	2.3°–26.7°	2.4°–26.7°	2.2°–25.0°	2.0°–27.7°
Index ranges	$-9 \le h \le 9$; $-10 \le k \le 10$; $-11 \le l \le 11$	$-9 \le h \le 9$; $-10 \le k \le 10$; $-11 \le l \le 11$	$-8 \le h \le 9$; $-10 \le k \le 10$; $-11 \le l \le 11$	$-9 \le h \le 9$; $-11 \le k \le 10$; $-14 \le l \le 14$
Reflections collected	7791	7664	6967	10,170
Independent reflections	2171 [*R*(int) = 0.052]	2173 [*R*(int) = 0.064]	1980 [*R*(int) = 0.066]	2894 [*R*(int) = 0.192]
Completeness to *θ*	26.7°, 99.5%	26.7°, 99.9%	24.5°, 99.9%	27.7°, 99.8%
Data/restraints/ parameters	2171/0/134	2173/0/134	1980/0/149	2894/0/144
Goodness-of-fit on F^2	1.14	1.02	1.05	0.91
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.052, *wR*2 = 0.143	*R*1 = 0.044, *wR*2 = 0.118	*R*1 = 0.029, *wR*2 = 0.075	*R*1 = 0.085, *wR*2 = 0.234
R indices (all data)	*R*1 = 0.0541, *wR*2 = 0.1428	*R*1 = 0.0554, *wR*2 = 0.113	*R*1 = 0.0319, *wR*2 = 0.0733	*R*1 = 0.1535, *wR*2 = 0.1985
Largest diff. peak and hole ($e\,Å^{-3}$)	0.70 and −0.36	0.49 and −0.53	0.76 and −1.19	1.11 and −0.74

present in the same plane while the two chlorides are axial. The coordinated pyrazole moieties show *trans* arrangement with respect to each other. The average bond lengths of Cu–N and Cu–Cl in **1** are 2.02 and 2.81 Å, respectively, while in **2** the Co–N and Co–Cl bond distances are 2.07 and 2.52 Å, respectively. The equatorial bond angles in **1** and **2** are equal [N–Cu/Co–N 180°], however, the bond angles for N–Cu–Cl 88.42 and N–Co–Cl 88.15 (7)° differ slightly but are comparable to previously reported analogous structures [25, 26]. A

Table 2. Selected bond lengths (Å) and angles (°) for **1–4**.

Compound **1**	Compound **2**	Compound **3**	Compound **4**
Cu1–N1 2.010(3)	Co1–N1 2.118(2)	Pd1–N1 2.021(2)	Zn1–N1 2.005(7)
Cu1–N3 2.021(3)	Co1–N3 2.129(2)	Pd1–N3 2.018(2)	Zn1–N3 2.004(7)
Cu1–Cl1 2.812(3)	Co1–Cl1 2.517(7)	Pd1–Cl1 2.298(8)	Zn1–Cl1 2.241(3)
Cu1–M1–N1A 180(1)	N1–Co1–N1A 180.(1)	N1–Pd1–N1 180(19)	N3–Zn1–N1 110.4(3)
N1–Cu1–N3 91.39(13)	N1–Co1–N3 90.22(9)	N1–Pd1–Cl1 89.92(7)	N3–Zn1–Cl1 110.3(2)
N1–Cu1–Cl1 88.42(7)	N1–Co1–Cl1 88.15(7)	Cl1–Pd1–Cl2 180(1)	N1–Zn1–Cl2 105.8(2)
Cl1–Cu1–Cl1A 180(1)	Cl1–Co1–Cl1A 180(1)		Cl1–Zn1–Cl2 117.2(9)

