Synthesis and Structure of a Copper(I) Complex with 1-Aminopyrene: Building of a 2D Structure Composed of Stacking Pyrene Rings

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The first copper(I) complex with aminopyrene [Cu(apyr)$_3$]ClO$_4$·MeOH is synthesized and characterized crystallographically; the most remarkable feature of the compound is its 2D structure connected through intra- and inter-molecular stacking of the aromatic rings.

One- and two-dimensional new materials with quasimetallic or semiconductive electrical properties have forced a progressive refinement of theoretical models as well as experimental expectation for cooperative phenomena in molecular solids. Donor–acceptor complexes of aromatic-electron systems often play an important role in these materials as an electronic donor.[1–3] It has been our interest to explore general approaches to the chemical synthesis of metal complex assemblies with the π–π interaction of aromatic rings.

[Cu(apyr)$_3$]ClO$_4$·MeOH **1** was prepared as follows. Copper wire was added to 0.1 mmol Cu(ClO$_4$)$_2$·6H$_2$O in MeOH, under ethylene, and the mixture stirred for 30 min at 0 °C. After removing the copper wire, 0.2 mmol apyr was added under argon. The yellow–green precipitate was filtered off, and then the filtrate was sealed in a glass tube under an argon atmosphere. Yellow–green crystals were obtained at −20 °C after two days.

The molecular structure of **1** is shown in Fig. 1. The Cu atom is coordinated by three amine groups in distorted trigonal geometry. The planes of pyr(1) and pyr(2) are parallel to each other, whereas the pyr(3) lies approximately perpendicular to the planes. The Cu atom has a T-shaped geometry because of the parallel arrangement of the pyr(1) and pyr(2),[4] the angle of N(1)–Cu–N(2) (131.3°) being larger than the others, N(2)–Cu–N(3) (112.8°) and N(1)–Cu–N(3) (115.8°). The Cu–N distances of 2.01(3) Å (av.) are between 1.890(8)–2.295(7) Å for $[CuN_3]^+$ type complexes.[4] MeOH is not coordinated.

