The first stable copper(II) complex containing four sulfide ligands: synthesis and structural characterization of [Pt$_2$(dppe)$_2$(μ-S)$_2$] and [Cu{Pt$_2$(dppe)$_2$(μ$_3$-S)$_2$}$_2$]$^{2+}$

Mercè Capdevila,[a] Yolanda Carrasco,[a] William Clegg,[b] Robert A. Coxall,[b] Pilar González-Duarte,*[a] Agustí Lledós,*[a] Joan Sola[a] and Gregori Ujaque[a]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain
[b] Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU

The synthesis and crystal structure of the novel heteropolymetallic aggregate [{Pt$_2$(dppe)$_2$(μ$_3$-S)$_2$}$_2$Cu]-[PF$_6$]$_2$ **2** and of its precursor [Pt$_2$(dppe)$_2$(μ-S)$_2$] **1** are reported; **2** has been further characterized by EPR and electronic spectroscopies and the hinged Pt$_2$S$_2$ rings in **1** and **2** have been rationalized by *ab initio* MP2 calculations.

The ability of [Pt$_2$L$_4$(μ-S)$_2$] (L = phosphine) to behave as a metalloligand towards Lewis acids of p- and d-block elements is well reflected in the literature by a wide range of homo- and hetero-metallic aggregates with various nuclearities and structures.[1] However, structural data in dimeric platinum sulfide complexes are scarce and contradictory. The partially determined X-ray structure of [Pt$_2$(PMe$_2$Ph)$_4$(μ-S)$_2$] shows a hinged Pt$_2$S$_2$ ring (θ = 121°),[2] but the ring is strictly planar in [Pt$_2$(dppy)$_4$(μ-S)$_2$] (dppy = 2-diphenylphosphanylpyridine).[3] Theoretical *ab initio* studies found a bent structure for the [Pt$_2$(PH$_3$)$_4$(μ-S)$_2$] complex.[4] Stimulated by the difficulty of stabilizating Cu^{II} in S$_4$ environments, relevant for the study of copper proteins, and based on the coordinative versatility of [Pt$_2$L$_4$(μ-S)$_2$], we targeted the synthesis of a copper(II) complex containing four sulfide ligands. The only X-ray structure of a heterometallic platinum sulfide aggregate, [{Pt$_2$(PPh$_3$)$_4$(μ$_3$-S)$_2$}Cu(PPh$_3$)]PF$_6$,[1a] contains copper as Cu^I. The closest precedents to copper(II) complexes contain alkyl persulfide[5] and disulfide[6] ligands. We report the synthesis and X-ray structure of [Pt$_2$(dppe)$_2$(μ-S)$_2$] **1** and pentametallic [Cu{Pt$_2$-(dppe)$_2$(μ$_3$-S)$_2$}$_2$](PF$_6$)$_2$ **2**, MP2 *ab initio* calculations for the [Pt$_2$(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$(μ-S)$_2$] complex **3** that can be taken as a model for **1**, and spectroscopic and magnetic features of **2**.

The preparation of **1**·2C$_6$H$_6$ from [PtCl$_2$(dppe)] and an excess of Na$_2$S in benzene by a standard method[7] led to a mixture of products. ^{31}P NMR measurements on aliquots of the reaction mixture allowed the determination of a satisfactory [PtCl$_2$(dppe)] : Na$_2$S : benzene ratio and of the appropriate reaction time. Slow evaporation of the mother-liquor gave orange crystals of **1**·2C$_6$H$_6$ in *ca.* 90% yield,† whose structure‡ consists of neutral dinuclear molecules devoid of crystallographic symmetry elements (Fig. 1). Each molecule shows a hinged Pt$_2$S$_2$ central ring (θ = 140.2°) with the two platinum atoms bridged by two sulfide anions, coordination being completed by chelating dppe ligands. The geometries at the individual Pt sites are approximately square planar.

