Isomerism in 1D Coordination Polymers of Cu(II) Complexes of *N*-(2-hydroxybenzyl)-L-valine: Influence of Solvent and Coordination Sphere on the Conformation

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Supporting Information

Infrared Spectra Typical vibrations have been assigned in the light of X-ray crystal structures. Some of the selected key IR bands of reduced Schiff base ligands have been assigned to ν(NH)(ca. 3194, 2967cm^{-1}), $\nu_{as}(CO_2^-)$(1640,1601cm^{-1}), $\nu_s(CO_2^-)$(1400cm^{-1}) and ν(CO)(1270cm^{-1}) based on the assignment of analogous H_2Sgly and H_2Sala. The ν(OH) band attributed to water is not observed for all the ligands.

The X-ray crystal structures of complexes showed that the metal atoms bonded to the ligands through phenolato, amine and carboxylato groups. The ν(NH), $\nu_{as}(CO_2^-)$, $\nu_s(CO_2^-)$ bands shifted upon complexation, showing that the coordination involves those groups. Compared to the ligands, the bands of ν(NH) in general red have shifted 30 cm^{-1} to 100 cm^{-1} upon complexation. However, the $\nu_s(CO_2^-)$ is moved to high energy and the trend in $\nu_{as}(CO_2^-)$ is not consistent for all complexes.

Table S1 Selected IR Absorption Bands (cm^{-1}) for ligands and complexes **1-4**.

Code	ν(OH)	ν(NH)	$\nu_{as}(CO_2^-)$	$\nu_s(CO_2^-)$	Δ^b	ν(CO) (phenolic)
H_2Sval	-	3194 (s, sp)	1640 (vs, sp)	1400(s, sp)	240	1270 (vs, sp)
		2967 (m, sp)	1601 (vs, sp)		201	
H_2Strp	-	3111 (m, sp)	1604 (vs, sp)	1370 (s, sp)		1275 (vs, sp)
H_2Sile	-	2953 (m, sp)	1595 (vs, sp)	1398 (s, sp)	197	1275 (vs, sp)
H_2Sleu	-	3214 (m, sp)	1639 (vs, sp)	1389 (s, sp)		1266 (vs, sp)
		2969 (m, sp)				
H_2Sphe	-	3193 (m, sp)	1597 (vs, sp)	1395 (s, sp)		1272 (vs, sp)
		3034 (m, sp)				
1	3446 (m, br)	3286 (m, sp)	1638 (vs, sp)	1390(s, sp)	248	1266 (vs, sp)
			1602 (vs, sp)	1370(s, sp)	232	
2	3424 (m, br)	3240 (s, sp)	1643 (vs, sp)	1395(s,sp)	248	1272 (s sp)
	3381(m, br)	2961 (m, sp)	1601 (vs, sp)	1374(s,sp)	227	
3	3427 (m, br)	3276 (m, sp)	1626 (vs, sp)	1372(s, sp)	254	1272 (vs, sp)
4		3293 (m, sp)	1655 (vs,sp)	1397(s, sp)	258	1260 (vs, sp)
		3202 (m, sp)	1599 (vs,sp)			

Legend: vs = very strong, s = strong, m = medium, sp = sharp, br = broad

Table S2. Hydrogen bond parameters for **1**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry
O7-H7A	0.90	2.57	129	3.217(9)	O6	[x+1, y, z]
O8-H8A	0.90	1.90	169	2.783(7)	O6	[x+1, y, z]
O8-H8B	0.90	2.22	148	3.013(9)	O6	[x+1/2, -y+3/2, -z+1]
O8-H8B	0.90	2.54	151	3.349(7)	O5	[x+1/2, -y+3/2, -z+1]
O9-H9A	0.91	1.93	163	2.814(7)	O3	[x-1/2, -y+1/2, -z+1]
O9-H9B	0.90	2.49	136	3.198(9)	O7	[x-1, y, z]
O9-H9B	0.90	2.58	112	3.036(7)	O2	[x-1, y, z]
C2-H2	0.93	2.39	122	2.991(8)	O5	
C7-H7C	0.97	2.48	135	3.239(7)	O3	[x-1/2,-y+1/2, -z+1]
C12-H12	0.93	2.46	130	3.139(8)	O2	
C12-H12	0.93	2.58	156	3.450(9)	O9	[x+1, y, z]
C17-H17A	0.97	2.58	135	3.345(9)	O9	

