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The first copper(I) complex containing a cyanato ligand. Synthesis and structural characterization of $[Cu(pyz)(\mu\text{-}NCO)]_n$ (pyz = pyrazine)

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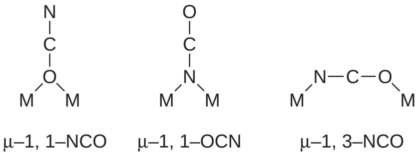
The first copper(I) complex containing a cyanato ligand, $[Cu(pyz)(\mu\text{-}1,1\text{-}NCO)]_n$ (pyz = pyrazine), has been synthesized and characterized.

The cyanate ion, NCO^- is known to co-ordinate to metals in both terminal and bridging modes. As a bridging ligand it can link a pair of metal centres in end-on (μ-1,1-OCN, μ-1,1-NCO) or end-to-end (μ-1,3-NCO) bonded fashion (see below).



μ–1, 1–NCO μ–1, 1–OCN μ–1, 3–NCO

Bi- and poly-nuclear copper cyanate systems are of considerable interest due to the broad range of their structural and magnetic properties,[1] and as synthetic models for the natural copper proteins and their derivatives.[2] However, the vast majority of studies have focused on copper(II) cyanato complexes.[1] On the other hand, while a lot of effort has been devoted to the study of copper(I) complexes of other pseudo-halides,[3] to the best of our knowledge, there is as yet no known example of a copper(I) complex containing a cyanato ligand of any type, terminal or bridging. Moreover, the preparation of the copper(I) cyanate salt itself has been described only once in the early literature, more than four decades ago.[4] We report here the first copper(I) complex $[Cu(pyz)(\mu\text{-}1,1\text{-}NCO)]_n$ (pyz = pyrazine) containing an end-on cyanato bridge bound by the nitrogen atom.

The reaction between copper(I) cyanate and pyrazine afforded a deep red 1 : 1 complex. That copper(I) cyanate has never been used in co-ordination chemistry may be due to its insolubility and/or instability in common solvents. Significantly, a concentrated solution of sodium or potassium cyanate can be used to dissolve polymeric $Cu^I(NCO)$, giving rise to a solution sufficiently stable to air oxidation. Using this procedure allowed us to grow single crystals of $[Cu(NCO)L]_n$†‡ by adding pyrazine in EtOH to the mixture, thus avoiding having to isolate any Cu^{II} impurities. This synthesis was found to be reproducible.

The complex is sufficiently stable against air-oxidation when well-dried. It is insoluble in many common solvents, *e.g.* water, methanol, ethanol, acetone, benzene, *etc.*, but soluble in DMF or DMSO giving rise to non-conducting solutions. In deuterated DMF or DMSO, however, the complex is not sufficiently soluble to allow NMR measurements.

The IR spectrum of $[Cu(pyz)(\mu\text{-}1,1\text{-}NCO)]_n$ shows characteristic asymmetric and symmetric NCO stretching vibrations at 2245, 2225 and 1330, 1316 cm^{-1}, respectively. These values are at substantially higher frequencies than the free-ion values,[5] and on the basis of earlier studies involving cyanate complexes,[6] this is consistent with N-bonding rather than O-bonding. In earlier studies,[7] it has been observed that δ_{NCO} is split by at most a few wavenumbers when the cyanate ion is terminal, while it typically shows a splitting of 30–50 cm^{-1} when the ion is bridging. The appearance of two peaks at 628 and 597 cm^{-1} in the spectrum of the present complex is, therefore, consistent with μ-1,1-cyanato bridge bound by the nitrogen atom. Additionally, the spectrum shows, as the most significant feature, a single band at 448 cm^{-1} (pyrazine) which corresponds to a symmetrical bridging pyrazine with a relatively weak interaction with the metal centre, its value being in the low frequency range for bridging pyrazines.[8]

