Electronic Supplementary Information (ESI)

Phenolate Based Metallomacrocyclic Xanthate Complexes of CoII/ CuII and Their Exclusive Deployment in [2:2] Binuclear N, O-Schiff Base Macrocycle Formation and in vitro Anticancer Studies†

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†Dedicated to Professor Pradeep Mathur on the occasion of his 60th Birthday
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General Methods and Materials. The reagents such as 4,4'-diaminodiphenyl ether (99%), CS2 (99%), 2-hydroxybenzaldehyde (98%) and 2-hydroxynaphthaldehyde (98%) were purchased from National Chemicals, Merck and Chemlabs, respectively. All other chemicals were obtained from commercial sources and were used without further purification. All the reactions and manipulations were performed under an inert atmosphere.

Analytical Methods. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyser 2400. Mass spectra were obtained on Thermo Scientific DSQ-II, Water’s QTOF and AB SCIEX 3200 Q TRAP LC/MS/MS system. IR (KBr pellets) spectra were recorded in the
4000–400 cm⁻¹ range using a Perkin-Elmer FTIR Spectrometer. The NMR spectra were obtained on a Bruker 400 MHz spectrometer in DMSO-d₆ unless otherwise noted. Single crystal X-ray analysis was carried out on Oxford diffraction X-Calibur and Agilent's Gemini diffractometer equipped with Eos CCD detector. UV–visible spectra were recorded on a Perkin Elmer Lambda 35 UV–vis spectrophotometer. TGA/DTA plots were obtained using SII TG/DTA 6300 in flowing N₂ with a heating rate of 10 °C min⁻¹. GC analysis was carried out on CLARUS500, PE AutoSystem type GC equipped with FID detector. Powder X-ray diffraction studies were performed on a ‘X Calibur, Eos, Gemini’ X-ray diffractometer using Cu source, CrysAlisPro data reduction: Agilent Technologies Version 1.171.36.28 program(s) used to process the data and the ‘POWDERX’ program for indexing the powder XRD data.

Synthesis

**Ligand precursors L¹ and L².** To a solution of 2-hydroxybenzaldehyde (3 mmol, 366.36 mg) or 2-hydroxynaphthaldehyde (3 mmol, 516.54 mg) in 10 mL of toluene containing 2-3 drops of glacial acetic acid were added 4, 4'-diaminodiphenyl ether (1 mmol, 200 mg) with rigorous stirring. The reaction mixture was refluxed for 2 hrs using Dean-Stark apparatus. This reaction is outlined in Scheme S1. The reaction mixture was cooled at room temperature and solvent was evaporated under vacuum, washed with chilled absolute ethanol followed by diethyl ether to yield the products **L¹** and **L²**. These compounds were dried under vacuum and samples were taken for analysis.

4,4'-bis(2-hydroxybenzylideneamino)diphenyl ether (L¹). Yield: ca 404 mg, 99%, Mp: 213 °C. Anal. Calcd for [C₂₆H₂₀N₂O₃]: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.40; H, 4.95; N, 6.89. Mass (MS ES+): 413.1730 (M+2Li), (42%); 414.1868 (M+2 Li+H), (10%). IR (KBr pellet, cm⁻¹): 3426m br ν(OH), 1618s ν(C=N).

**1H NMR (400 MHz, CDCl₃):** (δ from TMS) 6.970(td, 2H-Ph), 7.05(dd, 2H-Ph), 7.115(dt, 4H-Ph), 7.34(dt, 4H-Ph), 7.41(m, 4H-Ph), 8.659(s, 2H-N=C=H), 13.277(s, 2H-OH).

**13C NMR (400 MHz, CDCl₃):** (δ from TMS) 117.29, 119.16, 119.70, 122.61, 132.25, 133.20 (all CH of Ph), 161.19, 161.83(-N=C=H).

**DEPT 135 (400 MHz, CDCl₃):** (δ from TMS) 117.28, 119.16, 119.70, 122.60, 132.25, 133.29, 156.17 (all corresponds to Ph), 161.19, 161.83(–N=CH). DEPT 135 (400 MHz, CDCl₃): (δ from TMS) 117.28, 119.16, 119.70, 122.61, 132.25, 133.20 (all CH of Ph), 161.84(–N=CH).

4,4'-bis(2-hydroxynaphthylmethylideneamino)diphenyl ether (L²). 475 mg, 93% , Mp: 164 °C. Anal. Calcd for [C₃₄H₂₄N₂O₃]: C, 80.30; H, 4.76; N, 5.51. Found: C, 80.38; H, 4.72; N, 5.45. Mass (MS ES+): 510.52 (M+H); (30%). IR (KBr pellet, cm⁻¹): 3437s br ν(OH), 1619s ν(C=N).

**1H NMR (400 MHz, CDCl₃):** (δ from TMS) 7.159(m, 6H-Ph), 7.38(m, 6H-Ph), 7.55(td, 2H-Ph), 7.754(d, 2H-Ph), 7.84(d, 2H-Ph), 8.15(d, 2H-Ph), 9.39(s, 2H-N=C=H), 15.529(s, 2H-OH).

**13C NMR (400 MHz, CDCl₃):** (δ from TMS) 108.97, 118.94, 119.93, 121.72, 121.97, 123.57, 127.43, 128.07, 129.42, 133.10, 136.31, 141.59, 155.05, 155.82 (all corresponds to Ph), 168.69; (–N=CH).

**Scheme S1:** General scheme for the synthesis of diimines **L¹** and **L²**.

**Spectral Data**

**Characterization of L¹, L², Kₓxan¹ and Kₓxan².** The broad peak appeared in the region of 3426-3437 cm⁻¹ and the sharp peak in the region 1618-1619 cm⁻¹ for **L¹**-**L²** are attributable to the ν(OH) and ν(N=C) vibrations respectively which is characteristic of Schiff bases and suggest the
formation of desired structures. The IR bands appeared are in accordance to the literature reports of similar compounds.\textsuperscript{1} Disappearance of the IR absorption peak in the range of 3426-3437 cm\textsuperscript{-1} together with appearance of new bands in 1456-1493 cm\textsuperscript{-1} and 1084-1109 cm\textsuperscript{-1} region suggests the deprotonation of phenolic –OH and formation of –OCSS\textsubscript{2} moiety.

