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Synthesis and structural characterization of a disulphide-bridged tetranuclear palladium(II) complex derived from 3,5-diacetyl 1,2,4-triazole bis(4-ethylthiosemicarbazone)

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Abstract

A novel tetranuclear $[\text{Pd}_4(\mu_2\text{-}\eta^2\text{-S}_2)(\text{H}_2\text{L}^1)_2]$ complex, where H_2L^1 is the anion of 3,5-diacetyl-1,2,4-triazole bis(4-ethylthiosemicarbazone), was synthesized and structurally characterized by single crystal X-ray diffraction. The molecular structure shows an unexpected $\mu_2\text{-}\eta^2\text{-S}_2$ bridge, which is shared by all the four palladium atoms. Each trideprotonate 3,5-diacetyl-1,2,4-triazole bis(4-ethylthiosemicarbazone) ligand acts as a hexadentate in a symmetrical manner bridging two metal ions through the two adjacent nitrogen atoms of the central triazole ring. The molecular packing is characterized by hydrogen bond interactions to form a 3D supramolecular architecture with channels running down the c^* axis in which the lattice water molecules are encapsulated. © 2006 Published by Elsevier B.V.

Keywords: Bis(thiosemicarbazone); Crystal structure; 1,2,4-triazole; Disulphide-bridged; Tetranuclear palladium(II) complexes; Water molecules encapsulated

The use of the 1,2,4-triazole moiety as a part of a ligand system has gained great attention in recent years [1–4] by the fact that it represents a hybrid of pyrazole and imidazole with regard to the arrangement of their three donor atoms (Fig. 1).

Moreover, 1,2,4-triazoles exhibit a strong and typical property of acting as bridging ligands between two metal centers. In this bridging capacity, these ligands show a great coordination diversity, especially when the triazole unit is substituted with additional donor groups [5,6]. This structural diversity is also connected to the coordination modes of the neutral and anionic triazole ring. In addition to the ligand-metal interactions, hydrogen bonding plays a most important role in geometry of the coordination compounds of these ligands.

Among coordination chemistry, there is a rapidly growing interest in dinuclear and polynuclear metal complexes [7–9]. This arises from the awareness that pairs of metal ions appear to mediate certain chemical reactions differently from complexes of isolated metal centers. In previous papers [10,11], we have reported the first structurally characterized binuclear complexes of triazolate-containing bis(thiosemicarbazones), specifically palladium(II) complexes derived from 3,5-diacetyl-1,2,4-triazole bis(4-methylthiosemicarbazone) and 3,5-diacetyl-1,2,4-triazole bis(4-phenylthiosemicarbazone). In these complexes, the triazole units coordinate in a monodentate form through N^1 or N^2 atoms and the metal ions are linked by two thiosemicarbazone bridges. This asymmetrical arrangement of the ligands appears to be favoured by the formation of two intramolecular hydrogen bonds.

To extend the knowledge in this research field, particularly with respect to the co-ordination properties of the heterocyclic bis(thiosemicarbazones) and the stereochemistry

