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Cd(II) coordination compounds as heterogeneous catalysts for microwave-assisted peroxidative oxidation of toluene and 1-phenylethanol†

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The aroylhydrazone Schiff bases 2-hydroxy(2-hydroxybenzylidene)benzohydrazide (H_2L^1) and 2-amino(2-hydroxybenzylidene)benzohydrazide (H_2L^2) have been used to synthesize the new Cd(II) coordination polymer $[Cd(\mu\text{-}1\kappa ONO'\text{:}2\kappa O\text{:}3\kappa O''\text{-}L^1)(DMF)]_n$ (**1**) and the dinuclear complex $[Cd(1\kappa ONO'\text{:}2\kappa O\text{-}HL^2)(\kappa OO'\text{-}Ac)]_2\cdot 2DMF$ (**2**). Both **1** and **2** have been characterized by elemental analysis, FT-IR and single crystal X-ray diffraction analysis. The catalytic performances of **1** and **2** were evaluated towards the microwave (MW) assisted peroxidative oxidation (with *tert*-butylhydroperoxide, TBHP) of toluene and 1-phenylethanol under heterogeneous conditions. The MW-assisted peroxidative oxidation of toluene by a Cd(II) catalytic system is reported for the first time. At 50 °C, the **2**/TBHP/MW catalytic system shows good activity for toluene oxidation with a total (benzaldehyde + benzyl alcohol) product yield of 49% in 1 h, in the absence of any additives. In the case of neat solvent-free peroxidative oxidation of 1-phenylethanol the **1**/TBHP/MW catalytic system resulted in 24% total yield of acetophenone under optimized conditions. After the catalytic reactions, both **1** and **2** were successfully recovered and reused.

Introduction

Coordination polymers (CPs) are crystalline multifunctional materials widely used in gas storage and separation,[1,2] fluorescence and electrocatalytic sensors,[3,4] molecular recognition,[5,6] drug delivery,[7] synthesis of magnetic materials[8,9] and catalysis.[10,11] Aroylhydrazones, as ligands, can stabilize metal complexes in various coordination geometries and nuclearities,[12–22] their metal complexes can have a recognized potential to act as catalysts for oxidation reactions and some of them exhibit interesting magnetic properties.[11,19–22]

In this work, we have explored the heterogeneous catalytic activity of a new Cd(II) CP. Though cadmium compounds are known to be carcinogenic,[23] they have been used as versatile materials in different areas, particularly in the preparation of Metal–Organic Frameworks (MOFs) and CPs, semiconducting sulphides and metal nanoparticles.[24–27] There are different types of cadmium-based homogeneous[28–30] and heterogeneous[31–33] catalysts, semiconductors, *etc.*[34–36]

Herein, we report the syntheses of Cd(II) compounds, a coordination polymer $[Cd(\mu\text{-}1\kappa ONO'\text{:}2\kappa O\text{:}3\kappa O''\text{-}L^1)(DMF)]_n$ (**1**) and a dinuclear complex $[Cd(1\kappa ONO'\text{:}2\kappa O\text{-}HL^2)(\kappa OO'\text{-}Ac)]_2\cdot 2DMF$ (**2**), using two different aroylhydrazones. They have been screened as heterogeneous catalysts towards the peroxidative oxidation of toluene and 1-phenylethanol as model substrates of aromatic alkanes and secondary alcohols, respectively, and using *tert*-butyl hydroperoxide (TBHP) as the oxidizing agent, under microwave (MW) irradiation. Benzaldehyde is obtained as the main product from the oxidation of toluene whereas 1-phenylethanol produces acetophenone. These carbonyl compounds are useful starting materials in the industry of dyes, perfumes and pharmaceuticals[37–40] and building blocks for many organic compounds and fine chemicals.[41–46]

The establishment of sustainable conditions in catalytic oxygenation processes is a continuing demand and herein we explore the advantages of using microwave (MW) irradiation which provides a simpler and energy saving method compared to conventional heating.[47–55] The rate of the catalytic reaction under MW irradiation is also compared to the conventional heating. Peroxidative oxidation catalysed by Cd(II) complexes has been scaly reported[56,57] and MW-assisted peroxidative oxidation of alkyl benzene (toluene) by a heterogeneous Cd(II) system is now reported for the first time.

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Results and discussion

The Cd(II) coordination polymer [Cd(μ-1κONO′:2κO:3κO″-L^1)(DMF)]$_n$ (**1**) and the dinuclear complex [Cd(1κONO′:2κO-HL^2)(κOO′-Ac)]$_2$·2DMF (**2**) have been synthesized under solvothermal conditions (in DMF-MeOH) using two different aroylhydrazone Schiff bases, namely 2-hydroxy-(2-hydroxybenzylidene)benzohydrazide (H$_2$L^1) and 2-amino(2-hydroxybenzylidene)benzohydrazide (H$_2$L^2),[58–60] and Cd(OAc)$_2$·2H$_2$O (Scheme 1). In both cases, the ligand exhibits the keto form, but in **1** it behaves as a di-negative chelator (L^1)$^{2-}$ whereas in **2** it acts as a uni-negative chelator (HL^2)$^-$. In both complexes, phenolate oxygens at the *ortho*-position form phenoxido bridges. The phenolic –OH group present in the hydrazide moiety of H$_2$L^1 deprotonates during the reaction conditions and coordinates to another Cd(II) ion which helps to form 2D polymeric network of **1**. In the case of H$_2$L^2, the presence of –NH$_2$ group in the hydrazide moiety does not participate in coordination and thus **2** exists as dinuclear complex. Characterizations of **1** and **2** have been carried out by elemental analysis, IR spectroscopy and X-ray diffraction (single crystal) analysis. Besides the similar characteristic stretching signals of the ligands, the bands at 1602 and 1514 cm^{-1} in the IR spectrum of **2** correspond to the asymmetric and symmetric –COO stretching frequency of the acetate ligand.[61]