Schiff base precursors L\textsubscript{1}, L\textsubscript{2} and xanthate ligands K\textsubscript{2}xan\textsubscript{1}, K\textsubscript{2}xan\textsubscript{2} were characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR. The signals appeared at 8.659 and 9.39 ppm in \textsuperscript{1}H NMR spectra as well as signals appeared at 161.83 and 168.69 in \textsuperscript{13}C NMR spectra for the precursors L\textsubscript{1} and L\textsubscript{2} respectively are due to –N=CH moiety which are the characteristic signals for the Schiff base compounds. Phenolic –OH have been appeared as a broad singlet at 13.277 and 15.529 ppm for L\textsubscript{1} and L\textsubscript{2} respectively. The remaining signals observed in the NMR spectra in the range of 6.57-8.15 ppm could be assigned to the aromatic hydrogen atoms which are generally obtained as multiplets, as a result of coupling of aromatic protons and 108-162 ppm to aromatic carbon atoms of Schiff base precursors. \textsuperscript{1}H spectra of xanthate ligands K\textsubscript{2}xan\textsubscript{1} and K\textsubscript{2}xan\textsubscript{2} clearly showed the disappearance of signal for phenolic –OH which is previously present in L\textsubscript{1} and L\textsubscript{2} precursors. Generally, the most characteristic downfield signals appeared at 190.86 ppm and 190.24 ppm in the \textsuperscript{13}C NMR spectra of xanthate ligands K\textsubscript{2}xan\textsubscript{1} and K\textsubscript{2}xan\textsubscript{2}, respectively evidently confirms the formation of xanthate moiety from phenolic –OH. Due to the incorporation of xanthate moiety in the molecule leads to the shifting of electron density from aromatic ring to xanthate moiety which results into the downfield signal (0.5-1.0 ppm) for –N=CH moiety compared to respective Schiff base precursor.

**Mass spectral study.** Notably, similar reactivity is depicted by the similar fragmentation pattern observed for a set of compounds i.e. for compounds bearing similar functionalities in the molecular framework. The binuclear macrocyclic complexes 2, 6-7 were characterized by prominent molecular ion peak as shown in the mass spectra, summarized in Figure S1-S3.

![Image of mass spectra](image.png)

**Figure S1.** ES-MS of binuclear metallamacrocyclic Co\textsuperscript{II} xanthate complex 2.
Figure S2. ES-MS of binuclear metallamacrocyclic Co$^{II}$ N, O-Schiff base complex 6.

Figure S3. MALDI-TOF MS of binuclear metallamacrocyclic Cu$^{II}$ N, O-Schiff base complex 7.

The stacked IR spectra of K$_2$xan$^1$, its binuclear xanthate complex 1 and corresponding binuclear N,O-Schiff base complex 5 as well as K$_2$xan$^1$, its binuclear xanthate complex 3 and corresponding binuclear N,O-Schiff base complex 7 are given in Figure S4-S5, which clearly reveal the structural variations.

Figure S4: Representative IR spectra confirming the structural variation in K$_2$xan$^1$, 1 and 5.
Figure S5: Representative IR spectra confirming the structural variation in $\text{K}_2\text{xan}^1$, 3 and 7.

**NMR spectral data**

Figure S6. $^1\text{H}$ NMR spectrum for $\text{L}^1$

Figure S7. $^{13}\text{C}$ NMR spectrum for $\text{L}^1$
Figure S8. DEPT-135 NMR spectrum for \( \text{L}_1 \)

Figure S9. \(^1\text{H}\) NMR spectrum for \( \text{L}_2 \)

Figure S10. \(^{13}\text{C}\) NMR spectrum for \( \text{L}_2 \)
Figure S11. $^1$H NMR spectrum for $K_2$Xan$^1$

Figure S12. $^{13}$C NMR spectrum for $K_2$Xan$^1$

Figure S13. $^1$H NMR spectrum for $K_2$Xan$^2$
Powder XRD. The inadequate stability of the freshly synthesized xanthate ligands and their metal complexes in solvents, especially chlorinated solvents limited the crystallization attempts. Hence, the powder X-ray diffraction study performed on representative compounds (K$_2$xan$^1$, 1, 3, 5 and 7) and it suggests the microcrystalline nature of these samples. Further it helped us to understand structural characteristics like crystal lattice, lattice parameters. Notably, the results of the XRD analysis for xanthate ligand K$_2$xan$^1$ and its Co$^{II}$/Cu$^{II}$ complexes 1 and 3 as well as their corresponding Schiff base complexes 5 and 7 do not match well as they have different crystal packing. (Figure S15 and S16) In spite of their structural differences, there persists some obvious similarity in the patterns in these compounds because of the presence of the common molecular framework which remains intact during the course of the preparation.
Figure S16. Powder X-ray diffraction pattern for a set of compounds $K_2$xan $^1$, 3 and 7. The powder XRD data for these samples have been successfully indexed and refined by least square refinement with the help of commonly used program ‘POWDERX’ and the details of the indexed peak are given in Table S1.

Table S1. Power X-ray diffraction data for $K_2$xan$^1$, 1, 3, 5 and 7.

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<td>31</td>
<td>2</td>
<td>8</td>
<td>50.076</td>
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</table>

(d) 5: Orthorhombic (P): $a = 26.4$ Å, $b = 12.4$ Å, $c = 28.9$ Å; $\alpha = \beta = \gamma = 90^\circ$.

<table>
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<tr>
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<th>y</th>
<th>z</th>
<th>data</th>
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-S10-
In case of binuclear Schiff base complex 5 and 7, deviation between the experimental powder XRD pattern and simulated powder XRD pattern obtained from single crystal X-ray diffraction study shows that the bulk properties of these materials are different from the single crystals obtained upon very slow evaporation of solvent. Notably the powder XRD data could be indexed in the similar lattice system as that of single crystals for 5 and 7 however the differences in the cell parameters probably arise due to the involvement of solvent molecules stabilizing the crystal structure.

