[{Cu(bipy)(H_2O)Pt$(CN)_4$}$_2$]·2H_2O: the first synthesis and crystal structure of a discrete heterometallic square cyano-bridged compound with terminal cyano ligands

Larry R. Falvello* and Milagros Tomás*

Department of Inorganic Chemistry and Aragón Materials Science Institute, University of Zaragoza-C.S.I.C., Plaza San Francisco s/n E-50009 Zaragoza, Spain. E-mail: falvello@LRF1.unizar.es

Received (in Basel, Switzerland) 21st September 1998, Accepted 13th December 1998

The synthesis and crystal structure of a square cyano-bridged compound with terminal cyano ligands are presented together with a discussion of the influence of H_2O molecules on the stability of the terminal cyanides and therefore on the discrete nature of the compound.

The particular characteristics of the cyanide group have accorded it wide-ranging interest in various research areas.[1,2] One of the more interesting characteristics of $C{\equiv}N^-$ is its ability to act either as a terminal or as a bridging ligand. When it acts as a bridging ligand between metal atoms it usually gives rise to polymeric compounds[2] with 1-D, 2-D or 3-D networks. Except for some clusters such as those with the 'Mo_6Cl_8' core,[3] few discrete cyanide-containing molecules with more than three metal atoms have been synthesized and structurally characterized; and particularly rare are those with cyano–metal rings.[1]

Although square or distorted square cyano-bridged fragments, both homo- and hetero-nuclear, have been found embedded in polymeric compounds,[4–6] only very few discrete molecules with square cyano-bridged structures have been reported,[1] characterized mostly on the basis of molecular weight determinations.[7] Only two, the homonuclear compounds $[Cp_2Ti(CN)]_4$ and $[(\eta^2\text{-tmtch})Cu(CN)]_4$ (tmtch = 3,3,6,6,-tetramethyl-1-thia-4-cycloheptyne) have been fully characterized by single-crystal X-ray diffraction studies.[8] No structures of heteronuclear, square, cyano-bridged compounds have been reported.

It may be that the scant information available to date on discrete cyano-bridged ring compounds is the result of a scarcity of appropriate cyano-containing starting materials and the difficulty of obtaining crystalline compounds suitable for X-ray diffraction studies. We report here the synthesis of a discrete cyano-bridged ring using a 'stoichiometrically inappropriate' starting material and the preparation of single crystals by an unconventional method.

Polymerization can easily occur when the starting cyano compound contains more cyano groups than those required for the formation of the discrete ring. So it would seem that appropriate starting materials for obtaining discrete square homometallic $\{M(CN)\}_4$ or heterometallic $\{M(CN)M'(CN)\}_2$ rings should contain an average of one cyano group per metal. In fact, $[(\eta^2\text{-tmtch})Cu(CN)]_4$ was obtained beginning with CuCN, with only one CN group per metal center; and $[Cp_2Ti(CN)]_4$ was prepared using a starting material, $\{Cp_2TiCl\}_2$, which only incorporates one CN group per Ti upon reacting with NaCN.

Structures of discrete square cyano-bridged compounds with terminal CN groups are not known, but there are some examples of other kinds of compounds with terminal CN groups that do not form polymers.[6,9] For instance, in the compound $[\{Cu(dien)M(CN)_6\}_n][Cu(dien)(H_2O)(\mu\text{-}CN)M(CN)_5]_n$,[6] in addition to an unbounded chain of fused heterometallic rings, the discrete dianionic unit with five terminal cyanides, is also present.

