

New open-framework cobalt sulfate-oxalates based on molecular and chain-like building blocks

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Physical measurements:

IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N₂ with a heating rate of 10 °C/min. Single crystal X-ray diffraction data were collected on an Oxford Xcalibur diffractometer with graphite-monochromated MoK α ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL* program package.¹ The crystallographic data for compounds **3-4** are summarized in Table 1. Selected bond lengths for compounds **3-4** are listed in Tables 2 and 3.

Reference

1. G. M. Sheldrick, *Acta Cryst., Sect. A*, 2008, 64, 112.

Synthesis

Synthesis of Co₂(Hdeta)(H₂O)₂(SO₄)(C₂O₄)_{1.5} (1): A mixture of CoSO₄·7H₂O (0.281 g), H₂C₂O₄·2H₂O (0.126 g), and diethylenetriamine (0.103 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 8 d. The autoclave was subsequently allowed to cool to room temperature. Red crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (43.6 % yield based on cobalt).

Synthesis of Co_{1.5}(Haep)(SO₄)(C₂O₄) (2): A mixture of CoSO₄·7H₂O (0.422 g), H₂C₂O₄·2H₂O (0.126 g), and 1-(2-aminoethyl)piperazine (0.129 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 7 d. The autoclave was subsequently

allowed to cool to room temperature. Red crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (44.3 % yield based on cobalt).

Synthesis of $\text{H}_3\text{aep}\cdot\text{Co}_{1.5}(\text{H}_2\text{O})_3(\text{ox})_{1.5}\cdot 2\text{H}_2\text{O}\cdot 1.5\text{SO}_4$ (3): A mixture of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.281 g), $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.189 g), and 1-(2-aminoethyl)piperazine (0.129 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 8 d. The autoclave was subsequently allowed to cool to room temperature. Red crystals together with a large amount of unidentified pink powders were recovered by filtration, washed with distilled water, and finally dried at ambient temperature.

Synthesis of $\text{Ni}(\text{Hdeta})_2(\text{SO}_4)_2$ (4): A mixture of $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ (0.569 g), H_2SO_4 (0.201 g, 98 wt%), $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.126 g), and diethylenetriamine (0.309 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 9 d. The autoclave was subsequently allowed to cool to room temperature. Blue crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (21.2 % yield based on nickel).

Table 1. Reaction compositions and crystallization conditions for $\text{Co}_2(\text{Hdeta})(\text{H}_2\text{O})_2(\text{SO}_4)(\text{C}_2\text{O}_4)_{1.5}$ (**1**)

run	reactants (molar ratio)			crystallization conditions		product
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	deta	T (°C)	Time (days)	
1	1	1	1	150	8	Compound 1
2	1	1.5	1	150	8	unidentified powder
3	1	2	1	150	8	unidentified powder
4	2	1	1	150	8	unidentified powder
5	2	1.5	1	150	8	unidentified powder
6	2	2	1	150	8	unidentified powder

Table 2. Reaction compositions and crystallization conditions for $\text{Co}_{1.5}(\text{Haep})(\text{SO}_4)(\text{C}_2\text{O}_4)$ (**2**)

run	reactants (molar ratio)			crystallization conditions		product
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	aep	T (°C)	Time (days)	
1	1	1	1	170	8	Compound 2
2	1	1.5	1	170	8	Compound 3
3	1	2	1	170	8	unidentified powder
4	1.5	1	1	170	8	Compound 2
5	1.5	1.5	1	170	8	Compound 2
6	1.5	2	1	170	8	unidentified powder
7	2	1	1	170	8	Compound 2
8	2	1.5	1	170	8	unidentified powder

