σ-aromaticity in dinuclear copper(II) complexes: novel interaction between perchlorate anion and σ-aromatic [Cu_2X_2] (X = N or O) core

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Materials and Methods:

Materials and reagents. The starting materials for the synthesis of the ligands like acetylacetone (Merck), hydrazine hydrate (Rankem), formalin (Merck), are of reagent grade and used as received. Copper(II) perchlorate hexahydrate (Loba Chemie, India) was used for the preparation of complexes. Solvents like methanol, ethanol, chloroform, diethylether, acetonitrile (Merck, India) were of reagent grade and dried before use.

Synthesis of complexes.

Synthesis of [Cu_2(3,5-dimethyl-pyrazole)$_4$(1,1-N_3)$_2$(ClO_4)$_2$] (1).

0.50 mmol of $Cu(ClO_4)_2$•$6H_2O$ was solubilized in MeOH (15 ml) and stirred for few minutes and then 3,5-dimethyl-pyrazole (1.0 mmol) and sodium azide (1.50 mmol) in 1:2:3 mole ratio in MeOH were added and the solution turns into dark green. After six hours of stirring, the solution was filtered and kept in refrigerator. The green complexes thereby obtained were recrystallized from MeCN in presence of added perchlorate anion to get single crystals suitable for X-ray diffraction. Yield 60%, Anal. Calcd for $C_{20}H_{28}Cl_2Cu_2N_{14}O_8$,$CH_4$ O(M.W. 822.61)**:** C, 29.18; H, 3.40; N, 23.83. Found: C, 29.60; H, 3.78; N 23.03.

Synthesis of [Cu_2(3,5-di-methyl-pyrazole)$_2$(N-hydroxymethyl-3,5-dimethyl-pyrazole)$_2$ (ClO_4)$_2$] (2). 0.50 mmol of $Cu(ClO_4)_2$•$6H_2O$ in MeOH (15 ml) was reacted with 3,5-dimethyl-pyrazole (0.50 mmol) and N-hydroxymethyl-3,5-dimethyl-pyrazole (0.50 mmol) in 1:1:1 mole ratio in MeOH and the solution that turns into dark green was stirred for six hours and filtered and kept in refrigerator. The green complexes thereby obtained were recrystallized from MeCN in presence of added perchlorate anion to get single crystals suitable for X-ray diffraction. Yield 60%, Anal. Calcd for $C_{22}H_{34}Cl_2Cu_2N_8O_{10}$(M. W.768.57)**:** C, 34.35; H, 4.42; N, 14.57. Found: C, 34.60; H, 4.78; N 14.23.

DFT Calculations.

Geometries of complexes **1A** and **2** were fully optimized using B3LYP functional[1] as implemented in Gaussian 03[2] suit programs starting from the X-ray crystallographic structures and using LanL2DZ[3] effective core potentials and basis functions for the metal atom, Cu and 6-31+G(d) basis set for all others atoms. The nature of all the stationary points was confirmed by carrying out a normal mode analysis, where all vibrational frequencies were found to be positive.

X-Ray Crystallography. Single crystal X-ray data of **1** and **2** were collected at 296 and 120 K respectively on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073AÅ). Data integration and reductions were processed with SAINT+ software. Structures were solved by the direct method and then refined on F^2 by the full matrix least square technique with SHELX-97 software.[4] The extent of aromaticity or antiaromaticity of the four membered rings formed by the two Cu atoms is obtained from the calculated nucleus independent chemical shift (NICS) at the ring center, [NICS(0)] and at 1 Å above/below it, [NICS(1)], using gauge individual atomic orbital (GIAO) methods at B3LYP//LanL2DZ/6-31+G(d) level. We have also performed single point B3LYP//LanL2DZ/6-31+G(d) calculations for **1A** and **2** to get the energy for the interaction between σ-aromatic center and ClO_4^- anion.

