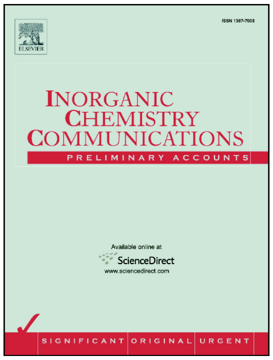

Copper(II) complex of the 2-pyridinecarbaldehyde aminoguanidine Schiff base: Crystal structure and catalytic behaviour in mild oxidation of alkanes

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Copper(II) complex of the 2-pyridinecarbaldehyde aminoguanidine Schiff base: Crystal structure and catalytic behaviour in mild oxidation of alkanes

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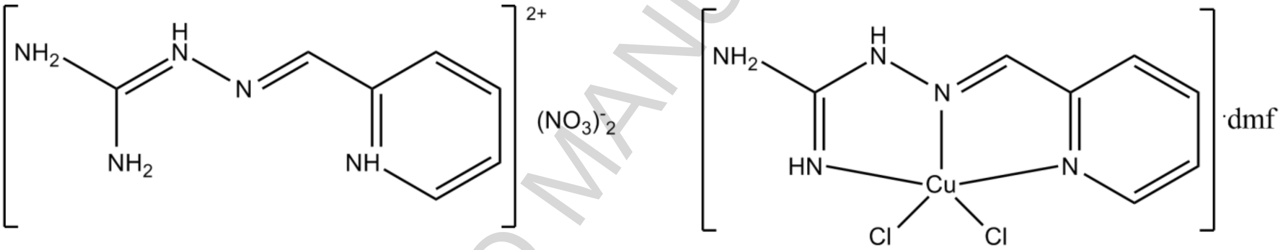
Keywords: 2-Pyridinecarbaldehyde; Aminoguanidine; Schiff base copper(II) complex; Crystal structure; Catalytic oxidation of cyclohexane, adamantane, *cis*-1,2-dimethylcyclohexane

Abstract

The new neutral dichloro-copper(II) Schiff base complex $[CuCl_2L]\cdot dmf$ **2**, where L results from condensation of 2-pyridinecarbaldehyde and aminoguanidine, was prepared, while the ligand itself was isolated in its protonated form as the dinitrate salt $(H_2L)(NO_3)_2$ **1**. Extended conjugation is responsible for the planarity of the H_2L^{2+} cation in **1**. On coordination, L forms two fused 5-membered chelate rings occupying three equatorial positions of the distorted square pyramidal copper polyhedron in **2**. The catalytic investigations disclosed a prominent activity of the copper compound **2** towards oxidation of cyclohexane with hydrogen peroxide in the presence of various promoters (nitric and acetic acids, pyridine and pyrrole), showing overall yields of products (cyclohexanol and cyclohexanone) up to 21 % based on the substrate.

The guanidine group is widely spread in biological molecules and has been of much interest in the field of natural product synthesis [1, 2] and drug development [3, 4]. Due to its unique role as a hydrogen-bond donor and its positive charge (upon protonation) the guanidine group is of importance for molecular recognition in chemical and biological systems [5, 6]. The utilization of guanidine derivatives as catalysts and superbases has also been explored [7–9]. Aminoguanidine (AG) has been extensively studied for the treatment of diabetic complications [10]. It is also one of the most studied quenchers of reactive carbonyl species (RCS) - endogenous or exogenous byproducts involved in the pathogenic mechanisms of different oxidative-based disorders [11]. Detoxification of RCS by carbonyl quenchers is a promising therapeutic strategy and investigation of conjugates of AG and arylaldehydes as well as their metal complexes has attracted increasing attention [12–14].

A challenging task in modern catalysis is the activation and functionalization of inert alkanes towards products of industrial significance [15]. It has been shown that coordination compounds of some transition metals, particularly copper, can catalyse the oxidation of alkanes C–H bonds under mild conditions using readily available oxidants, such as hydrogen peroxide [16–20]. In such processes, a crucial role can be played by promoters, which can turn the oxidation process in a desired way [21]. Therefore, the investigation of promoting effects is one of the milestones in this field of catalysis. Following our earlier studies on metal complexes with AG based Schiff bases [22, 23] and metal-catalysed C–H oxidation with peroxides [24–26], in this communication we describe the crystal structures and spectroscopic characterization of the 2-pyridinecarbaldehyde aminoguanidine Schiff base $(H_2L)(NO_3)_2$ **1** and the derived dichloro-Cu(II) complex $[CuCl_2L]\cdot dmf$ **2** (dmf – dimethylformamide, Scheme 1) as well as the catalytic activity of **2** in reactions of alkanes oxidation in the presence of various promoting agents.



Scheme 1. The Schiff base $(H_2L)(NO_3)_2$ **1** and derived dichloro-Cu(II) complex $[CuCl_2L]\cdot dmf$ **2**.

