B26

Spectroscopic Investigation of U(DBM)$_4$, U(TFBA)$_4$, Th(DBM)$_4$:U(IV), Th(TFBA)$_4$:U(IV) Single Crystals (DBM = 1,4-Dibenzoyl-1,3-butane dione, TFBA = 4,4,4-Trifluoro-1-phenyl-1,3-butane dione)

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Single crystals of U or Th(DBM)$_4$-solvate, U or Th(TFBA)$_4$ and Th(DBM)$_4$-solvate or Th(TFBA)$_4$ doped with U(IV), few tenths of cubic millimeters in size, have been grown at low temperature from benzene (DBM) or toluene (TFBA) solutions. Other conditions do not lead to so large single crystals.

All tetrakis-dibenzoylmethanato crystals exchange benzene molecules giving solvate crystals. They only can be kept unchanged in benzene saturated atmosphere. The yet unknown structure of these solvates are slightly different from the known 'dry' orthorhombic U(DBM)$_4$ (Pccn) [1, 2]. First investigation on U(DMB)$_4$ solvate essentially shows a 15% increasing of the *b* parameter and a 20% increasing of the orthorhombic volume cell. Space group is Pcbb. This probably means that benzene molecules insert themselves between the U(DBM)$_4$ layers of the dry crystals. In both structures, U lies on a C$_2$ crystallographic axis parallel to z. The structure of the tetrakis-trifluorobenzoylmethanato crystals is known to be tetragonal (I4$_1$/a) [3].

Polarized high resolution spectra of all these single crystals have been obtained between 4000 and 20000 Å in the temperature range 4–300 K. Some common features appear on these spectra. The thorium chelates show two bands. The Th(DBM)$_4$:U(IV) and Th(TFBA)$_4$:U(IV) which are the best resolved spectra among all the recorded ones, show about thirty vibronic bands, some of them having a width of 10 Å at 4 K.

A quite good polarization of Th(DBM)$_4$:U(IV) spectra is surprising for such an orthorhombic lattice. This means that probably the two optical axes are so close together that the crystal appears at 4 K as uniaxial. The 4 K polarized spectra look like very accurately the σ and π U^{4+} spectra in β-ThBr$_4$ and β-ThCl$_4$ matrix or UCl$_4$, all of them being uniaxial tetragonal crystals [4, 5] where point group symmetry of U^{4+} in D$_{2d}$. So, point group symmetry of U(IV) is close to D$_{2d}$ or another group whose characteristic table is the same.

These observations cannot be explained according to the above mentioned insertion of benzene molecules without any other changes in the positions of U in the lattice. In dry U(DBM)$_4$, point group symmetry of U(IV) is D$_{4d}$ or C$_2$ depending on whether the considered environment is a square antiprism of oxygen or the whole molecule. Spectra of Th(DBM)$_4$:U(IV) have been temporarily assigned on the D$_{2d}$ basis point group symmetry. Broadness of the lines leads to poorly significant values of the F_k and B^k_q parameters.

As expected for a tetragonal crystal and a S$_4$ point group symmetry for U(IV), polarization of Th(TFBA)$_4$:U(IV) is found and spectra of U(IV) are very different from those of D$_{2d}$ symmetry. σ lines are more numerous than π lines and this could indicate according to dipole selection rules for S$_4$, that ground state is two fold degenerate. Unfortunately no spectra of U(IV) have today been assigned in a such symmetry. The spectra we have recorded could be a basis for calculations.

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B27

Spectra of U^{4+} Ion at a Site of D$_{2d}$ Symmetry

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The optical spectra of U^{4+} ion (5 f^2) at a site of D$_{2d}$ symmetry were studied by different authors in various matrices as UCl$_4$ [1–5], ZrSiO$_4$ [6, 7], HfSiO$_4$ [8], ThSiO$_4$ [8] and ThBr$_4$ [9, 4]. There also exist data on magnetic susceptibility of UCl$_4$ [10–13] and USiO$_4$ [14] but most results do not agree with those obtained from optical spectra. At this point, one can note the disparity between the previous results concerning UCl$_4$, which was the most studied of all these crystals and mention the necessity of performing both optical and magnetic studies on single crystals of the same origin. A recent study of these issues leads to a better agreement [5, 15].