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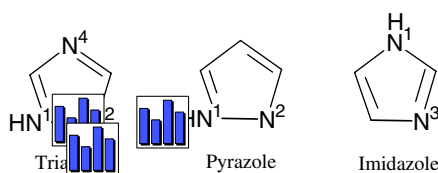
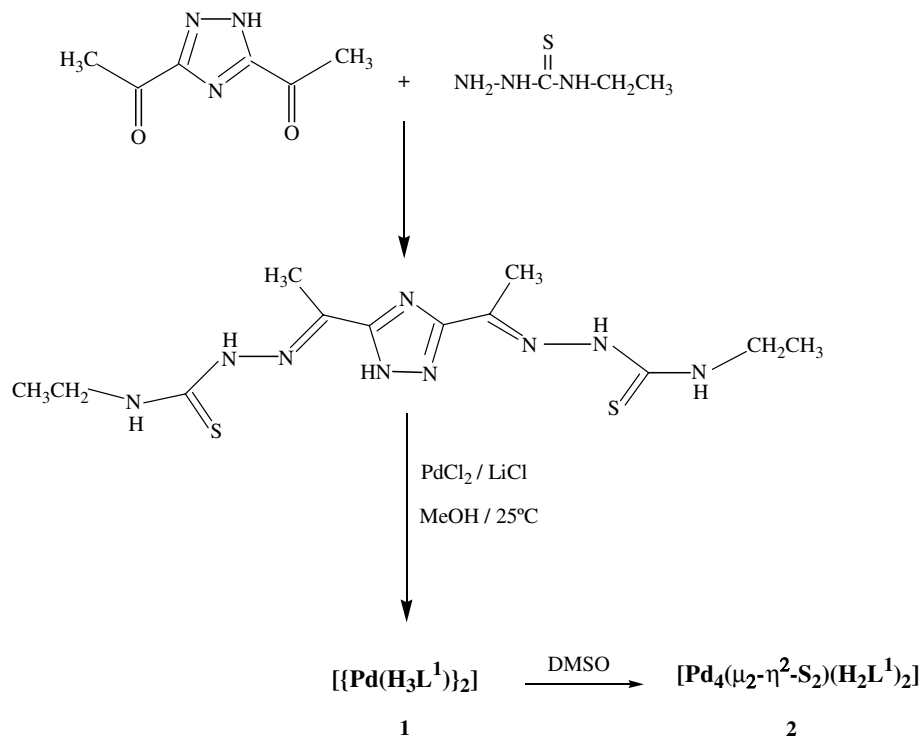


Fig. 1



Scheme 1.

57 and molecular structure of the complexes, we now report
58 on the synthesis, characterization and crystal structure of
59 the new tetranuclear $[\text{Pd}_4(\mu_2\text{-}\eta^2\text{-S}_2)(\text{H}_2\text{L}^1)_2]$ complex,
60 where H_2L^1 is the anion of 3,5-diacetyl-1,2,4-triazole
61 bis(4-ethylthiosemicarbazone). Each triazolone unit acts in
62 the N^1, N^2 -bridging mode and the two $[\text{Pd}_2(\text{H}_2\text{L}^1)]^+$
63 sub-units are linked via a disulphide bridge to give the tetranuclear
64 Pd(II) complex.

65 The ligand H_5L^1 was synthesized by reacting methanolic
66 solutions (20 mL) of 3,5-diacetyl-1,2,4-triazole (0.25 g,
67 1.6 mmol), previously synthesized [12], and the 4-ethylthio-
68 semicarbazide in a 1:2 molar ratio (0.38 g, 3.2 mmol).
69 The reaction mixture was treated under reflux for 6 h.
70 The pale yellow solid formed was filtered and washed with
71 cold MeOH and Et_2O and dried in vacuo.¹

washed with MeOH and Et_2O and dried in vacuo. The
found C, H, N and S percentages together with IR and
 ^1H NMR data allow us to postulate the obtaining of the
dimeric complex² $[\{\text{Pd}(\mu\text{-H}_3\text{L}^1)\}_2] \cdot 10\text{H}_2\text{O}$ (**1**), similar to
those found for palladium(II) complexes derived from
3,5-diacetyl-1,2,4-triazole bis(4-methylthiosemicarbazone)
and 3,5-diacetyl-1,2,4-triazole bis(4-phenylthiosemicarbazone).
Recrystallization of **1** from dimethylsulfoxide gave
orange crystals of compound **2** suitable for X-ray
diffraction.³

² $[\{\text{Pd}(\mu\text{-H}_3\text{L}^1)\}_2] \cdot 10\text{H}_2\text{O}$ (**1**): Anal. % Found: C, 26.10; H, 5.38, N, 22.77; S 11.77; $\text{C}_{24}\text{H}_{38}\text{N}_{18}\text{S}_4\text{Pd}_2 \cdot 10\text{H}_2\text{O}$ requires C, 26.21; H, 5.28, N, 22.93; S 11.65%. IR (KBr, cm^{-1}), $\nu = 3218$ (s, NH); $\nu = 1579$ (s, CN). ^1H NMR (d^6 -DMSO, ppm), $\delta = 15.32$ (s, NH-triazolic); $\delta = 12.49$; 10.86 (s, ^2NH); $\delta = 9.25$, 9.00 (t, ^4NH); $\delta = 3.61$ (m, CH_2); $\delta = 2.43$ (s, CH_3 -triazolic); $\delta = 1.10$ (m, CH_3).

