Supplementary Information for:

Self-assembly of Zn(salphen) complexes: Steric regulation, stability studies and crystallographic analysis revealing an unexpected dimeric 3,3′-t-Bu-substituted Zn(salphen) complex

Marta Martínez Belmonte, Sander J. Wezenberg, Robert M. Haak, Daniele Anselmo, Eduardo C. Escudero-Adán, Jordi Benet-Buchholz and Arjan W. Kleij*
akleij@iciq.es

Contents:

Page S2: Crystallographic comments

Page S3: \(^1\)H NMR comparison between dimers (5)_2 and (10)_2 and hetero-dimeric assembly 5·10.

Page S5: MALDI-TOF mass spectrometric analysis of 5·10.
Crystallographic comments

**Complex 2:**

The unit cell of this compound contains a CH₃CN molecule and one of the benzene rings at the main molecule is showing some disorder. The completeness of the data is 95%. The structure has an R1 value of 4.0%.

**Complex 5:**

The unit cell contains two half independent molecules of the complex. The unit cell contains also three independent molecules of CH₃CN. Some of the tert-butyl groups are disordered. The completeness of the data is 91%. The structure has an R1 value of 4.42%.

**Complex 6:**

The unit cell of this compound contains one molecule of CH₃CN and non relevant disorder was observed. The completeness of the data is 91%. The structure has an R1 value of 2.67%.

**Complex 9:**

The structure contains three molecules of CH₃CN and one of the tert-butyl groups is disordered in two positions. The structure has an R1 value of 8.28%.

**Complex 11:**

The structure is a solvate of 2,6-lutidine (2,6-dimethylpyridine). The 2,6-lutidine molecule is disordered in two overlaid positions (50:50) which are related through a C2-operation. The structure has an R1 value of 4.76%.

The residual electron density near the Zn atom is a residual artifact due to the presence of a second crystal that was not enough intense to perform a combined data reduction and absorption. This is also shown in the unusually large second term of the weighting scheme: 5.9979

**Complex 18:**

The unit cell does not contain solvent molecules and only diminutive disorder was observed. The completeness of the data is of 94%. This structure has an R1 value of 3.22%.

**Complex 19:**

The unit cell of this compound contains one molecule of CH₃CN and non relevant disorder was observed. The completeness of the data is 87%. The crystal measured was a twin (crystal ratio of 51:49) and for the absorption correction TWINABS was used
The structure has a R1 value of 5.7 %.
$^1$H NMR comparison between dimers (5)$_2$ and (10)$_2$ and hetero-dimeric assembly 5·10

Imine region of the $^1$H NMR ($d_6$-acetone) spectra of the respective species:

Full aromatic region:

In **GREEN**: complex 5, in **RED**: complex 10, and in **BLUE** hetero-complex 5·10.
$t$-Bu region:

In **GREEN**: complex 5, in **RED**: complex 10, and in **BLUE** hetero-complex 5·10.
MALDI-TOF mass spectrometric analysis of \textbf{5·10}.

\textbf{Calcd masses (molecular ions) of the DIMERS:}

See: \url{http://winter.group.shef.ac.uk/chemputer/isotopes.html}

For \((5)_2\): \(m/z = 1096 \ (100\%)
\)
For \((10)_2\): \(m/z = 1074 \ (100\%)
\)
For \(5\cdot10\): \(m/z = 1085 \ (100\%)
\)