**X-ray Crystallography**
### Table S2 Crystal data and structure refinement for compounds 5-8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>5</th>
<th>6</th>
<th>7, DMSO</th>
<th>7, 2CH$_2$Cl$_2$</th>
<th>8, CHCl$_3$8H$_2$O</th>
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<tbody>
<tr>
<td>CCDC Number</td>
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<td>986523</td>
<td>986525</td>
<td>986526</td>
<td>1426720</td>
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<td>Formula</td>
<td>C$<em>{36}$H$</em>{34}$Co$_2$N$_2$O$_6$</td>
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<td>C$<em>{36}$H$</em>{34}$Cu$_2$N$_2$O$_6$</td>
<td>C$<em>{36}$H$</em>{34}$Cu$_2$N$_2$O$_6$S</td>
<td>C$<em>{36}$H$</em>{34}$ClCu$_2$N$_2$O$_6$</td>
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<tr>
<td>Formula weight (amu)</td>
<td>930.71</td>
<td>1130.93</td>
<td>1018.06</td>
<td>1109.80</td>
<td>2526.66</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbca</td>
<td>Pbca</td>
<td>Pbca</td>
<td>Pbca</td>
<td>Pbca</td>
</tr>
<tr>
<td>a(Å)</td>
<td>26.3438(6)</td>
<td>11.840(3)</td>
<td>26.2828(4)</td>
<td>16.5132(3)</td>
<td>19.0398(9)</td>
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<tr>
<td>b(Å)</td>
<td>12.3067(3)</td>
<td>12.679(3)</td>
<td>12.25878(17)</td>
<td>14.6766(2)</td>
<td>21.6349(7)</td>
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<tr>
<td>c(Å)</td>
<td>28.9627(8)</td>
<td>37.680(8)</td>
<td>28.8218(4)</td>
<td>19.2170(3)</td>
<td>31.0856(15)</td>
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<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>4</td>
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<tr>
<td>Completeness to theta (%)</td>
<td>(θ = 72.16) 100</td>
<td>(θ = 26.08) 99.7</td>
<td>(θ = 29.31) 96.27</td>
<td>(θ = 25.00) 99.8</td>
<td>(θ = 26.08) 99.7</td>
</tr>
<tr>
<td>ρcalc/cm$^3$</td>
<td>1.317</td>
<td>1.334</td>
<td>1.456</td>
<td>1.592</td>
<td>1.333</td>
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<td>μ/mm$^{-1}$</td>
<td>5.965</td>
<td>0.647</td>
<td>1.020</td>
<td>1.209</td>
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<td>F(000)</td>
<td>3824.0</td>
<td>2328.0</td>
<td>4192.0</td>
<td>2264.0</td>
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<td>2θ range for data collection</td>
<td>CuKα (λ = 1.54184) (θ = 92) 36 to 140</td>
<td>MoKα (θ = 0.71073) (θ = 18) 54 to 170</td>
<td>MoKα (θ = 0.71073) (θ = 20) 58 to 165</td>
<td>MoKα (θ = 0.71073) (θ = 21) 58 to 165</td>
<td>MoKα (θ = 0.71073) (θ = 21) 58 to 165</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15</td>
<td>-14h ≤ 14, 0 ≤ k ≤ 15, -15 ≤ l ≤ 15</td>
<td>0 ≤ h ≤ 33, 0 ≤ k ≤ 15, -14 ≤ l ≤ 15</td>
<td>-19 ≤ h ≤ 19, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20</td>
<td>-28 ≤ h ≤ 28, -29 ≤ k ≤ 29, -31 ≤ l ≤ 31</td>
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<tr>
<td>Reflections collected</td>
<td>23584</td>
<td>58626</td>
<td>10072</td>
<td>17040</td>
<td>160890</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8695 [R$<em>{int} = 0.0385$, R$</em>{sigma} = 0.0507$]</td>
<td>11149 [R$<em>{int} = 0.0774$, R$</em>{sigma} = 0.0678$]</td>
<td>10072 [R$<em>{int} = 0.0000$, R$</em>{sigma} = 0.0254$]</td>
<td>4085 [R$<em>{int} = 0.0177$, R$</em>{sigma} = 0.0151$]</td>
<td>42728 [R$<em>{int} = 0.1895$, R$</em>{sigma} = 0.5255$]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>8695/0/577</td>
<td>11149/0/721</td>
<td>10072/0/632</td>
<td>4085/0/316</td>
<td>42728/2/793</td>
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<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.113</td>
<td>1.086</td>
<td>1.070</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Final R indices [1&gt;2σ(I)]</td>
<td>R$_1$ = 0.0593, wR$_2$ = 0.1861</td>
<td>R$_1$ = 0.0581, wR$_2$ = 0.1333</td>
<td>R$_1$ = 0.0391, wR$_2$ = 0.1117</td>
<td>R$_1$ = 0.0247, wR$_2$ = 0.0693</td>
<td>R$_1$ = 0.1272, wR$_2$ = 0.3435</td>
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<tr>
<td>R indices (all data)</td>
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<td>R$_1$ = 0.1301, wR$_2$ = 0.1555</td>
<td>R$_1$ = 0.0547, wR$_2$ = 0.1200</td>
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<tr>
<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>0.40/-0.28</td>
<td>0.44/-0.19</td>
<td>0.33/-0.62</td>
<td>0.42/-0.57</td>
<td>1.54/-0.55</td>
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</table>
Table S3 Selected structural parameters of 5-7 from single crystal X-ray study.

<table>
<thead>
<tr>
<th>Selected Bonds</th>
<th>Bond lengths (Å)</th>
<th>Selected Bonds</th>
<th>Bond angles (°)</th>
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<tr>
<td>O$_5$---Co$_1$</td>
<td>1.901(3)</td>
<td>N$_4$---Co$_1$---O$_5$</td>
<td>94.61(15)</td>
</tr>
<tr>
<td>O$_9$---Co$_1$</td>
<td>1.890(4)</td>
<td>N$_9$---Co$_1$---O$_9$</td>
<td>95.24(15)</td>
</tr>
<tr>
<td>O$_{10}$---Co$_2$</td>
<td>1.884(3)</td>
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</tr>
<tr>
<td>O$_{15}$---Co$_2$</td>
<td>1.908(4)</td>
<td>N$_{21}$---Co$<em>1$---O$</em>{21}$</td>
<td>140.78(19)</td>
</tr>
<tr>
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<tr>
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<td>1.988(4)</td>
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</tr>
<tr>
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<td>1.972(4)</td>
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<td>N$_{16}$---Co$_2$</td>
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<td>126.9(5)</td>
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<tr>
<td>N$_{16}$---C$_7$</td>
<td>1.432(6)</td>
<td>N$_{17}$---C$<em>7$---C$</em>{14}$</td>
<td>120.0(4)</td>
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<td>N$<em>4$---C$</em>{19}$</td>
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<td>N$<em>9$---C$</em>{32}$---C$_{64}$</td>
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<td>94.27(13)</td>
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<tr>
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<td>125.32(12)</td>
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<tr>
<td>O$_5$---Co$_2$</td>
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<td>127.7(4)</td>
</tr>
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<tr>
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<td>1.296(5)</td>
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</tr>
<tr>
<td>N$<em>4$---C$</em>{58}$</td>
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<tr>
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<td>O$_2$---Cu$<em>2$---N$</em>{22}$</td>
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</tr>
<tr>
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<td>148.32(8)</td>
</tr>
<tr>
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<td>1.9822(19)</td>
<td>O$_2$---Cu$<em>2$---N$</em>{21}$</td>
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</tr>
<tr>
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<td>N$<em>3$---C$</em>{15}$---C$_{27}$</td>
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</tr>
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<tr>
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</tr>
<tr>
<td>C$<em>{19}$---C$</em>{20}$---N$_2$</td>
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<td>C$_{11}$---O$<em>2$---C$</em>{24}$</td>
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Description of Crystal Packing Patterns. The aromatic moieties present in the molecular framework potentially provide a hydrophobic surface capable of participating in noncovalent interactions such as π...π, CH...π, CH...O, Cl...O and/or O...S in compounds 5-7. The details about non-covalent interactions like interatomic distances (Å), bond angles and α, β angles (°) are summarized in Table S2. The favorable α angles (angle between the line connecting Cg, H
atom and the normal to the phenyl ring plane) whereas the β angles (Figure S17) are large enough to facilitate CH...π interactions found in normal range, reflects strength of particular interactions.

