Synthesis, structure and properties of 
[Cu(L)(NCO)]X (L = tetradentate Schiff bases; X = ClO\textsubscript{4}, PF\textsubscript{6})

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Four copper(II) complexes of the type \([\text{Cu}(L)(\text{NCO})]X(1-4)\) \((L=N,N\textsuperscript{\prime}-(\text{bis(pyridin-2-yl)}\text{formylidene})\text{butane-1,4-diamine (bpfd)}\text{or N,N\textsuperscript{\prime}-(\text{bis(pyridin-2-yl})\text{benzylidene)butane-1,4-diamine (bpbd); X} = \text{ClO}\textsubscript{4}, \text{PF}\textsubscript{6})\) have been synthesised and characterised on the basis of microanalytical, spectroscopic, magnetic, electrochemical, and other physicochemical properties. X-ray diffraction study of complex 1 \((L = \text{bpfd}, X = \text{ClO}\textsubscript{4})\) reveals copper(II) ion in a distorted trigonal bipyramidal environment through coordination of the metal centre by two pyridine N atoms and two imine N atoms of the Schiff base with the fifth position occupied with N atom of terminal NCO. The tetradentate chelator is folded in the butylenic part. IR spectra of the complexes show asymmetric and symmetric stretching \(v_{\text{NCO}}\) vibrations at \(-2250\) and \(-1320\) cm\(^{-1}\) respectively indicating N-bonding of NCO. Electrochemical electron transfer study reveals Cu\(^{1+}\)-Cu\(^{2+}\) reduction in methanolic solutions.

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The chemistry of copper(II) azides is well documented\textsuperscript{1-5} through structural and magneto-structural characterisation of a plethora of mononuclear complexes of different dimensions. In contrast, copper(II) cyanates are relatively less explored\textsuperscript{6}. We wish to extend this area of research in combination with different Schiff bases\textsuperscript{5} of varied denticities. In the present note, neutral tetradeinate N-donor Schiff bases \((L)\) \(L = N,N\textsuperscript{\prime}-(\text{bis(pyridin-2-yl)}\text{formylidene})\text{butane-1,4-diamine (bpfd)}\) or \(N,N\textsuperscript{\prime}-(\text{bis(pyridin-2-yl})\text{benzylidene})\text{butane-1,4-diamine (bpbd)}\) have been used. Different mole ratios of metal ion, Schiff base and cyanate may produce\textsuperscript{6} mononuclear, di-, and polymeric cyanato complexes. A 1:1:2 molar ratio is likely to result in the mononuclear neutral compound \([\text{Cu}(L)(\text{NCO})_2]\) and a 1:1:1 ratio should yield dicationic dinuclear \([\text{Cu}(L)(\text{NCO})]_2^{2+}\) or polycationic polymer \([\text{Cu}(L)(\text{NCO})]_n^{n+}\). However, with both ratios, pentacoordinated mononuclear cationic complex of the type \([\text{Cu}(L)(\text{NCO})]^{2+}\) is afforded.

Herein, we report the synthesis and spectroscopic, magnetic and some physicochemical properties of mononuclear complexes of the type \([\text{Cu}(L)(\text{NCO})]X(1-4)\) \((L = \text{bpfd, bpbd; X} = \text{ClO}\textsubscript{4}, \text{PF}\textsubscript{6})\). In one case X-ray crystallographic study of \([\text{Cu}(\text{bpfd})(\text{NCO})]\text{ClO}\textsubscript{4}\) (I) has been made to define the coordination sphere.

Experimental

High purity pyridine-2-carboxaldehyde (Lancaster, UK), 2-benzoylpyridine (Lancaster, UK), butane-1,4-diamine (Lancaster, UK), copper nitrate tetrahydrate (E. Merck, India) sodium cyanate (Aldrich, USA), potassium hexafluorophosphate (Fluka, Germany) were used as received. Copper perchlorate hexahydrate was prepared by treatment of copper carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on steam-bath, filtration through a fine glass-frit, and preservation in a desiccator containing conc. sulphuric acid (E. Merck, India) for subsequent use. MeOH was purified and supporting electrolyte ([Et\textsubscript{4}N][ClO\textsubscript{4}]) was prepared as per literature methods\textsuperscript{5}. All other chemicals and solvents were AR grade and were used as received. The synthetic reactions and work-up were done in open air.