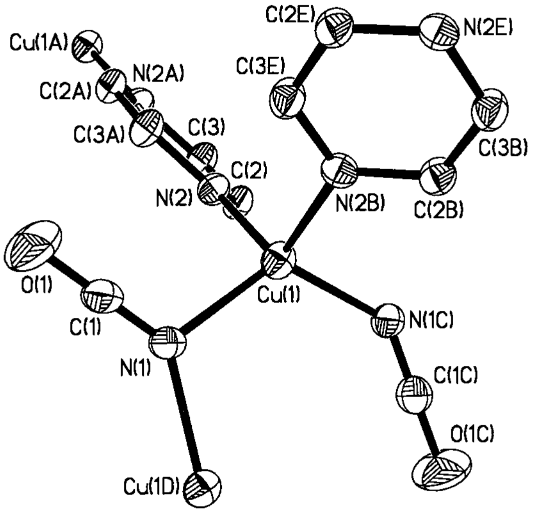


Fig. 1 Co-ordination diagram (40% probability ellipsoids) with atom labelling scheme of polymeric $[Cu(pyz)(NCO)]_n$. The cyanato group acts as a μ-N,N and the pyrazine molecules as μ-N,N′ bridging ligands. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Cu(1)···Cu(1D)[Cu(1C)] 3.333(1), Cu(1)···Cu(1A) 6.899(2), Cu(1)–N(1) 2.101(3), Cu(1)–N(1C) 2.035(3), Cu(1)–N(2)[N(2B)] 2.056(2); N(1)–Cu(1)–N(1C) 123.31(11), N(1)–Cu(1)–N(2)[N(2B)] 104.95(8), N(1C)–Cu(1)–N(2)[N(2B)] 104.87(8), N(2)–Cu(1)–N(2B) 114.37(13), Cu(1C)···Cu(1)···Cu(1D) 124.65(4); symmetry codes: A $-x, 1-y, 1-z$; B $x, 1/2-y, z$; C $-1/2+x, y, 3/2-z$; D $1/2+x, y, 3/2-z$; E $-x, -1/2+y, 1-z$.

A structure determination has shown the complex $[Cu(pyz)(NCO)]_n$ to possess a polymeric structure. Each distorted tetrahedrally bonded copper atom links two nitrogen atoms from two pyrazine ligands and the other two sites are occupied by nitrogen atoms from two cyanato ligands (Fig. 1). Thus the cyanate ion behaves as a μ-1,1 bridge bound *via* its nitrogen atom as inferred from the IR spectroscopy. The Cu(I)–μ-1,1-bridging cyanato sublattice [located at the mirror planes] forms chains along the *a*-axis. These chains are further connected *via* μ-N,N′ bridging pyrazine molecules to form a 3-D network (Fig. 2). This structure differs from those of the corresponding polymeric $[Cu(pyz)X]_n$ (X = NCS or N_3) complexes.[9] In the

