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Exploring coordination chemistry and reactivity of formazanate ligands

Travieso Puente, Raquel

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Exploring coordination chemistry and reactivity of formazanate ligands

Raquel Travieso Puente

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Rector Magnificus Prof. E. Sterken
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on
Friday 13 October 2017 at 11:00 hours

by

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born on 9 October 1987
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Esta tesis va dedicada a mi guía y mi ejemplo de vida.

A la sonrisa infinita, luchadora insaciable.

Esta tesis va dedicada a ti, Mamá.

*Queda prohibido llorar sin aprender,
levantarte un día sin saber qué hacer,
tener miedo a tus recuerdos.*

*Queda prohibido no sonreír a los problemas,
no luchar por lo que quieras,
abandonarlo todo por miedo,
no convertir en realidad tus sueños.
[...]*

*Queda prohibido no intentar comprender a las personas,
pensar que sus vidas valen más que la tuya,
no saber que cada uno tiene su camino y su dicha.*

*Queda prohibido no crear tu historia,
no tener un momento para la gente que te necesita,
no comprender que lo que la vida te da también te lo quita.
[...]*

*Queda prohibido no buscar tu felicidad,
no vivir tu vida con una actitud positiva,
no pensar en que podemos ser mejores,
no sentir que sin ti, este mundo no sería igual.*

~ ~ ~ ~ ~

*It is forbidden to cry without learning,
to wake up one day not knowing what to do,
to be afraid of your memories.*

*It is forbidden not to smile at problems,
not to fight for what you want,
to abandon everything because of fear,
not to transform your dreams into reality.
[...]*

*It is forbidden not to try to understand people,
to think that their lives are more valuable than yours,
not to know that each person has his own ways and his own joy.*

*It is forbidden not to create your history,
not to have a moment for the people who need you,
not to understand that whatever life gives you, it takes it away as well.
[...]*

*It is forbidden not to search for your happiness,
not to live your life with a positive attitude,
not to think that we can be better,
not to feel that, without you, this world wouldn't be the same.*

~ **Pablo Neruda** ~

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List of compounds

◆ Formazan ligands previously reported¹:

1-H: PhNHNC(*p*-tol)NNPh

2-H: MesNHNC(CN)NNMes

3-H: PhNHNC('Bu)NNPh

4-H: MesNHNC(*p*-tol)NNPh

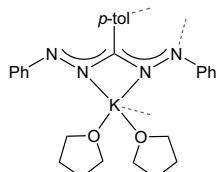
5-H: MesNHNC(*p*-tol)NNMes

6-H: C₆F₅NHNC(*p*-tol)NNMes

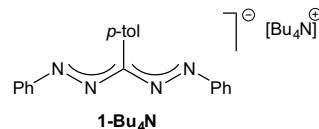
8-H: PhNHNC(C₆F₅)NNMes

9-H: C₆F₅NHNC(C₆F₅)NNMes

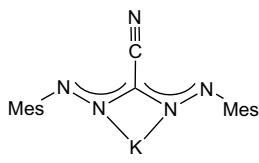
◆ Compounds presented in Chapter 2:



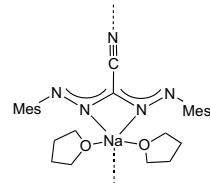
1-K (dimer): K[PhNNC(*p*-tol)NNPh]·2THF



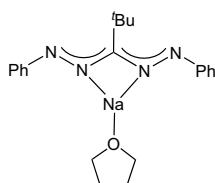
1-Bu₄N: [Bu₄N][PhNNC(*p*-tol)NNPh]



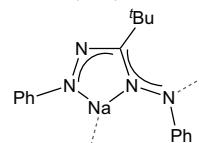
2-K: K[MesNNC(CN)NNMes]



2-Na (polymer):
Na[MesNNC(CN)NNMes]·2THF



3-Na_{THF}: Na[PhNNC('Bu)NNPh]·THF



3-Na (hexamer): Na[PhNNC('Bu)NNPh]

◆ Compounds presented in Chapter 3:

1-Mg: [PhNNC(*p*-tol)NNPh]₂Mg

1-Mg_{THF}: [PhNNC(*p*-tol)NNPh]₂Mg(THF)

3-Mg: [PhNNC('Bu)NNPh]₂Mg

3-Mg_{THF}: [PhNNC('Bu)NNPh]₂Mg(THF)

