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Two new copper(II) binuclear complexes with 2-[(E)-(pyridine-2yl-hydrazono)methyl]phenol: Molecular structures, quantum chemical calculations, cryomagnetic properties and catalytic activity



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ABSTRACT

The Schiff base is synthesized by the reaction of 2-hydrazinopyridine and salicylaldehyde. The copper(II) 2-[(E)-(pyridine-2yl-hydrazono)methyl]phenol (HL), were synthesized and characterized using various physicochemical techniques. The molecular structures of both binuclear complexes were evaluated by single-crystal X-ray analysis. Analysis of the supramolecular synthons and their effect on crystal packing is conferred in the context of crystal engineering. The electron paramagnetic spectra are reported as well. The electrochemical behavior of both complexes was explored using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The electronic and spectral properties are described by quantum chemical calculations (TD and DFT).The cryomagnetic investigation (2-300 K) reveal antiferromagnetic exchange coupling between two copper(II) centres of different strength: $J_{CuCu} = -21.6$ and $J_{CuCu} = -6.8$ cm⁻¹ for 1 and 2, respectively. The strong antiferromagnetic coupling between the copper centers found in 1 could be explained not only by magnetic exchange through hydrogen bonds but also through the π - π stacking of the Schiff base ligands. Both binuclear complexes exhibit catalytic activity toward the dismutation of superoxide anion at physiological pH. Although the activity in both complexes is lower than the native enzyme, they have potential as antioxidant SOD model for pharmaceutical applications.

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1. Introduction

The design of binuclear complexes using tridentate Schiff bases and bridging ligands have been carried out by many inorganic chemists [1–6]. The binuclear metal complexes with chelate ligands such as tridentate Schiff bases are interesting to study to mimic the biological properties of Cu-Zn superoxide dismutase [7]. In particular, copper(II) binuclear complexes are of significance owing to their structural versatility, and variety of magnetic couplings they can present [8–14]. Supramolecular interactions such as hydrogen bonds and π - π stacking show an important role in crystal engineering as they advance to directional molecular recognition

* Corresponding author. *E-mail address:* patelsatish33@yahoo.co.in (S.K. Patel). developments between molecules and therefore mediate selfassembly of defined supramolecular synthons [15]. The role of hydrogen-bonded supramolecular synthons is approved in crystal engineering [16]. Copper complexes have been studied extensively mainly because of its biologically relevant redox properties and to mimic the functions of proteins [7,15–20].

The metal complexes used in the study were binuclear copper (II) complexes **1** and **2** having a Schiff base ligand 2-[(E)-(pyridine-2yl hydrazono)methyl]phenol (HL), with one pyridine, one imine, one phenolic donor groups, and bridging pyrazine or perchlorate attached to it. The coordination behavior of transition metals with azo ligands (-C=N-NH- or -C-N=N-) is of importance for their π -acidity, functional coordination modes, and molecular structures, dye and pigmenting behavior, redox, photophysical and biological properties [21,22]. These properties are ascribed to the low-lying π^* orbitals of azo functionality. Hydrazones are an

example of azo chelate ligands. The coordination chemistry of hydrazone ligands is continuing to be an interesting field of research. Hydrazone is a class of compounds that have potential applications as catalysts [23,24], molecular sensors [25], luminescent probes [26], and also as therapeutic agents [27]. The biological properties and diversity of binding modes of such ligands inspired us to explore the nature of coordination as well as the structural features of binuclear copper(II) complexes with 2-[(E)-(pyridine-2yl hydrazono)methyl] phenol ligand. Both redox and cryomagnetic data were explored. Molecular structures of the present complexes were determined using a single-crystal X-ray diffraction technique. Further, both complexes were characterized by different physicochemical techniques viz., elemental analysis, infrared (IR), and UV-visible (UV-vis) spectroscopy and electrochemical techniques like cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Both complexes were also studied using electron paramagnetic resonance spectroscopy (EPR) and cryomagnetic technique. These two techniques are widely used for the identification and characterization of paramagnetic transition metal complexes [21,22,28-30]. Binuclear transition metal complexes show significant structural variation and can act as potent magnetic materials. These techniques enable important insight and binding properties of such transition metal complexes. Their antioxidant properties were also studied and it was demonstrated that copper(II) ion plays a key role in the mechanism of activity. Determination of the antioxidant activity in the reaction with superoxide radical-anion O_2^{-} is the most perspective approach.

We have already reported transition metal mono- and binuclear complexes bearing NNO/NOO donor set [5,31–33]. Thus, in continuation of these studies bearing similar donor set with heterocyclic bases, we report here the synthesis, structural characterization and electrochemical studies of copper(II) complexes with a new hydrazone Schiff base ligand 2-[(E)-(pyridine-2yl-hydrazono)methyl] phenol (HL) obtained from the condensation of 2-hydrazinopyridine and salicylaldehyde. Multinuclear metal clusters comprise a small subset of a larger family of metal-based supramolecular assemblies. The self-assembly of supramolecular structures compressed via metal-ligand coordinate bonds along with other weak interactions continues to attract considerable attention [34-36]. Of particular relevance to the present work are the many supramolecular complexes that utilize ligands which contain a pyridyl moiety. As a result, several supramolecular metal(II) complexes are well documented in the literature [37-40].

2. Experimental section

All used reagents and chemicals were of reagent grade. 2-hydrazinopyridine, salicylaldehyde, and copper(II) salts were purchased from Across Organics and used as supplied.

3. Caution

Although no problems were encountered during the synthesis of copper(II) complexes, perchlorate salts are potentially explosive and must be handled with extreme care.

3.1. Synthesis of Schiff base ligand (HL)

The Schiff base (HL) was synthesized according to the reported method [41,42]. The Schiff base 2-[(E)-(pyridine-2yl-hydrazono) methyl]phenol (HL) was synthesized by the condensation of 100 mL of 2-hydrazinopyridine (1.091 g, 10 mmol) and salicylalde-hyde (0.8 mL, 10 mmol) in presence of glacial acetic acid (0.5 mL, 10 mmol) in ethanol (20 mL). The reaction mixture was refluxed in a water bath for 3 h. The resulting pale yellow coloration

indicated the formation of the Schiff base ligand precursor (HL). During this period a yellow solid slowly precipitated. The solid mass was filtered, recrystallized from ethanol and characterized by analytical and spectral techniques. Yield: ~83%. Anal. Calcd. (%) for C₁₂H₁₁N₃O (M = 213.23 g mol⁻¹): C, 67.60; H, 5.20; N, 19.70. Found: C, 67.53; H, 5.02; N, 19.94. FT-IR bands (KBr, cm⁻¹) v(C=N) 1654 m, v(-OH) 3186b, v(-NH-) 2988 m (Fig. S1). ¹H NMR (CDCl₃, 400 MHz) δ = 10.73 (Ar-OH), 7.96 (CH = N) and 7.68 (-NH-), 7.26 (2H, py), 7.22 (4H, py), 6.96 to 6.85 (Ar-H) (Fig. S2).

3.2. Synthesis of $[Cu_2(\mu - ClO_4)(L)_2(H_2O)_2](ClO_4) \cdot H_2O(1)$

To a 20 mL methanolic solution of HL (0.213 g, 1 mmol), copper perchlorate hexahydrate (0.370 g, 1 mmol) was added and stirred for 2 h at room temperature. The green solution was left undisturbed fora few days for evaporation at ambient temperature to get green crystals. These green crystals were filtered off, washed with ether, and dried in a desiccator over calcium chloride. Yield: ~73%. Anal. Calcd. (%) for C₂₄H₂₆Cl₂Cu₂N₆O₁₃ (M = 804.49 g mol⁻¹): C, 35.83; H, 3.26; N, 10.45. Found: C, 35.63; H, 3.18; N, 10.64. Conductance (Λ_m /s cm² mol⁻¹) in DMSO 123. Electronic absorption spectrum in DMSO (λ_{max} , 648 nm ε , 167 M⁻¹ cm⁻¹). FT-IR bands (KBr, cm⁻¹): ν (C=N) 1563, ν (C=O) 1611, ν (ClO₄⁻) 1077 (Fig. S1).

