A Linear Trimeric Copper(I) Complex: Synthesis and Crystal Structure of a Copper(I) Complex of *N,N'*-Bis(*p*-tolylsulphonyl)pyridine-2,6-diaminato

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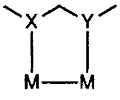
A pair of *N,N'*-bis(*p*-tolylsulphonyl)-pyridine-2,6-diaminato bridging ligands bind three copper(I) ions in a linear array with an average Cu–Cu distance of 2.467(1) Å.

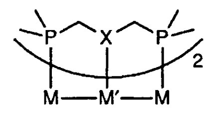
Many examples of binuclear metal complexes with bridging ligands, **1**, have been reported;[1] complexes of the type $[M_2(OAc)_4L_2]$ (M = Cu, Rh, Ru) are the most common. On the other hand, few examples of linear trimeric metallic complexes are known. Balch and coworkers have synthesized a series of homo- and hetero-trimetallic complexes **2**.[2] Beck and Strähle reported a trimeric linear copper(I) complex in a trigonal-planar cordination environment.[3]

Here we report a novel approach for the synthesis of the inexpensive ligand **4** which is capable of forming trimetallic complexes, and present the synthesis and structure of a trimeric copper(I) complex of *N,N'*-bis-(*p*-tolylsulphonyl)-pyridine-2,6-diaminato.



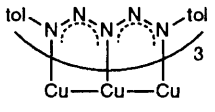
1

X, Y = O, S, N, P



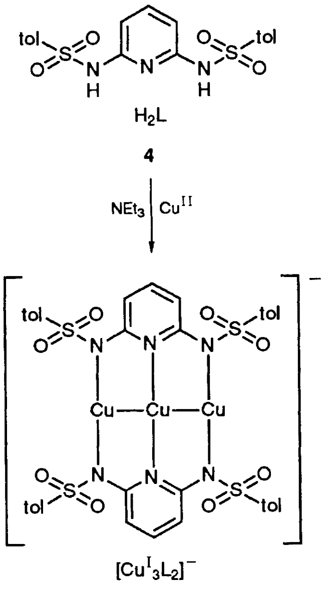
2

X = N, P, As
M = Ir, Au, Rh
M' = Ir, Au, Rh, Pd, Sn



3

tol = *p*-MeC$_6$H$_4$



The ligand was prepared by mixing in stoichiometric proportions 2,6-diaminopyridine and toluene-4-sulphonyl chloride (*p*-TsCl). A solution of *p*-TsCl (0.1 mol) in pyridine (40 ml) was added dropwise to a solution of 2,6-diaminopyridine (0.05 mol) in pyridine (40 ml) (the reaction is very exothermic). The brown solution, on being stirred for an hour, turned red-brown. It was then added dropwise to HCl (1 l; 15% aq.). The resulting brown precipitate was filtered off, washed and recrystallized from ethanol (yield 60%). H_2L, IR data: ν/cm^{-1} 3289 and 3225 (N-H); 1168 and 1156 (S=O).

The metal complex was prepared by the reaction of a hot alcoholic solution of the ligand (1 mmol in 20 ml), Et_3N (3 ml) and a hot alcoholic solution of $CuCl_2 \cdot 2H_2O$ (1 mmol in 20 ml). The mixture was boiled for 10 min, and then left to cool. After a few days, brown crystals were obtained (yield 15%); ν(S=O)/cm^{-1} 1139 and 1095.† The structure of the novel trimeric copper complex was determined by X-ray diffraction.‡

