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Mendeleev Commun., 2018, **28**, 202–204
Mendeleev Communications

Dinuclear copper(II) complex with novel N,N′,N″,O-tetradentate Schiff base ligand containing trifluoromethylpyrazole and hydrazone moieties

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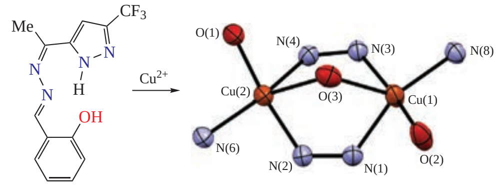
DOI: 10.1016/j.mencom.2018.03.032

A novel N,N′,N″,O-tetradentate Schiff base ligand was obtained by the condensation of salicylaldehyde and 5-(1-hydrazonoethyl)-3-(trifluoromethyl)pyrazole. Five-coordinated dinuclear copper(II) complex with this ligand was characterized by XRD analysis, magnetometry and voltammetry.

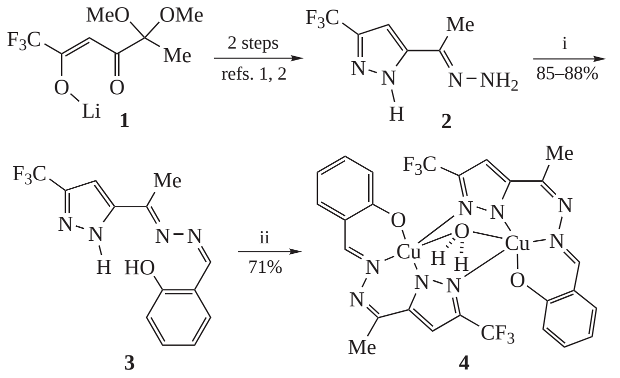


Wide-ranging application of Schiff bases in drug discovery and material science is well documented.[1] Due to their availability and strong metal-binding ability Schiff bases are highly in demand as ligands for coordination chemistry.[2] By variation of amino and keto counterparts it is possible to control the denticity of ligands, the nature of the donor atoms and the number of coordination centers. Transition metal complexes of Schiff bases have a great importance over the years due to their potential applications in industry, analytics and pharmacology.[3] Polynuclear copper(II) complexes are the efficient catalysts for C–H activation, oxidation and C–C cross-coupling reactions.[4,5] Dinuclear copper complexes with Cu–Cu distance of ~3 Å are interesting as corroborative models of the active site of catechol oxidase to elucidate the functional mechanism of the native enzyme and to develop the bio-inspired catalytic systems.[6] The redox potential of the physiologically accessible Cu^I/Cu^{II} couple varies dramatically depending on the ligand environment.[7] Dicopper(II) complexes represent the simplest case of magnetic interaction with only two unpaired electrons.[8] In this communication we described the preparation, structural characterization and electrochemical behavior of a novel dinuclear copper(II) complex based on original Schiff base.

Recently, we have elaborated a convenient synthetic approach to hydrazone-containing CF_3-pyrazole **2** starting from available lithium diketonate **1** bearing acetal fragment (Scheme 1).[9,10] We envisioned that the molecule of **2** could be effectively used in the construction of polydentate Schiff base ligands. In this context, hydrazones are of particular interest because they possess the enhanced hydrolytical and oxidative stability compared with that of imines.[1(*a*)] The condensation of pyrazole **2** with salicylaldehyde under reflux in ethanol gave Schiff base **3** without the use of acidic catalyst.[†] The structure of compound **3** was confirmed by NMR and elemental analysis data. Low-field signals of OH (δ ~ 11.1 ppm) and NH (δ ~ 14.3 ppm) groups in ^1H NMR spectrum indicate their participation in intramolecular H-bonding with hydrazone fragment of compound **3**.

