

Supplementary Materials for Transition Metal Complexes and Radical Anion Salts of 1,10-Phenanthroline Derivatives Annulated with a 1,2,5-Tiadiazole and 1,2,5-Tiadiazole 1,1-Dioxide Moiety: Multidimensional Crystal Structures and Various Magnetic Properties

Experimental Details

X-ray Crystal Structural Analyses

X-ray investigations were performed at 320 K and 120 K for $[\text{Fe}(\text{tdap})_2(\text{NCS})_2] \cdot \text{MeCN}$ and at 173 K for the other compounds. Crystals were mounted on a loop using oil (CryoLoop, Immersion Oil, Type B; Hampton Research Corp. Aliso Viejo, CA, USA) for low temperature measurements and on a quartz fiber using epoxy bond (Araldite Rapid; Huntsman Corp, The Woodlands, TX, USA) and set on a Rigaku RA-Micro007 with a Saturn CCD detector by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.710690 \text{ \AA}$) under a nitrogen stream. The frame data were integrated and corrected for absorption with the Rigaku/MSO CrystalClear package. The structures were solved by direct methods and standard difference map techniques, and were refined with full-matrix least-square procedures on F^2 by using the Rigaku/MSO CrystalStructure package. Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms in cobaltocenium ion of $[\text{CoCp}_2] \cdot \text{tdapO}_2$ were located in a difference Fourier map and refined isotropically. All other hydrogen atoms were placed at the calculated positions and refined using a riding model. Crystallographic parameters are shown in Table S1.

Magnetic Measurements

Magnetic susceptibility measurements for $[\text{M}(\text{tdap})_2(\text{NCS})_2] \cdot \text{MeCN}$ ($\text{M} = \text{Mn, Fe, Co, Ni, Zn}$) and $[\text{CoCp}_2] \cdot \text{tdapO}_2$ were carried out on polycrystalline samples on a MPMS-SL Quantum Design magnetometer. A quartz glass tube for $[\text{Fe}(\text{tdap})_2(\text{NCS})_2] \cdot \text{MeCN}$ and a plastic straw for the other compounds were used as the sample folder. Measurements were performed under 0.1 T for $[\text{M}(\text{tdap})_2(\text{NCS})_2] \cdot \text{MeCN}$ ($\text{M} = \text{Mn, Fe, Co, Ni, Zn}$) and under 3T for $[\text{CoCp}_2] \cdot \text{tdapO}_2$. The temperature dependences of the paramagnetic susceptibilities χ_p were calculated from theoretical fitting using the diamagnetic susceptibility as a fitting parameter.

Table S1. Crystallographic parameters.

	[Fe(tdap)₂(NCS)₂]•MeCN		[Co(tdap)₂(NCS)₂]	[Mn(tdap)₂(NCS)₂]•MeCN
	HS state	LS state		
Formula	C ₂₈ H ₁₅ N ₁₁ S ₄ Fe		C ₂₆ H ₁₂ N ₁₀ CoS ₄	C ₂₈ H ₁₅ N ₁₁ S ₄ Mn
Formula weight	689.59		651.62	688.68
Dimension/mm ³	0.18 × 0.15 × 0.09		0.10 × 0.05 × 0.01	0.15 × 0.07 × 0.06
<i>T</i> /K	320	120	173	173
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>a</i> /Å	11.7576(14)	11.525(2)	7.476(2)	11.7681(17)
<i>b</i> /Å	18.829(2)	18.670(3)	16.514(5)	18.664(3)
<i>c</i> /Å	13.3450(15)	12.992(2)	21.678(6)	13.3313(18)
<i>α</i> /°				
<i>β</i> /°	99.4530(15)	98.722(2)	96.728(4)	100.218(2)
<i>γ</i> /°				
<i>V</i> /Å ³	2914.3(6)	2763.2(8)	2657.8(13)	2881.7(7)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} /g cm ^{−3}	1.572	1.658	1.628	1.587
<i>μ</i> (Mo Kα)/cm ^{−1}	8.456	8.919	9.996	7.903
<i>F</i> (000)	1400.00	1400.00	1316.00	1396.00
2 $\theta_{\max}$ /°	54.9	54.9	55.0	55.0
Reflections collected	22443	21585	10575	22973
Unique reflections (<i>R</i> _{int})	6544 (0.025)	6206 (0.028)	2980 (0.050)	6556 (0.045)
Number of parameters	398	398	187	398
Final <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0366	0.0378	0.0474	0.0411
<i>wR</i> ₂ ^[b]	0.0958	0.0912	0.1172	0.1082
Goodness-of-fit	1.044	1.040	1.067	1.078

Table S1. Cont.

