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# Deaggregation properties and transmetalation studies of a zinc(II) salen-type Schiff-base complex†

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This paper reports the synthesis and the deaggregation properties of a Lewis acidic Zn(II) salen-type Schiff-base complex derivative from diaminomaleonitrile and a systematic detailed study of its transmetalation with other metal ions in solution. In a solution of non-coordinating solvents, the complex is in a dimeric form, while in coordinating solvents or upon addition of a Lewis base it is stabilized as monomeric adducts. Experiments done in two solvents with different Lewis basicities indicate a major role of the stability of the starting adduct in transmetalation. Thus, using nitrate or perchlorate salts, acetonitrile solutions of the complex give an immediate and complete transmetalation with Cu<sup>2+</sup>, while with Co<sup>2+</sup> and Ni<sup>2+</sup> a much slower transmetalation rate is observed. Instead, using chloride salts a fast and complete transmetalation is observed for divalent ions of the first transition series (Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>), indicating the role of the chloride in stabilizing the transition state of the transmetalation. On the other hand, DMF solutions of the complex are less prone to transmetalation, according with the greater basicity of the solvent and, hence, the greater stability of the related adducts with the complex. Therefore, the nature of the solvent and the counteranion allow controlling the transmetalation process of this Zn(II) Schiff-base complex.

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## 1. Introduction

Transition metal-based molecular materials are currently widely investigated for their functional properties.<sup>1–5</sup> Among them, zinc(II) complexes of Schiff-base ligands represent a promising class of materials with diverse optical and optoelectronic properties.<sup>6–12</sup> An interesting family is constituted by Lewis acidic Zn(salen)-type complexes, whose optical properties are mainly related to the absence/presence of a Lewis base.<sup>13,14</sup> In the first case, these complexes tend to dimerize/oligomerize in order to saturate their coordination sphere, while in the presence of Lewis bases they form monomeric adducts.<sup>15–17</sup> Aggregate species or monomeric adducts are characterized by very different optical spectroscopic properties, useful for using these complexes as chemosensors of Lewis bases.<sup>13,14,18</sup>

The stability of the Zn(salen)-Lewis base adducts is certainly an important feature for the chemistry of these complexes,

mainly related to the Lewis basicity of the coordinated species.<sup>19,20</sup> Therefore, the different stabilities of the adducts are expected to affect other properties of these complexes. One of these could be the ability of the Zn(II) ion to transmetalate with main group and/or transition metal ions. In this regard, few examples have been reported in the literature involving transmetalation of Zn(salen)-type complexes.<sup>21–23</sup> Transmetalation, or metal exchange, represents an unconventional approach in coordination and organometallic chemistry for its use in synthesis, catalysis, and sensing.<sup>24–29</sup>

Among Zn(salen)-type complexes, colourful derivatives from the 2,3-diaminomaleonitrile, Zn(salmal), are certainly those more interesting for their optical absorption and fluorescence emission properties upon deaggregation.<sup>30–37</sup> In order to further explore these varied characteristics, we have chosen a Zn(salmal) complex, **1**, having different substituents on the salicylidene rings. In particular, we found that the presence of 5-*tert*-butyl-bulky substituents makes this complex sufficiently soluble in a range of coordinating/non-coordinating solvents, giving us the possibility to explore its spectroscopic properties in solution, even in comparison to previous studies on amphiphilic Zn(salmal) complexes with longer alkyl substituents.<sup>30</sup> Moreover, in this work, a study on the transmetalation ability of this complex towards other metal ions is reported, in

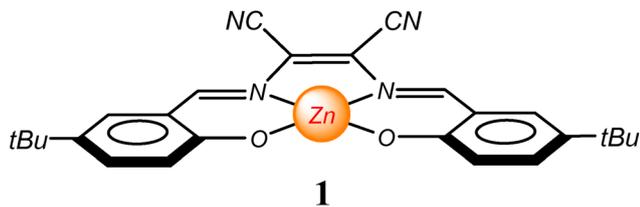
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relation to the nature of the starting adduct. This represents for the first time a systematic transmetalation study in solution for this family of complexes.



## 2. Results and discussion

### 2.1. Synthesis and characterization

The synthetic procedure for the preparation of complex **1** involves the reaction of 5-*t*-butyl-2-hydroxybenzaldehyde and 2,3-diaminomaleonitrile with  $\text{Zn}(\text{ClO}_4)_2$  in the presence of a base. The isolated compound is moderately soluble in the non-coordinating chloroform and other low-polar solvents and soluble in polar coordinating solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile (MeCN).