Complex **2** was isolated in an attempt to prepare a heterometallic Cu/Ni compound with the Schiff base ligand that was synthesized from the reaction of 2-pyridinecarbaldehyde with aminoguanidine freshly liberated from AG·HCl. The use of a zero-valent metal or a metal oxide as a source of metal ions along with a salt of another metal in reactions with proton-containing reagents or Schiff base ligands has yielded a number of heterometallic complexes that were successfully studied for catalytic applications [27–33]. In the current study, copper powder and $NiCl_2\cdot 6H_2O$ were reacted with the Schiff base formed *in situ* in dmf in a 1 : 1 : 2 molar ratio [34]. The isolated blue-green microcrystalline product was identified crystallographically [35] as the mononuclear Cu(II) Schiff base complex **2** which did not contain any nickel. The pro-ligand itself formed as the colourless dinitrate salt **1** in a similar synthetic procedure in methanol where nickel powder and $Cr(NO_3)_3\cdot 9H_2O$ were used instead of copper powder and nickel salt [34, 35]. The room temperature EPR spectrum of a polycrystalline sample of **2** exhibits an axial pattern with distinctly resolved *g* components: $g_{\|} = 2.242$, $g_{\perp} = 2.051$.

The crystal structure of **1** clearly shows that the pro-ligand molecule is protonated on the pyridyl and guanyl nitrogen atoms, N(1) and N(23), respectively, giving rise to a dicationic species (Fig. 1, Table S1). The newly formed imine bond, C21==N22, is in the *E* geometry. The C24–N25 and C24–N26 bond distances involving the two amino groups as well as the N25–C24–N26 angle indicate a considerable double-bond character of the guanidinium group. Distribution of partial π character in the bonding throughout the entire cation is evidenced by the shortening of the corresponding distances along the C2–C21–N22–N23–C24 series of atoms, as well as the proximity of the bond angles to the ideal value of 120° for the angles with *sp*2 atoms (Table S1). The extended conjugation is responsible for the planarity of the cation: the plane of the guanidinium moiety is twisted from the plane of the 2-pyridinium ring by only 6.01°. The structure and geometry of **1** are comparable to those found in tetraaquadichloronickelate dichloride [36] and tetrachlorocuprate hybrid salts [37] of the same Schiff base cation. In the crystal lattice, the dications and nitrate anions are involved in hydrogen bonds forming a 1-dimensional hydrogen bonded polymer (Fig. S1, Table S2). No π–π stacking is observed.

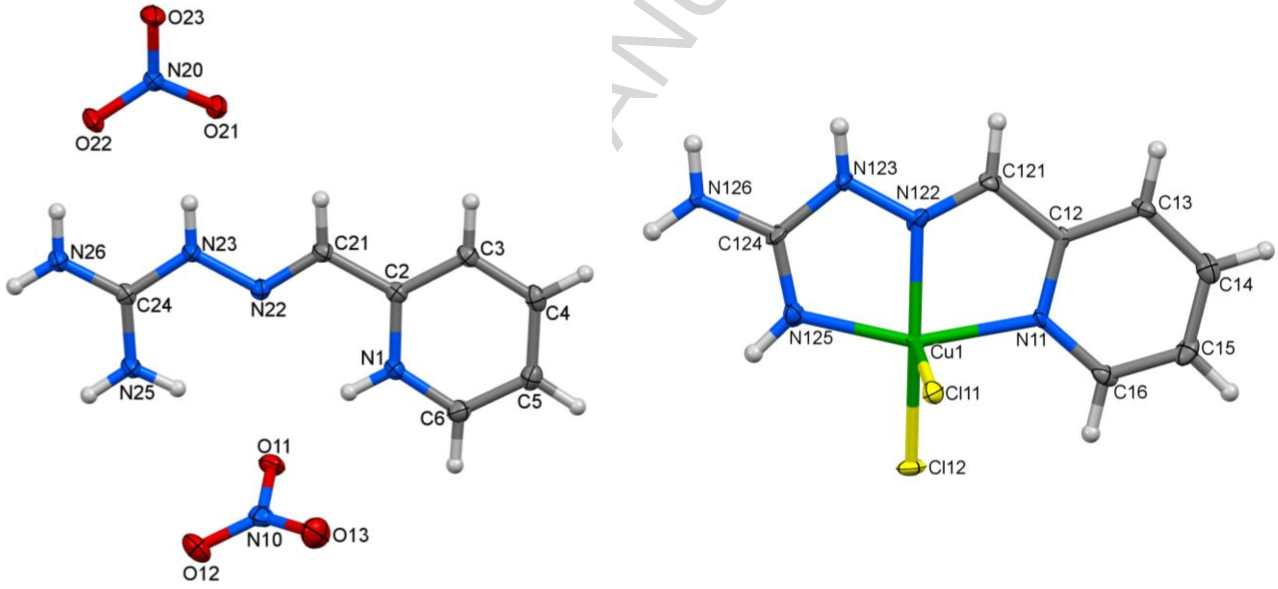
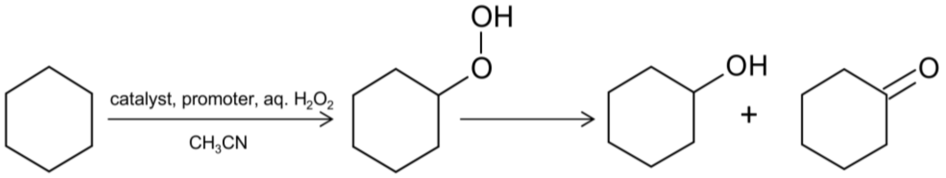


