

Synthesis, structure, and characterisation of a ferromagnetically coupled dinuclear complex containing Co(II) ions in high spin configuration and thiodiacetate and phenanthroline as ligands and of a series of isomorphous heterodinuclear complexes containing different Co:Zn ratios

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Table S1. Crystallographic parameters together with experimental details for **1**, **3**, and **4**. Crystal data of the Zn(II) and Cu(II) analogues are given for comparison.

For structures **1**, **3** and **4**, data were gathered at room temperature (293K) with an Oxford Diffraction Gemini CCD S Ultra Diffractometer, using Mo K α radiation. Absorption correction was performed with the Multi-scan Software provided in CrysAlis PRO, Oxford Diffraction (2015). General formula of the isomorphous series C₃₆H₃₀M₂N₄O₁₂S₃, with the cationic site **M** being, **1**: **M** = Co; **3**: **M** = Co:55%, Zn: 45%; **4**: **M** = Co: 25%, Zn: 75%; **6**(*): **M** = Zn; **7**(**): **M** = Cu

Table S1. Experimental details

	1	3	4	6 (*)	7 (**)
Cation (M)	Co	(Co: 55%, Zn: 45%)	(Co: 25%, Zn: 75%)	Zn	Cu
Formula weight	924.68	930.47	934.34	937.56	933.85
Crystal system, space group	Monoclinic, C2/c	Monoclinic, C2/c	Monoclinic, C2/c	Monoclinic, C2/c	Monoclinic, C2/c
Z	4	4	4	4	4
a, b, c (Å)	19.3064 (7), 14.3531 (5), 13.5255 (4)	19.3669 (8), 14.3494 (5), 13.5022 (5)	19.4449 (4), 14.3870 (3), 13.5165 (3)	19.6524 (6), 14.4247 (3), 13.6567 (4)	19.269 (9), 14.441 (2), 13.813 (4)
β (°)	105.974 (5)	106.231 (4)	106.473 (2)	106.958 (4)	107.49 (2)
V (Å³)	3603.3 (2)	3602.7 (2)	3626.09(15)	3703.07(3)	3665.8(54)
μ (mm⁻¹)	1.17	1.35	1.47	1.58	1.43
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30895, 4449, 3718	38617, 4610, 4174	19602, 4389, 3700		
R_{int}	0.047	0.036	0.044		
(sin θ/λ)_{max} (Å⁻¹)	0.680	0.687	0.685		
R[F²>2σ(F²)], wR(F²), S	0.034, 0.080, 1.39	0.024, 0.060, 1.05	0.031, 0.070, 1.05		
No. of reflections	4449	4610	4389		
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.81, -0.42	0.36, -0.35	0.31, -0.47		

Symmetry code: (i) 1/2-x, 1/2-y, -z

(*) Neuman, Burna et al. 2015; CSD code DUHXEL.

(**) Baggio, Garland et al. 1999; CSD code BEBQII

Table S2. Geometric parameters (Å, °)

	1	3	4	6	7
M—O1A	2.0425 (13)	2.0363 (9)	2.0366 (13)	2.0357(14)	1.976(3)
M—O3Aⁱ	2.0506 (13)	2.0595 (9)	2.0931 (12)	2.0724(14)	2.320(3)
M—N2	2.1017 (15)	2.0992 (11)	2.1080 (15)	2.0994(15)	2.016(3)
M—O3A	2.1125 (12)	2.0942 (10)	2.0661 (12)	2.1106(13)	1.974(3)
M—N1	2.1254 (15)	2.1227 (11)	2.1147 (15)	2.1176(16)	2.029(3)
M—S1A	2.6574 (5)	2.6081 (4)	2.5257 (5)	2.6841(6)	2.7241(17)
O1A—M—O3Aⁱ	92.97 (5)	92.93 (4)	92.67 (5)	93.37(6)	92.37(11)
O1A—M—N2	92.28 (6)	91.74 (4)	90.38 (6)	92.46(6)	91.44(12)
O3Aⁱ—M—N2	104.91 (6)	102.86 (4)	99.27 (5)	105.51(6)	99.69(10)
O1A—M—O3A	92.40 (5)	92.61 (4)	93.15 (5)	92.31(6)	92.18(11)
O3Aⁱ—M—O3A	78.83 (5)	78.82 (4)	78.78 (5)	78.70(5)	78.10(10)
N2—M—O3A	173.84 (6)	175.25 (4)	176.04 (5)	173.43(6)	175.84(11)
O1A—M—N1	164.52 (6)	165.20 (4)	165.64 (5)	164.16(6)	169.34(12)
O3Aⁱ—M—N1	101.61 (6)	100.28 (4)	98.02 (5)	101.74(6)	96.69(11)
N2—M—N1	79.06 (6)	78.89 (4)	78.49 (6)	79.05(6)	81.54(12)
O3A—M—N1	95.47 (5)	96.46 (4)	98.30 (6)	95.25(6)	95.17(11)
O1A—M—S1A	79.50 (4)	80.38 (3)	82.01 (4)	79.10(4)	80.64(9)
O3Aⁱ—M—S1A	155.88 (4)	157.22 (3)	159.63 (4)	155.48(4)	157.53(7)
N2—M—S1A	98.30 (4)	99.11 (3)	100.40 (4)	98.15(4)	101.80(9)
O3A—M—S1A	78.63 (4)	79.76 (3)	81.89 (4)	78.33(4)	80.84(8)
N1—M—S1A	88.99 (5)	89.73 (3)	91.01 (4)	88.82(4)	92.91(9)