Compound **3** represents a novel N_3O-tetradentate ligand with original structure. Pyrazole and salen moieties form the single coordination sphere through the deprotonation of pyrrole N atom and phenol group. At the same time, the additional coordination is possible *via* pyridine N atom of pyrazole thereby providing the formation of polynuclear metal complexes.[11] On the other hand, the ability of phenolate O atom to bridge metal ions often causes formation of dinuclear complexes.[11(*b*)] Therefore, there are two alternative possibilities to realize the multi-coordination with metal ions. In fact, the reaction of Schiff base **3** with $CuCl_2 \cdot 2H_2O$ in ethanol at room temperature produces a centrosymmetric dinuclear copper(II) complex **4** (see Scheme 1).[†] This reaction did not require the presence of a base in the reaction media to deprotonate NH group of pyrazole core or hydroxyl group of Schiff base. However, the choice of copper salt plays a crucial role in the synthesis of complex **4**. For example, when copper(II) acetate was used instead of copper(II) chloride, the complex formation was not observed under TLC monitoring.

According to XRD analysis data, compound **4** represents a neutral dinuclear complex $[Cu_2L_2(H_2O)]$, where L is deprotonated



Scheme 1 *Reagents and conditions*: i, salicylaldehyde, EtOH, ~20 °C, 2 h; ii, $CuCl_2 \cdot 2H_2O$, EtOH, ~20 °C.

[†] For synthesis and characteristics of 5-{1-[2-(hydroxybenzylidene)hydrazono]ethyl}-3-trifluoromethylpyrazole **3** and bis(5-{1-[2-(oxidobenzylidene)hydrazono]ethyl}-3-trifluoromethylpyrazol-1-yl)dicopper(II) monohydrate **4**, see Online Supplementary Materials.

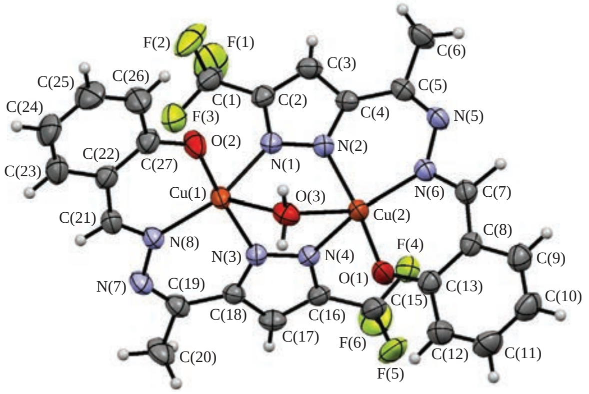


Figure 1 ORTEP view of dinuclear copper(II) complex **4**. Displacement ellipsoids are shown at the 50% probability level.

ligand **3** (Figure 1).[‡] Each Cu^{II} ion is five-coordinated by the three O,N,N′-donor atoms of one ligand, the N-donor atom from the second ligand and O atom of a bridging water molecule occupying the apical position. The Addison parameter (τ_5),[12] which is an index of distortion from square-pyramidal to trigonal-bipyramidal geometry, is 0.31 (see Online Supplementary Materials), thus indicating that both Cu^{II} centers in complex **4** adopt a distorted square-pyramidal geometry. Each ligand forms two six-membered chelate rings fused across the Cu^{II} ion. Two [CuL] units are linked by N$_{py}$ atoms of pyrazole moiety and O atom of bridging water molecule to construct the [Cu$_2$L$_2$(H$_2$O)] complex. In [CuL] chelate, the Cu^{II}–N$_{py}$ bond (~2.05 Å) is somewhat longer than Cu^{II}–N$_{pz}$ one (~1.93 Å). The intramolecular non-bonding Cu(1)–Cu(2) distance is 3.505 Å. The crystal packing is stabilized through the intermolecular hydrogen bonds OH···N between water molecule and N atoms of hydrazone group of the adjacent complex molecules (Figure 2, Table 1).

Table 1 Hydrogen-bond geometry in dinuclear copper(II) complex **4**.

Hydrogen bond D–H···A	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/deg
O(3)–H(3A)···N(7)	0.86	2.29	3.020	143
O(3)–H(3B)···N(5)	0.86	2.30	2.935	131

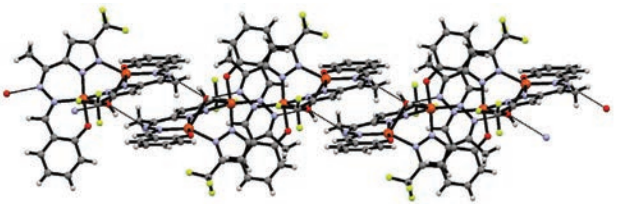


Figure 2 View of the 2D supramolecular structure of the Cu^{II} complex **4**.

