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Magnetic properties of polymeric framework materials with cobalt

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MAGNETIC PROPERTIES OF POLYMERIC
FRAMEWORK MATERIALS WITH COBALT

A Thesis Submitted
in Partial Fulfillment
of the Required for the Designation
University Honors

Cassara Higgins
University of Northern Iowa
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MAGNETIC PROPERTIES OF POLYMERIC MATERIALS WITH COBALT

This Study by: Cassara Higgins

Entitled: Magnetic Properties of Polymeric Framework Materials with Cobalt

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University Honors

Date

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Date

Dr. Jessica Moon, Director, University Honors Program

MAGNETIC PROPERTIES OF POLYMERIC MATERIALS WITH COBALT

Abstract:

Single molecule magnets (SMM) are a new class of materials that have not been well studied. Metal-organic frameworks (MOFs) created with cobalt(II) metal centers have unpaired $3d$ electrons, which gives the frameworks interesting magnetic properties. Cobalt(II) nitrate centers can be linked together by varying numbers of 4,4'-bipyridine (bpy) ligands to create six different framework structures: four-coordinate 1D chain, five-coordinate 1D ladder, 2D bilayer, and 3D brick wall, and six-coordinate 2D square grid and 2D rhombic grid. The effects of framework structure and Co(II)-Co(II) distance on Weiss temperatures and μ_{eff} were investigated. By understanding which parameters of a framework has the biggest influence on the magnetic properties, better SMM can be designed. All Weiss temperatures were negative and indicated very weak antiferromagnetic coupling interactions between the magnetic moments of the individual Co^{2+} with a small relation to framework directionality. The μ_{eff} of all frameworks indicated that there was significant spin-orbit coupling, but in all the frameworks all smaller than typically found for octahedral and tetrahedral Co^{2+} complexes. The Co(II)-Co(II) distances had little effect on the spin-orbit coupling or the coupling of the Co^{2+} atomic magnetic moments.

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Introduction:

Metal organic frameworks (MOFs) are crystalline materials. These crystals have metal centers (a single metal ion or a small cluster of metal ions) that are linked together by organic ligands¹. A ligand is a molecule or anion that is coordinated to a metal cation. Ligands with multiple metal binding sites can bridge between multiple metal cations or be non-bridging and form multiple bonds to one metal cation². To form MOFs, ligands that will bind to multiple different metal ions are used. When these ligand connecting the metal cations are large enough, pores are created within the framework, allowing small molecules to sit within them. The pore size varies with the framework, for those included in this thesis they range from 4 Å to 9 Å^{3,4}. There are thousands of combinations of ligands metal centers that can create different types of frameworks, and changing the conditions in which the MOFs are synthesized can change the structure of MOFs made from the same metal and organic linkers¹. MOFs have interesting and useful properties including gas sorption⁵, catalytic activity⁶, and magnetism⁷. In this project the magnetic properties of a series of related MOFs were investigated.

The cobalt atoms in the MOFs investigated in this project have the cobalt atom in a +2 oxidation state which means it will have one or three unpaired electrons. The electron spin of the unpaired electrons give rise to a spin magnetic moment. Thus each cobalt within a MOF crystal has at least one unpaired electron⁷. The magnetic moments of each individual cobalt atom has the capability to interact with the magnetic moments of the nearby cobalt atoms and either add together or cancel out according to how their magnetic moments align with each other. The overall order of order of the magnetic moments gives rise to magnetism for the material.

The long-range alignment of the magnetic moments results in different types of magnetism. Permanent magnets are generally ferromagnetic, where all of the magnetic moments

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align in the same direction. There are other types of magnetic behavior. Antiferromagnetic materials have magnetic moments align antiparallel, creating a net magnetic moment of zero for the material. Ferrimagnetic is where the atomic magnetic moments align antiparallel to each other but one direction has a larger magnitude atomic magnetic moment than the other. Which results in a material with a net magnetic moment in one direction⁸. Most materials with unpaired electrons are paramagnets. In paramagnets the atomic magnetic moments are disordered and do not align in any particular way, so there is no overall net magnetic moment for the material. If paramagnets are placed into a magnetic field or are cooled to low temperatures the magnetic moments of the unpaired electrons align. The fashion in which they align is characteristic to the materials and may be in any of the types explained above⁸. The type of magnetism exhibited by a material may also be dependent on temperature and change as the material is cooled. Figure 1 shows the different types of magnetism.

Paramagnetic	
Ferromagnetic	
Antiferromagnetic	
Ferrimagnetic	

Figure 1: Different types of magnetism that are exhibited by magnetic materials.

MAGNETIC PROPERTIES OF POLYMETRIC MATERIALS WITH COBALT

Single molecule magnets (SMM) are magnets that are only a single molecule. If the directionality of these moments can be closely controlled then there are further applications for them. Highly important potential applications for SMMs are quantum computing, high density data storage, and creating smaller electronics⁹. Before SMMs can be created and applied to the real world, there needs to be a strong base understanding to how molecular structure plays a role in their magnetic properties. The parameters examined are the distances between cobalt atoms, the coordination number of the cobalt, and the geometry of ligands around the cobalt atom. By understanding how the atomic magnetic moments in these MOFs interact, a material could be someday be engineered and used in every day electronics.

In order to test the effect of Co(II)-Co(II) distance and Co²⁺ coordination environment while keeping the types of ligands the same, a set of six different MOFs were analyzed. MOFs are a good system for varying Co(II)-Co(II) distance and Co²⁺ coordination environment while keeping the ligands bound to the cobalt ion the same since MOF structure is highly sensitive to the synthetic conditions. The metal center for all six MOFs is a single Co²⁺ linked by 4,4'-bipyridine (bpy) ligands. Each Co²⁺ atom is bonded to two nitrate ligands. The number of ligands varied with the structure. The coordination number is the number of total ligands bound to the metal atom. The coordination of the Co²⁺ is MOF specific and could be four, five, or six-coordinate. The 1D chain^{3, 10} (figure 2) has Co²⁺ linked together by two bpy. This framework also has an additional two aqua ligands which makes the Co²⁺ six-coordinate. When the frameworks were tested, they were dried overnight, which removed most aqua ligands to create a four-coordinate Co²⁺ framework. This creates a disordered four-coordinate system. The next set of frameworks have five-coordinate Co²⁺, created using a T-shape motif (figure 3a). Each Co²⁺ is linked with three bpy. This creates three frameworks: 1D ladder¹¹ (figure 3b), 2D bilayer^{3, 10}

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(figure 3c), and 3D brick wall (figure 3d)⁴. The 3D brick walls have very large pores which allows for three interpenetrating frameworks. The last two frameworks are six-coordinate Co^{2+} with four bpy ligands bonded to each Co^{2+} : 2D square grids (figure 4a) and 2D rhombic grids (figure 4b).