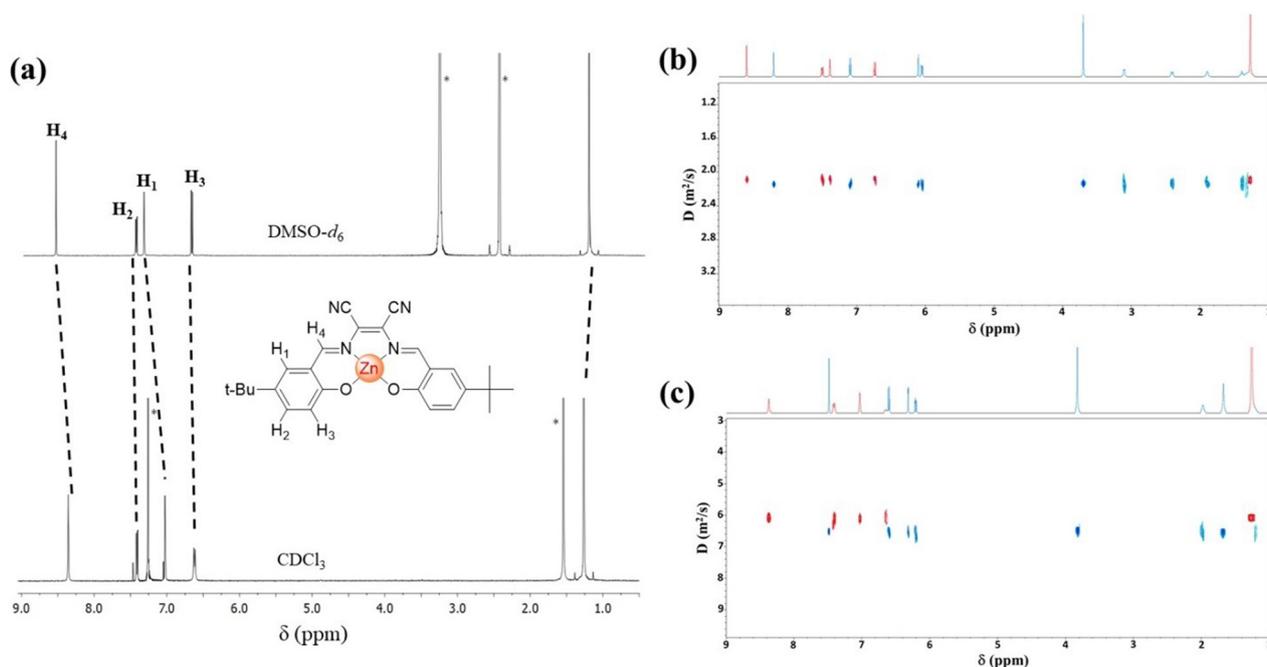
The  $^1\text{H}$  NMR spectrum of **1** in  $\text{DMSO-}d_6$  shows that the expected signals are consistent with its molecular structure. On switching to the spectrum in  $\text{CDCl}_3$ , a substantial up-field shift of the signals relative to  $\text{H}_1$  (0.36 ppm) and  $\text{H}_4$  (0.25 ppm) and a slight up-field shift of the signals relative to  $\text{H}_2$  (0.08 ppm) and  $\text{H}_3$  (0.11 ppm) protons are observed, in addition to a slight broadening of the  $\text{H}_3$  and  $\text{H}_4$  peaks

(Fig. 1a). As previously reported,<sup>30</sup> these significant shifts on passing from  $\text{DMSO-}d_6$  to  $\text{CDCl}_3$  are consistent with the formation of dimeric aggregates in a solution of the non-coordinating  $\text{CDCl}_3$  and the existence of 1:1 adducts,  $1 \cdot \text{DMSO-}d_6$ , in the coordinating  $\text{DMSO-}d_6$  solvent.

Diffusion-ordered NMR spectroscopy (DOSY) measurements further support this hypothesis. DOSY experiments were performed in the presence of a known reference compound.<sup>34</sup> In particular, the Schiff-base  $\text{Zn}(\text{II})$  complex derivative of *trans*-1,2-cyclopentanediamine<sup>38</sup> was used for DOSY measurements of **1** in  $\text{CDCl}_3$  (Fig. 1c). These indicate the presence of a single component in the diffusion dimension ( $D = 6.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), having a comparable diffusion coefficient of the reference compound ( $D = 6.55 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), with an estimated molecular mass of 1012 Da, in agreement with the calculated molecular mass (983.8 Da) for the dimer of **1**. DOSY measurements of **1** in  $\text{DMSO-}d_6$  were performed in the presence of the  $\text{Zn}(\text{II})$  complex derivative from *trans*-1,2-diaminocyclohexane<sup>39</sup> (Fig. 1b). A diffusion coefficient value of  $2.08 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  ( $D = 2.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for the reference compound) and an estimated mass of 571 Da, in agreement with the formation of an adduct with the solvent ( $1 \cdot \text{DMSO-}d_6 = 574 \text{ Da}$ ), are found, thus confirming the existence of monomeric species in solution of coordinating solvents.

### 2.2. Optical spectroscopic properties in solution and deaggregation experiments

The UV/vis optical absorption spectrum of **1** in  $\text{CHCl}_3$  shows two bands in the UV region ( $\lambda_{\text{max}} = 316 \text{ nm}$  and  $382 \text{ nm}$ ) and



**Fig. 1** (a) Comparison of the  $^1\text{H}$  NMR spectra of **1** in  $\text{DMSO-}d_6$  and  $\text{CDCl}_3$  solutions ( $1.0 \times 10^{-3} \text{ M}$ ). Asterisked peaks refer to water and residual DMSO and  $\text{CHCl}_3$  solvent signals.  $^1\text{H}$  NMR DOSY spectra of **1** in  $\text{DMSO-}d_6$  (b) and  $\text{CDCl}_3$  (c) solutions ( $1.0 \times 10^{-3} \text{ M}$ ). Red and blue signals refer to **1** and the internal reference species, respectively.



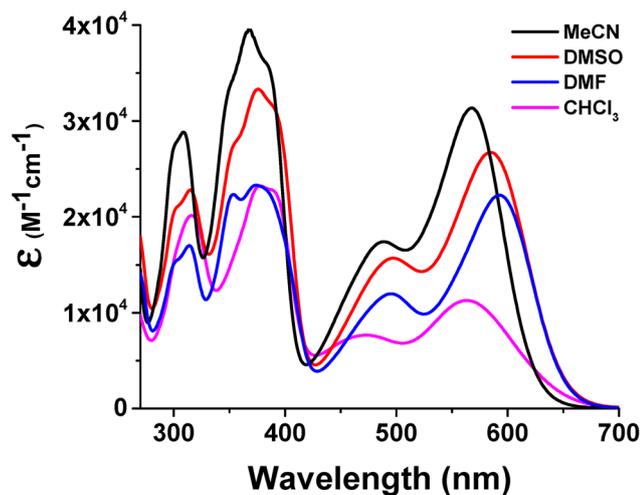


Fig. 2 Optical absorption spectra of **1** in various solvents.

two bands with lower intensity in the visible region, centred at  $\lambda_{\text{max}} = 473 \text{ nm}$  and  $570 \text{ nm}$  (Fig. 2). On changing to coordinating solvents (Fig. 2), a general hyperchromism of the absorption bands, more pronounced for the longer wavelength band, is observed which is also red-shifted ( $\lambda_{\text{max}} = 580 \text{ nm}$  in DMF), accompanied by an evident naked-eye colour change of the solution from red-wine to blue-violet (in DMF).

