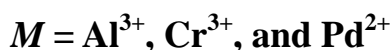


Supplementary Material for

More Examples of the 15-Crown-5···H₂O-*M*-OH₂···15-Crown-5 Motif,



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Abstract

Five structures of co-crystals grown from aqueous solutions equimolar in 15-crown-5 (or, 15C5) and $[M(\text{H}_2\text{O})_6](\text{NO}_3)_n$, $M = \text{Al}^{3+}$, Cr^{3+} , and Pd^{2+} , are reported. The H-bonding patterns in all are similar: metal complexes including the fragment *trans*-H₂O-*M*-OH₂ alternate with 15C5 molecules, to which they are hydrogen bonded, to form stacks. A literature survey shows that this H-bonding pattern is very common. In each of the two polymorphs of the compound $[\text{Al}(\text{H}_2\text{O})_6](\text{NO}_3)_3 \cdot 15\text{C}5 \cdot 4\text{H}_2\text{O}$ there are two independent cations; one forms H bonds directly to the 15C5 molecules adjacent in the stack while the other cation is H-bonded to two water molecules that act as spacers in the stack. These stacks are then crosslinked by H bonds formed by the three nitrate counterions and the three lattice water molecules. The H-bonded stacks in $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot (3/2)(15\text{C}5) \cdot \text{H}_2\text{O}$ are discrete rather than infinite; each unit contains two Cr^{3+} complex cations and three 15C5 molecules. These units are again crosslinked by the uncoordinated nitrate ions and a lattice water molecule. In $[\text{Pd}(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot 15\text{C}5$ the infinite stacks are electrically neutral and are not crosslinked. In $[\text{Pd}(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot 2(15\text{C}5) \cdot 2\text{H}_2\text{O} \cdot 2\text{HNO}_3$ a discrete, uncharged unit containing one Pd complex and two 15C5 molecules is “capped off” at either end by a lattice water molecule and an included nitric acid molecule. In all five structures the infinite stacks or discrete units form an array that is at least approximately hexagonal.