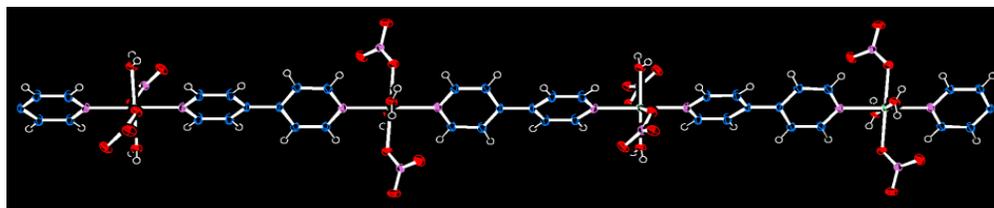


Figure 2: The hydrated Co^{2+} -bpy 1D chains. The tested chains were dehydrated to a four-coordinate disordered chain.

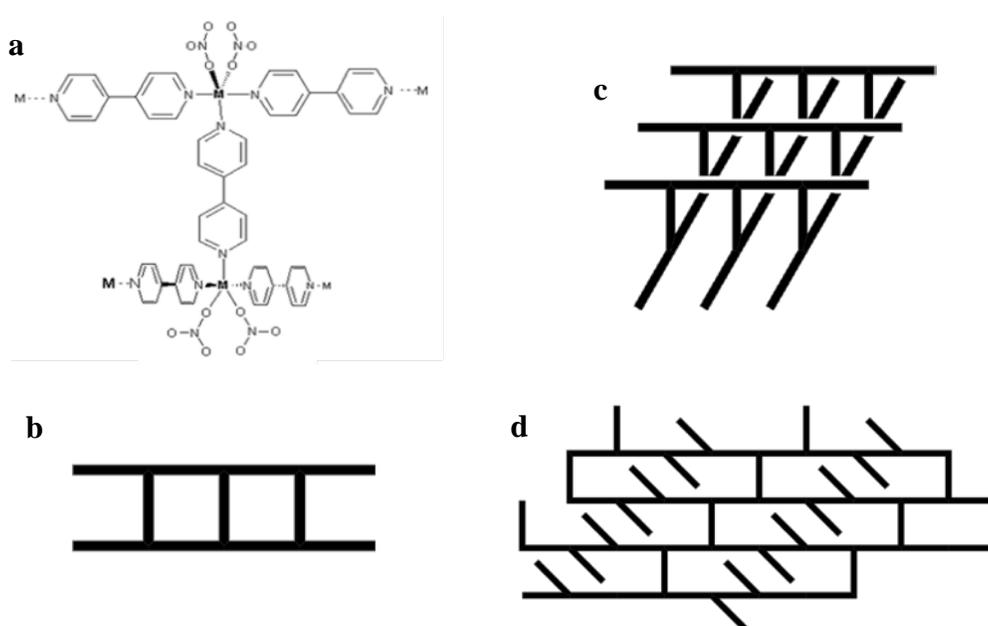


Figure 3: The five-coordinate Co^{2+} -bpy "T"-shaped linker is shown in a). The MOFs that it creates are the b) 1D ladder, c) 2D bilayer, d) 3D brick wall topologies.

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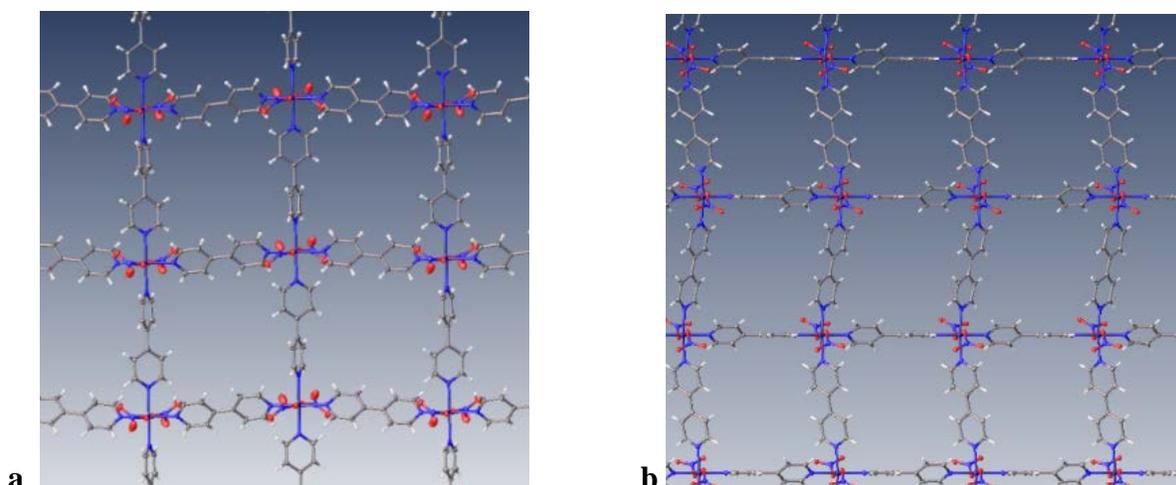


Figure 4: The six-coordinate Co^{2+} -bpy MOFs with the (a) 2D square grid and the (b) 2D rhombic grid topologies.

The DC magnetization was measured for each framework. The DC magnetization is the measurement of intensity of the magnetic dipole moment for the sample placed in an external DC magnetic field⁸. The DC magnetization was corrected for the background diamagnetism of the sample holder to produce m' (emu Oe^{-1}).

$$\chi_{\text{measured}} = \frac{m'}{\text{mass}_{\text{sample}}} \quad \text{Equation 1}$$

In equation 1 m' was divided by the sample mass to determine the measured χ or the magnetic susceptibility, for the system. Magnetic susceptibility is an indication for how strongly a material is influenced by an external magnetic field. A positive χ_{measured} indicates a paramagnetic system where a negative χ_{measured} indicates a diamagnetic system¹².