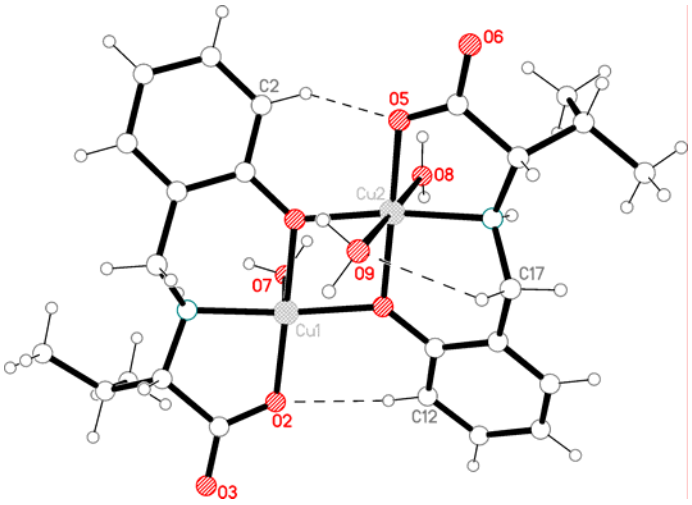

Figure S1. A view showing the intramolecular C-H···O bonds in **1**.

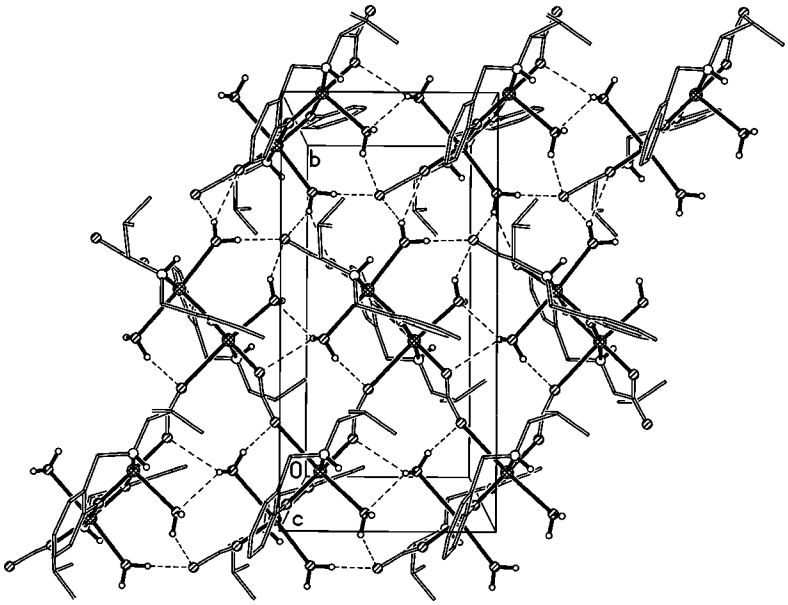

Figure S2. A view of packing structure of **1** in *ab* plane. Only selected hydrogen atoms are shown for clarity.

Table S3. Hydrogen bonding parameters for **2**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry
N2-H2	0.91	2.25	156	3.103(6)	O9	[x-1, y-1, z]
O7-H7A	0.90(3)	2.04(3)	173(4)	2.941(5)	O3	[x, y-1, z]
O7-H7B	0.90(3)	1.91(3)	172(3)	2.801(6)	O8	[1-x, ½-y, z]
O8-H8B	0.91(3)	1.85(3)	170(3)	2.746(7)	O9	[x, y-1, z]
O9-H9A	0.89(1)	2.23(3)	132(3)	2.905(6)	O2	[1+x, y, z]
O9-H9A	0.89(1)	2.05(2)	157(4)	2.897(6)	O3	[1+x, y, z]
C2-H2	0.93	2.31	141	3.090(6)	O5	
C4-H4	0.93	2.55	172	3.475(6)	O6	[1-x, ½+y, 1-z]
C20-H20	0.98	2.46	170	3.429(7)	O6	[-x, ½+y, 1-z]
C23-H23C	0.96	2.53	121	3.142(6)	O6	
C24-H24B	0.96	2.53	122	3.136(7)	O6	

