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COMMUNICATION

Unique Pt_5 metallacycle: $[Pt^{II}Cl(pyrrolidinedithiocarbamate)]_5$†‡

Diego Montagner*[a] and Pablo J. Sanz Miguel*[b]

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The neutral complex $[PtCl(PyDT)]_5$ (PyDT = $(CH_2)_4NCS_2^-$) represents the first example of a Pt_5 metallacycle. This unique architecture based on chiral *S*-bridged Pt^{II} monomers was prepared by thermal degradation of the reaction product of $PtCl_2$ and a pyrrolidinedithioester.

Dithiocarbamate complexes of transition metals have been widely studied,[1] focusing mainly on their antitumoral properties and flexible possibilities for molecular architectures. Due to their extremely versatile and robust motif, dithiocarbamates have been utilized for metal-directed self-assembly,[2] and more recently for the stabilization of gold nanoparticles.[3] They are well-known chemoprotective agents against heavy metal intoxication,[4] particularly against cisplatin,[5] the most prolific antitumoral drug. Recent tendencies aiming to reduce the toxicity of antitumoral drugs require the design of new molecules based on either nitrogen (analogue to cisplatin) or sulfur donor atoms (as carbamates).[6] Interesting results were obtained with Pt^{II}, Pd^{II} and Au^{III} compounds with ethylsarcosinedithio- and dimethyldithiocarbamates as ligands.[7] Complexes containing pyrrolidinedithiocarbamate (PyDT) are under investigation in order to develop potential antitumoral drugs, with Ru(III) complexes being the most active.[8]

The versatility of dithiocarbamates for molecular architectures lies in their ability to coordinate metals in different modes (Chart 1): as (i) monodentate ligands, involving one of the sulfur atoms, as (ii) bidentate ligands, with both donor S atoms coordinated to the same metal (as chelate) or to different (as bridging S) metals, and combining both modes, as (iii) tridentate and even (iv) as tetradentate ligands (Chart 1). The combination of such flexible ligands with the binding possibilities of transition metals results in a multitude of mono- and multinuclear, discrete and polymeric constructs.[9]

Here, we report the first example of a Pt_5 metallacycle, extending the existing series of platinum (Pt_2, Pt_3, Pt_4 and Pt_6) metallacycles.[10] Examples of discrete metallapentagons involving transition metals

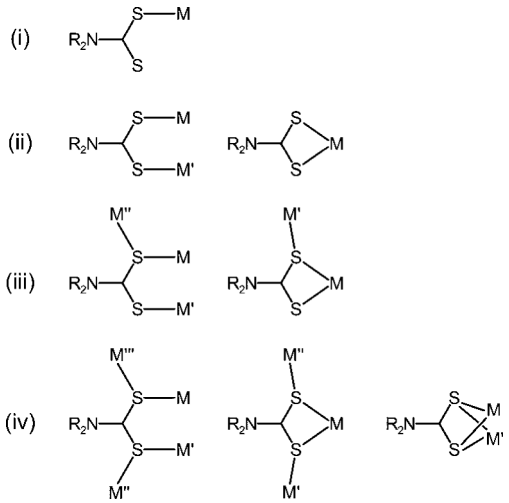
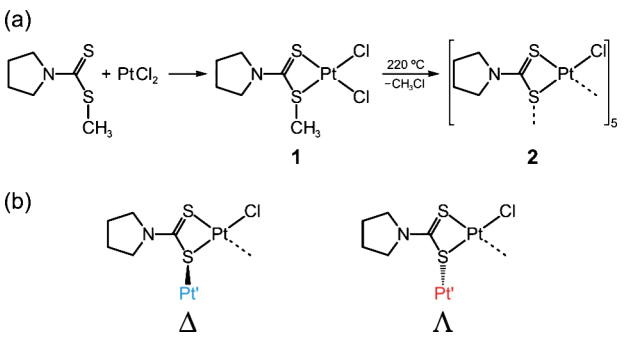


Chart 1

are not as common as other metallastructures, such as triangles, squares, hexagons or macrocycles.[11]

The reaction of $PtCl_2$ with pyrrolidinedithioester (PyDTM) yields $[PtCl_2(PyDTM)]$ (**1**), which after thermal degradation (220 °C)[6] produces $[PtCl(PyDT)]_5$ (**2**) (PyDT = pyrrolidinedithiocarbamate) (Scheme 1a). Crystals were grown by the slow evaporation of **2** in dichloroethane, crystallizing with two molecules of solvent.§ Dithiocarbamate complexes of general formula $[MCl(RDT)]_n$ can be stabilized by halogen (M = Pd; n = 2)[12] or sulfur (M = Pd, Pt; n = 2, 3)[13] bridging ligands.



