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Synthesis, X-ray structure and properties of a new nitrite-bound copper(II) complex with 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine in a $CuN_4(O)$ coordination

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Abstract—Synthesis and characterization of a nitrite-bound copper(II) compound $[Cu(L^4)_2(ONO)]ClO_4$ have been achieved (L^4 = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine]. The bidentate ligand L^4 provides a pyridine and a pyrazole donor site; however, they are separated by a methylene spacer. The complex has been structurally characterized and it belongs to only a handful of complexes having nitrito-bound mononuclear copper(II) centre. The metal atom has a distorted square pyramidal geometry with the copper atom displaced from the equatorial plane by 0.25 Å. In MeCN solution the green complex exhibits a broad ligand-field transition at 655 nm with a shoulder at 675 nm and in dichloromethane-toluene glass (80 K) it exhibits an EPR spectral feature characteristic of the unpaired electron in the $d_{x^2-y^2}$ orbital. Variable-temperature (80–300 K) magnetic susceptibility measurements in the solid state as well as room temperature measurement in MeCN solution reveal mononuclear magnetically dilute copper(II) centre. When examined by cyclic voltammetry (MeCN solution) it displays electrochemically irreversible Cu^{II}–Cu^{I} response [cathodic peak potential, E_{pc} (V *vs* saturated calomel electrode (SCE)): −0.32]. An oxidative response is observed at 1.14 V, probably due to bound-nitrite oxidation and is partially removed to generate a solvated complex at the electrode surface. The latter species gives rise to a reversible Cu^{II}–Cu^{I} redox response [$E_{1/2}$ = 0.41 V *vs* SCE]. © 1997 Elsevier Science Ltd

Keywords: 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine; nitrite-bound copper(II) complexes; X-ray structure; cyclic voltammetry; EPR spectra; absorption spectra; magnetism.

In the last few years we have investigated [1,2] the co-ordination chemistry of non-planar tridentate bis(pyrazol-1-yl-methyl)pyridine ligands (L^1–L^3) with divalent transition metal ions. These ligands contain both pyridine (soft) and pyrazole (hard) donors in a given ligand system. However, their electronic communication is prevented due to the placement of methylene spacers between the rings. The effects of such an electronic feature and the presence of methyl substituents near donor site (L^2 and L^3) were revealed in the spin-state behaviour of bis(ligand) complexes of iron(II) [2a] in the M^{III}–M^{II} reduction potentials of ML_2^{2+} species (M = Mn, Fe, Co and Ru) [1a–d] and in the X-ray structure of $[FeL_2^2][ClO_4]_2$ [2b]. Interestingly, these ligands provide six-membered boat conformations, when chelating a transition metal atom and exert a relatively weak field around the metal ion.

In continuation of our involvement with this class of relatively unexplored ligands [1–5], we have recently investigated [6] the co-ordinative behaviour of a closely similar bidentate ligand, 2-(pyrazol-1-ylmethyl)pyridine towards transition metal ions. Using a substituted variety of this ligand here we report the synthesis, X-ray structure and spectroscopic, magnetic and redox properties of a mononuclear nitrite-bound copper(II) complex $[Cu(L^4)_2(NO_2)]ClO_4$ [L^4 = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine]. An additional impetus derives from the current inter-

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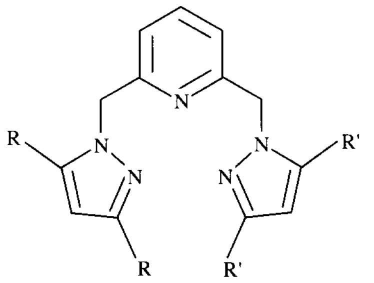

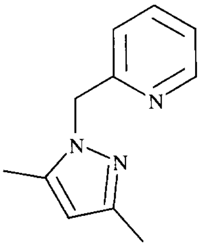

L^4

R, R' = H; L^1
R, H, R' = Me; L^2
R, R' = Me; L^3

est in the chemistry of mononuclear copper(II)-pyrazole complexes [7–10].