\textbf{Caution!} Perchlorate salts of metal ions are potentially explosive especially in presence of organic ligands. Only a small amount of the material should be prepared and handled with care.

Elemental analysis (C, H, N) was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000-300 cm\(^{-1}\)) were recorded using a Jasco FTIR (model 420) spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 \(M\) KCl solution and dry MeOH was used as

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solvent. UV-vis (in MeOH) and reflectance spectra were recorded on Jasco UV-vis-NIR (model V-570) spectrophotometer. Magnetic susceptibilities were measured with a PAR 155 vibrating sample magnetometer. Electrochemical measurements were made with a computer controlled EG & G PARC VersaStat (model 270) electrochemical instrument using a platinum disk working electrode. The solutions were IR-compensated and the results were collected at 25°C. The following parameters and relations were used: scan rate (v), 50 mV s⁻¹; formal potential \( E' = 0.5 \left( E_{pa} + E_{pc} \right) \), where \( E_{pa} \) and \( E_{pc} \) are anodic and cathodic peak potentials, respectively; \( \Delta E_p \) is the peak-to-peak separation. The potentials were referenced to a saturated calomel electrode (SCE) and are uncorrected for junction contributions.

**Preparation of bpfd and bpbd**

The Schiff base blocks, bpfd and bpbd, were prepared following a reported⁹th procedure. Details with bpfd is described: Pyridine-2-carboxaldehyde (0.214 g, 2 mmol) was refluxed with butane-1,4-diamine (0.088 g, 1 mmol) in dehydrated alcohol. After 10 h the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried and stored in vacuo over CaCl₂ for subsequent use [yield, 0.212 g (80%)]. Bpfd was prepared similarly by refluxing for 10 h 2-benzylopyridine (0.366 g, 2 mmol) instead of pyridine-2-carboxaldehyde with butane-1,4-diamine (0.088 g, 1 mmol) in 2:1 molar ratio [yield, 0.335 g (80%)]. Found: C, 72.4; H, 3.1; N, 21.3; Calc. C₁₆H₁₇N₄ (bpfd): C, 72.2; H, 3.0; N, 21.0%. IR: ν(C=N) = 1590 cm⁻¹; UV-vis, \( \lambda_{\text{max}} \): 245, 372 nm. Found: C, 80.7; H, 6.2; N, 13.5; Calc. C₂₈H₂₆N₄ (bpbd): C, 80.4; H, 6.3; N, 13.4%. IR: ν(C=N) = 1592 cm⁻¹; UV-vis, \( \lambda_{\text{max}} \): 240, 290 nm.

**Preparation of complexes**

Mononuclear complexes 1 and 3 were prepared from perchlorate salts of copper(II) using the same mole ratio (1:1:1) of the metal, bpfd/bpdb and cyanate. Complexes 2 and 4 were prepared using a 1:1:1:1 ratio of copper(II) nitrate, bpfd/bpdb, sodium cyanate and potassium hexafluorophosphate; these were also isolated by metathesis of respectively 1 and 3 with potassium hexafluorophosphate. Typical syntheses are described below.

\[ \text{[Cu(bpfd)(NCO)ClO}_4 \] (1) and [Cu(bpbd)(NCO)ClO}_4 \] (3) \]

A methanolic solution (5 ml) of bpfd (0.26 g, 1 mmol) was added dropwise to a solution of Cu(ClO₄)₂·6H₂O (0.37 g, 1 mmol) in the same solvent (10 ml). NaNCO (0.065 g, 1 mmol) in warm MeOH (5 ml) was added slowly to it. The green solution was filtered and the supernatant liquid was kept in air for slow evaporation. After a few days, the complex that separated out was washed with toluene and dried in vacuo over silica gel indicator [yield, 0.33 g (70%)]. Complex 3 was prepared similarly, using bpbd instead of bpfd [yield, 0.43 g (70%)].

\[ \text{[Cu(bpfd)(NCO)IPF}_6 \] (2) and [Cu(bpbd)(NCO)IPF}_6 \] (4) \]

