General X-ray Crystal Structure Information

Each crystal was mounted onto a thin glass fiber from a pool of Fluorolube™ and immediately placed under a liquid N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT Version 6.01 software. The structure refinement was performed using XSHELL 3.0 software. The data were corrected for absorption using the SADABS program within the SAINT software package.

Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the C, N, and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Table 1 lists the data collection parameters for 2 and 4 - 8. Table 2 and Table 3 list interatomic distances and angles for 2 and 4 – 8. We attempted numerous times to grow X-ray quality crystals of 3 but were unsuccessful. All CIF files were checked for errors using the free on-line Checkcif service provided by the International Union of Crystallography (available on the Web at http://www.iucr.org/acs/checkcif.html). Any problematic aspects of the structural solutions are discussed in the following paragraphs. Additional

information concerning the data collection and final structural solutions of these compounds can be found in the supplemental information or by accessing CIF files through the Cambridge Crystallographic Data Base.

$Ti(DMP)_4$ (2). The structure was solved in the triclinic space group P-1. The CheckCIF/Platon report found no serious problems with the structural data.

$[Rb_4(\mu\text{-}DMP)_4(THF)_2]_\infty$ (4). The structure was solved in the space group P2(1)2(1)2(1) using Patterson synthesis. This solution yielded the Rb, O, and some of the C atoms. Subsequent refinements yielded the remaining C atoms. THF was observed in the structural model as a disordered solvent. Attempts to structurally model the disordered (THF) failed and so the disordered (THF) was modeled using the PLATON/SQUEEZE program (Ver. 01-11-99). The SQUEEZE program located the solvent centers at (0.153 0.526 0.514), (0.347, 0.474 1.014), (0.653 0.974 0.486) and (0.847 0.026 –0.014). These four sites had a total potential volume of 714.3 $Å^3$ and electron count of 157 electrons/cell, consistent with four (THF) molecules. The disordered (THF) molecules were added to the contents of the unit cell during the final refinement series so that the proper crystal data could be calculated. Due to complications with Rb interactions it was difficult to model the hydrogen atoms. Therefore hydrogen atoms were left off of the structural model but were added to the formula during the final refinement.

The CheckCIF/Platon report found serious problems with the structural data primarily due to the use of the PLATON/SQUEEZE program to omit disordered solvent molecules, the polymeric nature of the complex, the fact that hydrogen atoms were left

off of the structural model but were added to the formula and the over quality of the structure.

$[Rb_2(\mu\text{-DIP})_2(\mu\text{-THF})]_\infty$ (5). The structure was solved in the orthorhombic space group P2(1)2(1)2(1). The CheckCIF/Platon report found a few serious problems with the structural data related to disordered C atoms (C9 and C13).

$[Rb(\mu\text{-ONep})_4(py)Ti(ONep)]_2$ (6). The structure was solved in the monoclinic space group P2(1)/c. The CheckCIF/Platon report only found serious problems related to a disordered C atom (C13).

$[Rb(\mu\text{-DMP})Ti(DMP)_4]_\infty$ (7). The structure was solved in the orthorhombic space group Pna2(1). The CheckCIF/Platon report found no serious problems with the structural data.

$[Rb(\mu\text{-DMP})_2(\mu\text{-ONep})_2Ti(ONep)]_\infty$ (8). The structure was solved in the space group P2(1)/c using a Patterson refinement. This solution yielded the Rb, O, and some of the C atoms. Subsequent refinements yielded the remaining C atoms. THF was observed in the structural model as a disordered solvent. Attempts to structurally model the disordered (THF) failed and so the disordered (THF) was modeled using the PLATON/SQUEEZE program (Ver. 01-11-99). The SQUEEZE program located the solvent centers at (0.513 0.292 0.945), (0.487 0.792 0.555), (0.513 0.208 0.445), (0.487 0.708 0.055). These four sites had a total potential volume of 830.8 $Å^3$ and electron count of 174 electrons/cell, consistent with four (THF) molecules. The disordered (THF) molecules were added to the contents of the unit cell during the final refinement series so that the proper crystal data could be calculated.

The CheckCIF/Platon report found serious problems with the structural data primarily due to the use of the PLATON/SQUEEZE program to omit disordered solvent molecules, the polymeric nature of the complex, and the over quality of the structure.