Table 3. Crystal data and structure refinement for compounds **3** and **4**

	3	4
Empirical formula	C ₉ H ₂₈ Co _{1.5} N ₃ O ₁₆ S _{1.5}	C ₈ H ₂₈ N ₆ N O ₈ S ₂
Formula weight	570.83	459.19
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1 (No.2)	<i>P</i> 2 ₁ / <i>c</i> (No.14)
<i>a</i> , Å	8.4423(6)	8.1281(4)
<i>b</i> , Å	9.2757(8)	10.5438(4)
<i>c</i> , Å	13.2415(8)	10.1264(6)
α , degree	92.184(7)	90
β , degree	95.486(5)	98.720(4)
γ , degree	92.025(7)	90
Volume, Å ³	1030.63(13)	857.81(7)
<i>Z</i>	2	2
<i>D</i> _c , g/cm ³	1.839	1.778
μ (Mo-K α), mm ⁻¹	1.458	1.427
Reflections collected	7621	3458
Independent reflections	3616	1506
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.0619, 0.1850	0.0315, 0.0750

Table 4. Select bond lengths (Å) for compound **3**^a

Co(1)-OW2	2.053(3)	Co(2)-O(2)#2	2.139(3)
Co(1)-OW1	2.058(4)	Co(2)-O(2)	2.139(3)
Co(1)-O(3)	2.085(3)	S(1)-O(8)	1.456(4)
Co(1)-O(5)	2.108(4)	S(1)-O(9)	1.470(4)
Co(1)-O(6)#1	2.118(3)	S(1)-O(10)	1.474(4)
Co(1)-O(1)	2.158(4)	S(1)-O(7)	1.475(4)
Co(2)-OW3	2.062(3)	S(2)-O(12)	1.365(17)
Co(2)-OW3#2	2.062(3)	S(2)-O(14)	1.386(15)
Co(2)-O(4)#2	2.078(3)	S(2)-O(11)	1.456(12)
Co(2)-O(4)	2.078(4)	S(2)-O(13)	1.571(15)

^a Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z;
#2 -x+1,-y,-z+1.

Table 5. Select bond lengths (Å) for compound **4**^a

Ni(1)-N(1)	2.092(2)	Ni(1)-O(1)#1	2.2015(17)
Ni(1)-N(1)#1	2.092(2)	S(1)-O(3)	1.463(2)
Ni(1)-N(2)#1	2.114(2)	S(1)-O(4)	1.470(2)
Ni(1)-N(2)	2.114(2)	S(1)-O(2)	1.4701(19)
Ni(1)-O(1)	2.2015(17)	S(1)-O(1)	1.4980(19)

^a Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2.

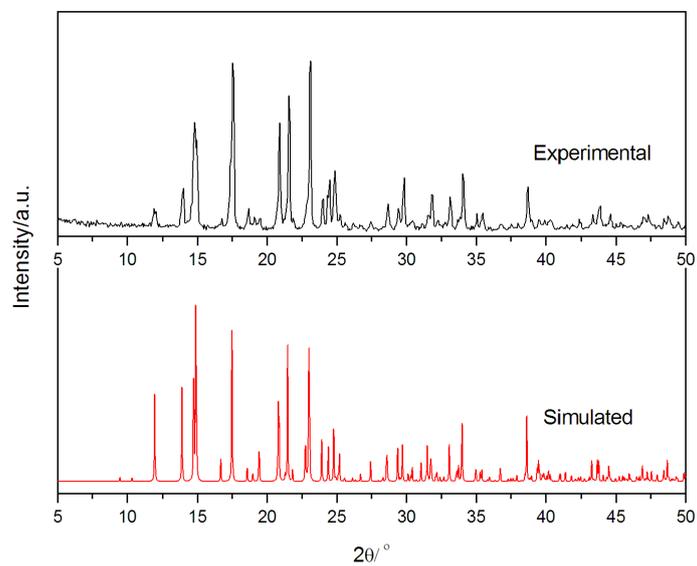


Fig. S1. Experimental and simulated powder XRD patterns of compound **1**.