Fig. 1. Molecular structures of $(H_2L)(NO_3)_2$ **1** (left) and one of the two independent molecules of $[CuCl_2L]$·dmf **2** (right) showing the atom numbering scheme. Non-H atoms are shown with displacement ellipsoids at the 50% probability level.

The copper complex **2** is formed of discrete $[CuCl_2L]$ neutral molecules and dmf molecules of crystallization. There are two crystallographically independent complex molecules in the asymmetric unit; both molecules have no crystallographically imposed symmetry and are similar (Table S3). In **2** the chelate tridentate ligands L coordinate to the copper atoms in a neutral form through the pyridine (N11, N21), azomethine (N122, N222) and imino (N125, N225) nitrogen atoms (Fig. 1). The Cu(II) coordination environments are distorted square pyramidal, with one of the chlorine atoms (Cl11 and Cl22) occupying the apical position. The Cu–N distances (Table S3) fall in the range of 1.951(12)–2.072(10) Å, the average equatorial and axial Cu–Cl distances being 2.225 and 2.678 Å, respectively. The *trans* angles at the metal atoms lie in the range of 156.1(4) to 163.2(4)°, the *cis* angles vary from 78.1(4) to 100.07(12)°. The neutral ligand molecules adopt an almost planar conformation. The coordination geometry around the metal atom has a close resemblance to that found in two polymorphic forms of the Cu(II) complex with a similar ligand which results from the condensation between 2-acetylpyridine and aminoguanidine-hydrogencarbonate [38]. The present study and earlier studies by others [38] demonstrate that the coordination mode of L that forms two fused 5-membered chelate rings is not affected by the presence of an additional substituent at the azomethine carbon atom. Both molecules of **2** are involved in N–H···O/Cl hydrogen bonding to form hydrogen bonded sheets parallel to the *ab* plane (Fig. S2, Table S2). The interactions between molecules are weak, the closest Cu···Cu intermolecular separation exceeding 5.76 Å. No π–π stacking is observed.

Complex **2** was tested as a catalyst in the mild oxidation of cyclohexane by aqueous hydrogen peroxide in acetonitrile in the presence of various promoting agents [39]. Cyclohexane has been used as a recognized substrate model for C–H bond activation investigations and the activity of metal catalysts can be improved by promoting agents of different types [18, 40–45]. The presence of strong protic acids (*e.g.* nitric, hydrochloric, trifluoroacetic acids) can hamper the undesired hydrogen peroxide decomposition (catalase-like activity) and may facilitate the formation of an unsaturated coordination environment around the metal cation upon partial ligand protonation [16, 32, 46–48]. Also the presence of a carboxylic acid (*e.g.* acetic, oxalic or pyrazinecarboxylic acid) can support the stabilization of transition states of metal catalysts [47, 48]. On the other hand, basic promoters (*e.g.* triethylamine, pyridine) can favor proton-shifts and transform a pro-catalyst into an active catalytic species [49, 50]. Taking this into account, we investigated the influence of promoters of different types, namely acid promoters (nitric and acetic acids), as well as basic ones (pyridine and pyrrole), on the catalytic activity of complex **2** (Scheme 2). No alkane oxidation products (or only traces) were obtained in the absence of the catalyst. The main final reaction products, after quenching of the samples with PPh_3, were cyclohexanol and cyclohexanone (Scheme 2).



Scheme 2. Catalytic oxidation of cyclohexane with H_2O_2, catalysed by complex **2**.

Complex **2** showed a prominent catalytic activity in the presence of all studied promoters at 50 °C with overall yields of oxygenated products of 15, 21, 19 and 20% (based on cyclohexane) with HNO_3, pyridine, HOAc and pyrrole promoters, respectively, achieved after 5 h reaction time. The products accumulation dependences (Fig. 2, top), monitored within 5 h time, reveal a sharp growth of products concentrations for pyridine, pyrrole and acetic acid, then reaching a plateau. In contrast, in the case of the nitric acid, the plateau was reached only after 2 h reaction time (Fig. 2, top).