Cu(NO₃)₂·4H₂O (0.24 g, 1 mmol) was dissolved in MeOH (10 ml). To this, bpfd (0.26 g, 1 mmol) dissolved in the same solvent (5 ml) was added slowly followed by NaNCO (0.065 g, 1 mmol). KPF₆ (0.18 g, 1 mmol) was added in one lot. The final solution was filtered, kept for slow evaporation and processed as in 1 to give pure 2; [yield: 0.38 g (75%)]. This was also prepared by metathesis of 1 (0.47 g, 1 mmol) with KPF₆ (0.18 g, 1 mmol) in MeOH-H₂O (2:1) mixture in better yield [yield: 0.41 g (80%)]. Using bpfd instead of bpfd yielded [0.50 g (75%)] 4. Metathesis of 3 (0.62 g, 1 mmol) with KPF₆ (0.18 g, 1 mmol) in MeOH-H₂O (2:1) affords 4 in higher yield [yield: 0.53 g (80%)].

**X-ray diffraction study**

Single crystals [size: 0.32 × 0.12 × 0.06 mm³] of 1 suitable for X-ray analysis were obtained by slow evaporation of a methanolic solution of the reaction mixture at 25°C. Diffraction data were measured at 213(2) K on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation (\( \lambda = 0.71073 \) Å). Crystallographic data and structure refinement parameters are given in Table 1. Of 11471 collected reflections, 4687 unique reflections were recorded using the o-scan technique. Data were corrected for Lorentz polarization effects and for linear-decay. Semi-empirical absorption corrections based on Ψ-scans were applied. The structure was solved by the heavy atom method using SHELXS-97⁹ and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier map the residual maxima and minima were 0.748 and -0.664 eÅ⁻³. All calculations were carried out using SHELXL-97¹⁰, ORTEP-3²¹.

**Results and discussion**

The tetradentate Schiff bases (bpfd and bpbd) were prepared by refluxing butane-1,4-diamine and pyri-
dine-2-carboxyaldehyde/2-benzoylpyridine in dry alcohol. The pentacoordinated mononuclear complex [Cu(bpfd)(NCO)]CIO₄ (1) initially formed in an MeOH solution containing a 1:1:2 mixture of Cu(CIO₄)₂·6H₂O, bpfd and NaNCO; a reactant ratio expected to yield a mononuclear species of the composition [Cu(L)(NCO)]₂. However, microanalyses showed a 1:1:1 ratio of metal, blocking ligand and the pseudodihalide, and in the IR spectrum presence of perchlorate bands was noticed. Reactant ratio corresponding to the product stoichiometry afforded better yields of 1. In an effort to get [Cu(L)(NCO)₃], the starting material was changed to Cu(NO₃)₂·4H₂O, and a 1:1:2 molar ratio of nitrate salt, ligand and the pseudodihalide produced a gummy mass of indefinite composition. However, addition of KPF₆ to the green reaction solution yielded shining microcrystalline powder of 2. The latter was also obtained from metathesis of 1 with KPF₆. Change of ligand from bpfd to bpbd showed similar behaviour and compounds 3 and 4 were isolated.

All the four complexes were characterised by elemental analysis, electrical conductivity, magnetic susceptibility, IR, UV-vis and reflectance spectra and electrochemistry. The results are consistent with the proposed mononuclear formulation. The air-stable moisture-insensitive complexes are powders, soluble in a range of common organic solvents such as methanol, ethanol, dichloromethane, acetone, but are insoluble in water. In methanol solutions they behave as 1:1 electrolytes as reflected in their Λₑ values. Room-temperature solid-phase magnetic susceptibility measurements show that copper(II) complexes have magnetic moment close to the spin-only value (S = ½), 1.73 BM, expected from discrete and magnetically non-coupled mononuclear 3d⁷ ion (Table 2). IR spectra show characteristic asymmetric and symmetric cyanate stretching vibration at ~2250 and ~1320 cm⁻¹, respectively. These are substantially higher than free ion value and are consistent with N-bonding rather O-bonding. The presence of ionic perchlorate bands at ~1090 and ~620 cm⁻¹ and ionic hexafluoro-