$[Pt(CN)_4]^{2-}$ compounds can react using the basic character of the Pt atom and have been extensively studied for their formation of conducting metal stacks.[10] $[Pt(CN)_4]^{2-}$ can also form complexes using its terminal CN ligands, giving rise to polynuclear compounds with 3-D networks such as in $[NMe_4][CuPt(CN)_4]$[11] or 2-D networks as in the Hofmann-type clathrates $[M(NH_3)_2Pt(CN)_4]$.[5] 1-D networks have been proposed for Zr or Hf in $[M(\eta^5\text{-}C_5H_5)_2Pt(CN)_4]_n$, although no X-ray diffraction data are available owing to the amorphous character of the solids.[12] $[Pt(CN)_4]^{2-}$ also reacts with rare earth metals, forming interesting 1-D networks that contain both terminal and bridging cyano groups.[13] However, to our knowledge no discrete heteronuclear compounds derived from $[Pt(CN)_4]^{2-}$ and containing bridging CN ligands, have been structurally characterized.

The reaction of $[NBu_4]_2[Pt(CN)_4]$ with $Cu(NO_3)_2{\cdot}2.5H_2O$ and 2,2′-bipyridyl produces the immediate precipitation of the deep blue solid $[\{Cu(bipy)(H_2O)Pt(CN)_4\}_2]{\cdot}2H_2O$ **1**.† The IR spectrum of compound **1** shows four absorptions in the CN region: 2208, 2195, 2156 and 2149 cm^{-1}. Those at 2208 and 2195 cm^{-1} correspond in all likelihood to the two *cis*-bridging CN groups, since bridging CN usually appears at higher energy than does terminal CN.[2] Thus, the bands at 2156 and 2149 cm^{-1} correspond to the two *cis*-terminal CN ligands. Crystals suitable for X-ray diffraction can be obtained—together with a variety of other compounds—by an unusual procedure, dissolution of compound **1** in a concentrated solution of NH_4OH and then slow evaporation of the NH_3. Compound **1** is very insoluble, and its solubility in NH_4OH is probably due to the coordination of NH_3 to the copper, which breaks the bridging cyanide system. The evaporation of the NH_3 regenerates the tetranuclear compound. This method, breaking the bridging cyanide system and slow regeneration of the insoluble compound, can probably be applied to the crystallization and even formation of other compounds, especially cyanide complexes. The magnetic properties and the nature of the other compounds are presently under study. Fig. 1 shows a view of one molecule of $[\{Cu(bipy)(H_2O)Pt(CN)_4\}_2]$.‡ The molecule consists of two $Pt(CN)_4$ fragments and two $Cu(bipy)(H_2O)$ moieties held together by CN bridges. The bridging cyanide ligands bind to platinum through their carbon atoms and to the copper centers through nitrogen, and the *cis*-disposition of the bridging CN moieties at each of the metal centers yields the square shape of the core of the complex. The molecule sits on a crystallographic inversion center. The square planar coordination about each platinum center is completed by two terminal CN groups. Each Cu center has a terminal chelating bipy ligand, which is nearly coplanar with the square core of the complex. The coordination about copper is completed by an apical aqua ligand [Cu–O 2.227(6) Å], giving a distorted square pyramidal coordination environment. As the molecule is centric, the two square pyramids at opposite corners of the Pt_2Cu_2 square have opposite polarities. There is also one unligated molecule of water in the crystallographic asymmetric unit, or two per molecule of complex **1**. Both the ligated [O(1)] and unligated [O(2)] water