These experimental findings are consistent with the presence of aggregate species in solution of non-coordinating solvents and monomeric adducts with the solvent axially coordinated in coordinating solvents, as previously found for analogous Zn(salmal) derivatives.<sup>30,31</sup> In fact, starting from solutions of **1** in non-coordinating solvents, the addition of a Lewis base leads to deaggregation with the formation of monomeric adducts having optical characteristics analogous to those observed in solution of coordinating solvents. Deaggregation can be accomplished using various Lewis bases, such as primary, secondary, and tertiary amines, aromatic amines, or ethers. Spectrophotometric titrations of  $\text{CHCl}_3$  solutions of **1** with pyridine (Fig. 3) and isopropylamine (Fig. S1†) are reported as representative examples. In all instances, the addition of the Lewis base involves the formation of a new, strong absorption band at longer wavelengths ( $\lambda_{\text{max}} = 595 \text{ nm}$ , for pyridine) responsible for the dramatic colour change of the solution (from red-wine to indigo). The curve fit analysis of the binding isotherm at  $595 \text{ nm}$  as a function of the concentration of pyridine added allowed the estimation of the binding constant ( $\log K$  value of 5.45) for the formation of the **1**·py adduct.

Pyridine has previously been used as a reference Lewis base to deaggregate a series of Zn(salen)-type complexes in non-coordinating solvents to rank their Lewis acidic character within the series.<sup>20</sup> Thus, the derived binding constant for the formation of the **1**·py adduct allows establishing the Lewis acidity of **1** in comparison to previously investigated complexes. In particular, a  $\log K$  value of 5.45 indicates a slightly weaker Lewis acidic character of **1** in comparison to that esti-

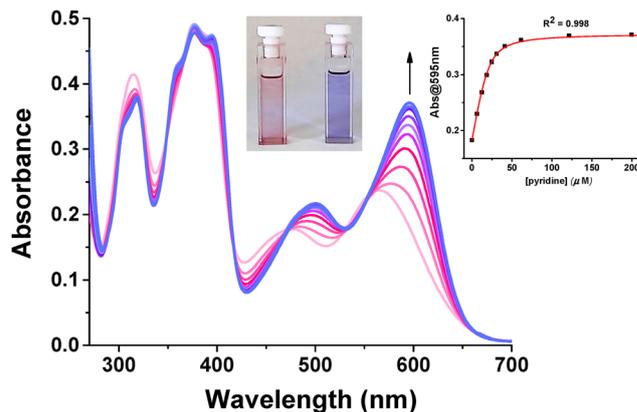


Fig. 3 Optical absorption titration curves of **1** ( $20 \mu\text{M}$  solution in  $\text{CHCl}_3$ ) with the addition of pyridine. The concentration of pyridine added varied from 0 to  $200 \mu\text{M}$ . Inset: variation of the absorbance at  $595 \text{ nm}$  as a function of the concentration of pyridine added and the fit of the binding isotherm (red line).

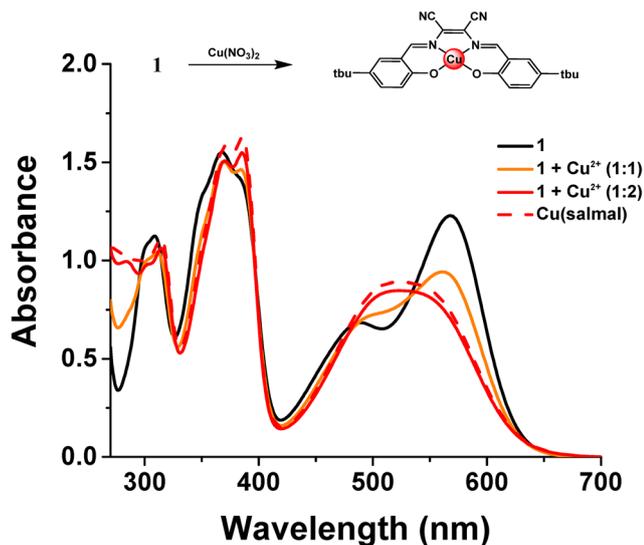
mated for the related Zn(salmal) complex having 4-alkoxy substituents in the salicylidene rings.<sup>20</sup>

### 2.3. Transmetalation studies

In order to explore the transmetalation ability of **1** towards several metal cations in relation to the stability of the starting adduct, two different solvents, MeCN and DMF, were considered. Both of them are coordinating solvents, but have different Lewis basicities.<sup>17</sup> Thus, different stabilities of the related adducts can be anticipated. In fact, the derived binding constants for the formation of the adducts, evaluated from spectrophotometric titrations upon deaggregation of **1** in  $\text{CHCl}_3$  (Fig. S2 and S3†),<sup>20</sup> indicate for the **1**·DMF adduct a  $\log K$  value of 2.95, more than two orders of magnitude larger than that for the **1**·MeCN adduct ( $\log K = 0.88$ ). Therefore, a different transmetalation behaviour of **1** is expected in these coordinating solvents.

Initially, nitrate salts of most common divalent and some trivalent cations were considered. The occurrence of transmetalation was first simply checked by optical absorption measurements immediately after the addition of stoichiometric amounts of aqueous solutions of nitrate salts to MeCN solutions of **1**. Except for  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Hg}^{2+}$  ions, which lead to the demetalation of **1** (*vide infra*), sizable changes in the optical absorption spectra of **1**, consistent with transmetalation, are observed only in the case of the addition of  $\text{Cu}(\text{NO}_3)_2$ , while the addition of all other cations involves small or negligible changes. In particular, the equimolar addition of  $\text{Cu}(\text{NO}_3)_2$  to **1** causes a decrease in the longer wavelength absorption band at  $\lambda_{\text{max}} = 567 \text{ nm}$  and the appearance of a new optical absorption feature at shorter wavelengths (Fig. 4). Upon addition of a 2-fold molar excess of  $\text{Cu}(\text{NO}_3)_2$ , the disappearance of the band at  $\lambda_{\text{max}} = 567 \text{ nm}$  and the definition of a new optical absorption band centred at  $\lambda_{\text{max}} = 524 \text{ nm}$  are observed, accompanied by a colour change of the solution from violet to magenta. These optical absorption changes





**Fig. 4** Optical absorption spectra of **1** (40.0  $\mu\text{M}$  solution in MeCN) before and after the addition of an equimolar and 2-fold molar excess of an aqueous solution of  $\text{Cu}(\text{NO}_3)_2$ . The optical absorption spectrum of  $\text{Cu}(\text{salmal})$  (dashed line) (40.0  $\mu\text{M}$  solution in MeCN) is reported for comparison.