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<th>Table 1 — Crystallographic data for [Cu(bpfd)(NCO)]CIO₄ (1)</th>
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| **Empirical formula**<br>**Formula weight**<br>**Temperature (K)**<br>**Wavelength (Å)**<br>**Crystal system**<br>**Space group**<br>**Dₐ (Mg m⁻³)**<br>**Volume (Å³)**<br>**Z**<br>**Unit cell dimensions a (Å)**<br>**b (Å)**<br>**c (Å)**<br>**α°, β°, γ°**<br>**F(000)**<br>**Crystal size (mm³)**<br>**μ (mm⁻¹)**<br>**0 ranges for data collection (°)**<br>**Reflections collected**<br>**Max. and min. transmission**<br>**Refinement method**<br>**Data/restraints/parameters**<br>**Goodness-of-fit on F²**<br>**Final R indices [I>2σ(I)]**<br>**R indices (all data)**<br>**Largest peak and hole (eÅ⁻³)**<br>**empirical formula**<br>**formula weight**<br>**temperature**<br>**wavelength**<br>**crystal system**<br>**space group**<br>**density**<br>**volume**<br>**z**<br>**cell dimensions**<br>**angles**<br>**size**<br>**mu**<br>**0 range**<br>**reflections**<br>**transmission**<br>**refinement method**<br>**data/restraints/parameters**<br>**goodness of fit**<br>**final r indices**<br>**r indices**<br>**largest peak and hole**<br>**Cu(H₂O)₄ClCu**<br>**C₃H₁₈N₂O₂ClCu**<br>**C₇H₁₈N₂O₄ClCu**<br>**C₇H₁₆N₂O₄PCu**<br>**C₇H₁₆N₂O₄PCu**<br>**CuCl₃·4H₂O**<br>**CuCl₃·4H₂O**<br>| **C**<br>**H**<br>**N**<br>**Λₑ² mol⁻¹ cm⁻²**<br>**μₐ β**<br>**UV-vis**<br>**Cu(H₂O)₄ClCu**<br>**E₂₉₅V (ΔE₉₅)**<br>**mm⁻¹ cm⁻²**<br>**nm**<br>**nm**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>**(r, dm³ mol⁻¹ cm⁻³)**<br>| 43.5<br>39.9<br>55.6<br>52.0<br>43.3<br>39.5<br>55.9<br>52.1<br>| 3.3<br>3.6<br>4.3<br>3.8<br>| 14.7<br>14.0<br>11.4<br>10.4<br>| 130<br>120<br>130<br>120<br>| 1.79<br>1.78<br>1.80<br>1.81<br>| 690 (8,490), 420 (9,020), 365 (22,030), 240 (25,370)<br>692 (8,570), 424 (9,590), 362 (22,370), 240 (25,810)<br>685 (10,550), 415 (10,790), 280 (24,110), 235 (26,590)<br>688 (10,860), 422 (11,010), 282 (24,550), 238 (26,860)<br>| 0.11 (100)<br>0.10 (100)<br>0.14 (100)<br>0.13 (100)<br><br>TABLE 2 — Analytical data of the complexes

*In MeOH solution at 298 K; † In solid state at 298 K; ‡ In MeCN solution at 298 K; † Working electrode is platinum.
phosphate at ~840 and ~540 cm\(^{-1}\) was also noticed. The \(\nu(\text{C}=\text{N})\) stretching vibrations of the metal bound Schiff bases are seen at ~1590 cm\(^{-1}\) (Table 2). All other characteristic L vibrations are seen in the 1600-600 cm\(^{-1}\) range. The reflectance spectra (e.g for I: \(\lambda\), 416, 695 nm) in nujol and electronic spectra (e.g for I: \(\lambda\), 420, 690 nm) in MeOH solutions also indicate a similar gross structure and electronic structure in solid state and in solution\(^{14}\). All the four complexes show similar spectral features which is consonance with similar structure of the cationic unit.