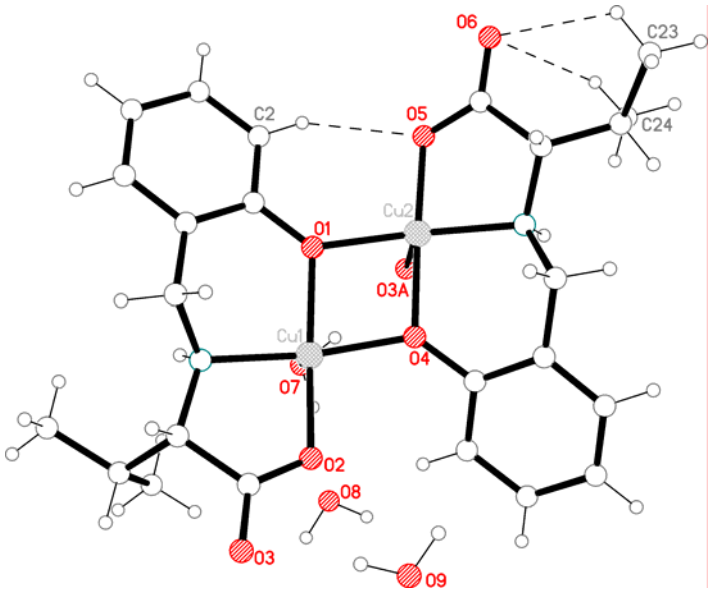

Figure S3. A view showing the intramolecular C-H···O bonds in **2**.

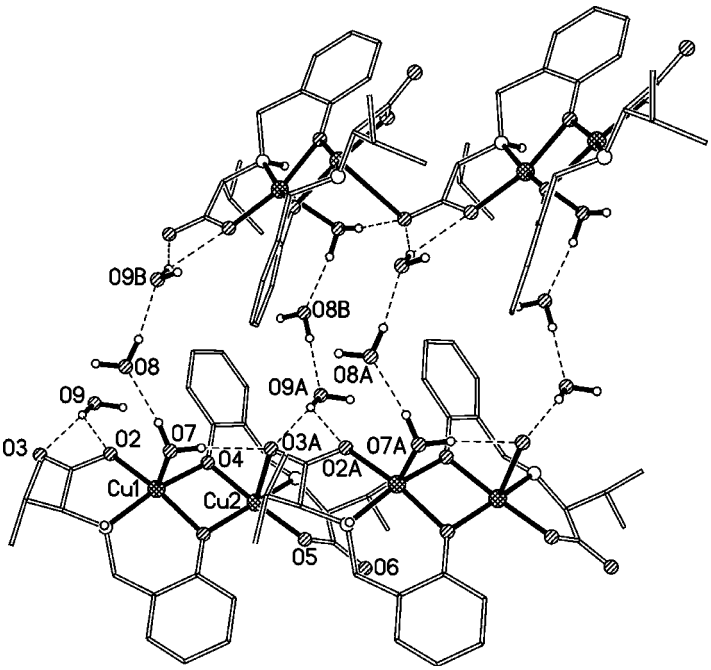

Figure S4. A view of the hydrogen bonding in the double stranded polymeric structure of **2**. Only selected hydrogen atoms are shown for clarity.

Table S4. Hydrogen bond lengths (Å) and angles (°) for **3**.