References

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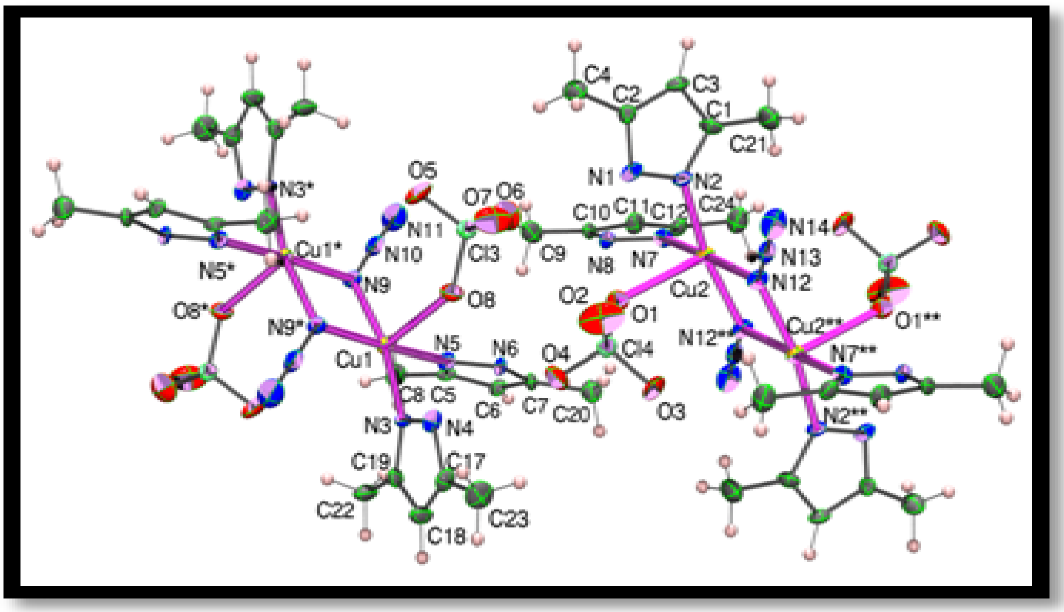
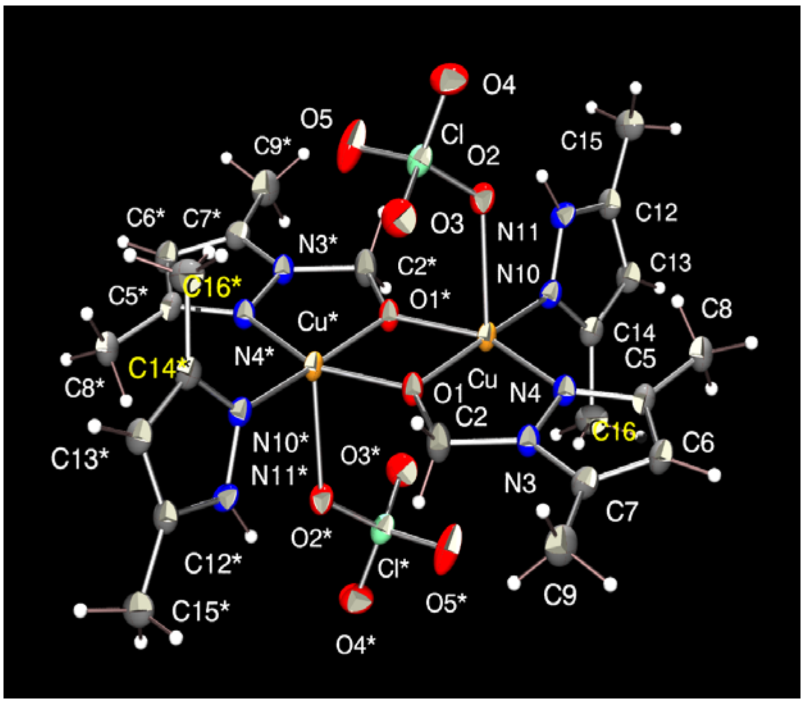
4. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. *Crystallogr.*, 2008, **64**, 112.

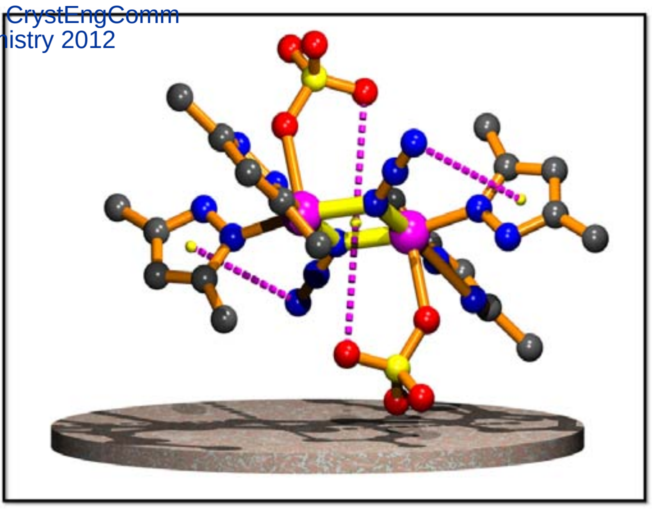
Crystal Structure.