Scheme 1

The metallacyclic structure of complex **2** is assembled from five chiral PtCl(PyDT) units (Fig. 1c). The PyDT moieties act as tridentate ligands, both chelating Pt and bridging the platinum

[a]*Dipartamento di Science Chimiche, Universita di Padova, 35131, Padova, Italy. E-mail: diego.montagner@unipd.it; Fax: +39 827-5161*
[b]*Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza- CSIC, 50009, Zaragoza, Spain. E-mail: pablo.sanz@unizar.es; Fax: +34 976-761187*

† Dedicated to Professor Bernhard Lippert on the occasion of his retirement.

‡ Electronic supplementary information (ESI) available: Instrumentation, synthesis procedures and TG-DTA studies. CCDC reference numbers 823484 (**2**) and 823485 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11475a

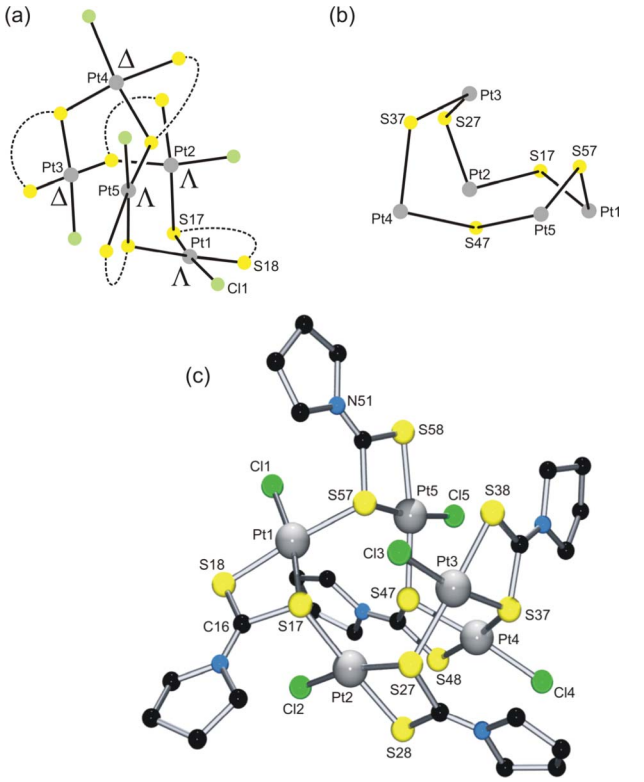


Fig. 1 Three different perspectives of complex **2**: (a) detail of the chirality of the monomer; (b) schematic view of the envelope conformation; (c) molecular structure.

atom (Pt′) of a vicinal monomer. Thus, the square planar coordination of each Pt^{II} unit consists of three sulfur atoms, with an additional chloride ligand occupying the fourth position. The chirality of the monomer originates from the orientation of the linked platinum atom (Pt′) of a vicinal monomer, which can be situated above (Δ) or below (Λ) the coordination plane of the platinum atom of the monomer (Scheme 1b).

As shown in Fig. 1a, three of the monomers (Pt1, Pt2, and Pt5) have identical chirality (Λ), whereas Pt3 and Pt4 are in the enantiomeric Δ configuration. As complex **2** crystallizes in the centrosymmetric space group $P\bar{1}$, both absolute configurations of complex **2** (Λ,Λ,Λ,Δ,Δ and Δ,Δ,Δ,Λ,Λ) are present in equal amounts in the crystal lattice.

