

**Table S1** Selected bond distance and bond angle maxima and minima, differences and means for static [Cu(chelate)<sub>3</sub>][Y]<sub>2</sub> complexes

**ELECTRONIC SUPPLEMENTARY MATERIAL**

|          | Cu-N(A)   | Cu-N(B)  | <b>Cu-N(C)</b> | Cu-N(D)  | Cu-N(E)   | <b>Cu-N(F)</b> | $T = R_{\text{in}}/R_{\text{out}}$ |
|----------|-----------|----------|----------------|----------|-----------|----------------|------------------------------------|
|          | /Å        | /Å       | /Å             | /Å       | /Å        | /Å             |                                    |
|          | In        | In       | <b>Out</b>     | In       | In        | <b>Out</b>     |                                    |
| Maximum  | 2.065(12) | 2.079(3) | 2.469(6)       | 2.079(5) | 2.048(9)  | 2.324(3)       | 0.8949                             |
| Minimum  | 2.004(5)  | 2.029(5) | 2.303(9)       | 2.020(5) | 2.003(13) | 2.214(6)       | 0.8661                             |
| $\Delta$ | 0.061     | 0.050    | 0.166          | 0.059    | 0.045     | 0.110          | 0.0288                             |
| Mean     | 2.041(6)  | 2.048(6) | 2.389(6)       | 2.042(6) | 2.021(6)  | 2.263(6)       | 0.8766                             |

|                     | Maximum  | Minimum   | $\Delta$ | Mean      |
|---------------------|----------|-----------|----------|-----------|
| $\alpha_1/^{\circ}$ | 81.6(5)  | 79.96     | 1.64     | 80.64(3)  |
| $\alpha_2/^{\circ}$ | 94.5(6)  | 92.76     | 1.74     | 93.77(3)  |
| $\alpha_3/^{\circ}$ | 93.63    | 89.97(19) | 3.66     | 91.95(8)  |
| $\alpha_4/^{\circ}$ | 95.97    | 94.1(5)   | 1.87     | 95.32(3)  |
| $\alpha_5/^{\circ}$ | 173.79   | 165.86    | 7.93     | 170.30(3) |
| $\alpha_6/^{\circ}$ | 168.6(5) | 162.01    | 6.59     | 165.97(3) |
| $\alpha_7/^{\circ}$ | 179.2(5) | 170.9(2)  | 8.30     | 175.63(3) |
| $\alpha_8/^{\circ}$ | 77.3(3)  | 76.2(4)   | 1.10     | 77.06(3)  |
| $\alpha_9/^{\circ}$ | 76.6(5)  | 74.01     | 2.59     | 75.20(3)  |

**Table S2** Selected bond distance and bond angle maxima and minima, differences and means for complexes of the [Cu(chelate)<sub>3</sub>][Y]<sub>2</sub> series with *T* > 0.9

**ELECTRONIC SUPPLEMENTARY MATERIAL**

|                   | Cu-N(A)    | Cu-N(B)   | <b>Cu-N(C)</b> | Cu-N(D)   | Cu-N(E)  | <b>Cu-N(F)</b> | <i>T</i> = <i>R</i> <sub>in</sub> / <i>R</i> <sub>out</sub> |
|-------------------|------------|-----------|----------------|-----------|----------|----------------|-------------------------------------------------------------|
|                   | /Å         | /Å        | /Å             | /Å        | /Å       | /Å             |                                                             |
|                   | In         | In        | <b>Out</b>     | In        | In       | <b>Out</b>     |                                                             |
| Maximum           | 2.129(9)   | 2.148(5)  | 2.270(10)      | 2.118(5)  | 2.120(9) | 2.252(5)       | 1.001                                                       |
| Minimum           | 2.039(3)   | 2.060(10) | 2.088(2)       | 2.044(9)  | 2.052(3) | 2.065(2)       | 0.9202                                                      |
| Δ                 | 0.090      | 0.088     | 0.182          | 0.074     | 0.068    | 0.187          | 0.0808                                                      |
| Mean              | 2.080(5)   | 2.093(6)  | 2.204(6)       | 2.084(6)  | 2.086(6) | 2.180(6)       | 0.9522                                                      |
|                   | Maximum    | Minimum   | Δ              | Mean      |          |                |                                                             |
| α <sub>1</sub> /° | 80.4(1)    | 78.2(1)   | 2.20           | 79.38(4)  |          |                |                                                             |
| α <sub>2</sub> /° | 98.42(9)   | 91.3(2)   | 7.12           | 94.07(2)  |          |                |                                                             |
| α <sub>3</sub> /° | 96.03      | 90.63(9)  | 5.40           | 93.66(3)  |          |                |                                                             |
| α <sub>4</sub> /° | 96.1(2)    | 92.67(9)  | 3.43           | 94.37(4)  |          |                |                                                             |
| α <sub>5</sub> /° | 175.72(13) | 166.7(1)  | 9.02           | 169.18(5) |          |                |                                                             |
| α <sub>6</sub> /° | 170.1(1)   | 163.7(4)  | 6.40           | 167.88(3) |          |                |                                                             |
| α <sub>7</sub> /° | 175.25     | 165.7(3)  | 9.55           | 169.05(3) |          |                |                                                             |
| α <sub>8</sub> /° | 78.62(9)   | 76.2(1)   | 2.42           | 77.75(4)  |          |                |                                                             |
| α <sub>9</sub> /° | 79.06(14)  | 76.1(4)   | 2.96           | 77.37(5)  |          |                |                                                             |