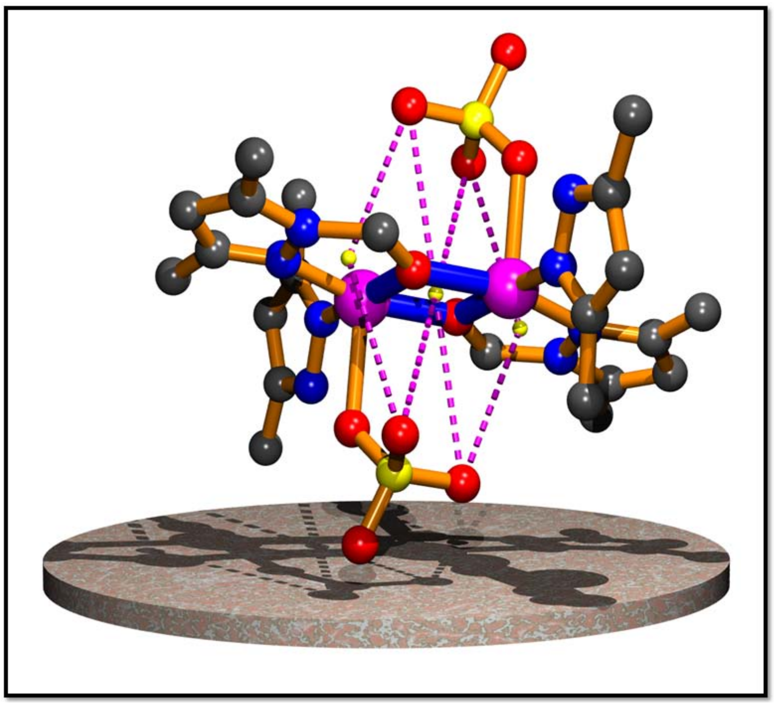
SUP Fig. S1 (a). ORTEP view of complex **1** with 30% thermal ellipsoid probability.



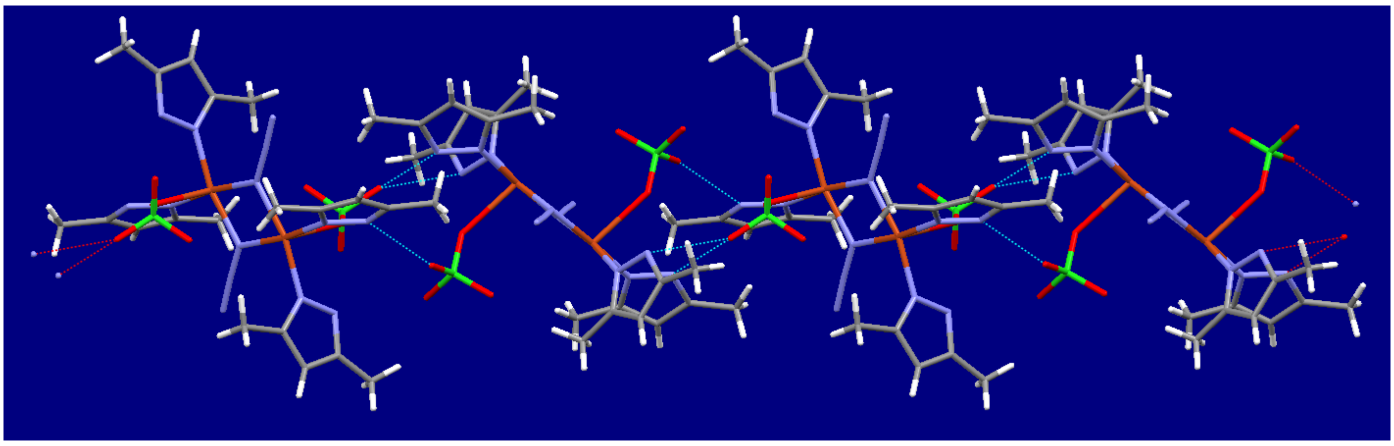
SUP Fig. S1 (b). ORTEP view of complex **1** with 30% thermal ellipsoid probability.