3.3. Synthesis of $[Cu_2(\mu-pyrazine)(L)_2](ClO_4)_2(\mathbf{2})$

To a 20 mL methanolic solution of HL (0.213 g, 1 mmol) copper (II) perchlorate hexahydrate (0.370 g, 1 mmol) was added with constant stirring. After 20 min pyrazine (0.040 g, 0.5 mmol) was added to the above solution with stirring. The resulting green solution was left for few days undisturbed for evaporation at ambient temperature to obtain green crystals. The crystals were collected by filtration and dried over calcium chloride desiccator. Yield: ~73%. Anal. Calcd (%) for $C_{28}H_{24}Cl_2Cu_2N_8O_{10}$ (M = 830.53 g/mol): C, 40.49; H, 2.91; N, 13.49. Found: C, 40.06; H, 2.48; N, 13.54. Conductance (Λ_m /s cm² mol⁻¹) in DMSO 235. The electronic absorption spectrum in DMSO (λ_{max} , 638 nm ε , 168 M⁻¹ cm⁻¹).FT-IR bands (KBr, cm⁻¹): v(C=N) 1561, v(C=O) 1610, $v(ClO_4)$ 1075 (Fig. S1).

4. Physical measurements

Elemental analyses were performed at SAIF, CDRI, Lucknow. The UV-vis spectra were recorded on a Shimadzu UV-1601. The Fourier transform infrared (FTIR) spectral data were obtained on a Perkin-Elmer IR α -T spectrophotometer. NMR spectra of ligand were recorded on a Bruker Avance III 400 MHz spectrometer. TMS was used as an internal standard. The electron paramagnetic resonance (EPR) spectra of copper(II) complexes in solid and solutions were measured on Varian E-line Century Series Spectrometer operating at X-band (9.25 G Hz) modulation frequency at room and low temperatures. The EPR spectra were calibrated with tetracyanoethylene(TCNE) as a field marker. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed with a BAS-100 electrochemical analyzer under a dry nitrogen atmosphere. Ag/AgCl electrode was used as the reference electrode and ferrocene as an internal standard in cyclic voltammetry [43]. Before the electrochemical measurements, a glassy carbon working electrode was polished, rinsed with distilled water, washed with DMSO, and dried. Magnetic susceptibility measurements were performed using a Quantum Design MPMSXL SQUID magnetometer operating under an applied *dc* magnetic field of 5000 Oe in the 2–300 K temperature range. Finely ground crystals of 1 (28.64 mg) and 2 (10.45 mg) were employed for the measurements. The data were corrected for the sample holder, the intrinsic

diamagnetic contributions of the compounds, and the temperature-independent paramagnetism.

4.1. X-ray crystallographic studies

Suitable air-stable single crystals for X-ray diffraction were obtained by slow cooling of methanolic solutions containing **1** and **2**. The X-ray diffraction data were measured on a Bruker D8 Venture diffractometer at 100(2) K. The intensity data were corrected for absorption. All non-hydrogen atoms were refined anisotropically. The structures were solved by the direct method [44] and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [45]. All geometrical calculations were performed using PLATON [46] and WINGX [47] programs. The hydrogen atom positions were initially estimated by geometry with anisotropic displacement data.

4.2. Biological (SOD) activity

The superoxide dismutase activity of complexes **1** and **2** was assayed by its ability to inhibit the reduction of nitroblue tetrazolium by alkaline DMSO in phosphate buffer solution [48–50]. The course of the reaction was monitored spectrophotometrically at 560 nm. A unit of antioxidant SOD activity is the concentration of the complex, which causes 50% (IC₅₀) inhibition of alkaline DMSO and mediated reduction of NBT. The catalytic rate constants were calculated as $K_{McCF} = K_{NBT}[NBT]/IC_{50}$, where $K_{NBT}(pH7.8) = 5.94 \times 10^4 M^{-1}S^{-1}$ [51,52].

4.3. Computational method

All DFT calculations were performed starting from the singlecrystal X-ray data. Theoretical calculations were performed regarding molecular structure optimization and HOMO-LUMO energies of complexes 1 and 2. All calculations were performed with the GAUSSIAN09 program [53], with the aid of the Gauss View visualization program. Full geometry optimizations were carried out using the density functional theory (DFT) method at the B3LYP level [54]. All elements except Cu were assigned the LANL2DZ basis set [55]. LANL2DZ with effective core potential for Cu atom was used [56]. The vibration frequency calculations were estimated to ensure that the optimized geometries represented the local minima and that there was only positive Eigenvalue. In the computational model, the cationic complex was taken into account. Vertical electronic excitations based on B3LYP optimized geometries were evaluated using the time-dependent density functional theory (TDDFT) formalism [57] in DMSO, using a conductor-like polarizable continuum model (CPCM) [58].

5. Results and discussion

5.1. Synthesis and general characterization

The synthetic route to prepare the Schiff base (HL) and the copper(II) complexes **1** and **2** are shown in Scheme 1. The formation of the Schiff base ligand precursor 2-[(E)-(pyridine-2yl hydrazone) methyl]phenol (HL) is supported by elemental analyses and infrared (IR) spectroscopy. The IR spectrum of HL shows v(N-H) at ~ 2990 cm⁻¹. The IR band at 1654 cm⁻¹ indicates the presence of an imine group as a result of the condensation of 2-hydrazinopyridine with salicylaldehyde. The absence of the bands at 3335 and 3305 cm⁻¹due to asymmetric and symmetric for $-NH_2$ stretching bonds modes indicates that the primary amine group of 2-hydrazinopyridine has completely condensed with the carbonyl group of salicylaldehyde. The most conclusive evidence that

supports the condensation of 2-hydrazinopyridine with salicylaldehyde is the single-crystal X-ray structures of **1** and **2** which demonstrate the coordination of the deprotonated Schiff base (L⁻)to the copper(II) center. Elemental analysis and FTIR data of **1** and 2 are consistent with the proposed formulae. The molar conductance data reveal the ionic nature of both complexes, 1 and 2, in accordance with the proposed formulations. Both complexes retain the band corresponding to v(N-H) with small shifts. The infrared spectra of both complexes **1** and **2** display a IR band at 1625 cm⁻¹ which could be assigned to azo (>C=N) stretching frequencies of the coordinated Schiff base (L⁻). The shift of this band on complexation towards lower frequency with respect to the free ligand also points out the coordination of the N-atom of the azomethine group. The coordination of the Schiff base is also substantiated by a band in the range \sim 410–490 cm⁻¹ for both complexes corresponding to M–O and M–N stretching vibrations [59]. The splitting of bands at 1210, 1121, 1000, and 911 cm⁻¹ indicates the presence of coordinated perchlorate in complex 1whereas in complex 2 the bridging mode of pyrazine is observed at 554 and 708 cm^{-1} [59,60]. Both complexes exhibit the presence of bands at 1092, 1012, 790 and 696, for complex 1, and 1091, 1013, 789, and 702 cm⁻¹, for complex **2**, that indicate a T_d symmetry of

5.2. Molecular geometries and supramolecular features: A crystallographic study

 ClO_4^- and suggest the presence of ionicClO_4^- [61,62].

The molecular structures of 1 and 2 were determined by singlecrystal X-ray diffraction (SCXRD) technique and ORTEP diagrams are shown in Figs. 1 & 2. The crystallographic parameters, bond angles, and bond parameters are presented in Tables 1-2 respectively. The molecular structure of 1 reveals that it is a binuclear perchlorate-bridged complex. Each of the subunits involves deprotonated tridentate (NNO) Schiff base ligand and one water molecule. In this complex two subunits are connected by bridging perchlorate anion. The copper-copper distance remains 4.867 Å, which is similar to other similar perchlorate bridged complexes [63]. As a result of the overall, the coordination in each copper(II) center is pentacoordinate and geometry of both copper(II) centers is distorted square pyramidal with $\tau = 0.1$ for Cu(1) and Cu(2), $[\tau = (\beta - \alpha)/60$, where, β and α are the two largest angles around the center atom; $\tau = 0$ and 1 for the perfect square pyramidal and trigonal bipyramidal geometries [64]. In complex 1 the square base of each copper(II) center is comprised by NNO of Schiff base (L⁻), with bond distances in the range 1.9086–1.968 Å and one oxygen atom of coordinating water molecule at a distance of 1.9590 Å, whereas the apical site is occupied by the oxygen atom of perchlorate anions at a longer distance of 2.4061 Å. For the coordination sphere of Cu(2), atoms O1B, N1B, N3B, and O2W define the basal plane while perchlorate O12 [Cu(2)-O(12) 2.9251(2) Å] occupies the axial position which is a short contact. The copper atom from the basal plane is shifted by 0.116 Å towards the axially bound perchlorate anion.