EXPERIMENTAL

Materials

All chemicals were obtained from commercial sources and used as received, unless stated otherwise. Acetonitrile (MeCN) was dried by distillation over CaH_2 and ethanol over $Mg(OEt)_2$. The ligand 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L^4) was prepared following a literature procedure [3,4a]. Tetra-*n*-butylammonium perchlorate was prepared and purified as before [11].

Synthesis of the copper complex

$[Cu(L^4)_2(NO_2)]ClO_4$. To a solution of copper(II) perchlorate hexahydrate (0.05 g, 0.14 mmol) in MeCN (2 cm^3) was added an MeCN solution (3 cm^3) of the ligand L^4 (0.05 g, 0.27 mmol). After stirring the solution for 2 min, an ethanolic solution (2 cm^3) of $NaNO_2$ (0.011 g, 0.16 mmol) was added dropwise and the solution magnetically stirred for 1 h at room temperature. The resulting green solution was filtered and left in the air for slow evaporation. After a day the green crystals thus formed were collected by filtration, washed with ethanol and air-dried. (Yield *ca* 87%.) Found: C, 44.9; H, 4.3; N, 16.7. Calc. for $C_{22}H_{26}N_7O_6ClCu$: C, 45.3; H, 4.5; N, 16.8%). IR (KBr, cm^{-1}, selected peaks): 1462 [ν(N=O)]; 1090 and 618 (ν [ClO_4^-]). Λ_M (298 K, MeCN): 142 Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [MeCN solution, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 975 (sh), 655 (130), 390 (1 100), 260 (8 250)]. Variable-temperature magnetic data (T in K, $\chi_M \times 10^{-3}$ in EMU mol^{-1}): 300, 1.655; 280, 1.683; 260, 1.923; 240, 1.790; 220, 2.034; 200, 2.339; 180, 2.501; 160, 2.949; 140, 3.215; 120, 3.594; 100, 4.227; 81, 5.212. X-ray quality single crystals were obtained by slow evaporation of an $MeCN/H_2O$ (3 : 1 *v*/*v*) solution at 298 K.

CAUTION! Although the preparation of the perchlorate salt described here has been done many times without incident, perchlorate salts of metal complexes with organic ligands have been known to explode spontaneously. Therefore, the preparation and handling of these perchlorate salts deserve special care.

Measurements

Solution electrical conductivity measurements were carried out with an Elico (Hyderabad, India) Type CM-82 T conductivity bridge. Spectroscopic data were obtained by using the following instruments: infrared spectra, Perkin–Elmer M-1320; electronic spectra, Perkin–Elmer Lambda 2; X-band EPR spectra, Varian E-109 C. Temperature-dependent (80–300 K) solid-state magnetic susceptibility was determined by the Faraday technique using a locally-built magnetometer [12], comprising an electromagnet (Polytronic Corporation, Bombay, India), a micro-balance (Sartorius, Germany) and a closed-cycle refrigerator (Cryo Industries, U.S.A.). All measurements were made at a main fixed field strength of ~ 10 kG. Solution-state magnetic susceptibility was determined by the NMR technique of Evans [13] in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. Susceptibilities were corrected using appropriate diamagnetic corrections [14]. Effective magnetic moments were calculated from $\mu_{eff} = 2.828\ [\chi_M T]^{1/2}$, where χ_M is the corrected molar susceptibility. Cyclic voltammetric measurements were performed by using a PAR model 370 electrochemistry system [11] with a platinum working electrode. Potentials are referenced to the saturated calomel electrode (SCE).