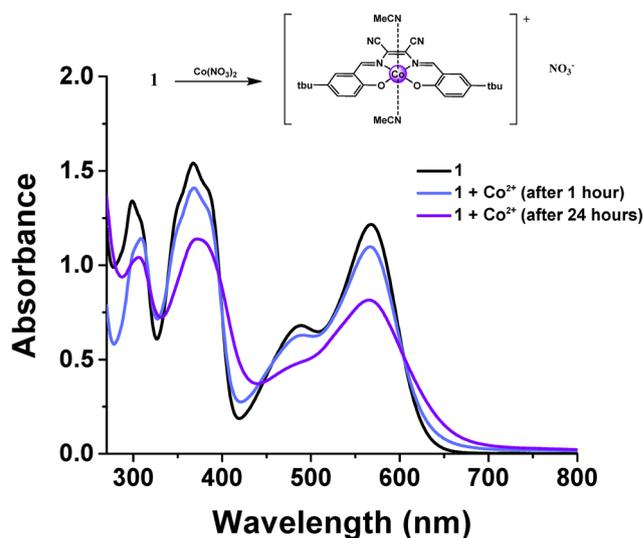
upon addition of  $\text{Cu}(\text{II})$  to MeCN solutions of **1** are in agreement with transmetalation. In fact, identical optical spectroscopic features are obtained from MeCN solutions of the synthesized and purified  $\text{Cu}(\text{salmal})$  complex (Fig. 4).  $^1\text{H}$  NMR titrations of **1** in  $\text{CD}_3\text{CN}$ , upon successive addition of a  $\text{Cu}(\text{NO}_3)_2$  solution in  $\text{D}_2\text{O}$ , indicate an increasing broadening of the proton signals, consistent with the transmetalation of the  $\text{Zn}^{2+}$  ion with the paramagnetic  $\text{Cu}^{2+}$  ion.<sup>40–42</sup> A complete disappearance of proton signals in the 4–9 ppm region is observed after the addition of a 2-fold molar excess of a  $\text{Cu}(\text{NO}_3)_2$  solution (Fig. S4<sup>†</sup>).

Transmetalated solutions of  $\text{Cu}(\text{salmal})$  are stable, as no optical absorption changes are observed even after several weeks. Moreover, analogous results are obtained using  $\text{Cu}(\text{ClO}_4)_2$  as the source of  $\text{Cu}^{2+}$  ions. Therefore, the addition of  $\text{Cu}^{2+}$  ions, either as nitrate or perchlorate, to MeCN solutions of **1** results in a fast and complete transmetalation, thus indicating that the  $\text{Cu}(\text{salmal})$  complex is thermodynamically more stable than the  $\text{Zn}(\text{II})$  analogue and the counteranion does not affect transmetalation. Transmetalation with  $\text{Cu}(\text{II})$  has been reported in the literature also for other families of  $\text{Zn}(\text{II})$  complexes.<sup>26,43–45</sup>

The observed dramatic variations in the optical absorption spectra upon the addition of a 2-fold molar excess of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Hg}^{2+}$  ions, as nitrate salts (Fig. S5<sup>†</sup>), with the almost disappearance of the longer wavelength band and the formation of a new strong optical absorption band at  $\lambda_{\text{max}} = 460$  nm, accompanied by a colour fading from violet to orange-yellow, cannot be ascribed to transmetalation. Rather, a demetalation process likely occurs, as a consequence of the acid hydrolysis of ferric and<sup>46</sup> aluminium salts<sup>47</sup> and  $\text{Hg}(\text{II})$  nitrate.<sup>48</sup> To support this hypothesis, spectrophotometric titrations of

MeCN solutions of **1** with aqueous perchloric acid were performed (Fig. S6<sup>†</sup>). Identical optical absorption spectral variations, such as those observed by addition of  $\text{Fe}(\text{III})$ ,  $\text{Al}(\text{III})$ , and  $\text{Hg}(\text{II})$  to MeCN solutions of **1**, are obtained. A complete demetalation of **1** occurs upon the addition of a 2.5-fold molar excess of the perchloric acid.

The transmetalation kinetics of the MeCN solutions of **1** upon the addition of 2-fold molar excess of the involved nitrate salts, left at room temperature, was further monitored by recording over time the optical absorption spectra. Except for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , no further appreciable changes, as compared to the measurements recorded immediately after the addition of various cations, were observed even after a week. In the case of  $\text{Co}^{2+}$ , a progressive hypochromism and broadening of the absorption bands at longer wavelengths of **1** are observed within 24 hours, suggestive of a transmetalation (Fig. 5). The  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$ , recorded 24 hours after the addition of 2-fold molar excess of  $\text{Co}(\text{NO}_3)_2$  in  $\text{D}_2\text{O}$ , shows sharp, shifted signals with respect to those of **1** (Fig. 6), indicating the formation of a low-spin diamagnetic  $\text{Co}(\text{III})$  complex upon aerobic oxidation of the  $\text{Co}^{2+}$  ion.<sup>49–53</sup> In particular, resonances of the imine  $\text{CH}=\text{N}$  (8.20 ppm) and aromatic (7.2–7.7 ppm) protons fall within the range of those found in other octahedral  $\text{Co}(\text{III})$  salen-type complexes, axially coordinated with two Lewis bases.<sup>54,55</sup> Instead, for  $\text{Ni}^{2+}$  a slow and progressive transmetalation is observed within seven days. The complete transmetalation of **1** with  $\text{Ni}^{2+}$  is demonstrated by the comparison of the optical absorption spectrum recorded after seven days, which is identical to that recorded for the synthesized  $\text{Ni}(\text{salmal})$  complex (Fig. 7). Perchlorate salts of  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$  give identical results. Interestingly, transmetalation experiments using  $\text{Ni}(\text{II})$  nitrate and heating the solution at 60  $^\circ\text{C}$ , under stirring, lead to a complete transmetalation after 3 hours (Fig. S7<sup>†</sup>), instead of seven days at



**Fig. 5** Optical absorption spectra of **1** (40.0  $\mu\text{M}$  solution in MeCN) before and after the addition of 2-fold molar excess of an aqueous solution of  $\text{Co}^{2+}$  ions (as nitrate salt) recorded after 1 and 24 hours.