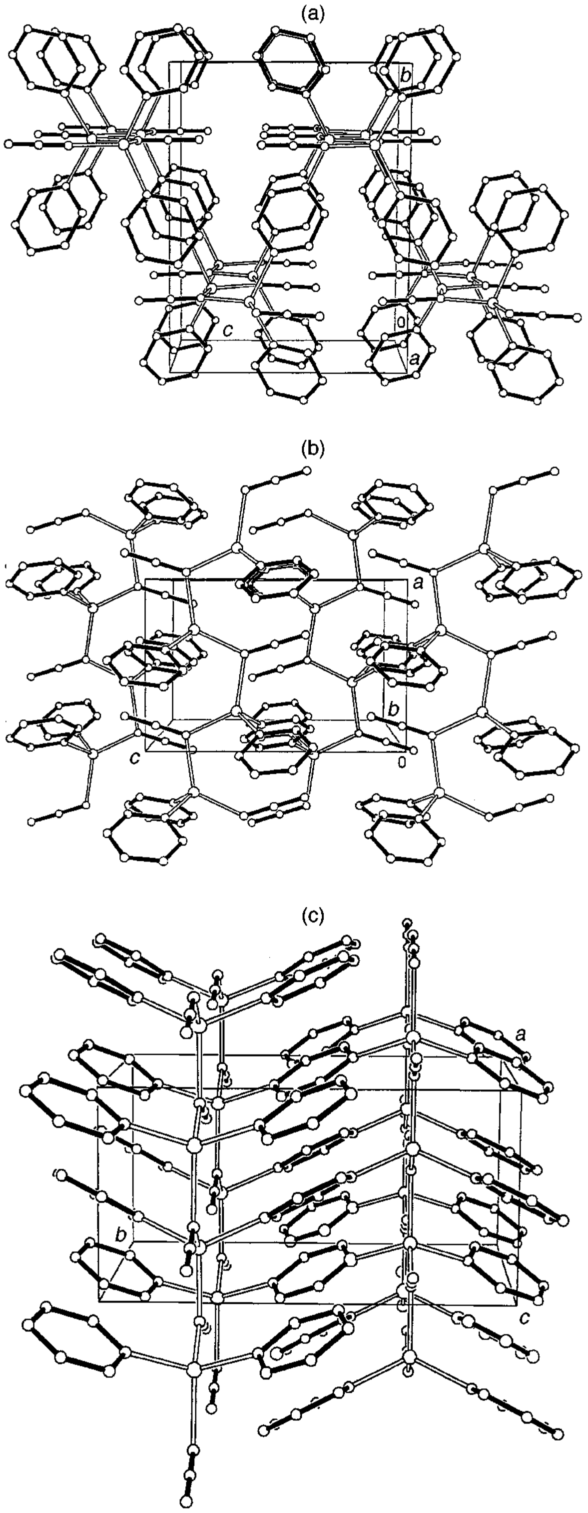


Fig. 2 Packing views of [Cu(pyz)NCO]$_n$ along the main axes of the unit cell: (a) along the *a*-axis; (b) along the *b*-axis; (c) along the *c*-axis. Atoms are represented as spheres with arbitrary size and hydrogen atoms are omitted for clarity. The Cu(I)–μ-N,N bridging cyanato sublattice [located at the mirror planes] forms chains along the *a*-axis. These chains are further connected *via* the μ-N,N′ bridging pyrazine molecules to form a 3-D network.

latter complexes the μ-1,3 bridging mode of the thiocyanate or azido ligand, along with the μ-N,N′ pyrazine resulted in two perpendicular 1-D zigzag chains crossing at the copper centres giving rise to a 2-D network structure. That the cyanate ion behaves as a μ-1,1 bridge means that a 2-D structure would not be formed and that therefore the 3-D network is the expected structure in this case.

The structural motif observed in the complex [Cu(pyz)(μ-NCO)]$_n$ represents both the first example of copper(I) complexes containing a cyanato ligand and also a new 3-D network. The preparation of this compound illustrates a new and potentially versatile approach to the construction of uncharged inorganic co-ordination networks and we are currently pursuing this methodology towards the synthesis of such new materials.

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Notes and references

† Preparation of [Cu(pyz)(μ-1,1-NCO)]$_n$. To an aqueous suspension of Cu(NCO) (2 mmol) a saturated aqueous solution of KNCO was added until a clear solution was obtained and any impurities filtered off. Pyrazine (4 mmol) dissolved in EtOH (*ca.* 10 ml) was then added and the final mixture allowed to stand over several days to yield large deep red crystals of the complex, along with an unknown pale red powder. Yield, *ca.* 20% [Found (calc.): C, 32.1 (32.34); H, 2.3 (2.17); N, 22.3 (22.62); Cu, 34.6 (34.23%)]. The complex was stored over *ca.* three months in a normal vial at room temperature without any sign of oxidation. IR (KBr disc): ν_1 (ν_{CN}) 2245s, 2225vs; ν_3 (ν_{CO}) 1330m, 1316m; δ_{NCO} 628m, 597m; ν_{16b} (pyrazine) 448 cm^{-1}. Electronic spectrum (solid Nujol mull): 420 (br), 500 nm (Cu^I→LCT).

‡ Crystal data for [Cu(pyz)(NCO)]$_n$: $C_5H_4CuN_3O$, $M = 185.65$, orthorhombic, space group *Pnma* (no. 62), $a = 5.904(2)$, $b = 11.593(3)$, $c = 9.038(4)$ Å, $U = 618.6(4)$ Å^3, $Z = 4$, $F(000) = 368$, $D_c = 1.993$ g cm^{-3}, μ(Mo-Kα) = 3.447 mm^{-1}, $T = 295(2)$ K. 573 unique reflections ($R_{int} = 0.0308$) were collected. At final convergence $R1$ [520 data with $I > 2\sigma(I)$] = 0.0261, $wR2$ (all 573 data) = 0.0655 for 53 parameters. CCDC reference number 186/1462. See http://www.rsc.org/suppdata/dt/1999/1923/ for crystallographic files in .cif format.

1 See for example, T. Otieno, S. J. Retting, R. C. Thompson and J. Trotter, *Inorg. Chem.*, 1993, **32**, 4384.
2 See for example, V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch and C. A. Reed, *J. Am. Chem. Soc.*, 1984, **106**, 4765.
3 See for example, (*a*) S.-M. Kuang, Z.-Z. Zhang, Q.-G. Wang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1997, 4477; (*b*) M. A. S. Goher, R.-J. Wang and T. C. W. Mak, *J. Coord. Chem.*, 1996, **38**, 151 and refs. therein.
4 E. Soederbarcy, *Acta Chem. Scand.*, 1975, **11**, 1622.
5 A. Maki and J. C. Decius, *J. Chem. Phys.*, 1959, **31**, 772.
6 (*a*) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 1286; (*b*) A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.
7 (*a*) R. A. Baily, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 1971, **6**, 407; (*b*) J. Nelson and S. M. Nelson, *J. Chem. Soc. A*, 1969, 1597.
8 T. Otieno, S. J. Retting, R. C. Thompson and J. Trottor, *Can. J. Chem.*, 1990, **68**, 1901.
9 M. A. S. Goher and F. A. Mautner, *Polyhedron*, in the press.

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