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COMPLEXATION OF COBALT(II) RHODANIDE WITH N,N',N'',N'''-
TETRAKIS(DIPHENYLPHOSPHORYLMETHYL)-1,4,7,10-
TETRAAZACYCLODODECANE

G.S. Tsebrikova^a, R.T. Barsamyan^b, I.N. Polyakova^c, V.P. Solov'ev^a, I.S. Ivanova^{a,c},
E.N. Pyatova^{a,c}, I.P. Kalashnikova^d, V.E. Baulin^{a,d} and A.Yu. Tsivadze^a

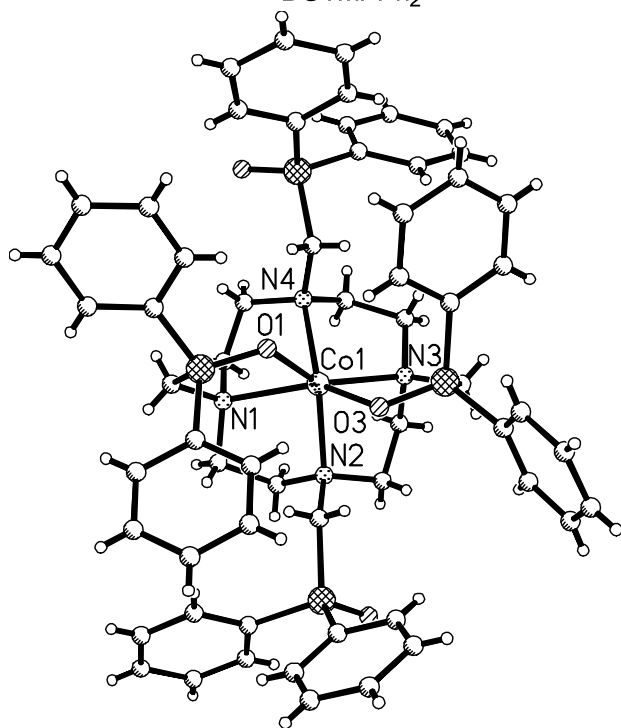
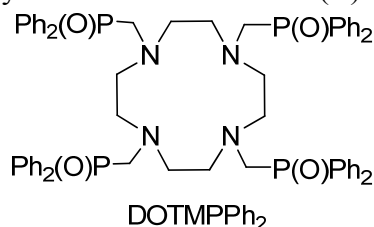
^a*Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, RUSSIA*

^b*Moscow Technological University, Moscow, RUSSIA*

^c*Kurnakov Institute of General and Inorganic Chemistry, RAS, Moscow, RUSSIA*

^d*Institute of Physiologically Active Compounds, RAS, Chernogolovka, RUSSIA*

In the crystal structure of complex $[\text{Co}(\text{DOTMPPh}_2)](\text{ClO}_4)$ studied earlier, Co atom is coordinated by four nitrogen atoms of the macrocycle and oxygen atoms of four phosphoryl groups in the shape of a twisted Archimedean antiprism. In an attempt to obtain complex cation of the same unusual coordination with the rhodanide anion, it was found that an acetonitrile solution contains complexes of the Co: DOTMPPh₂ = 1:1 and 2:1 compositions. The stability constants of the cobalt(II) rhodanide complexes with DOTMPPh₂ in acetonitrile



were estimated from UV-vis spectrophotometric data: $\log \beta_1 = 4.85 \pm 0.09$ ($\text{M}^{2+} + \text{L} = \text{M}^{2+}\text{L}$), $\log \beta_2 = 8.16 \pm 0.30$ ($2\text{M}^{2+} + \text{L} = \text{M}_2^{2+}\text{L}$). The IR, UV-vis, and ESR spectra of 2:1 complex in solid state and solution were studied. The X-ray diffraction study revealed that crystals grown from acetonitrile and ethanol solutions have the $[\text{Co}(\text{DOTMPPh}_2)]_2[\text{Co}(\text{NCS})_4] \cdot 2\text{CH}_3\text{CN}$ and $[\text{Co}(\text{DOTMPPh}_2)]_2[\text{Co}(\text{NCS})_4] \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ compositions. Solvent does not affect the coordination sphere of cobalt. In the $[\text{Co}(\text{DOTMPPh}_2)]^{2+}$ complex cation, the polyhedron of the cobalt atom is a distorted trigonal prism formed by four nitrogen atoms and oxygen atoms of only two phosphoryl groups. In the $[\text{Co}(\text{NCS})_4]^{2-}$ complex anion, Co atom is tetrahedrally coordinated by four N atoms of NCS⁻ anions.

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e-mail: tsebrikova@yandex.ru