D-H	d(D-H)	d(H..A)	d(H..A)	d(D…A)	A Symmetry
O13-H13A	0.89(2)	1.99(2)	143(2)	2.760(6)	O9
O13-H13B	0.89(3)	1.93(3)	148(2)	2.724(8)	O1S [-x+1, y-1/2, -z]
O14-H14A	0.92(3)	2.05(3)	144(2)	2.838(6)	O3 [x, y, z+1]
O14-H14B	0.91(3)	2.02(4)	162(2)	2.895(8)	O6
N1-H1	0.91	2.18	162	3.054(6)	O12 [-x+1, y+1/2, -z+1]
N4-H4	0.91	2.35	149	3.160(7)	O2 [x, y, z+1]
O1S-H1S	0.82(2)	2.21(5)	121(2)	2.724(9)	O13 [-x+1, y+1/2, -z]
C2-H2A	0.93	2.51	126	3.137(6)	O5
C7-H7b	0.97	2.56	128	3.239(7)	O13
C11A-H11B	0.96	2.56	116	3.107(7)	O3
C11B-H11F	0.96	2.32	125	2.978(9)	O6
C11C-H11H	0.96	2.52	173	3.478(8)	O5
C12-H12	0.93	2.56	126	3.201(6)	O2
C12A-H12C	0.96	2.49	169	3.433(9)	O12 [1-x, ½+y, 1-z]
C12D-H12K	0.96	2.45	121	3.048(9)	O12
C18-H18	0.98	2.47	131	3.203(7)	O8
C22-H22	0.93	2.37	143	3.155(6)	O11
C27-H27A	0.97	2.60	141	3.403(9)	O2s [1-x, y-1/2, 1-z]
C30-H30	0.98	2.54	101	2.889(7)	O9
C32-H32	0.93	2.49	129	3.159(6)	O8

