Electronic Supplementary Information

Diminishing accessibility of electrophilic nickel(II) centres on incorporating methyl spacer in the pendant side arm of a series of hetero-trinuclear nickel(II)/sodium complexes: DFT study using homodesmotic equation

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Table S1: Selected bond angles (°) of complexes **1**-**4**.

Bond angle	Complex 1	Complex 2	Complex 3	Complex 4
O(1)–Ni(1)–O(2)	81.81(1)	81.27(3)	84.29(14)	83.80(18)
O(1)–Ni(1)–N(1)	91.49(3)	92.20(2)	93.51(1)	92.50(2)
O(1)–Ni(1)–N(2)	158.45(4)	166.90(2)	166.47(2)	169.12(19)
O(1)–Ni(1)–N(5)	102.00(3)	98.20(2)	---	---
O(2)–Ni(1)–N(1)	171.71(4)	153.60(2)	167.63(17)	168.72(19)
O(2)–Ni(1)–N(2)	90.46(4)	89.60(4)	93.81(15)	93.90(2)
O(2)–Ni(1) –N(5)	100.40(3)	113.90(3)	---	---
N(1)–Ni(1)–N(2)	94.10(2)	93.90(2)	91.10(17)	91.60(2)
N(1)–Ni(1)–N(5)	85.70(3)	92.00(3)	---	---

N(2)–Ni(1)–N(5)	99.20(3)	94.20(2)	---	---
O(5)–Ni(2)–O(6)	82.11(1)	80.90(2)	84.04(15)	83.83(17)
O(5)–Ni(2)–N(3)	91.06(3)	92.60(2)	94.24(18)	93.0(2)
O(5)–Ni(2)–N(4)	174.88(4)	170.00(2)	167.9(2)	169.4(2)
O(6)–Ni(2)–N(3)	172.48(4)	167.20(2)	168.74(18)	169.5(2)
O(6)–Ni(2)–N(4)	92.80(2)	92.60(3)	93.1(2)	93.30(2)
N(3)–Na(1)–N(4)	94.10(2)	95.20(2)	---	---
O(1)–Na(1)–O(2)	62.21(13)	62.66(15)	61.58(12)	61.17(14)
O(1)–Na(1)–O(3)	65.76(14)	61.30(1)	63.05(12)	62.24(15)
O(1)–Na(1)–O(4)	124.67(15)	126.37(3)	120.26(14)	123.07(16)
O(1)–Na(1)–O(5)	139.65(15)	128.30(2)	130.84(14)	144.07(15)
O(1)–Na(1)–O(6)	142.82(3)	142.63(2)	145.45(14)	129.06(15)
O(1)–Na(1)–O(7)	84.47(1)	81.55(4)	86.30(13)	93.70(17)
O(1)–Na(1)–O(8)	86.58(1)	97.21(4)	90.43(13)	89.72(14)
O(2)–Na(1)–O(3)	127.02(2)	123.87(3)	122.35(13)	120.80(17)
O(2)–Na(1)–O(4)	62.47(14)	64.22(15)	61.13(13)	62.80(15)
O(2)–Na(1)–O(5)	128.51(15)	141.29(2)	146.99(14)	135.35(15)
O(2)–Na(1)–O(6)	140.27(2)	141.60(2)	129.56(14)	143.69(15)
O(2)–Na(1)–O(7)	80.38(1)	88.99(1)	92.55(14)	85.21(17)
O(2)–Na(1)–O(8)	98.84(1)	89.37(4)	84.27(14)	85.50(14)
O(3)–Na(1)–O(4)	165.59(2)	167.50(2)	176.53(14)	171.98(18)
O(3)–Na(1)–O(5)	87.00(15)	77.41(1)	84.43(12)	86.72(16)
O(3)–Na(1)–O(6)	89.46(2)	89.26(3)	90.51(13)	87.49(16)
O(3)–Na(1)–O(7)	85.54(3)	82.32(4)	98.78(14)	82.38(19)
O(3)–Na(1)–O(8)	87.25(3)	100.20(2)	81.33(15)	110.20(16)
O(4)–Na(1)–O(5)	78.83(14)	90.60(15)	92.31(12)	86.20(15)
O(4)–Na(1)–O(6)	85.56(2)	87.14(2)	86.87(14)	92.41(15)
O(4)–Na(1)–O(7)	85.77(2)	88.96(4)	80.69(14)	91.03(19)
O(4)–Na(1)–O(8)	102.57(3)	89.00(2)	99.43(16)	76.67(14)
O(5)–Na(1)–O(6)	59.23(14)	56.97(2)	61.47(12)	61.32(14)
O(5)–Na(1)–O(7)	63.30(14)	6.35(1)	62.11(13)	62.75(16)
O(5)–Na(1)–O(8)	122.88(15)	120.74(3)	121.59(14)	119.51(15)
O(6)–Na(1)–O(7)	122.49(1)	119.12(3)	121.37(13)	123.55(17)
O(6)–Na(1)–O(8)	63.93(15)	63.83(3)	62.35(13)	62.03(13)
O(7)–Na(1)–O(8)	170.24(4)	176.33(4)	176.25(14)	167.04(19)