Symmetry code: (i) 1/2-x,1/2-y,-z

Table S3. Hydrogen bonding interactions. Distances and angles are in Å and °, respectively.

Compound	<i>D—H</i>⋯<i>A</i>	<i>D—H</i> (<i>d</i>)	<i>H</i>⋯<i>A</i> (<i>d</i>)	<i>D</i>⋯<i>A</i> (<i>d</i>)	<i>D—H</i>⋯<i>A</i> (∠)
1	O1 <i>B</i> —H1 <i>B</i> ⋯O2 <i>A</i> ⁱⁱ	0.80 (1)	1.78 (1)	2.551 (2)	162 (2)
3	O1 <i>B</i> —H1 <i>B</i> ⋯O2 <i>A</i> ⁱⁱ	0.82 (1)	1.75 (1)	2.5463 (14)	164 (2)
4	O1 <i>B</i> —H1 <i>B</i> ⋯O2 <i>A</i> ⁱⁱ	0.81 (1)	1.75 (1)	2.547 (2)	165 (3)
6	O1 <i>B</i> —H1 <i>B</i> ⋯O2 <i>A</i> ⁱⁱ	0.84(5)	1.76(4)	2.550(2)	154(6)
7	O1 <i>B</i> —H1 <i>B</i> ⋯O2 <i>A</i> ⁱⁱ	0.70(5)	1.88(5)	2.580(5)	176(8)

Symmetry code: (ii) $-x+1/2, y+1/2, -z+1/2$.

Fig. S1. FTIR spectra of Thiodiacetic Acid (TDA, green line), phenanthroline (Phen, pink line), and **1** (black line).

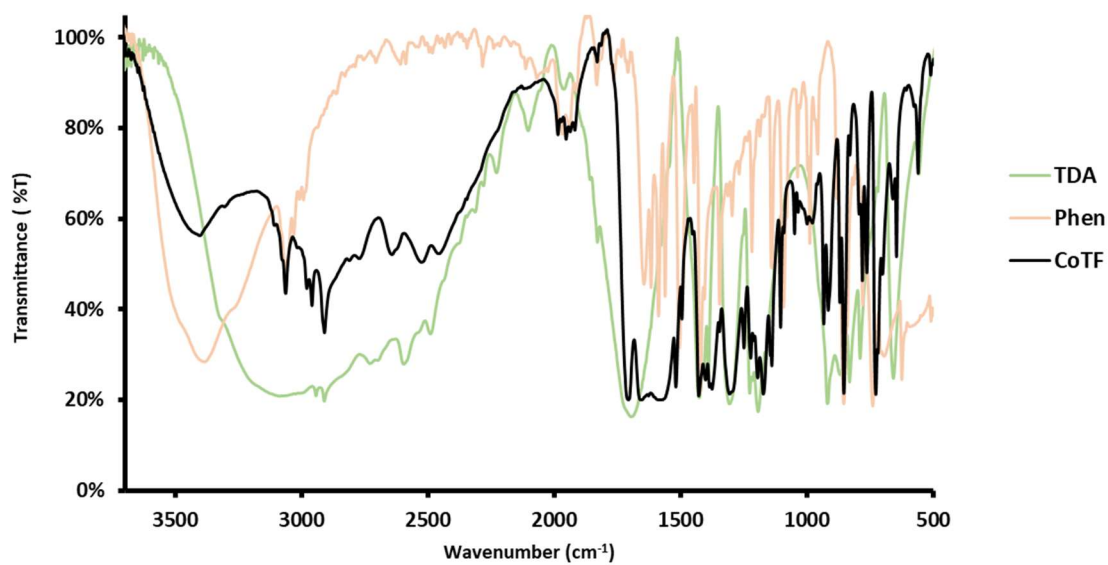


Fig. S2. Visible spectra of **1** and **5** in solid state (powder). Similar results were obtained in single-crystal samples. This figure was designed to compare peak positions and line shape of spectra in **1** and **5**. Note that the relative intensities of the bands are not indicative of the Co amount in each sample since we used a higher proportion of **5** in Na₂SO₄ to increase spectral sensitivity.

