Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Coordination polymers based on octacyanometalates(IV,V) and aliphatic polyamine cooper(II) tectons with [N_3] donor atom sets

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Contents

Table S1. The selected donor(D)-H)···H-acceptor(A) distances (Å) of possible hydrogen bonds in **3**

D···A		D···A	
O1···N3[a]	2.930	N6[a]···O1	2.964
O1···N2[a]	2.868	N6[a]···N1	3.313
O2···N2	3.125	N6[a]···O2	3.277
O2···N1[a]	3.055	N9A[a]···N1	3.105
		N9B[a]···N1	3.031
		N12···O2	3.066

[a]Atoms obtained by symmetry equivalent operations imposed by $P2_12_12$ space group.

Table S2 Selected Bond Lengths (Å) and Angles (deg) for $[Cu^{II}(tetrenH_2)]_2[W^{IV}(CN)_8]_2 \cdot 5H_2O$ **1**

$[W(1)(CN)_8]^{4-}$ and $[W(2)(CN)_8]^{4-}$

W1–C11	2.16(1)	C11–N11	1.13(1)	W1–C11–N11	178.3(9)
W1–C12	2.17(1)	C12–N12	1.15(1)	W1–C12–N12	176.6(8)
W1–C13	2.161(9)	C13–N13	1.15(1)	W1–C13–N13	178.7(9)
W1–C14a	2.172(9)	C14a–N14a	1.13(1)	W1–C14a–N14a	177.6(9)
W1–C15	2.17(1)	C15–N15	1.10(2)	W1–C15–N15	178.4(18)
W1–C16	2.15(1)	C16–N16	1.17(2)	W1–C16–N16	177.7(10)
W1–C17	2.19(1)	C17–N17	1.12(1)	W1–C17–N17	178.0(10)
W1–C18	2.17(1)	C18–N18	1.14(1)	W1–C18–N18	178.1(10)
W2–C21	2.167(9)	C21–N21	1.13(1)	W2–C21–N21	176.3(8)
W2–C22	2.17(1)	C22–N22	1.14(2)	W2–C22–N22	179.6(12)
W2–C23	2.17(1)	C23–N23	1.11(2)	W2–C23–N23	176.9(13)
W2–C24	2.18(1)	C24–N24	1.12(2)	W2–C24–N24	178.8(11)
W2–C25	2.15(1)	C25–N25	1.15(2)	W2–C25–N25	175.4(14)
W2–C26	2.17(1)	C26–N26	1.13(1)	W2–C26–N26	179.1(9)
W2–C27	2.19(1)	C27–N27	1.13(1)	W2–C27–N27	179.3(10)
W2–C28	2.18(1)	C28–N28	1.11(1)	W2–C28–N28	178.4(12)

$[Cu(1)(tetrenH_2)(NC)_2]^{2+}$

Cu1–N14	1.977(9)	Cu1–N14–C14	171.1(8)				
Cu1–N11	2.183(9)	Cu1–N11–C11	154.3(8)				
Cu1–N32	2.080(8)	N32–Cu1–N34	161.6(4)	N33–Cu1–N34	83.9(4)	N11–Cu1–N34	96.6(4)
Cu1–N33	1.998(8)	N33–Cu1–N14	159.5(4)	N34–Cu1–N14	95.2(4)	N11–Cu1–N14	101.8(4)
Cu1–N34	2.082(9)	N32–Cu1–N14	92.5(4)	N11–Cu1–N32	98.2(3)		
		N32–Cu1–N33	83.0(4)	N11–Cu1–N33	98.6(4)		

mer-$[Cu(2)(tetrenH_2)(NC)_3]^{+}$

Cu2–N21	1.960(8)	Cu2–N21–C21	175.8(9)				
Cu2–N12	2.266(9)	Cu2–N12–C12	146.5(8)				
Cu2–N28a	2.82	Cu2–N28a–C28a	148.6				
Cu2–N42	2.069(8)	N12–Cu2–N28a	176.5	N12–Cu2–N44	97.4(3)	N28a–Cu2–N44	82.7
Cu2–N43	2.016(9)	N21–Cu2–N43	176.0(4)	N21–Cu2–N42	94.1(4)	N28a–Cu2–N21	88.7
Cu2–N44	2.070(9)	N42–Cu2–N44	154.2(3)	N21–Cu2–N44	96.9(4)	N43–Cu2–N42	83.4(4)
		N12–Cu2–N42	104.8(3)	N28a–Cu2–N42	74.2	N43–Cu2–N44	84.1(4)
		N12–Cu2–N43	89.1(3)	N28a–Cu2–N43	87.5	N12–Cu2–N21	94.7(3)

Symmetry equivalent operation: (a) $-x, -y, -z+2$; the numbers given without the esd values have been read directly from ORTEP.