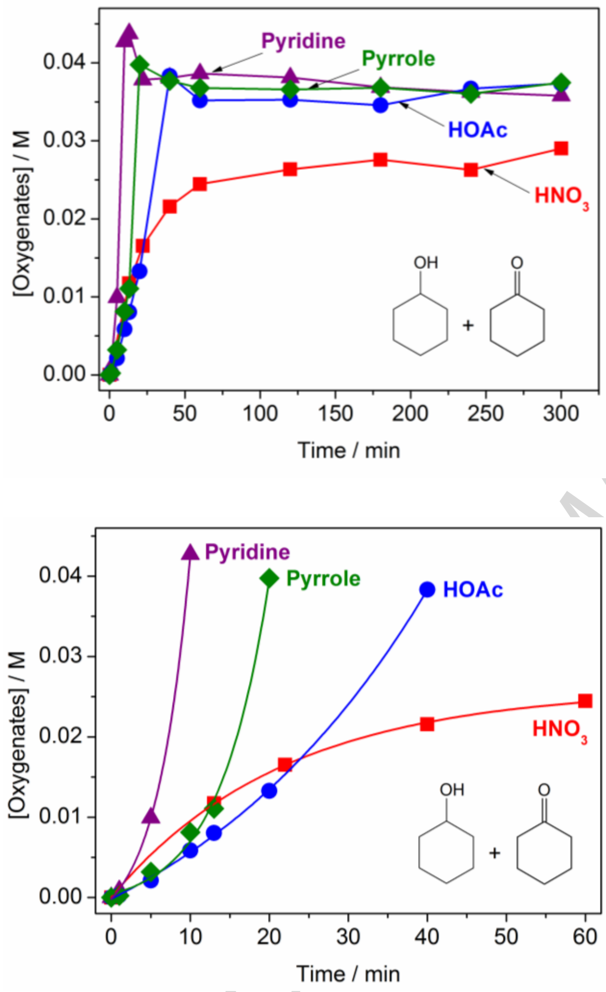


Fig. 2. Top: Accumulations of oxygenates (sums of cyclohexanol and cyclohexanone) with time in cyclohexane (0.2 M) oxidation with aq. H_2O_2 (1 M), catalysed by complex **2** (1×10^{-3} M) in the presence of HNO_3 (0.01 M) (red line), HOAc (0.01 M) (blue line), pyridine (0.01 M) (violet line) and pyrrole (0.01 M) (green line), in acetonitrile (total volume of the reaction solution was 5 mL) at 50 °C. Bottom: The initial periods of the respective catalytic dependences.

The accumulation with nitric acid promoter shows a gradual decay of the initial reaction rate W_0 of 2.0×10^{-5} M s^{-1}. Although the initial reaction rates for the other promoters (1.7×10^{-5}, 4.5×10^{-6}, 8.3×10^{-6} M s^{-1} for pyridine, pyrrole and acetic acid, respectively) are close to that for HNO_3, they exhibit an increase over time, reaching the *W* values of 3.8×10^{-4}, 1.1×10^{-4} and 2.6×10^{-5} M s^{-1}, respectively (22, 24 and 3 fold increase of *W*), before reaction stops and reaches a plateau region (Fig. 2, bottom). The presence of an auto-acceleration period suggests that complex **2** undergoes gradual transformation in solution and the species formed are more active than the initial structure. The auto-acceleration in copper-catalysed oxidation of cyclohexane with H_2O_2 was observed earlier for a tetranuclear complex in the presence of sulfuric acid promoter [51]. However, the observation of HOAc-caused auto-acceleration is unusual because acetic acid is commonly not expected to be an efficient promoter for copper catalysts in such a type of reactions [16].

The alcohol/ketone (A/K) ratios for all promoters, measured after addition of the solid PPh_3 to the reaction samples, are depicted in Fig. 3. At the beginning of reactions the A/K ratios are high for all promoters, lying in the range from 40 to 70. After reaching a plateau, the A/K ratio for the nitric acid appears at ca. 20 level, while for other promoters this parameter becomes much lower, ca. 3. High prevalence of cyclohexanol at the beginning of the reaction is in accord with formation of cyclohexyl hydroperoxide, Cy–OOH, which is quantitatively reduced to cyclohexanol by PPh_3, upon sample quenching [52]. At the plateau region, the comparable amounts of cyclohexanol and cyclohexanone for pyridine, pyrrole and acetic acid promoters (A/K of ca. 3) may account for decomposition of Cy–OOH in the reaction mixture. This process is assumed to produce mainly cyclohexanol and cyclohexanone, in nearly equal amounts. If the nitric acid promoter prevents the decomposition of Cy–OOH [16] then the cyclohexanol will dominate over the whole time range, resulting in an elevated A/K ratio (Fig. 3).