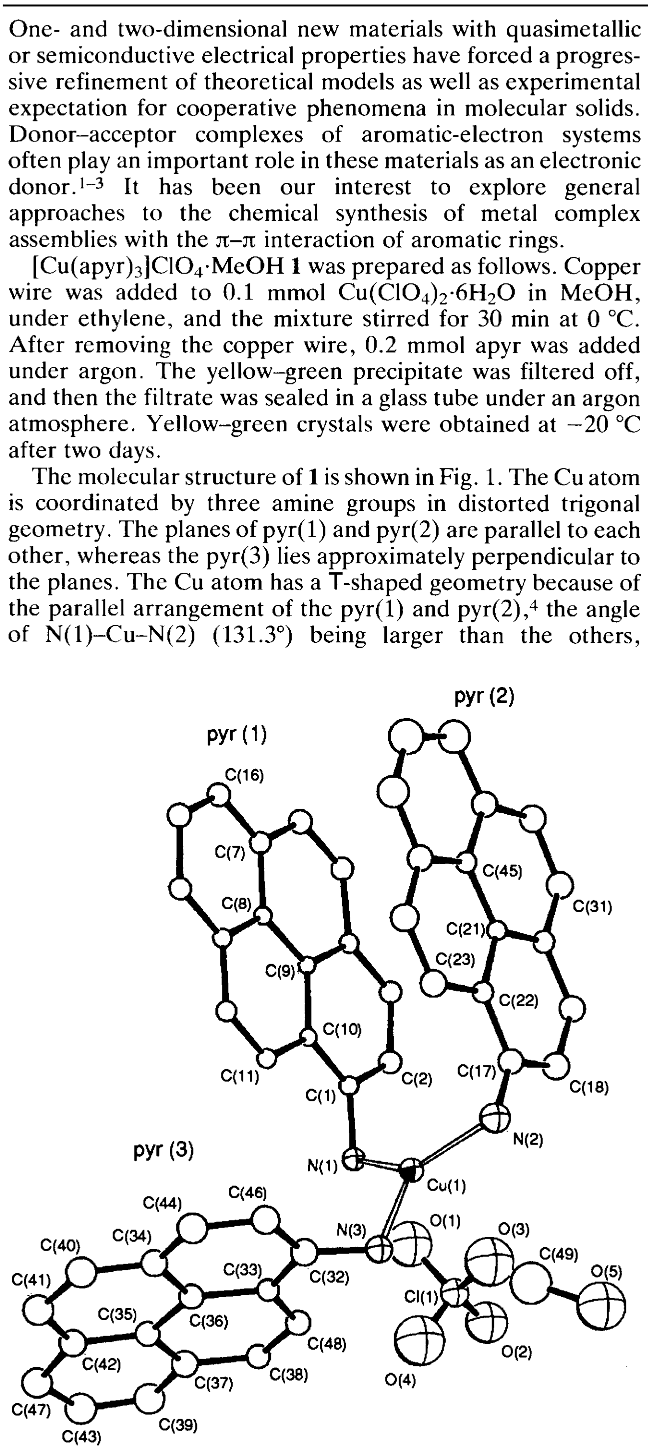

Fig. 1 Structure of Cu(apyr)$_3$ClO$_4$·MeOH **1**. Selected bond distances (Å) and angles (°): Cu–N(1) 2.01(1), Cu–N(2) 1.99(1), Cu–N(3) 2.04(1); N(1)–Cu–N(2) 131.3(6), N(1)–Cu–N(3) 115.8(6), N(2)–Cu–N(3) 112.8(6), Cu–N(1)–C(1) 110.2(9), Cu–N(2)–C(17) 110(1), Cu–N(3)–C(32) 113(1).

Fig. 2 shows the molecular packing of **1**. Interplane spacing is 3.46 Å between pyr(1) and pyr(2), indicative of an intramolecular π–π interaction. Furthermore, there are intermolecular π–π interactions between pyr(1) and pyr(1′), and pyr(2) and pyr(2′). The interplane spacing being 3.40 and 3.43 Å, respectively. The π–π interactions form an infinite stacking column of pyr(1) and pyr(2). In addition, these columns are connected through stackings of pyr(3) to form the two-dimensional structure, the interplanar distance between pyr(3) and pyr(3′) is 3.52 Å.

In the field of synthetic organic metals, pyrene and its derivatives have been used as new types of donors. The structures of several pyrene complexes with electron acceptors have been determined. The mean perpendicular separation between the donor and acceptor planes is in the range of 3.3–3.8 Å.[5–10] Radical salts of 2,7-bis(methylthio)-1,6-dithiapyrene(MTDTPY)[11] form uniform columnar stacks with interplanar distances of 3.40 Å. This value is shorter than the 3.48 Å of the TCNQ complex and the 3.47 Å of the chloranil(CHL) complex of MTDTPY.[12] The interplanar distances are generally in the order: Radical salts ⩽ D–A molecular complexes < neutral donors.[11–13] In complex **1**, the interplanar distances in the stacking columns [3.43 Å (av.)] are shorter than that of the free pyrene (3.52 Å).[14] This finding indicates that metal complex formation can also play an important role in the control of the distance of stacking planes.

The coordinating ability of aromatic amines (monodentate), such as benzeneamine, naphthylamine and aminophenanthrene to copper(I) are too weak to form stable complexes. To our knowledge, there are no such complexes characterized crystallographically, complex **1** would be the first example of this type complex. The stability of **1** can be explained by its higher lattice energy for the molecular interaction. However, the complex is still easily oxidized even in the solid state.

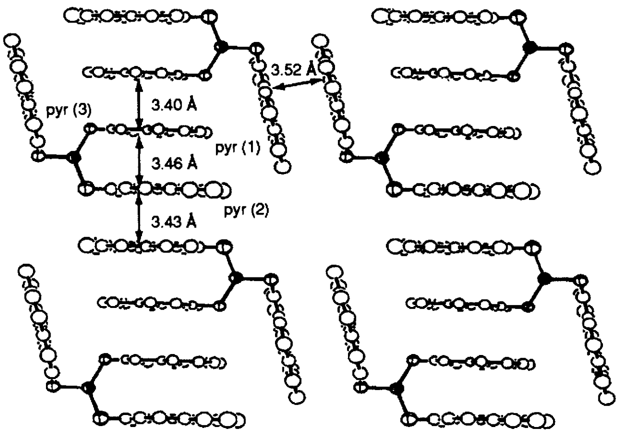

Fig. 2 Molecular packing of **1**

A *cis*-platinum complex is the only known example of a complex with 1-aminopyrene, but there was no crystal data reported.[15] A few metal complexes with pyrene were characterized crystallographically, and there were no π–π interactions between the pyr planes.[16–18]

Halogen doping of planar, conjugated metallomacrocycles has been shown to be an effective strategy for the synthesis of electrically conductive, low-dimensional compounds.[19–20] In our work, it is also noted that the complex **1** (an insulator) was treated with iodine in the gaseous diffusion method, (50 °C, five days) to give an electric conductivity of 4.5×10^{-4} S m^{-1} at room temp. Comparing the solid-state electronic spectra of iodine-doped **1** with the original, a broad peak exhibited at 660 nm, which is largely due to the polyiodide chains.[21] (I_3^- and I_5^-). Therefore, the complex was partially oxidized and exhibits some properties of radical salts.