³ Crystal data for $[\text{Pd}_4(\mu_2\text{-}\eta^2\text{-S}_2)(\text{H}_2\text{L}^1)_2] \cdot 4\text{DMSO} \cdot \text{H}_2\text{O}$ (**2**): $\text{C}_{32}\text{H}_{62}\text{N}_{18}\text{O}_3\text{Pd}_4\text{S}_{10}$, $M = 1515.18$, orthorhombic, space group $Pbca$, $a = 24.6317(6)$ Å, $b = 15.7255(3)$ Å, $c = 28.1872(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 10918.2(4)$ Å³, $T = 100(2)$ K, $Z = 8$, $D_c = 1.844$ Mg/m³, $F(000) = 6064$, $\mu = 14.500$ mm⁻¹, $\lambda = 1.54178$ Å, 46987 observed reflections, 10288 independent reflections [$R(\text{int}) = 0.0855$]. The final agreement factors are $R_1 = 0.0394$, $wR_2 = 0.0904$ with $I > 2\sigma(I)$ and R indices (all data) $R_1 = 0.0680$, $wR_2 = 0.1034$.

¹ $\text{H}_5\text{L}^1 \cdot \text{H}_2\text{O}$: Anal. % Found: C, 38.31; H, 6.31; N, 33.82; S, 17.59. $\text{C}_{12}\text{H}_{21}\text{N}_9\text{S}_2 \cdot \text{H}_2\text{O}$ requires: C, 38.60; H, 6.17; N, 33.78; S, 17.16. MS (FAB⁺ with mNBA matrix), $m/z = 356$ for $[\text{H}_5\text{L}^1 + \text{H}]^+$. IR (KBr, cm^{-1}), $\nu = 3354$, 3275, 3183 (s, NH); $\nu = 1596$ (s, CN), $\nu = 878$ (m, CS-thioamide IV band). ^1H NMR (d^6 -DMSO, ppm), $\delta = 15.16$ (s, NH-triazolic); $\delta = 12.65$; 10.95 (s, ^2NH); $\delta = 8.92$, 8.71 (t, ^4NH); $\delta = 3.70$ (m, CH_2); $\delta = 2.43$ (s, CH_3 -triazolic); $\delta = 1.26$ (m, CH_3).

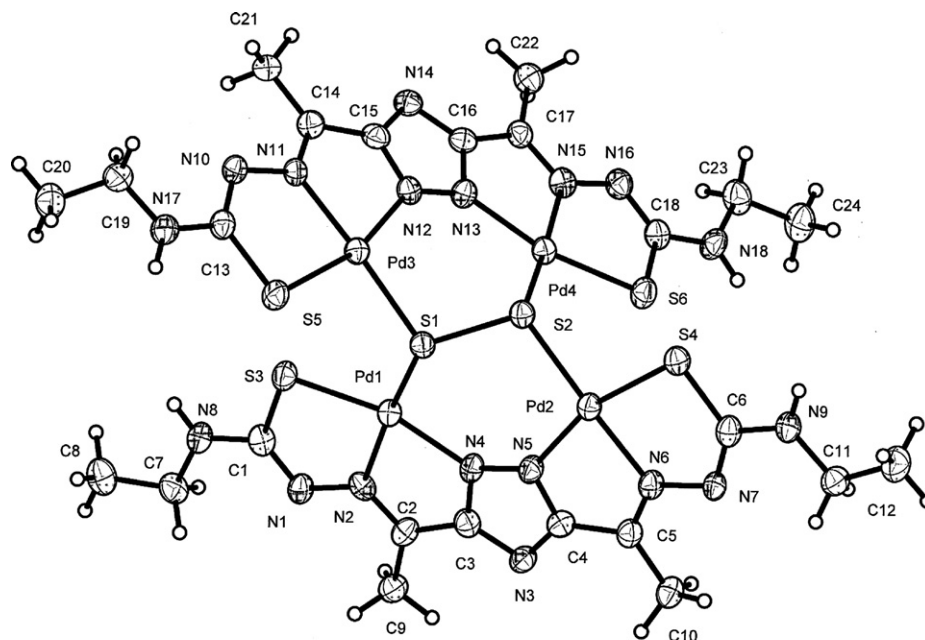


Fig. 2. Molecular structure of complex **2** displaying the atom numbering scheme.