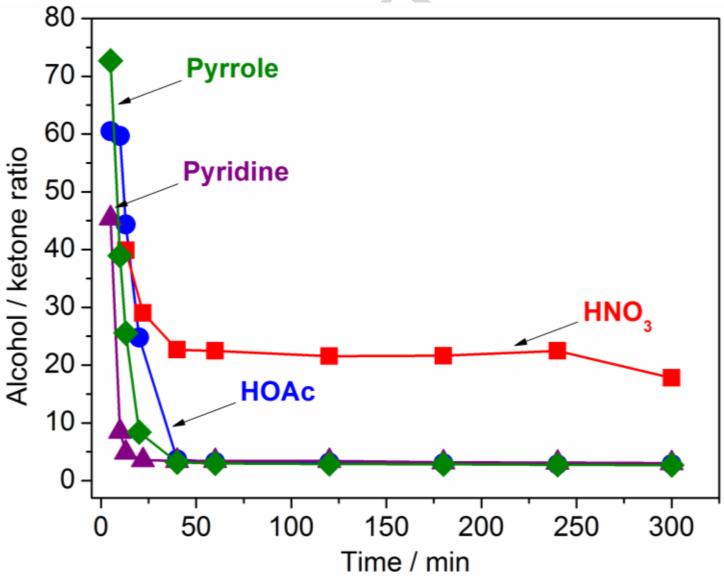


Fig. 3. The alcohol/ketone (A/K) ratios of the products (measured upon addition of PPh_3) for all studied promoters as functions of time (see Fig. 2 caption for reaction conditions).

The presence of cyclohexyl hydroperoxide, as a main reaction product, was directly confirmed by GC-MS methods, employing proper analytical conditions. The strong peaks of Cy–OOH (Fig. 4, bottom chromatograms) were observed for all promoters. These peaks completely disappeared after the samples were treated with solid PPh_3 (Fig. 4, top chromatograms), with a respective decrease of intensities of peaks of cyclohexanone, formed through spontaneous decomposition of Cy–OOH in GC injector and/or column [52, 53]. The presence of Cy–OOH accounts for a free radical reaction mechanism, where the reaction of the catalyst with hydrogen peroxide results in formation of hydroxyl radical, HO·, a very reactive attacking species [45]. HO· radicals abstract hydrogen from cyclohexane CyH to produce cyclohexyl radical Cy·, which is then trapped by dioxygen to give Cy–OO· radical. The latter may react either with substrate or oxidant to form Cy–OOH [46, 52, 54]. One should notice that this mechanism does not belong to a class of radical self-supporting chain reaction, as the concentrations of the substrate, oxidant and dioxygen in the reaction mixture are not sufficient for such type of processes [54].

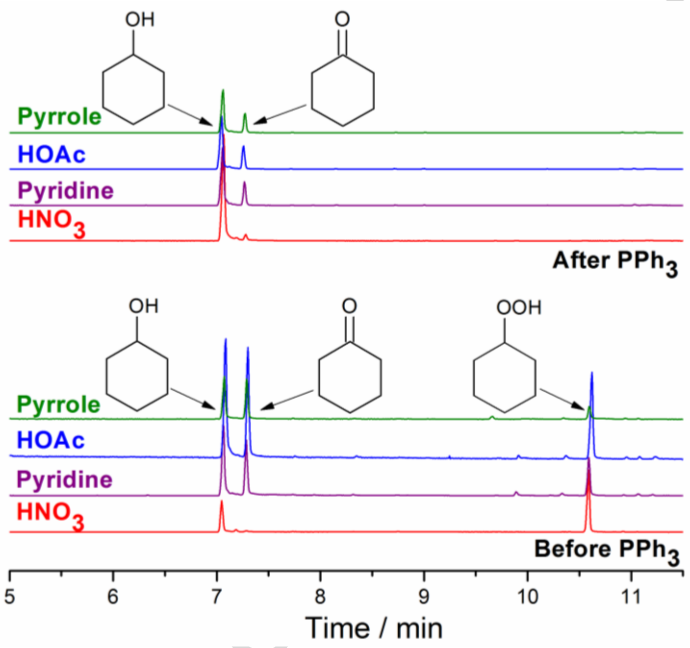


Fig. 4. Fragments of the chromatograms (see Fig. 2 caption for reaction conditions), showing the main reaction products (recorded before and after addition of solid Ph_3P, bottom and top, respectively). The large peak of cyclohexyl hydroperoxide, seen at 10.6 min (four bottom chromatograms), completely disappears after addition of Ph_3P (four top chromatograms).

The hydroxyl radical is typically non-selective due to its very high reactivity. Hence, the respective catalytic systems commonly exhibit relatively low bond-, regio- and stereo-selectivities [55-57]. Thus, these tests are commonly used to prove the assumption about the presence of HO· radicals as C–H attacking species. The accumulations of main products in the course of adamantane oxidation, catalysed by the complex **2** in the presence of nitric acid promoter, are depicted in Fig. 5. The yield of 20% based on substrate was achieved, with $W_0 = 1.4 \times 10^{-5}$ M s^{-1}. The alcohols dominate and the normalized 2° : 3° ratio ranges from 1 : 2.6 to 1 : 2.9. This value is close to those observed for hydroxyl radical attack of adamantane (1 : 2) [58].

Interestingly, careful investigation of the chromatogram reveals the presence, in a small amount, of a chlorinated product, 1-chloroadamantane (Fig. S3), which formation is also in agreement with a free-radical process in the system. The chloro-ligands of **2** can be the chlorine source for the chlorinated hydrocarbon [21].