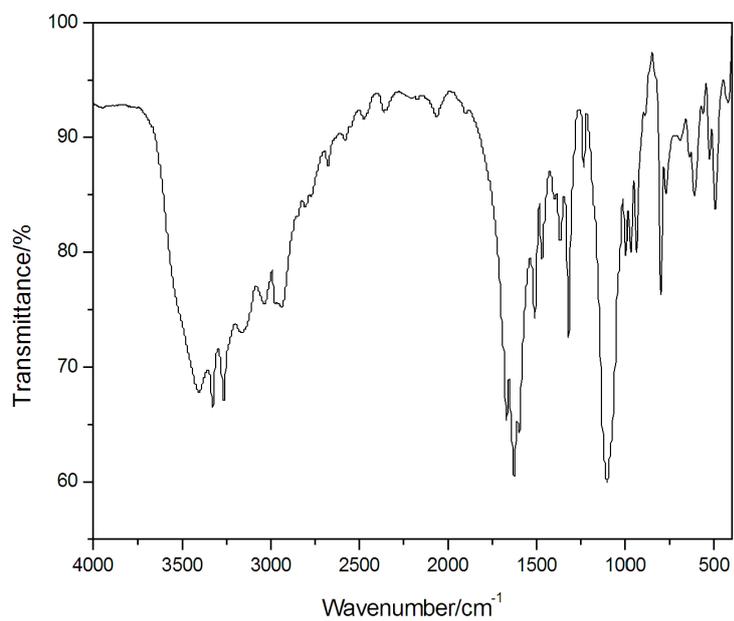


Fig. S2. IR spectrum of compound **1**.

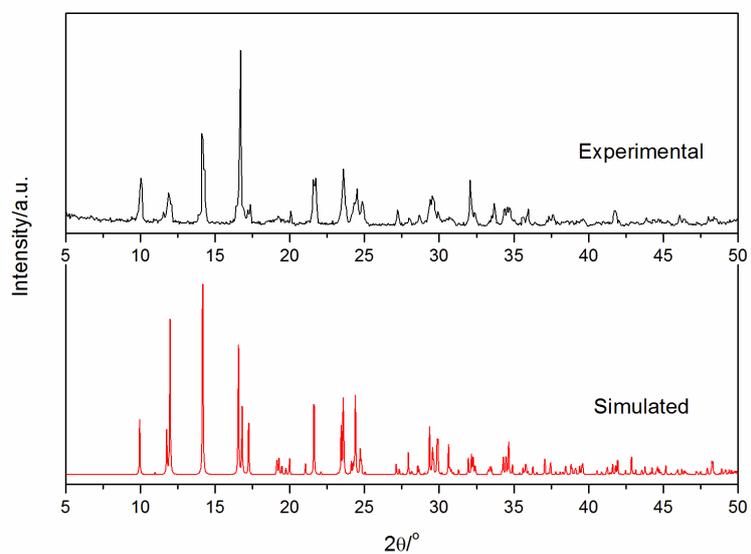


Fig. S3. Experimental and simulated powder XRD patterns of compound **2**.

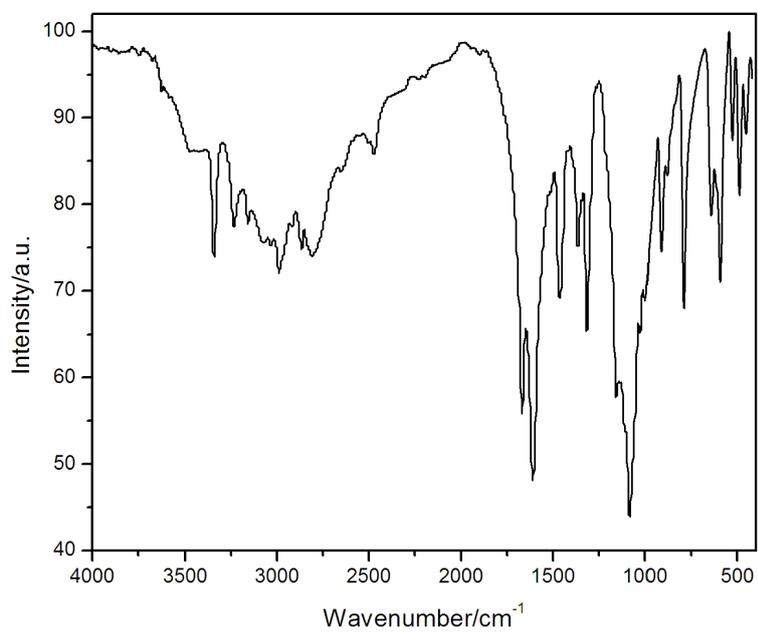


Fig. S4. IR spectrum of compound **2**.