Table S4. Significant intermolecular interactions [Interatomic distances (Å), and bond angles (°)] found in compounds 5-7.

<table>
<thead>
<tr>
<th>Interactions</th>
<th>D─H…A</th>
<th>D─H</th>
<th>H…A</th>
<th>D…A</th>
<th>&lt;DHA</th>
<th>&lt;α</th>
<th>&lt;β</th>
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<tbody>
<tr>
<td>CH...π</td>
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<tr>
<td>H24...π</td>
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<td>3.521</td>
<td>176.87</td>
<td>5.3</td>
<td>176.87</td>
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<tr>
<td>(Cg: C22 C60 C53 C46 C63 C44) 10 atoms</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>H61...π</td>
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<td>2.751</td>
<td>3.583</td>
<td>149.11</td>
<td>11.99</td>
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<tr>
<td>(Cg: C49 C59 C57 C52 C33 C55) 10 atoms</td>
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<td>2.12</td>
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<tr>
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<td>H62...π</td>
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<td>2.850</td>
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<tr>
<td>(Cg: C11 C35 C42 C54 H49 C20 C13) 10 atoms</td>
<td></td>
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<tr>
<td>CH...O</td>
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</tr>
<tr>
<td>H8...O5/O15</td>
<td>0.931</td>
<td>2.471</td>
<td>3.278</td>
<td>145.20</td>
<td>...</td>
<td>...</td>
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<td>(Bifurcated)</td>
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<td>H21...O15</td>
<td>0.931</td>
<td>2.491</td>
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Figure S17. Protocol for CH...π interactions: d is the distance between the phenyl ring centroid (Cg) and the H atom; V is the vector normal to the plane of phenyl ring; α is the angle between the d and V vector, and β is the C–H...Cg angle.

For instance, the intermolecular interactions H61...π, H49...π (5) and H39...π (7.DMSO) lead to the formation of infinite 1D helical chain with helical pitch 28.963Å and 28.822 Å, respectively (which is equivalent to its unit cell parameter c). A representative view is provided in Figure S18a for 7.DMSO (Other views are depicted in Supporting Information, Figure S19-S21). The presence of N-naphthyl substituents in 6 alters the packing pattern and indeed forms, infinite 1D saw shape molecular stacking along the b-axis involving H6...π or H15...π and π...π interactions. (Figure S18b) Mutually all the noncovalent interactions in 5, 6 and 7.DMSO lead to the formation of an infinite 3D molecular network consisting of voids occupied by corresponding solvent molecules, that are translated in infinite channels as shown in Figure S18c-e. In case of 7.CH2Cl2, solvent molecules played a crucial role in directing the crystal packing patterns of this molecule. For instance, π...π and Cl...O interactions lead to an attractive helical arrangement along c axis, however, all these noncovalent interactions mutually leads to the formation of a 3D infinite supramolecular assembly consisting relatively smaller voids occupied by CH2Cl2 molecules, compared to 7.DMSO. Moreover, the two closing π...π interactions involve half of the linker moiety of two molecules which oriented adjacent molecule in anti fashion. Notably, differential stereoelectronic factors associated with CH2Cl2 molecules have efficiently tuned the noncovalent interactions, involving CH2Cl2 molecules in CH...O interactions that together with effective CH...π, π...π interactions have resulted into the formation of unique 3D interlocked undulated architecture as illustrated in Figure S18f.
Figure S18. (a) CH...π interactions forming infinite 1D helical chain, (b) packing pattern illustrating an infinite 1D saw shape molecular stacking, (c) 3D supramolecular assembly formed through noncovalent interactions capped stick and spacefill model (H are omitted for clarity) a view along the b-axis (2.2.2) for 7.DMSO (d) Formation of 3D infinite interlocked undulated architecture through noncovalent interaction in 7.CH₂Cl₂.

Other packing patterns:
5: Interestingly, the H61...π (Cg: C49 C59 C57 C52 C33 C55) interactions can be used to generate 1D infinite helicate along b-axis whereas H49...π (Cg: C35 C11 C13 C20 C54 C42) interactions forms another helicate along c-axis, with helical pitch 28.963 Å (Figure S19). The H24...π (Cg: C22 C60 C53 C46 C63 C44) interactions are associated with two CH...O interactions viz. H8...O5/O15 and H21...O15, which are closing contact, hence forms macrocyclic assembly.

Figure S19. (a) and (b) Formation of helicates along b- and c-axis through noncovalent interactions.
6: The H21...π(Cg: N4 C59 C60) donor-acceptor interactions are closing contact which holds two molecules exactly in *anti* manner and are associated with H61...π interaction, which leads to the formation of two molecular finite ‘S-shaped’ self-assembly. Additionally, 1D wavy arrangement along c-axis and 1D stacking along a-axis have been formed through H42...π and H42...π interactions, respectively. (Figure S20 a-b) Four double helical macrocyclic molecular units are situated at four diagonal corners of the unit cell of 6 whereas dimensionality is extended predominantly through CH...π and CH...O interactions to the formation of infinite 3D architecture consisting of number of voids.

7.2CH$_2$Cl$_2$: The π...π interactions align molecules in *anti* and lead to 1D packing (Figure 21a) and Cl...O interactions in cooperation with CH...O interactions, pack the molecules in ac plane via dichloromethane (Figure 21b). Notably, distinct crystal packing pattern is observed when DMSO is switched over to CH$_2$Cl$_2$, for instance smaller voids are generated due to crystal packing which are occupied by CH$_2$Cl$_2$ molecules. Hydrogen of CH$_2$Cl$_2$ molecules are also involved in CH...O interactions with both the chelated phenolic oxygens of either side.
Figure S21.  (a) View of the layer formed by the π...π-stacking interactions (b) Molecular packing in ac plane via dichloromethane molecules. (c) Helical chain-like packing along the c-axis. (d) Molecular packing view along a-axis (2.2.2) in complex 7.CH₂Cl₂, H atoms and solvent molecules were omitted for clarity.