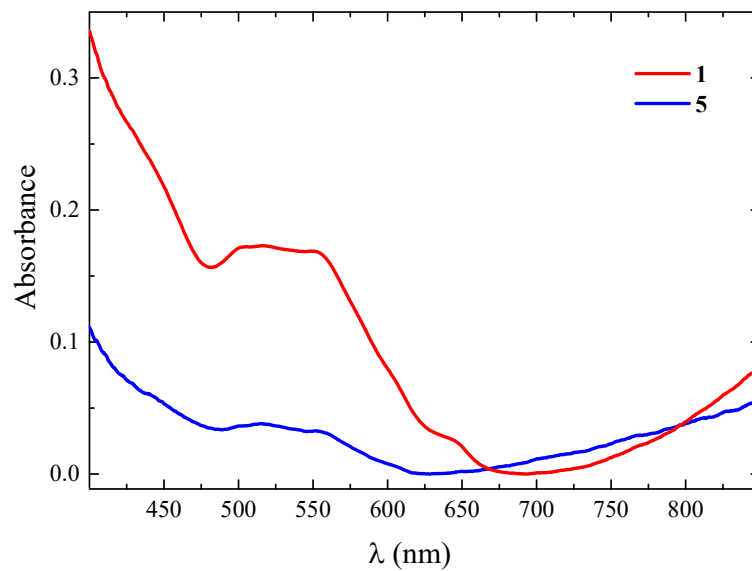


Fig. S3. Powder X-ray diffractograms of **1-5**.

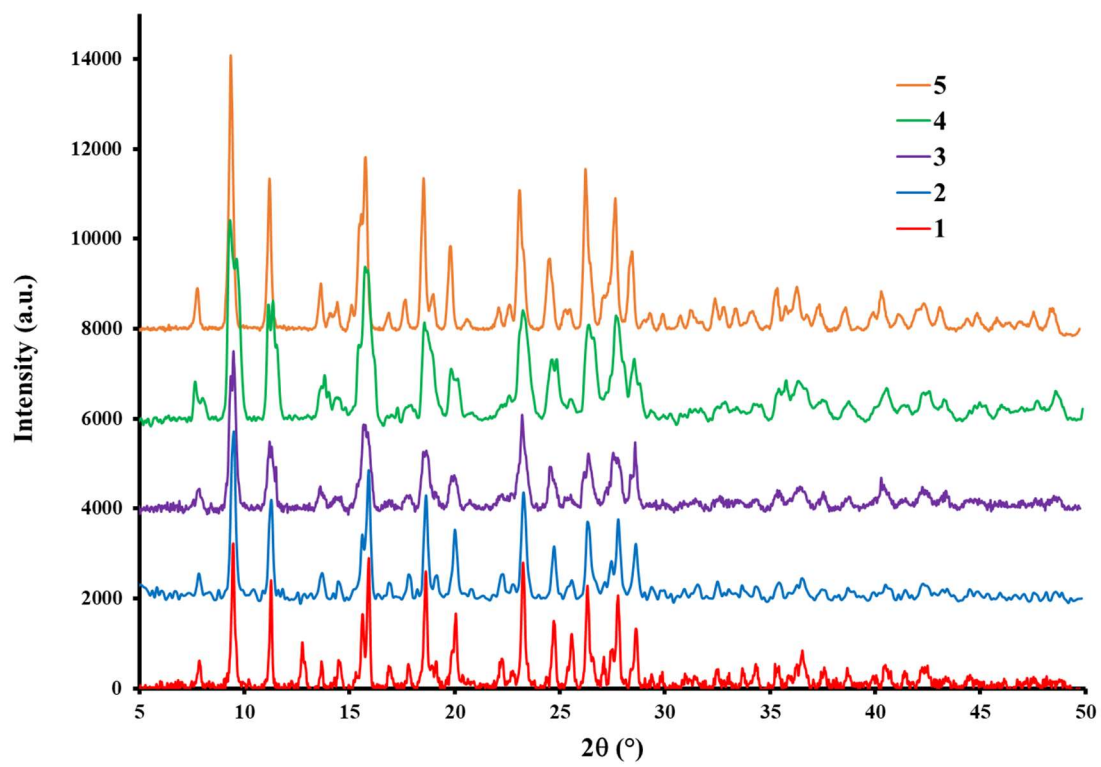


Fig. S4. Structural superposition of the dinuclear units of **1**, **3**, **4**, **6** (solid lines), and **7** (dash lines).

