Electronic Supplementary Material (ESI) for Dalton Transactions

Stacking of metal chelating rings with π-systems in mononuclear complexes of copper(II) with 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (chloranilic acid) and 2,2'-bipyridine ligands

Supplement

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S1 Crystallographic details

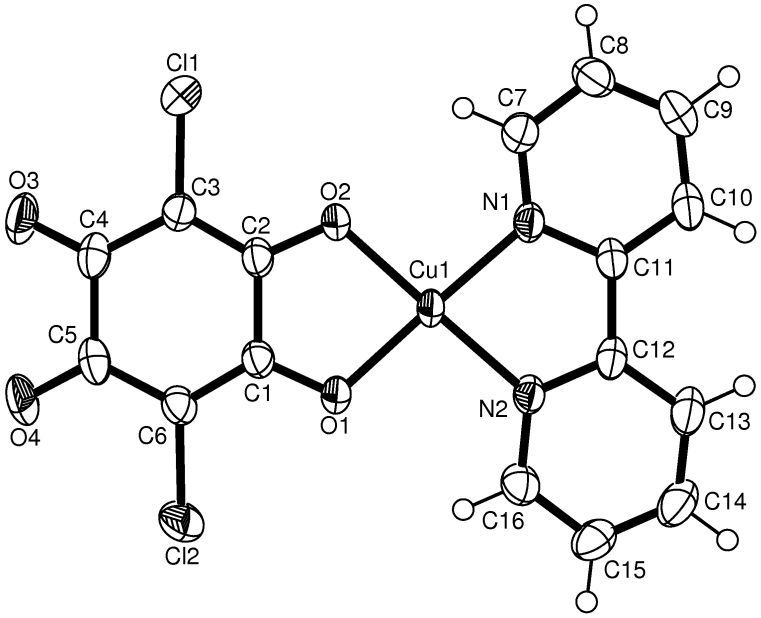

Figure S1 ORTEP-3 drawing of the complex [Cu(CA)(bpy)] (**1b**). Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

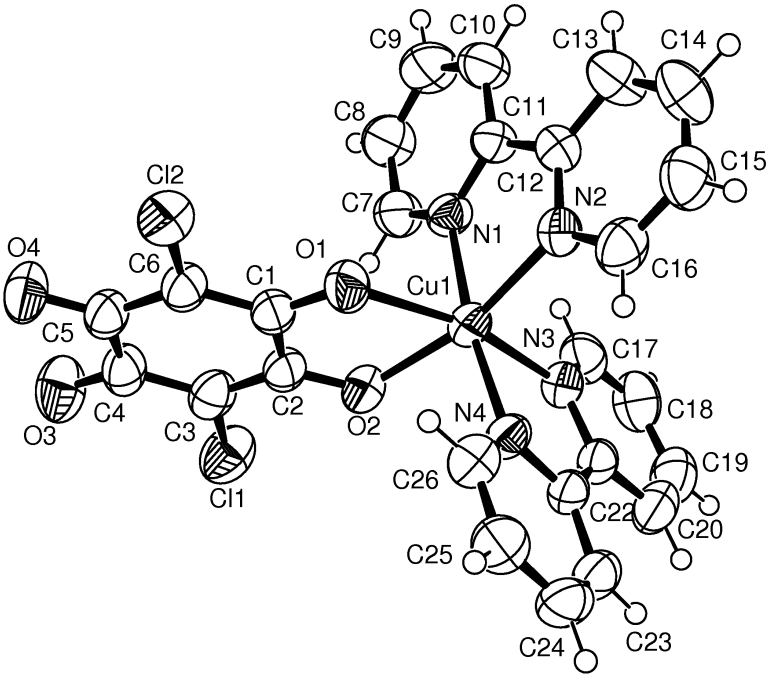

Figure S2 ORTEP-3 drawing of a complex [Cu(CA)$(bpy)_2$] from the dihydrate **4**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

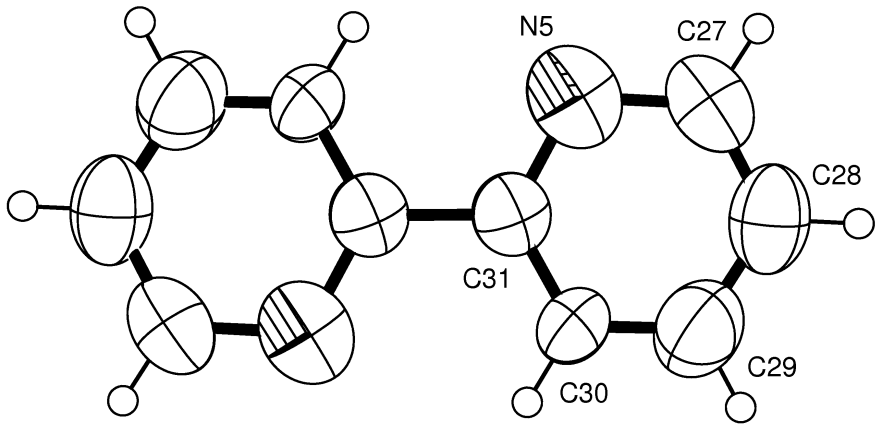

Figure S3 ORTEP-3 drawing the uncoordinated bipy molecule from **3**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii. The crystallographic inversion centre is located at the midpoint of the C31-C31^{i} bond.