**UV-visible absorption and Emission.** The UV–visible absorption (10⁻⁴ M) and emission (10⁻⁴ M) property of ligand precursors (L¹, L²), potassium salt of xanthate ligands (K₂xan¹, K₂xan²), binuclear xanthate macrocyclic complexes (1–4) as well as binuclear N,O-Schiff base macrocyclic complexes (5-8) were investigated at room temperature from DMSO solution.
samples. The differential electronic spectra of 1-8 shown in Figure S22a-b clearly suggest alterations in the structural features of the molecular framework. The shorter absorption band ~315 nm is assigned to $\pi \rightarrow \pi^*$ (phenyl) transitions and the longer absorption band ~360 nm is assigned to $n \rightarrow \pi^*$ (imine) transitions while the absorption band in the range of 390-490 nm could be attributable to the intraligand charge transfer in respective compounds.

It appears that the $\lambda_{\text{max}}$ value for all the compounds arises due to phenyl $\pi \rightarrow \pi^*$ transitions do not show any significant change with the change in the functionality. As expected, the band due to imine $n \rightarrow \pi^*$ transitions appeared in ligand precursors $L^1$, $L^2$ remains unaffected in corresponding xanthate ligands $K_2\text{xan}^1$, $K_2\text{xan}^2$ and bimetallic xanthate complexes 1-4, however a distinguishable blue shift of 10-15 nm in 5-8 as compared to the similar transitions observed in $L^1$ and $L^2$, clearly underlines the participation of imine moiety in complex formation. Further ligand precursors $L^1$, $L^2$ display strong bands due to charge transfer transitions at 395 and 480 nm respectively, predominantly arises due to the presence of phenolic hydroxyl moiety present in conjugation with imine (–CH=N-) functionality. These bands significantly shifted towards higher wavelength ca 444 nm and 490 nm upon formation of $K_2\text{xan}^1$, $K_2\text{xan}^2$ ligands respectively. These bands undergo substantial blue shifts upon complexation with metal ions. For instance a hefty blue shift of 39 nm (1), 57 nm (2) and 29 nm (4) has been observed. In contrast a minor red shift of approx 8 nm in the charge transfer transition band (444 nm) of $K_2\text{xan}^1$ ligand is observed upon complexation with Cu$^{II}$ ion. In addition to these transitions, all complexes 1-8 exhibit a weak d-d transition bands in the visible region of the spectrum. The cobalt complexes 1-2 and 5-6 displayed a weak absorption band in the range of 531- 565sh nm suggesting distorted tetrahedral geometry around the Co$^{II}$ centers whereas copper complexes 3-4 and 7-8 displayed a weak band in the range of 670- 690 nm suggesting distorted square planar / tetrahedral geometry around the Cu$^{II}$ centers.

Figure S22. UV-visible absorption spectra of Schiff base precursors, xanthate salts, binuclear xanthate complexes and binuclear Schiff base complexes at room temperature in 10^{-4} M DMSO solution: (a) $L^1$, $K_2\text{xan}^1$, 1, 3, 5 and 7; (b) $L^2$, $K_2\text{xan}^2$, 2, 4, 6 and 8.
The fluorescence spectra of ligand precursors (L\textsuperscript{1}, L\textsuperscript{2}), potassium salt of xanthate ligands (K\textsubscript{2}xan\textsuperscript{1}, K\textsubscript{2}xan\textsuperscript{2}), binuclear xanthate macrocyclic complexes (1-4) as well as binuclear N,O-Schiff base macrocyclic complexes (5-8) shown in Figure S23, clearly suggests that L\textsuperscript{1} and K\textsubscript{2}xan\textsuperscript{1} display very weak intensity band at 432, 513 and 520 nm at λ\textsubscript{ex} 360 and 318 nm respectively however L\textsuperscript{2} and K\textsubscript{2}xan\textsuperscript{2} display very strong bands 519 and 532 nm at λ\textsubscript{ex} 318 and 497 nm respectively with a significant Stokes shift. Besides the Co\textsuperscript{II} N, O-Schiff base complex 5 is found to be highly fluorescent, display a high sharp intensity 410 nm at λ\textsubscript{ex} 314 with a Stokes shift of ≈ 138 nm. As copper (II) is generally a fluorescence quencher, all the Cu\textsuperscript{II} complexes display no significant fluorescence properties. The observed trend of fluorescence spectra and concomitant bathochromic shifts of intramolecular charge-transfer emissions by coordination compounds were previously observed in dithiocarbamate\textsuperscript{4}, dialkoxo-bridged\textsuperscript{5} and Salen-type\textsuperscript{6} complexes. The appearance of more number of bands upon excitation of a single wavelength as well as high fluorescence behaviour of the complexes may be attributed to the reduction of photoinduced electron transfer process on complex formation.\textsuperscript{7} In conclusion the results of emission study suggest that the emission intensities are dependent on not only on the extended conjugation but also on rigidity in the molecule, which suppresses the distortion of the molecular framework and the concomitant nonradioactive decay process.

**Theoretical Investigations.** All calculations were performed with the Gaussian 03 program suite.\textsuperscript{8} The geometry for all the model compounds discussed herein was fully optimized (Figure S24) by density functional theory at the DFT B3LYP/lanl2dz level. Such type of basis set has been used with good success in a number of studies involving similar species, having good agreement with experimental results.\textsuperscript{9} Molecular orbitals were generated using GaussView 3.0 program.
Figure S24. An optimized geometry for the minimum energy conformation at B3LYP/lanl2dz level for 1 (a), 2 (b), Kxan-1 (c), 5 (d), 7 (e), L₁ (f).

The outcomes of theoretical study are in good agreement with the experimental data. The flexibility associated with the linker along with the desired orientations of xanthate moieties of K₂xan¹ is essentially the key factor involved in the macrocyclization process, leading to binuclear complexes 1-4. It appears that the optimized structures adopt a unique orientation to diminish the steric and electronic factors associated with them. For instance, boat shaped macrocyclic architectures are obtained as a lower energy conformation in case of binuclear xanthate complexes 1 and 3, whereas double helical macrocyclic architectures are obtained for binuclear N, O-Schiff base complexes 5 and 7. These architectures are exemplified in Figure S25-S26.
Figure S25. Complex 1 forming boat shaped macrocyclic architecture represented by capped sticks (a) and spacefill (b) models.

