

Di- and oligo-nuclear nickel complexes with oxalic amidinato bridging ligands: syntheses, structures and catalytic reactions†

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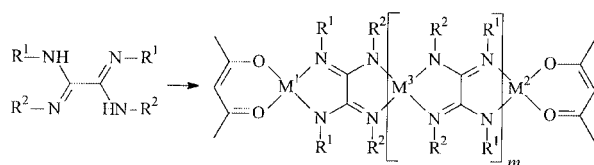
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A new family of di-, tri- and tetra-nuclear Ni(II) complexes containing oxalic amidinates as bridging ligands is described in which both peripheral Ni centres are catalytically active in the oligomerization or polymerization of ethylene or in the selective cross coupling of Ar–X with Ar'–MgX.

Di- or oligo-nuclear metal complexes of late d metals connected via the conjugated π -system of oxalic amidinato ligands ('oxam') are attractive candidates for catalytic reactions, because the ligands are easily accessible and their steric and electronic properties can be easily modified. Furthermore, systems with different metals in peripheral positions enable catalysts to be designed in which either one or two metals are catalytically active. In addition, the metal coordinated at the opposite side of an active metal centre may be used for fine tuning the catalytic activity.

Since oxalic amidinato ligands tend to form ill-defined polymers with metal salts^{1,2} their coordination chemistry is very limited.^{3–6} Neither dinuclear d⁸ metal complexes nor tri- or oligo-metallic complexes are known. Furthermore, catalytic C–C-linking reactions are also unknown.

Surprisingly, the Ni(II) complexes **1–4** (Scheme 1, $m = 0$) are obtained by reacting Ni(acac)₂ in toluene or THF with a variety of oxalamidines. Recrystallisation from toluene resulted in red-brown diamagnetic crystalline complexes in 35–60% yields. According to ¹H NMR spectroscopy on **1–5** the ratio of acac to oxalic amidine ligand was 2:1 supporting dimeric structures (Scheme 1).‡



- 1** $m = 0$, R¹, R² = phenyl, M¹, M² = Ni
2 $m = 0$, R¹, R² = tolyl, M¹, M² = Ni
3 $m = 0$, R¹, R² = mesityl, M¹, M² = Ni
4 $m = 0$, R¹ = tolyl, R² = mesityl, M¹, M² = Ni
5 $m = 0$, R¹, R² = mesityl, M¹ = Ni, M² = Zn
6 $m = 1$, R¹, R² = mesityl, M¹, M² = Ni, M³ = Zn

Scheme 1

The solid state structure of the key complex **4** was determined by X-ray diffraction and Fig. 1 displays its molecular structure.§

As expected, the oxalamidinate acts as bridging ligand connecting two (acac)Ni(II) fragments with both metal centres essentially planar. Although **4**, containing different N-substituents, may exist as two isomers, to our surprise only one isomer was observed, in which both metal centres have different coordination environments: one metal is surrounded by two

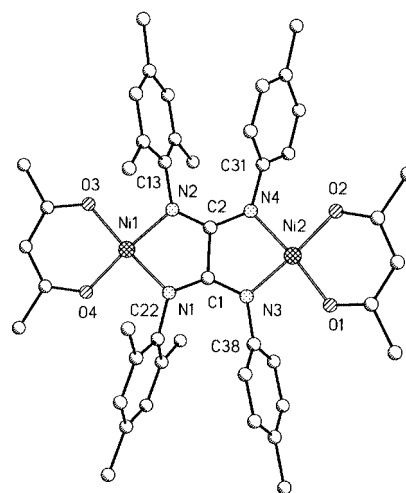


Fig. 1 Molecular structure of **4**. Selected bond distances (Å) and bond angles (°): Ni1–N1 1.880(8), Ni2–N2 1.886(8), Ni1–O3 1.841(7), Ni1–O4 1.843(7), Ni2–N3 1.879(8), Ni2–N4 1.902(8), Ni2–O1 1.845(7), Ni2–O2 1.854(7), C1–C2 1.518(13), N1–C1 1.304(12), N2–C2 1.311(12), N3–C1 1.316(13), N4–C2 1.334(12); O4–Ni1–N1 90.3(3), O3–Ni1–N2 90.9(3), N2–Ni1–N1 83.9(3), O3–Ni1–O4 94.8(3), O1–Ni2–N3 89.7(3), O2–Ni2–N4 91.4(3), N3–Ni2–N4 84.5(4), O1–Ni2–O2 94.4(3).

mesityl–N groups, the other by two *p*-tolyl–N groups. The aromatic substituents are oriented to the ligand plane at an angle of 90°. The ¹H NMR spectrum confirms the presence of only one isomer in solution. Complexes **1–5** can be considered as the first members of a series of oxalamidinato complexes of general composition L_nM¹(oxam)[M³(oxam)]_mM²L_n ($m = 0$).