IR spectra

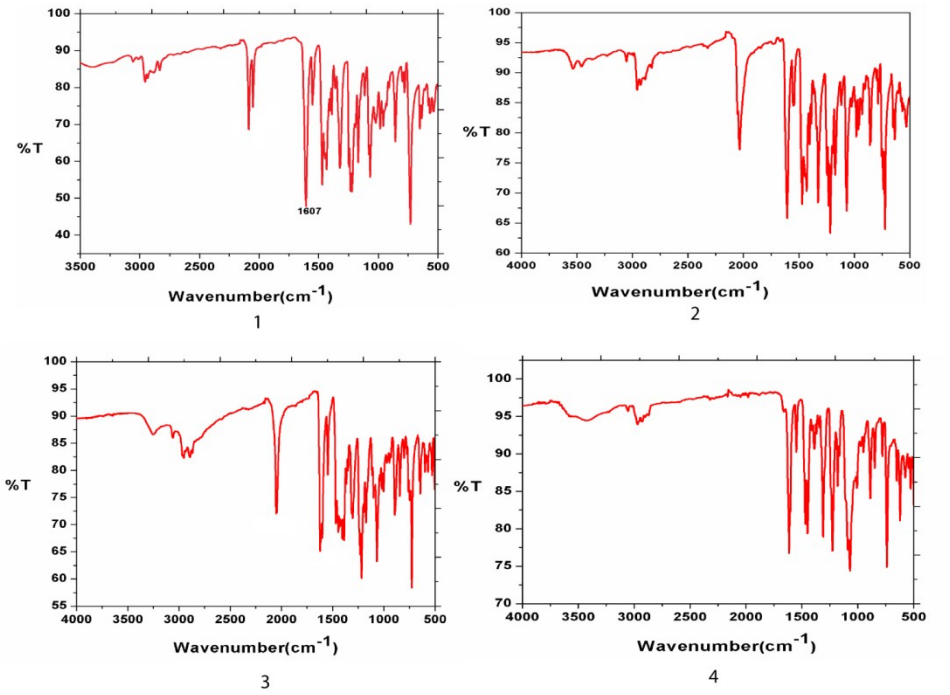

Fig. S1: IR spectrum of complexes 1-**4**

UV-VIS spectra

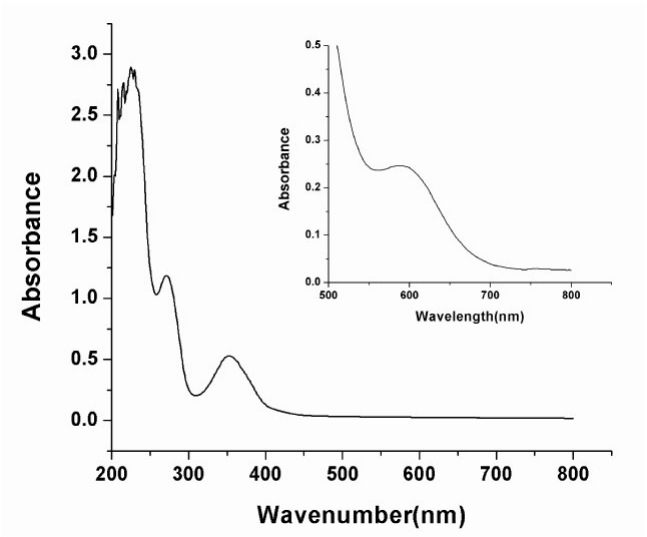

Fig. S2: Electronic spectrum of complex **1**. Inset shows the selected small range (500-800 nm) electronic spectrum of the complex.

