# Supplementary Materials

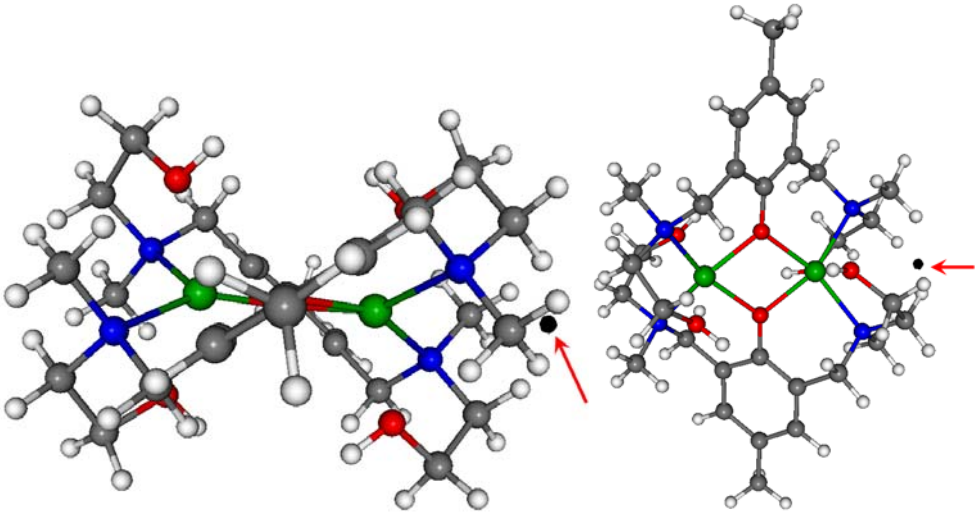

**Figure 1** View of the highest residue (pointed by the red arrow) for two orientations of the cobalt complex. Blue: N atoms, red: O atoms, gray: C atoms, green: Co atoms. The black isosurface is drawn for 0.5 e.Å$^{-3}$

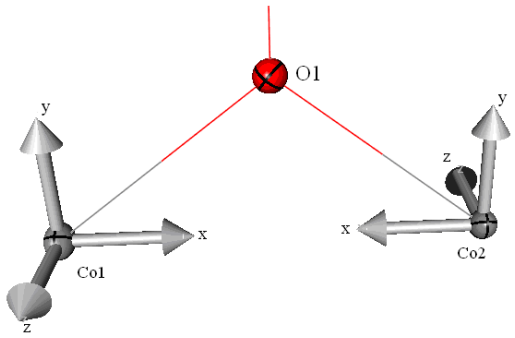


**Figure 2** Local axes of the Co atoms for the multipole refinement: X axis is along the Co···Co direction (**b** axis), Z axis is perpendicular to the $Co_1$-$O_1$-$Co_2$-$O_{1i}$ plane and Y completes the basis set (in the plane of the bridge).

The d-orbital density is:

$$\rho = \sum_i \sum_j P_{ij} \phi(d_i)\phi(d_j)$$

Where $\phi(d_i)$ the atomic d-orbital basis set and Pij is is the population of the ij product. The cross term is $\phi(d_i)\phi(d_j)$ with i≠j and should be zero for the highest symmetry environments.

**Table 1** Cross terms for the different d-orbital models (obtained with ERD, Sabino & Coppens( 2003)).

| | Option | dz²/xz | dz²/yz | $dz^2/x^2-y^2$ | dz2/xy | dxz/yz | dxz/x²-y² | dxz/xy | dyz/x²-y² | dyz/xy | dx²-y²/xy | Sum(di/dj)² |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Co_1$ | I | -0.059 | -0.112 | -0.010 | -0.272 | -0.421 | -0.155 | -0.046 | -0.088 | 0.151 | -0.101 | 0.334 |
| $Co_1$ | II | 0.034 | -0.059 | 0.000 | 0.289 | 0.4401 | 0.048 | 0.043 | 0.040 | -0.035 | 0.063 | 0.294 |
| $Co_2$ | I | -0.033 | -0.011 | -0.0058 | -0.205 | -0.399 | -0.127 | 0.125 | -0.032 | 0.322 | 0.069 | 0.344 |
| $Co_2$ | II | 0.0312 | -0.037 | 0.000 | 0.207 | 0.404 | 0.044 | 0.221 | 0.043 | -0.220 | 0.198 | 0.349 |