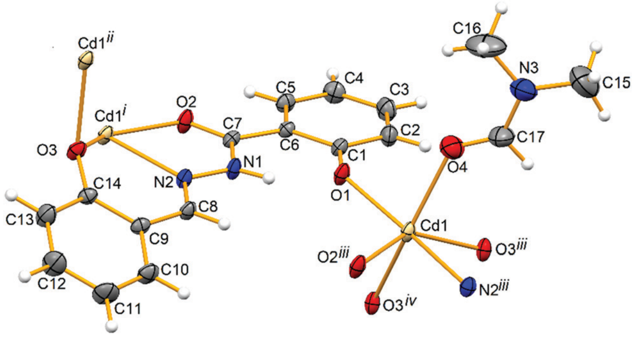
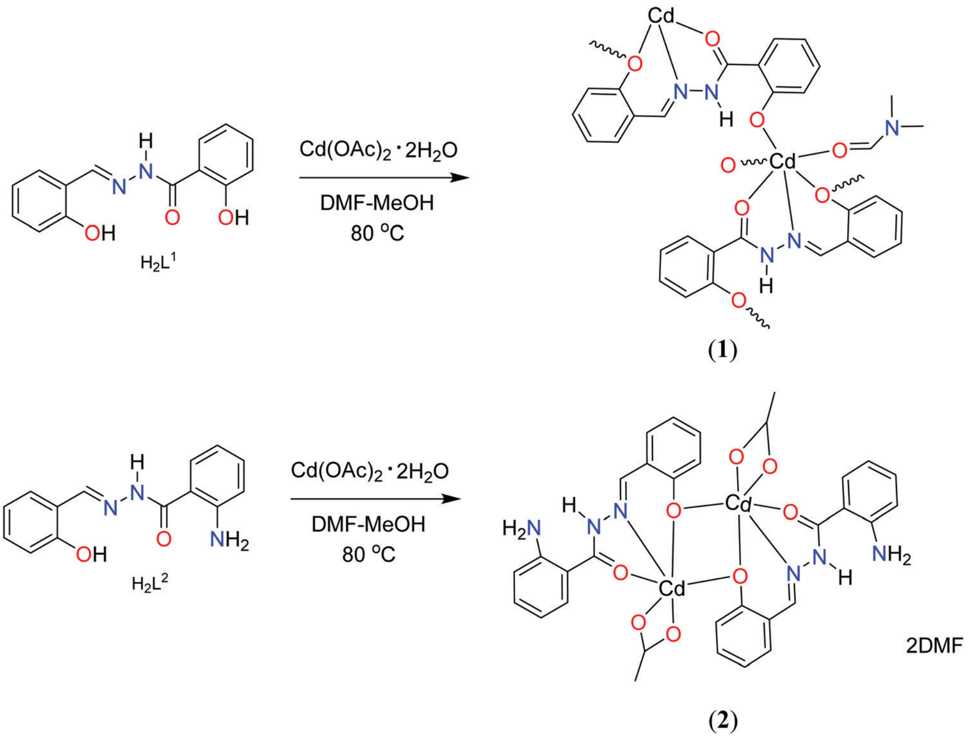


Fig. 1 Ellipsoid plot of **1** (drawn at 30% probability level) with atom numbering scheme. Symmetry operations to generate equivalent atoms: (i) 1 − *x*, 1/2 + *y*, 1.5 − *z*; (ii) *x*, 1/2 − *y*, −1/2 + *z*; (iii) 1 − *x*, −1/2 + *y*, 1.5 − *z*; (iv) *x*, 1/2 − *y*, 1/2 + *z*. Selected bond distances (Å) and angles (°): Cd1–O1 2.172(2), Cd1–O2^{iii} 2.327(2), Cd1–O3^{iii} 2.271(2), Cd–O3^{iv} 2.314(3), Cd1–O4 2.384(3), Cd1–N2^{iv} 2.320(3), N1–N2 1.375(4), C1–O1 1.321(4), C7–O2 1.255(4), C14–O3 1.322(4); O1–Cd1–N2^{iv} 163.08(10), O2^{iii}–Cd1–O3^{iii} 143.67(9), O3^{iv}–Cd1–O4 164.09(11).

X-ray structures

X-ray quality crystals of **1** and **2** were obtained under solvothermal synthesis from a mixture of DMF/methanol.

The asymmetric unit of **1** contains one ligand (L^1)$^{2-}$, one DMF molecule and one Cd(II) ion (Fig. 1). The aroylhydrazone ligand is in the dianionic keto form and symmetry expansion reveals a 2D polymeric structure with a metal-to-ligand ratio of 1 : 1, where every (L^1)$^{2-}$ moiety bridge chelate the metals in the following way (Fig. 2): one of the cations *via* the O$_{\text{keto}}$-, the N$_{\text{imine}}$- and the O$_{\text{phenolate}}$-atoms, this latter atom also binding a second cation, and the other O$_{\text{phenolate}}$ coordinating to a third cadmium. The Cd(II) cations have distorted octahedral NO$_5$ geometries and are located in the least-square planes constructed with the basal coordinating atoms from two symmetry related L^1 ligands; the apical positions are engaged with the



Scheme 1 Syntheses of **1** and **2**.

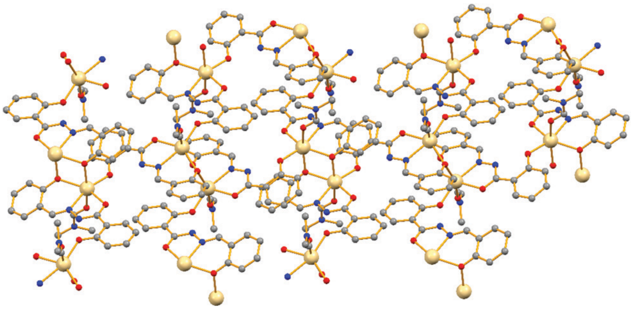


Fig. 2 Ball and stick representation of the 2D polymeric structure of **1** (arbitrary view).

O-atom of a third L^1 moiety and the O_{DMF}. The $(L^1)^{2-}$ assemblies are not planar (the least-square planes of the phenyl groups make an angle of 28.85°) and are stacked in the polymeric structure. No classical H-bond interactions were found in **1**, except the intramolecular contacts involving the H_{imine} atoms and the $O_{phenolate}$.

The asymmetric unit of **2** consists of a $(HL^2)^-$ ligand ONO′ coordinated to a cadmium center and one chelating acetate anion; a crystallization DMF solvent molecule is also present. Symmetry expansion leads to the formation of a dinuclear species with an inversion center in the middle of a $\{Cd_2O_2\}$ core (Fig. 3). As found in **1**, the aroylhydrazone ligands are in the keto form and chelate by means of the $O_{phenolate}$-, the O_{keto}- and the N_{imine}-atoms; the former type of atoms act as bridging bidentate donors to two metal cations. Despite the 6-membered NO_5 environments, every Cd(II) center exhibits a geometry that resembles a square pyramid in which the chelating acetate, as a whole, occupy the apical site. Relative to the least-square plane formed by the basal binding atoms, the metal is displaced 0.804 Å towards the acetate. The $(HL^2)^-$ ligand is also not planar (the least-square planes of the phenyl groups make an angle of 20.12°). Contrasting with **1**, the structure of **2** reveals H-bond interactions involving the donor N_{imine} and the acceptor $O_{acetate}$ [$d_{D\cdots A}$ 2.839(2) Å, $\angle_{D-H\cdots A}$ 163(3)°], and the donor N_{amine} and the acceptor O_{DMF} [$d_{D\cdots A}$ 2.952(4) Å, $\angle_{D-H\cdots A}$ 169(2)°] therefore generating a 2D infinite network (Fig. 4).