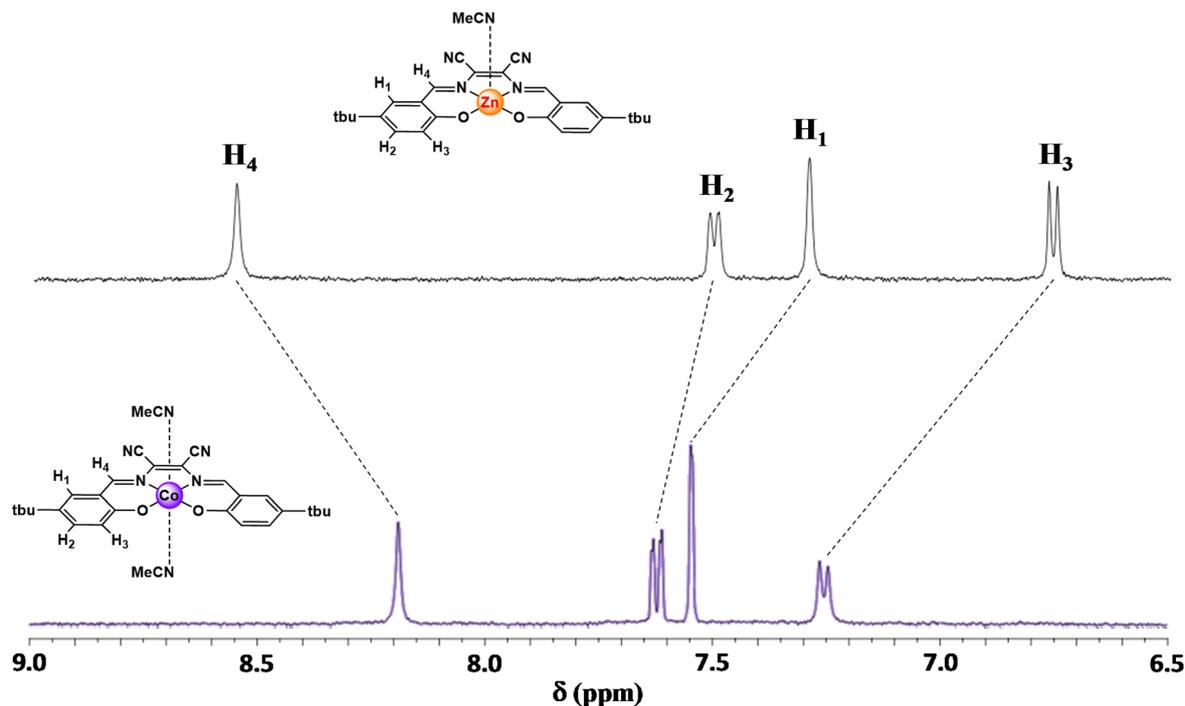


Fig. 6 Comparison of  $^1\text{H}$  NMR spectra of **1** ( $1.0 \times 10^{-4}$  M) in  $\text{CD}_3\text{CN}$  before (top) and after the addition of 2-fold molar excess of a  $\text{D}_2\text{O}$  solution of  $\text{Co}(\text{NO}_3)_2$  recorded after 24 hours (down).

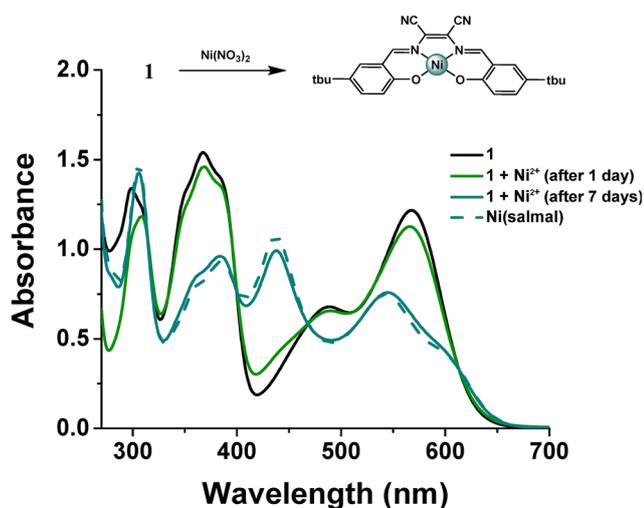


Fig. 7 Optical absorption spectra of **1** ( $40.0 \mu\text{M}$  solution in MeCN) before and after the addition of 2-fold molar excess of an aqueous solution of  $\text{Ni}^{2+}$  ions (as nitrate salt) recorded after 1 and 7 days. The optical absorption spectrum of  $\text{Ni}(\text{salmal})$  (dashed line) ( $40.0 \mu\text{M}$  solution in MeCN) is reported for comparison.

room temperature. Therefore, in this case, the temperature dramatically affects the transmetallation kinetics.

The possible effect of other counteranions on transmetallation was also investigated. Surprisingly, the addition of stoichiometric amounts of metal chlorides to MeCN solutions of **1** lead to very different results from those previously obtained for

nitrate or perchlorate salts (Fig. 8). In fact, optical absorption measurements recorded immediately after the addition of 2-fold molar excess of various chlorides (30 min for  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$ ) indicate substantial spectral changes for all the involved divalent metal ions of the first transition series, including  $\text{Mg}(\text{II})$ , consistent with transmetallation. These absorption spectral changes are in agreement with those found for the homologous series of  $\text{M}(\text{salmal})$ -type complexes.<sup>21,56,57</sup>

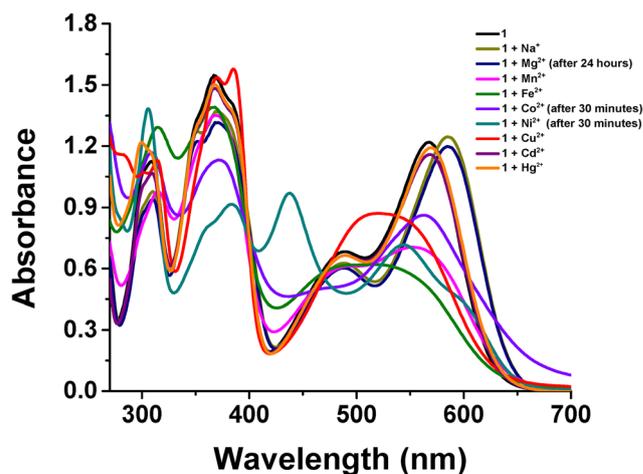


Fig. 8 Optical absorption spectra of **1** ( $40.0 \mu\text{M}$  solution in MeCN) before and after the addition of 2-fold molar excess of several cations (as aqueous solutions of chloride salts).