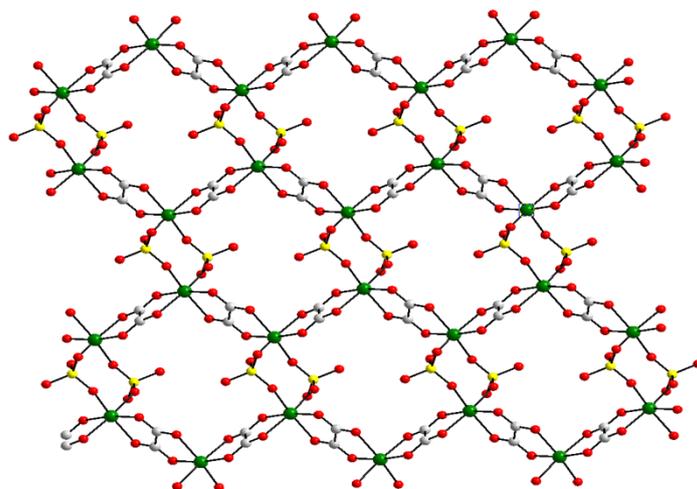


Fig. S5. The cobalt sulfate-oxalate layer present in the structure of compound **2**.

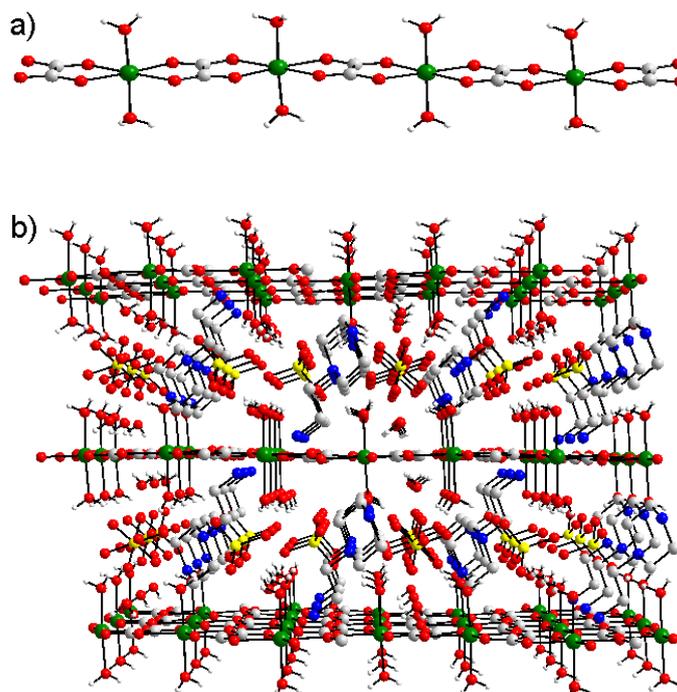


Fig. S6. (a) A view of the $\text{Co}(\text{H}_2\text{O})_2(\text{ox})$ chain in compound **3**; (b) A perspective view of the structure of **3**.

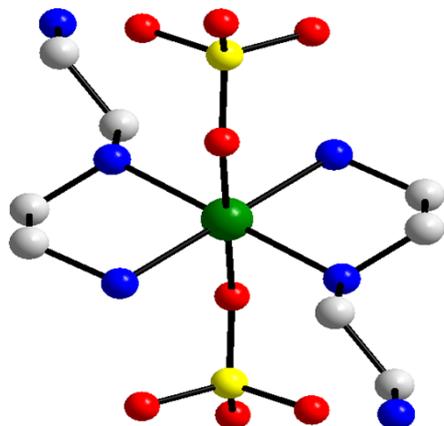


Fig. S7. The molecular structure of compound **4**. Color code: nickel, green; sulfur, yellow; oxygen, red; nitrogen, blue; carbon, gray.

