**A Combined** **NMR Crystallographic and PXRD Investigation of the Structure-Directing Role of Water Molecules in Orotic Acid and its Lithium and Magnesium Salts**

Ann-Christin Pöppler, David Walker and Steven P. Brown

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

1. **Magres-files for the different calculation including initial CIF files as well as those obtained directly after geometry optimization, single molecule calculations and the files for the symmetric and asymmetric magnesium orotate dehydrate. All calculations were run and analyzed by Ann-Christin Pöppler.**
2. **Orotic Acid Monohydrate (1): The following data was used in Figures 4 and 6.**

OROTAC01.cif

orotic\_2008-out.cif

orotic\_full\_NMR.magres

orotic\_molecule\_water\_NMR.magres

orotic\_molecule\_orotic\_acid\_NMR.magres

1. **Lithium Orotate Monohydrate (2): The following data was used in Figures 1-3.**

SIMZOD01.cif

li-out.cif

li\_full\_NMR.magres

li\_full\_without\_Li\_NMR.magres

li\_orotate\_molecule\_NMR.magres

li\_water\_molecule\_NMR.magres

1. **Magnesium Orotate Octahydrate (3): The following data was used in Figures 7 and 11.**

SIMZUJ.cif

mg-out.cif

mg\_full\_NMR.magres

mg\_water\_molecule\_NMR.magres

mg\_hexaquo\_molecule\_NMR.magres

mg\_orotate\_molecule\_NMR.magres

1. **Magnesium Orotate Dihydrate (Figure 11):**

dihydrate\_sym.cif

dihydrate\_asym.cif

dihydrate\_sym\_NMR.magres

dihydrate\_asym\_NMR.magres

1. **TGA: raw files (.txt) with both values of the mass [mg] and the heatflow [mW] at certain times/temperatures. The first two datasets are shown in the ESI, while the two magnesium orotate datasets were used in Figure 8. The TGA measurements were carried out by Ann-Christin Pöppler with the help of David Hammond.**

orotic\_acid\_monohydrate.txt (recorded on 14.04.2015)

lithium\_orotate\_2.txt (recorded on 14.04.2015)

magnesium\_orotate\_2.txt (recorded on 14.04.2015)

mg orotate after vacuum.txt (recorded on 15.04.2016)

1. **PXRD experiments: raw files as recorded under a) ambient condition or b) vacuum. All experiments were recorded by Ann-Christin Pöppler and David Walker.**
2. **Ambient condition: The first two datasets are shown in the ESI; the two mg\_orotate datasets are shown in the ESI as well as Figure 9. All diffraction experiments were recorded on 14.04.2015.**

Orotic Acid Sigma-Aldrich 5-60-1Hr30min.asc

Li\_orotate\_5-60-1Hr30min\_1.asc

Mg\_orotate\_5-60-1Hr30min.asc

Mg\_orotate\_dried\_5-60-1Hr30min.asc

1. **Vacuum: The file No Vac as well as #1, 2, 3, 5, 7 were used to create the plot shown in Figure 9, top. These experiments were carried out from 03.-04.09.2015.**

Mg-Orotate RT No Vac 5-30-1Hr.xy

Mg-Orotate RT Vac 5-30-1Hr #1.xy

Mg-Orotate RT Vac 5-30-1Hr #10.xy

Mg-Orotate RT Vac 5-30-1Hr #2.xy

Mg-Orotate RT Vac 5-30-1Hr #3.xy

Mg-Orotate RT Vac 5-30-1Hr #4.xy

Mg-Orotate RT Vac 5-30-1Hr #5.xy

Mg-Orotate RT Vac 5-30-1Hr #6.xy

Mg-Orotate RT Vac 5-30-1Hr #7.xy

Mg-Orotate RT Vac 5-30-1Hr #8.xy

Mg-Orotate RT Vac 5-30-1Hr #9.xy

1. **NMR experiments: raw files as recorded for the three compounds by Ann-Christin Pöppler**
2. **Orotic Acid Monohydrate**