Crystal structure determination of $[Cu(L^4)_2(ONO)]ClO_4$

Intensities and lattice parameters of a green plate-shaped crystal (dimensions: 0.09 × 0.41 × 0.49 mm) were measured on a Enraf Nonius CAD4 diffractometer (University of Louisville) at ambient temperature by using graphite monochromated Mo-K_α radiation. No decomposition of the crystal occurred

Table 1. Summary of X-ray crystallographic data for $[Cu(L^4)_2(ONO)]ClO_4$

Chemical formula	$C_{22}H_{26}ClCuN_7O_6$
M_r	583.49
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	13.186(5)
b (Å)	20.824(7)
c (Å)	9.677(4)
β (°)	90.19(3)
U (Å^3)	2657(1)
λ (Å)	(Mo-K_α) (0.710 93)
T (K)	295
Z	4
D_{calc} (g cm^{-3})	1.458
μ (mm^{-1})	0.972
Scan type	ω-2θ
$2\theta_{max}$ (°)	50.0
Reflections measured	5123
Observed reflections $[I > 3\sigma(I)]$	3041
$F(000)$	1204
Least-squares parameters	346
Data : parameter ratio	8.79
Maximum, minimum peak in final difference map (e Å^{-3})	0.46, −0.55
Maximum Δ/σ	0.02
Max., min. transmission factors	0.86, 1.21
R^a	0.052
$R_w{}^b$	0.052
Goodness of fit^c	2.32

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$.

$^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 1/\sigma^2 (F_o)$.

^{c}Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_r)]^{1/2}$, N_o and N_v are the number of observations and variables respectively.

Table 2. Selected bond lengths (Å) and angles (°) in the cationic part of $[Cu(L^4)_2(ONO)]ClO_4$

Cu—O(1)	2.091(5)	Cu—N(1)	2.007(4)
Cu—N(3)	2.155(4)	Cu—N(4)	2.002(4)
Cu—N(6)	2.063(4)	O(1)—N(7)	1.260(6)
O(2)—N(7)	1.199(6)		
O(1)—Cu—N(1)	86.6(2)	O(1)—Cu—N(3)	103.1(2)
O(1)—Cu—N(4)	89.2(2)	O(1)—Cu—N(6)	156.6(2)
N(1)—Cu—N(3)	89.0(2)	N(1)—Cu—N(4)	174.0(2)
N(1)—Cu—N(6)	94.9(2)	N(3)—Cu—N(4)	96.1(2)
N(3)—Cu—N(6)	100.3(2)	N(4)—Cu—N(6)	87.3(2)
O(1)—N(7)—O(2)	111.2(6)	Cu—O(1)—N(7)	110.3(4)

during data collection. The intensity data was subjected to Lorentz and polarization correction and an empirical absorption correction using the program DIFABS [15] was applied. Neutral-atom scattering factors [16a] and anomalous dispersion terms [16b,c] for non-hydrogen atoms were taken from the literature.

The structure was solved by heavy-atom Patterson methods [17] using the TEXSAN [18] software package. All non-hydrogen atoms, with exception of disordered atoms, were refined anisotropically. Hydrogen atoms were included but not refined. The perchlorate was found to be disordered. Each of the oxygens was disordered over three positions, a multiplicity factor for each set of the disordered oxygen atoms was refined so that the total multiplicity was unity. With this model the structure converged to the observed R values.

Crystal data and a summary of experimental results are presented in Table 1. Selected bond distances and angles associated with the cation are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

RESULTS AND DISCUSSION

Synthesis and selected properties

A straightforward reaction between the bidentate ligand L^4, copper(II) perchlorate hexahydrate and $NaNO_2$ in C_2H_5OH-MeCN mixture affords a deep green crystalline solid. Microanalytical, IR and solution electrical conductivity data [19] suggest that this complex has the composition $[Cu(L^4)_2(NO_2)]ClO_4$. It should be noted, however, that the presence of co-ordinated NO_2^- could not be identified confidently from its IR spectrum as severe overlapping with ligand vibrations and broad and intense ionic perchlorate band occur; however, an enhancement of vibrations in the expected range [21] was clearly observed. It was finally confirmed by X-ray structural analysis (*vide infra*). It is worth mentioning here that the impetus for investigating the binding of nitrite ion derives from the current interest in synthesizing models for the substrate adduct of copper containing nitrite reductase [20,21]. The substrate binding site in the enzyme is a mononuclear copper(II) centre with three histidine nitrogen coordination [20b,c]. Therefore it should be noted that this complex is not expected to serve as a structural model of this enzyme.