89 **Scheme 1** shows the reactions used to form the neutral
90 tetranuclear complex **2** and its molecular structure is shown
91 in **Fig. 2**.

92 The presence of a disulphide ligand presumably formed
93 by the oxidation of some ligand molecules, is to be noted in
94 fact the reductive character of thiosemicarbazones is well
95 known and especially when solutions are heated or allowed
96 to crystallise over several days even at room temperature
97 [13,14].

98 The structure contains two planar subunits of
99 $[\text{Pd}_2(\text{H}_2\text{L}^1)]^+$ linked via a disulphide bridge, four dimethylsulphoxide molecules and one water molecule of crystallization. Due to the sp^3 hybridization of the bridging sulphur atoms, the molecule is appreciably twisted with bridge angles $\text{Pd}(3)\text{--S}(1)\text{--Pd}(1)$ $109.28(6)$, $\text{Pd}(1)\text{--S}(1)\text{--S}(2)$ $114.19(7)$, $\text{S}(2)\text{--S}(1)\text{--Pd}(3)$ $108.06(7)$, $\text{Pd}(4)\text{--S}(2)\text{--Pd}(2)$ $107.07(6)$, $\text{Pd}(2)\text{--S}(2)\text{--S}(1)$ $109.13(7)$, $\text{S}(1)\text{--S}(2)\text{--Pd}(4)$ $113.06(7)^\circ$ to result in a roof-shaped structure. The S–S distance of the $\mu\text{-S}_2$ group [$2.125(18)$ Å] is slightly longer than that found in disulphide complexes ($2.01\text{--}2.09$ Å) [15].

109 This complex crystallizes in the high symmetry *Pbca*
110 space group with $Z = 8$. The geometry around each palladium atom is essentially planar with two nitrogen, iminic and triazolic, and two sulphur, thioamide and disulphide-bridge, atoms defining the N_2S_2 coordination sphere. Each trideprotonate 3,5-diacetyl-1,2,4-triazole bis(4-ethylthiosemicarbazone) ligand acts as a hexadentate in a symmetrical manner bridging two metal ions through the two adjacent nitrogen atoms of the central triazole ring. The disulphide bridge is shared by all the four palladium atoms resulting in the formation of two central six-membered $\text{Pd}_2\text{N}_2\text{S}_2$ chelate rings which are not coplanar. The four palladium

atoms form a Pd_4 core (**Fig. 3**) with $\text{Pd} \cdots \text{Pd}$ separation
121 of ~ 3.7 Å for $\text{Pd}(1) \cdots \text{Pd}(3)$ and $\text{Pd}(2) \cdots \text{Pd}(4)$, linked
122 by a S–S bridge, and ~ 4.3 Å for $\text{Pd}(1) \cdots \text{Pd}(2)$ and
123 $\text{Pd}(3) \cdots \text{Pd}(4)$, linked by a N–N triazole bridge, these distances
124 are too long to make a direct metal–metal bond. 125

The Pd–N and Pd–S bond distances in the range
126 $1.997(5)\text{--}2.028(5)$ Å and $2.254(15)\text{--}2.310(15)$ Å, respectively,
127 are comparable with those reported for Pd(II) thiosemicarbazone complexes [16,17]. The C–S bond lengths of
128 $1.766(6)$, $1.776(6)$, $1.778(6)$ and $1.783(6)$ Å are within the
129 normal range of a C–S single bond, indicating that the thiosemicarbazone moieties adopt the thiol tautomeric form.
130 The C–N and N–N bond distances are intermediate
131 between formal single and double bonds, pointing to exten- 132
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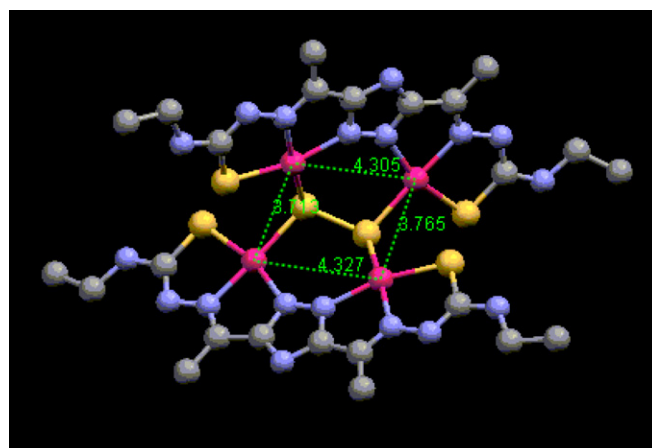


Fig. 3. A view of structure **2** showing the distances between the palladium ions.