The model of this complex constitutes many inter- and intramolecular hydrogen bonds. These hydrogen bonds are responsible for forming various heterosynthons viz., $R_2^1(6)$, $R_2^2(6)$, $R_2^2(8)$ and $R_6^6(3)$. These graph set motifs (heterosynthons) are shown in Fig. 1(b). In the crystal packing of **1**, the O2W and C7A atoms are intermolecularly hydrogen-bonded to perchlorate oxygen atoms (O22 and O21) via a pair of O2W-H2W1···O22 and C7-H7AA···O21 hydrogen bonds leading to the formation of inversion dimmers of the dimer with $R_6^6(34)$ graph set motif (cyclic dimmers) [65] (Fig. 1b). Such hydrogen bonds are also responsible for dimer like association, function, and dynamics of biological and chemicals



Scheme 1. Synthetic route of HL and complexes 1 and 2.

models [66]. The hydrogen bonds are given in Table S1. These various hydrogen bonds form the supramolecular network (Fig. S3).

The comparison of bond distances Cu(1)-O(11) [2.4061 (18)A] and Cu(2)-O(12) [2.925 (2)A] confirms the possibility of a bridging dinuclear structure. The Cu-N and Cu-O bond distances are smaller 1.969(2), 1.948(2) and 1.9086(18 A) suggesting the domination of the deprotonated Schiff base (L⁻) in bonding. It is found that Cu-N pyridyl bonds are 0.021-0.042 A larger than Cu-N imine bonds showing the strength of azomethine nitrogen coordination. The unit cell packing diagram of complex **1** viewed along the *a*-axis is shown in Fig. 1(d). It is clear from the packing diagram that the molecules are packed in a two-dimensional manner with two coordinated water molecules.

The structure of complex 2 is different from that of 1 with respect to the coordination environment of the copper(II) center. In this complex, each copper atom has distorted square planar geometry. In each subunit, the copper center is coordinated by one pyridine nitrogen, one imine nitrogen, and one phenolic oxygen atom of the tridentate deprotonated Schiff base (L⁻) and the nitrogen atom of bridged pyrazine ligand. Some of the angles around the copper(II) center $\sim 172^\circ$ and $\sim 87^\circ$ indicating a distorted square planar geometry around each copper(II) center [67,68]. Also, bond angles are around copper centers deviate from 90° confirming a distorted square planar geometry for this binuclear complex. Yang and co-workers [69] have suggested the geometry index (τ_4) for four coordinate complexes $\tau_4 = \frac{360-(\alpha+\beta)}{141^\circ}$, where α and β are the two largest angles in the four coordinate species subtracted from 360°, all divided by 141° A perfect tetrahedral structure yields $\tau_4 = 1$ while a square planar structure gives $\tau_4 = 0$. The $\tau_4 = -0.2-0.3$ of this complex reflects the distorted square planar geometry. The Cu-Cu distance in a dinuclear unit is 6.807A, which is in agreement with those reported in the literature [70]. The bite angles $N(1) - Cu - N(3) = 82.42(8)^{\circ}$ and $O(1) - Cu - N(3) = 92.06(7)^{\circ}$ are generated by the chelating of deprotonated Schiff base (L⁻) [71]. Two noncoordinated perchlorate anions are present to neutralize the charge of the complex. These anions are located at both side of the cation in such a way that it forms symmetric hydrogen bonds(C13 - H13A...O11, C7 - H7A...O12 and N2 - H2B...O13) leading to the formation of inversion dimers with $R_2^2(8)$ and $R_4^4(34)$ graph-set ring motif (cyclic dimmers) [65] (Fig. 2b). The cohesion of packing in **2** is further insured by Cl-O- $C_g[\pi]$ weak contracts.

Lone pair-aryl $\pi(lp \cdots \pi)$ interactions are operated by lone pair electrons of oxygen atoms of ionic perchlorates and π electrons of bridging pyrazine ligand (Fig. 2c). These lp – $\pi(aryl)$ interactions are also responsible for dimer like association, function, and dynamics of biological and chemical models [66]. The unit cell diagram of complex **2** shown along the *b*-axis is shown in Fig. 2(d). In this diagram, it can be observed that the molecules are in a twodimensional manner with parallel arrangements of the rings with two ionic perchlorates.

5.3. EPR spectroscopy

The X-band electron paramagnetic resonance (EPR) spectra of both complexes in polycrystalline solids at room temperature (RT) and in DMSO $(3.0 \times 10^{-3} \text{M})$ solutions at liquid nitrogen temperature (LNT) were recorded to obtain information about the nuclearity and coordination geometry in the complexes (Fig. 3). The epr spectra of both complex **1** and **2** in polycrystalline samples are typical of *S* = 1 systems [72,73]. The polycrystalline samples at RT exhibit the expected spectral features of singlet–triplet transition ($\Delta M_s = \pm 2$) at a low magnetic field ($g_e \approx 4$) [74]. These











(c)

Fig. 1. (a) ORTEP view of 1, (b) partial packing diagram (dimer of dimer model), and (c) packing diagram along *a*-axis.













Fig. 2. (a) ORTEP view of complex **2**, (b) partial packing diagram (dimer of dimer model) showing H-bondings with synthons, (c) $lp - \pi(aryl)$ centroid interactions, and (d) packing diagram with ionic perchlorate.

Table 1

Crystal data and structure refinement parameters of synthesized copper(II) complexes.

Empirical formulaC24 H26 Cl2 Cu2 N6 O13Formula weight804.49	C ₂₈ H ₂₄ Cl ₂ Cu ₂ N ₈ O ₁₀ 830.53 100(2)
Formula weight 804.49	830.53 100(2)
	100(2)
Temperature (K) 100(2)	0.71072
Wavelength (Å) 0.71073	0.71073
Crystal system Triclinic	Triclinic
Space group P-1	P-1
a (Å) 8.0343(3)	6.7110(3)
b (Å) 11.2399(5)	10.8068(4)
c (Å) 17.2657(7)	11.1131(4)
α (°) 105.094(3)	99.618(3)
β (°) 100.673(3)	94.535(3)
γ (°) 92.804(3)	106.393(3)
Volume (Å ³) 1471.56(11)	755.52(5)
Z 2	1
Density (calculated) (Mg/ 1.816 m ³)	1.825
Absorption coefficient 1.705 (mm ⁻¹)	1.659
F(000) 816	420
Theta range for data 1.248 to 30.628 collection (°)	2.004 to 33.271
Index ranges $-11 \le h \le 11$,	−10≤ <i>h</i> ≤10,
<i>−</i> 16≤ <i>k</i> ≤16, <i>−</i> 24≤ <i>l</i> ≤24	<i>−</i> 16≤ <i>k</i> ≤16,
	<i>−</i> 17 <i>≤l≤</i> 17
Reflections collected 50,750	21,193
Independent reflections 9056 [R(int) = 0.0719]	5762 [<i>R</i> (int) = 0.0612]
Completeness to 100.0% theta = 25.242°	99.6%
Absorption correction None	None
Refinement method Full-matrix least-	Full-matrix least-
squares on F ²	squares on F ²
Data/ 9056/9/456	5762/0/226
restraints/parameters	
Goodness-of-fit on F^2 1.050	1.017
Final R indices [I greater $R1 = 0.0398$,	R1 = 0.0480,
than 2sigma(<i>I</i>)] w <i>R</i> 2 = 0.0931	wR2 = 0.0876
R indices (all data) $R1 = 0.0672$,	R1 = 0.0898,
wR2 = 0.1016	wR2 = 0.1006
Extinction coefficient n/a	n/a
Largest diff. peak and hole 0.680 and -0.777 (e·Å ⁻³)	0.755 and -1.231