Electroactivity of the complexes was studied in MeOH solutions using cyclic voltammetry and coulometry at platinum working electrodes. A one-electron reductive response is observed presumably due to electrode reaction shown in Eq (1):

\[
\text{[Cu}^{II}(\text{L})(\text{NCO})]^{+} + e \rightleftharpoons \text{[Cu}^0(\text{L})(\text{NCO})]
\]  

(1)

The electrode process in CV is reproducible in the potential range of 0.08 to -0.08 V with no trace of decomposition as reflected in smooth cyclic voltammogram. The one-electron stoichiometry of couple I was confirmed by comparison of current height with that of standard copper(II)-copper(I) couple, since attempted coulometry at potentials more cathodic than \(E_{pce}\) gave continuous coulomb count due to some unidentified side reactions\(^{16}\). The similar pattern in electron transfer behaviour of all the complexes at about same potential once again corroborates similar structure of the cationic units.

X-ray studies

In order to define the coordination sphere, single-crystal X-ray diffraction study was made in one case, viz. I. An ORTEP diagram with atom numbering scheme of the mononuclear unit in I is shown Fig. 1. Selected interatomic bond lengths and bond angles are listed in Table 3. The crystal lattice consists of \([\text{Cu}(\text{bpfld})(\text{NCO})]^+\) cations and \(\text{ClO}_4^-\) anions. The coordination polyhedron around metal centre is best described as distorted trigonal bipyramid (tbp) with CuN\(_5\) chromophore. The coordination includes a tetradentate Schiff base (bpfld) ligated by two pyridine nitrogens (N1, N4), two imine nitrogens (N2, N3) and one terminal cyanate nitrogen (N5). The equatorial positions are occupied by one imine nitrogen (N3), one pyridine nitrogen (N1) and the cyanate nitrogen (N5) while the axial positions are occupied by the remaining imine (N2) and pyridine (N4) nitrogen atoms. The distortion from ideal tbp geometry is due to the asymmetric nature of the Schiff base and the deviations of the refine angles (90°/120°) formed at the metal centre. Butylenic part of the Schiff base N3-C10-C9-C8-C7-N2 is to some extent puckered (Fig. 1). The equatorial Cu-N distances [1.947(4)-2.209(3) Å] as well as the bond angles [102.03(14)-148.90(14)]\(^\circ\)] show significant variations. The axial Cu-N distances [Cu1-N2 2.011(3) Å, Cu1-N4 2.002(3) Å] are however close. The lowest value [1.947(4) Å] of Cu1-N5 distance indicates stronger coordination of the anionic cyanate over neutral Schiff base. The three bite angles N4-Cu1-N3, N3-Cu1-N2 and N2-Cu1-N1 are 81.13(13), 94.53(13) and 78.81(12)\(^\circ\)i.e., respectively. The larger bite in N3-Cu1-N2 arises due to seven membered puckered loop formed from the butylenic arm and is almost of similar value to non-bite angle [96.52(12)\(^\circ\)], N1-Cu1-N4. The axial bond angle, N2-Cu1-N4 [172.30(14)\(^\circ\)], deviates slightly from the ideal value (180\(^\circ\)). The sum (359.97)\(^\circ\) of the equatorial angles N1-Cu1-N3 [109.04(12)\(^\circ\)], N3-Cu1-N5 [148.90(14)\(^\circ\)] and N5-

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<td>2.209(3)</td>
<td>2.011(3)</td>
<td>2.017(3)</td>
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<th>Bond angles (°)</th>
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<td>94.35(15)</td>
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Fig. 1—ORTEP representation of monomeric \([\text{Cu}(\text{bpfld})(\text{NCO})]\)\(\text{ClO}_4\) (I) with atom labelling scheme and 20% probability ellipsoids for all non hydrogen atoms.
Cu1-N1 [102.03(14)°] are very close to 360.00°; so the atoms N1, N3, N5 and Cu1 are almost in a same plane. In the terminal cyanate ligand the N5-C17 distance [1.163(5) Å] is longer than the C17-O5 length [1.203(5) Å] which indicates that the nitrogen (N5) atom of NCO⁻ is coordinated to copper(II) centre. The NCO⁻ ion is coordinated in a linear fashion as seen from its N5-C17-O5 angle [177.6(5)°].

The X-ray structures of the other three complexes could not be solved due to difficulties in obtaining single crystals. However, similarity in IR, UV-vis, reflection spectra, and electrochemical electron transfer properties show cognate solid state and solution structures.

Supplementary data
Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre No 227528 for 1. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References