A novel trinuclear copper(II) complex bridged by tren: $[Cu_3(tren)_4][Pt(CN)_4]_3 \cdot 2H_2O$

Iris P. Y. Shek,[a] Tai-Chu Lau,*[a] Wing-Tak Wong[b] and Jing-Lin Zuo[c]

[a] *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Hong Kong, P. R. China. E-mail: bhtclau@cityu.edu.hk*
[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China*
[c] *Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

Received* (*in Montpellier, France*) *24th June 1999, Accepted 10th September 1999

Reaction of copper(II) acetate with tren [tris(2-aminoethyl)amine] and $K_2[Pt(CN)_4]$ produced a novel trinuclear copper(II) complex, $[Cu_3(tren)_4][Pt(CN)_4]_3 \cdot 2H_2O$; the cation consists of three $Cu(tren)^{2+}$ units connected by an additional tren ligand.

Tris(2-aminoethyl)amine (tren) has been widely used as a tetradentate ligand[1] for binding to metals to form octahedral complexes of the type $[M(tren)XY]^{n+}$ or five-coordinate complexes of the type $[M(tren)X]^{n+}$.[1] However, there are very few complexes that feature tren as a bridging ligand binding two or more metals. An example is $[Mn_2O_2(tren)_2](CF_3SO_3)_3$, where each tren ligand is coordinated to two manganese atoms.[2] We report here the synthesis and structure of a novel trinuclear copper(II) complex, $[Cu_3(tren)_4][Pt(CN)_4]_3 \cdot 2H_2O$, that has an unprecedented structure consisting of three $Cu(tren)^{2+}$ units connected together by an additional tren ligand.

The trinuclear copper complex was prepared by mixing aqueous solutions of $Cu(CH_3CO_2)_2 \cdot H_2O$ and tren in a mole ratio of 1 : 1.4.† Crystals suitable for X-ray crystallography were obtained using $[Pt(CN)_4]^{2-}$ as the counter ion. The IR spectrum (KBr) shows ν(NH) at 3317, 3265 and 3165 cm^{-1}. The ν(CN) bond occurs at 2127 cm^{-1}, which is identical to that of $K_2[Pt(CN)_4]$, indicating that $[Pt(CN)_4]^{2-}$ is not coordinated to Cu. There is also a broad peak at 3440 cm^{-1} due to ν(OH).

The structure of the complex was determined by X-ray crystallography.‡ It consists of a $Cu_3(tren)_4^{6+}$ cation with three $[Pt(CN)_4]^{2-}$ anions. Three $Cu(tren)^{2+}$ units are linked together by a fourth tren ligand (Fig. 1). The three copper atoms are arranged in the form of an unsymmetrical triangle with long Cu–Cu distances of 6.64 [Cu(1)–Cu(2)], 7.54 [Cu(1)–Cu(3)] and 8.07 [Cu(2)–Cu(3)] Å. This is in contrast to other trinuclear copper complexes,[3–5] which have short Cu–Cu distances of around 3 Å. Each five-coordinate Cu in each tricopper unit is bonded to the four nitrogens of a tren ligand, with the fifth position being occupied by one of the primary amine groups of the bridging tren ligand. The coordination geometry of Cu(2) and Cu(3) are best described as distorted trigonal bipyramidal, with geometric parameters[6] τ being equal to 0.84 and 0.85, respectively. For Cu(1), τ is 0.60, suggesting that the geometry is almost intermediate between trigonal bipyramidal and square pyramidal. The Cu–N distances in each $Cu(tren)^{2+}$ unit range from 2.029 to 2.169 Å; these values are similar to those reported for mononuclear and binuclear copper(II) tren complexes.[7–12] The Cu–N(bridging tren) distances are also similar to the Cu–N distances in each $Cu(tren)^{2+}$ unit; Cu(1)–N(2), Cu(2)–N(3) and Cu(3)–N(4) distances are 2.011(8), 2.004(8) and 2.048(9) Å, respectively. Each $Cu_3(tren)_4^{6+}$ cation is also linked to the $[Pt(CN)_4]^{2-}$ anions through –N–H···N≡C– hydrogen bonding.

The magnetic susceptibility of the complex (analytically pure powder) was studied in the temperature range of 75–300 K. The complex obeys the Curie–Weiss law with a Curie constant of 1.46 cm^3 K mol^{-1} and a Weiss temperature, θ, of −29.5 K (Fig. 2). The μ_{eff} for the complex at room temperature is 3.24 μ_B, it decreases slowly to 2.88 μ_B at 75 K. The magnetic properties of this complex will be further studied.

In conclusion, we have described an unusual trinuclear copper complex formed by self-assembly of Cu^{2+} and tren. The synthesis of other $M_3(tren)_4^{n+}$ species is currently under investigation.

Acknowledgements

We thank the Hong Kong Research Grants Council, the City University of Hong Kong, the University of Hong Kong, and