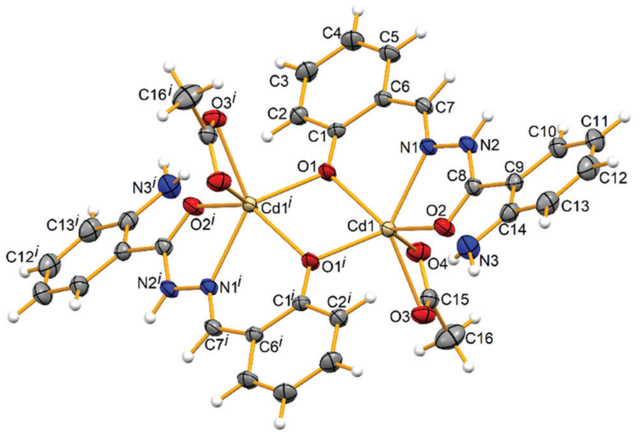


Fig. 3 Ellipsoid plot of **2** (drawn at 30% probability level) with atom numbering scheme. DMF molecule of crystallization is omitted for clarity. Symmetry operation to generate equivalent atoms: (i) $1 - x$, $1 - y$, $1 - z$. Selected bond distances (Å) and angles (°): Cd1–O1 2.1946(14), Cd1–O1^i 2.2824(13), Cd1–O2 2.3345(14), Cd1–O3 2.3903(16), Cd1–O4 2.3086(17), Cd1–N1 2.2993(16), N1–N2 1.385(2), C1–O1 1.328(2), C8–O2 1.254(2), C14–N3 1.368(3); O1–Cd1–O2 135.50(6), O1–Cd1–N1 133.71(6).

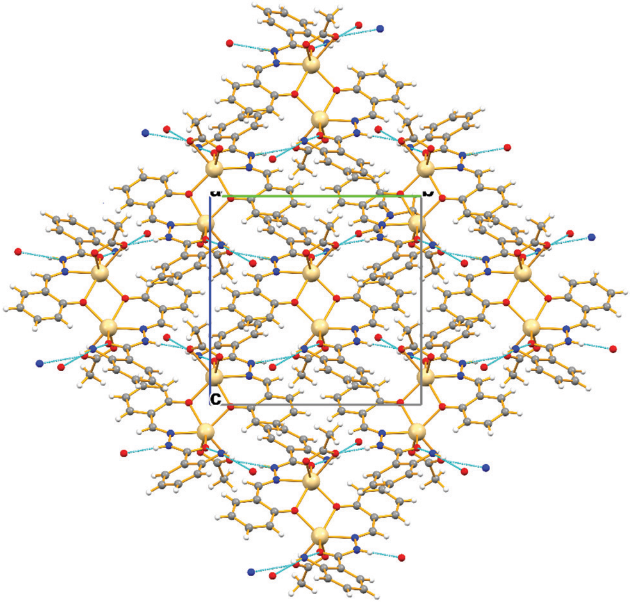
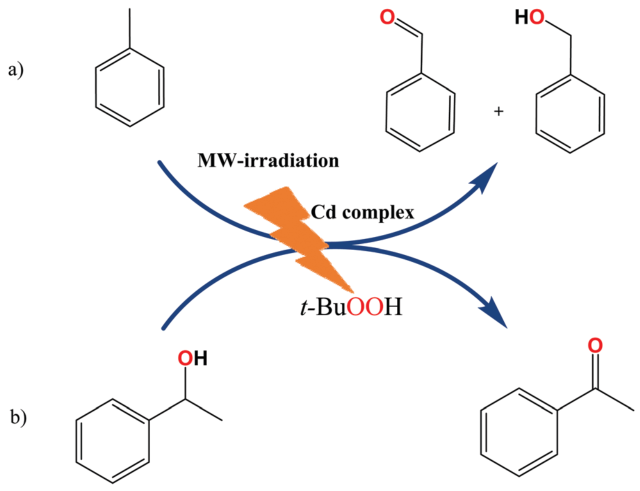


Fig. 4 A view (down the crystallographic *a* axis) of the infinite 2D network derived from H-bond interactions (represented in light-blue dashed lines).

Catalytic studies

To examine the catalytic performance of Cd(II) complexes **1** and **2** under microwave irradiation, we have selected toluene and 1-phenylethanol as model substrates for the peroxidative oxidation of alkanes and alcohols, respectively. All the reactions were carried out under mild conditions, using *t*-BuOOH as oxidant (Scheme 2).



Scheme 2 Microwave-assisted peroxidative oxidation of toluene (a) and 1-phenylethanol (b) by **1** and **2**.

Microwave-assisted peroxidative oxidation of toluene by the Cd(II) compounds

The microwave-assisted peroxidative oxidation of toluene (Scheme 2a and Table 3) was undertaken under low MW irradiation (5 W) in acetonitrile at 50 °C for 1 h (typically) and using *t*-BuOOH (aq. 70%, 2 eq.) as oxidant, in the presence of $[Cd(\mu\text{-}1\kappa ONO'{:}2\kappa O{:}3\kappa O''\text{-}L^1)(DMF)]_n$ (**1**) or $[Cd(1\kappa ONO'{:}2\kappa O\text{-}HL^2)(\kappa OO'\text{-}Ac)]_2{\cdot}2DMF$ (**2**). Both complexes are active as catalysts, being **2** the most promising one. Under the above-mentioned reaction conditions, toluene is oxidized to yield predominantly benzaldehyde, along with some amount of benzyl alcohol. For longer reaction periods, residual amounts of benzyl acetate and benzoic acid among other oxidation products were detected (GC-MS). The simple cadmium acetate $Cd(OAc)_2{\cdot}2H_2O$ was also tested for comparative purposes and, under typical reaction conditions (1 h, 50 °C, 5 W) less than 1% total yield (entry 15, Table 1) was reached, thus showing the importance of the N and O donor ligands in the metal coordination sphere in order to increase the catalytic performance. Despite this, the ligands HL^1 and HL^2 do not exhibit any activity by themselves (entries 16 and 17, Table 1), demonstrating also the key role played by the metal coordination entity.

An examination of the reaction kinetic profile of the toluene oxidation in the presence of **2** during 3 hours at 50 °C shows that the reaction proceeds gradually to yield increasing amounts of the major reaction products (benzaldehyde and benzyl alcohol) (Fig. 5) up to a maximum total yield of *ca.* 49%. The selectivity towards benzaldehyde is always above 90% (Fig. 6) even during the initial reaction period.

A highly favorable effect of MW irradiation is observed in this study, even with the very low power of 5 W. Hence, *e.g.* for the **2**/TBHP/MW system, 68% of total product yield (benzaldehyde + benzyl alcohol) was obtained after 24 h reaction using conventional heating and stirring at 50 °C in acetonitrile with TBHP (70% aqueous solution) as oxidant, 15% using H_2O_2 (30% aqueous solution) or less than 2% when using atmospheric oxygen instead, while under a low microwave power (5 W) already 39.5% or 49% of total product yield was achieved after only 1 or 3 h reaction, respectively, at 50 °C (entries 8 or 9, respectively, Table 1). A very interesting achievement is the considerable yield of *ca.* 22% obtained after 1 h reaction under MW irradiation and in the absence of any added solvent (entry 11, Table 1).

The temperature of 50 °C was found to be the optimum one for this catalytic system. Attempt to perform the peroxidative oxidation of toluene in the presence of **2** at a lower temperature of 30 °C resulted in an important yield drop. The temperature rises from 50 to 80 °C resulted in a decrease in the total yield from 39.5 to 31%, respectively (entries 8 and 10, Table 1), suggesting the formation in higher amount of the unwanted benzoic acid (oxidation of benzyl alcohol to benzaldehyde and sequential oxidation to benzoic acid).

