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# Unusual shift of a nitro group in a phenylhydrazo- $\beta$ -diketone $\dagger$

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A novel *para* to *meta* shift of a nitro group at the phenyl ring of 3-(2-hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione (H<sub>2</sub>L<sup>1</sup>, 1), with formation of the new 3-(2-hydroxy-3,5-dinitrophenylhydrazo)pentane-2,4-dione (H<sub>2</sub>L<sup>2</sup>, 2), occurs upon nitration of 1 with an equimolar amount of NaNO<sub>2</sub>, under basic conditions. 2 acts as a polydentate ligand for the synthesis of the polymeric potassium  $[K(\mu_5-HL^2)]_n$  (3) and monomeric nickel(II) [Ni(H<sub>2</sub>O)<sub>3</sub>(L<sup>2</sup>)]·H<sub>2</sub>O (4) compounds. They have been fully characterized, including single crystal X-ray analysis, and the complexes feature metal–organic (in 3) or supramolecular (in 4) 3D networks. The topological analysis of 3 reveals a uninodal 5-connected underlying net with the point symbol of (4<sup>6</sup>.6<sup>4</sup>) and a very rare 5/4/t5 topology, which had not yet been observed in coordination polymers.

# Introduction

Nitro compounds are very important and widely used chemicals<sup>1</sup> due to their versatile reactivities and simplicity to prepare. In particular, the nitro functionality can readily be introduced into an aromatic ring and replaced by a number of nucleophiles.<sup>2</sup> In fact, the ability of the nitro group as a leaving group is, in many cases, comparable with that of fluorine and is better than those of chlorine or bromine.<sup>2c</sup> Oxygen, carbon and sulfur nucleophiles were successfully used in reactions with activated nitroaromatics towards various applications. Transformation of 2-methoxy-4-nitroaniline into an important hepatitis C drug candidate VX-497 (merimepodib)<sup>3</sup> can be mentioned as an example among many others.<sup>1</sup> Hence, the search for new conversions within the nitro compounds is of significance for the synthesis of chemicals of practical importance.

Generally, nitroaromatic compounds can be prepared by a classic electrophilic substitution: nitric and sulfuric acids produce the nitronium ion that performs the nitration.<sup>1</sup> Another known method is the Zincke nitration in which a halo-substituent of a phenol or cresol is replaced by a nitro group, *via* treatment with nitric acid or sodium nitrite.<sup>1a</sup> Lately, nitrations by metal nitrate salts or nitrogen oxides in the presence of catalysts have been developed.<sup>1a</sup> Current research in this area is focusing on attaining a nitro group with the highest nucleofugacity under mild reaction conditions.<sup>1a</sup> However, to the best of our knowledge, no examples

of nitration with simultaneous shift of a  $NO_2$  group from *para* to *meta* position of an aromatic ring are known.

Nitroaromatic azoderivatives of β-diketones (NABD) constitute an important class of nitro compounds, which have been applied as analytical reagents<sup>4a,b</sup> or for further organic synthesis,<sup>4c</sup> while their complexes can be used as catalysts for some C–C coupling<sup>4d</sup> or oxidation reactions.<sup>4e</sup> Moreover, NABD are found to display analgesic, antipyretic, and antibacterial properties.<sup>4c</sup> Thus, the achievement of a new type of functionalization within the aromatic part of NABD should be of significance in the above areas of application.

Therefore, the main aims of the current work are: (*i*) to achieve a further nitration of the phenyl ring of a NADB, illustrated by 3-(2-hydroxy-4-dinitrophenylhydrazo)pentane-2,4-dione ( $H_2L^1$ , 1); (*ii*) to see if such a nitration would induce any further reaction at the aromatic ring; (*iii*) to use the thus synthesized dinitro derivative for the preparation of new metal coordination compounds.