**Table 2** Topological properties at selected bond critical points (i refer to the applied symmetry: -x, y, -z+1/2)

| Bond | d (Å) | ρ(CP) (e.Å$^{-3}$) | $\nabla^2\rho$(rc) (e.Å$^{-5}$) | $d_{1\text{-bcp}}$ (Å) | $\lambda_1$ (e.Å$^{-5}$) | $\lambda_2$ (e.Å$^{-5}$) | $\lambda_3$ (e.Å$^{-5}$) |
|---|---|---|---|---|---|---|---|
| C1-O1 | 1.3364(5) | 2.12 | -16.0 | 0.514 | -17.4 | -16.1 | 17.5 |
| C1-C2 | 1.4114(6) | 2.05 | -17.8 | 0.705 | -15.7 | -12.8 | 10.71 |
| C2-C3 | 1.3933(6) | 2.08 | -17.9 | 0.686 | -15.91 | -12.76 | 10.77 |
| C3-C4 | 1.4005(7) | 2.10 | -18.4 | 0.696 | -16.0 | -13.3 | 10.8 |
| C4-C5 | 1.3974(7) | 2.09 | -18.1 | 0.704 | -15.9 | -13.0 | 10.8 |
| C5-C6 | 1.4008(6) | 2.05 | -17.4 | 0.710 | -15.6 | -12.6 | 10.8 |
| C6-C1 | 1.4100(6) | 2.07 | -17.8 | 0.704 | -16.0 | -12.6 | 10.7 |
| C4-C11 | 1.5070(7) | 1.67 | -12.4 | 0.744 | -11.7 | -10.8 | 10.1 |
| Ring phenyl | | 0.15 | 3.47 | | -1.15 | -0.26 | 1.74 |

**Table 3** Integrated charges calculated by WinXPRO (Stash & Tsirelson, 2002) and NEWPROP (Souhassou & Blessing, 1999) programs.