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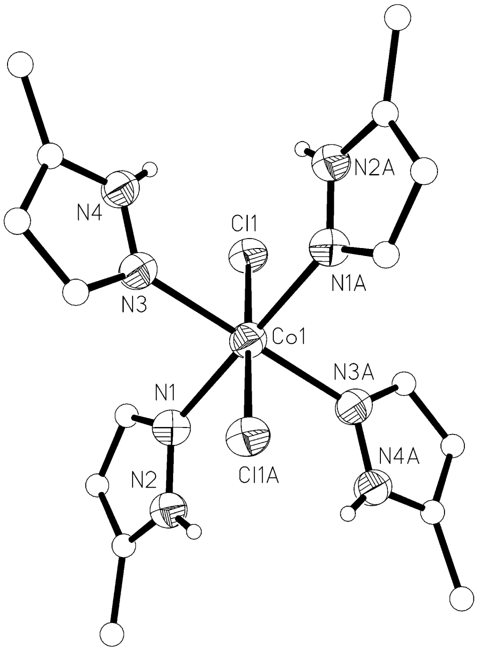

Figure 1. Molecular structure of **2**, thermal ellipsoids with 50% probability level, hydrogens except N–H are omitted for clarity. Selected bond lengths and angles are given in table 2.

comparison of the structures of **1** and **2** shows that certain structural features can be related to the ionic size in the expected manner. The M–N bond distance Co–N = 2.07 Å and Cu–N = 2.02 Å follows the order of ionic size, i.e. Co(II) and Cu(II). The data show that the sequence was not followed by the M–Cl bond and the Cu–Cl bond was longer than the

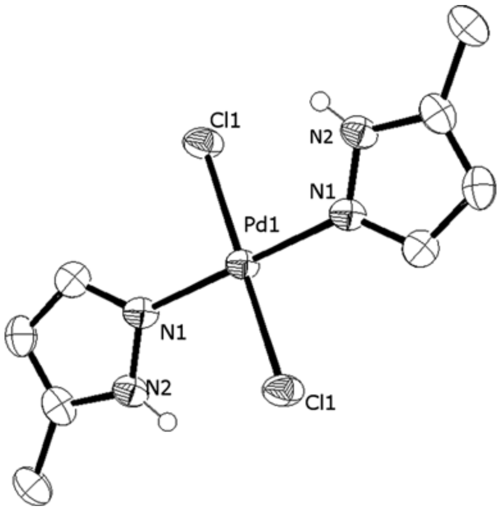

Figure 2. Molecular structure of **3** with thermal ellipsoids drawn at 50% probability level. All hydrogens except N–H are omitted for clarity. For selected bond lengths and angles see table 2.

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Co–Cl bond (2.81 and 2.52 Å, respectively). We did not find any reasonable justification in the literature, but the difference is probably due to the contamination of copper salt by bromine.

We were further interested to structurally characterize the 3-methylpyrazole complexes of Pd and Zn, and thus reacted two equivalents of 3-methylpyrazole with the corresponding MCl_2 [M = Pd (**3**); Zn (**4**)]. Complex **3** adopts square planar arrangement (figure 2), in which identical ligands are present in the *trans* position with respect to each other, adopting nearly identical bond angles [N–Pd–Cl 89.92(7)° and 90.08(7)°]. Likewise in **1** and **2**, the pyrazole ligands are *trans* to each other and prefer coordination through the second isomeric form (scheme 1). The observed Pd–N distance (2.018(2) Å) falls in the range observed for other Pd complexes [6(b)]. The Pd–Cl bond distance (2.298(8) Å) is shorter than the Pd–Cl bond distance reported for complexes bearing mixed ligands, including triarylphosphine. The difference so observed may clearly be traced to the difference in ligands attached to the Pd center [27, 28]. The geometry around the Pd center in **3** is more symmetrical if compared with other complexes containing the Pd–Cl moiety [27, 28], where the *trans* effect of the phosphine ligand causes major distortion. The crystals of **4** were small and led to poor data (*wR*2 23%), but still the connectivities were established and found in accord with the data obtained for the other structures as discussed above. Interestingly the Zn complex (**4**) also coordinates two pyrazole ligands in tetrahedral geometry (figure 3), according to the tendency and stability of Zn(II) tetrahedral complexes [29]. The average Zn–N bond length of 2.00 Å is in the range known for other Zn complexes [30].

