Yes, Solvent Molecules Do Matter: Solvatomorphism and Polymorphism of cis-2,2-tetrakis(monothiosuccinimidato)dimolybdenum(II)

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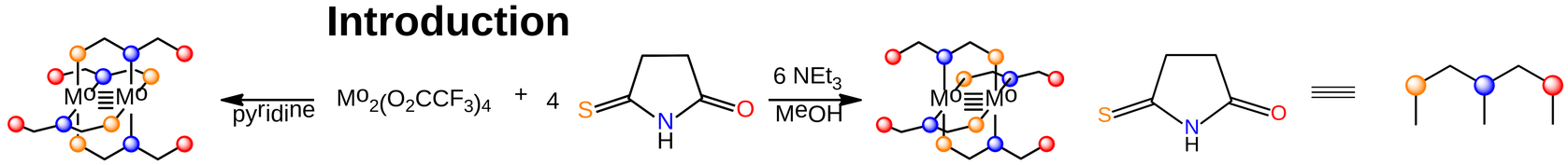
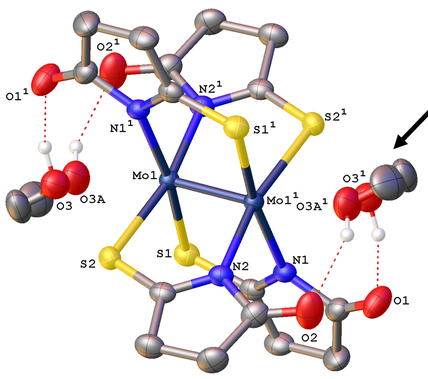
Introduction

While there are many $[Mo_2]^{4+}$ compounds known in the literature, most have limited reactivity in their axial positions. We have shown that dimolybdenum thioamidate ($Mo_2(SN)_4$) compounds can make axial chemistry of the $[Mo_2]^{4+}$ unit more accessible. Most $Mo_2(SN)_4$ compounds form the *trans*-2,2 isomer, which is thermodynamically favored due to sterics. However, the thioamide ligand monothiosuccinimde has the unique ability to form either the *trans*-2,2 and *cis*-2,2 isomers selectively based on the solvent used in the reaction. Crystallographic characterization of solvatomorphs and polymorphs of the *cis*-2,2 isomer suggest a reason for this selectivity.



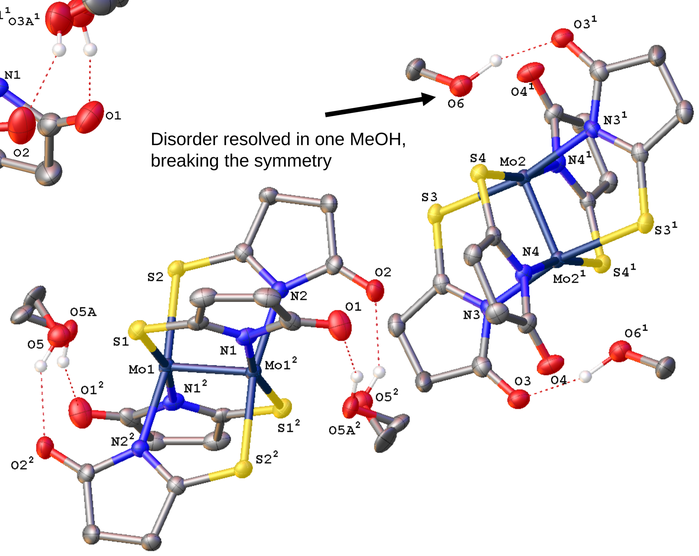
MeOH Solvatomorph

Form 1 (200K)



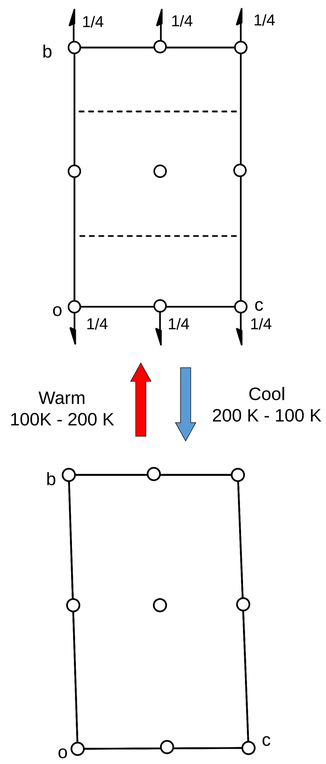
Disordered MeOH molecule able to form hydrogen bonds with either O1 or O2