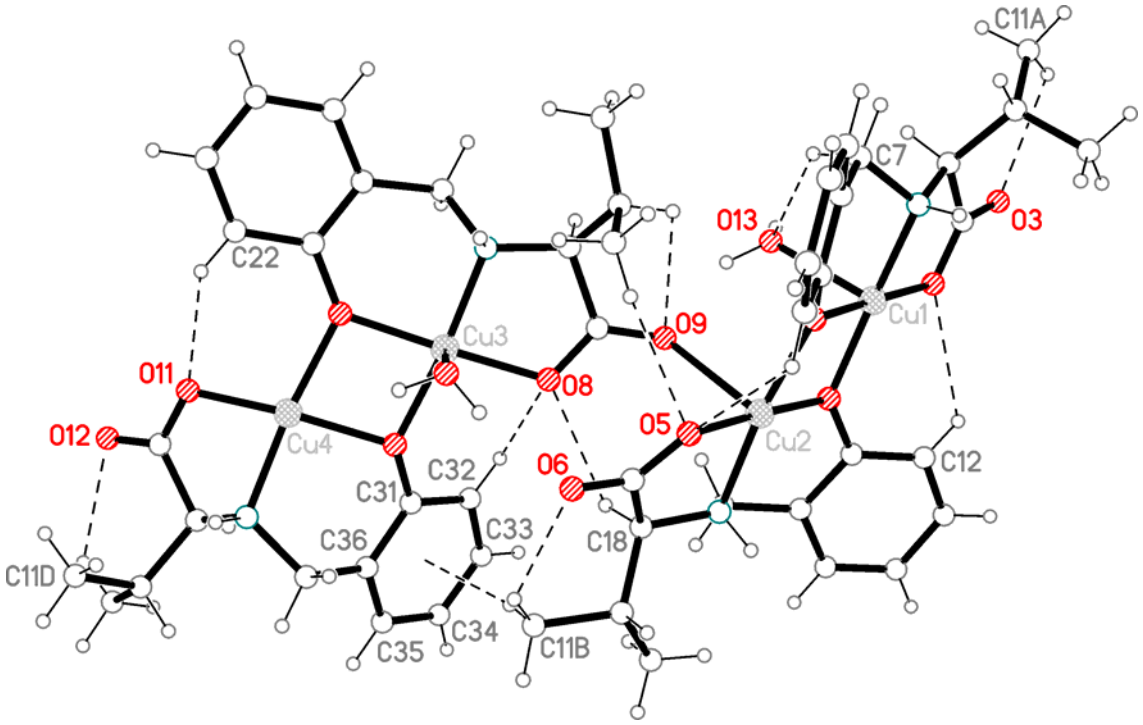

Figure S5. A view showing the intramolecular C-H···O and C-H···π bonds in **3.**

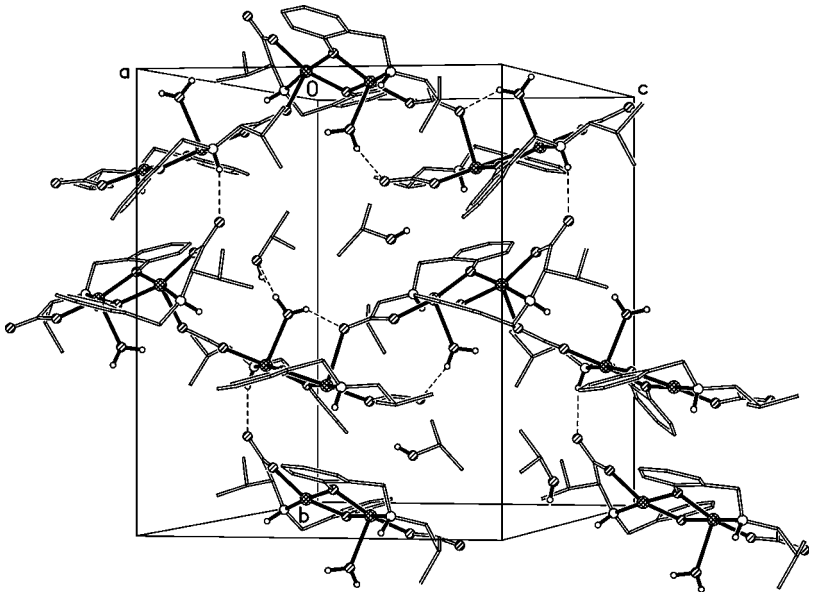

Figure S6. A portion of the structure showing the hydrogen-bonded 1D coordination polymeric structure in **3**. Only selected hydrogen atoms are shown for clarity.

Table S5. Hydrogen bond lengths (Å) and angles (^{o}) for **4**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry
N1-H1	0.91	2.23	163	3.112(7)	O12	[-x+2, y+1/2, -z+1]
N4-H4	0.91	2.33	145	3.121(8)	O2	
O13-H13B	0.91	2.09	135	2.810(9)	O11	[-x+2, y+1/2, -z+1]
O13-H13B	0.91	2.24	148	3.054(9)	O12	[-x+2, y+1/2, -z+1]
O14-H14A	0.90	1.96	171	2.858(7)	O3	
O14-H14B	0.90	2.10	141	2.848(8)	O6	[x, y, z-1]
O1S-H1S	0.82	2.01	149	2.740(9)	O9	[x, y, z+1]
O2SA-H2S1	0.82	2.42	165	3.22(2)	N3	[-x+2, y+1/2, -z]
C2-H2A	0.93	2.48	126	3.122(7)	O5	
C7-H7B	0.97	2.50	129	3.204(7)	O1s	
C12-H12	0.93	2.51	129	3.177(7)	O2	
C11B-H11D	0.96	2.34	126	2.997(9)	O6	
C30-H30	0.98	2.55	103	2.924(9)	O9	
C32-H32	0.93	2.55	129	3.213(7)	O8	
C12A-H12C	0.96	2.39	164	3.32(1)	O12	[2-x, y + ½, 1-z]
C12D-H12K	0.96	2.38	124	3.03(1)	O12	
C18-H18	0.98	2.52	127	3.202(8)	O8	[x, y, 1+z]
C27-H27A	0.97	2.33	138	3.12(2)	O2Sa	[2-x, y + ½, -z]
C11C-H11H	0.96	2.51	160	3.431(9)	O5	[x, y, 1-z]