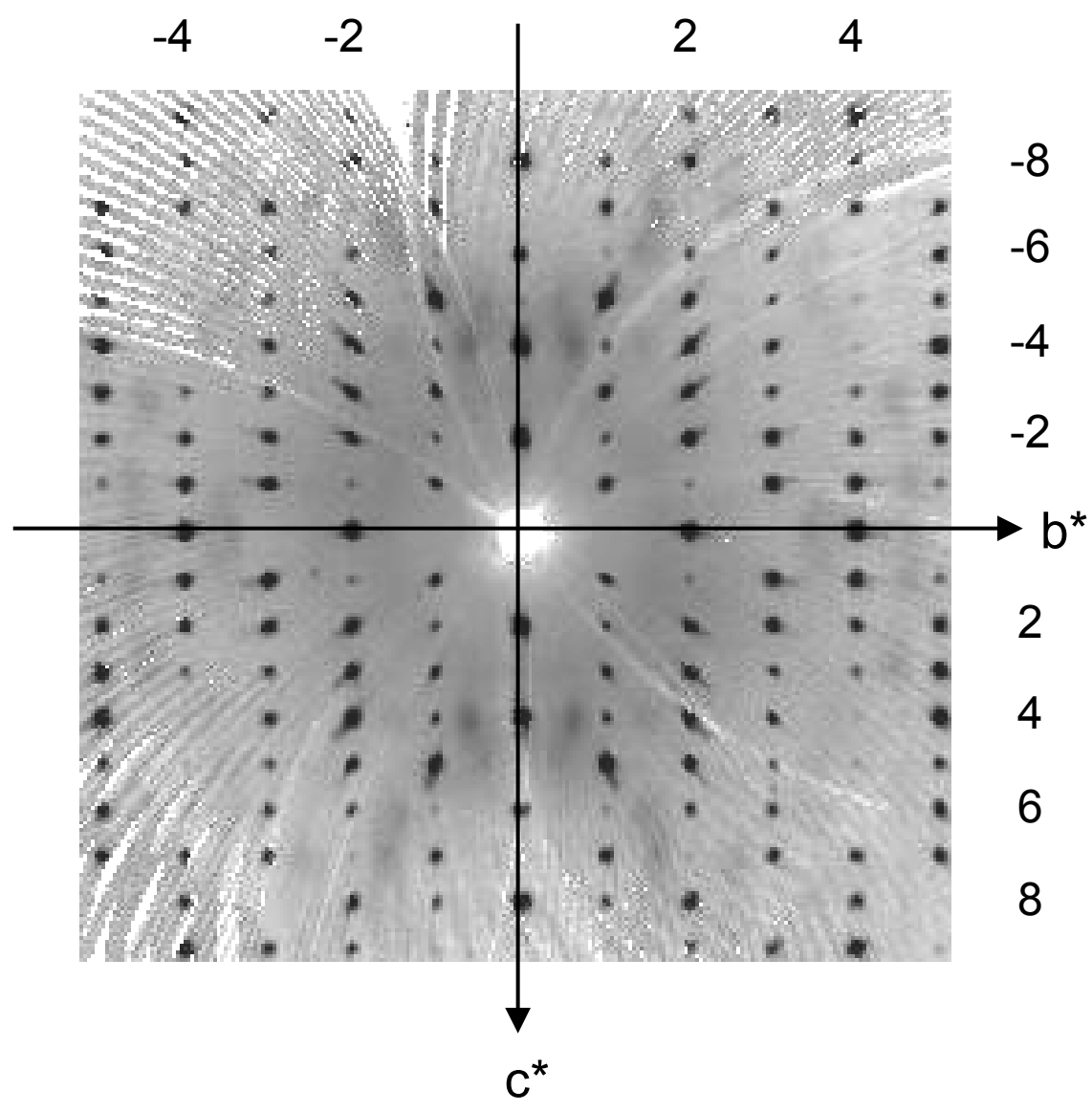
Items Included

1. List of structures retrieved from the CSD (2 pp.)
2. Reciprocal lattice slices for Cr compound showing diffuse scattering (3 pp.)
3. Details of disorder of “inner” 15-crown-5 ring in the Cr compound (1 pg.)