**Table S3** Values for  $R_{\text{IN}}/\text{\AA}$ ,  $R_{\text{OUT}}/\text{\AA}$ ,  $|R_{\text{IN}} - \text{RTO}|/\text{\AA}$  and  $|R_{\text{OUT}} - \text{RTO}|/\text{\AA}$  for the  $[\text{Cu}(\text{chelate})_3][\text{Y}]_2$  series of complexes complexes corresponding to the  $Q_\theta$  component of the JT active  $e$  vibration

**ELECTRONIC SUPPLEMENTARY MATERIAL**

| Structure                                  | 8b        | 11a      | 6         | 10        | 11b      |          |           |
|--------------------------------------------|-----------|----------|-----------|-----------|----------|----------|-----------|
| $R_{\text{IN}}/\text{\AA}$                 | 2.084(11) | 2.076(3) | 2.086(4)  | 2.088(9)  | 2.101(5) |          |           |
| $R_{\text{OUT}}/\text{\AA}$                | 2.169(10) | 2.256(3) | 2.211(3)  | 2.230(10) | 2.208(5) |          |           |
| $ R_{\text{IN}} - \text{RTO} /\text{\AA}$  | 0.066     | 0.074    | 0.064     | 0.062     | 0.049    |          |           |
| $ R_{\text{OUT}} - \text{RTO} /\text{\AA}$ | 0.019     | 0.106    | 0.061     | 0.080     | 0.058    |          |           |
|                                            |           |          |           |           |          |          |           |
| Structure                                  | 4c        | 4d       | 9         | 1         | 5        | 7        | 8a        |
| $R_{\text{IN}}/\text{\AA}$                 | 2.031(3)  | 2.033    | 2.037(13) | 2.036(5)  | 2.033(2) | 2.047(3) | 2.052(10) |
| $R_{\text{OUT}}/\text{\AA}$                | 2.345(3)  | 2.338    | 2.328(12) | 2.296(6)  | 2.337(3) | 2.346(3) | 2.293(10) |
| $ R_{\text{IN}} - \text{RTO} /\text{\AA}$  | 0.119     | 0.117    | 0.113     | 0.114     | 0.117    | 0.103    | 0.098     |
| $ R_{\text{OUT}} - \text{RTO} /\text{\AA}$ | 0.195     | 0.188    | 0.178     | 0.146     | 0.187    | 0.196    | 0.143     |

**Table S4** The relative contributions in Å from the  $Q_\theta$  and  $Q_\varepsilon$  components of the JT active  $e$  vibration