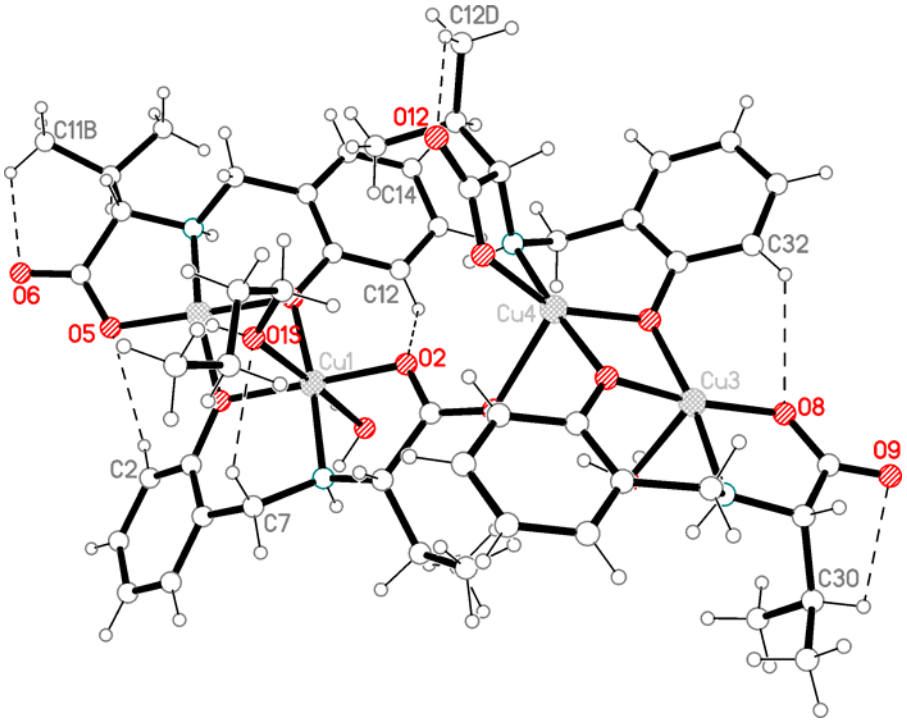

Figure S7. A view showing the intramolecular C-H···O bonds in 4.

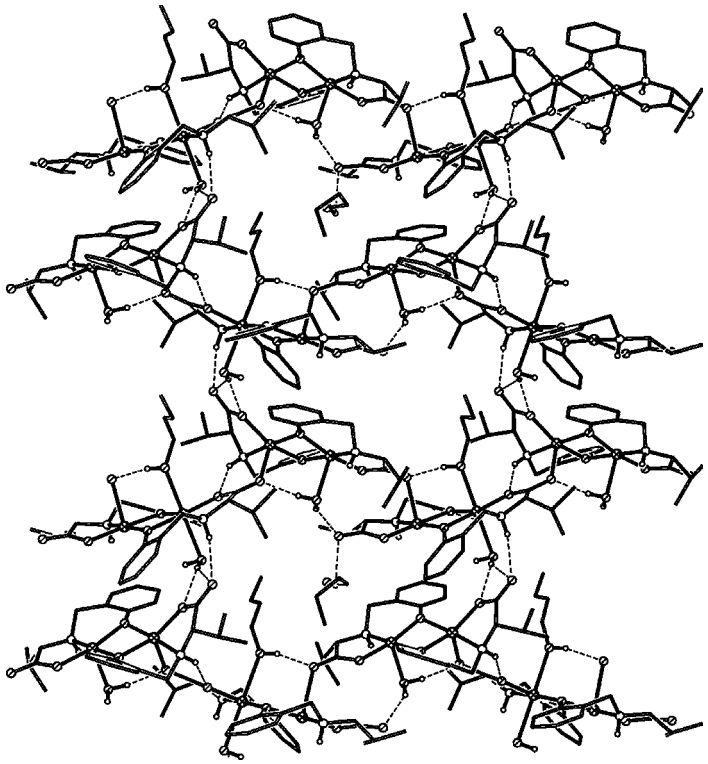

Figure S8. A section of 2D sheet in **4**. Only selected hydrogen atoms are shown for clarity.