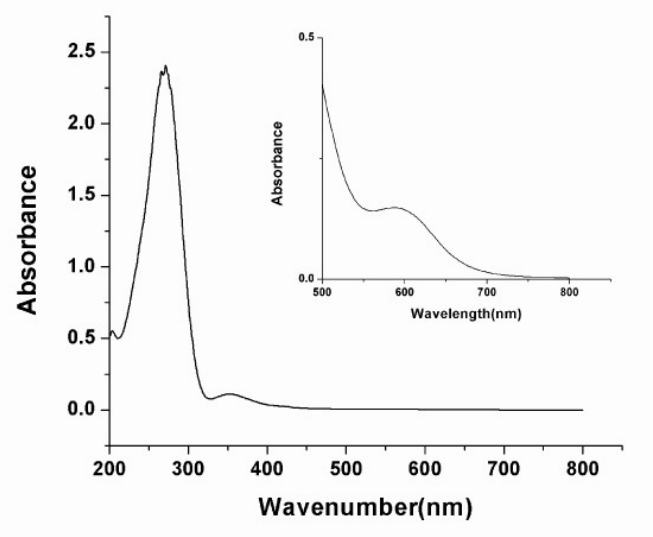

Fig. S3: Electronic spectrum of complex **2**. Inset shows the selected small range (500-800 nm) electronic spectrum of the complex.

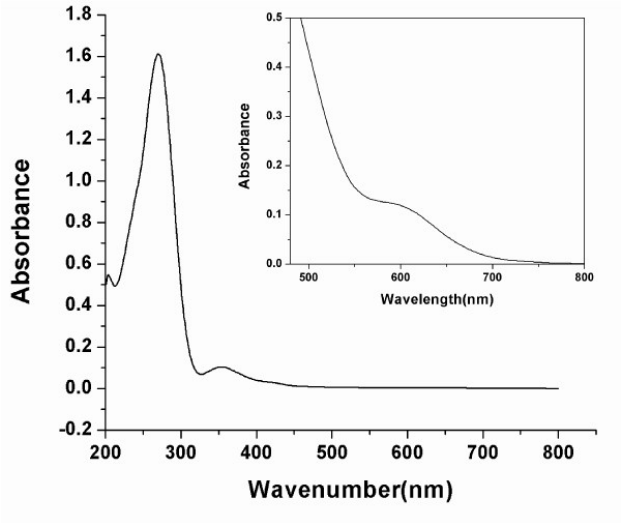

Fig. S4: Electronic spectrum of complex **3**. Inset shows the selected small range (500-800 nm) electronic spectrum of the complex.