Figure S26. Complex 5 forming double helical macrocyclic architecture represented by capped sticks (a) and spacefill (b) models.

An optimized geometry of complexes 1, 5 and 7 suggests distorted tetrahedral coordination sphere at both the metal centers however complex 3 adopts distorted square planar geometry around both the Cu$^{II}$ centers. The geometrical parameters of the binuclear $N$, O-Schiff base macrocyclic complexes 5 and 7 are well compared with their experimental parameters obtained from single crystal X-ray study (Table S3) and these validate the optimized electronic structural models of compounds under investigation. The small difference between the geometrical parameters obtained theoretically and from X-ray crystallography of compound 5 is probably emerged due to the presence of large number of non-covalent interactions offered by the spacer moiety intending an extra stability to the macrocyclic architecture.

Table S5. Selected structural parameters obtained from theoretical investigations and X-ray study for 1, 3, 5 and 7.

| Entry | Selected Bond | Bond Length (Å) | | | Selected Bond | Bond Length (Å) | | |
|-------|---------------|----------------|---|---|---------------|----------------|---|
|       |               | Theoretical    | X-ray | Geometrical | X-ray |      | | |
| 5     | O–Co          | 1.917, 1.921   | 1.890, 1.900, 1.906, 1.884 | O–Co–N | 94.08, 94.54 | 94.62, 95.29, 93.46, 91.71 | 94.24, 91.07 |
|       | N–Co          | 2.047, 2.043   | 1.991, 1.953, 1.972, 1.985 | O–Co–O | 117.61 | 117.14, 127.68, 126.35, 126.88 |
|       | N–C (imine)   | 1.312, 1.309   | 1.284, 1.288, 1.301 | N–Co–N | 123.70 | 127.14, 127.0, 126.7, 126.88 |
|       | O–C (ether)   | 1.387, 1.381   | 1.381, 1.396, 1.384, 1.379 | C–C–N | 128.16, 128.43 | 126.35, 126.88 |
|       | Co$_1$–Co$_2$ | 11.259 | 11.750 | C–N–Co | 118.64, 118.65, 119.32 | 127.70, 127.0, 121.61, 122.85, 121.95 | 126.75, 127.47, 127.49 |
|       |               |               |      | C–O–Co | 124.93, 126.49 | 124.63, 128.86 | 115.42, 117.92 |
|       |               |               |      | C–O–C (ether) | 118.88 |              | |
| 7     | O–Cu          | 1.930 | 1.888, 1.893 | O–Cu–N | 93.33 | 94.11-94.92 |
|       | N–Cu          | 2.029 | 1.957, 1.976 | N–Cu–N | 104.34 | 98.12 |
|       | N–C           | 1.421 | 1.299-1.434 | O–Cu–O | 96.22 | 92.80 |
|       |               |               |      | N–Cu–O | 139.48-139.53 | 145.29-145.89 | |
|       |               |               |      | C–C–N | 128.20 | 125.87-126.82 | |
|       |               |               |      | C–N–Cu | 122.10-122.11 | 121.48-122.76 | |
|       |               |               |      | C–O–Cu | 128.84-128.85 | 123.16-127.69 |
|       |               |               |      | C–O–C | 118.32 | 115.91 |
**Table S6.** Computational calculation data for complex 1, 3, 5, 7

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**Frontier molecular orbital analysis.** The character of the frontier orbitals and the HOMO–LUMO energy gap greatly contribute to the photo-physical properties of the complexes and thus analysis of frontier molecular orbitals need prime consideration for prediction of the possible reactivity of the molecule.\(^\text{10}\)

**Figure S27.** Comparison of the frontier molecular orbitals derived from DFT calculation at the B3LYP/LAN2DZ level; for (a) L\(_1\) and K\(_{\text{kxan-1}}\), (b) Complexes 1, 3, 5 and 7.

Due to the effective conjugation, HOMO and LUMO in L\(^1\) are delocalized over all the phenyl rings whereas HOMO of K\(_{\text{kxan}}\)^\(^1\) is mainly delocalized over phenyl rings adjacent to ethereal
oxygen and to a little extent to the xanthate moieties. Expectedly, LUMO of K$_2$xan$^1$ is mainly localized over a xanthate moiety and potassium attached to xanthate as illustrated in Figure S26a. The electron density in the HOMO for binuclear xanthate complexes 1 and 3 is predominantly delocalized over the phenyl moieties adjacent ethereal with oxygen, while metal chelated xanthate moieties are mainly contributed for LUMO as shown in Figure S27b. The transformation of the binuclear xanthate complexes to their corresponding binuclear N,O-Schiff base analogues can be explained by the localization of LUMO at metal chelated xanthate moiety in complexes 1 and 3 which emphasizes the vulnerability of xanthate moiety under nucleophilic conditions. The HOMO for 5 and 7 is predominantly delocalized over spacer moiety; the $\pi$-orbitals of two peripheral phenyl moieties of linker unit are commonly contributing to the high extent for the delocalization of the HOMO. However, the LUMO in 5 is mainly delocalized over the length of the one of the ligand portion and it is delocalized over peripheral phenyl moieties in 7 with minor contribution by the phenyl moieties attached to ethereal oxygen as shown in Figure S27b. On the other hand, for both the compounds the contribution from the metal atom in their HOMOs and LUMOs is extremely negligible. Thus, frontier molecular analysis suggests that the chelated xanthate moiety can preferentially react with nucleophilic species and all the complex molecules can show an efficient CH-$\pi$ and $\pi$-$\pi$ donor-acceptor ability.

Furthermore, the significant decrease in the energy difference between HOMO-LUMO is observed upon reaction of L$_1$ (3.7829 eV) with CS$_2$ leading to the Kxan-1 (3.2543 eV), due to higher electron density and extended conjugation. We have also found that the energies of HOMO and LUMO of 1 and 3 are lower than that of 5 and 7, energy difference between HOMOs is smaller but LUMOs are greatly differentiated by energy. The energy difference between HOMO-LUMO for xanthate complexes (3.4646 eV for 1 and 3.3941 eV for 3) is significantly lower compared to their corresponding Schiff base complexes (3.5688 eV for 5 and 3.6303 eV for 7), could be due to the presence of flexible skeletal structures of the xanthate ligand. Additionally, this study also revealed the greater contribution of copper towards decrease of the HOMO-LUMO energy difference in xanthate complexes in spite of identical molecular framework except metal centers, however reverse trend is observed in Schiff base complexes. The lower energies of HOMO in copper containing complexes (3 and 7) over their cobalt centered congeners (1 and 5) also suggest their superior stability. Interestingly, the HOMO– LUMO gap values for the entire investigated compound are in the range of 3.38–3.79 eV which reveals the possible semiconducting properties of the compounds$^{11}$ and increases the potential applicability of this class of compounds towards semiconducting materials.