Table S3 Selected Bond Lengths (Å) and Angles (deg) for $[Cu^{II}(tetrenH_2)][Cu^{II}(tetrenH)][W^{V}(CN)_8][W^{IV}(CN)_8]\cdot 2.5H_2O$ **2**

W(1) and W(2)

W1–C11	2.134(16)	C11–N11	1.17(2)	W1–C11–N11	176.9(14)
W1–C12	2.14(2)	C12–N12	1.16(3)	W1–C12–N12	178.8(19)
W1–C13	2.184(19)	C13–N13	1.11(2)	W1–C13–N13	176.0(17)
W1–C14	2.11(2)	C14–N14	1.17(3)	W1–C14–N14	178.1(19)
W1–C15	2.14(2)	C15–N15	1.13(3)	W1–C15–N15	177(2)
W1–C16	2.138(18)	C16–N16	1.14(3)	W1–C16–N16	177.3(18)
W1–C17	2.194(19)	C17–N17	1.13(2)	W1–C17–N17	178.2(17)
W1–C18	2.184(19)	C18–N18	1.10(2)	W1–C18–N18	173.4(19)
W2–C21	2.16(2)	C21–N21	1.13(3)	W2–C21–N21	179(2)
W2–C22	2.18(2)	C22–N22	1.11(2)	W2–C22–N22	174.5(18)
W2–C23	2.18(2)	C23–N23	1.13(3)	W2–C23–N23	177.2(18)
W2–C24	2.143(18)	C24–N24	1.15(2)	W2–C24–N24	178.7(17)
W2–C25	2.16(3)	C25–N25	1.13(3)	W2–C25–N25	177(2)
W2–C26	2.18(3)	C26–N26	1.13(3)	W2–C26–N26	179(2)
W2–C27	2.16(2)	C27–N27	1.11(3)	W2–C27–N27	176(2)
W2–C28	2.18(2)	C28–N28	1.14(3)	W2–C28–N28	179(2)

Cu(3)

Cu3–N33	2.021(16)	Cu1–N11	1.971(17)	Cu1–N11–C11	167.1(14)
Cu3–N34	2.036(19)	Cu1–N16a	2.431(18)	Cu1–N16a–C16a	149.6(16)
Cu3–N32	2.08(2)	Cu1–N18b	2.446(16)	Cu1–N18b–C18b	175.2(19)
N11–Cu3–N33	176.1(7)	N11–Cu3–N32	97.1(8)	N18b–Cu3–N32	89.7(8)
N16a–Cu3–N18b	175.6(7)	N11–Cu3–N34	94.3(7)	N18b–Cu3–N33	88.9(7)
N32–Cu3–N34	167.3(8)	N16a–Cu3–N32	87.8(8)	N18b–Cu3–N34	84.0(7)
N11–Cu3–N16a	90.5(6)	N16a–Cu3–N33	87.3(6)	N32–Cu3–N33	86.0(9)
N11–Cu3–N18b	93.5(6)	N16a–Cu3–N34	97.7(8)	N33–Cu3–N34	82.8(8)

Cu(4)

Cu4–N42	2.060(16)	Cu4–N12	1.944(19)	Cu4–N12–C12	172.1(17)
Cu4–N43	2.019(17)	Cu4–N22	2.287(16)	Cu4–N22–C22	149.9(18)
Cu4–N44	2.032(20)	Cu4–N28c	3.114(19)	Cu4–N28c–C28c	148.4
N12–Cu4–N43	172.7(7)	N12–Cu4–N44	94.5(8)	N28c–Cu4–N43	90.7(7)
N22–Cu4–N28c	174.6(7)	N22–Cu4–N43	90.1(7)	N28c–Cu4–N44	92.4(8)
N42–Cu4–N44	158.3(8)	N22–Cu4–N44	94.9(8)	N43–Cu4–N44	86.7(9)
N12–Cu4–N42	93.1(7)	N22–Cu4–N42	106.3(6)	N42–Cu4–N43	83.3(8)
N12–Cu4–N28c	82.0(8)	N28c–Cu4–N42	68.5(8)	N12–Cu4–N22	97.0(7)

Symmetry equivalent operations: (a) $1 - x, -y, 1 - z$; (b) $x - 1, -y, -z + 1$; (c) $x - 1, y, z$; the numbers given without the esd values have been read directly from ORTEP

Table S4. Selected distances and angles for $[Cu(dien)]_2[W(CN)_8]\cdot 4H_2O$ **3**.