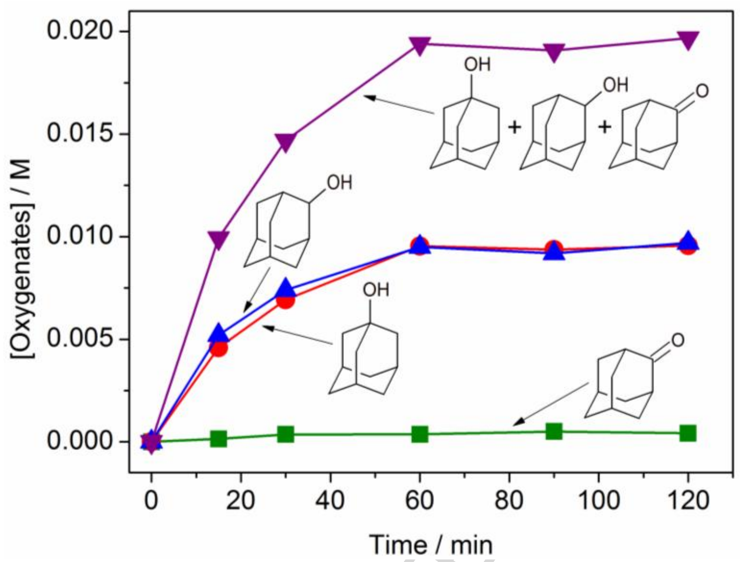


Fig. 5. Accumulations of oxygenates with time in adamantane (0.1 M) oxidation with aq. H_2O_2 (1 M), catalysed by complex **2** (1×10^{-3} M) in the presence of HNO_3 (0.01 M) in acetonitrile (total volume of the reaction solution was 5 mL) at 50 °C.

A further evidence for the presence of the non-selective hydroxyl radical was obtained through the oxidation of *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH) under the same conditions as adamantane. The accumulation of the sum of all oxidation products ($W_0 = 3.9 \times 10^{-5}$ M s^{-1}) is depicted in Fig. 6. The sum of all reaction products gave 21% of the maximum yield based on the substrate with low retention of stereoconfiguration (*cis*/*trans* ratio of tertiary alcohols was up to only 1.3, Fig. 6, inset). A free radical mechanism foresees the epimerization of stereoconfiguration of substrate [32, 56]. The observed *cis*/*trans* ratio in the case of the complex **2** is low, thus confirming the assumption about hydroxyl radicals. The averaged normalized 1° : 2° : 3° selectivity was 1 : 7 : 43. The amount of primary alcohol is quite low and can be explained by the presence of two closely located electron-rich tertiary C–H bonds, which are much more “attractive” for oxidation than methyl groups. As reaction by-products, those of ring cleavage were detected, particularly 2,7-octanedione derived upon further oxidation (Fig. S4).

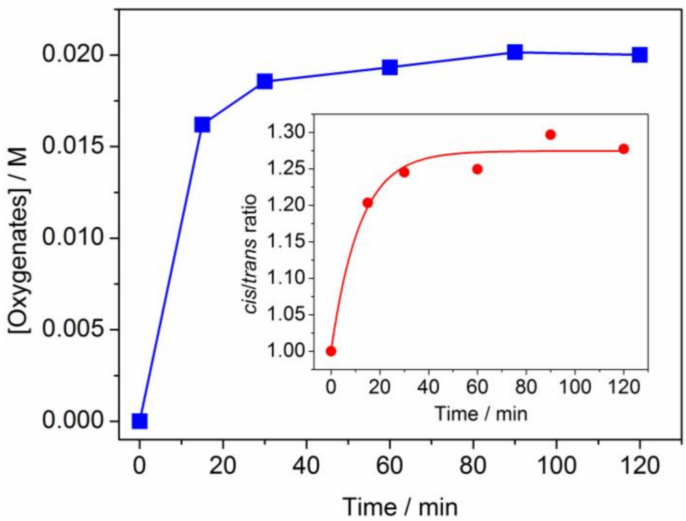


Fig. 6. Accumulation of oxygenates (sum of reaction products, alcohols and ketones, formed through the oxidation of primary, secondary and tertiary C-H bonds) with time in *cis*-1,2-dimethylcyclohexane (0.1 M) oxidation with aq. H_2O_2 (1 M), catalysed by complex **2** (1×10^{-3} M) in the presence of HNO_3 (0.01 M) in acetonitrile (total volume of the reaction solution was 5 mL) at 50 °C. Inset: the *cis*/*trans* ratio of the tertiary oxygenates as a function of time.