To understand the preference for the bent structure of **1** we have optimized complex **3** at the MP2 level§ yielding a hinged structure with θ = 118.8°. This result indicates the intrinsic preference of **3** to adopt a bent structure and allows us to disregard crystal packing effects as the cause for hinging. The energy difference with respect to an optimized structure with a fixed θ = 180° is 30.1 kJ mol^{-1} in favour of the former. This energy difference between the bent and planar forms is small enough for changes in the size of the terminal ligands to cause significant variations in the dihedral angle. Thus, **3** is more hinged (θ = 118.8°) than **1** (140.2°) and a further increase in the
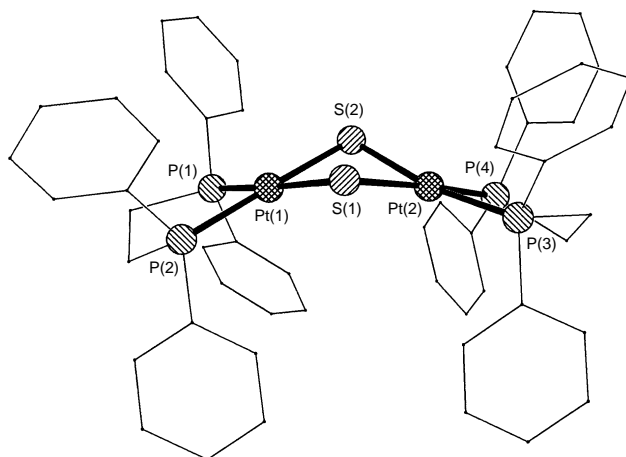

Fig. 1 View of the structure of [Pt$_2$(dppe)$_2$(μ-S)$_2$] in **1** with hydrogen atoms omitted, showing labelling of key atoms. Selected bond lengths (Å) and angles (°) of the Pt$_2$S$_2$ ring: Pt(1)–S(2) 2.3412(12), Pt(1)–S(1) 2.3554(12), S(1)–Pt(2) 2.3581(13), S(2)–Pt(2) 2.3437(12); S(2)–Pt(1)–S(1) 83.73(4), Pt(1)–S(1)–Pt(2) 88.60(4), Pt(1)–S(2)–Pt(2) 89.28(4), S(2)–Pt(2)–S(1) 83.61(4).

steric hindrance about P atoms, as happens in [Pt$_2$(dppy)$_4$(μ-S)$_2$], leads to planarity. Optimization of **3** with a fixed θ = 140° gives an energy only 10.0 kJ mol^{-1} above than that for θ = 118.8°. It is likely that the great coordinative versatility of [Pt$_2$L$_4$(μ-S)$_2$] is due to the low energy cost associated with the bending process. Moreover, this low energy cost would allow a ring reversal process and thus a fluxional behaviour in solution.[11]

Mixing Cu(PF$_6$)$_2$ with **1** (1 : 2 molar ratio) in methanol gave rise to a dark solution that afforded red crystals of **2**·0.5Et$_2$O.‡ As shown in Fig. 2, the crystallographically non-symmetrical cation [Cu{Pt$_2$(dppe)$_2$(μ$_3$-S)$_2$}$_2$]$^{2+}$ comprises two {Pt$_2$S$_2$} butterflies linked through sulfur to the Cu^{II} ion. The long S···S distance (3.1 Å) in each Pt$_2$S$_2$ moiety indicates the lack of a disulfido bond. The deviations from square-planarity around all platinum atoms are small and the hinge angles between PtS$_2$P$_2$ planes are 118.4 and 121.1°. There is a near-symmetrical chelation of both disulfide metalloligands **1** to the Cu^{II} centre. The distorted tetrahedral environment about the heterometal is shown by the two acute S–Cu–S bite angles of *ca.* 83.6° and by a torsion angle, ω = 60°, between the two S–Cu–S planes. Among the numerous geometries of the heterometal in the environment of [Pt$_2$L$_4$(μ-S)$_2$] there is no example where the former is tetrahedrally coordinated to two [Pt$_2$L$_4$(μ-S)$_2$] molecules.