W1-C1	2.161(3)	C1-N1	1.151(4)	N1-C1-W1	177.3(3)
W1-C2	2.162(3)	C2-N2	1.149(5)	N2-C2-W1	177.3(4)
W1-C3	2.162(3)	C3-N3	1.146(5)	N3-C3-W1	177.7(3)
W1-C4	2.143(3)	C4-N4	1.153(4)	N4-C4-W1	174.9(3)
Cu1-N4	1.947(3)	C4-N4-Cu1	161.2(4)		
Cu1-N1a	2.290(3)	C1a-N1a-Cu1	140.7(3)		
Cu1-N6	2.037(5)	N4-Cu1-N9B	167.3(3)	N1a-Cu1-N9A	91.6(3)
Cu1-N9A	2.033(11)	N4-Cu1-N9A	166.6(3)	N1a-Cu1-N9B	89.1(3)
Cu1-N9B	2.020(10)	N12-Cu1-N6	160.9(3)	N6-Cu1-N9A	75.5(4)
Cu1-N12	2.027(6)	N4-Cu1-N12	92.6(2)	N6-Cu1-N9B	93.1(4)
		N4-Cu1-N6	94.88(19)	N12-Cu1-N9B	76.9(3)
		N4-Cu1-N1a	99.28(14)	N12-Cu1-N9A	93.9(3)
		N6-Cu1-N1a	99.71(18)		
		N12-Cu1-N1a	96.4(2)		

Symmetry equivalent operation: (a) $-x+1/2, y+1/2, -z$.

Table S5. Selected distances and angles for $[Cu(dien)]_2[Mo(CN)_8]\cdot 4H_2O$ **4**.

Mo1-C1	2.157(2)	C1-N1	1.151(3)	N1-C1-Mo1	177.3(3)
Mo1-C2	2.161(3)	C2-N2	1.149(4)	N2-C2-Mo1	177.3(4)
Mo1-C3	2.162(3)	C3-N3	1.155(4)	N3-C3-Mo1	177.7(3)
Mo1-C4	2.149(2)	C4-N4	1.147(3)	N4-C4-Mo1	174.9(3)
Cu1-N4	1.949(2)	C4-N4-Cu1	161.5(3)		
Cu1-N1a	2.291(2)	C1a-N1a-Cu1	140.7(2)		
Cu1-N6A	2.165(6)	N6A-Cu1-N12B	169.8(2)	N1a-Cu1-N6A	98.23(16)
Cu1-N6B	1.841(7)	N6A-Cu1-N12A	156.0(3)	N1a-Cu1-N6B	101.6(2)
Cu1-N9A	2.021(5)	N6B-Cu1-N12A	146.6(3)	N1a-Cu1-N12A	102.5(3)
Cu1-N9B	2.017(5)	N6B-Cu1-N12B	161.0(3)	N1a-Cu1-N12B	91.7(2)
Cu1-N12A	1.885(7)	N6A-Cu1-N9A	80.2(2)	N1a-Cu1-N9A	92.18(14)
Cu1-N12B	2.174(7)	N6A-Cu1-N9B	97.9(2)	N1a-Cu1-N9B	89.27(15)
		N6B-Cu1-N9A	69.2(3)	N4a-Cu1-N6A	90.87(17)
		N6B-Cu1-N9B	86.9(3)	N4a-Cu1-N6B	101.1(2)
		N9A-Cu1-N12A	87.0(3)	N4a-Cu1-N12A	97.6(2)
		N9A-Cu1-N12B	97.0(2)	N4a-Cu1-N12B	90.0(2)
		N9B-Cu1-N12A	70.6(3)	N4a-Cu1-N9A	166.41(16)
		N9B-Cu1-N12B	79.6(2)	N4a-Cu1-N9B	166.81(16)
		N4-Cu1-N1a	99.26(10)		

Symmetry equivalent operation: (a) $-x+1/2, y+1/2, -z$.