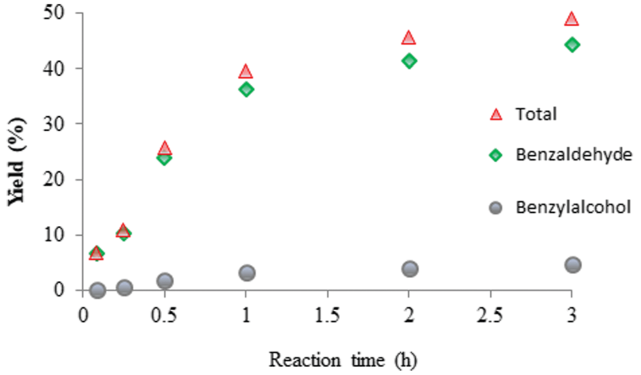


Fig. 5 Yields of the major products of oxidation of toluene (benzaldehyde and benzyl alcohol) catalyzed by **2** along time (0.083–3 h). Reaction conditions: [toluene] = 1.67 M; [**2**] = 3.3 × 10^{-3} M; [TBHP] = 3.3 M, in NCMe, under MW irradiation (5 W).

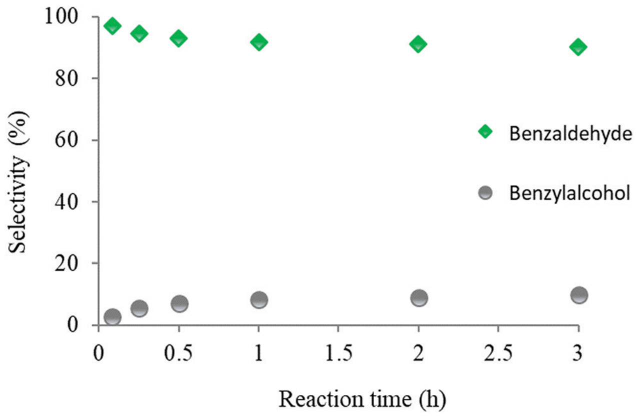


Fig. 6 Selectivity of the major products of oxidation of toluene (benzaldehyde and benzyl alcohol) catalyzed by **2** along time (0.083–3 h). Reaction conditions: [toluene] = 1.67 M; [**2**] = 3.3 × 10^{-3} M; [TBHP] = 3.3 M, in NCMe, under MW irradiation (5 W) during 0–180 min.

Table 1 Yields (benzaldehyde and benzyl alcohol) in the microwave-assisted oxidation of toluene by TBHP at 50 °C with **1** or **2** as catalyst[a]

			Yield[b] (%)			
Entry	Catalyst	Co-catalyst (μmol)	Benzaldehyde	Benzyl alcohol	Total	TON[c]
1	**1**	—	13.7	3.9	17.6	88
2[d]		—	18.6	6.5	25.1	126
3[e]		—	11.5	0.2	11.7	59
4[f]		—	5.2	0.3	5.5	28
5		TEMPO (30)	1.9	—	1.9	10
6		HNO_3 (7)	2.5	0.4	2.9	15
7		HNO_3 (35)	0.5	—	0.5	3
8	**2**	—	36.2	3.3	39.5	198
9[d]		—	44.2	4.9	49.1	246
10[e]		—	30.3	0.7	31.0	155
11[f]		—	21.6	0.2	21.8	109
12		TEMPO (30)	3.1	0.1	3.2	16
13		HNO_3 (7)	2.2	—	2.2	11
14		HNO_3 (35)	0.5	—	0.5	3
15	$Cd(OAc)_2{\cdot}2H_2O$	—	0.6	—	0.6	3
16	HL^1	—	—	—	—	—
17	HL^2	—	—	—	—	—

[a] Reaction conditions: toluene (1.67 M), catalyst precursor **1** or **2** (3.3 × 10^{-3} M), TBHP (70% aq. 3.3 M), NCMe (3 mL), 50 °C, 1 h, MW (5 W). [b] Moles of products (benzaldehyde or benzyl alcohol)/100 mol of toluene, determined by GC. [c] Turnover number (TON) = number of moles of products per mol of Cd(II) compound. [d] 3 h reaction. [e] Reaction performed at 80 °C, 10 W. [f] Solvent-free conditions.

In the present system, especially in the presence of **2**, higher yields of oxidized products at moderate temperature (50 °C) were achieved after 1 h (39.5% total yield, entry 8, Table 1), compared with those reported *e.g.* for nanoparticles of cadmium peroxide CdO_2 for which a total yield of 30% was obtained after 1 h at 180 °C.[62] To check the heterogenous character of the catalysts we have performed powder XRD of the compounds (**1** and **2**) before and after catalytic reactions (Fig. S1, ESI†). Similar powder patter as well as same elemental analyses suggest that the compounds remain unchanged after catalytic reactions. The reusability of the most active catalyst **2** was also explored. Compound **2** was isolated by centrifugation after catalyzing the microwave-assisted oxidation of toluene by TBHP for 1 h at 50 °C (Table 1, entry 8) and reused in 4 more cycles. It was found that for the reaction performed for 1 h, there was a reduction of *ca.* 11% yield in the 2nd cycle compared to the first cycle. Between the 2nd and 3rd cycles a 7% yield reduction was detected, and between 3rd, 4th and 5th cycles there was no significant change (Fig. 7).

The mechanism of this reaction should initially involve the formation of oxygen-based radicals $t\text{-BuOO}^\bullet$ and $t\text{-BuO}^\bullet$ (eqn (1) and (2)) upon oxidation or reduction of the oxidant *t*-BuOOH by Cd^{II} or Cd^{I} metal centers, respectively.[17,63,64]

The $t\text{-BuOO}^\bullet$ radical can undergo dismutation to the $t\text{-BuO}^\bullet$ radical and O_2, and the $t\text{-BuO}^\bullet$ radical can abstract an H atom from toluene (RH) to form the benzyl radical $R^\bullet$ (eqn (3)) which upon reaction with O_2 forms the benzyl peroxyl radical $ROO^\bullet$ (eqn (4)) which upon dismutation leads to ROH (benzyl alcohol) and benzaldehyde (plus O_2). Furthermore, H-abstraction from toluene (RH) by the $ROO^\bullet$ radical originates ROOH (plus $R^\bullet$) (eqn (5)) which upon reduction by a Cd^{I} center, forms the benzyloxyl $RO^\bullet$ radical (plus hydroxide) (eqn (6)) that leads to benzyl alcohol (plus $R^\bullet$) by H-abstraction from toluene (eqn (7)).[63]

The selectivity for benzaldehyde (our main product) can be favoured by the terminal reaction of $ROO^\bullet + t\text{-BuOO}^\bullet$ to yield the aldehyde (plus *t*-BuOH and O_2) (eqn (8)) or by further metal promoted oxidation of benzyl alcohol with *t*-BuOOH.[63]

The dinuclear Cd(II) complex $[\text{Cd}(1\kappa ONO'{:}2\kappa O\text{-HL}^2)(\kappa OO'\text{-Ac})]_2\cdot 2\text{DMF}$ (**2**) exhibits a catalytic activity similar to that (*ca.* 39% total yield and high selectivity) of the mononuclear aroylhyrazone-Cu(II) complex $[\text{Cu}(\kappa NOO'\text{-HL})\text{Cl}(\text{CH}_3\text{OH})]$ and higher than that of the 1D aroylhyrazone-Cu(II) coordination polymer $[\text{Cu}(1\kappa NOO',2\kappa O',3\kappa O''\text{-L})]_n$ studied by us as catalysts for the oxidation of toluene under similar reaction conditions.[17] This shows that cadmium complexes may become important players in a game that is being dominated by more studied transition metal centers, such as those typically used in oxidation reactions of alkanes, namely of copper or iron.