The EPR spectrum of **2** in CH$_2$Cl$_2$ solution displays a signal at g_{iso} = 2.056. The hyperfine coupling constant to the copper ion (I = 3/2) A_{iso} was determined to be 58.5 × 10^{-4} cm^{-1}. The spectrum of a powdered sample of **2**, which consists of a nearly axial signal with no appreciable changes either at room
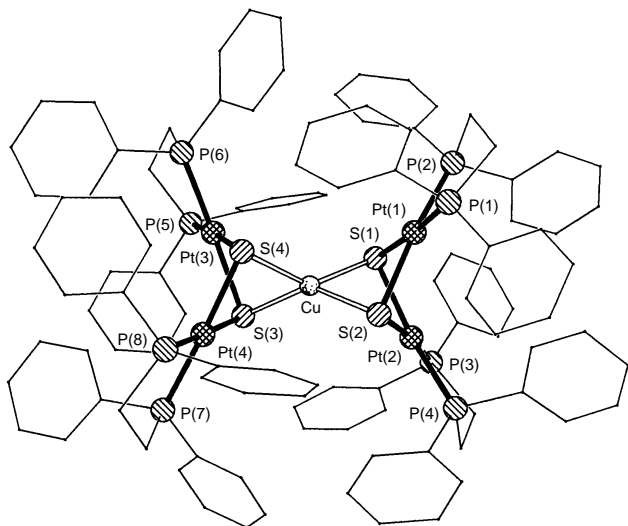
Fig. 2 The structure of the $[Cu\{Pt_2(dppe)_2(\mu_3\text{-}S)_2\}_2]^{2+}$ cation in **2** with key atoms labelled. Selected bond lengths (Å) and angles (°) of the $Cu\{Pt_2S_2\}_2$ core: Pt(1)–S(2) 2.355(2), Pt(1)–S(1) 2.375(3), S(1)–Pt(2) 2.362(2), S(2)–Pt(2) 2.365(2), S(1)–Cu 2.320(2), S(2)–Cu 2.318(3), S(4)–Cu 2.303(3), S(3)–Cu 2.316(3), S(3)–Pt(4) 2.359(3), S(3)–Pt(3) 2.364(3), S(4)–Pt(4) 2.366(2), S(4)–Pt(3) 2.372; S(2)–Pt(1)–S(1) 81.66(8), Pt(1)–S(1)–Pt(2) 80.86(7), Pt(1)–S(2)–Pt(2) 81.20(7), S(2)–Pt(2)–S(1) 81.75(8), S(2)–Cu–S(1) 83.65(8), S(4)–Cu–S(3) 83.54(9), S(3)–Pt(3)–S(4) 81.02(9), Pt(3)–S(3)–Pt(4) 82.98(8), Pt(3)–S(4)–Pt(4) 82.65(8), S(3)–Pt(4)–S(4) 81.26(8).

temperature or at 115 K, shows a partially good resolution of the copper hyperfine splitting, probably brought about by magnetic dilution afforded by the bulky phenyl groups of the dppe ligands on the diamagnetic $[Pt_2(dppe)_2(\mu\text{-}S)_2]$ moieties. Simple first-order spectral analysis yielded $g_z = 2.114$, $g_y = 2.055$ and $g_x = 1.994$, and $A_z = 124.4 \times 10^{-4}$, $A_y = 37 \times 10^{-4}$ and $A_x = 36 \times 10^{-4}$ cm^{-1}. These results agree with the distorted tetrahedral geometry and show that the heterometal is a copper(II) ion rather than copper(I) coordinated to a $[Pt_2(dppe)_2(\mu\text{-}S)_2]^+$ radical moiety. The unpaired electron resides in the d_{xy} orbital of the metal centre (with sulfur donor-atoms between the x and y axes).[12] No evidence of delocalization of the unpaired electron onto the platinum(II) ions has been found. Comparison of these features with EPR spectral patterns of the blue copper sites[13] indicates that $g_{x,y}$ and $A_{x,y}$ are similar, but those of the corresponding parallel parameters deviate significantly. This can be attributed to the different nature of the donor atoms bound to Cu and to the more flattened tetrahedral geometry about this metal centre in the case of the $[Cu\{Pt_2\text{-}(dppe)_2(\mu_3\text{-}S)_2\}_2]^{2+}$ cation.[14]