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Footnote

† *Crystal data* for **1**: $CuClO_5N_3C_{49}H_{37}$, $M = 846.85$, triclinic, space group $P\bar{1}$, $a = 14.446(9)$, $b = 16.487(2)$, $c = 8.715(2)$ Å, $\alpha = 93.65(1)°$, $\beta = 104.39(3)°$, $\gamma = 87.06(4)°$; $U = 2005(1)$ Å^3, $Z = 2$, $D_c = 1.391$ g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, crystal dimensions 0.2 × 0.3 × 0.2 mm.

Intensity data in the range $2\theta < 50.0°$ were collected by the ω-2θ scan technique using a Rigaku AFC5R automatic diffractometer. The structure was solved by a direct method (MITHRIL and DIRDIF) and was refined using least-squares techniques. The final R and R_w values were 0.068 and 0.069, respectively, based on 1674 observed reflections [$I > 3.20\ \sigma(I)$] and 532 variable parameters.

Atomic coordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. S. Miller, *Extended linear chain compounds*, Plenum, New York, 1981–1983, vols. 1–3.

2 J. S. Miller, J. C. Calabrese, R. L. Harlow, D. A. Dixon, J. H. Zhang, W. M. Reiff, S. Chittipeddi, M. A. Selover and A. J. Epstein, *J. Am. Chem. Soc.*, 1990, **112**, 5496.

3 M. Munakata, S. Kitagawa, N. Ujimaru, M. Nakamura and M. Maekawa, *Inorg. Chem.*, 1993, **32**, 826.

4 M. Munakata, M. Maekawa, S. Kitagawa, S. Matsuyama and H. Masuda, *Inorg. Chem.*, 1989, **28**, 4300.

5 C. K. Prout and I. J. Tickle, *J. Chem. Soc., Perkin Trans.*, 1973, 734.

6 C. K. Prout, I. J. Tickle and J. D. Wright, *J. Chem. Soc., Perkin Trans.*, 1973, 528.

7 C. K. Prout, T. M. Orley, I. J. Tickle and J. D. Wright, *J. Chem. Soc., Perkin Trans.*, 1973, 523.

8 J. C. Barnes, J. A. Chudek, R. Foster, F. Jarrett, F. Mackie and J. Paton, *Tetrahedron*, 1984, **40**, 1595.

9 I. Ikemoto and H. Kuroda, *Acta Crystallogr. Sect. B*, 1968, **24**, 383.

10 F. H. Herbstein and J. A. Snyman, *Phil. Trans.*, 1969, **A264**, 635.

11 A. Kawamoto, J. Tanaka, A. Oda, H. Mizumura, I. Murata and K. Nakasuji, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2137.

12 K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto and J. Tanaka, *J. Am. Chem. Soc.*, 1987, **109**, 6970.

13 K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama and J. Tanaka, *J. Am. Chem. Soc.*, 1986, **108**, 3460.

14 A. Camerman and J. Trotter, *Acta Crystallogr.*, 1965, **18**, 636.

15 T. Osa, H. Hino, S. Fujieda, F. Shimizu and M. Arakawa, *Chem. Pharm. Bull.*, 1986, **34**, 1881.

16 T. Hasegawa, M. Sekine, W. P. Schaefer and H. Taube, *Inorg. Chem.*, 1991, **30**, 449.

17 I. M. Vezzosi, A. F. Zanoli, L. P. Battaglia and A. B. Corradi, *J. Chem. Soc., Dalton Trans.*, 1988, 191.

18 G. Bombieri, G. Peyronel and I. M. Vezzosi, *Inorg. Chim. Acta*, 1972, **6**, 349.

19 M. Cowie, A. Gleizes, G. W. Grynkwich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.

20 J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffmann and T. J. Marks, *J. Am. Chem. Soc.*, 1977, **99**, 287.

21 L. D. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewruf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2937.