Distances and angles around the five platinum atoms are compiled in Table 1. In all cases, deviations from the best plane defined by the platinum and four donor atoms do not exceed 0.04(2) Å (S38). Typical angle values for platinum are observed due to the chelation of the dithiocarbamate species. The internal chelate S–Pt–S angles are almost identical, ranging from 75.38(14)° (S37–Pt3–S38) to 76.19(14)° (S47–Pt4–S48). Analogous Pt–Cl and Pt–S bond distances and angles were found in the related species $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$.[14] The tridentate coordination of the PyDT ligand (*cf.* Chart 1) results in slight differences regarding the Pt–S bond lengths, depending on the coordination mode of the sulfur atoms: chelating-S or chelating-bridging-S. The distance between Pt^{II} and the sulfur atom participating only in chelate binding is almost unaltered for the five platinum atoms (from Pt3–S38, 2.295(4) Å to Pt5–S58, 2.311(4) Å), as also occurs for Pt–Cl (from Pt5–Cl5, 2.307(4) Å to Pt4–Cl4, 2.332(4) Å). For the Pt–S distances involving chelating-bridging-S atoms, it is observed that the chelating distance is significantly shorter compared to the bridging distance (Pt1–S17, 2.305(4) Å and Pt2–S17, 2.337(4) Å; Pt2–S27, 2.286(4) Å and Pt3–S27, 2.318(4) Å; Pt3–S37, 2.296(4) Å and Pt4–S37, 2.309(4) Å; Pt4–S47, 2.272(4) Å and Pt5–S47, 2.302(4) Å; Pt5–S57, 2.295(4) Å and Pt1–S57, 2.305(4) Å). This is probably a consequence of the unusually different hybridization assumed by both sulfur atoms. In the case of the Pt1 monomer, the sp^2-hybridized S18 atom displays a shorter bond length to C16 (1.670(17) Å) in comparison to the C16–S17 distance (1.789(17) Å) shown by the sp^3 hybridized S17 atom, *trans* to Cl1. This situation is analogous in the other four monomers (C26–S27, 1.765(15) Å and C26–S28, 1.707(15) Å; C36–S37, 1.778(14) Å and C36–S38, 1.711(14) Å; C46–S47, 1.765(13) Å and C46–S48, 1.700(14) Å; C56–S57, 1.758(15) Å and C56–S58, 1.720(15) Å).

The core of the complex consists of an unsymmetrical $(Pt–S)_5$ crown of the unusual type $A^2{}_5A^2{}_5$.[15] In addition to the above-described Pt–S distances and S–Pt–S angles of the platinum coordination sphere (Table 1), the Pt–S–Pt angles are slightly distorted from ideal sp^3 hybridization (Pt1–S17–Pt2, 112.11(17)°; Pt2–S27–Pt3, 109.62(16)°; Pt3–S37–Pt4, 113.84(16)°; Pt4–S47–Pt5, 115.84(15)°; Pt5–S57–Pt1, 111.06(17)°). The platinum atoms within the crown adopt an envelope-like conformation, in which Pt1, Pt2, Pt4 and Pt5 roughly lie on the same plane (maximum deviation of 0.1382(3) Å for Pt5), Pt3 being out of the plane by 2.9803(17) Å (Fig. 1b). Pt–Pt distances between adjacent corners within the crown are similar (Pt1–Pt2, 3.8511(14) Å; Pt2–Pt3, 3.7627(15) Å; Pt3–Pt4, 3.8586(16) Å; Pt4–Pt5, 3.8760(13) Å; Pt5–Pt1, 3.7917(11) Å). Likewise, the S–S distances in the crown are within the same range (S17–S27, 3.490(5) Å; S27–S37, 3.649(5) Å; S37–S47, 3.417(5) Å; S47–S57, 3.376(5) Å; S57–S17, 3.453(5) Å). The mutual dispositions (dihedral angles) of the Pt^{II} coordination planes are as follows (Pt2/Pt4, 10.9(1)°; Pt3/Pt5, 19.5(1)°;

Table 1 Selected bond distances (Å) and angles (°) in **2**

Pt1–S17, 2.305(4)	Pt2–S27, 2.286(4)	Pt3–S37, 2.296(4)	Pt4–S47, 2.272(4)	Pt5–S57, 2.295(4)
Pt1–S18, 2.296(4)	Pt2–S28, 2.302(4)	Pt3–S38, 2.295(4)	Pt4–S48, 2.310(4)	Pt5–S58, 2.311(4)
Pt1–S57, 2.305(4)	Pt2–S17, 2.337(4)	Pt3–S27, 2.318(4)	Pt4–S37, 2.309(4)	Pt5–S47, 2.302(4)
Pt1–Cl1, 2.315(4)	Pt2–Cl2, 2.311(5)	Pt3–Cl3, 2.330(4)	Pt4–Cl4, 2.332(4)	Pt5–Cl5, 2.307(4)
S17–Pt1–S18, 76.09(15)	S27–Pt2–S28, 75.76(15)	S37–Pt3–S38, 75.38(14)	S47–Pt4–S48, 76.19(14)	S57–Pt5–S58, 75.61(13)
S17–Pt1–S57, 97.04(14)	S27–Pt2–S17, 98.02(15)	S37–Pt3–S27, 104.51(13)	S47–Pt4–S37, 96.50(13)	S57–Pt5–S47, 94.50(13)
S18–Pt1–Cl1, 93.63(17)	S28–Pt2–Cl2 92.50(16)	S38–Pt3–Cl3, 95.71(16)	S48–Pt4–Cl4, 96.01(16)	S58–Pt5–Cl5, 96.08(15)
S57–Pt1–Cl1, 93.24(16)	S17–Pt2–Cl2, 93.69(16)	S27–Pt3–Cl3, 84.43(15)	S37–Pt4–Cl4, 91.26(16)	S47–Pt5–Cl5, 93.82(15)
S18–Pt1–S57, 173.13(15)	S28–Pt2–S17, 173.70(15)	S38–Pt3–S27, 177.23(16)	S37–Pt4–S48, 172.54(14)	S47–Pt5–S58, 169.99(13)
S17–Pt1–Cl1, 169.72(16)	S27–Pt2–Cl2, 168.11(16)	S37–Pt3–Cl3, 171.05(15)	S47–Pt4–Cl4, 172.12(15)	S57–Pt5–Cl5, 171.68(15)