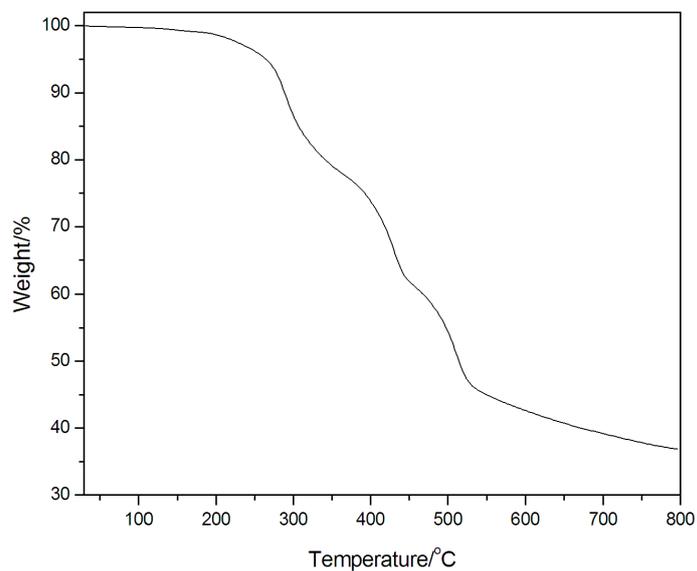


Fig. S8. TGA curve of compound **1**.

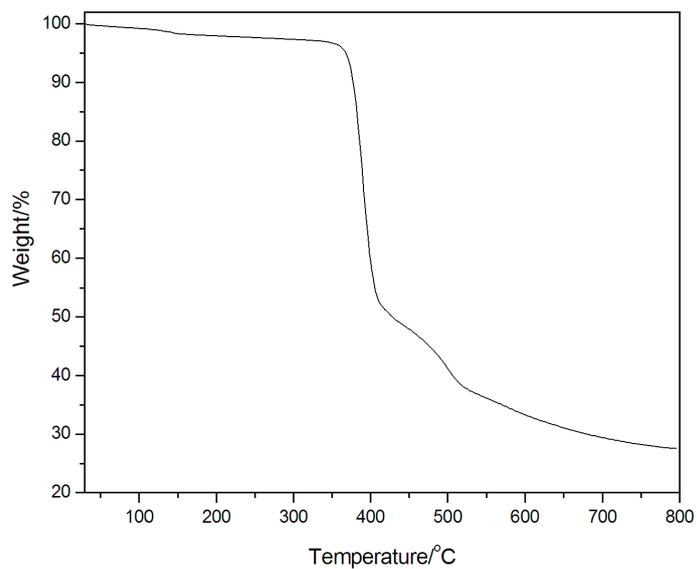


Fig. S9. TGA curve of compound **2**.

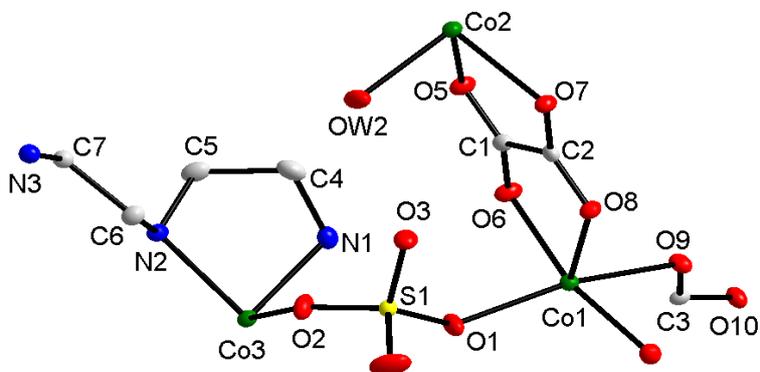


Fig. S10. ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 30% probability displacement ellipsoid.