The ESI-MS analysis of the transmetalated MeCN solutions after the addition of a 2-fold molar excess of various metal chlorides indicates the presence of a molecular peak for  $M(\text{salmal})$  ( $M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ) complexes. In particular, the ESI-mass spectra of the transmetalated solutions with  $\text{Mn}(\text{II})$ ,  $\text{Fe}(\text{II})$ , and  $\text{Co}(\text{II})$  show an intense peak related to the  $[\text{M}(\text{salmal})]^+$  ion (Fig. S8†). Instead, those with  $\text{Mg}(\text{II})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Cu}(\text{II})$  show the presence of the  $[\text{M} + \text{H}]^+$  molecular ion (Fig. S9†). Moreover, the optical absorption measurements of these transmetalated solutions with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  show identical spectra to those recorded using the nitrate or perchlorate salts of  $\text{Cu}(\text{II})$ ,  $\text{Co}(\text{II})$ , and  $\text{Ni}(\text{II})$ , although transmetalation for the latter two ions took place in a much longer time.  $^1\text{H}$  NMR measurements of the transmetalated  $\text{CD}_3\text{CN}$  solutions of **1**, recorded after the addition of a 2-fold molar excess of  $\text{NiCl}_2$  in  $\text{D}_2\text{O}$ , show a spectrum identical to that recorded for the  $\text{Ni}(\text{salmal})$  complex in  $\text{CD}_3\text{CN}$  solution (Fig. S10†).  $^1\text{H}$  NMR titrations of **1** in  $\text{CD}_3\text{CN}$ , after the successive addition of  $\text{CoCl}_2$  in  $\text{D}_2\text{O}$ , show the appearance in the  $^1\text{H}$  NMR spectrum of a new distinct set of sharp signals, strongly shifted with respect to those of **1** (Fig. S11†) and identical to those observed upon the addition of  $\text{Co}(\text{NO}_3)_2$  to **1**. No further changes in the  $^1\text{H}$  NMR spectra are observed after the addition of 2-fold molar excess of  $\text{CoCl}_2$ . DOSY experiments, performed after the addition of a half-molar amount of  $\text{CoCl}_2$  to a  $\text{CD}_3\text{CN}$  solution of **1**, indicate the presence of a single component in the diffusion dimension ( $D = 11.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), having a diffusion coefficient comparable to that of the **1**- $\text{CD}_3\text{CN}$  adduct used as the reference species ( $D = 12.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). These data are consistent with the presence of a monomeric  $\text{Co}(\text{III})$  complex in solution. The identical chemical shift of signals found either upon transmetalation with perchlorate or chloride salts (Fig. S12†) suggests that the anions are out of the coordination sphere of the  $\text{Co}(\text{III})$  complex. Therefore, the overall data suggest that after the transmetalation of **1** with the  $\text{Co}^{2+}$  ion, the complex evolves towards the formation of a low-spin diamagnetic  $[\text{Co}(\text{salmal})]^+$  species, whose hexacoordination is fulfilled by the coordination of the solvent.<sup>58,59</sup> The  $^1\text{H}$  NMR spectra of transmetalated solutions with  $\text{Mn}^{2+}$ , recorded immediately after the addition of 2-fold molar excess of  $\text{MnCl}_2$ , show the complete disappearance of all proton signals, according with the formation of a paramagnetic complex.<sup>40</sup> While transmetalated solutions of **1** with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  (oxidized to  $\text{Co}^{3+}$ ) are stable over time, those transmetalated with  $\text{Fe}^{2+}$  completely decompose within 30 min and those with  $\text{Mn}^{2+}$  gradually decompose within a few days.

In the case of  $\text{Mg}^{2+}$ , the transmetalated  $\text{Mg}(\text{salmal})$  complex initially formed successively evolves (within 24 hours) towards the formation of the adduct (Fig. S13†). Analogously, the addition of  $\text{Na}(\text{I})$  chloride to MeCN solutions of **1** leads to the formation of chloride adducts by solvent displacement with the chloride ion.<sup>14,60–63</sup> Indeed, spectrophotometric titrations of **1** in MeCN with an aqueous solution of tetrabutylammonium chloride (TBACl) show analogous optical absorption changes as those observed upon addition of  $\text{Mg}(\text{II})$  and  $\text{Na}(\text{I})$  chlorides, indicating the formation of stable 1:1 **1**- $\text{Cl}^-$ - $\text{TBA}^+$  adducts with a saturation point after the addition of *ca.* 1.6-fold molar excess of TBACl (Fig. S14†). Finally, the addition of the remaining  $\text{Cd}(\text{II})$  and  $\text{Hg}(\text{II})$  chlorides to **1** does not involve any optical absorption change, presumably because of their presence in the molecular form in solution.<sup>64,65</sup>

In order to assess the role of the chloride ion in the transmetalation process, further experiments were done. For this study, we have chosen the  $\text{Ni}^{2+}$  ions because with tetradentate ligands it gives stable square planar complexes, without the need for any auxiliary ligands/solvent.<sup>66–68</sup> Therefore, the stability of the transmetalated  $\text{Ni}(\text{salmal})$  complex will be not affected by the nature of the counteranion.