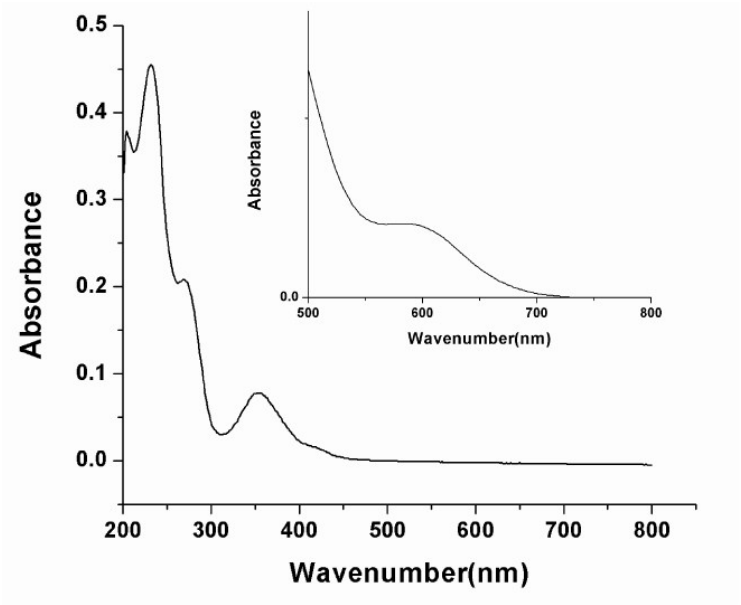

Fig. S5: Electronic spectrum of complex **4**. Inset shows the selected small range (500-800 nm) electronic spectrum of the complex.

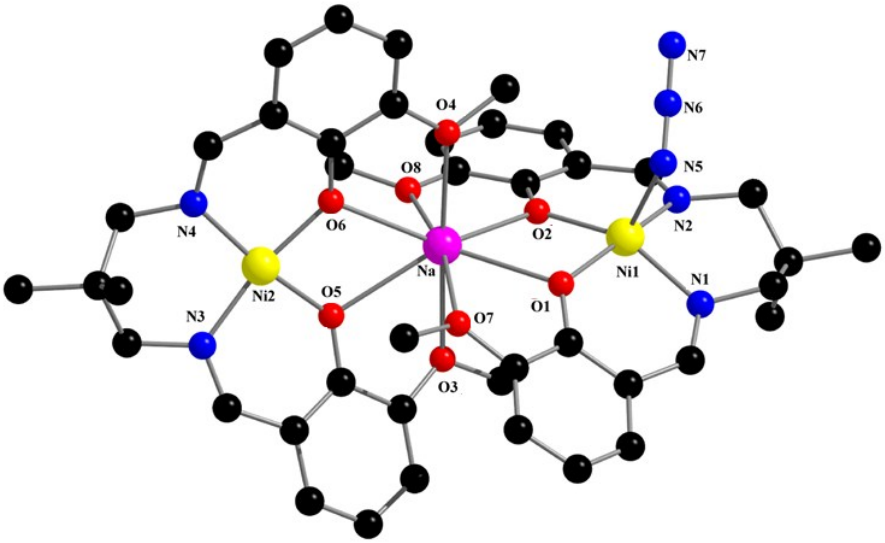

Fig. S6: Perspective view of the complex **2** with selective atom-numbering scheme. Non coordinated carbon-dioxide molecule has been omitted for clarity.

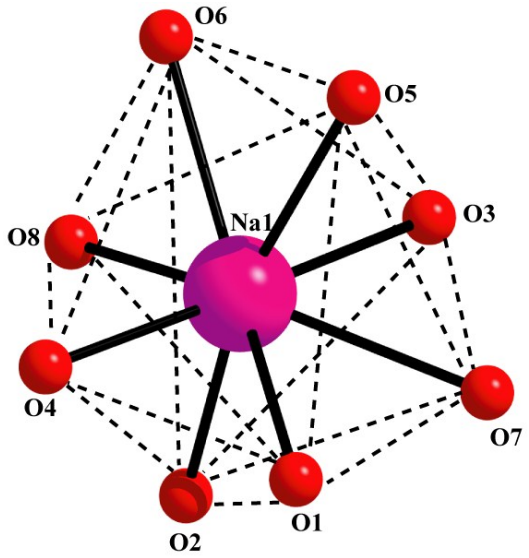

Fig. S7: Trigonal dodecahedral geometry of sodium(I) in complex **2**.