observations are in agreement with the antiferromagnetic interaction between the copper(II) ions in the binuclear complexes [5,75–79]. In spin coupled systems, spin Hamiltonian parameter (H) for an S = 1state interacting with a magnetic field (H) is given as:

$$H = g\beta H_s + DS_z^2 + E(S_x^2 - S_y^2) - (2/3)D$$

where *D* and *E* are the zero-field splitting parameters. The values for $g_{\parallel}, g_{\perp}, D$ and E which fit with experimental X-band spectra of bridged systems are presented in Table 4. The values for both complexes are in the range. Thus, EPR spectra are in agreement with the geometry confirmed by single-crystal X-ray analysis. The exchange parameter G, which characterizes the exchange interaction between copper centers in polycrystalline compounds, was estimated using the expression $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ [76–82]. The estimated *G*, values for **1** and **2** are less than 4 (G < 4), suggesting that there is an exchange interaction between copper centers (Table 3). The low values of G of both complexes indicate a $d_{x^2-v^2}$ the ground state has a weak exchange coupling which may be propagated through $[Cu - N_2/O_2Cl - Cu]$ cores [83,84]. The low-temperature EPR spectra of samples dissolved in DMSO indicate the existence of different species in solution and yielded the values $(g_{\scriptscriptstyle \parallel}>g_{\scriptscriptstyle \perp}>g_{\scriptscriptstyle e})$ for 1 and **2** consistent with the $d_{x^2-y^2}$ ground state for copper(II) ions typical for square pyramidal and square planar geometry [85-87] (Fig. 3).

The EPR parameters g_{\parallel} , g_{\perp} and A_{\parallel} (cm⁻¹) and d-d energies were used to estimate the bonding parameters (α^2 , β^2 and γ^2). These bonding parameters are used to measure the covalency in the inplane σ -bonding, in-plane π -bondings and out-of-plane π -bondings. The orbital reduction factors (K_{\parallel} and K_{\perp}) were also estimated for the present complexes. The value of $K_{\parallel} \simeq K_{\perp} \simeq 0.77$ is for pure sigma bonding [88] and in-plane π -bonding, $K_{\parallel} < K_{\perp}$, while for out-of-plane π -bonding $K_{\perp} < K_{\parallel}$. In both complexes, it is found that $K_{\parallel} < K_{\perp}$ which indicates in-plane π -bonding. Other bonding parameters (α^2 and β^2) value is found to be less than 1.0 and therefore indicating the covalent nature of the bonds.

5.4. Electrochemical studies

The electrochemical studies of both complexes 1 and 2 were examined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV)in DMSO $(3.0 \times 10^{-3} \text{M})$ in the presence of 0.1 Mtetrabutylammonium perchlorate (TBAP) as the supporting electrolvte in the potential range -1.0 to 0.6 V (Fig. 4). The cyclic voltammogram of both complexes shows a similar type of pattern (Fig. 4). The cyclic voltammogram of complexes shows two redox processes (Table 4). The corresponding redox peaks observed in the CVs of each complex (1 and 2) were verified by comparing the voltammogram at different scan rates maintaining the identical experimental conditions and also by comparing its wave height with that of the ferrocene/ferrocenium couple. Both redox processes are irreversible and identical numbers of electrons as supported by differential pulse voltammetric (DPV) experiments. DPV is a good technique for identifying reduction peaks having small differences in the peak potentials, provided the two peaks differ in their formal potential by more than 0.18 V.

5.5. Electronic spectra

UV-visible spectra of both complexes have been recorded in 3.0×10^{-3} M DMSO. UV-visible spectroscopy is one of the most used methods for characterizing the transition metal complexes. The *d*-*d* spectra of present complexes are of little help in these two complexes since the *d*-*d* transitions are masked by strong charge transfer transitions. These bands observed at a higher concentration at 648 nm in **1** and 638 nm in **2**are assigned to *d*-*d* transitions (in in-set) (Fig. 5). Furthermore, a shoulder at ~ 980 nm is observed for both complexes. The apperence of a ~ 980 nm is indicative of bridging mode of sulphate anion and pyrazine coligands. The intense band noticed in the UV- the region is due to the overlap of the transition of the azomethane with the charge transfer band from bridging perchlorate oxygen to the vacant *d* orbital (N/O \rightarrow M) of the copper (II) [22,89,90].

5.6. Catalytic activity

Both complexes (**1** and **2**) are exhibit catalytic activity toward antioxidant SOD which was evaluated using the alkaline DMSOnitroblue tetrazolium (NBT) assay method [49,91,92]. The obtained SOD results show how much superoxide radical production was inhibited for each concentration of complex **1** and **2**. The IC₅₀ value i.e. concentration of metal complexes which inhibits 50% of the O_2^- /NBT reaction is used in the equation of the line which relates the different concentrations of the complexes analyzed with the respective percentage of NBT photoreduction inhibition. As the reaction proceeds, the photoreduction of NBT to MF⁺ is measured at 560 nm. The dismutation of superoxide anions takes place at physiological pH. Additionally, the SOD data of similar complexes of biologically important ligands as well as the values of the best SOD models reported in the literature so far are also presented in

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Coordination bond lengths [Å] and angles [°] for complexes 1 and 2.

	X-ray	DFT		X-ray	DFT
Complex 1 Bond length					
Cu(1)-O(1A)	1.9086(18)	1.9086	Cu(2)-O(1B)	1.8811(18)	1.8812
Cu(1)-N(1A)	1.948(2)	1.9481	Cu(2)-N(1B)	1.9351(19)	1.9351
Cu(1)-O(1 W)	1.9590(18)	1.9590	Cu(2)-O(2 W)	1.9577(17)	1.9577
Cu(1)-N(3A)	1.969(2)	1.9692	Cu(2)-N(3B)	1.977(2)	1.9773
Cu(1)-O(11)	2.4061(18)	2.4061	O(12)-Cu(2)	2.925(2)	2.9251
Perchlorate anion					
Cl(1)-O(14)	1.435(2)	1.4345	Cl(2)-O(23)	1.414(2)	1.4143
Cl(1)-O(13)	1.4441(19)	1.4441	Cl(2)-O(24)	1.420(2)	1.4210
Cl(1)-O(11)	1.4460(19)	1.4460	Cl(2)-O(22)	1.429(2)	1.4293
Cl(1)-O(12)	1.452(2)	1.4523	Cl(2)-O(21)	1.459(2)	1.4591
Bond angle					
O(1A)-Cu(1)-N(1A)	91.96(8)	91.9643	O(1B)-Cu(2)-N(1B)	93.06(8)	93.0588
O(1A)-Cu(1)-O(1 W)	91.40(8)	91.4009	O(1B)-Cu(2)-O(2 W)	93.11(8)	93.1113
N(1A)-Cu(1)-O(1 W)	170.77(8)	176.1223	N(1B)-Cu(2)-O(2 W)	164.22(9)	164.2159
O(1A)-Cu(1)-N(3A)	172.14(8)	176.3804	O(1B)-Cu(2)-N(3B)	170.92(8)	176.0681
N(3A)-Cu(1)-O(11)	90.23(7)	90.2367	N(1B)-Cu(2)-N(3B)	81.65(9)	81.6510
N(1A)-Cu(1)-N(3A)	81.76(9)	81.7629	O(2 W)-Cu(2)-N(3B)	93.90(8)	93.8985
O(1 W)-Cu(1)-N(3A)	94.11(8)	94.1089	O(1B)-Cu(2)-O(12)	83.00(7)	83.9961
O(1A)-Cu(1)-O(11)	95.83(7)	95.8313	N(1B)-Cu(2)-O(12)	121.20(7)	121.1959
N(1A)-Cu(1)-O(11)	103.28(8)	103.2847	O(2 W)-Cu(2)-O(12)	74.01(7)	73.9961
O(1 W)-Cu(1)-O(11)	84.91(7)	84.9102	N(3B)-Cu(2)-O(12)	93.39(7)	93.3926
Perchlorate anion					
O(14)-Cl(1)-O(13)	110.38(12)	110.3816	O(23)-Cl(2)-O(24)	110.7(2)	110.6653
O(14)-Cl(1)-O(11)	109.49(12)	109.4981	O(23)-Cl(2)-O(22)	109.92(16)	109.9263
O(13)-Cl(1)-O(11)	109.11(12)	109.1132	O(24)-Cl(2)-O(22)	109.58(16)	109.5801
O(14)-Cl(1)-O(12)	109.77(12)	109.7753	O(23)-CI(2)-O(21)	109.41(14)	109.4246
O(13)-Cl(1)-O(12)	108.63(11)	108.6263	O(24)-CI(2)-O(21)	108.94(14)	108.9431
O(11)-CI(1)-O(12)	109.42(12)	109.4221	O(22)-CI(2)-O(21)	108.21(13)	108.2113
Complex 2					
Bond length					
Cu = O(1)	1.8651(17)	1.8651	Cu = N(3)	1.958(2)	1.9581
Cu-N(1)	1.9366(18)	1.9366	Cu-N(4)	2.0183(18)	2.0183
Bond angle	00.00(7)	00.0000		00.00(7)	0.0 700 1
O(1)-Cu-N(1)	92.06(7)	92.0638	O(1)-Cu-N(4)	86.80(7)	86.7981
V(1) - Cu - N(3)	1/2.83(/)	1/6.1224	N(1)-Cu-N(4)	1/2.69(8)	1/8.6688
N(1)-CU-N(3)	82.42(8)	82.4225	N(3)-CU-N(4)	99.25(8)	99.2464