In conclusion, the Schiff base of 2-pyridinecarbaldehyde and aminoguanidine and the derived dichloro-Cu(II) complex were synthesised and crystallographically characterized. The planar neutral Schiff base ligand occupies three equatorial positions of the distorted square pyramidal copper polyhedron. The complex **2** was found to be an active catalyst in the oxidation of cyclohexane with hydrogen peroxide in the presence of various promoters. The basic aromatic N-heterocycles, namely pyridine (Py) and pyrrole, were the most efficient promoting agents. Nitric acid, a commonly accepted promoter for copper complexes, was found to exhibit considerably weaker activity, also showing no acceleration of the reaction rate (in contrast to pyridine, pyrrole and acetic acid promoters). The highest yield of products, achieved for the **2**/Py/H_2O_2 cyclohexane oxidizing system, was 21 %. For all the promoters, the formation of large quantities of cyclohexyl hydroperoxide (Cy–OOH) was directly detected by GC-MS methods. Cyclohexyl hydroperoxide as a main reaction product suggests a free-radical pathway with hydroxyl radicals as attacking species. Such assumption is in accord with the observed 2° : 3° carbons selectivity in the oxidation of adamantane and epimerization of *cis*-1,2-dimethylcyclohexane when oxidized to the respective tertiary alcohols. Finally, the formation of a C–Cl chlorinated by-product also confirms the involvement of the alkyl radical with subsequent Cl-coupling. In the case of cyclohexane and adamantane the respective cyclic structures retained their integrities, while in the case of *cis*-1,2-dimethylcyclohexane substrate the ring cleavage by-product 2,7-octanedione was observed. This work may lead to the development of a new family of metal catalysts based on aminoguanidine Schiff base ligands for mild oxidation of alkanes.

Acknowledgement

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Appendix A. Supplementary material

CCDC 1513756 and 1513757 contain the supplementary crystallographic data for this paper. Structural data (Tables and Figures); fragments of the chromatograms showing the reaction products of oxidation of adamantane and *cis*-1,2-dimethylcyclohexane.

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[34] **Synthesis of 1**: to Ni powder (0.06 g, 1 mmol), $Cr(NO_3)_3\cdot 9H_2O$ (0.40 g, 1 mmol) and AG·HCl (0.22 g, 2 mmol) in methanol (10 ml), 2-pyridinecarbaldehyde (0.19 ml, 2 mmol) was added and the mixture was heated to 323 K with magnetic stirring. A white powder of **1** started to precipitate in 30 min; total dissolution of the nickel powder was not achieved. The reaction mixture was filtered and the X-ray quality crystals of **1** deposited next day from the resulting blue-grey solution. They were collected by filter-suction, washed with dry Pr^iOH and finally dried in air. 1H NMR (400 MHz, DMSO-*d*6, s, singlet; br, broad; d, doublet; t, triplet): 12.07, s (1H, NH guanidinium group); 8.71, m (1H, Py); 8.37, d (1H, Py, J = 7.6 Hz); 8.21, s (1H, CH=N azomethine); 8.06, t (1H, Py, J = 7.3 Hz); 7.89, br (4H, NH2); 7.57, m (1H, Py); 5.15, br (NH, Py). IR (ν/cm^{-1}): 3338s, 3240s, 3190s, 2940m, 2904m, 2830m, 1656s, 1630s, 1610m, 1578m, 1544m, 1470m, 1384vs, 1352s, 1226w, 1168w, 1050w, 770w, 706w, 584m, 544m, 510m, 436w.

Synthesis of 2: to Cu powder (0.06 g, 1 mmol), $NiCl_2\cdot 6H_2O$ (0.24 g, 1 mmol) and AG·HCl (0.22 g, 2 mmol) in dmf (5 ml) 2-pyridinecarbaldehyde (0.19 ml, 2 mmol) was added and the mixture was heated to 323 K under magnetic stirring until total dissolution of the copper powder was observed (1 hour). The resulting brown solution was filtered and allowed to stand at room temperature. Green microcrystals of **2** were formed over several days. They were collected by filter suction, washed with dry Pr^iOH and finally dried in air (yield: 37%). IR (ν/cm^{-1}): 3404m, 3324s, 3256m, 3200m, 3150s, 3090m, 3034m, 2986m, 2940m, 2874m, 2762m, 1656s, 1638s, 1604m, 1544s, 1508w,

1498w, 1466m, 1450m, 1418m, 1386w, 1344m, 1292w, 1272m, 1220s, 1168s, 1104m, 1022m, 890w, 780m, 750m, 646m, 568m, 518w, 460w, 416w.

[35] **Crystal data for $(H_2L)(NO_3)_2$ 1**: $C_7H_{11}N_5\cdot 2(NO_3)$, M = 289.23, colourless rod, monoclinic, space group $P2_1/c$, $a = 5.7627(2)$, $b = 26.9810(7)$, $c = 7.7665(2)$ Å, $\beta = 102.559(3)°$, $V = 1178.67(6)$ Å^3, Z = 4, $D_c = 1.63$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.14 mm^{-1}, T = 100 K. Total 13825 reflections, 4108 unique, $R_{int} = 0.037$. Refinement of 4108 reflections (181 parameters) converged at final $R[F^2 > 2\sigma(F^2)] = 0.049$, $wR(F^2) = 0.114$, gof = 1.06.