5. Electrochemistry

For electrochemical characterization, cyclic and DP voltammetric techniques were used. The CVs of the compounds shown in figure 4 indicate that **1**, **2**, and **4** exhibit a single cathodic peak at −0.69, −0.81, and −0.71 V, respectively, with no corresponding anodic signal in the reverse scan. Hence, these compounds follow one-step irreversible reduction. On the contrary, **3** shows a two-step reversible redox behavior as evidenced by the appearance of two cathodic waves with corresponding anodic peaks in the reverse scan. In the positive potential window of GCE, all the compounds were stable as no oxidation peak appeared.

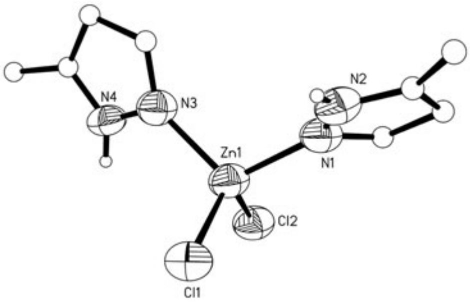

Figure 3. Molecular structure of **4** with 50% probability level with partial numbering scheme. Hydrogens (CH) are omitted for clarity. Selected bond lengths and angles are summarized in table 2.

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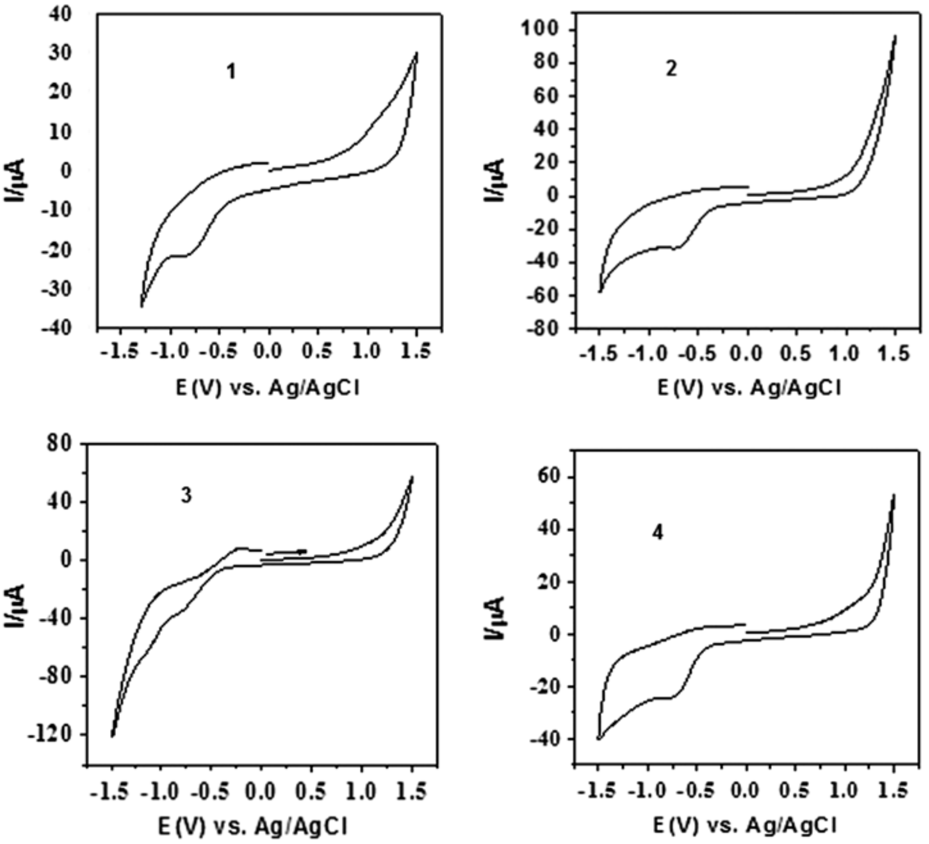

Figure 4. CVs of 2 mM solutions of **1–4** at scan rate of 100 mVs^{-1} at pH 4 using 50% ethanol and 50% BR buffer.