Starting from a MeCN solution of **1**, the addition of a 2-fold molar excess of  $\text{Ni}(\text{ClO}_4)_2$  followed by the addition of an equimolar amount (with respect to perchlorate ions) of chloride ions, as  $\text{NaCl}$ , leads to a complete transmetalation within 30 min, as that obtained using  $\text{NiCl}_2$  (Fig. S15†). The same occurs also in the presence of a stoichiometric excess of perchlorate anions added as  $\text{TBAClO}_4$ . Identical results are obtained upon adding  $\text{NaCl}$  to **1** before the addition of  $\text{Ni}(\text{ClO}_4)_2$ . Moreover, if one-half molar amount of  $\text{NaCl}$  is added to **1**, a complete transmetalation occurs in a much longer time (*ca.* 2 days). It then turns out that the chloride anion plays a role in stabilizing the transition state of the transmetalation (Scheme 1).

In order to investigate the transmetalation process starting from a different adduct, **1**-DMF, analogous experiments were performed using solutions of the complex **1** in DMF. The addition of 2-fold molar excess of either nitrate or perchlorate of the involved cations does not produce any appreciable change in the optical absorption spectra measured immediately after the addition of the cations, except for some small variations for  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  (Fig. S16†). A complete transmetalation of **1** with  $\text{Cu}^{2+}$  occurs after *ca.* 20 hours (Fig. S17†), in striking contrast to the immediate transmetalation observed in MeCN.



Scheme 1 Proposed mechanism for the chloride-assisted transmetalation process of **1** by  $\text{NiCl}_2$ .



**Table 1** Transmetalation behaviour<sup>a</sup> of **1** (including the time required for a complete transmetalation) in two different solvents towards metal cations, upon the addition of 2-fold molar excess of aqueous solutions of various metal salts at room temperature without stirring

Solvent	Counteranion	Na <sup>+</sup>	Mg <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>
MeCN	Nitrate/perchlorate	nt	nt	nt	nt	24 h	7 days	<i>t</i> <sub>0</sub>	nt	dm	nt
	Chloride	ad	<i>t</i> <sub>0</sub> <sup>b</sup>	<i>t</i> <sub>0</sub> <sup>c</sup>	<i>t</i> <sub>0</sub> <sup>c</sup>	30 min	30 min	<i>t</i> <sub>0</sub>	nt	nt	—
DMF	Nitrate/perchlorate	nt	nt	nt	nt	30 h	100 h	20 h	nt	dm	nt
	Chloride	ad	ad	ad <sup>c</sup>	dm <sup>c</sup>	5 h	50 h	5 min	nt	nt	—

<sup>a</sup> nt = no transmetalation; *t*<sub>0</sub> = transmetalation immediately after the addition of the metal salt; dm = demetalation; ad = 1-chloride adduct formation. <sup>b</sup> Subsequent adduct formation. <sup>c</sup> Subsequent decomposition.

On the other hand, the addition of metal chlorides to DMF solutions of **1** again leads to very different results than those observed in MeCN. An almost complete transmetalation (within 5 min) occurs only in the case of the addition of CuCl<sub>2</sub> (Fig. S18†). Instead, the addition of the other chlorides (Na<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>) gives absorption changes analogous to those observed upon titration of **1** in DMF with TBACl (Fig. S19†), thus indicating the formation of 1-chloride adducts. However, for Co(II) and Ni(II), the chloride adducts initially formed successively evolve, at different times, into the transmetalated species. In the case of Co(II), transmetalation is observed after 5 hours, while for Ni(II) a complete transmetalation occurs after *ca.* 50 hours (Fig. S20†). Instead, for Mn(II) a subsequent gradual decomposition is observed. Analogously, as observed for MeCN solutions of **1**, the addition of HgCl<sub>2</sub> and CdCl<sub>2</sub> to DMF solutions of **1** does not involve any absorption change. Finally, the addition of FeCl<sub>2</sub> to DMF solutions of **1** leads first to demetalation and then to decomposition. Titrations of DMF solutions of **1** with perchloric acid indicate a complete demetalation upon the addition of a 3.75-fold molar excess of acid (Fig. S21†). In comparison with the demetalation of **1** in MeCN, this is in agreement with the greater stability of the 1-DMF adduct. The transmetalation behaviour of **1** in MeCN and DMF towards the involved metal cations is summarized in Table 1.

In summary, DMF solutions of **1** are less prone to transmetalation than MeCN solutions, and this different behaviour can be related to the greater stability of the 1-DMF adduct, which is consequently reflected by the slower transmetalation kinetics.

### 3. Conclusions

This paper reports the synthesis and the deaggregation properties of a Lewis acidic Zn(salen)-type complex, and a systematic study on the transmetalation in solution with other metal ions. Although the transmetalation process is thermodynamically driven, its kinetics is strongly affected by the stability of the 1-solvent adducts and the nature of the counteranion of the incoming cation. While MeCN is a solvent with a weak Lewis basicity, yielding adducts suitable for a facile transmetalation, DMF possessing a stronger Lewis basicity forms more stable adducts and is less prone to transmetalation. Moreover, the presence of the chloride anion significantly

accelerates the kinetics of the process in MeCN solutions, with a fast and complete transmetalation for divalent ions of the first transition series, indicating a major involvement of the chloride ion in the transmetalation mechanism. Therefore, the nature of the solvent and the counteranion allow controlling the transmetalation process of this Zn(salen) complex. In conclusion, the interesting transmetalation results emerging from this study certainly deserve further investigations within the family of Zn(salen)-type Schiff-base complexes as these findings can be exploited for the straightforward synthesis of new M(salen)-type complexes and for sensing specific cations.

## 4. Experimental

### 4.1. Materials and general procedures

All the chemicals used were purchased from Sigma-Aldrich (Merck) and used as received. Zinc perchlorate hexahydrate was used for the template synthesis of complex **1**. *Caution: Perchlorate salts of metal compounds in the presence of organics are potentially explosive. Only small amounts of the material should be cautiously handled.* Chloroform stabilized with amylene was used for spectrophotometric measurements. It was purified as follows before use: left overnight in anhydrous K<sub>2</sub>CO<sub>3</sub>, filtered and stored over molecular sieves (3 Å) in the dark under an argon atmosphere. DMF was dried over molecular sieves (3 Å). CDCl<sub>3</sub> was stored over molecular sieves (3 Å), while all the other deuterated solvents were used as received. All reactions were performed under an inert atmosphere of nitrogen.