Table S6. The selected donor(D)-acceptor(A) distances (Å) of possible hydrogen bonds in **1**

D···A		D···A		D···A	
O1···N16[a]	2.948	N31···N13	2.925	N41···N17[a]	3.015
O1···N24[a]	3.202	N31···N26	3.045	N41···N22	2.926
O1···N27[a]	3.160	N31···N27	3.202	N41···N26[a]	2.920
O2···N11	3.303	N31···N27[a]	2.884	N41···O3	3.132
O2···N18	3.219	N31···O1	3.097	N42···N28[a]	3.010
O2···N18[a]	2.868	N32···O1	2.922	N43···N12	3.009
O3···N17[a]	3.322	N33···O2	2.969	N44···N12	3.261
O4···N25[a]	3.102	N35···N22[a]	3.290	N44···N25[a]	3.258
O4···N28	2.807	N35···N23	3.005	N44···N28[a]	3.281
O5···N16	2.899	N35···N26[a]	3.211	N45···N15[a]	2.923
O5···N24	2.759			N45···N25[a]	3.021
				N45···O4	2.823
				N45···O5	3.036

[a]Atoms obtained by symmetry equivalent operations imposed by P-1 space group

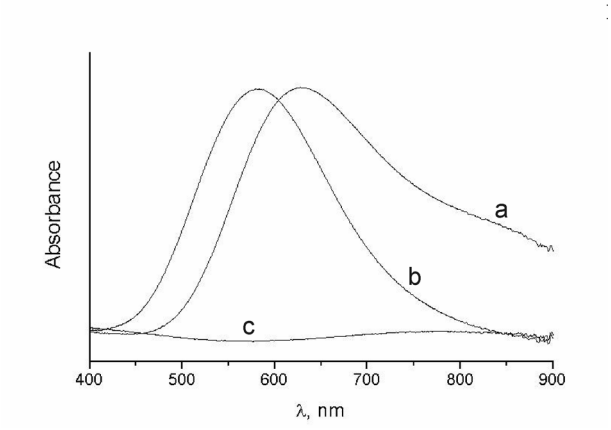

Fig. S1. Electronic spectra of $[Cu^{II}(tetren)]^{2+}$ at different pH: (a) $[Cu^{II}(tetren)]^{2+}$ at pH > 6, (b) $[N_3]$ chelation forms ($[Cu^{II}(tetrenH_2)]^{4+}$ and/or $[Cu^{II}(tetrenH)]^{3+}$) at pH 3–5, and (c) $[Cu(OH_2)_6]^{2+}$ (pH < 2).

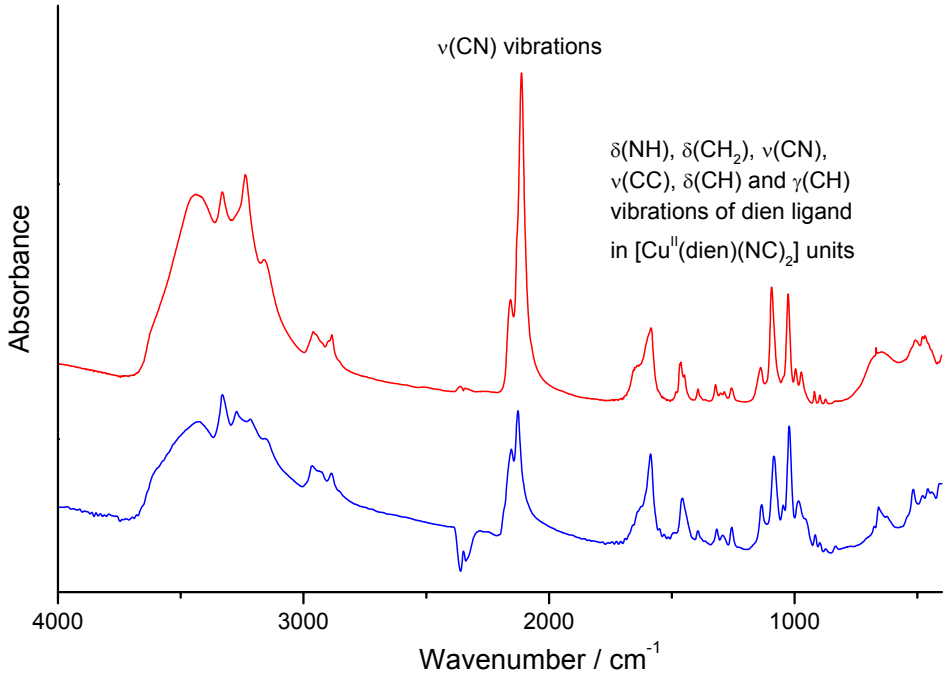

Fig. S2. The dependence of the intensities of ν(CN) stretching frequencies on the oxidation state of octacyanotungstate moiety. A comparison of relative absorbance of ν(CN) bands (2200-2000 cm^{-1}) *vs* δ(NH), δ(CH_2), ν(CN), ν(CC), δ(CH_2) and γ(CH) bands characteristic of dien ligand (1700-850 cm^{-1}) in [Cu^{II}(dien)(NC)2] units in cyano-bridged compounds of W(IV) and W(V): [Cu^{II}(dien)]$_2$[$W^{IV}(CN)_8$]·4H_2O **3** (red, this work) and K[Cu^{II}(dien)]$_4$[$W^{V}(CN)_8$]$_3$ ·8H_2O (blue, ref. 6 in this work).

