Acta Cryst. (2002). A**58** (Supplement), C317

STRUCTURAL STUDIES OF THE BORON COORDINATION COMPOUND WITH THIOUREA

I. Zviedre[1] V. Belsky[2] V. Zavodnik[3] J. Schwartz[4]
[1]Institute of Inorganic Chemistry of The Riga Technical University Miera Str.34 SALASPILS LV-2169 LATVIA [2]L. Karpov Institute of Physical Chemistry, Moscow, Russia [3]L. Karpov Institute of Physical Chemistry, Moscow, Russia [4]Institute of Inorganic Chemistry of the Riga Technical University, Riga, Latvia

In the course of systematic structural studies of dicitratoborates the investigation of the crystal structure of $NH_2CSHNH_2[(C_6H_6O_7)_2B]$ has been carried out. The dicitratoborate complex with thiourea (L) was synthesized according to [1]. The structure is formed by cations of thiourea $(HL)^+$ and spiran-type complex anions $[(C_6H_6O_7)_2B]^-$. In the complex anions two citric acid resides are coordinated bidentatically to the BO_4-terahedron. The values of the chemical bond lengths and bond angles in the complex anions are in accordance with those determined earlier for the crystal structures of dicitratoborates. The boron-containing five-membered rings are approximately planar. The cation $(NH_2CSHNH_2)^+$ is protonated at the sulphur atom. The protonation gives rise to delocalization of p-electron density at the C-S and N-C bonds. The bond lengths are: C-S 1.738(2) Å; N-C 1.317(3) Å and 1.298(3) Å. The bond C(sp^2)-S is lengthened for 0.10 Å, but the C(sp^2)-N bonds are shortened for 0.04 Å in average in the cation $(HL)^+$ when compared with the neutral molecule (L). In the crystals each organic cation is bonded with three nonidentical complex anions by five hydrogen bonds N-H···O (2+2) and S-H···O. The complex anions are bonded directly by four strong hydrogen bonds O-H···O (length from 2.589 to 2.692 Å). Crystal data: $NH_2CSHNH_2[(C_6H_6O_7)_2B]$, triclinic, space group *P*-1, a = 9.630(1) Å, b =10.320(2) Å, c=10.914(2) Å; α=76.86(1)°, β=88.80(1)°, γ=64.26(1)°; V=947.7(3)Å^3; Z=2; dx=1.641 g·cm^{-3}; R=0.0246, wR2=0.0661.

[1] G.Sergeeva, N.Burnashova, J.Schwartz.Compounds of borodicitric acid with urea and thiourea, Latvian Journal of Chemistry, (1991), 5: 553-558.

Keywords: CRYSTAL STRUCTURE, BORON COMPLEXES, THIOUREA

Acta Cryst. (2002). A**58** (Supplement), C317

STRUCTURAL AND SPECTROSCOPIC MOTIFS OF ARTIFICIAL DI-IRON SUB-SITES OF ALL-IRON HYDROGENASE

S. C. Davies[1] J. E. Barclay[2] S. P. Best[2] S. Borg[1] D. J. Evans[1] S. J. George[1] D. L. Hughes[1] A. Le Cloirec[1] M. Razavet[1] C. J. Pickett[1]
[1]Biological Chemistry Department John Innes Centre Colney Lane NORWICH NR4 7UH UK [2]School of Chemistry, University of Melbourne, Parkville, 3052 Victoria, Australia