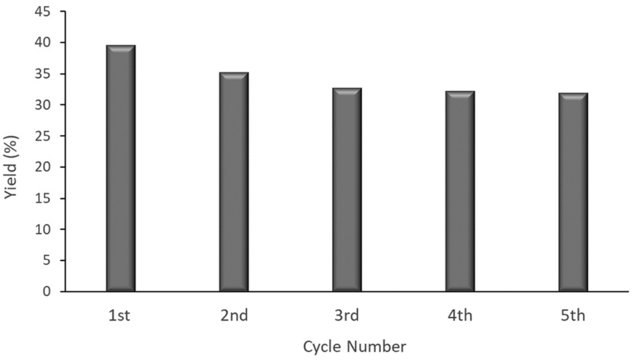


Fig. 7 Recycling studies for **2**. Reaction conditions: toluene (1.67 M), catalyst precursor **2** (3.3×10^{-3} M), TBHP (70% aq. 3.3 M), NCMe (3 mL), 50 °C, 1 h, MW (5 W).

$$\text{Cd(II)} + t\text{-BuOOH} \rightarrow \text{Cd(I)} + t\text{-BuOO}^\bullet + \text{H}^+ \qquad (1)$$

$$\text{Cd(I)} + t\text{-BuOOH} \rightarrow \text{Cd(II)} + t\text{-BuO}^\bullet + \text{HO}^- \qquad (2)$$

$$t\text{-BuO}^\bullet + \text{RH} \rightarrow t\text{-BuOH} + \text{R}^\bullet \qquad (3)$$

$$\text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet \qquad (4)$$

$$\text{ROO}^\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}^\bullet \qquad (5)$$

$$\text{ROOH} + \text{Cd(I)} \rightarrow \text{Cd(II)} + \text{RO}^\bullet + \text{HO}^- \qquad (6)$$

$$\text{RO}^\bullet + \text{RH} \rightarrow \text{ROH} + \text{R}^\bullet \qquad (7)$$

$$\text{ROO}^\bullet + t\text{-BuOO}^\bullet \rightarrow \text{RHO} + t\text{-BuOH} + \text{O}_2 \qquad (8)$$

Microwave-assisted solvent-free peroxidative oxidation of 1-phenylethanol by the Cd(II) compounds

The oxidations 1-phenylethanol (Scheme 2, reaction b) using *t*-BuOOH (aq. 70%, 2 eq.) as the oxidizing agent, were carried out following a previously reported procedure.[55,65] Under typical conditions, the catalyst **1** or **2** (10 μmol) was placed in the reaction tube as well as 1-phenylethanol (2.5 mmol) and *t*-BuOOH (5 mmol, aq. 70%), in the absence of any added solvent. The reactions were performed for 1 hour at 80 or 120 °C and under low-power (5 or 15 W) microwave irradiation. Acetophenone is the only oxidized product detected by GC-MS chromatography in the abovementioned conditions. The results in terms of yield and of turnover number (TON, moles of product/mol of catalyst) are summarized in Table 2.

Table 2 Selected results for the MW-assisted oxidation of 1-phenylethanol by TBHP with **1** or **2** as catalyst[a]

Entry	Catalyst	Temperature (°C)	Additive (μmol)	Yield[b] (%)	TON[c]
1	**1**	80	—	12	30
2		120	—	24	60
3		80	TEMPO (30)	15	38
4	**2**	80	—	9	23
5		120	—	13	33
6		80	TEMPO (30)	7	18
7		120	TEMPO (30)	10	25
8		80	Hpca (50)	5	10
9	$\text{Cd(OAc)}_2\cdot 2\text{H}_2\text{O}$	80	—	3	8

[a] Reaction conditions (unless stated otherwise): 2.5 mmol of substrate, 10 μmol (0.4 mol% *vs.* substrate), 5 mmol of *t*-BuOOH (aq. 70%), 80 or 120 °C, 1 h, microwave irradiation (5–15 W). [b] Molar yield (%) based on 1-phenylethanol, *i.e.* moles of acetophenone per 100 mol of 1-phenylethanol determined by GC. [c] Turnover number (TON) = number of moles of acetophenone per mol of Cd(II) compound.

Under the above conditions (120 °C and 1 h reaction time) and in the presence of **1** (catalyst/substrate molar ratio of 0.4%) a substantial conversion of 1-phenylethanol into acetophenone was already reached (24% yield, entry 2, Table 2).

The presence of 2,2,6,6-tetramethylpiperydil-1-oxyl (TEMPO) radical has not a considerable significant effect on the acetophenone yield in both catalytic systems. While in the presence of **1** a slight increase on the acetophenone yield from 12 to 15% (in the absence and in the presence of TEMPO, respectively, entries 1 and 3, Table 2) is observed, in the system catalyzed by **2** even a small decline is observed (from 9 to 7% in the absence and in the presence of TEMPO, respectively, entries 4 and 6, Table 2).

The effect of an acidic additive was tested by using the heteroaromatic 2-pyrazynecarboxylic acid (Hpca) in the **2**/TBHP/MW system and also an inhibiting effect was observed, *e.g.*, a yield drop from 9 to 5% was detected in the absence and in the presence [n(acid)/n(catalyst **2**) = 5], respectively, when the reaction was performed at 80 °C during 1 h.

The temperature has an accelerating effect on the conversion of 1-phenylethanol and at 120 °C yields of 24% and 13% were obtained after 1 h reaction in the presence of **1** or **2**, respectively (Table 2, entries 2 and 5), which are considerably higher than those observed at 80 °C (12 and 9%, respectively) (Table 2, entries 1 and 4).

The replacement of **1** or **2** by the precursor salt, cadmium(II) acetate dihydrate resulted in a strong decrease of activity (compare *e.g.*, entries 1 and 9, Table 2) indicating again the important role of the Schiff base ligand in the catalytic performance of the Cd(II) compounds for the oxidation reaction.

The formation of acetophenone catalyzed by **1** and **2** does not occurred when Ph_2NH or $CBrCl_3$ (well known[66] oxygen- or carbon-radical traps, respectively), are added to the reaction mixture, suggesting the involvement of radical species in the oxidation mechanism. Therefore, we believe that the mechanism may involve (see above) the metal-assisted generation of ^{t}BuOO$^•$ and t-BuO$^•$ radicals upon oxidation or reduction of t-BuOOH, respectively, which further behave as hydrogen atom abstractors from the alcohol[64,67] with possible involvement of the Schiff-based ligand in proton transfer steps. Compared with other Cd(II) Schiff-based heterogeneous catalysts,[68] the catalytic activity of the present Cd compounds **1** and **2** proved to be comparable (slightly higher) for the alcohol oxidation reaction,[68] the most promising catalyst **1** being recovered and reused for at least 3 consecutive cycles. For the reaction performed at 120 °C for 1 h, it was verified that there was no significant change in the yield between the first and second cycles, but it decreased by *ca.* 15% from the second to the third round. The loss of activity could indicate the occurrence of catalyst partial deactivation.