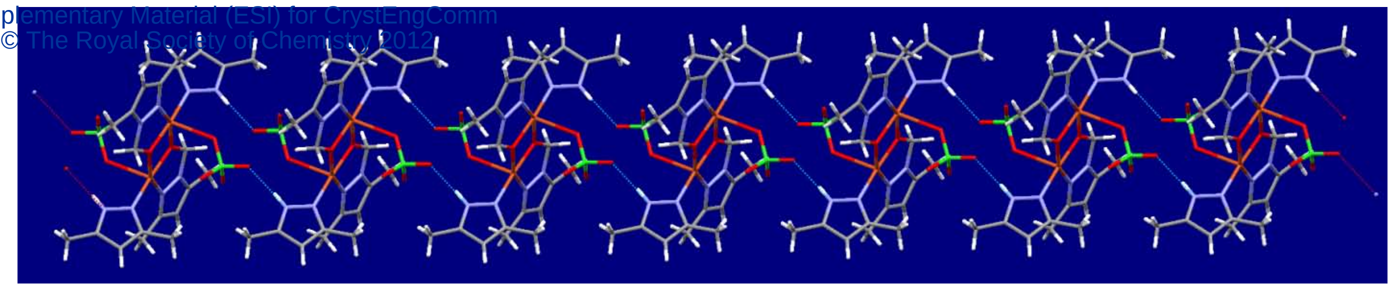
SUP Fig. S1c. ClO_4^-....σ and azide…π interaction in complex **1A**



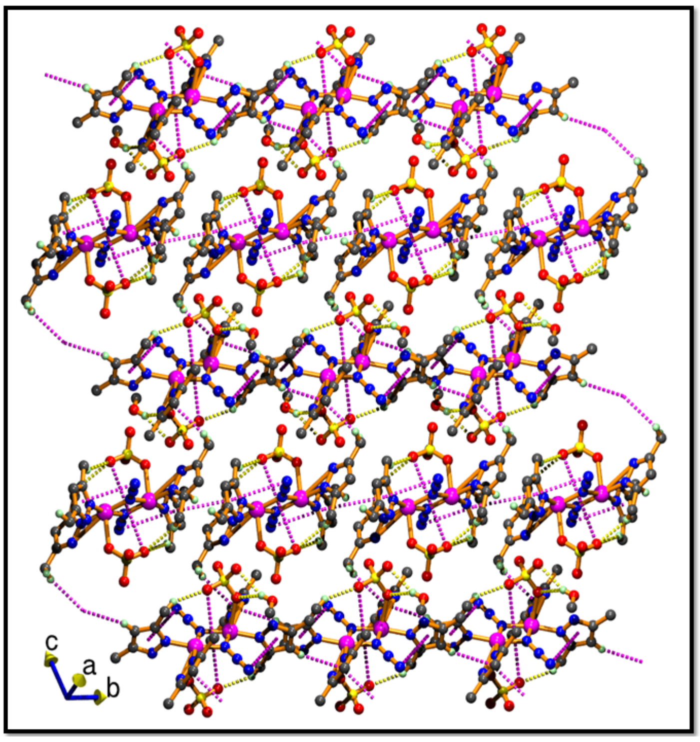
SUP Fig. S1d. ClO_4^-....σ and ClO_4^-....π (metallacycle) interactions in complex **2**