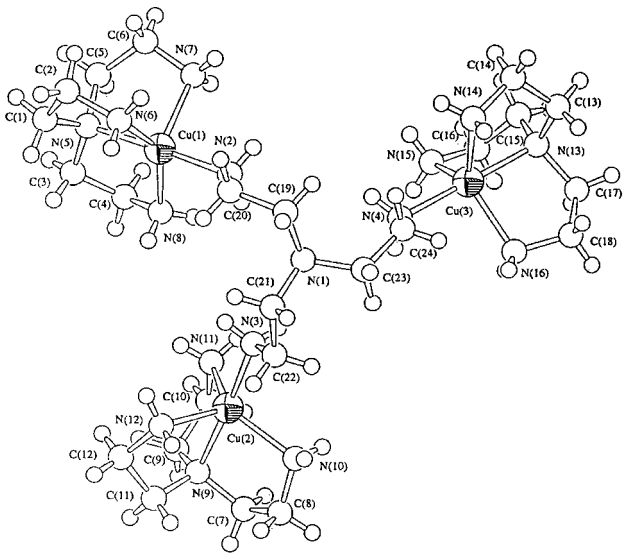

Fig. 1 Perspective view of the cation in $[Cu_3(tren)_4][Pt(CN)_4]_3 \cdot 2H_2O$. Selected bond lengths (Å): Cu(1)–N(2) 2.011(8), Cu(1)–N(5) 2.068(8), Cu(1)–N(6) 2.066(8), Cu(1)–N(7) 2.169(8), Cu(1)–N(8) 2.029(9), Cu(2)–N(3) 2.004(8), Cu(2)–N(9) 2.071(7), Cu(2)–N(10) 2.066(8), Cu(2)–N(11) 2.066(9), Cu(2)–N(12) 2.109(8), Cu(3)–N(4) 2.048(9), Cu(3)–N(13) 2.051(7), Cu(3)–N(14) 2.053(8), Cu(3)–N(15) 2.135(9), Cu(3)–N(16) 2.039(8).

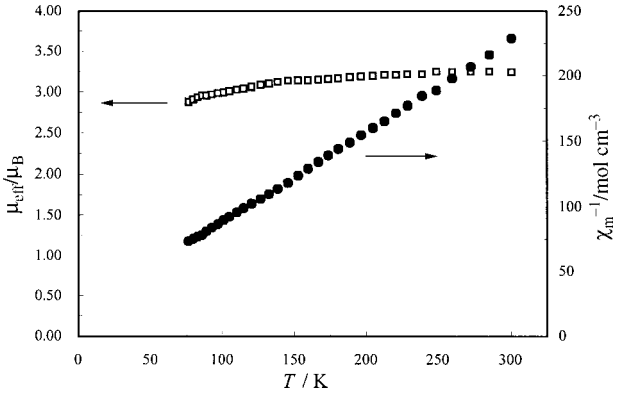

Fig. 2 Magnetic data for powdered samples of $[Cu_3(tren)_4][Pt(CN)_4]_3 \cdot 2H_2O$ at 75–300 K.

the State National Nature Science Foundation of China for financial support.

Notes and references

† Tris(2-aminoethyl)amine (0.1 g, 0.68 mmol) was added to a solution of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.1 g, 0.5 mmol) in water (10 ml) and the mixture was stirred at room temperature for 1 h. A solution of $K_2[Pt(CN)_4]$ (0.23 g, 0.6 mmol) in water (5 ml) was then added. The resulting light blue precipitate was filtered, washed with ethanol and then ether. Slow evaporation of the filtrate gave pale blue crystals suitable for X-ray crystallography. Yield: 74%. Anal. calcd for $C_{36}H_{76}N_{28}O_2Cu_3Pt_3$: C, 25.28; H, 4.45; N, 22.94. Found: C, 25.10; H, 3.58; N, 22.6390.

‡ Crystal data: $Cu_3Pt_3N_{28}C_{36}H_{76}O_2$, $M = 1709.09$, monoclinic, space group $P2_1/a$ (#14), $T = 298$ K, $a = 16.714(2)$, $b = 14.082(1)$, $c = 24.612(2)$ Å, $\beta = 100.78(2)°$, $U = 5690.6(10)$ Å^3, $Z = 4$, graphite monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu = 84.77$ cm^{-1}, of 45 505 reflections, 10 728 were unique with $R_{int} = 0.07$; the data were corrected for Lorentz and polarization effects; the structure was solved by direct methods (SHELXS86) and expanded using Fourier techniques (DIRFDIF94), the final cycle of full-matrix least-squares refinement was based on 8206 observed reflections [$I > 1.50\sigma(I)$] and 639 variable parameters. $R = 0.048$, $R_w = 0.056$ with a goodness-of-fit of 1.48.

CCDC reference number of 440/141. See http://www.rsc.org/suppdata/nj/1999/1049/ for crystallographic files in .cif format.

1 D. A. House, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, p. 23.
2 K. S Hagen, W. H. Armstrong and H. Hope, *Inorg. Chem.*, 1988, **27**, 969.
3 M. Angaroni, G. A. Ardizzoia, T. Beringhelli, G. La Monica, D. Gatteschi, N Masciocchi and M. Moret, *J. Chem. Soc., Dalton Trans.*, 1993, 3685.
4 S. Kannan, M. R. A. Pillai, P. A. Droege, S. Jurisson and C. L. Barnes, *Inorg. Chim. Acta*, 1997, **254**, 397.
5 M. H. W. Lam, Y. Y. Tang, K. M. Fung, X. Z. You and W. T. Wong, *Chem. Commun.*, 1997, 957.
6 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
7 Z. L. Lu, C. Y. Duan, Y. P. Tian, Z. W. Wu, J. J. You, Z. Y. Zhou and T. C. W. Mak, *Polyhedron*, 1997, **16**, 909.
8 Z. L. Lu, C. Y. Duan, Y. P. Tian, X. Z. You, H. K. Fun and B. C. Yip, *Polyhedron*, 1996, **15**, 1769.
9 A. Ludi and H. U. Gudel, *Struct. Bonding* (*Berlin*), 1973, **14**, 1.
10 L. A. Gentil, J. A. Olasle and G. E. Riggutie, *Inorg. Chim. Acta*, 1991, **179**, 89.
11 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 1911.
12 M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.

Letter 9/05080I