The electrostatic potential (ESP) of molecules are widely used as a powerful tool for exploring the properties and locating potential sites within the molecules for the interactions with other moieties and thus it provides insights into molecular association. For instance, the surface property of drug molecule reveals the potential sites of interactions with biomolecules which is useful to estimate the mode of action.$^{12}$
The localization of slight negative potential around –OH in \( \mathbf{L}^1 \) and very high positive potential around potassium centers and quite negative potential around sulfur atoms in \( \mathbf{K}_2\text{xan}^1 \) can be clearly seen in Figure S28. Furthermore, the localization of low positive potential at aromatic hydrogen atoms moderately negative potential around N/O/S in macrocyclic complex 1 (a), 3 (b), 5 (d) and 7 (e) could be clearly revealed from mapping of electrostatic potential surface (Figure S28). This has indeed generated a scope for the use of these macrocyclic complexes with variable cavity size and tuneable electronic environment as ditopic receptors to interact with suitable guest species (\textit{vide supra}). Gejji et al. have depicted the exploitation of molecular electrostatic potential from density functional calculations to understand the host-guest interactions.\textsuperscript{13} In this context, the surface potential of binuclear xanthate macrocyclic complexes 1 and its Schiff base analogue 5 clearly explain the sensing ability of various metal ions using fluorescence spectroscopy (\textit{vide supra}).

**Cartesian Coordinates for Optimized Geometries:**

**Table S7.** Cartesian coordinates for optimized geometry of \( \mathbf{L}^1 \).

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Table S12. Cartesian coordinates for optimized geometry of 7.

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**Notes:**

Cartesian coordinates for optimized geometry of 7.
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Anticancer Activity

![Anticancer Activity](image)

**Figure S29.** % Cytotoxicity observed for investigated compounds against HEP 3B (a) and IMR 32 (b) at different concentrations.

In analogy to the literature reports on antitumour activity of similar compounds, our hypothesis on binuclear Co\textsuperscript{II}/Cu\textsuperscript{II} xanthate complexes induce cytotoxicity might involve multiple mode of action leading to the cell death, can be explained by several previously observed effects of isostructural dithiocarbamate complexes and complexes derived from \(N, O\)- donor ligands. 1,1-dithio moieties are known to exert cytotoxicity through antiangiogenesis effects, inhibition of numerous metalloenzymes and NF-KB-related gene-expression and modulation of cellular
metabolism, which lead to tissue damage. The decomposition and metabolic products of a transition metal 1,1-dithio complexes in vivo, ca free 1,1-dithio moieties, CS2 are reportedly able to arrest the cell proliferation. Dou and co-workers reported several studies concerning the cytotoxic activity of discrete, transition metal complexes, including complexes based on S, N and/ or O- donor ligands. Electrochemical and stability data suggests that the most stable dithiocarbamate complexes proved to be most cytotoxic in vitro and also against the cisplatin-resistant. Recent investigations highlights the electronic density analysis of different dithiocarbamate metal complexes to correlate their toxicity as well as the ability to inhibit proteasome and induce apoptosis in human cancer cells. It has appeared that the dithiocarbamate complexes holding higher electronic density over sulfur atom within the complex are more active against the JAMM domain of the 26S proteasome. Due to presence of almost similar structural and electronic features in dithiocarbamate and xanthate complexes, analogous mode of action for the antitumor activity could be expected for both of them. Beyond this, the possibility of transchelation reactions with physiological molecules and metabolic products of xanthate complexes could alter the intracellular metal constitutions which lead to the cytotoxic activity. Further, cobalt and copper complexes are also known to target DNA under physiological conditions via an oxidative pathway and induce cytotoxicity.

Moreover, several stereoelectronic parameter made available by DFT study are known to provide insight in the mechanisms related to membranes transportations, revealing possible interactions with biological macromolecules or intracellular receptors and thus provide a possible rationalization for the structure activity relationships (SARs) of these compounds. The stability and reactivity of the molecules towards possible biological receptors such as electron rich or electron deficient regions are reportedly depends on the frontier orbitals, as HOMO energy is closely related to susceptibility to electrophilic attack while LUMO energy is closely related to susceptibility to nucleophilic attack.

**Table S13. Parameters obtained from the computational investigations and cytotoxic activity for model compounds.**

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<th>Compound</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>HOMO-LUMO gap (eV)</th>
<th>Dipole moment (Debye)</th>
<th>Charges on chelated atoms (S/N,O) and metal center</th>
<th>IC₅₀ values</th>
<th>HEP 3B μM (1mL) ±SE</th>
<th>IMR 32 μM (1mL) ±SE</th>
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<tr>
<td>L₁</td>
<td>-5.59</td>
<td>3.7829</td>
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<td>137.8±13.9</td>
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<td>Kxan-1</td>
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<td>3.2543</td>
<td>17.2480</td>
<td>S –(0.380-0.394), K (0.821-0.824)</td>
<td>17.8±2.9</td>
<td>23.2±1.4</td>
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<td>2.6945</td>
<td>S – (0.020-0.036), Co (0.052)</td>
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<td>3</td>
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<td>S (0.015-0.028), Cu –(0.103-0.109)</td>
<td>8.1±0.8</td>
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<td>5</td>
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<td>3.5688</td>
<td>0.4366</td>
<td>N – (0.566-0.571), O – (0.654- 0.661), Co (0.749-0.750)</td>
<td>69.7±3.6</td>
<td>99.7±6.6</td>
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<td>7</td>
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<td>3.6303</td>
<td>0.0139</td>
<td>N – (0.545), O – (0.606), Cu (0.607)</td>
<td>19.2±2.1</td>
<td>13.2±1.1</td>
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</table>

**Induction of Apoptosis study**

-S35-
Figure S30: Flow cytometry density plots of HEP 3B and IMR 32 upon treatment with $K_2\text{xan}^1$, binuclear macrocyclic complexes 1, 3, 6 and 7.
Figure S31. Flow cytometry data revealing apoptotic/ necrotic/live cell population of HEP 3B and IMR 32 cells upon treatment of $K_2\text{xan}^1$, binuclear macrocyclic complexes 1, 3, 6 and 7.