Form 2 (100 K)



Disorder resolved in one MeOH, breaking the symmetry

Metrical Comparison



Warm 100K - 200 K

Cool 200 K - 100 K

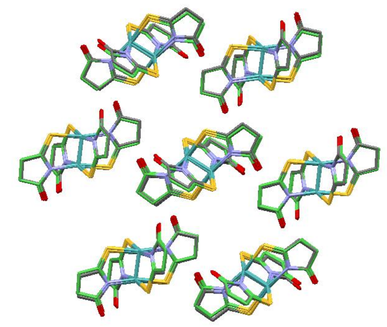
Upon cooling, loss of 2-fold screw axis and c-glide

	Form 1	Form 2
Temperature/K	200.0	100.0
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	9.0133(5)	8.990(3)
b/Å	14.7157(12)	14.717(7)
c/Å	10.0976(7)	10.048(4)
α/°	90	89.646(17)
β/°	111.403(4)	112.528(13)
γ/°	90	88.73(2)
Volume/Å³	1246.95(15)	1227.6(9)
Z	2	2
Data/restraints/parameters	2451/39/180	8926/0/333
Goodness-of-fit on F²	1.063	0.978
Final R indexes [I>=2σ (I)]	R_1 = 0.0183 wR_2 = 0.0449	R_1 = 0.0516 wR_2 = 0.1177
Final R indexes [all data]	R_1 = 0.0196 wR_2 = 0.0455	R_1 = 0.0740 wR_2 = 0.1270

	Form 1	Form 2
Mo-Mo (Å)	2.1429(18)	2.1408(3)
Mo-N_{avg} (Å)	2.161(10)	2.159(2)
Mo-S_{avg} (Å)	2.495(4)	2.4942(7)
Mo-O_{ax} (Å)	2.6533(6)	2.679(2)

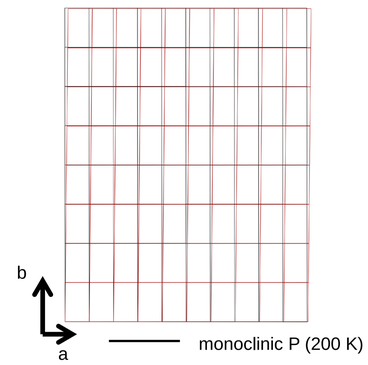
Structurally identical in spite of different unit cells

Structural Overlay



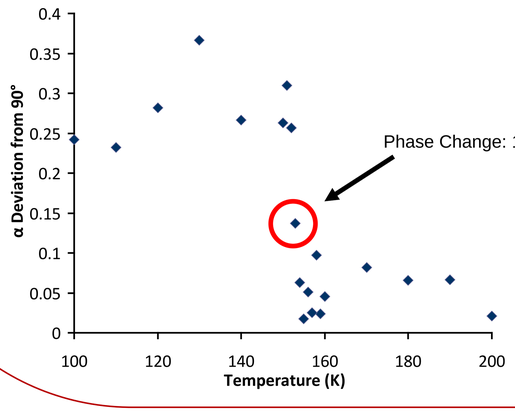
RMSD = 0.218 for 15 molecules
Form 1 gray carbons, Form 2, green carbons