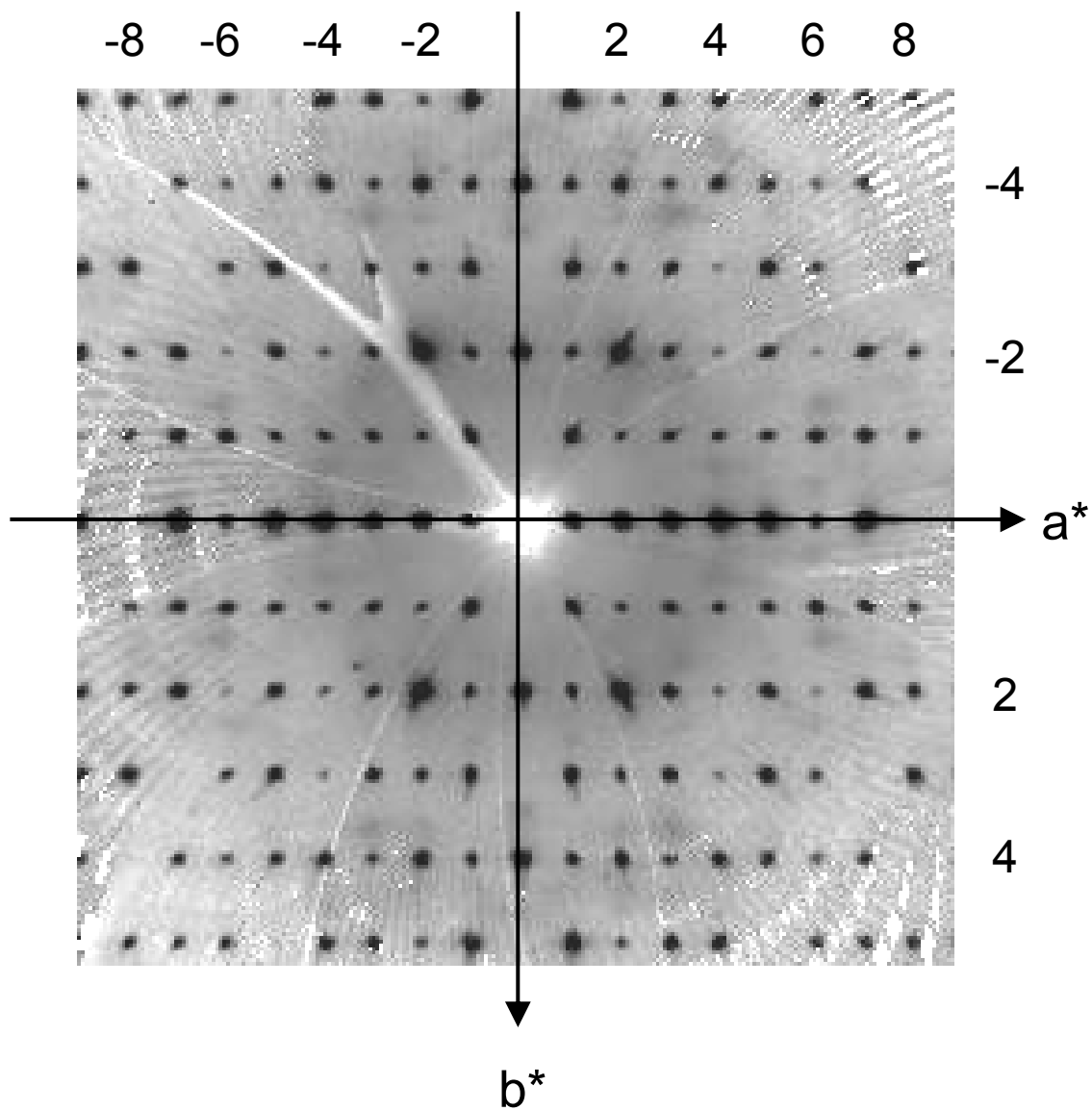
Refcode	R value	M	M Oxidation State	Charge of Complex	average M-OH2 distance	Motif (if unusual)	Comments
DUCNEU	0.050	Zn	2	0	2.00		
FANRUH	0.044	Sn	4	0	2.12		distances don't agree with POGDUK01
FAYVEG01	0.035	Y	3	3+	2.34		chains crosslinked
FILVOL	0.052	Gd	3	3+	2.39		chains crosslinked
FILVUR	0.036	Lu	3	3+	2.32		chains crosslinked
GEMXIF	0.045	Th	4	0	2.53		
GOHTAY	0.031	Nd	3	3+	2.49		chains crosslinked
HEYBET	0.054	Ni, Cu	2. 2	2+, 2-	2.03, 1.94	AB chains	chains crosslinked
KAPFOW	0.060	U	6	0	2.43		
KEQBUE	0.028	Mo	6	0	2.27		chains crosslinked
KOKDIX	0.066	Y	3	0	2.34	discrete	aggregate is uncharged
KUPHAE	0.078	Cu	2	0	1.92		
KUPHEI	0.029	Cu	2	0	1.94		chains crosslinked
KUZJEU	0.047	Cu, Mg	2. 2	2+, 2-	1.95, 2.02	AB chains	chains crosslinked
LIGVUS	0.053	La	3	0	2.61		
LIWCAV	0.085	Cr	3	0	2.01		chains crosslinked
NASSUV	0.038	Cd	2	1-	2.29	discrete	aggregate includes 2+ cation and so is uncharged
NIKZUC01	0.072	U	6	0			chains crosslinked
NILBAL01	0.042	U	6	1-	2.41	AB chains	B = H5O2+ ions
POGDUK01	0.079	Sn	4	0	2.41		distances don't agree with FANRUH
PUJCIG	0.033	Yb	3	3+	2.31		chains crosslinked
PXCDCB	0.086	Cu	2	0	1.97		
ROLBOK	0.031	Ni	2	2+	2.04		chains crosslinked (second polymorph)
ROLBOK01	0.064	Ni	2	2+	2.04		chains crosslinked
ROLBUQ	0.037	Ni	2	2+	2.05	AB chains	chains crosslinked
ROLCAV	0.036	Ni	2	2+	2.04	AB chains	chains crosslinked
ROLCEB	0.043	Ni	2	0	2.02		chains crosslinked but by CH...O interactions
SONRIW	0.043	La	3	0	2.55		
TONFEH	0.035	La	3	0	2.54		two 3+ ions in each dimer; chains crosslinked
VEBWUU	0.065	Zr	4	0	2.28		

VEDHOB	0.042	Eu	3	0	2.38	discrete	aggregate is uncharged
VUKKOB	0.026	In	3	0	2.20		
WIDPOO	0.036	V	4	0	2.00		
XEMFUQ	0.058	Er	3	0	2.29		chains crosslinked
XEMGAX	0.082	Ni	2	2+	2.03		chains crosslinked
XEMGEB	0.066	Ni	2	2+	2.04		chains crosslinked
XEMGIF	0.029	Ni	3	2+	2.04		chains crosslinked
XEMGOL	0.031	Ni	2*2	2+	2.04		chains crosslinked
XIGSEL	0.043	Fe	3, 3*2	2*3+, 4+	2.01	discrete	aggregate has charge 10+; units crosslinked by nitrate ions
YICCIW	0.040	Er	3	3+	2.33		chains crosslinked
ZOCYUL	0.067	Fe	3	0	2.04		
average R	0.049						
maximum R	0.086						
total number	41					22	charge 0
discrete	4					2	charge 1+ or 1-
AB chains	5					10	charge 2+ (plus 2 more with 2+/2-)
						6	charge 3+
chains crosslinked	23					1	XIGSEL
						41	sum
Deleted Hits:							
CARYUP	0.150	Zn	2	0	2.00		no coords for crown, which is disordered
CIGSAM	0.117	Cu	2	0	1.99		
FUVFIL	0.111	U	6	2+	2.38	discrete	M(15C5) ₃ aggregate has charge 1+
GOHTEC	0.109	Nd	3	1+	2.44		chains crosslinked
TUVYUE	0.120	Sc	3	1+	2.2?		no coords but structure shown in paper