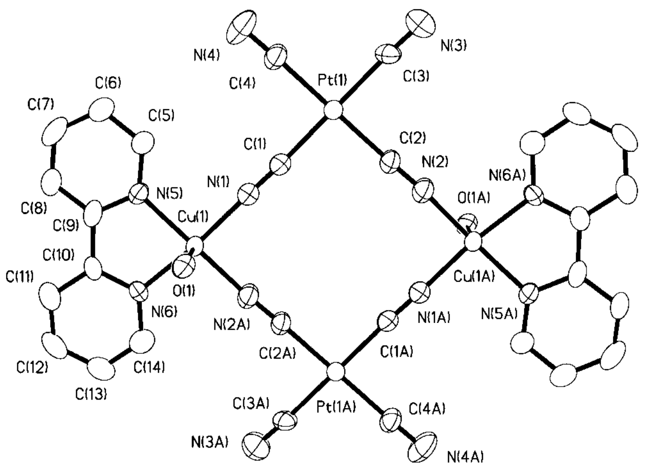

Fig. 1 Crystal structure of **1** with atom labelling scheme (50% probability ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 1.973(8), Pt(1)–C(2) 1.973(7), Pt(1)–C(3) 1.985(8), Pt(1)–C(4) 1.987(8); Cu(1)–N(1) 1.958(7), Cu(1)–N(2A) 1.961(6), Cu(1)–N(5) 2.010(6), Cu(1)–N(6) 1.994(6), Cu(1)–O(1) 2.228(6), C(1)–N(1) 1.145(10), C(2)–N(2) 1.144(10), C(3)–N(3) 1.114(11), C(4)–N(4) 1.136(10); N(5)–Cu(1)–N(6) 81.5(3).

molecules are involved in significant hydrogen bonds. The bound water molecule acts as an H-bond donor to the terminal nitrogen atom N(4) of another molecule, with O(1)···N(4′) 2.82(1) Å. The free water molecule acts as a hydrogen bond donor to terminal nitrogen atom N(3) of two different molecules, with O(2)···N(3′) 2.85(1) Å and O(2)···N(3″) 2.94(1) Å. So the terminal nitrogen atoms of both pendant cyanide ligands serve as hydrogen bond acceptors in the extended structure. There is also a hydrogen bond between the bound and free water moieties, with O(1)···O(2) 2.76(1) Å.

The fact that the apical water molecule in the coordination environment of copper is not substituted by cyanide nitrogen to give rise to an extended structure can be explained as the result of several factors. First of all, the fifth and sixth coordination constants of copper are relatively small, especially when the first four ligands are nitrogen donors.[14] So a factor internal to the molecule, the propensity of copper not to accept a fifth nitrogen donor, may be responsible for the incorporation of water and the concomitant impediment to polymer formation. It remains true, however, that cases exist in which cyanide participates in a copper coordination environment consisting of five nitrogen atoms; the $[(Cu(dien)M(CN)_6\}_n]^{n-}$ chain is just such an example.

The hydrogen bonding that is found in the solid is also a key factor, and may be crucial, in determining the structure that we observe, since the formation of significant hydrogen bonds satisfies the nucleophilicity of the terminal nitrogen atoms and serves as a blocking factor, both spatially and electronically, against coordination of these nitrogen atoms to other metal centers.

In conclusion, the use of a starting material with excess cyanide in an environment favorable to the formation of hydrogen bonds with the cyanide nitrogen as acceptor, can give rise to discrete molecules with terminal cyanide ligands such as the tetranuclear square heterometallic complex **1**.

Funding by the Dirección General de Enseñanza Superior (Spain) under grant PB95-0792 is gratefully acknowledged. The authors thank Dr J. M. Williams for helpful suggestions.

Notes and references

† *Experimental procedure and selected data*: an acetone solution of 0.200 g (0.254 mmol) of $[NBu_4]_2[Pt(CN)_4]$ was added to an aqueous solution of 0.058 g (0.25 mmol) of $Cu(NO_3)_2\cdot 2.5H_2O$ and bipy (0.040 g, 0.25 mmol). The precipitate of complex **1** was filtered off after being stirred for 15 min. The solid was washed with acetone and dried (77% yield). Crystals suitable for X-ray analysis were obtained by dissolving compound **1** in a concentrated solution of NH_4OH and then letting the NH_3 evaporate slowly. Satisfactory elemental analysis was obtained. IR: ν(OH): 3504–3261 cm^{-1}; bipy: 1612, 1605 and 773 cm^{-1}.