Table 5 for comparison [6,31,91,93–95]. The high SOD activity can be associated with the coordinately metal centers and the flexibility of the used tridentate Schiff base, which would permit molecular rearrangement along the catalytic pathway [96]. SOD enzymes have demonstrated pharmacological efficacy in some animal models of ROS-related diseases [97]. Their therapeutic use has been limited by their high production cost, molecular size, and antigenic activity [98]. Synthetic SOD mimetic compounds of low molecular weight could compensate for the limitations of SOD because of the lack of antigenicity, higher stability in solution, longer half-life, and lower production cost [99,100]. The lower SOD activity of these complexes compared to the best SOD models can be interpreted by considering a possible correlation between the strength of the equatorial field and the SOD activity [100]. Complex 2 showed less SOD activity than 1. In complex 2 Cu(II) ion experiences a strong equatorial field which makes difficult for the O_2^{-} radical to bind axially, due to the coordination of the metal by four nitrogen atoms. Similar SOD data have been obtained for other copper(II) complexes [101]. The present complexes based on SOD may be considered as potent SOD mimics [93-95,102,103].

5.7. Quantum chemical calculations

The structure of both binuclear complexes was also optimized by DFT methods [104–106]. Based on the SCXRD analysis, a distorted square pyramidal for **1** and a distorted square planar for **2** was considered. In Table 2, the comparison between experimental and calculated bond parameters is summarized. As expected, calculated values of bond distances and bond lengths slightly divert from those observed experimentally. Such discrepancy of bond parameters occurs owing to the crystal packing which modifies the parameters of the relaxed molecules. The density functional theory (DFT) method at the B₃LYP level is used to calculate the HOMO-LUMO energies for complexes **1** and **2**. The HOMO-LUMO energies are popular quantum mechanical descriptors that play an important role in governing a wide range of chemical interactions [107]. These energy levels are shown in Fig. 6. During HOMO-LUMO analysis of **1** and **2**, the fifth-highest and highest occupied MO's (HOMO and HOMO-5), the lowest and lowest unoccupied MO's (LUMO and LUMO + 5) are considered. Energy gaps are shown in Table 6. The energy gap was estimated at 16.0568 eV for **1** and 4.7435 eV for **2**. The energy gap for **1** is greater than **2**.

Graphical representations of the Mulliken atomic spin densities of both complexes were calculated using B3LYP/LanL2DZ basic set for comparative purposes (Fig. 7). The delocalization of the single unpaired electron is to the $d_{x^2-y^2}$ orbital with a less contribution of d_{z^2} of both copper centers and donor atoms of both complexes. The π -conjugated hydrocarbon network of Schiff base and tridentate ligand also carry spin density in both complexes due to the spin-polarization mechanism [108,109].

5.8. Magnetic measurements

The cryomagnetic susceptibility data for complexes 1 and 2 were measured in the temperature range 2–300 K. Plots of



Fig. 3. EPR spectra of complexes (a) 1 and (b) 2 (half field spectra of complexes 1 and 2 indicated in the inset).

magnetic susceptibility vs. temperature are shown in Figs. 8 and 10. The magnetic measurements obtained for **1** agree with previously reported data [110]. The value obtained for the $\chi_M T$ product of **1** at 300 K is 0.83 cm³·K·mol⁻¹, slightly larger than the one expected for two isolated copper(II) ions with a g value of 2. This value is constant until approximately 90 K. Further cooling of the sample leads to a decrease of $\chi_M T$ caused by antiferromagnetic interactions. This decrease is especially pronounced bellow 50 K, reaching a value of 0.02 cm³·K·mol⁻¹ at 2 K. The $\chi_M vs T$ plot shows a maximum at 18 K, indicative of antiferromagnetic coupling, and a small paramagnetic tail bellow 4.4 K (Fig. 8).

The magnetic data of **1** were fitted using the following equation that considers an intradimer coupling (*J*) through the Bleany-Bowers expression and the existence of a small $S = \frac{1}{2}$ paramagnetic impurity (*P*), responsible of the small paramagnetic tail observed in the $\chi_{\rm M}$ data and the *plateau* at low temperature in the $\chi_{\rm M}$ data:

$$\chi_{M} = (1 - P) \frac{2Ng^{2}\beta^{2}}{3KT} \frac{3}{3 + \exp(-\frac{J}{KT})} + 0.375 \frac{P}{T}$$

(Derived from the *H* = -*J*S1·S2Hamiltonian. *N*, β and *k* have their usual meanings).

The best fit of our data ($\sigma^2 = 1.8 \times 10^{-5}$) led to g = 2.16, J = -21.6 and P = 0.05. The fit estimates the existence of a paramagnetic impurity of a 5% that could not be anticipated by the elemental analysis (35.64% C; 3.35% H; 10.35% N) obtained for the sample batch used for the magnetic measurements. An antiferromagnetic exchange pathway, Cu1Cu2, through hydrogen bonds was proposed in the literature [110]. However, the magnitude of this coupling could be explained by an additional exchange through π - π interactions, which looks particularly strong between the Schiff base ligands bonded to Cu2 centers [111] (Fig. 9). This hypothesis is supported by the spin density structure around the ligands of **1** deduced from DFT calculations.

The dinuclear **2** complex displays a constant value, 0.79 cm³- \cdot K·mol⁻¹, of the molar magnetic susceptibility-temperature product ($\chi_{M}T$) from 300 K to approximately 35 K. This value is consistent with the existence of two *S* = ½ ions in the structure (calculated Curie constant of 0.75 cm³·K·mol⁻¹). Lowering the



Fig. 4. (a) Cyclic voltammogram of complexes 1-2 in DMSO $(3.0 \times 10^{-3} M)$ solution, (b) DPV of complexes 1-2 in DMSO $(3.0 \times 10^{-3} M)$ solution.

Table 3	
EPR parameters of	copper(II) complexes.

EPR parameter	1	2
Polycrystalline state (298 K)		
S S S S S S S S S S S S S S S S S S S	2.187	2.185
g	2.074	2.074
G	2.52	2.50
$D (cm^{-1})$	0.019	0.033
$E (cm^{-1})$	0.00	0.01
Frozen solution in DMSO (77 K)		
S	2.251	2.222
g	2.251	2.207
g_{\perp}	2.067	2.068
$A_{\parallel}(1)$	175	127
A _∥ (2)	175	175
f(cm)(1)	138	190
f(cm)(2)	138	138
α ²	0.768	0.727
β^2	0.951	0.993
γ^2	1.011	1.084
K _∥ (1)	0.761	0.721
K _∥ (2)	0.761	0.696
K_{\perp}	0.776	0.788
$E_{d-d}/\lambda_{max}(cm^{-1})$	15,432	15,677



Fig. 5. Absorption spectra of 3.0×10^{-3} M DMSO solution of complexes 1 and 2.