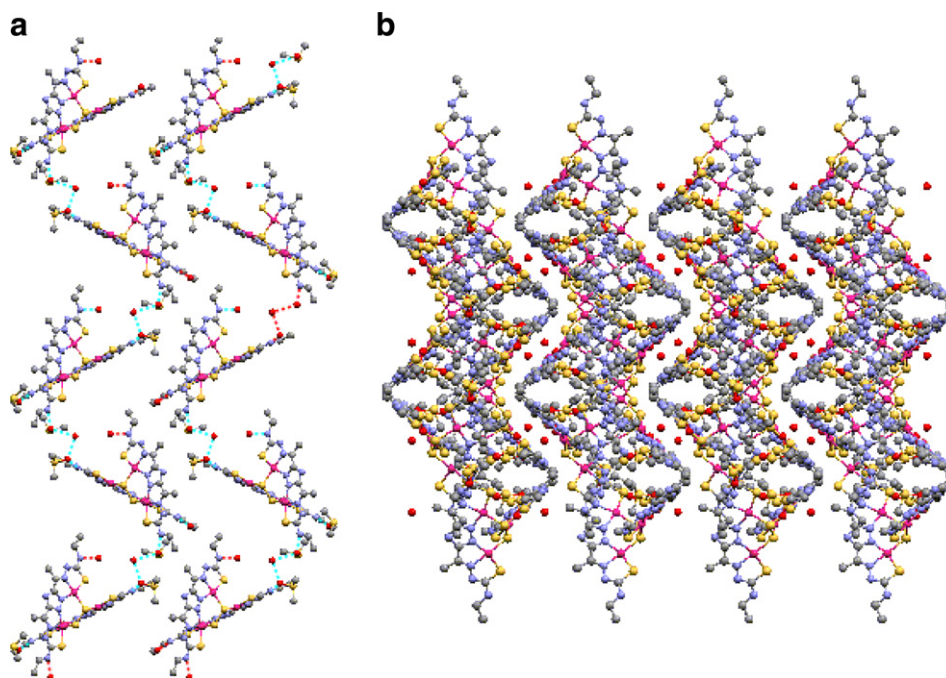


Fig. 4. Network illustrations of complex 2. (a) A view along the *a*-axis showing the hydrogen bond interactions. (b) Packing diagram viewed down the *c**-axis.

135 sive delocalization over the entire 3,5-diacetyl-1,2,4-triazole
136 bis(thiosemicarbazone) skeleton.

137 Fig. 4a shows the existence of intermolecular hydrogen
138 bonds involving the uncoordinated terminal nitrogen
139 atoms of the molecule and the oxygen atoms of the dimethylsulphoxide
140 and water molecules, which are responsible for the formation of the strand
141 along the crystallographic *a* axis. The molecular packing is characterized
142 by hydrogen bond interactions with the formation of a framework type
143 structure having two types of well-defined channels: the oval monodimensional
144 channels, perpendicular to *c** axis, and the zig-zag channels running down
145 the *c** axis in which the lattice water molecules are located as shown in
146 Fig. 4b.

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154 Appendix A. Supplementary material

155 Full crystallographic details have been deposited in
156 CIF format with the Cambridge Crystallographic Data Centre. CCDC 611952
157 contains the supplementary crystallographic data for this paper. These data
158 can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>,
159 or from the Cambridge Crystallographic Data Centre, 12 Union Road,
160 Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-408; e-mail: depos-

it@ccdc.cam.ac.uk. Supplementary data associated with
163 this article can be found, in the online version, at
164 [doi:10.1016/j.inoche.2006.09.016](https://doi.org/10.1016/j.inoche.2006.09.016).
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