Experimental

General materials and procedures

The synthetic part of this study was performed under atmospheric air. Commercially available reagents and solvents were used as received, without further purification or drying. The metal source, namely $Cd(OAc)_2{\cdot}2H_2O$, was used for the synthesis of complexes.

C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets; wavenumbers are in cm^{-1}. The ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet, Rheinstetten, Germany) spectrometer. Tetramethylsilane was used as the internal reference and the chemical shifts are reported in ppm. The catalytic tests performed under microwave (MW) irradiation were undertaken in a focused Anton Paar Monowave 300 microwave incorporating a rotational system and an IR temperature detector, using a 10 mL capacity reaction tube with a 13 mm internal diameter. Gas chromatographic (GC) measurements were carried in a FISONS Instruments GC 8000 series gas chromatograph with a capillary DB-WAX column (30 m × 0.32 mm) and a FID detector under the following conditions: program 120 °C for 1 min, 10 °C min^{-1}, 200 °C for 1 min, injector at 240 °C and helium as the carrier gas. Gas Chromatography-Mass Spectrometry (GC-MS) analyses were performed using a PerkinElmer Clarus 600 °C (Shelton, CT, USA) instrument (He as the carrier gas). The ionization voltage was 70 eV. Gas chromatography was conducted in the temperature-programming mode, using a SGE BPX5 column (30 m × 0.25 mm × 0.25 m). All reaction products achieved from the catalytic oxidation reactions were identified by their retention times, confirmed with those of commercially available samples. The mass spectra of reaction products were compared to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer. Powder X-ray diffraction (PXRD) was conducted in a D8 Advance Bruker AXS (Bragg Brentano geometry) theta-2theta diffractometer, with copper radiation (Cu Kα, λ = 1.5406 Å) and a secondary monochromator, operated at 40 kV and 40 mA. Flat plate configuration was used, and the typical data collection range was between 5° and 40°.

Syntheses of the pro-ligands H_2L^1 and H_2L^2

The aroylhydrazone Schiff base pro-ligand 2-hydroxy(2-hydroxybenzylidene)benzohydrazide (H_2L^1) and 2-amino(2-hydroxybenzylidene)benzohydrazide (H_2L^2) (Scheme 1) were prepared by a reported method[58–60] upon condensation of the 2-hydroxybenzohydrazide or 2-aminobenzohydrazide with 2-hydroxybenzaldehyde.

Synthesis of the Cd(II) compounds

[Cd(μ-1κONO′:2κO:3κO″-L^1)(DMF)]$_n$ (1). A mixture of 2 mL DMF solution of H_2L^1 (5 mg, 0.02 mmol) and 5 mL methanolic solution of $Cd(OAc)_2{\cdot}2H_2O$ (5 mg, 0.02 mmol) was sealed in a capped glass vessel and heated to 80 °C for 48 h and, after subsequent gradual cooling to room temperature, good quality crystals were isolated by filtration, washed 3 times with methanol, and then dried open in air. This compound is insoluble in common organic solvents and water. Yield: 58% (based on Cd). Anal. calc. for **1** ($C_{17}H_{17}CdN_3O_4$): C, 46.43; H, 3.90; N, 9.56. Found: C, 46.37; H, 3.86; N, 9.53. IR (KBr; cm^{-1}): 3476 ν(OH) 3157 ν(NH), 1663 ν(C═O), 1189 ν(N–N).

[Cd(1κONO′:2κO-HL^2)(κOO′-Ac)]$_2$·2DMF (2). This compound was synthesized using a similar procedure as mentioned in the case of **2** but H_2L^2 was used instead of H_2L^1.

Anal. calc. for **2** ($C_{38}H_{44}Cd_2N_8O_{10}$): C, 45.75; H, 4.45; N, 11.23. Found: C, 45.72; H, 4.41; N, 11.20. IR (KBr; cm^{-1}): 2986 ν(NH), 1684 ν(C=O), 1176 ν(N–N).

X-ray measurements

Good quality single crystals suitable for X-ray diffraction of **1** and **2** were immersed in cryo-oil, mounted on Nylon loops and measured at 297 K. Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite mono chromated Mo Kα (λ 0.71073) radiation. Data were collected using phi and omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART[69] software and refined using Bruker SAINT[69] on all the observed reflections. Absorption corrections were applied using SADABS.[70] Structures were solved by direct methods by using SHELX-97[71] and refined with SHELXL-2014.[72] Calculations were performed using WinGX version 2014.1.[73] All non-hydrogen atoms were refined anisotropically. The H-atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model, using U_{iso} defined as $1.2U_{\mathrm{eq}}$ or $1.5U_{\mathrm{eq}}$ of the parent carbon atoms for phenyl or methyl groups, respectively. The N-bound hydrogen atoms were located in the difference Fourier synthesis and refined. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the atoms were employed. Crystallographic data and processing parameters are presented in Table 3.

Catalytic studies

The microwave-assisted (MW) peroxidative oxidations of toluene and 1-phenylethanol were performed in an appropriate Pyrex tube (10 mL capacity reaction tube with a 13 mm internal diameter) which was placed in an Anton Paar Monowave 300 reactor fitted with a rotational system and an IR temperature detector. For toluene oxidation, the concentrations of the reactants in NCMe (3 mL) were as follows: toluene (1.67 M), catalyst precursor **1** or **2** (3.3×10^{-3} M), TBHP (70% aq. 3.3 M), 50 °C, 1–3 h, MW (5 W). After the reaction, 90 μL of cycloheptanone (internal standard) and 10 mL of diethyl ether (for extraction) were added and after stirring, a sample was analysed by GC. For the solvent-free oxidation of 1-phenylethanol, the following conditions were applied: 2.5 mmol of the alcohol, 10 μmol (0.4 mol% *vs.* substrate) of [Cd(μ-1κONO′:2κO:3κO″-L^1)(DMF)]$_n$ (**1**) or [Cd(1κONO′:2κO-HL^2)(κOO′-Ac)]$_2$·2DMF (**2**), 5 mmol of *t*-BuOOH (aq. 70%). The sealed tube was placed in the microwave reactor and the system was left under stirring and under irradiation (5 or 15 W), at 80 or 120 °C for 1 h. After reaction, 150 μL of benzaldehyde (internal standard) and 2.5 mL of NCMe (for extraction) were added and the mixture stirred. Similarly, a sample from the upper organic layer was analysed by GC and the product yield determined using the internal standard method. Blank experiments (without metal catalyst) were also performed to confirm the catalytic activities of Cd(II) complexes, however no oxidation products were detected.