**1H (56 kHz, 600 MHz):** orotic\_acid\_56kHz\_1H\_600 (recorded on 11.04.2015)

**13C CP MAS (10 kHz, 500 MHz):** orotic\_acid\_10kHz\_13C\_CPMAS\_500 (recorded on 29.09.2014)

**14N-1H\_HMQC (600 MHz):** orotic\_acid\_56kHz\_HMQC\_14N (recorded on 10.12.2014)

**15N CP MAS (500 MHz):** orotic\_acid\_10kHz\_15N\_CPMAS\_500 (recorded on 01.10.2014)

**600, Figure 4a:** orotic\_acid\_56kHz\_BABA\_no\_cooling\_600 (recorded on 13.04.2015)

**850, Figure 4b:** orotic\_acid\_60kHz\_BABA\_cooling (recorded on 18.07.2015)

**850 Figure 5:** orotic\_acid\_1H\_35kHz, orotic\_acid\_1H\_40kHz, orotic\_acid\_1H\_45kHz, orotic\_acid\_1H\_50kHz, orotic\_acid\_1H\_55kHz, orotic\_acid\_1H\_60kHz (recorded on 17.07.2015)

**Anhydrate (BABA, 30 kHz, 500 MHz):** orotic\_acid\_anhydrate\_30kHz\_BABA\_500 (recorded on 02.12.2014)

1. **Lithium Orotate Monohydrate**

**Figure 2a, 1H (56 kHz, 600 MHz):** lithium\_orotate\_55kHz\_1H\_600 (recorded on 25.02.2015)

**Figure 2b, BABA, 600 MHz:** lithium\_orotate\_55kHz\_BABA\_600 (recorded on 26.02.2015)

**7Li (10 kHz, 500 MHz):** lithium\_orotate\_10kHz\_7Li \_500 (recorded on 27.02.2015)

**13C CP MAS (30 kHz, 500 MHz):** lithium\_orotate\_30kHz\_13C\_CPMAS\_500 (recorded on 05.02.2015)

**14N-1H\_HMQC (600 MHz):** lithium\_orotate\_55kHz\_HMQC\_14N (recorded on 26.02.2015)

**15N CP MAS (500 MHz):** lithium\_orotate\_10kHz\_15N\_CPMAS\_500 (recorded on 28.02.2015)

1. **Magnesium Orotate Octa- and Dihydrate**

**Figure 7a, 1H (30 kHz, 500 MHz):** magnesium\_orotate\_30kHz\_1H\_500\_a (recorded on 04.02.2015)

**Figure 7b, 1H (30 kHz, 500 MHz):** magnesium\_orotate\_30kHz\_1H\_500\_b (recorded on 05.02.2015)

**Figure 7c, 1H (30 kHz, 500 MHz):** magnesium\_orotate\_30kHz\_1H\_500\_c (recorded on 01.03.2015)

**Figure 7d, 1H (60 kHz, 600 MHz):** magnesium\_orotate\_60kHz\_1H\_600\_d (recorded on 05.03.2015)

**BABA (30 kHz, 500 MHz):** magnesium\_orotate\_BABA\_changing (recorded on 05.02.2015)

**13C CP MAS (10 kHz, 500 MHz):** magnesium\_orotate\_12500Hz\_13C\_CPMAS\_500\_PXRD\_evacuation (recorded on 19.10.2015); magnesium\_orotate\_10kHz\_13C\_CPMAS\_500\_after\_drying (recorded on 01.03.2015)

**13C-1H refocused INEPT:** magnesium\_orotate\_12500Hz\_INEPT\_after\_PXRD (recorded on 20.10.2015)

**Noesy-like spin-diffusion MAS (60 kHz)**: magnesium\_orotate\_60kHz\_1H\_spin\_diff (recorded on 06.03.2016)