The trimetallic complex [(acac)Ni(oxam)Zn(oxam)Ni(acac)] **6** is the first example of the next generation of this series ($m = 1$, M¹, M² = Ni; M³ = Zn, oxam = tetramesityloxalamidine) which was prepared by reacting of 2 equiv. of oxam with ZnEt₂ in toluene, followed by addition of 2 equiv. of Ni(acac)₂ in good yields.

The Ni₂Zn₂ complex **7** is the first example of a tetrametallic complex of the above-mentioned range prepared from 2 equiv. of ZnEt₂ and 3 equiv. of bis(mesityl)bis(*p*-tolyl)oxalamidine in THF, followed by reaction with 2 equiv. of Ni(acac)₂. Red crystalline complex **7** was isolated upon recrystallisation of the product from toluene. Elemental analyses, mass spectra, and the ¹H NMR spectrum confirm its composition. Its X-ray structure (Fig. 2) shows that both peripheral Ni centres have the same planar environment as in **4**, while the two central Zn atoms are tetrahedrally coordinated.

Table 1 shows that all the complexes are catalytically active towards ethylene when activated with MAO or Et₃Al. In contrast to the well established Ni catalysts for the SHOP process,⁷ in which negatively charged P–O ligands support the oligomerization of ethylene, we observed both oligomerization and polymerization of ethylene (Table 1).

A comparison of **2** (runs 1 and 2 in Table 1) and **3** (runs 5 and 6 in Table 1) clearly shows that the *p*-tolyl groups in **2** promote the oligomerization of ethylene; however, substitution by

† Electronic supplementary information (ESI) available: general procedures and full spectroscopic characterisation of complexes **1–7**. See <http://www.rsc.org/suppdata/cc/b0/b000791i/>

Table 1 Catalytic reactions of 1–7 with ethylene in the presence of MAO or Et₃Al^a

Run	Precat.	Cocatalyst	C ₄ /C ₆ (%)	Polymer (%)	Polymer selectivity (%)	M _w	M _n	D = M _w /M _n
1	2	MAO (300)	33	—	—	—	—	—
2	3	MAO (2)	—	4	100	357000	244000	1.46
3	3	MAO (6)	—	24	100	673000	451000	1.49
4	3	MAO (20)	2	42	95	491000	185000	2.66
5	3	MAO (300)	9	74	89	157000	88000	1.78
6	3	MAO (1000)	6.5	54	89	75000	30000	2.49
7	3	AlEt ₃ (300)	—	62	92	246000	165000	1.49
8	4	MAO (300)	16	16	50	237000	117000	2.02
9	6	MAO (300)	7	82	92	189200	132700	1.43
10	7	MAO (300)	24	2	—	—	—	—
11	Ni(acac) ₂	MAO (300)	38	—	—	—	—	—

^a General conditions: 0.031 mmol catalyst, 10 bar ethylene, 20 ml toluene, 16 h reaction time, room temperature; run 9: most of the polymer was insoluble, only the molecular weight of the soluble fraction was determined.

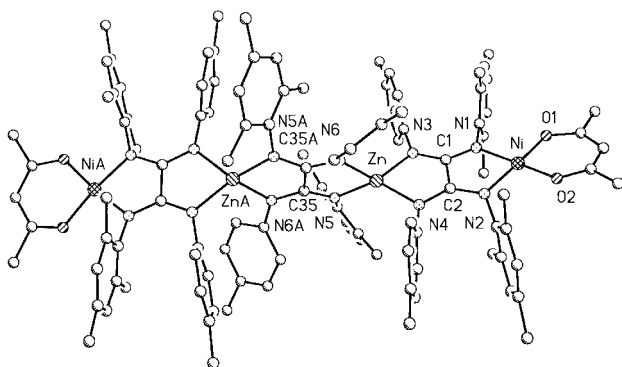


Fig. 2 Molecular structure of 7. Selected bond distances (Å) and angles (°): Ni–O1 1.840(4), Ni–O2 1.864(4), Ni–N1 1.897(4), Ni–N2 1.885(4), Zn–N3 2.002(4), Zn–N4 2.007(4), Zn–N5 1.996(5), Zn–N6 2.000(5), C1–N1 1.309(6), C1–N3 1.334(7), C2–N2 1.312(7), C2–N4 1.344(7), C1–C2 1.524(8), C35–N5 1.343(7), C35–N6A 1.338(7), C35–C35A 1.518(12), dihedral angle between planes (Ni–O1–O2)/(Ni–N1–N2) 6.9(2), (Zn–N2–N4)/(Zn–N5–N6) 100.8(2). Symmetry transformations used to generate equivalent atoms: A $-x + 3/2, y, -z + 1$.

mesityl groups (in **3**) results in the formation of a selective polymerization catalyst. In contrast to recently described 1,2-diimine or salicylaldiminato complexes of d⁸ metals, where very bulky substituents have to be used for selective polymerization,^{8–11} in the oxalic amidinato complexes only two additional *ortho*-methyl groups are necessary to switch the reaction from oligomerization to polymerization of ethylene. Since both oligomerization and the polymerization of ethylene occur using **4** as catalyst which contains two different coordination spheres, we can conclude that *both* metals are catalytically active (runs 3 and 4 in Table 1). If the reaction with **3** was carried out heating the reaction mixture from room temperature to 69 °C within 10 min (50 bar ethylene) then 3.7 g of polyethylene was produced giving a TOF of 102 000 h⁻¹.