Table 3 Crystal data and structure refinement details for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{17}H_{17}CdN_3O_4$	$C_{38}H_{44}Cd_2N_8O_{10}$
Formula weight	439.73	997.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.0012(10)	12.732(2)
b/Å	13.1453(11)	12.938(2)
c/Å	12.5273(12)	13.914(2)
β/°	101.791(4)	113.651(6)
V (Å^3)	1773.4(3)	2099.7(6)
Z	4	2
D_{calc} (g cm^{-3})	1.647	1.578
F000	880	1008
μ (Mo Kα) (mm^{-1})	1.257	1.077
Rfls. collected/unique/observed	28 675/3628/3171	33 215/4309/3725
R_{int}	0.0309	0.0277
Final R_1[a], wR_2[b] ($I \geq 2\sigma$)	0.0293, 0.0728	0.0208, 0.0494
Goodness-of-fit on F^2	1.164	1.120

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\mathrm{w}R(F^2) = [\sum \mathrm{w}(|F_o|^2 - |F_c|^2)^2/\sum \mathrm{w}|F_o|^4]^{\frac{1}{2}}$.

Conclusions

The Cd(II) compounds [Cd(μ-1κONO′:2κO:3κO″-L^1)(DMF)]$_n$ (**1**) and [Cd(1κONO′:2κO-HL^2)(κOO′-Ac)]$_2$·2DMF (**2**) have been applied as heterogeneous catalysts in the oxidation of toluene and 1-phenylethanol. Peroxidative oxidations catalysed by Cd(II) complexes are not yet well explored and in this study we have reported for the first time the MW-assisted peroxidative oxidation of an alkyl benzene (toluene) by an heterogeneous Cd(II) system. The **2**/TBHP/MW system is more active in the toluene oxidation at moderate temperature (50 °C), achieving a total (benzaldehyde + benzyl alcohol) product yield of 49% after 1 h, in absence of any additives, whereas 68% of total product yield was obtained after 24 h reaction using conventional heating. The **1**/TBHP/MW catalytic system shows a better catalytic activity in the solvent-free peroxidative oxidation of 1-phenylethanol (24% yield of acetophenone). After the catalytic reactions, both **1** (for the 1-phenylethanol oxidation) and **2** (for the toluene oxidation) were successfully recovered and reused.

This study shows a promising catalytic activity of Cd(II) complexes in peroxidative oxidation reactions, namely those for which Cu(II) and Fe(II or III) complexes provide typical catalysts, and the obtained results encourage further extension to other oxidation reactions and/or to different Cd(II) complexes with benzohydrazide ligands.

Conflicts of interest

There are no conflicts to declare.

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References

1 E. D. Bloch, L. J. Murray, W. L. Queen, S. Chavan, S. N. Maximoff, J. P. Bigi, R. Krishna, V. K. Peterson, F. Grandjean, G. J. Long, B. Smit, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14814–14822.

2 W.-W. Fan, Y. Cheng, L.-Y. Zheng and Q.-E. Cao, *Chem. – Eur. J.*, 2020, **26**, 2766–2779.

3 S. K. Ujjain, P. Ahuja and R. K. Sharma, *J. Mater. Chem. B*, 2015, **3**, 7614–7622.

4 X. Rao, T. Song, J. Gao, Y. Cui, Y. Yang, C. Wu, B. Chen and G. Qian, *J. Am. Chem. Soc.*, 2013, **135**, 15559–15564.

5 L. Shao, J. Yang and B. Hua, *Polym. Chem.*, 2018, **9**, 1293–1297.

6 L. Gu, H.-Z. Zhang, W.-H. Jiang, G.-F. Hou, Y.-H. Yu and D.-S. Ma, *RSC Adv.*, 2017, **7**, 45862–45868.

7 S. Bera, A. Chowdhury, K. Sarkar and P. Dastidar, *Chem. – Asian J.*, 2020, **15**, 503–510.

8 Q. Yue and E.-Q. Gao, *Coord. Chem. Rev.*, 2019, **382**, 1–31.

9 M. Sutradhar, E. C. B. A. Alegria, T. Roy Barman, M. F. C. Guedes da Silva, C.-M. Liu and A. J. L. Pombeiro, *Front. Chem.*, 2020, **8**, 157, DOI: 10.3389/fchem.2020.00157.

10 Z. Zhou, C. He, L. Yang, Y. Wang, T. Liu and C. Duan, *ACS Catal.*, 2017, **7**, 2248–2256.

11 F.-X. Bu, M. Hu, L. Xu, Q. Meng, G.-Y. Mao, D.-M. Jiang and J.-S. Jiang, *Chem. Commun.*, 2014, **50**, 8543–8546.

12 M. Sutradhar and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2014, **265**, 89–124.

13 M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2015, **301-302**, 200–239.

14 M. Sutradhar, M. V. Kirillova, M. F. C. Guedes da Silva, L. M. D. R. S. Martins and A. J. L. Pombeiro, *Inorg. Chem.*, 2012, **51**, 11229–11231.

15 M. Sutradhar, L. M. D. R. S. Martins, S. A. C. Carabineiro, M. F. C. Guedes da Silva, J. G. Buijnsters, J. L. Figueiredo and A. J. L. Pombeiro, *ChemCatChem*, 2016, **8**, 2254–2266.

16 M. Sutradhar, L. M. D. R. S. Martins, T. Roy Barman, M. L. Kuznetsov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *New J. Chem.*, 2019, **43**, 17557–17570.

17 M. Sutradhar, E. C. B. A. Alegria, T. R. Barman, F. Scorcelletti, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Mol. Catal.*, 2017, **439**, 224–232.

18 M. Sutradhar, N. V. Shvydkiy, M. F. C. Guedes da Silva, M. V. Kirillova, Y. N. Kozlov, A. J. L. Pombeiro and G. B. Shul'pin, *Dalton Trans.*, 2013, **42**, 11791–11803.

19 M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, C.-M. Liu and A. J. L. Pombeiro, *Eur. J. Inorg. Chem.*, 2015, 3959–3969.

20 M. Sutradhar, M. V. Kirillova, M. F. C. Guedes da Silva, C.-M. Liu and A. J. L. Pombeiro, *Dalton Trans.*, 2013, **42**, 16578–16587.

21 M. Sutradhar, T. Roy Barman, E. C. B. A. Alegria, M. F. C. Guedes da Silva, H.-Z. Kou, C.-M. Liu and A. J. L. Pombeiro, *Dalton Trans.*, 2019, **48**, 12839–12849.

22 M. Sutradhar, E. C. B. A. Alegria, M. F. C. Guedes da Silva and C.-M. Liu, *Molecules*, 2018, **23**, 2699.

23 M. P. Waalkes and R. R. Misra, in *Cadmium carcinogenicity and genotoxicity*, ed. L. W. Chang, L. Magos and T. Suzuli, CRC Press, Taylor & Francis Group, Boca Raton, FL, USA, 1996, pp. 231–243.

24 A. Karmakar, G. M. D. M. Rúbio, M. F. C. Guedes da Silva, A. P. C. Ribeiro and A. J. L. Pombeiro, *RSC Adv.*, 2016, **6**, 89007–89018.