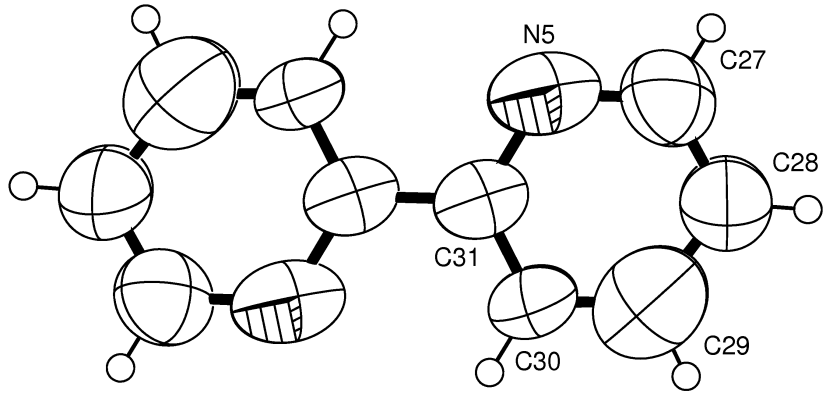

Figure S4 ORTEP-3 drawing the uncoordinated bipy molecule from **4**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii. The crystallographic inversion centre is located at the midpoint of the C31-C31^{i} bond.

Table S1 Geometric parameters of C-H···O hydrogen bonds in **1b**, **3** and **4**.

	D–H / Å	H···*A* / Å	*D*···*A* / Å	*D*–H···*A* / º	Symm. op. on *A*
1b					
C9–H9···O3	0.93	2.49	3.169(4)	130	–1/2+*x*, –1/2+*y*, *z*
C10–H10···O4	0.93	2.39	3.320(4)	176	–1/2+*x*, –1/2+*y*, *z*
C13–H13···O4	0.93	2.54	3.462(4)	173	–1/2+*x*, –1/2+*y*, *z*
C7–H7···O2	0.93	2.56	3.063(4)	115	*x*, *y*, *z*
C16–H16···O1	0.93	2.55	3.056(4)	114	*x*, *y*, *z*
3					
C7–H7···O1	0.93	2.52	3.031(6)	115	*x*, *y*, *z*
C8–H8···O4	0.93	2.48	3.093(8)	124	–*x*, 1–*y*, 1–*z*
C10–H10···O2	0.93	2.44	3.334(7)	161	–*x*, 1–*y*, –*z*
C23–H23···O5	0.93	2.38	3.205(9)	147	1+*x*, 1+*y*, –*z*
C26–H26···O2	0.93	2.46	3.123(8)	128	*x*, *y*, *z*
4					
C7–H7···O2	0.93	2.48	3.037(10)	118	*x*, *y*, *z*
C9–H9···O6	0.93	2.46	3.146(12)	131	1+*x*, *y*, *z*
C14–H14···O5	0.93	2.39	3.147(14)	142	–1+*x*, 1+*y*, *z*
C15–H15···O6	0.93	2.59	3.406(12)	147	*x*, *y*, *z*
C23–H23···O2	0.93	2.49	3.342(8)	153	1–*x*, –*y*, 1–*z*
C25–H25···O5	0.93	2.59	3.433(12)	150	2–*x*, –*y*, *z*
C26–H26···O6	0.93	2.58	3.401(10)	148	1–*x*, 1–*y*, –*z*

Table S2 Crystallographic, data collection and refinement details of the structure **1b**.

Compound	**1b**
Empirical formula	$C_{16}H_8Cl_2CuN_2O_4$
Formula wt. / g mol^{-1}	426.68
Crystal dimensions / mm	0.22 x 0.15 x 0.11
Space group	*C* 2/*c*
a / Å	25.0006(6)
b / Å	7.4597(2)
c / Å	17.2095(4)
α / °	90
β / °	104.509(3)
γ / °	90
Z	8
V / Å^3	3107.16(13)
D_{calc} / g cm^{-3}	1.824
μ / mm^{-1}	5.395
Θ range / °	3.65 – 65.11
T / K	293(2)
Radiation vawelength	1.54179 (Cu*K*α)
Diffractometer type	Xcalibur Nova
Range of *h*, *k*, *l*	$-29 < h < 28$; $-7 < k < 8$; $-19 < l < 7$
Reflections collected	4763
Independent reflections	2430
Observed reflections ($I \geq 2\sigma$)	2129
Absorption correction	Multi-scan
R_{int}	0.0215
R (F)	0.0360
R_w (F^2)	0.1057
Goodness of fit	1.067
H atom treatment	Constrained
No. of parameters	227
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.811; -0.624

S2 IR spectra

IR data (KBr, cm^{-1}):

1a $\tilde{\nu}$ = 1643 (m), 1629 (sh), 1605 (w), 1555 (s), 1538 (vs), 1521 (vs), 1474 (m), 1449 (m), 1366(s), 1318 (m), 1301 (sh), 1269 (w), 1256 (w), 1244 (w), 1174 (w), 1159 (m), 1124 (w), 1106 (w), 1073 (w), 1056 (w), 1037 (m), 1023 (w), 999 (m), 846 (s), 775 (m), 729 (m), 669 (w), 653 (w), 610 (w), 601 (sh), 569 (m), 445 (w), 417 (w).