‡ (a) *Crystal structure data*: crystal dimensions, 0.32 × 0.26 × 0.12 mm; monoclinic, space group $P2_1/c$; a = 8.5573(8), b = 26.064(3), c = 7.5950(7) Å, β = 91.976(9)°, V = 1693.0(3) Å^3; D_c = 2.177 Mg m^{-3}; $2\theta_{max}$ = 55.0°; Mo-Kα radiation, $\lambda(\bar{\alpha})$ = 0.71073 Å; ω–θ scans; T = 298–299 ± 1 K; L_p corrections applied; μ = 9.53 mm^{-1}; max., min. relative transmission = 1.000, 0.370; absorption corrections based on 26 ψ-scans of reflections with bisecting-mode Eulerian equivalent χ ranging from −27 to +50°; 4251 data measured, 3863 unique, R_{int} = 0.0274; structure solution by direct methods; 3863 data used in refinement to F^2, no σ limit; 222 parameters. All hydrogen atoms were observed in a difference Fourier map, but those of the bipy ligand were placed at idealized positions and refined as riding atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent carbon atoms. The hydrogen atoms of the H_2O moieties were initially placed at the positions at which they were located in the difference Fourier map and were refined as riding atoms with independent isotropic displacement parameters. $R1$ = 0.0383 [calculated for 3125 $|F| > 4\sigma(|F|)$]; $wR2$ = 0.1050 for all F^2; quality of fit = 1.046. Max., min. residual difference density: +1.31, −1.20 e Å^{-3}. (b) *Crystallographic software*: data reduction and L_p corrections, XCAD4B (K. Harms, 1995); absorption corrections and molecular graphics, SHELXTL Rel. 5.05/VMS, ©1996, Siemens Analytical X-Ray Systems, Inc., Madison, WI; direct methods, SHELXS-97, ©1997, George M. Sheldrick; structure refinement, SHELXL-97, ©1997, George M. Sheldrick. CCDC 182/1126. See http://www.rsc.org/suppdata/cc/1999/273/ for crystallographic files in .cif format.

1 H. Vahrenkamp, A. Geib and G. N. Richardson, *J. Chem. Soc., Dalton Trans.*, 1997, 3643.
2 K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283.
3 D. H. Johnston, C. L. Stern and D. F. Shriver, *Inorg. Chem.*, 1993, **32**, 5170.
4 G. W. Beall, W. O. Milligan, J. Korp and I. Bernal, *Inorg. Chem.*, 1977, **16**, 2715; H. J. Buser, D. Schwarzenbach, W. Petter and A. Ludi, *Inorg. Chem.*, 1977, **16**, 2704.
5 T. Iwamoto, T. Nakano, M. Morita, T. Miyoshi, T. Miyamoto and Y. Sasaki, *Inorg. Chim. Acta*, 1968, **2**, 313.
6 G. O. Morpurgo, V. Mosini, P. Porta, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1981, 111; D. G. Fu, J. Chen, X. S. Tan, L. J. Jiang, S. W. Zhang, P. J. Zheng and W. X. Tang, *Inorg. Chem.*, 1997, **36**, 220.
7 F. Stocco, G. Stocco, W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, 1971, **10**, 2639; B. L. Shaw and G. Shaw, *J. Chem. Soc.*, 1971, 3533.
8 P. Schinnerling and U. Thewalt, *J. Organomet. Chem.*, 1992, **431**, 41; F. Olbrich, J. Kopf and E. Weiss, *J. Organomet. Chem.*, 1993, **456**, 293.
9 S. Takano, T. Naito and T. Inabe, *J. Mater. Chem.*, 1998, **8**, 511; M. Zhou, B. W. Pfennig, J. Steiger, D. Van Engen and A. B. Bocarsly, *Inorg. Chem.*, 1990, **29**, 2456.
10 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987, pp. 139–204.
11 R. W. Gable, B. F. Hoskins and Richard Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 762.
12 J. A. Abys, G. Ogar and W. M. Risen, *Inorg. Chem.*, 1981, **20**, 4446.
13 D. W. Knoeppel and S. G. Shore, *Inorg. Chem.*, 1996, **35**, 1747; D. W. Knoeppel and S. G. Shore, *Inorg. Chem.*, 1996, **35**, 5328.
14 B. J. Bathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 5, pp. 533–774.

Communication 8/07324D