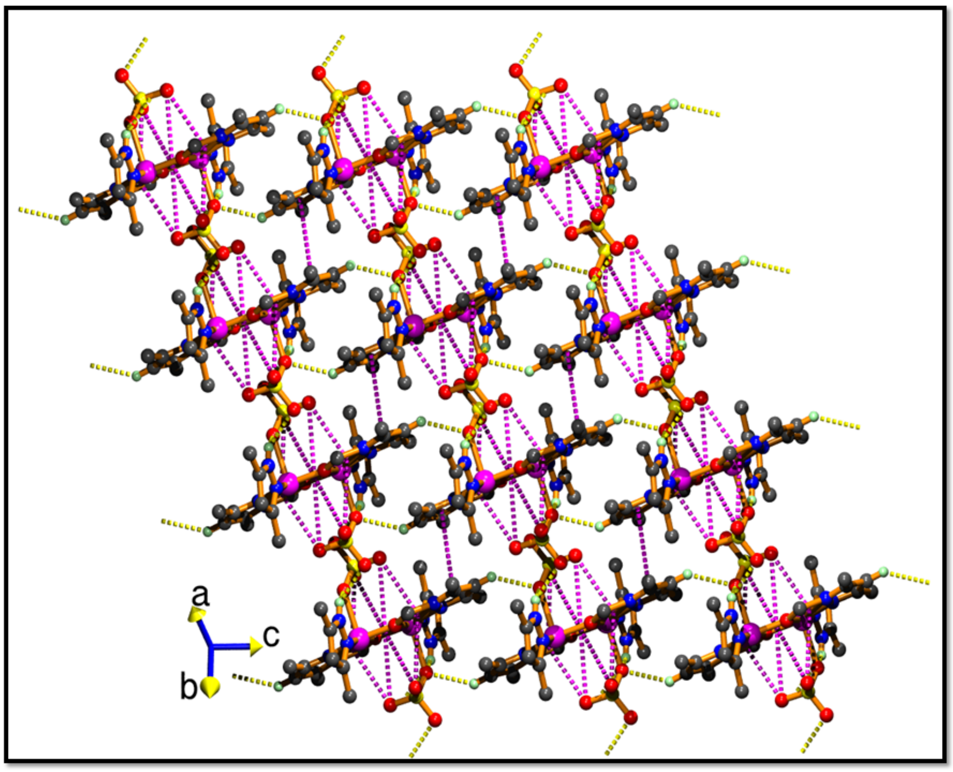
SUP Fig. S2a. N-H(Pyrazole)...O-ClO_3 and O(MeOH)....N-H (pyrazole) H-bonding interactions in **1**.



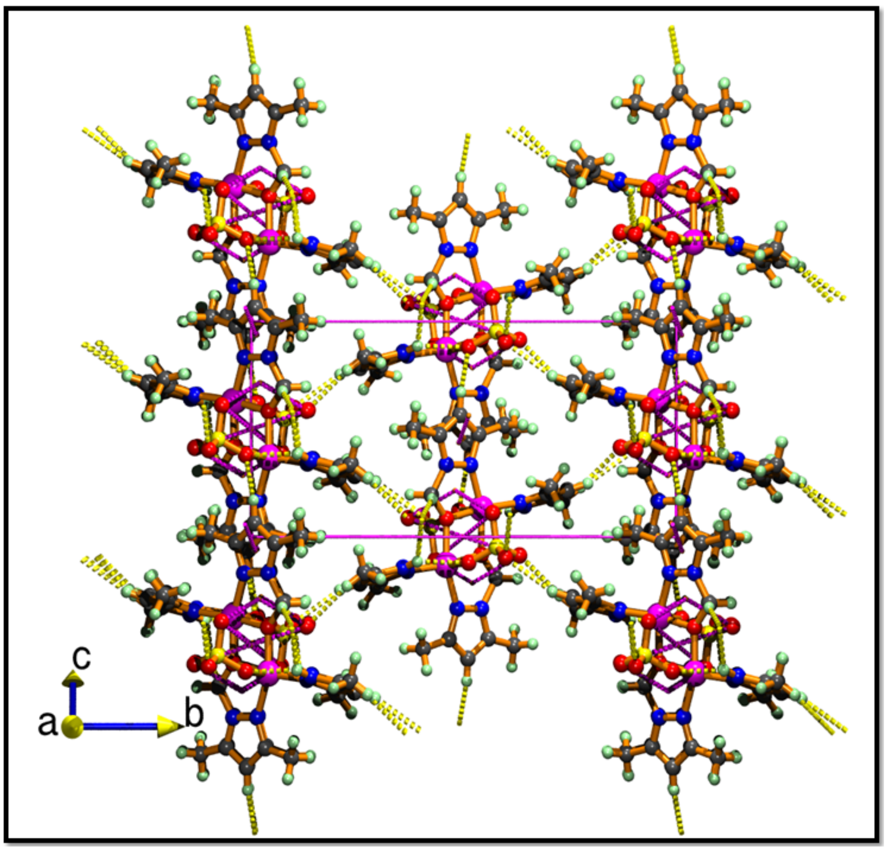
SUP Fig. S2b. N-H(Pyrazole)...O-ClO$_3$ H-bonding interactions in complex **2**.