Crystal structure of $[Cu(L^4)_2(ONO)]ClO_4$

The asymmetric unit consists of one molecule of $[Cu(L^4)_2(ONO)]^+$ and one non-co-ordinating perchlorate anion. The structure of the cationic part is depicted in Fig. 1. The copper(II) ion is coordinated by two pyridyl nitrogens, two pyrazole nitrogens and one oxygen atom of NO_2^-. Thus this is a nitrito-bound five-co-ordinate copper(II) complex. The coordination environment around the Cu atom is best described as a distorted square pyramidal with a trigonal bipyramidal component of, $\tau = 0.29$ [$= (\beta - \alpha)/60$, where β = N(1)—Cu—N(4) 174.0° and

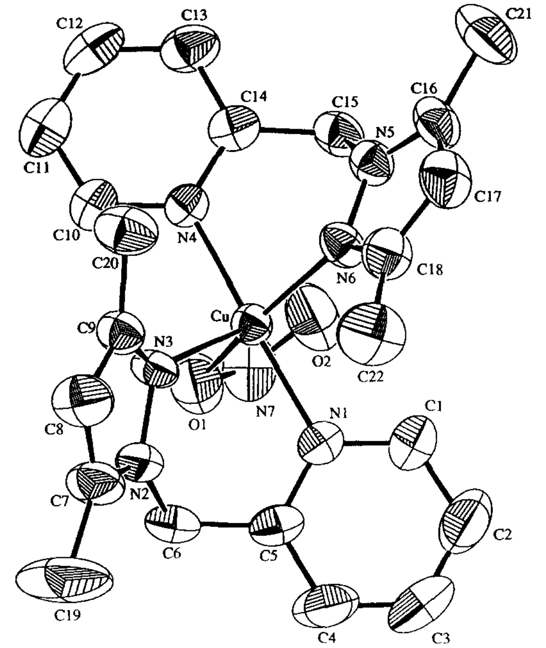

Fig. 1. Molecular structure and atomic numbering scheme for the cation in $[Cu(L^4)_2(ONO)]ClO_4$.

α = O(1)—Cu—N(6) 156.6°]; for a perfect square pyramidal and trigonal bipyramidal geometries the value of τ is zero and unity, respectively [22]. The basal plane of the square pyramid is defined by N(4) and N(6) atoms of an L^4 ligand, N(1) pyridine atom of the other ligand, and O(1) of the nitrite ion. The N(3) pyrazole nitrogen atom of the second ligand forms the axial bond. The Cu atom is displaced from the equatorial plane towards the axial pyrazole nitrogen by 0.25 Å. The two pyridyl nitrogens are *trans* to each other. There exists an inverse correlation [23] between the displacement parameter and the Cu-(apical) distance in square pyramidal copper(II) complexes. The present data nicely fits in the expected trend.

The average copper(II)-N(pyridine) distance of 2.005 Å is comparatively shorter than that found for similar complexes [4b,6,21a–c]. The copper(II)-O(nitrite) distance of 2.091(5) Å is appreciably longer than closely similar copper(II)-nitrito complexes (2.012(5) Å [21a], 1.938(2) Å [21b,c] and 1.962(6) [21d]). The equatorial copper(II)–N(pyrazole) distance of 2.063(4) Å is significantly longer than the related complexes [4b,5a,6–9]. In fact, the bond is even longer or on the higher end of that observed for copper(II) complexes with sterically crowded tris(pyrazolyl)hydroborate complexes [20a]. Interestingly, the axial Cu-N(pyrazole) bond distance of 2.155(4) Å is quite long. To the best of our knowledge, within the mononuclear copper(II) complexes of pyrazole donors, this is the first report of a long axially coordinated Cu(II)–N(pyrazole) bond. We believe that the observed bonding effect is the manifestation of the steric crowding created by the pyrazole ring methyl substituents near the donor site of the L^4 ligands.