# **Results and discussion**

#### Synthesis and characterization

3-(2-Hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione (H<sub>2</sub>L<sup>1</sup>, **1**) was described by us earlier,<sup>4e</sup> and thus will not be discussed in detail here. We have now unexpectedly observed that, in this compound, the nitro group of the aromatic ring shifts from the *para* position (relative to the hydrazo group) to the *meta* position, upon nitration with sodium nitrite in the presence of KOH in MeOH, to form 3-(2-hydroxy-3,5-dinitrophenylhydrazo)pentane-2,4-dione (H<sub>2</sub>L<sup>2</sup>, **2**, Scheme 1, Route A–B). During the course of these reactions, we have isolated the possible intermediate compound [K( $\mu_5$ -HL<sup>2</sup>)]<sub>n</sub> (**3**) as red rod-like X-ray quality crystals. In addition, a similar compound [Na( $\mu$ -HL<sup>2</sup>)]<sub>n</sub> (**5**) has been obtained as a microcrystalline powder when using NaOH instead

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Scheme 1 Reactions of 1 and derived products. Experiments were run in MeOH at r.t., unless stated otherwise.

of KOH. However, due to the poor quality of the crystals, this sodium complex was not characterized by X-ray diffraction, and thus its composition is assumed on the basis of other methods and by analogy with **3**. It should be mentioned that both **3** and **5** can be easily converted to **2** upon treatment with HCl (Scheme 1, Route B).

Interestingly, the nitro shift does not occur under the same reaction conditions if 2-hydroxy-4-nitroaniline or 3-(4-nitrophenylhydrazo)pentane-2,4-dione (Scheme 2), which are related to 1 but do not bear both the hydroxo and the hydrazo groups simultaneously, are used as starting materials. The shift also does not proceed upon attempted reaction of 1 with sodium nitrite in the absence of potassium hydroxide (Scheme 1, Route C), indicating thus that the presence of alkali is essential. On the other hand, the reaction of 1 with potassium hydroxide, in the absence of the nitrite, gives simply its potassium salt 6 (Scheme 1, Route D), which can be reconverted to 1 by treatment with HCl (Route F). Hence, the observed nitro shift only occurs upon nitration in basic medium, *i.e.*, when all the mentioned reagents (1, NaNO<sub>2</sub> and KOH) are combined.



Scheme 2 2-Hydroxy-4-nitroaniline (a) and 3-(4-nitrophenylhydrazo)-pentane-2,4-dione (b).

To examine whether the nitro shift could also occur in the presence of a transition metal centre, we have studied the reaction of **1** with nickel(II) chloride. Although Ni(II) reacts with **1** in MeOH solution,<sup>4f</sup> simple solvent evaporation from the reaction mixture containing NiCl<sub>2</sub> and **1** gives the starting materials (Scheme 1, Route E). However, if the nickel(II) salt is treated with **1** in the

presence of sodium nitrite and KOH in MeOH, the nitro group shift, deprotonation and coordination occur in one pot, and the mononuclear complex  $[Ni(H_2O)_3(L^2)]\cdot H_2O$  (4) can be isolated (Route J) as green X-ray quality crystals. This compound can also be prepared from 2 upon its deprotonation with KOH in the presence of NiCl<sub>2</sub> (Route H), although the direct reaction of the Ni(II) salt with 2 does not proceed (Route G).

Although the IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra of **1** and **2** are rather similar, there are some distinctive features. Thus, the IR spectra of **1** and **2** reveal the presence of v(OH) vibrations at *ca*. 3461 and 3466 cm<sup>-1</sup>, and v(NH) bands at 3095 and 3099 cm<sup>-1</sup>, correspondingly. The carbonyl stretching vibrations [1638 v(C=O)and 1626  $v(C=O\cdots H)$  cm<sup>-1</sup> for **1**, and 1633 v(C=O) and 1613  $v(C=O\cdots H)$  cm<sup>-1</sup> for **2**] demonstrate<sup>4c</sup> that, in the solid state, **1** and **2** are stabilized in the H-bonded hydrazo forms. As in the case of **1**,<sup>4e</sup> the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2** in DMSO-*d*<sup>6</sup> solution at room temperature indicate that this compound exists in the hydrazo form rather than in the enol-azo or keto-azo forms. The NMR spectra show a separation of the methyl peaks (see Experimental section) of the two acetyls in **2**, thus supporting that one of these groups participates in hydrogen bonding with the hydrazone NH moiety.<sup>4,5</sup>