The electronic spectrum of **2** in acetonitrile solution shows a very broad band with maximum intensity at $\nu_1 = 8550$ cm^{-1} (1170 mm, $\varepsilon = 740$ dm^3 mol^{-1} cm^{-1}), a band at $\nu_2 = 17\,700$ cm^{-1} (565 nm, $\varepsilon = 4400$ dm^3 mol^{-1} cm^{-1}), and a very strong absorption between 320 and 220 nm ($\varepsilon > 20\,000$ dm^3 mol^{-1} cm^{-1}). The position of ν_1 reveals that the distorted tetrahedral geometry of the copper ion in complex **2** is preserved in solution and compares well with the estimated value of 9800 cm^{-1} for the higher energy d–d band of a tetrahedral CuCl$_4$ core with the same degree of distortion ($\omega = 61°$) as **2**.[15] On the basis of an idealized D_2 symmetry the ν_1 band is assigned to the $^2B_1 \rightarrow {}^2A$ ($d_{z^2} \rightarrow d_{xy}$) transition. Following the EPR behaviour, both the position and the intensity of ν_2 are close to those of the characteristic band of the blue copper sites appearing at *ca.* 600 nm in stellacyanin, plastocyanin and azurin proteins. Therefore, ν_2 is assigned to a $\sigma(S) \rightarrow d_{xy}(Cu)$ LMCT transition.[13]

Notes and References

1 (*a*) H. Liu, A. L. Tan, Y. Xu, K. F. Mok and T. S. A. Hor, *Polyhedron*, 1997, **16**, 377 and references therein; (*b*) V. W. W. Yam, P. K. Y. Yeung and K. K. Cheung, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 739.

2 C. E. Briant, C. J. Gardner, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.,* 1984, 2645.

3 V. W. W. Yam, P. K. Y. Yeung and K. K. Cheung, *J. Chem. Soc., Chem. Commun.,* 1995, 267.

4 M. Capdevila, W. Clegg, P. González-Duarte, A. Jarid and A. Lledós, *Inorg. Chem.,* 1996, **35**, 490.

5 E. John, P. K. Bharadwaj, K. Krogh-Jespersen, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.,* 1986, **108**, 5015.

6 K. Fujisawa, Y. Moro-oka and N. Kitajima, *J. Chem. Soc., Chem. Commun.,* 1994, 623.

7 R. Ugo, G. La Monica, S. Cenini, A. Segre and F. Conti, *J. Chem. Soc. A,* 1971, 522.

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzew-ski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andrés, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. De Frees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian 94; Gaussian Inc., Pittsburg PA, 1995.

9 C. Möller and M. S. Plesset, *Phys. Rev.,* 1934, **46**, 618.

10 (*a*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.,* 1985, **82**, 299; (*b*) W. R. Wadt and P. J. Hay, *J. Chem. Phys.,* 1985, **82**, 284; (*c*) A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.,* 1993, **208**, 237; (*d*) W. J. Hehre, R. E. Stewart and J. A. Pople, *J. Chem. Phys.,* 1969, **51**, 2657.

11 N. Duran, P. González-Duarte, A. Lledós, T. Parella, J. Sola, G. Ujaque, W. Clegg and K. A. Fraser, *Inorg. Chim. Acta,* 1997, **265**, 89.

12 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.,* 1970, **5**, 143.

13 K. W. Penfield, R. R. Gay, R. S. Himmelwright, N. C. Eickman, V. A. Norris, H. C. Freeman and E. I. Solomon, *J. Am. Chem. Soc.,* 1981, **103**, 4382.

14 U. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.,* 1979, 600.

15 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem.,* 1979, **18**, 148.