| ATOM | Net Charge (e) NEWPROP | Net Charge (e) WinXPRO | ATOM | Net Charge (e) NEWPROP | Net Charge (e) WinXPRO | ATOM | Net Charge (e) NEWPROP | Net Charge (e) WinXPRO |
|---|---|---|---|---|---|---|---|---|
| Co1 | 0.8 | 0.8 | C115 | 0.1 | 0.0 | H103 | -0.1 | 0.2 |
| Co2 | 0.9 | 0.8 | C116 | 0.1 | 0.0 | H104 | 0.1 | 0.3 |
| B | 1.6 | 1.9 | C117 | -0.2 | -0.6 | H105 | 0.0 | 0.2 |
| O1 | -1.4 | -1.4 | C118 | -0.2 | -0.4 | H106 | 0.0 | 0.2 |
| O5 | -1.3 | -1.4 | C119 | -0.4 | -0.4 | H108 | 0.0 | 0.2 |
| O6 | -1.3 | -1.5 | C120 | -0.1 | -0.2 | H109 | 0.0 | 0.2 |
| O7 | -0.8 | -1.1 | C121 | 0.0 | -0.2 | H110 | -0.1 | 0.1 |
| O8 | -1.1 | -1.2 | C122 | 0.0 | -0.1 | H111 | -0.1 | 0.1 |
| N1 | -1.1 | -1.1 | C123 | -0.1 | -0.3 | H112 | 0.0 | 0.2 |
| N4 | -1.1 | -1.1 | C124 | -0.1 | -0.2 | H114 | 0.2 | 0.4 |
| C1 | 0.4 | 0.6 | C125 | -0.1 | -0.6 | H115 | 0.0 | 0.2 |
| C2 | -0.2 | -0.2 | C126 | 0.7 | 0.9 | H116 | 0.0 | 0.2 |
| C3 | -0.1 | -0.3 | C127 | -0.6 | -1.1 | H117 | 0.0 | 0.2 |
| C4 | -0.1 | -0.1 | H1 | 0.7 | 0.8 | H118 | 0.0 | 0.3 |
| C5 | -0.1 | -0.2 | H2 | 0.6 | 0.8 | H120 | 0.0 | 0.2 |
| C6 | -0.2 | -0.1 | H3 | 0.1 | 0.3 | H121 | 0.0 | 0.2 |
| C7 | 0.2 | -0.1 | H5 | 0.0 | 0.2 | H122 | 0.0 | 0.2 |
| C10 | 0.2 | -0.3 | H7a | 0.0 | 0.2 | H123 | 0.0 | 0.2 |
| C11 | 0.0 | -0.5 | H7b | 0.0 | 0.2 | H124 | 0.1 | 0.3 |
| C12 | 0.2 | -0.1 | H10a | 0.1 | 0.3 | H125 | 0.2 | 0.4 |
| C13 | 0.1 | -0.2 | H10b | 0.0 | 0.2 | H126 | 0.1 | 0.3 |
| C15 | 0.1 | -0.3 | H10c | 0.0 | 0.2 | H127 | 0.0 | 0.2 |
| C23 | 0.1 | -0.2 | H11a | 0.1 | 0.3 | H128 | 0.1 | 0.3 |
| C24 | 0.3 | 0.0 | H11b | 0.1 | 0.3 | H129 | 0.1 | 0.4 |
| C29 | 0.3 | 0.0 | H11c | 0.1 | 0.3 | H130 | 0.3 | 0.4 |
| C101 | -0.5 | -0.5 | H12a | 0.1 | 0.2 | H01 | 0.6 | 0.8 |
| C102 | -0.1 | -0.2 | H12b | 0.0 | 0.2 | H02 | 0.6 | 0.8 |
| C103 | -0.1 | -0.2 | H13a | 0.0 | 0.2 | | | |
| C104 | -0.1 | -0.2 | H13b | 0.1 | 0.3 | | | |
| C105 | -0.1 | -0.2 | H15a | 0.1 | 0.3 | | | |
| C106 | -0.1 | -0.3 | H15b | 0.0 | 0.2 | | | |
| C107 | -0.4 | -0.5 | H15c | 0.0 | 0.2 | | | |
| C108 | -0.1 | -0.3 | H23a | 0.1 | 0.2 | | | |
| C109 | 0.0 | -0.1 | H23b | 0.1 | 0.3 | | | |
| C110 | -0.1 | -0.3 | H24a | 0.0 | 0.2 | | | |
| C111 | 0.0 | -0.2 | H24b | 0.1 | 0.2 | | | |
| C112 | -0.1 | -0.3 | H29a | 0.1 | 0.3 | | | |
| C113 | -0.3 | -0.4 | H29b | -0.1 | 0.2 | | | |
| C114 | 0.0 | -0.3 | H102 | 0.0 | 0.3 | | | |

**Table 4** Integrated basin volumes calculated by WinXPRO (Stash & Tsirelson, 2002) and NEWPROP (Souhassou & Blessing, 1999) programs.