The χ_{measured} includes the diamagnetic magnetic susceptibility from the paired electrons present in the sample. Diamagnetism is the phenomenon where the paired electrons in every molecule becomes weakly magnetic due to the induced current when they are placed in a strong magnetic field. The vector of the magnetic moments of the induced current from the paired

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electrons is antiparallel to the external field. This effect is observed in most materials¹³. Only the magnetic susceptibility of the unpaired electrons are useful for a SMM, so the diamagnetic contributions are subtracted out. Each framework has a χ_D that can be calculated from the chemical formula of the framework. The diamagnetic corrections of each framework were determined using the values of χ_D for the individual components reported by Bain and Berry¹². These corrections are negative because the alignment is in the opposite direction of the induced paramagnetism¹². The magnetic susceptibility, χ_g , of the Co^{2+} is determined in equation 2.

$$\chi_g = \chi_{measured} - \chi_D \quad \text{Equation 2}$$

The way that χ_g changes as a function of temperature reveals the magnitude and nature of the interactions between the magnetic moments of the Co^{2+} atoms. This is determined by plotting χ_g as a function of temperature and fitting the data using a non-linear curve fit of the Curie-Weiss Law. The equation used for the fit is shown in equation 3.

$$\chi = \chi_0 + \frac{C}{T-\Theta} \quad \text{Equation 3}$$

From the fit, the Curie constant, C ($\text{emu K Oe}^{-1} \text{g}^{-1}$) and the Weiss temperature, Θ (K) for each MOF is determined. χ_0 is used to account for the presence of impurities in the sample and assists in the fitting of the data¹²⁻¹³.

The original Curie Law proposed by Pierre Curie contained only C/T and was developed to describe the increasing randomization of the magnetic moments as temperature increases. The Curie Law assumes that there is no interaction between the magnetic moments of separate atoms. The Weiss temperature is a correction for the interactions between internal localized moments. Weiss called these interactions molecular fields. When Θ equals T the susceptibility diverges and a phase transition occurs. A positive Θ indicates the alignment of the molecular fields with the applied field or a ferromagnetic interaction¹⁴. When Θ is negative, it indicates an

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antiferromagnetic interaction. The Weiss temperature for isolated Co^{2+} ions is -20 K^7 . The smaller the Weiss temperature, the better the material would be for a SMM. Interactions or coupling between Co^{2+} atoms does not allow for tunability of each individual magnetic moment.

From the Curie constant, the effective magnetic moment was calculated.

$$\mu_{eff}^2 = \frac{3Ck_B}{N\mu_B^2} \quad \text{Equation 4}$$

Where k_B is the Boltzmann constant and μ_B is the Bohr magneton. N is the number of cobalt atoms per gram of sample. μ_{eff} is important because it describes spin-orbit coupling. The magnetic moment of an atom is comprised to the spin-only interactions and the spin-orbit coupling. When an electron spins, a magnetic field is created perpendicular the direction of the spin of the electron. As the electron orbits around the cobalt nucleus, it creates a second magnetic field perpendicular to its movement. These two magnetic fields are not in the same direction, so the coupling between them gives rise to spin-orbit coupling. The μ_{eff} is also dependent on the g-factor and quantum number J . The g-factor is an atom specific constant that is known. J is comprised of the spin quantum number (S) added and the angular momentum quantum number (L). This is shown in equation 5.

$$\mu_{eff} = g \sqrt{J(J+1)} \quad \text{Equation 5}$$

Cobalt(II) is generally high spin meaning it has three unpaired electrons so S equals $3/2$. The spin-only component of the atom is when J is equal to S . For high spin cobalt the spin-only magnetic moment (μ_s) is 3.87 . The typical μ_{eff} for high spin octahedral Co^{2+} is 4.7 to $5.2 \mu_B$ and for high-spin tetrahedral Co^{2+} is 4.5 to $4.8 \mu_B^7$. In a SMM, the closer μ_{eff} is to μ_s , the easier it is to manipulate and control the magnetism. An ideal μ_{eff} would be equal to μ_s .

The Weiss temperature and the magnitude of the spin-orbit coupling has not been previously reported for these frameworks. The six different MOFs are comprised of the same

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metal center and organic linker. The only changes in the frameworks is the environment around the cobalt atoms and the Co(II)-Co(II) distances. This allows us to look for correlations between the Weiss temperature and μ_{eff} while changing these variables. By understanding which variables have a bigger impact on the couplings of the different systems, better SMMs could be engineered in the future.

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Experimental Methods:

MOF crystals were synthesized for magnetic measurements. These crystals included 1D chains, 1D ladders, 2D bilayers, 3D brick walls, 2D square grids, and 2D rhombic grids. All of the crystals were dried. This was done because they contained a range of different solvent molecules in their pores which could influence communication pathways within the MOFs.

Materials List:

4,4'-bipyridine, Acros, 98%, anhydrous

Cobalt (II) nitrate hexahydrate, Alfa Aesar, 97.7%, dried over anhydrous calcium-sulfate

Ethanol, Acros, absolute, 200 proof, 99.5%

Methanol, VWR International, 99.8%

Pyridine, Acros, 99%

Toluene, Alfa Aesar, 99.7%

Benzene, Alfa Aesar, 99%

Benzyl alcohol, Alfa Aesar, 99%

All syntheses were completed in a fume hood. Personal protective equipment worn included goggles, gloves, and lab coat. All solvents used are flammable, and benzene and pyridine are carcinogenic.

Synthesis Methods of MOFs:

1D chains The 1D chain crystals were synthesized via a direct mixing method^{3, 10}. 1.5714 g of bpy was dissolved in 70 mL of ethanol. 2.8931 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved

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in 160 mL of ethanol and 14 mL of water. The bpy solution was added to the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The orange crystals were collected out of the Erlenmeyer flask and placed into a 20 mL vial in mother liquor two days after synthesis. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

1D ladder The 1D ladder crystals were synthesized via a direct mixing method^{11, 15}. 1.1637 g of bpy was dissolved in 50 mL of methanol. 1.1133 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL of methanol. The bpy solution was added to the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The maroon crystals were collected out of the Erlenmeyer flask and placed into a 20 mL vial in mother liquor two days after synthesis. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

2D bilayer The 2D bilayer crystals were synthesized via a direct mixing method^{3, 10}. 1.8926 g of bpy was dissolved in 400 mL of ethanol. 2.3622 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 400 mL of ethanol. The bpy solution was added to the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The maroon crystals were collected out of the Erlenmeyer flask and placed into a 20 mL vial in mother liquor two days after synthesis. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

3D brick wall The 3D brick wall crystals were synthesized using a slow diffusion method¹⁶. 0.0245 g of bpy was dissolved in 4 mL of benzene in a 12 mL vial. A 0.8 mL methanol middle layer was added. 0.0305 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 4 mL of methanol. The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was placed on top. The crystals were left to grow for two weeks. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

2D square grids The 2D square grid crystals were synthesized using a slow diffusion method¹⁶. 0.0805 g of bpy was dissolved in 3 mL of benzyl alcohol in a 12 mL vial. A 3 mL benzyl alcohol layer middle layer was added. 0.10 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a mixture of 3 mL of methanol and 0.35 mL of pyridine. Then the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was

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placed on top. The crystals were collected after 3 months and placed into two sealed vials with mother liquor. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

2D rhombic grids The 2D grid crystals were synthesized using a slow diffusion method¹⁶. 0.0245 g of bpy was dissolved in 3 mL of toluene in a 12 mL vial. A 2 mL toluene middle layer was added. 0.0305 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 3 mL of methanol. The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was placed on top. Some crystals were placed in a 4 mL vial and dried at 80 °C for a week.