Table 3. Parameters determined from CV.

Parameters	**1**	**2**	**3**	**4**
D ($\mathrm{cm}^2\,\mathrm{s}^{-1}$)	3.15×10^{-6}	5.02×10^{-6}	4.6×10^{-6}	4.14×10^{-6}
K_s ($\mathrm{cm\,s}^{-1}$)	2.18×10^{-4}	3.6×10^{-4}	2.99×10^{-4}	2.86×10^{-4}
A	0.42	0.45	0.35	0.4
$\mathrm{Ep} - \mathrm{Ep}_{112}$ (mV)	114	106	136	119

The values of the diffusion coefficients (D) and heterogeneous rate constants (K_s) listed in table 3 were evaluated using Randles–Sevcik and Reinmuth equations [31, 32]. DPV is a sensitive electrochemical technique which can be reliably used for the determination of the involvement of protons during electron transfer reactions. The DP voltammogram of **3** is shown in figure 4. In the pH range 2–7, the peak shifts to more negative potentials with increasing pH of the medium, thus indicating the involvement of protons during the electron transfer reaction (figure 5, **2**) [33]. Similar behavior was observed for the other compounds under the same experimental conditions.

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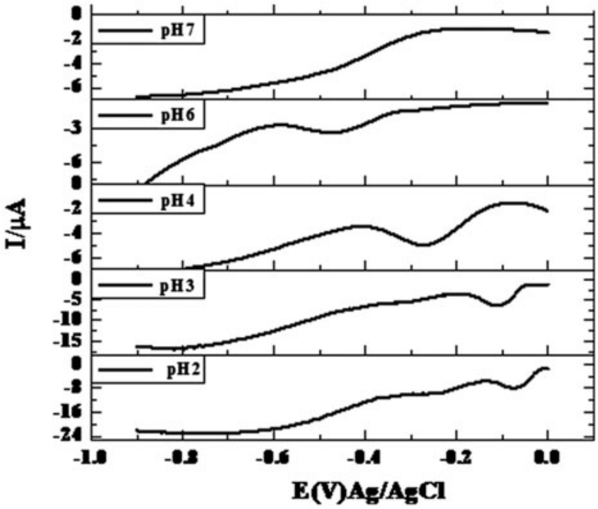

Figure 5. DP voltammograms of 2 mM solution of **2** recorded at 5 mVs^{-1} in pH 2–7.

6. Conclusion

The 3-methylpyrazole complexes of M(II) (M = Cu, Co, Pd, and Zn) are easily accessible as a result of reaction with MCl_2 salt. The corresponding mononuclear compounds were structurally characterized to elucidate the mode of coordination of the pyrazole derivative. The number of ligands coordinated, and thus the resulting geometry of the complexes, depends on the metal center. The CV results show that **1**–**4** in buffered aqueous ethanol media reduce at a GCE in a pH-dependent diffusion controlled manner. All the analytes were resistant to oxidation. CV shows irreversible nature of **1**, **2**, and **4** reduction, while **3** follows a two-step reversible redox behavior. Physical parameters like diffusion coefficient, rate constant, and charge transfer coefficient were determined. DPV showed the electron transfer reactions to be accompanied with the transfer of protons. The compounds so obtained bear the MCl_2 moiety, which makes the resultant compounds useful synthons for further transformation, especially for the development of supramolecular chemistry.

Supplementary material

The X-ray crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 980919 (**1**), CCDC 980920 (**2**), CCDC 980918 (**3**) and CCDC 980921 (**4**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

S.A.K. is grateful to Higher Education Commission (HEC) Pakistan for fellowship under “5000 indigenous PhD scholarships” at the University of Malakand and a six month fellowship under the "International Research Support Initiative Program" IRSIP as a graduate research trainee, Anorganische Chemie II, Universität Bayreuth, Bayreuth, Germany. We are also thankful to an anonymous reviewer for his valuable suggestions.

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