| ATOM | Volume (Å$^3$) NEWPROP | Volume (Å$^3$) WinXPRO | ATOM | Volume (Å$^3$) NEWPROP | Volume (Å$^3$) WinXPRO | ATOM | Volume (Å$^3$) NEWPROP | Volume (Å$^3$) WinXPRO |
|---|---|---|---|---|---|---|---|---|
| Co1 | 11.3 | 10.7 | C115 | 13.0 | 13.2 | H103 | 8.1 | 6.9 |
| Co2 | 11.0 | 10.5 | C116 | 11.5 | 11.7 | H104 | 8.1 | 7.2 |
| B | 3.2 | 2.5 | C117 | 15.5 | 16.5 | H105 | 7.8 | 6.5 |
| O1 | 13.2 | 13.0 | C118 | 14.3 | 14.6 | H106 | 6.8 | 5.9 |
| O5 | 15.1 | 15.3 | C119 | 11.4 | 10.6 | H108 | 6.9 | 6.0 |
| O6 | 14.7 | 15.0 | C120 | 12.1 | 12.2 | H109 | 7.5 | 6.7 |
| O7 | 19.8 | 21.0 | C121 | 13.1 | 12.9 | H110 | 9.4 | 8.3 |
| O8 | 18.6 | 18.0 | C122 | 14.1 | 13.9 | H111 | 8.8 | 7.8 |
| N1 | 8.8 | 8.6 | C123 | 13.8 | 13.6 | H112 | 7.0 | 6.4 |
| N4 | 8.7 | 8.6 | C124 | 13.9 | 14.0 | H114 | 6.9 | 5.8 |
| C1 | 8.8 | 8.4 | C125 | 15.5 | 17.3 | H115 | 10.1 | 8.9 |
| C2 | 10.5 | 9.9 | C126 | 7.9 | 7.0 | H116 | 7.9 | 7.6 |
| C3 | 12.5 | 12.5 | C127 | 13.9 | 16.1 | H117 | 6.9 | 6.7 |
| C4 | 11.8 | 10.9 | H1 | 1.9 | 0.9 | H118 | 7.6 | 6.3 |
| C5 | 12.2 | 12.1 | H2 | 2.1 | 1.2 | H120 | 7.9 | 6.6 |
| C6 | 9.9 | 9.4 | H3 | 6.4 | 5.5 | H121 | 8.7 | 7.8 |
| C7 | 8.0 | 9.3 | H5 | 7.6 | 6.8 | H122 | 8.9 | 8.5 |
| C10 | 10.0 | 11.9 | H7a | 6.8 | 6.4 | H123 | 8.4 | 6.6 |
| C11 | 12.6 | 15.2 | H7b | 5.4 | 4.8 | H124 | 7.4 | 6.2 |
| C12 | 7.9 | 9.0 | H10a | 7.2 | 6.6 | H125 | 4.8 | 4.0 |
| C13 | 8.8 | 10.1 | H10b | 6.1 | 5.5 | H126 | 5.0 | 4.7 |
| C15 | 9.7 | 11.5 | H10c | 7.5 | 6.9 | H127 | 6.5 | 5.3 |
| C23 | 8.4 | 9.6 | H11a | 6.8 | 6.0 | H128 | 5.3 | 5.0 |
| C24 | 8.2 | 9.7 | H11b | 7.1 | 7.1 | H129 | 6.8 | 5.6 |
| C29 | 7.9 | 9.2 | H11c | 9.0 | 7.9 | H130 | 7.8 | 7.2 |
| C101 | 11.4 | 10.7 | H12a | 5.1 | 4.6 | H01 | 1.8 | 0.9 |
| C102 | 12.1 | 12.5 | H12b | 7.7 | 7.2 | H02 | 1.8 | 1.0 |
| C103 | 12.8 | 12.7 | H13a | 7.5 | 6.9 | | | |
| C104 | 14.4 | 14.6 | H13b | 6.7 | 5.8 | | | |
| C105 | 14.6 | 14.5 | H15a | 6.3 | 5.7 | | | |
| C106 | 11.5 | 11.8 | H15b | 6.2 | 5.4 | | | |
| C107 | 11.0 | 11.0 | H15c | 6.8 | 6.1 | | | |
| C108 | 13.4 | 13.7 | H23a | 7.9 | 7.4 | | | |
| C109 | 12.6 | 13.2 | H23b | 6.2 | 5.5 | | | |
| C110 | 13.4 | 14.0 | H24a | 7.4 | 6.7 | | | |
| C111 | 12.4 | 13.1 | H24b | 6.7 | 6.0 | | | |
| C112 | 11.3 | 12.1 | H29a | 7.3 | 6.8 | | | |
| C113 | 11.0 | 10.8 | H29b | 6.6 | 5.9 | | | |
| C114 | 12.1 | 14.6 | H102 | 6.9 | 5.9 | | | |

## References

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