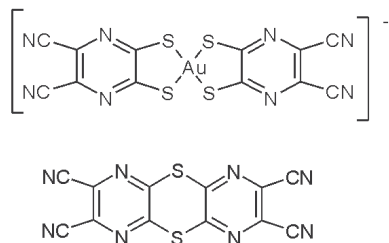


s13.m35.p20 **5,6-Dicyano-2,3-dithiopyrazine (dcdmp) Chemistry; Au(III)(dcdmp)₂ Complex, Charge Transfer Salts with TTF Type Donors and (tctata).** I.C. Santos^a, D. Belo^a, E.B. Lopes^a, M.T.Duarte^b, R.T.Henriques^b and M. Almeida^a, ^aDep. Química, Instituto Tecnológico Nuclear, Estrada Nacional 10, 2685-953 Sacavém, Portugal, ^bDep. Eng. Química, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: icsantos@itn.mces.pt

Keywords: Charge transfer salts; Metal bisdithiolates

As an effort to explore new complexes of the 2,3-dicyano-5,6-dimercaptopyrazine (dcdmp) ligand with different transition metals, different salts containing both the Au(dcdmp)₂- complex and the new species 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene (tctata), were obtained and characterized[1]. To the best of our knowledge tctata, together with bis(quinoxaline)-2,2',3,3'-disulfide[2] and 1,4,6,9-tetraazathianthrene are the only azathiaantrenes displaying an essentially planar geometry, while all others present significant molecular dihedral angles ranging from 132 to 143°. n-Bu₄N Au(dcdmp)₂ crystallises in monoclinic space group C2/c, Z=8 with unit cell parameters a=35.147(4)Å, b=9.527(1)Å, c=21.792(2)Å and β=109.626(8)°. Its crystal structure consists of almost regular columns of [Au(dcdmp)₂]⁻, stacked along b, surrounded by n-Bu₄N⁺ cations. n-Bu₄N AuBr₂ (tctata) crystallises in triclinic space group P-1, Z=2, with unit cell parameters a=10.986(1)Å, b=13.230(2)Å, c=13.791(1)Å, α=79.150(9)°, β=69.663(6)°, γ=70.254(9)°. The crystal packing is made by zigzag chains of tctata separated by layers of cations, with AuBr₂ anions located in alternated cavities between the tctata chains and the cation layers. At last, n-Bu₄N [Au(dcdmp)₂] (tctata) crystallises in monoclinic space group P2₁/n, Z=4, with unit cell parameters a=10.693(2)Å, b=40.308(7)Å, c=10.870(1)Å, β=92.16(1)°. Its crystal structure can be seen has a mix of those of the two preceding compounds. It consists of bidimensional layers composed of out of registry parallel zigzag chains of alternating tctata and [Au(dcdmp)₂]⁻ units. The adjacent layers are separated by layers of [nBu₄N]⁺.



Finally charge transfer salts of Au(dcdmp)₂ with BEDT-TTF, TMTSF and TTF donors were obtained and characterised by X-ray diffraction, and electrical transport measurements. These salts all have a 1:1 stoichiometry. Electrical conductivity at room temperature show values between 10² and 10⁻⁴ S/cm, depending on the donor molecule. The lowest conductivity was observed for ET[Au(dcdmp)₂], 7x10⁻⁴ S/cm with an activation energy of 206 meV, while for the TTF complex an electric conductivity of 192 S/cm was observed[3].

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s13.m35.p21 **Hydrothermal Synthesis and the Crystal Structure of Boratokankrenit - (Na, Ca)₂[NA₆(AlSiO₄)₆](BO₃)·2H₂O.** A. F. Shirinova, H. R. Samedov, C. G. Ragimov, M. J. Chiragov, *Baku State University, Russia*. E-mail: afashf@rambler.ru

Keywords: Boratokankrenit; Hydrothermal crystallization; Chemistry of alumoborosilicates

In order to help understand the crystal chemistry of alumoborosilicates the system CaO-Al₂O₃-SiO₂-B₂O₃-H₂O has been investigated by the hydrothermal crystallization method. The single transparent crystal with elongated habitus has been obtained in the 0,5:1:4:0,5 correlation oxides and concentration of NaOH - 25%. According to the result of powder diagrams and chemical analysis the single crystals were canerit with chemical composition 3,55 Na₂O·CaO·3Al₂O₃·6SiO₂·0,5B₂O₃. The lattice constant of the hexagonal unit cell are a=12.745 (4), c=5.180 (2), V=728.6 (4) Å³ at T=298 K, Z=1, d_c=2,666 g/cm³, space group P6₃, F(000)=492, μ=0,702 mm⁻¹. 10833 reflection were recorded on automatic Enraf - Nonius CADY diffractometer with MoKα radiation.

The structure has been determined by direct method and refined in the full matrix approach for non-hydrogen atoms.

The water molecules are situated in special positions on the three fold axes statistically disordered around this axes in positions with 1/3 of occupancy factors. The boron atoms situated on the 6₃ axes in the two multiple positions and connecting with him three oxygen atoms are situated in the six multiple positions also statistically disordered with occupancy factor 1/2. The sodium and calcium atoms are statistically disordered in the two multiple positions on the three fold axes.

The structure has been solved and refined to R=0,027 for 2889 independent reflection by using the SHELXTL (PC Version 5.10) programs.

The structure of boratocanrenit can be described as three dimensional framework of Al and Si-tetrahedra. The sodium atoms and BO₃ group are occupied in large 12-members hexagonal rings. The 6-members rings are occupied by the Na and Ca atoms.

The average interatomic distances in the Si and Al tetraedra (Si-O)_{av}=1.614 Å, (Al-O)_{av}=1,741 valency angles <(O-Si-O)_{av}=109.47° and <(Al-O-Al)=109.45°. The polyhedral -Na-O distances range from 2,3737 to 2,9211 Å and (Na,Ca)-O(H₂O) distances from 2,351 to 2,945 Å. The inter atomic distances in the BO₃ group are 1.409 Å.