The catalytic reaction of **6**/MAO with ethylene shows that the Zn moiety in the middle of **6** increases the selectivity towards polymerization compared with **3** (Table 1, runs 5 and 9). This demonstrates the possibility for fine tuning the catalytic activity by using different metals. The tetranuclear complex **7**, however, is a dimerization catalyst when activated with MAO. The complexes can also be used as catalysts in other C–C coupling reactions such as the polymerization of styrene (*e.g.*: 3/300 equiv. MAO/4000 equiv. styrene yielded 94% polystyrene) or cross coupling, *e.g.* of mesitylmagnesium bromide (500 equiv.) with *p*-tolyl bromide (500 equiv.) to give mesityl–4-tolyl in 99% selectivity and an overall yield of 95% when **4** in THF at ambient temperature was used.

In conclusion, we have shown that di-, tri- and tetra-nuclear complexes of late d metals with oxalamidates can easily be prepared and used in a number of catalytic C–C-linking reactions. Both peripheral Ni centres are catalytically active in these complexes.

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Notes and references

‡ Satisfactory microanalysis have been obtained. *Selected spectroscopic data*: for **4**: C₄₄H₅₀N₄O₄Ni₂: MS (EI): *m/z* 816 (42%, M + 2⁺); δ_H(toluene-d₈, 25 °C): 0.89, 0.94 (CH₃-acac, 2 × s, 12H), 1.89, 1.9 (*p*-CH₃, 2 × s, 12H), 2.68 (*o*-CH₃-mes, s, 12H), 4.62, 4.68 (CH-acac, 2 × s, 2H), 6.25 (CH-mes, s, 4H), 6.37, 6.71 (CH-tol, AA'BB', 8H).

For **7**: C₁₁₂H₁₂₂N₁₂Ni₂O₄Zn₂: δ_H(THF-d₈, 25 °C): 1.01, 1.04, 1.29, 1.39, 1.48, 1.64, 1.83, 1.88, 1.90, 1.99, 2.03, 2.08, 2.12, 2.20, 2.25, 2.30, 2.34, 2.48 (CH₃, 72H), 4.97, 5.00 (CH-acac, 2H), 5.75, 5.79, 5.89, 5.93, 6.02–6.29 (m, CH-aryl, 23H), 6.44, 6.48, 6.56, 6.61, 6.65 (m, CH-aryl, 6H), 7.08–7.2 (m, CH-aryl, 7H).

§ *Crystal data* for **4**:¹² C₄₄H₅₀N₄Ni₂O₄, M_r = 816.30, brown prism, size 0.40 × 0.35 × 0.10 mm, monoclinic, space group P2₁/n, *a* = 12.696(2), *b* = 8.873(1), *c* = 36.989(4) Å, β = 98.278(6)°, *V* = 4123.5(9) Å³, *T* = –90 °C, *Z* = 4, D_c = 1.315 g cm⁻³, μ(Mo–Kα) = 9.59 cm⁻¹, F(000) = 1720, 4609 reflections with *h*(–13/13), *k*(0/9), *l*(–41/40), measured in the range 2.81 ≤ θ ≤ 23.27°, completeness θ max = 98.7%, 3331 independent reflections, R_{int} = 0.089, 2607 reflections with F_o > 4σ(F_o), 487 parameters, 0 restraints, R_{1obs} = 0.080, wR_{2obs} = 0.231, R_{1all} = 0.108, wR_{2all} = 0.271, GOF = 1.074, largest difference peak and hole: 0.385, –0.563 e Å⁻³.

For **7**:¹² C₁₁₂H₁₂₂N₁₂Ni₂O₄Zn₂, M_r = 1948.38, red prism, size 0.32 × 0.28 × 0.20 mm, monoclinic, space group I2/a, *a* = 22.2023(8), *b* = 21.6541(6), *c* = 25.343(1) Å, β = 105.960(2)°, *V* = 11714.5(7) Å³, *T* = –90 °C, *Z* = 4, D_c = 1.125 g cm⁻³, μ(Mo–Kα) = 7.71 cm⁻¹, F(000) = 4176, 22567 reflections for *h*(–27/27), *k*(–26/27), *l*(–31/31), measured in the range 3.01° ≤ θ ≤ 26.42°, completeness θ max = 98.9%, 11922 independent reflections, R_{int} = 0.091, 6125 reflections with F_o > 4σ(F_o), 615 parameters, 0 restraints, R_{1obs} = 0.086, wR_{2obs} = 0.217, R_{1all} = 0.175, wR_{2all} = 0.261, GOF = 1.010, largest difference peak and hole: 0.927, –0.451 e Å⁻³.

CCDC 182/1615. See <http://www.rsc.org/suppdata/cc/b0/b000791i/> for crystallographic files in .cif format.

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