Pt2–Pt4/Pt3–Pt5, 72.1(2)°; Pt1/Pt2–Pt4, 83.3(2)°; Pt1/Pt3–Pt5, 63.17(9)°).

The reaction of complex **2** with different P- or S-donor ligands results in facile cleavage of the Pt^{II}–S bridge, leading to different mononuclear species, such as [PtCl(PyDT)(PPh_3)] (**3**) or [PtCl(PyDT)(DMSO)] (**4**) (ESI‡).

Crystals of **3** suitable for X-ray analysis were obtained by the slow addition of *n*-pentane to a dichloromethane solution.¶ The structure of complex **3** is somewhat related to that of the monomers of **2**, including the PyDT and chloride ligands, and a PPh_3 group, which formally substitutes the second bridged PyDT ligand (Fig. 2). Both S atoms of the PyDT ligand in **3** act only as chelates, thus no sp^3 hybridization is expected for the sulfur atoms, contrary to the situation observed in **2**. This is clearly observable in the C–S distances, which are almost identical (C16–S17, 1.738(7) Å; C16–S18, 1.716(7) Å). The distances and angles around Pt1 and within the molecule are normal (ESI‡) and similar to related complexes, such as [$M(S_2CNEt_2)(PPh_3)Cl$] (M = Pd, Pt).[16]

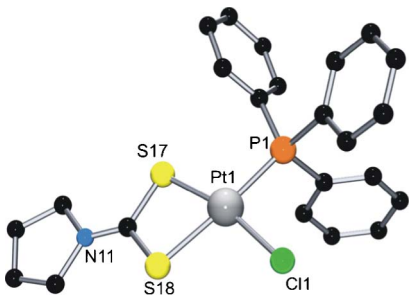


Fig. 2 View of [PtCl(PyDT)(PPh_3)] (**3**).

In conclusion, the self-assembly of five PtCl(PyDT) monomers of different chirality results in a unique Pt_5 metallacyclic structure, $[PtCl(PyDT)]_5$ (**2**), with two possible enantiomers (Λ,Λ,Λ,Δ,Δ and Δ,Δ,Δ,Λ,Λ). With this PyDT chelating ligand, a pentamer is the smallest possible construction, stabilizing the two different (sp^2 and sp^3) hybridizations of the S atoms. This work also extends the existing examples of discrete Pt^{II} metallacycles, with potential applications based on a dithiocarbamate-platinum tandem.

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Notes and references

§ $[PtCl(PyDT)]_5 \cdot 2CH_3ClCH_3Cl$ (**2**): $C_{29}H_{48}Cl_9N_5Pt_5S_{10}$, M = 2081.82, orange blocks, triclinic, space group $P\bar{1}$, a = 11.862(2), b = 14.543(3), c = 16.207(3) Å, α = 80.60(3), β = 78.97(3), γ = 74.89(3)°, V = 2630.3(9) Å^3, Z = 2, D_c = 2.629 g cm^{-3}, T = 150(2) K, with Mo-Kα (λ = 0.71073), 9497 reflections collected, 9147 unique (R_{int} = 0.0363), R_1 [$I > 2\sigma(I)$] = 0.0533, wR_2 (F, all data) = 0.1254, GoF = 0.990.‡

¶ $[PtCl(PyDT)(PPh_3)] \cdot 0.5CH_2Cl_2$ (**3**): $C_{47}H_{48}Cl_4N_2P_2Pt_2S_4$, M = 1363.03, colorless blocks, triclinic, space group $P\bar{1}$, a = 9.571(2), b = 10.278(3), c = 14.367(3) Å, α = 89.79(3), β = 86.21(3), γ = 62.91(3)°, V = 1254.9(5) Å^3, Z = 1, D_c = 1.804 g cm^{-3}, T = 150(2) K, with Mo-Kα (λ = 0.71073), 6366 reflections collected, 6015 unique (R_{int} = 0.0212), R_1 [$I > 2\sigma(I)$] = 0.0397, wR_2 (F, all data) = 0.0975, GoF = 0.994.‡

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