### 4.2. Physical measurements

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ESI-MS spectra were recorded on a Thermo Fisher API 2000 mass spectrometer. ESI-MS spectra were achieved using MeCN solutions of complex **1** (40 μM) immediately after the addition of aqueous solutions of the chloride salts, except for Ni(II) and Co(II), for which ESI-MS spectra were achieved 30 min after the addition of NiCl<sub>2</sub> and CoCl<sub>2</sub>. <sup>1</sup>H NMR experiments were performed at 27 °C on a Varian Unity S 500 (499.88 MHz for <sup>1</sup>H) spectrometer. Tetramethylsilane (TMS) has been used as the internal reference for all NMR experiments. <sup>1</sup>H DOSY measurements in CDCl<sub>3</sub> were performed using the Zn<sup>II</sup> complex derivative of the *trans*-1,2-diaminocyclopentane as the reference species (double helicate Zn<sub>2</sub>L<sub>2</sub> structure, 863.6



Da),<sup>38</sup> while the Zn<sup>II</sup> complex derivative of the *trans*-1,2-diaminocyclohexane was used as the reference for DOSY measurements in DMSO-*d*<sub>6</sub> (adduct with DMSO, 530 Da).<sup>39</sup> Further experimental details are reported elsewhere.<sup>34,38,39</sup> UV/vis optical absorption spectra were recorded at room temperature using an Agilent Cary 60 spectrophotometer.

#### 4.3. Spectrophotometric titrations and transmetalation experiments

Solutions of Lewis bases and metal salts were added to solutions of the complex **1** using Rainin (METTLER TOLEDO) positive displacements pipettes. Titrations were performed using a 1 cm path length cuvette. At least three replicate titrations were performed for each Lewis base. Experimental details of the determination of binding constants are reported elsewhere.<sup>60</sup> Transmetalation experiments were performed at room temperature, without stirring, and monitored immediately after the addition of aqueous metal salt solutions and over time. Aqueous solutions of metal salts were obtained by dissolving salts in distilled water and used as prepared. The addition of distilled water or D<sub>2</sub>O to MeCN solutions of **1** does not involve any change in the optical absorption nor <sup>1</sup>H NMR spectra, indicating that no demetalation/decomposition occurs.

#### 4.4. Syntheses

**Complex 1.** To a solution of 2,3-diaminomaleonitrile (0.108 g, 1.00 mmol) in methanol (15 ml), 5-*tert*-butyl-2-hydroxybenzaldehyde (342 μl, 2.00 mmol) was added and the resulting solution was heated at reflux with stirring for 2 h under a nitrogen atmosphere. Then, zinc(II) perchlorate hexahydrate (0.559 g, 1.50 mmol) and triethylamine (1.0 ml) were added and the formation of a dark precipitate was observed. The mixture was heated at reflux with stirring under a nitrogen atmosphere for 24 h. After cooling, the dark-brown precipitated product was collected by filtration, washed with methanol and dried under vacuum. The product (0.430 g) was crystallized from chloroform (50 ml), filtered, washed with chloroform, and dried under vacuum. Dark-brown powder (0.333 g, 68%). C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Zn (491.90): calcd C, 63.49; H, 5.33; N, 11.39; found C, 63.51; H, 5.34; N, 11.42. ESI-MS: *m/z* = 491 [M + H<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 8.60 (s, 2H, CH=N), 7.49 (dd, <sup>3</sup>J<sub>HH</sub> = 9 Hz, <sup>4</sup>J<sub>HH</sub> = 3 Hz, 2H; ArH), 7.39 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 1H; ArH), 6.76 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 2H; ArH), 1.26 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ = 31.39, 34.03, 112.26, 118.20, 121.97, 124.41, 131.82, 136.12, 136.97, 164.20, 173.55.

**Cu(salmal).** To a solution of 2,3-diaminomaleonitrile (0.054 g, 0.50 mmol) in ethanol (10 ml), 5-*tert*-butyl-2-hydroxybenzaldehyde (171 μl, 1.00 mmol) was added and the resulting solution was heated at reflux with stirring for 30 min under a nitrogen atmosphere. Afterwards, copper(II) acetate monohydrate (0.091 g, 0.50 mmol) was added and the formation of a red precipitate was observed. The mixture was heated at reflux with stirring under a nitrogen atmosphere for 24 h. After cooling, the red precipitated product was collected by filtration, washed with methanol and dried under vacuum.

Brown powder (0.114 g, 46%) C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Cu (490.07): calcd C, 63.72; H, 5.35; N, 11.43; found C, 63.75; H, 5.38; N, 11.46. ESI-MS: *m/z* = 490 [M + H<sup>+</sup>].

**Ni(salmal).** To a solution of 2,3-diaminomaleonitrile (0.054 g, 0.50 mmol) in ethanol (10 ml), 5-*tert*-butyl-2-hydroxybenzaldehyde (171 μl, 1.00 mmol) was added and the resulting solution was heated at reflux with stirring for 30 min under a nitrogen atmosphere. Afterwards, nickel(II) acetate tetrahydrate (0.124 g, 0.50 mmol) was added and the formation of a black precipitate was observed. The mixture was heated at reflux with stirring under a nitrogen atmosphere for 24 h. After cooling, the red precipitate product was collected by filtration, washed with methanol and dried under vacuum. Black powder (0.146 g, 60%) C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Ni (485.21): calcd C, 64.36; H, 5.40; N, 11.55; found C, 63.40; H, 5.44; N, 11.60. ESI-MS: *m/z* = 485 [M + H<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ = 8.28 (s, 2H, CH=N), 7.63 (dd, <sup>3</sup>J<sub>HH</sub> = 9 Hz, <sup>4</sup>J<sub>HH</sub> = 3 Hz, 2H; ArH), 7.56 (d, <sup>3</sup>J<sub>HH</sub> = 3 Hz, 1H; ArH), 7.04 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 2H; ArH), 1.30 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 30.82, 34.07, 77.00, 77.25, 109.29, 118.85, 121.97, 122.12, 122.65, 127.56, 137.39, 140.80, 155.78, 168.10.

## Conflicts of interest

There are no conflicts of interest to be declared.

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