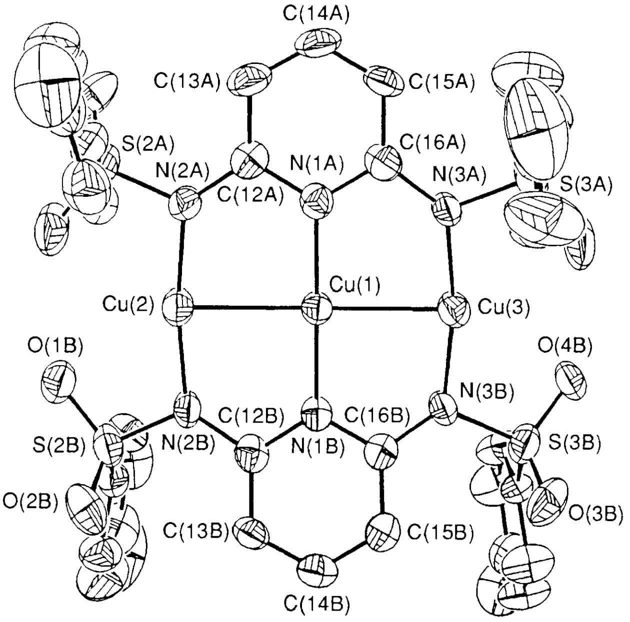


Fig. 1 ORTEP drawing of the $[Cu_3L_2]^-$ anion. Pertinent bond lengths (Å) and angles (°): Cu(1)-Cu(2) 2.466(1), Cu(2)-Cu(3) 2.468(1), Cu(1)-N(1A) 1.944(6), Cu(1)-N(1B) 1.949(6), Cu(2)-N(2A) 1.884(6), Cu(2)-N(2B) 1.881(6), Cu(3)-N(3A) 1.883(6), Cu(3)-N(3B) 1.890(6); all N-C 1.363(9)-1.386(9), average 1.374(9); Cu(2)-Cu(1)-Cu(3) 178.32(6), N(1A)-Cu(1)-N(1B) 178.0(2), N(2A)-Cu(2)-N(2B) 170.8(2), N(3A)-Cu(3)-N(3B) 170.1(2).

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† Satisfactory elemental analyses were obtained.

‡ *Crystal data*: $(HNEt_3)[Cu_3L_2]$, monoclinic, space group $P2_1/c$, a = 15.414(3), b = 25.091(6), c = 12.978(4) Å, β = 107.47(2)° V = 4787(2) Å^3; D_m = 1.55, D_c = 1.56 g cm^{-3}, Z = 4; CAD4 diffractometer with graphite-monochromated Mo-Kα radiation. Ψ scan absorption correction was made; 6234 unique reflections were measured and 3249 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R = 0.040 and R_w = 0.029. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The structure consists of triethylammonium cations and trimeric copper(I) complex anions. The structure of the anion is shown in Fig. 1. The most interesting feature of the structure is that the bridging ligands bind three copper(I) ions in a linear array. The Cu–Cu distances, 2.466(1) and 2.468(1) Å, are short, comparable with the distances found in $[Cu_2(napy)_2](ClO_4)_2$ (napy = 1,8-naphthyridine) [2.506(2) Å],[4] in $[Cu_2(form)_2]$ (form = *N,N′*-di-*p*-tolylformamidinato) [2.497(2) Å],[5] in $[Cu_2(dpt)_2]$ (dpt = 1,3-diphenyltriazenato) (2.451 Å),[6] in $[Cu_2(dpt)_4]$ [2.441(2) Å],[7] and in $[Cu_2(ptsampy)_4]$ (ptsampy = *p*-tolylsulphonylpyridineaminato) [2.516(2) Å].[8] They are 0.012 Å longer than the shortest Cu–Cu distances known, 2.348 and 2.358 Å observed in $[Cu_3(tolN_5tol)_3]$.[3] The average Cu–N distances, 1.885(6) Å, for the terminal copper atoms and 1.947(6) Å for the central copper atom, are also short, but comparable with those for two-coordinated Cu^I ions in $[Cu_2(napy)_2](ClO_4)_2$ [1.908(5) Å], in $[Cu_2(form)_2]$ [1.873(7) Å], and in $[Cu_2(dpt)_2]$ (1.918 Å), but shorter than those in $[Cu_2(dpt)_4]$ [2.020(7) Å], in $[Cu_2(ptsampy)_4]$ [2.010(5) Å], and in $[Cu_2(tolN_5tol)_3]$ (2.03 Å for the terminal and 1.95 Å for the central copper). The present trimetric Cu^I complex, which is coordinatively unsaturated and has short Cu–Cu distances, might be considered as a model for Cu^I clusters[9] and heterogeneous Cu surfaces.

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References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988.
2 A. L. Balch, V. J. Catalano and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 2010 and references therein.
3 J. Beck and J. Strahle, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 409.
4 M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi and H. Masude, *Inorg. Chim. Acta*, 1990, **167**, 181.
5 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077.
6 I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1961, **14**, 480.
7 M. Corbett, B. F. Hoskin, N. J. McLeod and B. P. O'Day, *Aust. J. Chem.*, 1975, **28**, 2377.
8 H. Cheng, P. Cheng, C. Lee and S. Peng, *Inorg. Chim. Acta*, 1991, in the press.
9 K. M. Merz, Jr., and R. Hoffmann, *Inorg. Chem.*, 1988, **27**, 2120.