The pyridyl and pyrazole rings are each planar. However, a pyridyl ring of a given ligand is twisted to a pyrazole ring by an angle of 52.58 or 59.92°. Thus the six-membered chelate rings exist in boat conformations, as is observed in compounds of these kinds of ligands [2b,4a,b].

UV–vis and EPR spectra

In MeCN solution the green complex displays a broad ligand-field band at 655 nm with a shoulder at 975 nm, suggesting a five-coordinate geometry [23] (*vide* X-ray structure). The high-energy transition at 260 nm is assigned to the metal-perturbed intraligand transition. The other high energy transition at 390 nm is attributed to various ligand-to-metal charge-transfer (LMCT) transitions.

The EPR spectrum of this complex in dichloromethane-toluene glass (80 K) is displayed in Fig. 2, which suggests that the unpaired electron is in the $d_{x^2-y^2}$ orbital, with expected stronger axial interaction ($g_\parallel = 2.266$, $g_\perp = 2.060$, $A_\parallel = 160$ G) [23,24].

Magnetism

We have investigated variable-temperature (80–300 K) magnetic susceptibility behaviour of this compound in the solid state using Faraday method. The complex follows the Curie–Weiss law. The $1/\chi_M$ *vs* *T* plot is linear. The effective magnetic moment of the complex in the solid-state (300 K) is 1.99 μ_B. The corresponding solution state moment is 1.94 μ_B. The values are in the range of 1.8–2.0 μ_B expected for copper(II) complexes in a magnetically dilute environment [23].

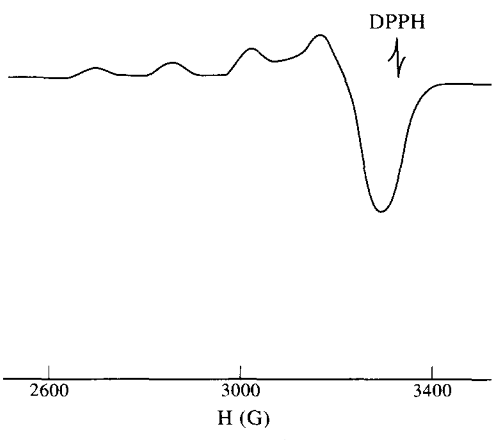

Fig. 2. EPR spectrum of $[Cu(L^4)_2(ONO)]ClO_4$ in dichloromethane-toluene glass at 80 K.

Redox properties

Due to the presence of copper(II)-bound nitrite ion [20,21] we have investigated the redox behaviour of this complex in some detail. It exhibits a one-electron (based on current heights of authentic compounds under similar conditions) [1a–d,3] Cu^{II}–Cu^{I} redox process ($E_{pc} = -0.32$ V *vs* SCE) with a large cathodic to anodic peak separation, implying an irreversible nature of the electrode process. A second irreversible reduction for the Cu^{I}–Cu^{0} redox process is observed at ~ -0.6 V. The cyclic voltammetric scans are presented in Fig. 3. It is worth noting the two overlapping responses in the range 0.2–0.4 V during the anodic scan. Repetitive scanning exhibits a similar feature. This behaviour is most probably due to oxidations of both N-bound and O-bound copper(I)-nitrite species formed at the electrode surface, during cathodic scan. We believe that the response at 0.36 V is due to N-bound NO_2^- and the response at 0.22 V is due to O-bound NO_2^-, implying a redox-driven linkage isomerisation of the NO_2^- ion. In fact, Tanaka *et al.* observed [21c] a closely similar redox behaviour with their $[Cu(H_2O)(tpa)][ClO_4]_2$ (tpa = tris[(2-pyridyl) methyl]amine), in the presence of $[Bu_4N'']$ $[NO_2]$ in MeCN.