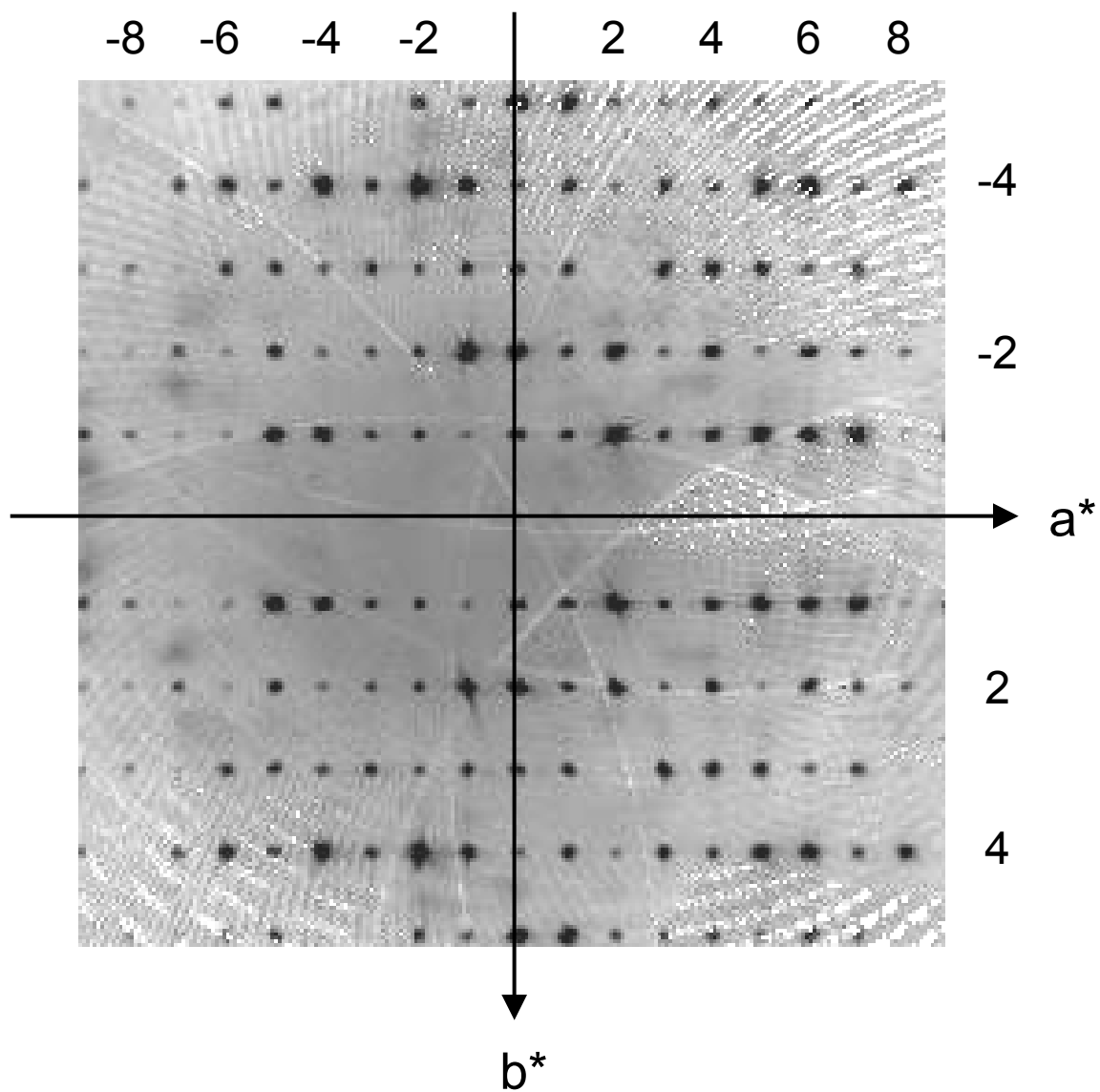
0kl Slice of the Reciprocal Lattice for
 $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot \text{H}_2\text{O}$ at 90 K



hk0 Slice of the Reciprocal Lattice for
 $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot \text{H}_2\text{O}$ at 90 K



hk3 Slice of the Reciprocal Lattice for
 $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot \text{H}_2\text{O}$ at 90 K



Inner 15-Crown-5 Rings in
 $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot \text{H}_2\text{O}$ at 90 K