Table 4

Electrochemical data for binuclear copper(II) complexes 1 and 2 in DMSO $(3.0 \times 10^{-3} M)$ containing 0.1 M TBAP as a supporting electrolyte.

Complex	$E_{pc1}(V)$	$E_{pa1}(V)$	$E_{pc2}(V)$	$E_{pa2}(V)$	$DE_{pc1}(V)$	$DE_{pc2}(V)$	$\Delta_{Dpc}(V)$	$E^1_{1/2}(V)$	$\textit{E}_{1/2}^2(V)$	$\Delta E_{1/2}(V)$
1	0.127	0.388	-0.492	0.193	0.208	$-0.473 \\ -0.469$	0.681	0.257	-0.149	0.406
2	0.080	0.425	-0.519	0.256	0.192		0.661	0.254	-0.131	0.385

Table 5

SOD activities (IC₅₀ values kinetic catalytic constant and SOD activity) Cu(II) complexes.

Compound	IC ₅₀	$K_{M_{C}CF} (molL^{-1})^{-1}S^{-1}$	SOD activity (μM^{-1})	Reference
$[Cu(L)(H_2O)_2](NO_3)$	6	55.44	166.66	6
$[Cu_2(L^1)_2(HL^2)_2(H_2O)](NO_3)22H_2O$	38	8.75	26.31	96
$[Cu_2(L^1)_2(HL^2)_2]$ (NO ₃) ₂ ·H ₂ O	35	9.50	28.57	96
[Cu ₂ (bdpi)(CH ₃ CN) ₂](ClO ₄) ₃ CH ₃ CN 3H ₂ O	0.32	_	31.25	99
[(bipy) ₂ Cu–Im–Cu(bipy) ₂] (ClO4) ₃ ·CH ₃ OH	22	15.12	45.45	100
[Cu ₂ (Me ₄ bdpi)(H ₂ O) ₂](ClO ₄)34H2O	1.1	_	909.09	99
[Cu(L)(neocuprin)](NO ₃)·H ₂ O	21	15.84	47.62	31
[Cu ₂ (2-(2-pyridyl)benzimidazole) ₂ (L) ₂](ClO ₄)	17	19.57	58.82	31
$[Cu(L)(H_2O)(NO_3)] \cdot H_2O$	8	41.58	125.00	6
[Cu(idb)]	1.18	-	847.5	101
1	3.9	85.24	256.41	This work
2	8.6	38.87	116.27	This work

 $K_{M_{C}CF} = K_{NBT} \times (NBT) / IC_{50}, K_{NBT} = 5.94 \times 10^{-4} M^{-1} S^{-1}, \text{[NBT]} = 56 \ \mu\text{M}, \text{ SOD activity} = 1000 / IC_{50} \ (\mu\text{M}^{-1}).$



Fig. 6. Frontier molecular diagram of complexes (a) 1 and (b) 2.

 Table 6

 Theoretical transition levels between HOMO and LUMO frontier orbital were calculated by B3LYP/LanL2DZ method in complexes 1 and 2.

Level	MO Energy (eV)		$\Delta E (eV)$	
	1	2	1	2
НОМО	-7.2514	-5.4773	16.0568	4.7435
LUMO	8.8054	-0.7338		
HOMO-1	-7.2354	-5.4773	16.0490	4.7446
LUMO + 1	8.8136	-0.7327		
HOMO-2	-7.9338	-5.5368	18.0535	4.9385
LUMO + 2	10.1197	-0.5983		
HOMO-3	-7.3932	-5.5347	18.5714	5.1402
LUMO + 3	11.1782	-0.3945		
HOMO-4	-8.3510	-5.5510	17.5864	5.5157
LUMO + 4	9.2354	-0.0353		
HOMO-5	-7.1592	-5.5510	17.1891	5.5157
LUMO + 5	10.0299	-0.0353		

temperature further results in a sharp decrease of the $\chi_M T$ product, ascribed to intradimer antiferromagnetic interactions (Fig. 10).

The existence of antiferromagnetic interactions is also supported by the maximum at 6.4 K observed in the representation of the temperature dependence of the molar magnetic susceptibility (Fig. 9). Taking into account the dimeric nature of **2**, the experimental data were fitted using the Bleany-Bowers equation to

estimate the *J* and *g* values. The best fit of the data $(\sigma^2 = 1.6 \times 10^{-4})$ with this model led to *g* and *J* values of 2.08 and -6.8 cm^{-1} , respectively. The value of the coupling constant obtained from this fit agrees well with that of other similar copper(II) complexes in which pyrazine bridges mediate antiferromagnetic interactions with |J| values in the range of 3 to 12 cm⁻¹ [6,112].



Fig. 7. Graphical illustrations of the Mulliken atomic spin densities for the ground state (S = 1/2) of 1 and 2 with a surface threshold level of 0.004.



Fig. 8. Temperature dependence of χ_M (blue circles) and $\chi_M T$ (red squares) of **1**. Solid lines represent the fit of the experimental data as described in the main text.

6. Conclusions

Based on the single crystal X-ray crystallography and theoretical techniques, molecular geometries, weak interactions, electronics and catalytic properties of two new binuclear complexes (1 and 2) have been investigated. In perchlorate bridged binuclear complex 1, both copper(II) centers have square pyramidal geometry



Fig. 10. Temperature dependence of χ_M (blue circles) and $\chi_M T$ (red squares) of **2**. Solid lines represent the fit of the experimental data as described in the main text.

whereas in pyrazine bridged binuclear complex **2**, both copper centers have square planar geometry. Both complexes showed two reduction waves. Spin density on both copper(II) center was also calculated. Cryomagnetic magnetic susceptibility measurements showed that both complexes exhibit antiferromagnetic interactions. From the coupling parameter (J_{CuCu}) values of **1** and **2**, it is confirmed that **1** possesses stronger antiferromagnetic interaction



Fig. 9. Representation of the structure of **1** showing its main *π*-*π* interactions. The shortest distances between atoms of different units are given inÅ. Perchlorates are omitted for clarity.

compared to **2**, probably due to exchange through H-bonds and also through π - π stacking. The supramolecular chemistry of supramolecular synthons is also observed. It is capable of further self-assembly into chains and sheets. Both complexes showed good antioxidant SOD activity, which indicated that both complexes have the potential possibility to sure as antioxidant SOD mimics for pharmaceutical applications.

CRediT authorship contribution statement

R.N. Patel: Conceptualization, Supervision, Visualization, Writing - original draft, Writing - review & editing. **S.K. Patel:** Project administration, Investigation, Methodology. **D. Kumhar:** . **Nirmala Patel:** Formal analysis. **A.K. Patel:** Resources, Software. **R.N. Jadeja:** Conceptualization, Project administration, Resources, Software, Visualization. **Neetu Patel:** . **R.J. Butcher:** Validation. **M. Cortijo:** Validation. **S. Herrero:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC No. 1957632 and 1957633 contain the supplementary crystallographic data for compounds **1** and **2** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.htmL, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j. poly.2020.114687.