A Physical Property Measurement System (PPMS) by Quantum Design was used to complete the magnetic susceptibility measurements. The PPMS creates an external magnetic field around the sample. It then varies the temperature. During the change in temperature it measures the DC magnetization of the sample. The temperature was varied from 300 to 4 K. The DC magnetic field used was 1000 Oe and the AC magnetic field was 3 Oe with a 1 kHz frequency. Sample size of each MOF was 5-10 mg. After the data was collected it was analyzed using Origin. The DC magnetization was measured by the PPMS in emu. The measured DC magnetization was divided by the DC magnetic field, 10,000 Oe, to give the DC magnetization in units of emu Oe^{-1} . The background was previously determined for this system to be 0.0030 emu in a 20,000 Oe DC magnetic field. The background was subtracted from the DC magnetization. The data collected was analyzed using the Curie-Weiss Law.

Results:

The raw data from the PPMS was processed using equations 1 and 2. Figures 5 thru 10 are the χ_g vs temperature data for all six MOFs dried. The data was fitted using the Curie-Weiss Law (equation 3).

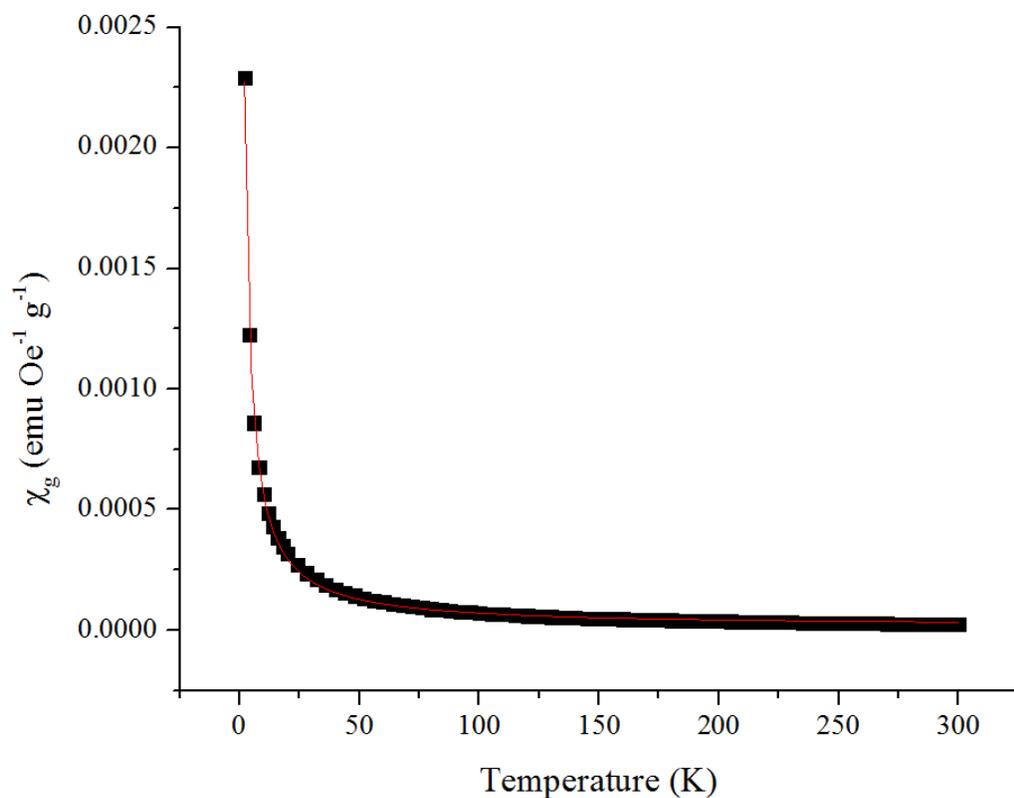


Figure 5: Curie-Weiss fit for the 1D chains.

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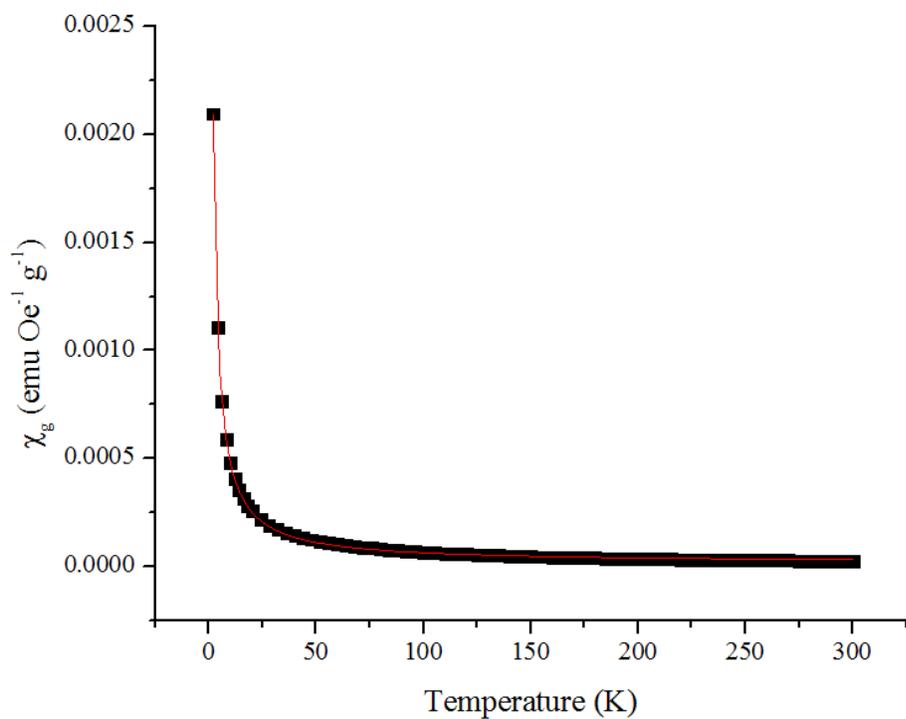


Figure 6: Curie-Weiss fit for the 1D ladder.