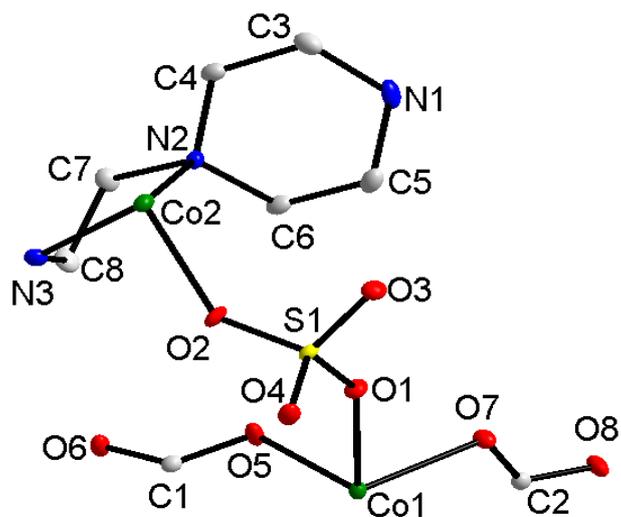


Fig. S11. ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 30% probability displacement ellipsoid.

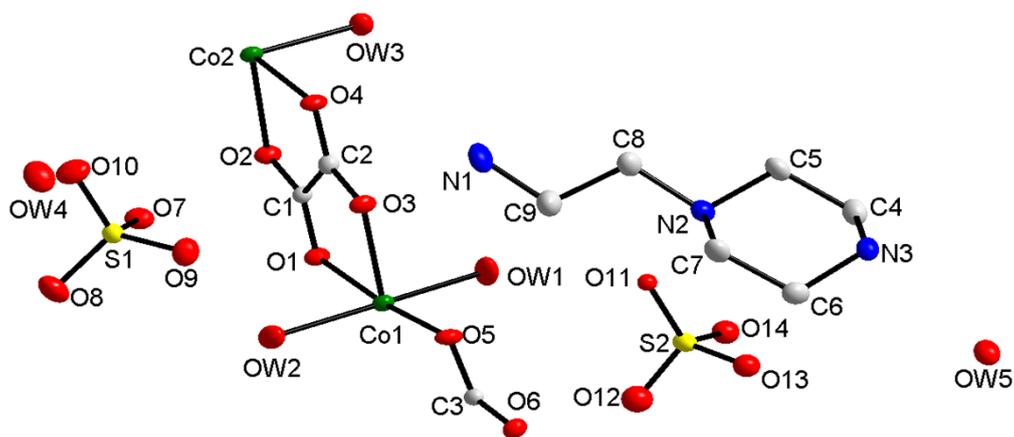


Fig. S12. ORTEP plot of the asymmetric unit of compound **3**, showing the labeling scheme and the 30% probability displacement ellipsoid.

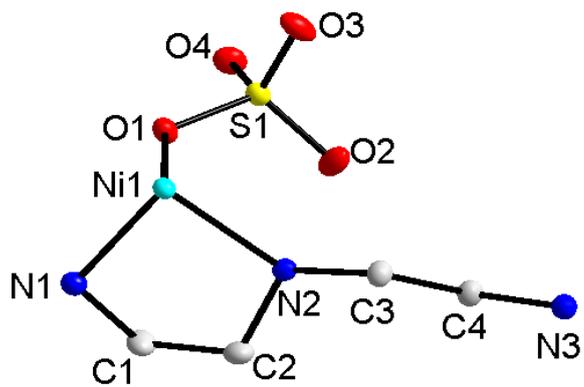


Fig. S13. ORTEP plot of the asymmetric unit of compound **4**, showing the labeling scheme and the 30% probability displacement ellipsoid.