

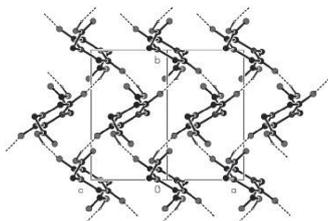
s13.m42.p3 **Rectangular Rings in 2,5-Dioxo-piperazine-1,4-diacetic acid.** Ana Matos Beja^a, Manuela Ramos Silva^a, José António Paixão^a, Abílio J.F.N. Sobral^b, Lúcia M.L.Cabral^b, A.M.d'A Rocha Gonsalves^b. ^aCEMDRX, FCT, Universidade de Coimbra, 3004-516 Coimbra, Portugal. ^bDepartamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal. E-mail: ana@pollux.fis.uc.pt

Keywords: Piperazine; Hydrogen bond

Molecules of the title compound, C₈H₁₀N₂O₆, crystallize in a monoclinic unit cell with P2₁/c space group and occupy centres of symmetry in the crystal structure [1]. The six-membered ring assumes an extremely flattened conformation (almost planar), with the substituent on nitrogen nearly perpendicular to the ring.



The ideal geometry of the isolated molecule, as determined by ab-initio Hartree-Fock quantum mechanical calculations[2], is slightly more puckered than that observed in the solid state. Detailed comparison between experimental and calculated molecular geometry will be made. In the crystal structure, a strong hydrogen bond joins neighbouring molecules. The H-bond pattern will be analysed according to Etter's graph-set analysis[3]. The formation of chains and of an unusual network of rectangular rings will be shown and described.

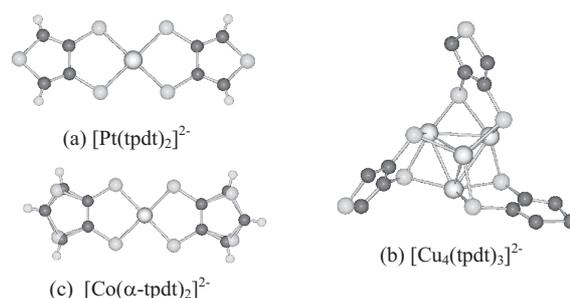


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 [2] Schimdt *et al.* *J. Comput. Chem.* **14** (1993), 1347-1363.
 [3] Bernstein *et al.* *Angew. Chem. Int. Ed. Engl.* **34** (1995), 1555-1573.

s13.m42.p4 **Metal Bisthiophenedithiolates as Building Blocks in Molecular Materials.** D. Belo^a, M.J. Figueira^a, J.Mendonça^a, H.Alves^a, I.C. Santos^a, E.B. Lopes^a, L.C. Pereira^a, M.T. Duarte^b, V. Gama^a, R.T. Henriques^b, M. Almeida^a, C.Rovira^c and J.Veciana^c; ^aDep. Química, Instituto Tecnológico Nuclear, Estrada Nacional 10, P-2685-953 Sacavém, Portugal. ^bDep. Eng. Química Av. Rovisco Pais, P-1049-001 Lisboa, Portugal. ^cInstitut De Ciencia De Materials De Barcelona, Csci, E-08193 Bellaterra, Espana; E-mail: Dbelo@Itm.Mces.Pt

Keywords: Transition metal complexes; Dithiophene ligands

In this communication we report the synthesis and characterization of new transition metal complexes based on dithiophene ligands: [M(α -tpdt)_y]^{x-}, [M(dtpdt)_y]^{x-} and [M(tpdt)_y]^{x-} (α -tpdt=2,3-thiophenedithiolate, dtpdt=4,5-dihidro-2,3- thiophenedithiolate, and tpdt=3,4-thiophenedithiolate with M=Au, Ni, Co, Cu and Pt)[1,2] and evaluate their potential as building blocks for the preparation of new electric or magnetic materials. The crystal structure of these complexes, obtained by single crystal x-ray diffraction show in general a square planar coordination geometry (y=2) except for Cu which presents the less common geometry based Cu₄S₆ clusters with y=3 as for Cu₄(tpdt)₃. The crystal structures corroborate the ability of these thiophene ligands to establish contacts through the peripheral sulphurs atoms. Cyclic voltametry studies confirm their relatively low oxidation potentials, when compared with other bisdithiolenes complexes. Some of these bisdithiophene complexes can be easily oxidised to a stable neutral species. An important results is the neutral complex Au(α -tpdt)₂ that, characterized as a polycrystalline sample, displays properties of a metallic system, with a room temperature electrical conductivity of 7 S/cm and a thermoelectric power of 5.5 μ V/K. The bisdithiophene complexes, obtained either as nBu₄N or tetraphenylphosphonium salts were combined with TTF based donors in order to obtain molecular conductors or with decamethylmetallocenium cations to obtain magnetic materials and some examples will be shown. Among the mettalocenium salts the magnetic characterisation of [Fe(Cp*)₂][Ni(α -tpdt)₂] reveals, below 2 K, a metamagnetic behaviour with a critical field up to 0.06 T.



- [1] D. Belo *et al.* *Chem. Eur. J.*, 2001, 7, 511.
 [2] D. Belo *et al.* *Eur. J. Inorg. Chem.*, 2001, 3127-3133.