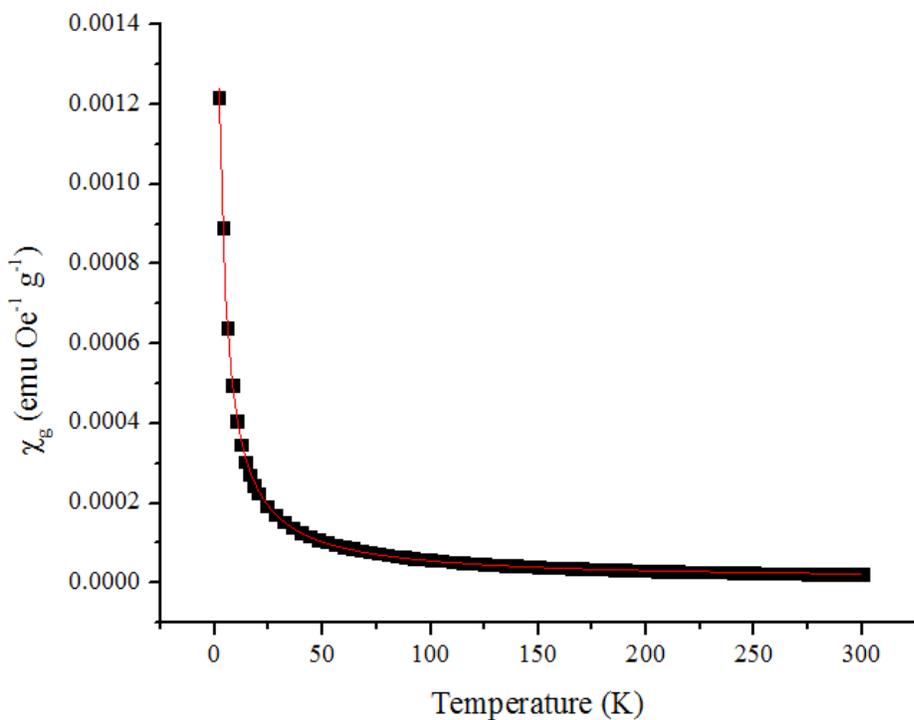


Figure 7: Curie-Weiss fit for the 2D bilayer.

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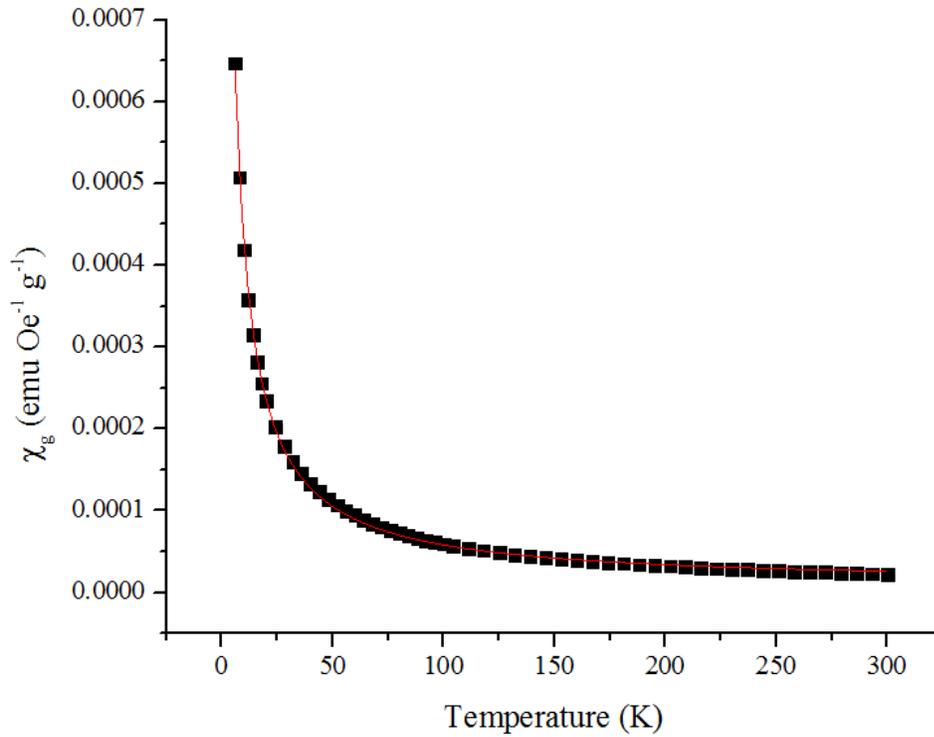


Figure 8: Curie-Weiss fit for the 3D brick wall.

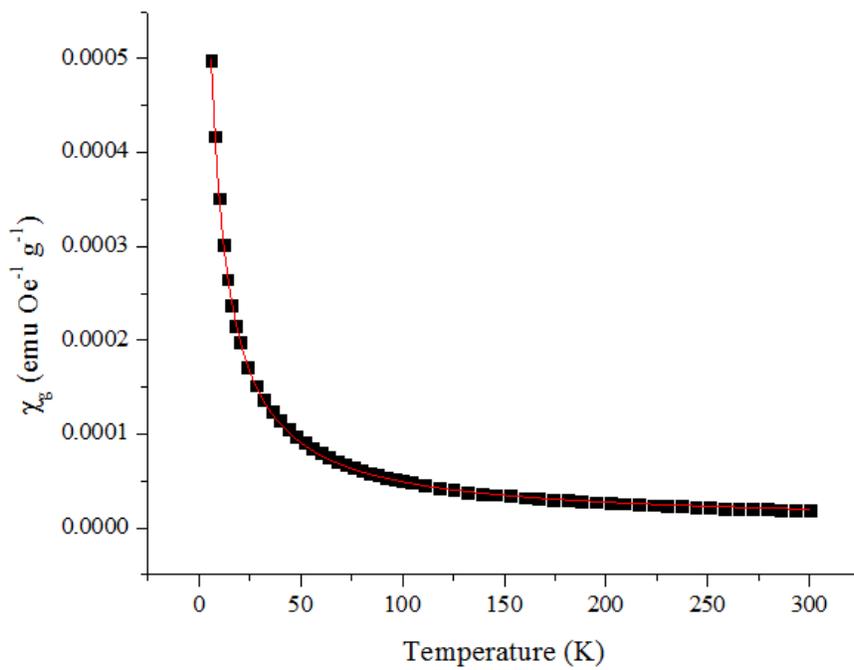


Figure 9: Curie-Weiss fit for the 2D square grid.