Thermogravimetric Analysis

The thermogravimetric analysis of bimetallic xanthate/ $N,O$-Schiff base macrocyclic complexes 1-8, were performed under $N_2$ atmosphere at a heating rate of 10 $^\circ$C /min from room temperature to 550 $^\circ$C. The thermal analysis data and corresponding thermogram are summarized in Table S12 and Figure S31, respectively. A single or multi stage mass loss for these compounds was observed with DTG and corresponding DTA curves which are ascribed to endothermic and/or exothermic elimination of molecular fragments due to the thermal degradation. The bimetallic xanthate macrocyclic complexes 1-4, exhibit an insignificant mass loss of ~ 1% in initial stage which could be assigned to the loss of solvent impurities. Further mass loss of 12.44, 8.07, 4.2 and 3.52 % observed in the second stage of degradation is attributed to the loss of $\text{CS}_2$/ SCO ligand fragments. The maximum rate of decomposition seen on DTG curves for 1-4 is 360.2, 442.3, 327.8 and 337.6 $^\circ$C respectively. Contrarily, among bimetallic $N,O$-Schiff base complex 5-8, complex 5 display an endothermic peak at 147.2 $^\circ$C on DTA curve without mass loss suggesting phase changes occurring due to its melting. Further it exhibits a single stage degradation started at 200 $^\circ$C and continues at 550 $^\circ$C with maximum rate of decomposition observed at 269.8 $^\circ$C on DTG curve. Other complexes 6-8 showed two stages of degradation involving the loss of naphthyl/ $\text{CH}_2\text{Cl}_2$ fragments in the first stage followed by a continuous mass loss with a maximum rate of degradation at 467.5, 373.9 and 358.3 $^\circ$C observed on corresponding DTG curves. It may be noted that the thermogravimetric study of complex 7 has been performed with the crystals obtained from $\text{CH}_2\text{Cl}_2$/hexane solvent mixture. The association of two $\text{CH}_2\text{Cl}_2$ molecules with the crystals is indeed confirmed by its thermogram, disclosing a mass loss of 14.8% at 212 $^\circ$C corresponding to 2$\text{CH}_2\text{Cl}_2$ molecules (calc. 16.5%). This is consistent with the results of single crystal X-ray analysis of 7.

Table S14. Thermogravimetric analysis of binuclear xanthate/ $N,O$-Schiff base macrocyclic complexes 1-8.

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<th>Entry</th>
<th>DTA ($^\circ$C) (µV)</th>
<th>DTG ($^\circ$C) (µg/min)</th>
<th>Significant Mass loss % (temp range $^\circ$C)</th>
<th>Inference</th>
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<td>1</td>
<td>188.5 (8.21)</td>
<td>188.1 (45.2) 360.2 (20.3)</td>
<td>1.22 % (upto 100) 12.44 % (100-250) 22.71 % (250-550) 36.37 % (50-550)</td>
<td>1st stage: Insignificant mass loss of solvent impurities. 2nd stage: Loss of $\text{CS}_2$ molecules (calc. 12.3 %). 3rd stage: Decomposition continues after 550 $^\circ$C. Maximum rate of decomposition observed at 188.1 $^\circ$C on DTG curve.</td>
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<tr>
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<td>442.3 (62.2)</td>
<td>1.49 % (upto 100) 8.07 % (100-350) 23.43 % (350-550) 32.99 % (100-550)</td>
<td>1st stage: Insignificant mass loss of solvent impurities. 2nd stage: Loss of 2SCO fragment (calc. 8.35 %). 3rd stage: Decomposition continues after 550 $^\circ$C. Maximum rate of decomposition observed at 442.3 $^\circ$C on DTG curve.</td>
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### DTG curve.

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<td>298.7 (2.42)</td>
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<td>25.4% (250-550)</td>
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<td>30.1% (50-550)</td>
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</table>

- **1st stage:** Insignificant mass loss of solvent impurities.
- **2nd stage:** Loss of SCO fragment (calc. 4.9%).
- **3rd stage:** Decomposition continues after 550 °C.

- **Maximum rate of decomposition observed at 327.8 °C on DTG curve.**

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<td>1st</td>
<td>264.2 (3.32)</td>
<td>3.52% (50-100)</td>
</tr>
<tr>
<td>2nd</td>
<td>303.5 (4.46)</td>
<td>35.68% (100-550)</td>
</tr>
<tr>
<td>3rd</td>
<td>329.8 (2.84)</td>
<td>39.20% (50-550)</td>
</tr>
<tr>
<td></td>
<td>362.8 (-1.60)</td>
<td></td>
</tr>
</tbody>
</table>

- **1st stage:** Decomposition continues after 550 °C.
- **2nd stage:** Loss of SCO (calc. 4.1%).
- **3rd stage:** Decomposition continues after 550 °C.

- **Maximum rate of decomposition observed at 337.6 °C on DTG curve.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>147.2 (25.8)</td>
<td>47.8% (200-550)</td>
</tr>
</tbody>
</table>

- An endothermic peak at 147.2 °C appeared on DTA curve without mass loss suggesting phase changes occurring due to its melting.
- **Maximum rate of decomposition observed at 269.8 °C on DTG curve.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>212.1 (7.75)</td>
<td>14.8% (150-250)</td>
</tr>
<tr>
<td>2nd</td>
<td>349.1 (6.50)</td>
<td>35.2% (250-550)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0% (50-550)</td>
</tr>
</tbody>
</table>

- **1st stage:** Decomposition continues after 550 °C.
- **2nd stage:** Loss of 2CH<sub>2</sub>Cl<sub>2</sub> (calc. 14.8%).
- **Maximum rate of decomposition observed at 373.9 °C on DTG curve.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>364.6 (39.59)</td>
<td>12.2% (50-250)</td>
</tr>
<tr>
<td>2nd</td>
<td>358.3 (93.1)</td>
<td>48.5% (250-550)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.7% (100-550)</td>
</tr>
</tbody>
</table>

- **1st stage:** Loss of naphthyl (calc. 16.5%).
- **2nd stage:** Decomposition continues after 550 °C.
- **Maximum rate of decomposition observed at 358.3 °C on DTG curve.**
Figure S32. DTG/DTA/TG curves a-h for binuclear xanthate/ N,O-Schiff base macrocyclic complexes 1-8, respectively.

References:
3. ‘POWDERX” – A program for indexing and refinement of X-ray data written by Dr. V. K. Wadhavan, Bhabha Atomic research Center, private communication.