1b $\tilde{\nu}$ = 1647 (m), 1629 (w), 1605 (w), 1538 (s), 1523 (vs), 1514 (s), 1474 (m), 1448 (m), 1366 (s), 1317 (m), 1305 (m), 1268 (w), 1254 (w), 1167 (sh), 1123 (w), 1109 (w), 1074 (w), 1055 (w), 1036 (m), 1023 (w), 999 (m), 846 (s), 774 (m), 730 (m), 669 (w), 653 (w), 601 (m), 572 (m), 521 (w), 419 (w).

2 $\tilde{\nu}$ = 3423 (m, br), 1647 (m), 1626 (w), 1605 (m), 1538 (s), 1523 (vs), 1513 (s), 1474 (m), 1448 (m), 1372 (s), 1317 (m), 1306 (sh), 1268 (w), 1254 (w), 1226 (sh), 1167 (w), 1159 (w), 1123 (w), 1108 (w), 1074 (w), 1055 (w), 1036 (m), 1023 (w), 1012 (m), 999 (m), 846 (s), 775 (m), 730 (m), 668 (w), 653 (m), 600 (m), 572 (m), 520 (w), 419 (w).

3 and 4 $\tilde{\nu}$ = 3424 (m, br), 1648 (m), 1628 (w), 1605 (m), 1511 (vs), 1474 (m), 1448 (m), 1369 (s), 1317 (m), 1306 (sh), 1268 (w), 1253 (w), 1168 (w), 1158 (w), 1123 (w), 1108 (w), 1055 (w), 1036 (w), 1102 (w), 999 (w), 846 (s), 775 (m), 730 (m), 668 (w), 653 (w), 601 (m), 572 (m), 520 (w), 420 (w).

S3 Additional data on the compound 1b

Preparation of [Cu(CA)(bpy)] (1b). After mixing a methanol solution (4 mL) of $CuCl_2 \cdot 2H_2O$ (17.6 mg; 0.1 mmol) with a methanol solution (4 mL) of 2,2'-bipyridine (16.1 mg; 0.1 mmol), reaction mixture became cloudy and a green precipitate immediately formed. It was removed by filtration and the clear solution was carefully laid above an aqueous solution (5 mL) of H_2CA (21.1 mg; 0.1 mmol) into a test tube. Deep dark violet, almost black, prismatic single crystals with well-developed {100} planes were formed after few weeks. The yield was ~96%. According to the results of X-ray structure analysis, **1b** is identical to the previously reported structure of (2,2'-bipyridyl-κ^2N,N')(chloranilato-κ^2O,O')-copper(II)[48].

Table S3 Geometry of the coordination sphere of Cu(II) in **1b** (Å, °).

	1b*
Cu1 - O1	1.921 (2)
Cu1 - O2	1.920 (2)
Cu1 - N1	1.950(2)
Cu1 - N2	1.956 (2)
O1 - Cu1 - O2	84.80 (9)
O1 - Cu1 - N2	96.13(9)
O1 - Cu1 - N1	177.4 7(10)
O2 - Cu1 - N2	178.98 (10)

Table S4 Geometric parameters of the $\pi\cdots\pi$ interactions involving five-membered metal chelating rings and aromatic rings of the ligands in **1b**.

$\pi\cdots\pi$	Cg[a]···Cg / Å	α[b]	β[c]	Cg···plane(Cg2) / Å	Offset / Å	Symm. op. on Cg2
Cu1→O2···Cu1→O2	3.4925(15)	0	19.65	3.2891(10)	1.174	1–*x*, 1–*y*, 2–*z*
Cu1→O2···C1→C6	3.9698(16)	1.77(13)	34.57	3.2854(10)	1.86[d]	1–*x*, 1–*y*, 2–*z*
Cu1→N2···C1→C6	3.9358(16)	2.31(13)	31.34	3.3316(10)	1.73[d]	1–*x*, –*y*, 2–*z*
Cu1→N2···C1→C6	3.6087(16)	2.31(13)	25.63	3.2002(10)	1,38[d]	1–*x*, 1–*y*, 2–*z*
N1→C11···C1→C6	3.4230(17)	3.57(14)	8.43	3.4106(12)	0.50[d]	1–*x*, –*y*, 2–*z*

[a] Cg = centre of gravity of the interacting ring.

[b] α = angle between planes of two interacting rings.

[c] β = angle between Cg···Cg line and normal to the plane of the first interacting ring.

[d] Offset can be calculated only for the strictly parallel rings (α = 0.00°). For slightly inclined rings (α ≤ 3°) an approximate value is given.