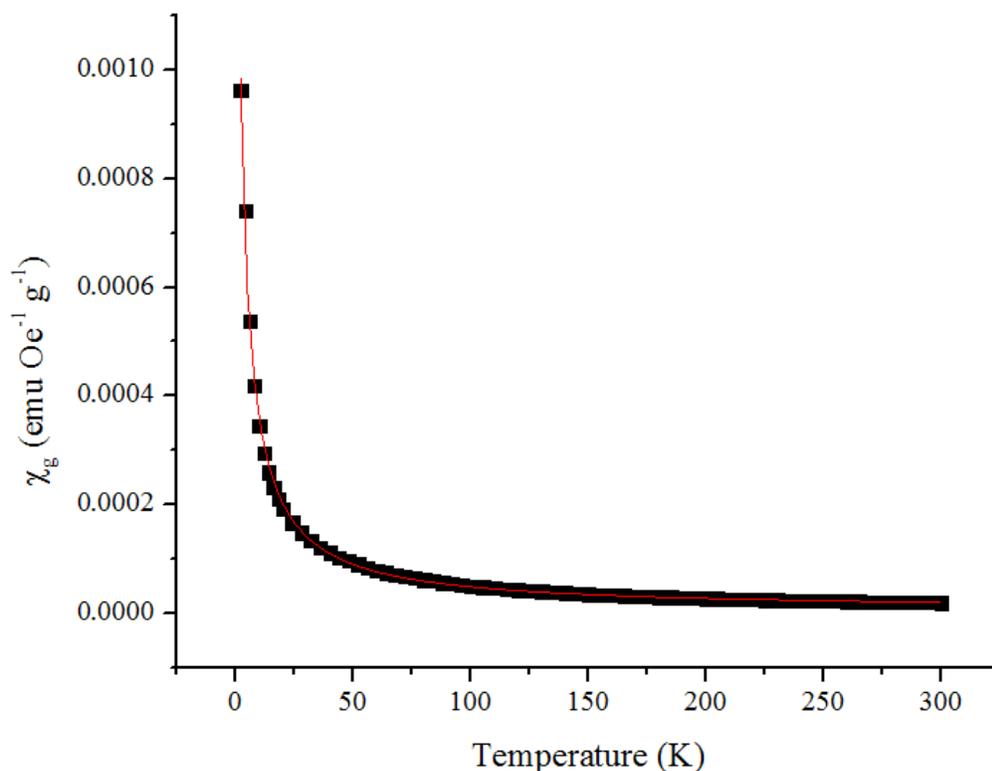


Figure 10: Curie-Weiss fit for the 2D rhombic grid.

The Weiss temperatures and Curie constants are recorded below in table 1. In table 1 the Curie constants are reported per mole. From the Curie constants the μ_{eff} was determined using equation 4.

Table 1: The fitted data for the six dried frameworks reported in per mole values of cobalt.

Framework	Weiss Temp (K)	Curie Constant (emu K Oe ⁻¹ mol ⁻¹)	μ_{eff} (μ_B)	R ² from fit
1D Chain	-0.56 ± 0.04	1.95 ± 0.02	3.95 ± 0.08	0.998
1D Ladder	-0.34 ± 0.02	2.00 ± 0.01	4.00 ± 0.08	0.999
2D Bilayer	-2.09 ± 0.07	2.10 ± 0.03	4.10 ± 0.08	0.998
3D Brick Wall	-1.88 ± 0.11	2.07 ± 0.02	4.06 ± 0.08	0.999
2D Square Grid	-3.24 ± 0.10	2.26 ± 0.02	4.26 ± 0.09	0.999
2D Rhombic Grids	-2.54 ± 0.09	2.20 ± 0.04	4.19 ± 0.08	0.997

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In table 2 is measured distanced between cobalt atoms within the structures. These distances were determined using the solved structure of the crystals from single crystal x-ray diffraction data.

Table 2: Distances between cobalt atoms in each framework measured in angstroms.

Framework	Distance (Å)	Number of Co²⁺ at that distance
1D Chains¹⁰	6.93	4
	7.38	2
	10.43	4
	11.38	4
	11.74	2
	12.53	4
	13.65	8
	13.86	4
	14.75	6
1D Ladders¹⁵	6.16	2
	6.32	1
	6.68	1
	6.79	1
	7.89	1
	8.08	2
	8.26	1
	8.30	2
	8.33	1
	10.33	1
	10.36	2
	10.37	2
	10.38	1
	10.41	1
	10.45	1
	10.50	1
	10.55	2
	10.61	2
	10.65	1

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	11.30	1
	11.33	1
	11.34	1
	11.3434	2
	11.37	1
	11.38	1
	11.38	2
	11.40	1
	11.40	1
	11.42	2
	11.79	1
	11.79	1
	11.86	2
	11.87	1
	11.94	1
	12.10	1
	12.11	1
	12.16	1
	12.29	1
	12.86	1
	12.88	1
2D Bilayer¹⁷		
	6.08	1
	6.13	2
	6.67	2
	8.64	2
	8.71	2
	9.51	2
	9.99	2
	10.65	4
	11.29	2
	11.32	4
	11.32	1
	11.62	4
	12.2	2
	12.85	4
	12.88	2
	12.90	4

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3D Brick Wall¹⁶	6.60	2
	8.30	1
	9.77	1
	10.77	2
	10.98	1
	11.21	1
	11.27	1
	11.39	1
	11.97	2
	12.02	1
	12.17	1
	12.84	2
	12.86	1
2D Square Grid¹⁶	9.06	2
	9.86	2
	11.17	4
	11.37	2
	11.46	2
	12.98	2
2D Rhombic Grid¹⁶	7.68	
	9.68	
	11.45	2
	11.50	2
	12.29	4
	12.83	4

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Discussion:

The negative Weiss temperatures indicate antiferromagnetic interactions between the localized moments within the molecular materials. Overall there seems to be little relation between the coordination number and geometry of the framework and the strength antiferromagnetic interactions. The four-coordinate 1D chain has a very small interaction -0.56 K. The 1D ladder which is a five-coordinate framework with an even weaker interaction of -0.34 K. However the other two five-coordinate frameworks, 2D bilayer and 3D brick walls have stronger interactions of -2.09 K and -1.88 K. Lastly the six-coordinate frameworks had the strongest antiferromagnetic interactions of the dried frameworks. The 2D square grids had the strongest interaction of -3.24 K, the 2D rhombic grids were a bit weaker at -2.54 K. There seems to be a weak correlation in terms of directionality of the framework and magnitude of the Weiss temperature. The 1D structures have the smallest magnitude, followed by the 3D, framework and then the 2D frameworks. However, this data is inconclusive because all the Weiss temperatures are quite small in magnitude.

When looking at the distances between the cobalt atoms in table 2, the 1D chains, 1D ladders, 2D bilayers, and 3D brick walls have several cobalt atoms in a closer proximity to each other ($< 9 \text{ \AA}$). The other frameworks also tend to have a few cobalt atoms within 9 \AA of each other, but not as many. It would appear that the frameworks with more close Co(II) atoms, the weaker the antiferromagnetic interactions with the exception of the 2D bilayer. While the MOFs with fewer close Co(II) atoms have stronger antiferromagnetic interactions.