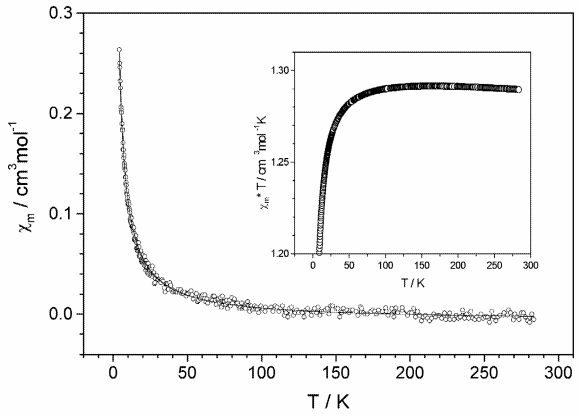

Fig. S3. The temperature dependence of molar magnetic susceptibility of **2** and the best fit of Curie-Weiss law. Inset: the temprature dependence of product $\chi \cdot T$.

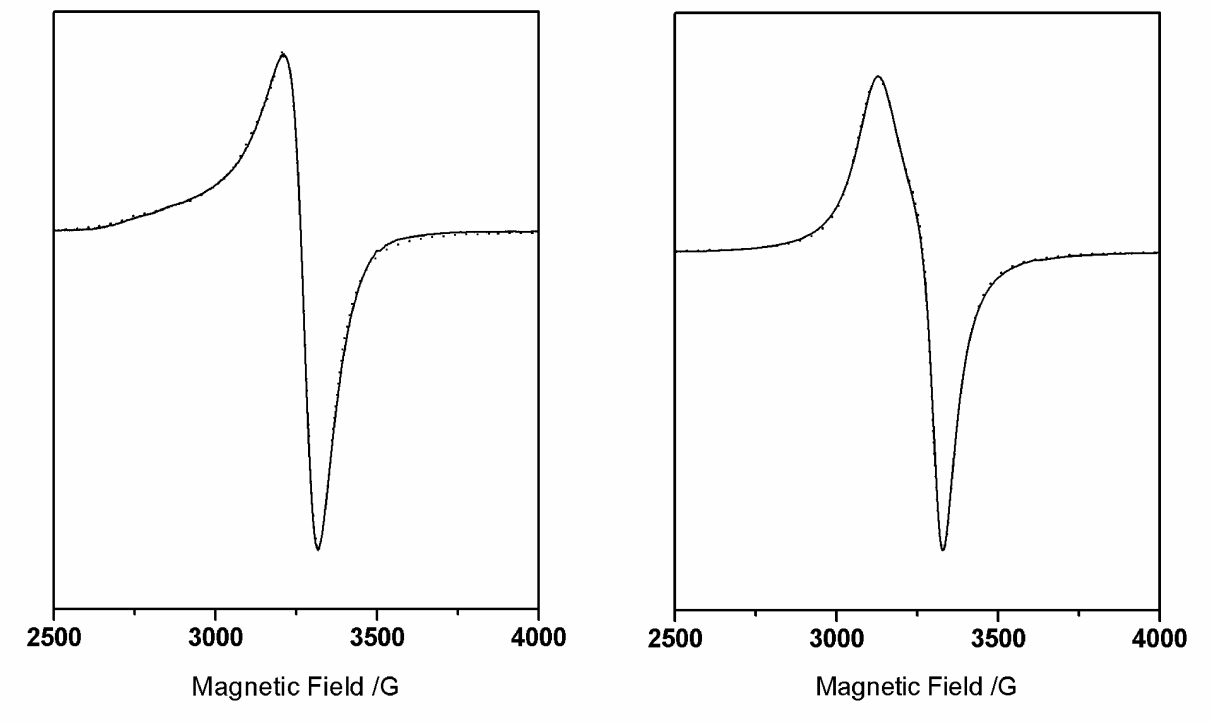

Fig. S4. The ESR spectra of **1**·3H_2O (left) and **2**·10.5H_2O (right) at 77 K; (—) – the experimental line, (· · ·) – the simulated line.