Crystal data $[CuCl_2L]\cdot$dmf 2: $C_7H_9Cl_2CuN_5\cdot C_3H_7NO$, M = 370.73, green plate, orthorhombic, space group $Pca2_1$, $a = 12.8536(6)$, $b = 6.1472(2)$, $c = 37.350(2)$ Å, $V = 2951.1(2)$ Å^3, Z = 8, D_c = 1.669 Mg m^{-3}, μ(Mo $K\alpha$) = 1.85 mm^{-1}, T = 100 K. Total 14003 reflections, 5716 unique, R_{int} = 0.092. Refinement of 5716 reflections (323 parameters) converged at final $R[F^2 > 2\sigma(F^2)] = 0.089$, $wR(F^2) = 0.229$, gof = 1.05. Absolute structure parameter 0.36(4). Anisotropic displacement parameters were employed for the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Some atoms were refined with displacement parameters restrained to reasonable values. The displacement parameters of other atoms related by a pseudo-inversion centre were constrained to be equal.

The structure was refined in the orthorhombic non-centrosymmetric space group $Pca2_1$ with two crystallographically independent complex molecules in the asymmetric unit that are similar. This appears unusual, however, the structure did not solve in space group *Pcam* and there was no indication from Checkcif that the structure could be in a space group of higher symmetry or that the structure has an inversion centre. There was also no indication from the frames that one of the axial lengths should be doubled. It would appear that the structure is pseudo-centrosymmetric, perhaps as a result of the cooling of the crystal: the structure may be centrosymmetric at room temperature but non-centrosymmetric at lower temperatures. However, this could not be tested as the sample had deteriorated in the interim.

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[39] **Catalytic oxidation of alkanes.** To 5 μmol of solid catalyst weighed into the reaction flask, 4.1 mL CH_3CN, 40–100 μmol of promoter (HNO_3, HOAc, pyridine and pyrrole were used in acetonitrile solutions, typically 0.5–1 mL of promoter was mixed with 9 mL of CH_3CN), 0.5 mL of CH_3NO_2 stock solution (internal standard; 1 mL of CH_3NO_2 mixed with 9 mL of CH_3CN), 108 μL (1 mmol) of cyclohexane or 70 μL (1 mmol) of *cis*-1,2-dimethylcyclohexane and 0.28 mL (5 mmol; 50% aqueous) of H_2O_2 were added in this order at 50 °C under vigorous stirring (CAUTION: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). In the case of solid adamantane (1 mmol) as a substrate, it was placed into the vial prior to the addition of acetonitrile solution. At the end of the reaction, aliquots (ca. 0.5 mL) of the reaction mixture were carefully transferred into a vial containing an excess (ca. 150 mg) of solid Ph_3P. A Perkin-Elmer Clarus 500 gas chromatograph with a BP-20 capillary column (SGE, 30 m × 0.32 mm × 25 μm) and a Perkin-Elmer Clarus 600 gas chromatograph, equipped with a Perkin-Elmer Clarus 600 C mass-spectrometer (electron impact), with a BPX5 capillary column (SGE, the same dimensions) and helium carrier gas were used for quantitative analyses of the reaction mixtures.

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Copper(II) complex of the 2-pyridinecarbaldehyde aminoguanidine Schiff base: Crystal structure and catalytic behaviour in mild oxidation of alkanes

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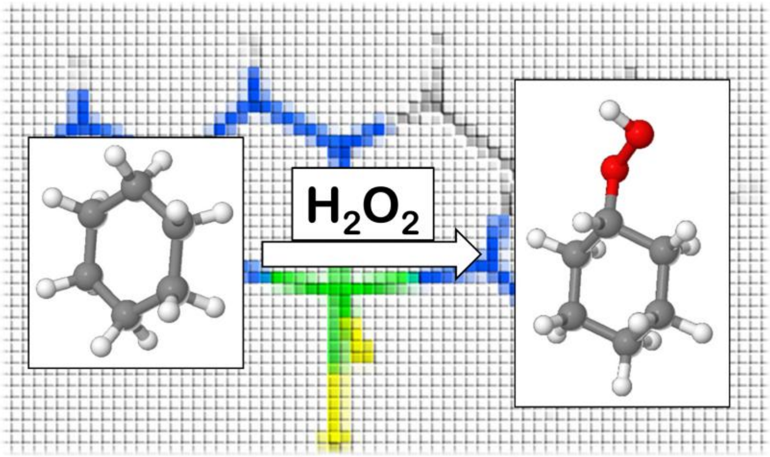
Graphical abstract



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Highlights

- Aminoguanidine based organic ligand (**1**) and its copper complex (**2**) are synthesized.

- **1** and **2** are characterized by X-ray crystallography and spectroscopic methods.

- The protonated ligand cation in **1** is planar due to extended conjugation.

- On coordination, the neutral ligand forms two fused 5-membered chelate rings.

- **2** acts as catalyst in oxidation of cyclohexane with H_2O_2 in the presence of promoters.