In a 2012 paper by J. G. Malecki the magnetic properties of complexes six different cobalt were reported. All of the complexes had a single Co^{2+} atom with two thiocyanate or chloro ligands and then either 2 or 4 other ligands. These complexes are pictured in figure 11.

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The first four complexes $[\text{Co}(\text{SCN})_2(\beta\text{-pic})_4]$, $[\text{Co}(\text{SCN})_2(\text{pyCH}_2\text{OH})_2]$, $[\text{Co}(\text{SCN})_2(\text{py}(\text{CH}_2)_3\text{OH})_2]$, and $[\text{Co}(\text{SCN})_2(\text{CH}_3\text{OH})_4(\text{tzpyrim})_2]$ are six-coordinate. They had Weiss temperatures that are respectively -0.2 K, -0.3 K, -0.3 K, and -5.3 K. The fifth complex is four-coordinate, $[\text{Co}(\text{SCN})_2(\text{urotrop})_2]$, with a Weiss temperature of 1.2 K. The positive value indicates the molecular moment interactions in this complex are ferromagnetic. The last complex is three-coordinate, $[\text{Co}(\text{DMIM})_3]\text{Cl}_2\cdot\text{H}_2\text{O}$, with a Weiss temperature of -0.1 K¹⁸.

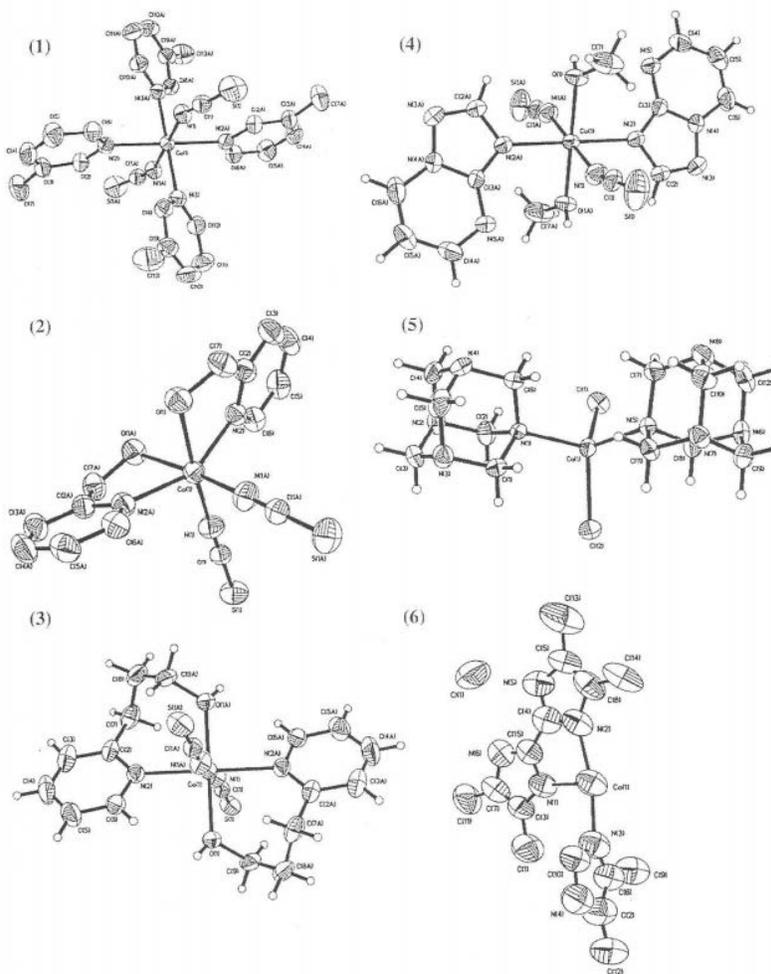


Figure 11: The six cobalt (II) complexes reported by Malecki. $\text{Co}(\text{SCN})_2(\beta\text{-pic})_4$ (1), $[\text{Co}(\text{SCN})_2(\text{pyCH}_2\text{OH})_2]$ (2), $[\text{Co}(\text{SCN})_2(\text{py}(\text{CH}_2)_3\text{OH})_2]$ (3), and $[\text{Co}(\text{SCN})_2(\text{CH}_3\text{OH})_4(\text{tzpyrim})_2]$ (4) are six-coordinate, $[\text{Co}(\text{SCN})_2(\text{urotrop})_2]$ (5) is four-coordinate, and $[\text{Co}(\text{DMIM})_3]\text{Cl}_2\cdot\text{H}_2\text{O}$ (6) is three-coordinate¹⁸.

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In a separate paper two other six-coordinate cobalt(II) complexes are reported by R. March. These are $[\text{Co}(\text{MeC}_5\text{H}_3\text{NCOO})_2(\text{H}_2\text{O})_2]$ and $[\text{CoCl}_2(\text{C}_5\text{H}_4\text{NCOOPr}^i)_2]$. The structures showed that the cobalt(II) coordination compounds were discrete mononuclear complexes. These complexes are shown in figure 12. The first is held together through a hydrogen bonding network and the second has only van der Waals forces. The respective Weiss temperatures of these two complexes are -11.0 K and -7.8 K ¹⁹. These antiferromagnetic interactions are much stronger than the interactions observed in the frameworks studied in this project.

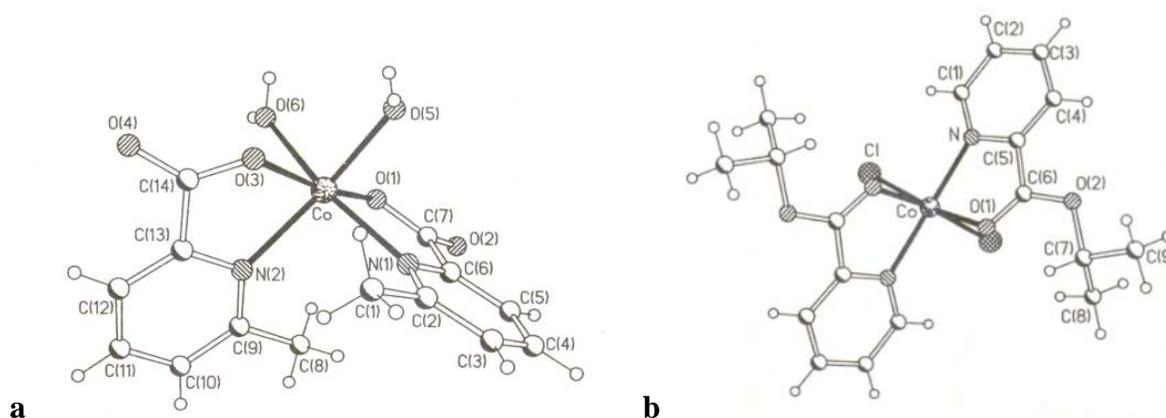


Figure 12: a) Structure of $[\text{Co}(\text{MeC}_5\text{H}_3\text{NCOO})_2(\text{H}_2\text{O})_2]$ complex and b) Structure of $[\text{CoCl}_2(\text{C}_5\text{H}_4\text{NCOOPr}^i)_2]$ complex¹⁹.