**ELECTRONIC SUPPLEMENTARY MATERIAL**

|                                                 | <b>1</b> | <b>3</b>  | <b>4c</b> | <b>4d</b> | <b>5</b>  | <b>6</b>   |            |
|-------------------------------------------------|----------|-----------|-----------|-----------|-----------|------------|------------|
| Cu-N(A,E)/Å                                     | 2.018(5) | 2.083(2)  | 2.028(3)  | 2.035     | 2.030(2)  | 2.093(3)   |            |
| Cu-N(B,D)/Å                                     | 2.054(5) | 2.077(2)  | 2.032     | 2.032     | 2.037(2)  | 2.079(4)   |            |
| $\Delta[\text{Cu-N(B,D)-Cu-N(A,E)}]/\text{\AA}$ | 0.036    | -0.006    | 0.006     | -0.003    | 0.007     | -0.014     |            |
| $ R_{\text{OUT-RTO}} /\text{\AA}$               | 0.146    | 0.073     | 0.195     | 0.188     | 0.187     | 0.061      |            |
|                                                 | <b>7</b> | <b>8a</b> | <b>8b</b> | <b>9</b>  | <b>10</b> | <b>11a</b> | <b>11b</b> |
| Cu-N(A,E)/Å                                     | 2.028(3) | 2.052(9)  | 2.084(11) | 2.034(13) | 2.125(9)  | 2.046(3)   | 2.069(5)   |
| Cu-N(B,D)/Å                                     | 2.067(3) | 2.053(10) | 2.084(11) | 2.041(14) | 2.052(10) | 2.106(3)   | 2.133(5)   |
| $\Delta[\text{Cu-N(B,D)-Cu-N(A,E)}]/\text{\AA}$ | 0.039    | 0.001     | 0.000     | 0.007     | -0.073    | 0.060      | 0.064      |
| $ R_{\text{OUT-RTO}} /\text{\AA}$               | 0.196    | 0.143     | 0.019     | 0.178     | 0.080     | 0.106      | 0.058      |

**Table S5** The relative contributions in Å from the  $Q_\theta$  and  $a_{2u}$  components of the  $[\text{Cu}(\text{chelate})_3][\text{Y}]_2$  series of complexes

**ELECTRONIC SUPPLEMENTARY MATERIAL**

|                                             | <b>1</b> | <b>3</b>  | <b>4c</b> | <b>4d</b> | <b>5</b>  | <b>6</b>   |            |
|---------------------------------------------|----------|-----------|-----------|-----------|-----------|------------|------------|
| $\Delta[\text{Cu-N(C)-Cu-N(F)}]/\text{\AA}$ | 0.164(6) | 0.023(2)  | 0.216(3)  | 0.215     | 0.212(3)  | 0.018(3)   |            |
| $ R_{\text{OUT-RTO}} /\text{\AA}$           | 0.146    | 0.073     | 0.195     | 0.188     | 0.187     | 0.061      |            |
|                                             | <b>7</b> | <b>8a</b> | <b>8b</b> | <b>9</b>  | <b>10</b> | <b>11a</b> | <b>11b</b> |
| $\Delta[\text{Cu-N(C)-Cu-N(F)}]/\text{\AA}$ | 0.043(3) | 0.020(10) | 0.000     | 0.014(12) | 0.080(10) | 0.008(5)   | 0.013(6)   |
| $ R_{\text{OUT-RTO}} /\text{\AA}$           | 0.196    | 0.143     | 0.019     | 0.178     | 0.080     | 0.106      | 0.058      |

**Table S6** The bond distances (in Å), *T* values and coordinate bond summation values for the CuL<sub>6</sub> EO complexes  
**ELECTRONIC SUPPLEMENTARY MATERIAL**

|           | <b>L</b> | <b>Cu-N(A)</b> | <b>Cu-N(B)</b> | <b>Cu-N(E)</b> | <b>Cu-N(D)</b> | <b>Cu-N(F)</b> | <b>Cu-N(C)</b> | <b><i>T</i></b> | <b>Sum</b> |
|-----------|----------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|------------|
| <b>12</b> | N        | 2.061(6)       | 2.078(6)       | 2.061(6)       | 2.078(6)       | 2.353(7)       | 2.353(7)       | 0.880           | 12.984     |
| <b>13</b> | N        | 2.027(26)      | 2.066(25)      | 2.040(23)      | 2.131(24)      | 2.350(28)      | 2.459(26)      | 0.859           | 13.073     |
| <b>14</b> | N        | 2.164(3)       | 2.164(3)       | 2.164(3)       | 2.164(3)       | 2.173(6)       | 2.173(6)       | 0.996           | 13.002     |
| <b>15</b> | O        | 1.974(2)       | 2.079(2)       | 1.974(2)       | 2.079(2)       | 2.167(2)       | 2.167(2)       | 0.935           | 12.440     |
| <b>16</b> | O        | 1.968(2)       | 2.021(2)       | 1.968(2)       | 2.021(2)       | 2.223(2)       | 2.223(2)       | 0.897           | 12.424     |
| <b>17</b> | O        | 2.002(9)       | 2.035(9)       | 1.981(9)       | 2.028(9)       | 2.156(9)       | 2.201(10)      | 0.923           | 12.403     |