Concerning a possible mechanistic pathway of the nitro shift reaction, we believe it is initiated by an interaction of **1** with the alkali, *i.e.* KOH. Multiple interactions of potassium(1) ions with carbonyl, hydroxo and nitro groups can occur. Deprotonation of the hydrazo moiety in **1** by KOH with K<sup>+</sup> addition to one carbonyl group would account for the formation of the X–N=Nmoiety [X = CH<sub>3</sub>C(–OK)=C–C(=O)CH<sub>3</sub>] in **3**. This is shown in Scheme 3, step **A**, wherein deprotonation of the *ortho*-OH group also occurred, with addition of KOH, to form a charge-assisted hydrogen bonding system (CAHB).<sup>6</sup>

Activation of the *meta* (3) C–H bond (with adjacent electron withdrawing -OK and  $-NO_2$  groups in the aromatic ring) and the above formation of the CAHB system enhance the 3-C–H proton mobility and carbon atom nucleophilicity, facilitating the



Scheme 3 Proposed mechanism for the nitro group shift upon nitration in the conversion of 1 to 3.

attack of a NO<sub>2</sub> group (nitration) at that position (3) (Scheme 3, steps **B** and **C**). The presence of two nitro groups in adjacent ring positions would be electronically and sterically unfavourable, what promotes the transfer of the group from the *para* (4) to the *meta* (5) position which bears the C–H bond activated in a related way to that described above, resulting in the formation of **3** (Scheme 2, steps **D–F**). This proposed route appears to be supported by ESI-MS analysis of the reaction mixture, which shows, apart from the anionic form of **1**,  $[1-2H]^-$  (ESI-MS<sup>-</sup>, m/z = 263), the possible parent ions of the suggested intermediates I and II (ESI-MS<sup>+</sup>,  $[I+H]^+ m/z = 465$  and  $[II+H]^+ m/z = 522$ , Scheme 3).

## X-ray crystal structures

 $[K(\mu_5-HL^2)]_n$  (3). The asymmetric unit of 3 consists of a potassium ion and one µ5-HL2 moiety (Fig. 1a). Each multidentate  $\mu_5$ -HL<sup>2</sup> ligand simultaneously binds five symmetrically generated K1 atoms (Fig. 1b), thus giving rise to an infinite 3D noninterpenetrating network (Fig. 2). While both oxygen atoms of the N4-nitro group in HL<sup>2</sup> are coordinated to only a metal cation, the N3-nitro moiety is bridging, by means of its O31 oxygen atom, to three potassium ions (Fig. 1b). Additionally, the O1 atom is also connected to two K1 atoms. All oxygen atoms of the  $\mu_5$ -HL<sup>2</sup> ligand, except O3, are bound to K1 atoms that adopt a ninecoordinate  $\{KO_9\}$  environment (Fig. 1c). It is filled by oxygen atoms from five different HL<sup>2</sup> moieties, namely (i) the O31 and O32 atoms of the N3-nitro group of one HL<sup>2</sup> ligand, (ii) the O31 and O1 atoms of other two HL<sup>2</sup> moieties, (iii) the O41 and O42 atoms of the N4-nitro group of the fourth HL<sup>2</sup> ligand, and (iv) the O2 atom of the fifth HL<sup>2</sup> moiety. The K–O bond lengths lie in the 2.718(6)–3.223(6) Å range (Fig. 1), their elongated nature being in agreement with the high coordination number of the metal.<sup>7</sup> The overall polymeric structure of 3 can also be described as a collection of the cyclic 1D chain  $[K_3(\mu_2-O)_2(\mu_3-O)_3]_n$  motifs that run along the *a* axis, being driven by the  $\mu_2$ -O1 and  $\mu_3$ -O31 atoms (Fig. 1d), with the corresponding  $K1 \cdots K1^{ii}$ ,  $K1 \cdots K1^{iii}$ and  $K1 \cdots K1^i$  separations of 3.862(3), 4.896(3) and 5.653(4) Å, respectively. Multiple 1D motifs are stacked into a complex 3D framework (Fig. 2) via the repeating O41-K1<sup>iv</sup> and O42-K1<sup>iv</sup>

bonds. Although some coordination polymers of alkaline earth metals bearing derivatives of  $\beta$ -diketones have been reported,<sup>7b</sup> the corresponding compounds composed of alkali metals remain rather scant.