Considering the Co^{2+} complexes reported in this thesis and the Co^{2+} complexes from the other papers, it appears that the coordination geometry of the Co^{2+} has little effect on the Weiss temperature. The first four six-coordinate complexes reported by Malecki had very small negative Weiss temperatures¹⁸. The two six-coordinate complexes reported by March have much stronger interactions. This could be an indication that the communication pathways between cobalt atoms is a larger factor in the Weiss temperature than the coordination number of the Co(II). The complexes are held together through weaker interactions, hydrogen bonding and van der Waals, while the MOFs are held together by organic ligands.

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Overall the Weiss temperatures measured in this thesis are very small in comparison to the -20 K that is determined for isolated Co^{2+} ions⁷. This means the interactions between cobalt atoms for these frameworks is very weak. There seems to be little correlation between the magnitude of the Weiss temperature and Co(II)-Co(II) distances or coordination number. There was a small correlation in framework directionality. It is possible that the ligands bound to the cobalt atom could affect this interaction, which could explain the range of Weiss temperatures between the MOFs reported here and the other Co^{2+} complexes reported in literature.

Using the Curie constants obtained from the fits, the μ_{eff} was determined using equation 4. The four-coordinate 1D chain has a μ_{eff} of 3.95 μ_{B} . The five-coordinate MOFs had similar μ_{eff} values of 4.00 μ_{B} for the 1D ladder, 4.10 μ_{B} for the 2D bilayer, and 4.06 μ_{B} for the 3D brick walls. The six-coordinate frameworks had the largest μ_{eff} . The 2D square grids had a value of 4.26 μ_{B} and the 2D rhombic grids was a bit smaller at 4.19 μ_{B} . The spin-only magnetic moment, μ_{s} , is 3.87 μ_{B} . The μ_{eff} for all of the reported frameworks is larger than μ_{s} which indicates significant spin-orbit coupling.

The Co(II) complexes reported by Malecki had a range of μ_{eff} values. The four six-coordinate MOFs had μ_{eff} of 3.99 μ_{B} ($[\text{Co}(\text{SCN})_2(\beta\text{-pic})_4]$), 4.28 μ_{B} ($[\text{Co}(\text{SCN})_2(\text{pyCH}_2\text{OH})_2]$), 3.51 μ_{B} ($[\text{Co}(\text{SCN})_2(\text{py}(\text{CH}_2)_3\text{OH})_2]$), and 3.87 μ_{B} ($[\text{Co}(\text{SCN})_2(\text{CH}_3\text{OH})_4(\text{tzpyrim})_2]$). The four-coordinate complex, $[\text{Co}(\text{SCN})_2(\text{urotrop})_2]$, had a μ_{eff} of 4.45 μ_{B} . The three-coordinate complex, $[\text{Co}(\text{DMIM})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ had a μ_{eff} of 3.74 μ_{B} ¹⁸. In the two six-coordinate complexes, $[\text{Co}(\text{MeC}_5\text{H}_3\text{NCOO})_2(\text{H}_2\text{O})_2]$ and $[\text{CoCl}_2(\text{C}_5\text{H}_4\text{NCOOPr}^i)_2]$, reported by March the μ_{eff} values were 5.08 μ_{B} and 5.17 μ_{B} , respectively, at 300K¹⁹.

The μ_{eff} for the MOFs reported in this paper correlates with the coordination geometry of the Co^{2+} . The four-coordinate Co^{2+} has a smaller μ_{eff} than the six-coordinate. The three

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frameworks with the T-shape, five-coordinate motif all have similar μ_{eff} although the frame connectivity varies greatly. The Co(II)-Co(II) distances once again don't seem to have a major effect on the μ_{eff} values. All of the μ_{eff} reported are smaller than the typical μ_{eff} for high spin octahedral Co^{2+} (4.7 to 5.2 μ_{B}) and for high-spin tetrahedral Co^{2+} (4.5 to 4.8 μ_{B})⁷.

When comparing the μ_{eff} of the literature complexes and the six MOFs, μ_{eff} varies greatly between the complexes with no distinct correlations in Co(II)-Co(II) distance or coordination number. This may suggest that the ligands used to connect the Co^{2+} atoms could play an important role in the strength of the spin-orbital coupling within the complexes.

Conclusion:

There is a lack in understanding in which aspects of MOF structure have the largest influence on the magnetic properties of its metal centers. The effects of Co(II)-Co(II) distance, coordination number, and the connectivity of metal centers on the interactions between metal centers and the spin-orbit coupling were examined.

The six MOFs examined all exhibited antiferromagnetic interactions between the magnetic moments shown by the negative Weiss temperatures. The MOFs with a 1D framework directionality tended to have a weaker interaction than the 2D or 3D MOFs. The Weiss temperatures were all very small in magnitude, indicating weak coupling between metal centers. As the coordination number of the cobalt(II) increased the μ_{eff} of the MOF increased as well. The connectivity of the metal centers seemed to have little effect on the μ_{eff} of the MOFs. The Co(II)-Co(II) distance of the MOFs seemed to have little effect on the Weiss temperature and the spin-orbit coupling.

These results are all constructive for the understanding for how to engineer SMM. Weak interactions between Co^{2+} makes it possible to control the directionality of spin for each individual metal center. For high-density information storage, information is currently stored as 1s and 0s. This can be translated into spin up and spin down of magnetic moments. The result that Co(II)-Co(II) distances in the range observed in the MOFs have little effect on the Weiss temperature and μ_{eff} is a valuable result. The closer molecular magnets can be placed together results in higher density of information storage.

There is still room for additional work with these MOFs. All of these MOFs contain guest molecules in their pores. In this study the MOFs magnetic properties were studied after removal of the guest molecules in the pores. Measurements could also be done with the guest molecules

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left in the pores. Some of these guest solvent molecules could also be exchanged for others as well. There is a possibility the presence of guest solvent molecules changes the communications pathways within the MOFs. Some guest solvents provide hydrogen bonding within the frameworks. Hydrogen bonding is present in the 1D chains before they are dried and contain water ligands.

The results presented add further to the growing body of research on the magnetic capabilities of MOFs. In addition it further analyzes which parameters of a framework plays a larger role in the magnetic properties of the framework. By understanding the factors that influence Weiss temperature and μ_{eff} , better SMM could be designed and applied to electronics in the future.

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