4-Mg: [MesNNC(*p*-tol)NNPh]₂Mg

4-Mg_{THF}: [MesNNC(*p*-tol)NNPh]₂Mg(THF)

6-Mg: [C₆F₅NNC(*p*-tol)NNMes]₂Mg

6-Mg_{THF}: [C₆F₅NNC(*p*-tol)NNMes]₂Mg(THF)

8-Mg: [PhNNC(C₆F₅)NNMes]₂Mg

9-Mg: [C₆F₅NNC(C₆F₅)NNMes]₂Mg

1-Ca: [PhNNC(*p*-tol)NNPh]₂Ca(THF)₂

3-Ca: [PhNNC('Bu)NNPh]₂Ca(THF)₂

4-Ca: [MesNNC(*p*-tol)NNPh]₂Ca(THF)₂

5-Ca: [MesNNC(*p*-tol)NNMes]₂Ca(THF)₂

Other compounds reported previously used for comparison¹:

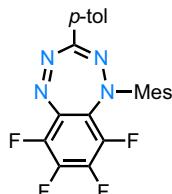
1-Zn: [PhNNC(*p*-tol)NNPh]₂Zn

3-Zn: [PhNNC('Bu)NNPh]₂Zn

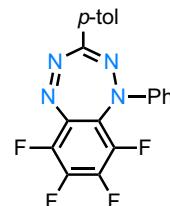
4-Zn: [MesNNC(*p*-tol)NNPh]₂Zn

6-Zn: [C₆F₅NNC(*p*-tol)NNMes]₂Zn

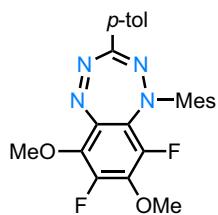
◆ Compounds presented in Chapter 4 and 5



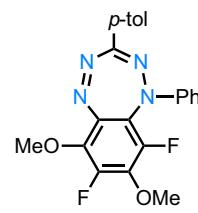
Tetrazepine 4.1



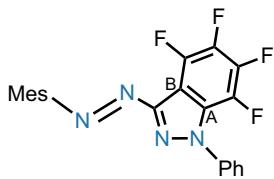
Tetrazepine 4.2



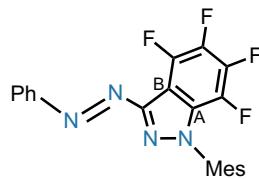
Tetrazepine 4.1^{OMe}



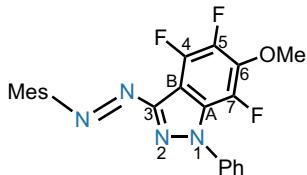
Tetrazepine 4.2^{OMe}



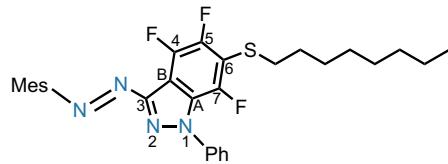
Azoindazole 4.3



Azoindazole 4.4



Azoindazole 4.3^{OMe}



Azoindazole 4.3^{SC8H17}

◆ Compounds presented in Chapter 6:

1-ZnO*i*Pr: {[PhNNC(*p*-tol)NNPh]ZnO*i*Pr}₂

1-ZnO*t*Bu: {[PhNNC(*p*-tol)NNPh]ZnO*t*Bu}₂

1-ZnOPh: {[PhNNC(*p*-tol)NNPh]ZnOPh}₂

5-ZnO*i*Pr: {[MesNNC(*p*-tol)NNMes]ZnO*i*Pr}₂

1-MgOC(CH₃Ph)₂: {[PhNNC(*p*-tol)NNPh]MgOCCH₃(Ph)₂}₂

Other compounds reported previously¹:

1-ZnMe: [PhNNC(*p*-tol)NNPh]ZnMe

3-ZnMe: [PhNNC('Bu)NNPh]₂ZnMe

4-ZnMe: [MesNNC(*p*-tol)NNPh]₂ZnMe

5-ZnMe: [MesNNC(*p*-tol)NNMes]ZnMe

◆ Compounds presented in Chapter 7:

1-Fe: [PhNN(*p*-tol)NNPh]₂Fe

[1-Fe][NBu₄]: [Bu₄N][(PhNN(*p*-tol)NNPh)₂Fe]

(1) Chang, M.-C. *Thesis: Formazanate as a Redox-Active, Structurally Versatile Ligand Platform*; 2016.