To get a further insight into the intricate 3D network of 3, we have performed its topological analysis using the TOPOS software package,<sup>8</sup> and following the concept of the simplified underlying net.9 Hence, upon contracting the HL<sup>2</sup> moieties to their centroids, the structure of 3 can be considered as an underlying net composed of the topologically equivalent 5-connected K1 and HL<sup>2</sup> nodes (Fig. 3). The topological analysis<sup>8</sup> of this net discloses a uninodal 5-connected framework with the point (Schläfli) symbol of  $(4^{6}.6^{4})$ and the 5/4/t5 or sqc518 topology, according to classifications in the RCSR<sup>10</sup> or EPINET<sup>11</sup> databases, respectively. To our knowledge,<sup>8</sup> the present type of topology has been encountered in the crystal structures of only two organic compounds, trans-5-(1methylethyl)-2-oxo-4-imidazolidinecarboxamide12a and 3-amino-1*H*-pyrazolo(3,4-c)pyridazine,<sup>12b</sup> which form supramolecular Hbonded 3D networks. Hence, compound 3 represents the first example of a coordination polymer with the 5/4/t5 topology.

[Ni(H<sub>2</sub>O)<sub>3</sub>(L<sup>2</sup>)]-H<sub>2</sub>O (4). In contrast to the polymer 3, the crystal structure of 4 (Fig. 4a) is composed of mononuclear units, in which the six-coordinate Ni1 atoms exhibit a distorted octahedral {NO<sub>5</sub>} coordination geometry. The L<sup>2</sup> moiety occupies equatorial sites acting as a tridentate N,O<sub>2</sub>-ligand by means of the deprotonated aromatic *ortho* hydroxyl group (O1), one of the diazo nitrogen atoms (N1) and a carbonyl oxygen atom (O2). The aqua ligand O3 fills the remaining equatorial position, while the O4 and O5 water molecules lie in the axial sites. The bonding parameters in 4 are comparable to those of other metal complexes with phenylazo-β-diketone ligands.<sup>4,5</sup> Furthermore, owing to the presence of four water molecules, the overall crystal structure is stabilized by multiple O–H…O hydrogen bonds, which give rise to a 3D supramolecular network.

# Conclusions

In the present work, we have described an interesting and, to our knowledge, unprecedented nitro group shift upon nitration



**Fig. 1** Structural fragments of **3**: (a) ellipsoid plot of the asymmetric unit with atom numbering scheme (50% probability ellipsoids), (b) metal environment of the ligand, (c) coordination geometry of the potassium ion, and (d) repeating 1D cyclic chain  $[K_3(\mu_2-O)_2(\mu_3-O)_3]_n$  motif. The H atoms are omitted for clarity. Colour codes: K (purple), C (gray), N (blue), O (red). Selected distances (Å) and angles (°): O1–K1 2.718(6), O2–K1<sup>*i*</sup> 2.825(6), O1–K1<sup>*i*</sup> 2.726(6), O31–K1 2.890(5), O31–K1<sup>*i*</sup> 2.934(6), O31–K1<sup>*i*</sup> 3.222(6), O41–K1<sup>*i*</sup> 2.868(6), O42–K1<sup>*i*</sup> 2.966(6), C1–O1 1.275(8), C6–N1 1.401(9), C12–O2 1.233(10), C13–N2 1.340(10), N1–N2 1.303(9), K1 ··· K1<sup>*i*</sup> 3.862(3), K1 ··· K1<sup>*i*</sup> 4.896(3), K1 ··· K1<sup>*i*</sup> 5.653(4), K1 ··· K1<sup>*i*</sup> 10.472(3); O1–K1–O31 57.66(17), N1–N2–C13 121.1(7), N2–N1–C6 120.3(6). Symmetry operators: (*i*) 1 – *x*, *y*, *z*, (*ii*) 2 – *x*, –*y*, 2 – *z*, (*iii*) 3 – *x*, –



**Fig. 2** Complex 3D network of **3** (rotated view along the *a* axis). The H atoms are omitted for clarity. Colour codes: K (purple), C (gray), N (blue), O (red).