	[Co(tdap) ₂ (NCS) ₂] •MeCN	[Ni(tdap) ₂ (NCS) ₂] •MeCN	[Cu(tdap) ₂ (NCS) ₂] •MeCN	[Zndap) ₂ (NCS) ₂] •MeCN
Formula	C ₂₈ H ₁₅ N ₁₁ S ₄ Co	C ₂₈ H ₁₅ N ₁₁ S ₄ Ni	C ₂₈ H ₁₅ N ₁₁ S ₄ Cu	C ₂₈ H ₁₅ N ₁₁ S ₄ Zn
Formula weight	692.67	692.44	697.29	699.12
Dimension/mm ³	0.12 × 0.09 × 0.08	0.07 × 0.07 × 0.04	0.20 × 0.20 × 0.20	0.15 × 0.10 × 0.10
<i>T</i> /K	173	173	173	173
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>a</i> /Å	11.6350(18)	9.491(2)	11.6129(19)	11.6761(11)
<i>b</i> /Å	18.691(3)	15.380(4)	18.761(3)	18.7392(17)
<i>c</i> /Å	13.203(2)	19.967(5)	13.179(2)	13.2026(12)
<i>α</i> /°				
<i>β</i> /°	99.627(3)	102.708(4)	98.535(2)	99.4276(13)
<i>γ</i> /°				
<i>V</i> /Å ³	2830.8(8)	2843.2(12)	2839.5(8)	2849.7(5)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} /g cm ^{−3}	1.625	1.617	1.631	1.629
<i>μ</i> (Mo Kα)/cm ^{−1}	9.448	10.193	11.066	11.982
<i>F</i> (000)	1404.00	1408.00	1412.00	1416.00
2 $\theta_{\max}$ /°	55.0	55.0	55.0	55.0
Reflections collected	22649	11326	22632	22576
Unique reflections (<i>R</i> _{int})	6409 (0.043)	3192 (0.041)	6405 (0.039)	6487 (0.026)
Number of parameters	398	202	398	398
Final <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0438	0.0394	0.0471	0.0298
<i>wR</i> ₂ ^[b]	0.1126	0.0890	0.1074	0.0711
Goodness-of-fit	1.062	1.072	1.089	1.049

Table S1. Cont.

	[Mn(tdap) ₂ Cl ₂]	[Cu ₂ (tdap) ₂ (NCS) ₂]	[Cu ₂ (tdap) ₂ (NCS) ₄]	[CoCp ₂]•tdapO ₂
Formula	C ₂₄ H ₁₂ N ₈ S ₂ Cl ₂ Mn	C ₂₆ H ₁₂ N ₁₀ S ₄ Cu ₂	C ₁₄ H ₆ N ₆ S ₃ Cu	C ₂₂ H ₁₆ N ₄ O ₂ SCo
Formula weight	602.38	719.78	417.97	459.39
Dimension/mm ³	0.20 × 0.20 × 0.01	0.15 × 0.05 × 0.01	0.10 × 0.05 × 0.02	0.10 × 0.07 × 0.01
T/K	173	173	173	173
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c (#15)	P2 ₁ /c (#14)	P $\bar{1}$ (#2)	Pbca (#61)
a/Å	8.277(3)	9.1233(17)	8.2240(19)	8.274(4)
b/Å	12.142(5)	19.608(4)	8.314(2)	16.528(7)
c/Å	22.935(9)	7.5173(14)	11.979(3)	27.116(12)
α/°			102.996(3)	
β/°	93.665(6)	109.386(2)	105.900(4)	
γ/°			90.120(3)	
V/Å ³	2300.1(16)	1268.5(4)	765.7(3)	3708(3)
Z	4	2	2	8
D _{calc} /g cm ^{−3}	1.739	1.884	1.813	1.646
μ(Mo Kα)/cm ^{−1}	10.221	20.482	18.436	10.679
F(000)	1212.00	720.00	418.00	1880.00
2θ _{max} /°	54.9	55.0	55.0	55.0
Reflections collected	8983	9991	6169	26180
Unique reflections (R _{int})	2618 (0.071)	2810 (0.062)	3376 (0.023)	4254 (0.065)
Number of parameters	169	191	218	312
Final R ₁ [I > 2σ(I)] ^[a]	0.0519	0.0309	0.0307	0.0683
wR ₂ ^[b]	0.1150	0.0813	0.0741	0.1385
Goodness-of-fit	1.131	0.859	1.063	1.141

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^[b] $wR_2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$.