Unit Cell Overlay

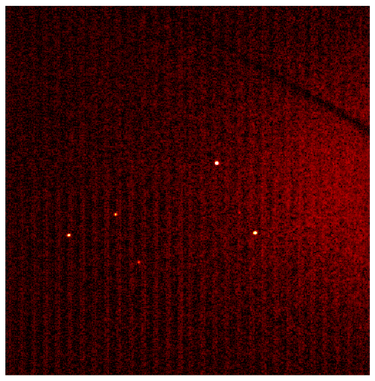


Phase Transition

Unit cells taken at temperatures ranging from 100 K to 200 K reveal phase change

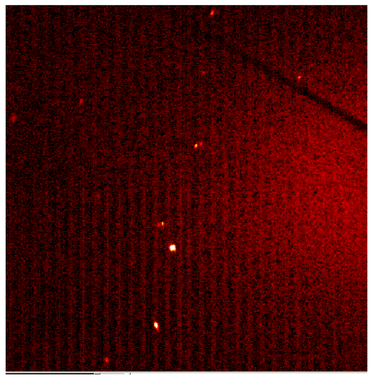


Twinning



Warm 100K – 200K

Cool 200K – 100K



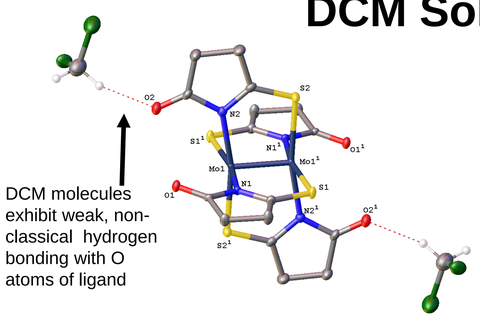
Upon cooling to 100 K, the diffraction pattern shows split diffraction spots, indicating non-merohedral twinning

Twin Law

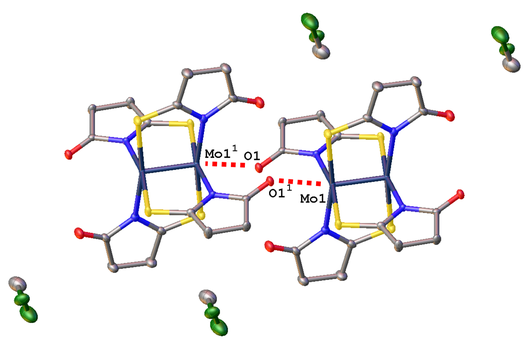
$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$$

The twin law is a 2-fold rotation around *b*, consistent with change from monoclinic to triclinic

DCM Solvatomorph



DCM molecules exhibit weak, non-classical hydrogen bonding with O atoms of ligand



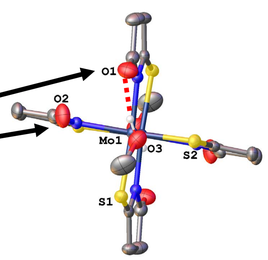
Close-contact between pendant oxygen atoms and axial position of Mo_2 in place of MeOH

Hydrogen bonding and axial coordination present in both solvatomorphs

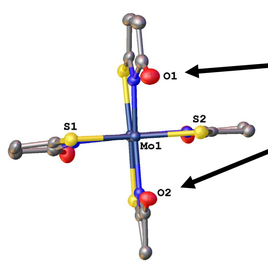
Temperature/K	100(1)
Crystal system	monoclinic
Space group	$P2_1/c$
***a*/Å**	9.101(4)
***b*/Å**	20.55(1)
***c*/Å**	7.445(4)
α/°	90
β/°	110.31(2)
γ/°	90
Volume/Å³	1306(1)
Final R indexes [I>=2σ (I)]	R_1 = 0.0366 wR_2 = 0.0833
Final R indexes [all data]	R_1 = 0.0509 wR_2 = 0.0884

Comparison between *cis*-2,2 and *trans*-2,2 complexes

cis arrangement of oxygen atoms allows coordination of MeOH in axial Mo_2 site



cis-2,2



trans-2,2

trans arrangement of oxygen atoms precludes coordination of MeOH and subsequent formation of hydrogen bonds

Ability to form hydrogen bonds makes *cis*-2,2 isomer more stable in MeOH than *trans*-2,2 isomer

Summary and Conclusions

- Two solvatomorphs of *cis*-2,2-$Mo_2(SNO5)_4$ identified and structurally characterized
- MeOH solvatomorph undergoes reversible phase transition between monoclinic P and triclinic P lattices
- Non-merohedral twin forms upon cooling below transition temperature
- Transition temperature 153 ± 1 K
- Hydrogen bonding and axial coordination contribute to stabilization of *cis*-2,2-$Mo_2(SNO5)_4$ relative to *trans*-2,2-$Mo_2(SNO5)_4$