25 J. W. Shin, J. M. Bae, C. Kim and K. S. Min, *Inorg. Chem.*, 2013, **52**, 2265–2267.

26 C. T. Dameron, R. N. Reese, R. K. Mehra, A. R. Kortan, P. J. Carroll, M. L. Steigerwald, L. E. Brus and D. R. Winge, *Nature*, 1989, **338**, 96–597.

27 S. R. Lingampalli, U. Gupta, U. K. Gautam and C. N. R. Rao, *ChemPlusChem*, 2013, **78**, 837–842.

28 B. K. Park, G. H. Eom, S. H. Kim, H. Kwak, S. M. Yoo, Y. J. Lee, C. Ki, S.-J. Kim and Y. Kim, *Polyhedron*, 2010, **29**, 773–786.

29 W.-G. Jia, D.-D. Li, C. Gu, Y.-C. Dai, Y.-H. Zhou, G. Yuan and E.-H. Sheng, *Inorg. Chim. Acta*, 2015, **427**, 226–231.

30 L. Rout, P. Saha, S. Jammi and T. Punniyamurthya, *Adv. Synth. Catal.*, 2008, **350**, 395–398.

31 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**(3), 1151–1152.

32 S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**(9), 2607–2614.

33 D. Shi, Y. Ren, H. Jiang, J. Lu and X. Cheng, *Dalton Trans.*, 2013, **42**, 484–491.

34 T. Kanno, T. Oguchi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, 1980, **21**(5), 467–470.

35 P. A. Kohl and A. J. Bard, *J. Am. Chem. Soc.*, 1977, **99**(23), 7531–7539.

36 J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, 1978, **82**(12), 1397–1399.

37 F. Brühne and E. Wright, *Benzaldehyde, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, vol. 5, pp. 223–233.

38 D. G. Lee and U. A. Spitzer, *J. Org. Chem.*, 1970, **35**, 3589–3590.

39 B. L. Ryland and S. S. Stahl, *Angew. Chem., Int. Ed.*, 2014, **53**, 8824–8838.

40 M. Trincado, D. Banerjee and H. Grutzmacher, *Energy Environ. Sci.*, 2014, **7**, 2464–2503.

41 X. H. Li, J. S. Chen, X. C. Wang, J. H. Sun and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 8074–8077.

42 R. H. Liu, X. M. Liang, C. Y. Dong and X. Q. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 4112–4113.

43 R. F. Nie, J. J. Shi, W. C. Du, W. S. Ning, Z. Y. Hou and F. S. Xiao, *J. Mater. Chem. A*, 2013, **1**, 9037–9045.

44 S. J. Liu, N. Zhang, Z. R. Tang and Y. J. Xu, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6378–6385.

45 M. Sutradhar, E. C. B. A. Alegria, T. R. Barman, F. Scorcelletti, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Mol. Catal.*, 2017, **439**, 224–232.

46 M. N. Kopylovich, A. Mizar, M. F. C. Guedes da Silva, T. C. O. MacLeod, K. T. Mahmudov and A. J. L. Pombeiro, *Chem. – Eur. J.*, 2013, **19**, 588–600.

47 M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Appl. Catal., A*, 2015, **493**, 50–57.

48 S. Horikoshi and N. Serpone, *Microwaves in Catalysis: Methodology and Applications*, JohnWiley & Sons, Hoboken, NJ, USA, 2015.

49 M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, E. C. B. A. Alegria, C.-M. Liu and A. J. L. Pombeiro, *Dalton Trans.*, 2014, **43**, 3966–3977.

50 A. K. Rathi, M. B. Gawande, R. Zboril and R. S. Varma, *Acc. Chem. Res.*, 2014, **47**, 1338–1348.

51 A. de la Hoz, Á. Díaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, 2005, **34**, 164–178.

52 M. C. Lubinu, L. De Luca, G. Giacomelli and A. Porcheddu, *Chem. – Eur. J.*, 2011, **17**, 82–85.

53 H.-C. Lin, J.-F. Pan, Y.-B. Chen, Z.-P. Lin and C.-H. Lin, *Tetrahedron*, 2011, **67**, 6362–6368.

54 D. D. Young, J. Nichols, R. M. Kelly and A. Deiters, *J. Am. Chem. Soc.*, 2008, **130**, 10048–10049.

55 M. Alexandru, M. Cazacu, A. Arvinte, S. Shova, C. Turta, B. C. Simionescu, A. Dobrov, E. C. B. A. Alegria, L. M. D. R. S. Martins, A. J. L. Pombeiro and V. B. Arion, *Eur. J. Inorg. Chem.*, 2014, 120–131.

56 R. Jlassi, A. P. C. Ribeiro, M. Mendes, W. Rekik, G. A. O. Tiago, K. T. Mahmudov, H. Naïli, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Polyhedron*, 2017, **129**, 182–188.

57 D. Shi, Y. Ren, H. Jiang, J. Lua and X. Cheng, *Dalton Trans.*, 2013, **42**, 484–491.

58 M. Sutradhar, G. Mukherjee, M. G. B. Drew and S. Ghosh, *Inorg. Chem.*, 2007, **46**, 5069–5075.

59 M. Sutradhar, T. R. Barman, G. Mukherjee, M. G. B. Drew and S. Ghosh, *Polyhedron*, 2012, **34**, 92–101.

60 M. Sutradhar, T. R. Barman, M. G. B. Drew and S. Ghosh, *J. Mol. Struct.*, 2012, **1020**, 148–152.

61 T. R. Barman, M. Sutradhar, M. G. B. Drew and E. Rentschler, *Polyhedron*, 2013, **51**, 192–200.

62 S. R. Lingampalli, U. Gupta, U. K. Gautam and C. N. R. Rao, *ChemPlusChem*, 2013, **78**, 837–842.

63 T. C. O. Mac Leod, M. V. Kirillova, A. J. L. Pombeiro, M. A. Schiavon and M. D. Assis, *Appl. Catal., A*, 2010, **372**, 191–198.

64 M. V. Kirillova, M. L. Kuznetsov, Y. N. Kozlov, L. S. Shul'pina, A. Kitaygorodskiy, A. J. L. Pombeiro and G. B. Shul'pin, *ACS Catal.*, 2011, **1**, 1511–1520.

65 M. Sutradhar, E. C. B. A. Alegria, K. T. Mahmudov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *RSC Adv.*, 2016, **6**, 8079–8088.

66 J. M. Mattalia, B. Vacher, A. Samat and M. Chanon, *J. Am. Chem. Soc.*, 1992, **114**, 4111–4119.

67 M. S. Dronova, A. N. Bilyachenko, A. I. Yalymov, Y. N. Kozlov, L. S. Shul'pina, A. A. Korlyukov, D. E. Arkhipov, M. M. Levitsky, E. S. Shubina and G. B. Shul'pin, *Dalton Trans.*, 2014, **43**, 872–882.

68 A. Karmakar, L. M. D. R. S. Martins, S. Hazra, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2016, **16**, 1837–1849.

69 Bruker, *APEX2*, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

70 G. M. Sheldrick, *SADABS. Program for Empirical Absorption Correction*, University of Gottingen, Germany, 2000.

71 G. M. Sheldrick, *SHELX97. Programs for Crystal Structure Analysis (Release 97-2)*. University of Göttingen, Germany, 1997.

72 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.

73 L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.