The hydrogenases catalyse the reversible interconversion of protons to dihydrogen. Recently, the X-ray crystal structures of all-iron hydrogenase from Clostridium pasteurianum and Desulfovibrio desulfuricans were reported. The active site, the H-centre, in each is comprised of a 6-Fe cluster, with 2 [$4Fe_4S$] clusters forming an electron transfer pathway from the site to the surface of the protein. In the active site, a [$4Fe_4S$] cluster is linked through a cysteinyl sulfur to a novel [$2Fe_3S$] unit, the sub-site, which is ligated by CO and CN^-. Model chemistry can provide an understanding of the spectroscopic properties of H-centre redox states and mechanistic insights into how the enzyme works. There has been considerable debate as to whether the epr active redox state of the sub-site comprises an Fe(I)-Fe(II) or Fe(III)-Fe(II) pair. The Fe(I)-Fe(II) state is unprecedented in biology and recent structural and spectroscopic data for synthetic sub-site assemblies, including, the first class of artificial [$2Fe_3S$] assemblies [1 and references therin], now support its occurrence in the above system. Artificial sub-sites may provide new materials for electrocatalysis of hydrogen evolution/uptake, a key aspect of energy transduction relevant to progress towards an Hydrogen Economy.

1. M. Razavet, S. C. Davies, D. L. Hughes, and C. J. Pickett, Chem. Commun., 2001, 847 ; M. Razavet , S. J. George, S. A. Fairhurst, S. J. Borg, S. P. Best and C. J. Pickett, Chem. Commun., 2002, in press.

Keywords: STRUCTURAL MOTIFS ALL-IRON HYDROGNASE IRON-SULFUR CLUSTERS

Acta Cryst. (2002). A**58** (Supplement), C317

BIOLOGICALLY ACTIVE COPPER(II) AND PLATINUM(IV) COMPLEXES WITH CYTOKININ-DERIVED COMPOUNDS

M. Malon Z. Travnicek J. Marek
Faculty of Science, Palacky University Dept. of Inorganic Chemistry Krizkovskeho 10 OLOMOUC CZ-771 47 CZECH REPUBLIC

Biologically active mononuclear Cu(II) and Pt(IV) complexes have been synthesized and structurally characterized in the course of our systematic investigations of cytokinin-derived compounds [1,2]. The composition of the complexes, resulting from a single crystal X-ray analysis, is following: $[Cu(2OHbapH)_2Cl_3]Cl\cdot 2H_2O$ (1) (2OHbap = 6-(2-hydroxybenzylamino)purine), $[Cu(3OHbapH)_2Cl_3]Cl\cdot 2H_2O$ (2) (3OHbap = 6-(3-hydroxybenzylamino)purine), $[Cu(4FbapH)_2Cl_2(H_2O)]Cl_2$ (3) (4Fbap = 6-(4-fluorobenzylamino)purine) and $(roscH_2)_2[PtCl_6]Cl_2\cdot 4H_2O$ (4) (rosc = 2-(1-ethyl-2-hydroxyethylamino)-6-benzylamino-9-isopropylpurine). A coordination geometry is trigonal-bipyramidal in all the copper(II) complexes. Each of two protonationed purine-derived ligands is bonded to the copper(II) ion via the N9 atom. The compound (4) consists of two twice-protonationed rocs cations, one $[PtCl_6]^{2-}$, two Cl^- anions and four uncoordinated water molecules. The compounds have been tested for their possible cytotoxic activity against G-361, HOS, K-562 and MCF7 cell lines. A cytokinin activity has been also determined for the copper(II) complexes. X-ray data were collected at 120 K on a four-circle kappa-axis diffractometer KUMA KM-4 equipped with an Oxford Cryostream cooler and a CCD detector. All crystal structures were determined and refined using a SHELX97 program package. Crystal data: (1) $C_{24}H_{26}N_{10}O_4Cl_4Cu$, monoclinic $P2_1/n$, a = 14.8725(6), b = 8.3546(4), c = 23.3856(9) Å, β = 95.079(4)°, Z = 4, reflections collected / unique 14673 / 5069 [R(int) = 0.0501], R1(obs) = 0.0434, wR2(obs) = 0.0937. (2) $C_{24}H_{26}N_{10}O_4Cl_4Cu$, monoclinic $P2_1$, a = 7.3794(7), b = 27.282(3), c = 14.369(2) Å, β = 93.193(11)°, Z = 4, Reflections collected / unique 10481 / 7780 [R(int) = 0.0437], R1(obs) = 0.0569, wR2(obs) = 0.1391. (3) $C_{24}H_{24}Cl_4CuF_2N_{10}$, triclinic *P*-1, a = 7.2851(5), b = 13.4033(7), c = 15.3589(9) Å, α = 92.018(4), β = 94.604(5), γ = 90.889(5)°, reflections collected / unique 9769 / 5931 [R(int) = 0.0534], R1(obs) = 0.0441, wR2(obs) = 0.1081. (4) $C_{38}H_{64}Cl_8N_{12}O_6Pt$, monoclinic $P2_1/n$, a = 17.8564(14), b = 6.9720(4), c = 21.353(2) Å, β = 95.784(7)°, Reflections collected / unique 12896 / 4654 [R(int) = 0.0992], R1(obs) = 0.0691, wR2(obs) = 0.1714.