The solid-state FT-IR spectrum of ligand **3**, in addition to the bands attributed to the aliphatic and aromatic C–H and C–F stretching vibrations, contains characteristic bands of hydrazone and pyrazole moieties, which appears in the range of 1626–1559 cm^{-1}. In the spectrum of Cu^{II} complex **4**, these bands are low-frequency shifted to 1619–1527 cm^{-1}, thereby indicating the coordination of ligand nitrogen atoms with metal ion. The absence of intense high-frequency absorption bands corresponding to the stretching vibrations of OH and NH groups also confirms the complexation through N$_3$O-coordination mode. However, the appearance of a wide low-intensity absorption band in the field of ~3330–3400 cm^{-1} indicates the presence of water molecule participating in intermolecular interactions in complex **4**. The bands at 556 and 472 cm^{-1} corresponding to ν(Cu–N) and ν(Cu–O), respectively, are also detected for the Cu^{II} complex.

Temperature dependence of the effective magnetic moment (μ_{eff}) is shown in Figure 3.[§] The μ_{eff} value is 2.20 μB at 300 K and decreases with lowering temperature down to 0.07 μB at 2 K. The high temperature value is somewhat lower than theoretical spin only value of 2.45 μB for two non-interacting Cu^{II} ions with spins $S = 1/2$. Decrease in the μ_{eff} with lowering temperature indicates the presence of antiferromagnetic exchange interactions between spins of Cu^{II} ions. A remnant value of the μ_{eff} at low temperature is due to a small amount (~0.2%) of paramagnetic admixture. In accordance with the XRD analysis data, the model for exchange coupled dimer (spin Hamiltonian $H = -2JS_1S_2$) was used for the analysis of the experimental $\mu_{eff}(T)$ dependence. The best fit values of g-factor and exchange coupling parameter J are 1.99(±0.01) and –68.0(±0.4), respectively.

The cyclic voltammograms of 0.005 M solutions of ligand **3** and its complex **4** recorded in the range of potentials 0.8 to –1.2 V are shown in Figure 4.[¶] Ligand **3** is electro-inactive in the studied potential region. In the cathode branch of the

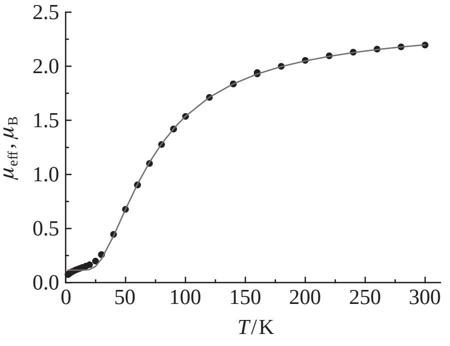


Figure 3 The $\mu_{eff}(T)$ dependence for the Cu^{II} complex **4**. Solid line is theoretical curve.

[‡] The XRD experiment for the single crystal of C$_{26}$H$_{20}$Cu$_2$F$_6$N$_8$O$_3$ was accomplished on an Xcalibur 3 diffractometer by standard procedure [MoKα-irradiation, graphite monochromator, ω-scans with 1° step at 295(2) K]. Empirical absorption correction was applied. Using Olex2,[13] the structure was solved with the ShelXS[14] structure solution program using Direct Method and refined with the ShelXL[13] refinement package using least-squares minimization. All non-hydrogen atoms were refined in the anisotropic approximation; H-atoms were added in the calculated positions and refined in the ‘rider’ model.