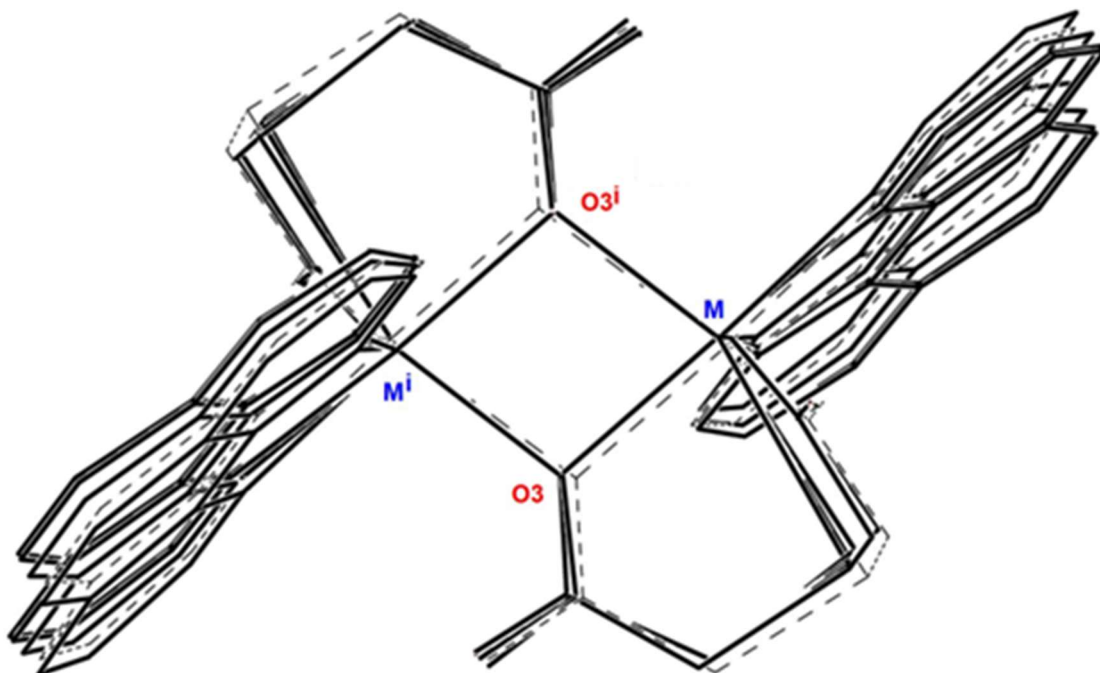
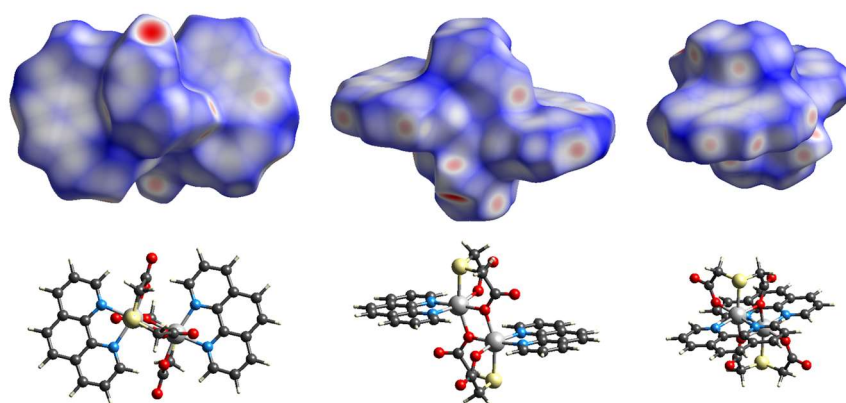


Fig. S5. **a)** Perspective views of Hirshfeld surface of **1** mapped with d_{norm} . Neighbouring molecules are not drawn for clarity. **b)** Perspective view of Hirshfeld surface of **1** and the closest neighbouring A- and B-type dimers (see also Figure 2, upper panel, in the text). The intense red region corresponds to the interaction between two tda molecules that bridge two magnetically inequivalent Co(II) ion dimers at 19.925 Å (Figure 2 in the text, lower panel). The Hirshfeld surfaces were calculated using Crystal Explorer Ver. 21.5 based on the X-ray data of **1**.

a)



b)