This work was supported by the Grant Agency of the Czech Republic, grant nos. 203/00/0152 and 203/02/0436.

1. Z. Travnicek, M. Malon, Z. Sindelar, K. Dolezal, J. Rolcik, V. Krystof, M. Strnad, and J. Marek, J. Inorg. Biochem., 84(1-2), 23-32 (2001). 2. M. Malon, Z. Travnicek, M. Marysko, R. Zboril, M. Maslan, J. Marek, K. Dolezal, J. Rolcik, V. Krystof, and M. Strnad, Inorg. Chim. Acta, 323,119-129 (2001).

Keywords: CYTOKININ COPPER(II) PLATINUM(IV)

Acta Cryst. (2002). A**58** (Supplement), C317

DERIVATIVES OF SUBSTITUTED 3-TRICHLOROGERMYL PROPIONIC ACID

M. Parvez[1] K. Hans[1] S. Ali[2] M. Mazhar[2]
[1]University of Calgary Chemistry 2500 University Drive N.W. CALGARY ALBERTA T2N 1N4 CANADA [2]Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan

Organogermanium chemistry has received a great impetus in the recent years due to the low toxicity of organogermanium compounds, such as germatrans, spirogermanium, germa-gama-lactones, etc. In continuing our work in the studies of biologically active organogermanium compounds, we have synthesized a number of compounds. The crystal structures of three of these have been determined and will be presented in the poster. Crystal data (I): $C_{31}H_{32}GeO_2$, FW = 509.15, monoclinic, $P2_1/c$, a = 10.5010(5), b = 16.3680(6), c = 18.1040(7) Å, β = 123.410(2)°, V = 2597.5(2) Å^3, Z = 4, Dx = 1.320 Mg/m^3, T = 170 K, F(000) = 1064, R = 0.054, GoF = 1.03, for 5870 reflections collected on a KappaCCD diffractometer, and using full-matrix least-squares calculations on F^2 with the aid of SHELXL97. Crystal data (II): $C_{27}H_{23}FGeO_2$, FW = 471.04, monoclinic, $P2_1/c$, a = 9.7278(1), b = 17.9075(3), c = 13.5408(2) Å, β = 110.907(1)°, V = 2203.51(5) Å^3, Z = 4, Dx = 1.420 Mg/m^3, T = 170 K, F(000) = 968, R = 0.027, GoF = 1.03, for 5026 reflections collected on a KappaCCD diffractometer, and using full-matrix least-squares calculations on F^2 with the aid of SHELXL97. Crystal data (III): $C_{31}H_{32}GeO_2$, FW = 509.15, monoclinic, $P2_1/c$, a = 10.9842(3), b = 13.7103(4), c = 20.2450(5) Å, β = 113.857(1)°, V = 2788.33(13) Å^3, Z = 4, Dx = 1.213 Mg/m^3, T = 170 K, F(000) = 1064, R = 0.043, GoF = 1.01, for 6347 reflections collected on a KappaCCD diffractometer, and using full-matrix least-squares calculations on F^2 with the aid of SHELXL97.

References

Sheldrick, G.M. (1997). SHELXL97. Program to Refine Crystal Structures. University of Gottingen, Germany.

Keywords: ORGANOGERMANIUM, PROPIONIC ACID DERIVATIVES, CRYSTAL STRUCTURES