Sup Fig S2c. CH…pi interaction and hydrogen bonding in **1** leads to 2D supramolecular sheet**.**



SUP Fig S2d: Hydrogen bonding and pi-pi interaction in **2** leads to supramolecular sheet.



SUP Fig S2e: Packing of supramolecular sheets in **2** through hydrogen bonding.

SUP Table S1. Some important Bond Distances (Ǻ) and bond angles of complexes **1** and **2**.

1A	**Complex 1A** **Bond distances(Å)**
Cu1 -O8	2.372(6) [2.07]]
Cu1 -N3	1.991(8) [2.258]
Cu1 -N5	1.995(8) [2.056]
Cu1 -N9	1.965(7) [2.105]
Cu1 -N9_a	1.973(8) [2.037]
Cu1...Cu1	3.087 [3.287]
	Bond Angles (°)
N3 -Cu1 -N5	92.0(3) [75.8]
O8 -Cu1 -N3	88.9(3) [98.37]
O8 -Cu1 -N5	87.5(3) [98.6]
O8 -Cu1 -N9_a	95.9(3) [94.5]
N3 -Cu1 -N9_a	94.1(3) [101.5]
N5 -Cu1 -N9	96.7(3) [93.8]
N5 -Cu1 -N9_a	173.0(3) [166.8]
N3 -Cu1 -N5	92.0(3) [75.8]
1B	Bond Distances**(Å)**
Cu2 -N12_b	1.987(7)
Cu2 -N2	2.003(7)
Cu2 -N7	1.971(8)
Cu2 -O1	2.406(6)
Cu2 -N12	1.956(8)
Cu1...Cu1	3.119
	Bond Angles(°)
O1 -Cu2 -N12	100.1(3)
O1 -Cu2 -N12_b	98.1(3)
N2 -Cu2 -N7	94.6(3)
N2 -Cu2 -N12	92.6(3)
N2 -Cu2 -N12_b	167.0(3)
N7 -Cu2 -N12	171.2(3)
N7 -Cu2 -N12_b	97.0(3)
N12 -Cu2 -N12_b	75.4(3)
O1 -Cu2 -N2	88.7(3)
O1 -Cu2 -N7	85.1(3)

	Complex 2
	Bond distances (Å)
Cu -O1	1.9159(16) [1.967]
Cu -O2	2.3909(17) [2.425]
Cu -N4	1.9695(18) [2.05]
Cu -N10	1.9586(18) [2.01]
Cu -O1_a	1.9352(15) [1.997]
Cu...Cu	3.029 [3.179]
	Bond Angles (°)
O1 -Cu -O2	97.52(6) [104.3]
O1 -Cu -N4	82.04(7) [80.3]
O1 -Cu -N10	171.44(7) [166.7]
O1 -Cu -O1_a	76.29(6) [73.3]
O2 -Cu -N4	100.09(7) [102.3]
O2 -Cu -N10	88.61(7) [85.8]
O1_a -Cu -O2	88.35(6) [99.2]
N4 -Cu -N10	102.84(7) [106.2]
O1_a -Cu -N4	157.62(7) [149.4]
O1_a -Cu -N10	98.02(7) [96.9]

SUP Table S2: Hydrogen Bond table (Å)

	Complex – 1				
O1S-H1S···O7	0.82	2.36	3.151(13)	162	.
O1S-H1S···O8	0.82	2.48	3.130(12)	138	.
C9-H9C···O6	0.96	2.57	3.401(13)	145	.
C21-H21C···O3	0.96	2.45	3.267(13)	143	2-x,2-y,2-z
C22-H22A···O5	0.96	2.49	3.360(12)	151	1-x,1-y,1-z
C24-H24C···O3	0.96	2.56	3.378(13)	143	2-x,2-y,2-z
	Complex – 2				
D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	<DH···A(°)	symmetry
N11-H11···O2	0.88	2.37	2.928(2)	122	.
N11-H11···O4	0.88	2.28	2.936(3)	131	1-x,-y,1-z
C2-H2A···O4	0.99	2.56	3.529(3)	166	-1+x,y,z
C6-H6···O2	0.95	2.54	3.273(3)	134	-x,-y,-z
C13-H13···O4	0.95	2.54	3.458(3)	162	1/2-x,1/2+y,1/2-z
C15-H15B···O3	0.98	2.51	3.450(3)	160	1/2-x,1/2+y,1/2-z