When the anodic scanning was continued further an irreversible oxidative response at 1.14 V was observed. This must be due to oxidation of bound ligand (copper(II)-bound NO_2^- to NO_3^- could be a possibility). On scan reversal at 1.4 V, a reversible [25] cyclic response at $E_{1/2} = 0.40$ V is clearly observable. We assign this couple as due to the Cu^{II}–Cu^{I} redox process for the solvated species like $[Cu(L^4)_2(MeCN)_2]^{2+}$ or $[Cu(L^4)_2(MeCN)(OH_2)]^{2+}$. This behaviour implies that the solvated species is generated at the electrode surface due to irreversible ligand oxidation (*vide supra*).

Interestingly, the Cu^{II}–Cu^{I} couple for this solvated species is fairly positive [5a,10,26] which deserves special attention. It is well established [10,24,26] that for nitrogen donor ligands the following factors influence to destabilize Cu^{II} centre and hence to raise the Cu^{II}–Cu^{I} reduction potential. They include: (i) reducing ligand field strength around copper(II) by decreasing ligand σ donor ability or by constraining copper(II) geometry; (ii) introduction of alkyl or aryl substituents near the ligand donor site, which effectively results in a more hydrophobic environment, and (iii) use of π-accepting ligand to favour copper(I) state. Based on the ^{1}H NMR results (co-ordination-induced shifts) of bis(ligand) ruthenium(II) complexes of L^1 and L^3 and the fact that pyrazoles are poor π-accepting ligands [1c], we are inclined to believe that metal-to-ligand (pyridine) π-back donation is less important in this species and hence the present result is due to a combination of the first two factors.

Two results emerge from the above studies. (i) Compared to the case of Tanaka *et al.* (potential shift between water-bound and nitrite-bound in MeCN is 270 mV) [21c] the potential for nitrite-bound Cu^{II}–Cu^{I} couple for the present complex is $\sim$700 mV more negative than the solvent bound couple. (ii) The Cu^{II}–Cu^{I} redox potential for the solvent bound species is fairly positive.

CONCLUSIONS

In this work we have synthesized and characterized a nitrite-bound mononuclear copper(II) complex using two bidentate supporting ligands containing both pyridine and pyrazole in a given non-planar ligand. It should be noted here that very few structurally characterized mononuclear five-co-ordinate copper(II)-nitrito complexes using biologically relevant ligands are known [21]. Electrochemical experiments reveal that the copper(II) state in the title complex is reasonably stabilized with respect to the solvent bound species.

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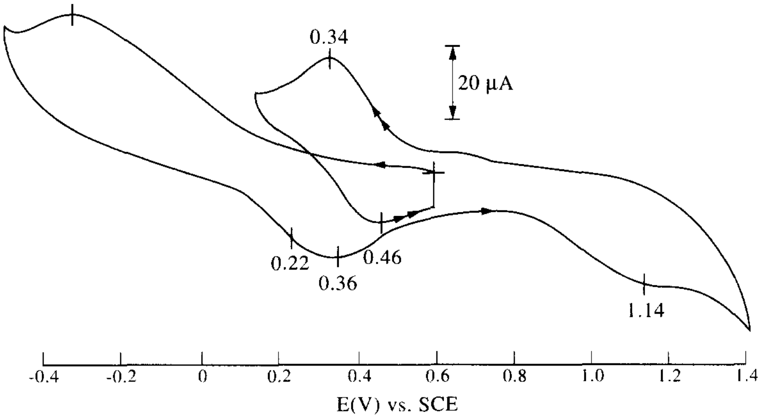

Fig. 3. Cyclic voltammograms of $[Cu(L^4)_2(ONO)]ClO_4$ (1.5 mol dm^{-3}) in MeCN (0.15 mol dm^{-3}) $[NBu_4^n]ClO_4$ at a platinum electrode; scan rate 50 mV s^{-1}. The response due to Cu^{I}–Cu^{0} is not shown.

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