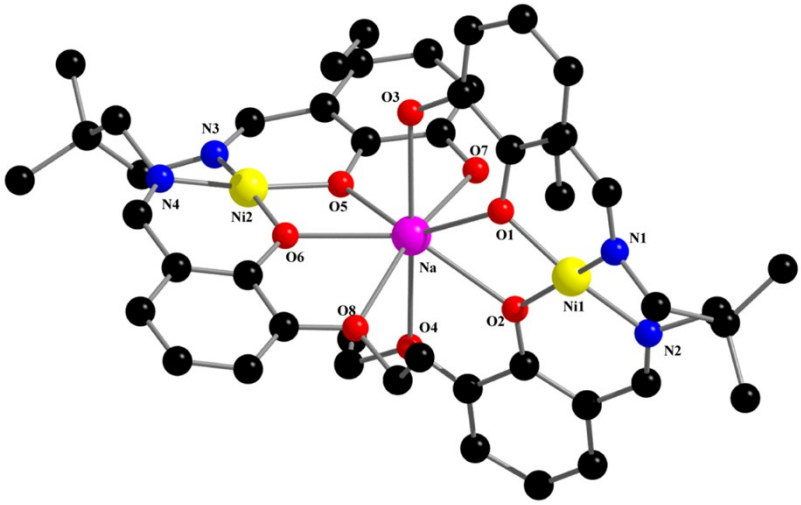

Fig. S8: Perspective view of complexes **4** with selective atom-numbering scheme. Non coordinated perchlorate counter anion has been omitted for clarity.

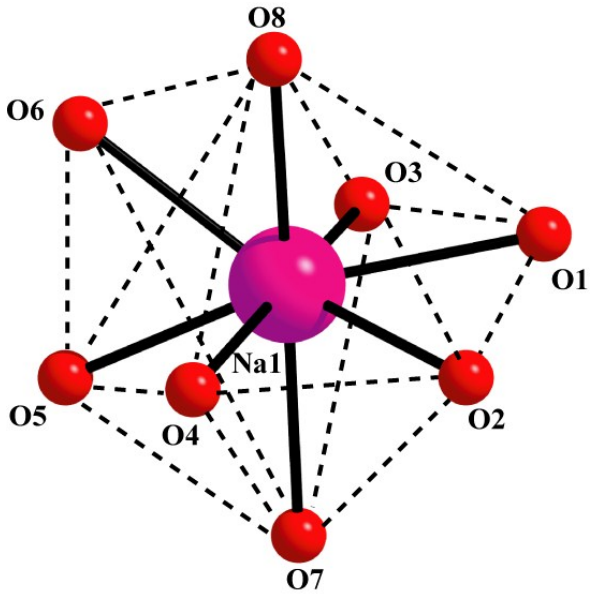

Fig. S9: Trigonal dodecahedral geometry of sodium(I) in complex **4**.

Hirshfeld Surface Analysis

Hirshfeld surfaces[1-2] and the associated two-dimensional (2D) fingerprint[3-5] plots were estimated using Crystal Explorer [6].

Two distances, d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest nucleus internal to the surface), are defined for each point on the Hirshfeld isosurface. The d_{norm} presents a surface with a red−white−blue color scheme, where bright red spots emphasize shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. The normalized contact distance (d_{norm}) based on d_e and d_i is defined by

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vwd}} + \frac{(d_e - r_e^{vdw})}{r_e^{vwd}}$$

where r_i^{vdW} and r_e^{vdW} refers to the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations.