Crystal data for **4**. C$_{26}$H$_{20}$Cu$_2$F$_6$N$_8$O$_3$, $M = 733.58$, triclinic, $a = 8.6169(5)$, $b = 13.5327(6)$ and $c = 13.9359(7)$ Å, $\alpha = 115.897(5)°$, $\beta = 105.431(4)°$, $\gamma = 92.827(4)°$, $V = 1383.26(12)$ Å^3, $T = 295(2)$ K, space group $P\bar{1}$, $Z = 2$, μ(MoKα) = 1.624 mm^{-1}, 14300 reflections measured, 7574 unique (R_{int} = = 0.0347) which were used in all calculations. The final $R_1 = 0.0784$, $wR_2 = 0.1499$ (all data) and $R_1 = 0.0459$, $wR_2 = 0.1174$ [$I > 2\sigma(I)$]. Largest diff. peak/hole: 0.54/–0.63 e Å^{-3}.

CCDC 1574959 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] The magnetic susceptibility of the polycrystalline sample was measured with a Quantum Design MPMSXL SQUID magnetometer in the temperature range 2–300 K with magnetic field of up to 5 kOe. Field dependence of molar magnetization at 2 K is linear. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

[¶] Cyclic voltammograms were recorded using Autolab PGSTAT128N with three electrodes cell [3 mm diameter glassy carbon disc working electrode (Metrohm 6.1204.110), glassy carbon rod auxiliary electrode and Ag/AgCl as reference electrode (Metrohm 6.0726.100) were used]. The glassy carbon working electrode was cleaned with alumina polish prior to each scan. 0.1 M [Bu$_4$NH$_4$]$^+$BF$_4^-$ solution in DMF was used as supporting electrolyte. The solutions were deoxygenated by purging with argon for 5 min before measuring.

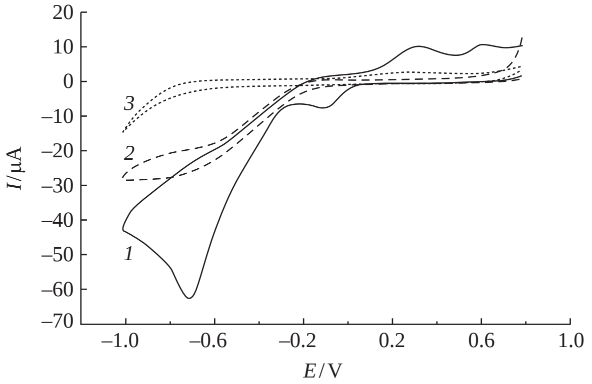


Figure 4 Cyclic voltammograms of solutions of (*1*) complex **4**, (*2*) ligand **3** and (*3*) supporting electrolyte (0.1 M $[\mathrm{Bu_4N}]^+\mathrm{BF_4^-}$ in DMF) recorded using a disc glassy carbon electrode, scanning sweep is 100 mV s^{-1}.

cyclic voltammograms of the complex **4**, two recovery peaks are observed at potentials of –0.08 and –0.68 V. In the anodic branch there are two oxidation peaks at 0.32 and 0.62 V. The obtained voltammograms demonstrate a probable sequential two-step electroreduction of the central Cu$^{\mathrm{II}}$ atoms to Cu$^{\mathrm{I}}$ (peak at –0.08 V) and Cu$^{\mathrm{I}}$ to Cu^0 (peak at –0.68 V). The irreversibility of the reduction process is presumably due to the chemical reaction of reduced species that occurs after the electron transfer.

In summary, a polydentate Schiff base was synthesized by the reaction of trifluoromethylated pyrazole bearing hydrazone moiety with salicylaldehyde. A dinuclear copper(II) complex was obtained with the participation of N,N′,N″,O-coordination mode of the ligand. The redox potentials of copper(II) complex were determined.

This work (synthetic part and structure characterization) was supported by the Russian Foundation for Basic Research (grant no. mol_a_dk 16-33-60048). The electrochemical investigations were supported by the Russian Science Foundation (project no. 17-13-01096). ASB is grateful to the FASO (0333-2017-0001). BDN acknowledges the State Program for Supporting of Leading Scientific Schools of the Russian Federation (grant no. NSh-8922.2016.3). VIS is grateful to the Ural Branch of the Russian Academy of Sciences (grant no. 18-3-3-16).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.032.

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Received: 26th September 2017; Com. 17/5357