References

- [1] R. Karmakar, C.R. Choudhury, D.L. Hughes, G.P.A. Yap, M.S.E. Fallah, C. Desplanches, J.-P. Sutter, S. Mitra, Inorg. Chim. Acta 359 (2006) 1184-1192.
- [2] C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhuri, S. Koner, Polyhedron 25 (2006) 2191–2197.
- [3] S. Banerjee, M.G.B. Drew, C.-Z. Lu, J. Tercero, C. Diaz, A. Ghosh, Eur. J. Inorg. Chem. (2005) 2376–2383.
- [4] N.R. Sangeetha, S. Pal, Polyhedron 19 (2000) 1593-1600.
- [5] Y. Singh, R.N. Patel, S.K. Patel, A.K. Patel, N. Patel, R. Singh, R.J. Butcher, J.P. Jasinski, A. Gutierrez, Polyhedron 171 (2019) 155–171.
- [6] Y.P. Singh, R.N. Patel, Y. Singh, D.C. Lazarteb, R.J. Butcher, Dalton Trans. 46 (2017) 2803–2820.
- [7] N. Petrovic, A. Comi, M.J. Ettinger, J. Biol. Chem. 271 (1996) 28331–28334.
 [8] P. Kapoor, A. Pathak, R. Kapoor, P. Venugopalan, M. Corbella, M. Rodriguez, J.
- Robles, A. Llobet, Inorg. Chem. 41 (2002) 6153–6160.
- [9] M. Rodri-guez, A. Llobet, M. Corbella, Polyhedron 19 (2000) 2483-2491.
- [10] M. Rodri-guez, A. Llobet, M. Corbella, A.E. Martell, Reibenspies, J. Inorg. Chem. 38 (1999) 2328–2334.

- [11] E. Pardo, J. Faus, M. Julve, F. Lloret, M.C. Mun-oz, J. Cano, X. Ottenwaelder, Y. Journaux, R. Carrasco, G. Blay, I. Fernandez, R. Ruiz-Garci-a, J. Am. Chem. Soc. 125 (2003) 10770–10771.
- [12] G. Psomas, C.P. Raptopoulou, L. Iordanidis, C. Dendrinou-Samara, V. Tangoulis, D.P. Kessissoglou, Inorg. Chem. 39 (2000) 3042–3048.
- [13] S. Ferlay, A. Jouaiti, M. Loi, M.W. Hosseini, A. De Cian, P. Turek, New J. Chem. (2003) 1801–1805.
- [14] J. Cano, E. Ruiz, P. Alemany, F. Lloret, S. Alvarez, J. Chem. Soc., Dalton Trans. (1999) 1669–1676.
 [15] K.J. Humphreys, K.D. Karlin, S.E. Rokita, J. Am. Chem. Soc. 124 (2002) 8055–
- 8066.
- [16] K. Jitsukawa, M. Mizutani, H. Arii, I. Kubo, Y. Izu, T. Ozawa, H. Masuda, Chem. Lett. 33 (2004) 1302–1303.
 [17] Y. Singh, R.N. Patel, Y.P. Singh, A.K. Patel, N. Patel, R. Singh, R.J. Butcher, J.P.
- Jasinski, E. Colacio, M.A. Palacios, Dalton Trans. 46 (2017) 11860–11874.
- [18] R.N. Patel, Y. Singh, Y.P. Singh, R.J. Butcher, A. Kamal, I.P. Tripathi, Polyhedron 117 (2016) 20-34.
- [19] R.N. Patel, V.P. Sondhiya, K.K. Shukla, D.K. Patel, Y. Singh, Polyhedron 50 (2013) 139–145.
- [20] R.N. Patel, Y. Singh, Y.P. Singh, A.K. Patel, N. Patel, R. Singh, R.J. Butcher, J.P. Jasinski, E. Colacio, M.A. Palacios, New J. Chem. 42 (2018) 3112–3136.
- [21] S. Roy, M. Bohme, S.P. Dash, M. Mohanty, A. Buchholz, W. Plass, S. Majumder, S. Kulanthaivel, I. Banerjee, H. Reuter, W. Kaminsky, R. Dinda, Inorg. Chem. 57 (2018) 5767–5781.
- [22] A. Bianchi, E. Delgado-Pinar, E. Garcia-Espana, C. Giorgi, F. Pina, Coord. Chem. Rev. 260 (2014) 156–215.
- [23] J. Pisk, B. Prugovecki, D. Matkovic-Calogovic, T. Jednacak, P. Novak, D. Agustin, V. Vrdoljak, RSC Adv. 4 (2014) 39000–39010.
- [24] O. Pouralimardan, A.C. Chamayou, C. Janiak, H.H. Monfared, Inorg. Chim. Acta 360 (2007) 1599–1608.
- [25] M. Bakir, O. Green, W.H. Mulder, J. Mol. Struct. 873 (2008) 17-28.
- [26] C. Basu, S. Chowdhury, R. Banerjee, H.S. Evans, S. Mukherjee, Polyhedron 26 (2007) 3617–3624.
- [27] M. Alagesan, N.S.P. Bhuvaneshb, N. Dharmaraj, Dalton Trans. 42 (2013) 7210– 7223.
- [28] W.E. Antholine, B. Bennett, G.R. Hanson, Copper Coordination Environments, in: S.K. Misra (Ed.), Multifrequency Electron Paramagnetic Resonance: Theory and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.
- [29] J. Jezierska, V. Kokozay, A. Ozarowski, Res. Chem. Intermed. 33 (2007) 901– 914.
- [30] F.E. Mabbs, Chem. Soc. Rev. 22 (1993) 313-324.
- [31] Y.P. Singh, R.N. Patel, Y. Singh, R.J. Butcher, P.K. Vishakarma, R.K.B. Singh, Polyhedron 122 (2017) 1–15.
- [32] A.K. Patel, R.N. Jadeja, H. Roy, R.N. Patel, S.K. Patel, R.J. Butcher, J. Mole. Struct. 1185 (2019) 341–350.
- [33] S.K. Patel, R.N. Patel, Y. Singh, Y.P. Singh, D. Kumhar, R.N. Jadeja, H. Roy, A.K. Patel, N. Patel, N. Patel, A. Banerjee, D. Choquesillo-Lazarted, A. Gutierrez, Polyhedron 161 (2019) 198–212.
- [34] S.R. Seidel, P.J. Stang, Acc. Chem. Res. 35 (2002) 972–983.
- [35] J.-M. Lehn, PNAS 99 (2001) 4763-4768.
- [36] B.J. Holliday, C.A. Mirkin, Angew. Chem. Int. Ed. 40 (2001) 2022-2043.
- [37] F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, J. Am. Chem. Soc. 123 (2001) 7740-7741.
- [38] Y.K. Kryschenko, S.R. Seidel, D.C. Muddiman, A.I. Nepomuceno, P.J. Stang, J. Am. Chem. Soc. 125 (2003) 9647–9652.
- [39] M. Barboiu, G. Vaughan, R. Graff, J.-M. Lehn, J. Am. Chem. Soc. 125 (2003) 10257–10265.
- [40] R.N. Patel, D.K. Patel, V.P. Sondhiya, K.K. Shukla, Y. Singh, A. Kumar, Inorg. Chim. Acta 405 (2013) 209–217.
- [41] S. Mamour, D. Mayoro, T.E. Ibrahima, G. Mohamed, B.A. Hamady, J. Ellena, Acta Cryst. Sect. E 74 (2018) 642–645.
- [42] M.S. Shongwe, K.S. Al-Barhi, M. Mikuriya, H. Adams, M.J. Morris, E. Bill, K.C. Molloy, Chem. Eur. J. 20 (2014) 9693–9701.
- [43] R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854-2855.
- [44] G.M. Sheldrick, Acta Cryst. A 46 (1990) 467-473.
- [45] Acta Crystallogr. Vnir. Gottingen: Gottingen, Germany, 1997.
- [46] A.L. Spek, Acta Crystallogr. D 65 (2009) 148–155.
- [47] L.J. Ferrugia, J. Appl. Crystallogr. 45 (2012) 849-854.
- [48] R.N. Patel, A. Singh, K.K. Shukla, D.K. Patel, V.P. Sondhiya, J. Coord. Chem. 64 (2011) 902–919.
- [49] R. Konecny, J. Li, C.L. Fisher, V. Dillet, D. Bashford, L. Noodleman, Inorg. Chem. 38 (1999) 940–950.
- [50] R.G. Bhirud, T.S. Srivastava, Inorg. Chimca Acta 173 (1999) 121–125.
- [51] Z.R. Liao, X.F. Zheng, B.S. Luo, L.R. Shen, D.F. Li, H.L. Liu, W. Zhao, Polyhedron 20 (2001) 2813–2821.
- [52] R.N. Patel, Y.P. Singh, Y. Singh, R.J. Butcher, J.P. Jasinski, Polyhedron 133 (2017) 102–109.
- [53] R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. 256 (1996) 454-464.
- [54] G.A. Petersson, M.A. Al-Laham, J. Chem. Phys. 94 (1991) 6081–6090.
- [55] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270–283.
- [56] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.

Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian O9, Revision D.01, Gaussian Inc., Wallingford, CT, 2009.

- [57] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 224 (2003) 669– 681.
- [58] T. Mosmann, J. Immunol. 65 (1993) 55–63.
- [59] K. Nakamoto, John Wiley & Sons, Inc., New York-London, 1963.
- [60] R.N. Patel, Y.P. Singh, Y. Singh, R.J. Butcher, J.P. Jasinski, Polyhedron 129 (2017) 164–181.
- [61] B.J. Hathaway, A.E. Underhill, J. Chem. Soc. (1961) 3091-3096.
- [62] R.N. Patel, Y.P. Singh, Y. Singh, R.J. Butcher, Polyhedron 104 (2016) 116–126.
 [63] B. Cheng, P.H. Fries, J.-C. Marchon, W.R. Scheidt, Inorg. Chem. 35 (1996)
- 1024–1032. [64] A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984.) 1349–1356.
- [65] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, Angew. Chem. Int. Ed. 34 (1995) 1555–1573.
- [66] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer-Verlog Berlin, 1996, pp. 3–14.
- [67] M. Gonzalez-Álvarez, G. Alzuet, J. Borrás, L. del Castillo-Agudo, S. Garcia-Granda, J.M. Montejo-Bernardo, Inorg. Chem. 44 (2005) 9424–9433.
- [68] T. Suksrichavalit, S. Prachayasittikul, C. Nantasenamat, C. Isarankura-Na-Ayudhya, V. Prachayasittikul, Eu. J. Med. Chem. 44 (2009) 3259–3265.
- [69] L. Yang, D.R. Powell, R.P. Houser, Dalton Trans. (2007) 955–964.
- [70] J. Lu, T. Paliwala, S.C. Lim, C. Yu, T. Niu, A.J. Jacobson, Inorg. Chem. 36 (1997) 923–929.
- [71] R. Atencio, K. Ramírez, J.A. Reyes, T. González, P. Silva, Inorg. Chim. Acta 358 (2005) 520–526.
- [72] J. Lewis, F.E. Mabbs, L.K. Royston, W.R. Smail, J. Chem. Soc., A (1969) 291-296.
- [73] N.D. Chasteen, R.L. Belford, Inorg. Chem. 9 (1970) 169–175.
- [74] J. Reedijk, D. Knetsch, B. Nieuwenhuijse, Inorg. Chem. Acta 5 (1971) 568–572.
 [75] W.E. Estes, J.R. Wasson, J.W. Hall, W.E. Hatfield, Inorg. Chem. 17 (1978) 3657–
- 3664.
- [76] R.C. Aggarwal, N.K. Singh, R.P. Singh, Inorg. Chem. 20 (1981) 2794–2798.
- [77] W.A. Alves, S.A.A. Filho, R.H.A. Santos, A.M.C. Ferreira, Inorg. Chem. Commun. 6 (2003) 294–299.
- [78] O. Kahn, Moleculer Magneetism, Wiley VCH, Newyork, 1993.
- [79] R.N. Patel, Inorg. Chim. Acta 363 (2010) 3838-3846.
- [80] E.B. Seena, M.R.P. Kurup, Polyhedron 26 (2007) 829-836.
- [81] J.R. Wasson, C. Trapp, J. Phy. Chem. 73 (1969) 3763-3772.
- [82] B.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143-207.
- [83] S.K. Jain, B.S. Garg, Y.K. Bhoon, D.L. Klayman, J.P. Scovill, Spectrochim Acta A 41 (1985) 407–413.

- [84] M.J. Bew, B.J. Hathaway, R.J. Fereday, J. Chem. Dalton Trans. (1972) 1229– 1237.
- [85] E. Garribba, G. Micera, J. Chem. Educ. 83 (2006) 1229–1232.
- [86] G. Kolks, C.R. Frihart, P.K. Coughlin, S.J. Lippard, Inorg. Chem. 20 (1981) 2933– 2940.
- [87] C.-L. O'Young, J.C. Dewan, H.R. Lilienthal, S.J. Lippard, J. Am. Chem. Soc. 100 (1978) 7291–7300.
- [88], Comprehensive Coordination Chemistry Vol. 5 (1987) 533.
- [89] H. Okawa, M. Tadokoro, Y. Aratake, M. Ohba, K. Shindo, M. Mitsumi, M. Koikawa, M. Tomono, D.E. Fenton, J. Chem. Soc., Dalton Trans. (1993) 253–258.
- [90] J.V. Folgado, R. Ibanez, E. Coronado, D. Beltran, J.M. Savariault, J. Galy, Inorg. Chem. 27 (1988) 19–26.
- [91] R.N. Patel, Y.P. Singh, Y. Singh, R.J. Butcher, M. Zeller, RSC Adv. 6 (2016) 107379–107398.
- [92] R.G. Bhirud, T.S. Srivastava, Inorg. Chim. Acta 173 (1990) 121-125.
- [93] H. Ohtsu, Y. Shimazaki, A. Odani, O. Yamauchi, W. Mori, S. Itoh, S. Fukuzumi, J. Am. Chem. Soc. 122 (2000) 5733–5741.
- [94] R.N. Patel, N. Singh, K.K. Shukla, V.L.N. Gundla, U.K. Chauhan, J. Inorg. Biochem. 99 (2005) 651–663.
- [95] X. Meng, M. Wang, N. Jiang, D. Zhang, L. Wang, C. Liu, J. Agric. Food Chem. 60 (2012) 11211–11221.
- [96] A. Maroz, G.F. Kelso, R.A.J. Smith, D.C. Ware, R.F. Anderson, J. Phys. Chem. A 112 (2008) 4929–4935.
- [97] J.B. -Haberle, J.S. Rebouças and I. Spasojevic, Redox Signaling, 2010, 13, 877– 918.
- [98] D.P. Riley, Chem. Rev. 99 (1999) 2573-2587.
- [99] R.S. Nicholson, I. Shain, Anal. Chem. 37 (1965) 178–190.
- [100] S.W. Feldberg, L. Jeftic, J. Phys. Chem. 76 (1972) 2439-2446.
- [101] C. Amar, E. Vilkas, J. Foos, J. Inorg. Biochem. 17 (1982) 313-323.
- [102] N.A. Roberts, P.A. Robinson, Br. J. Rheumatol. 24 (1985) 128-136.
- [103] J.A. Tainer, E.D. Getzoff, J.S. Richardson, D.C. Richardson, Nature 306 (1983) 284–287.
- [104] G. Micera, E. Garribba, Int. J. Quantum Chem. 112 (2012) 2486–2498.
- [105] L. Pisano, K. Varnagy, S. Timári, K. Hegetschweiler, G. Micera, E. Garribba,
- Inorg. Chem. 52 (2013) 5260–5272. [106] D. Sanna, K. Várnagy, N. Lihi, G. Micera, E. Garribba, Inorg. Chem. 52 (2013) 8202–8213.
- [107] R.N. Patel, Y. Singh, Y.P. Singh, R.J. Butcher, J. Coord. Chem. 69 (2016) 2377– 2390
- [108] S.K. Silverman, D.A. Dougherty, J. Phys. Chem. 97 (1993) 13273-13283.
- [109] A. Rajca, Chem. Rev. 94 (1994) 871-893.
- [110] J. Tang, J.S. Costa, A. Golobi, B. Kozlev, A. Robertazzi, A.V. Vargiu, P. Gamez, J. Reedijk, Inorg. Chem. 48 (2009) 5473–5479.
- [111] Y.-H. Chi, J.-M. Shi, H.-N. Li, W. Wei, E. Cottrill, N. Pan, H. Chen, Y. Liang, L. Yu, Y.-Q. Zhang, C. Hou, Dalton Trans. 412 (2013) 15559–15569.
- [112] V. Selmani, C.P. Landee, M.M. Turnbull, J.L. Wikaira, F. Xiao, Inorg. Chem. Commun. 13 (2010) 1399–1401.