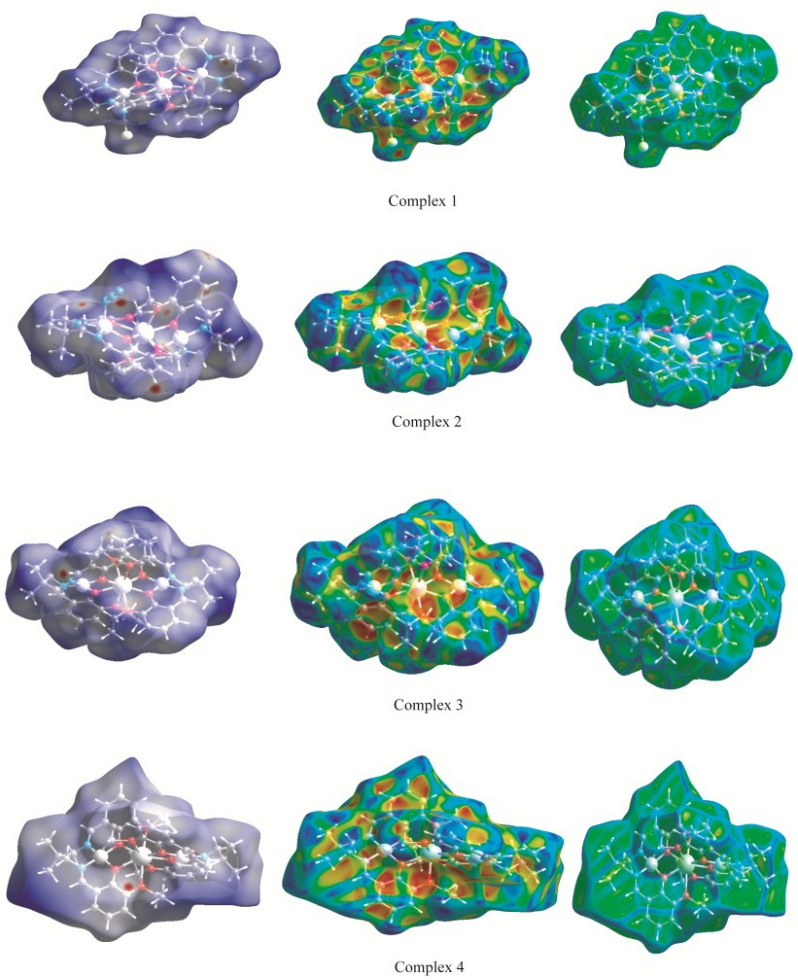

Fig. S10: Hirshfeld surfaces mapped with d_{norm} (left column), shape index (middle) and curvedness (right column) of complexes **1**-**4**.

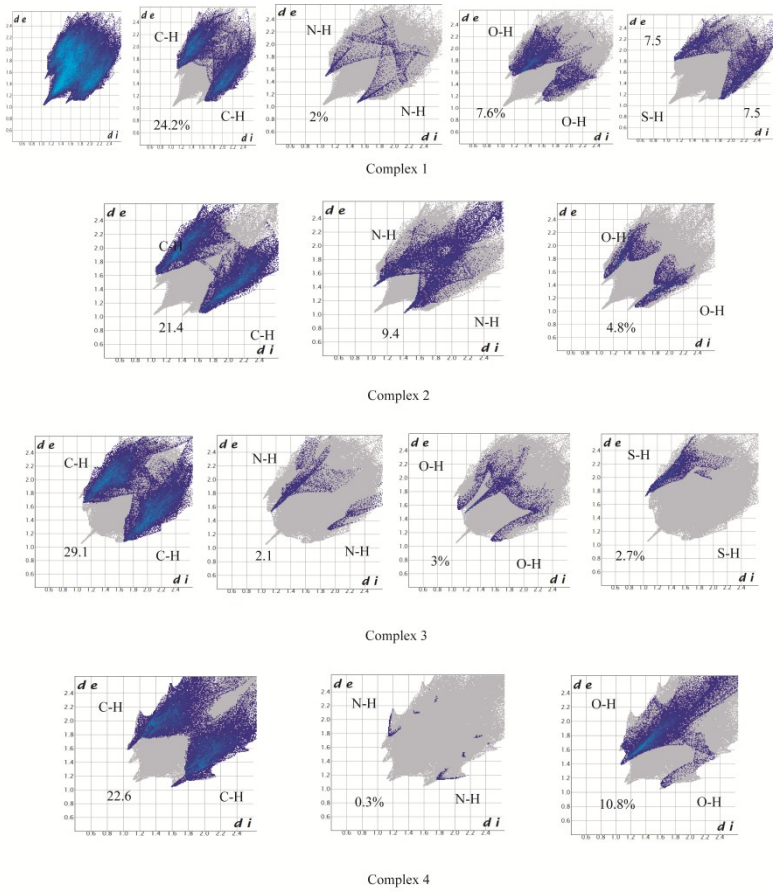

Fig. S11: Fingerprint plot: Full (extreme left), resolved into H···C/C···H (second from the left), H···N/N···H (second from the right) and H···O/O···H (extreme right) contacts contributed to the total Hirshfeld Surface area of complexes **1-4**.

References

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