**Fig. 3** (a) Simplified underlying 3D net of **3** with the 5/4/t5 (sqc518) topology. (b) Fragment of a 1D cyclic chain motif. The topologically equivalent 5-connected K1 nodes and centroids of HL<sup>2</sup> nodes are shown as violet and yellow sticks, respectively. Rotated views along the *a* (a) or *b* (b) axes.

at a phenyl ring, in 1, that leads to the generation of a new dinitrophenylhydrazo- $\beta$ -diketone, 2. This unusual reaction thus broadens the scope of organic transformations known for aromatic nitro derivatives. Also, the coordination behaviour



Fig. 4 Ellipsoid plot of 4 with atom numbering scheme (50% probability ellipsoids, H atoms and crystallization  $H_2O$  molecule are omitted for clarity). Selected bond distances (Å) and angles (°): Ni1–O1 2.035(3), Ni1–O2 2.031(3), Ni1–O3 2.035(3), Ni1–O4 2.091(3), Ni1–O5 2.121(3), Ni1–N1 1.974(3), N1–N2 1.275(5), C10–O2 1.261(5), C1–O1 1.281(5), C8–O6 1.233(6); N1–Ni1–O1 82.35(13), N1–Ni1–O2 86.55(13), N1–Ni1–O3 175.94(13).

of **2** towards potassium and nickel(II) ions has been studied, giving rise to novel poly- and mononuclear compounds **3** and **4**, respectively. Hence, the current study also extends to K and Ni centres the application of various azoderivatives of  $\beta$ -diketones in coordination chemistry, which is mainly limited to complexes of Cu and Zn.<sup>4,5</sup>

A noteworthy feature of **3** consists in the formation of a 3D metal–organic network, driven by 5-connected potassium and  $\mu_5$ -HL<sup>2</sup> nodes, the topological analysis of which reveals a uninodal net with a very rare 5/4/t5 topology. To our knowledge, compound **3** represents the first example of a coordination polymer with the present type of topology.

Further research should focus on probing the observed shift at other aromatic substrates, and on widening the still underexplored application of various azoderivatives of  $\beta$ -diketones in the design of coordination and supramolecular networks.

# **Experimental section**

#### Materials and instrumentation

All the synthetic work was performed in air and at room temperature (r.t., ca. 20 °C). All the chemicals were obtained from commercial sources (Aldrich) and used as received, except for 1 that was prepared according to a published procedure.4e The 1H and <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Bruker Avance II + 300 (UltraShield<sup>TM</sup> Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts ( $\delta$ ) are reported in ppm using tetramethylsilane as the internal reference. The infrared spectrum (4000-400 cm<sup>-1</sup>) was recorded on a BIO-RAD FTC 3000MX instrument in KBr pellets. C, H, N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 psi nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution.

### Synthesis and analytical data for compounds 1-6

**Compound 1**<sup>4e</sup>. Calcd for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub> (M = 265.22): C 49.81, H 4.18, N 15.84%; found C 49.85, H 4.17, N 15.39%. MS (ESI): m/z: 266 [1+H]<sup>+</sup>. IR (KBr): 3461 (s, br) v(OH), 3095 (s, br) v(NH), 1638 (s) v(C=O), 1626 (s) v(C=O····H), 1598 (s) v(C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.45 (s, 3H, CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 7.73–7.86 (m, 3H, Ar–H), 11.55 (s, 1H, OH), 14.17 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} (75.468 MHz, DMSO- $d_6$ ):  $\delta$  = 26.55 (CH<sub>3</sub>), 31.38 (CH<sub>3</sub>), 110.21 (Ar–H), 114.31 (Ar–H), 116.30 (Ar–H), 135.36 (C=N), 135.62 (Ar–NH–N), 143.64 (Ar–NO<sub>2</sub>), 145.68 (Ar–OH), 196.50 (C=O), 197.42 (C=O) ppm.

Synthesis of 2 from 3 or 5. To 41.9 mg (0.1 mmol) of 3 [or 40.3 mg (0.1 mmol) of 5] in methanol (50 mL) was added HCl ( $2.2 \mu$ L, 2.0 mmol, 33% in H<sub>2</sub>O), which caused the precipitation of a yellow solid that was then filtered off, washed with methanol on a filter and dried in air to give 2.

**Compound 2.** Yield: 40% (based on **3**), yellow powder, soluble in ethanol, acetone and methanol and insoluble in chloroform. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O<sub>7</sub> (M = 310.20): C 42.59, H 3.25, N 18.06%; found C 42.25, H 3.17, N 18.03%. MS (ESI): m/z: 311 [**2**+H]<sup>+</sup>. IR (KBr): 3466 (s, br) v(OH), 3099 (s, br) v(NH), 1633 (s) v(C=O), 1613 (s) v(C=O···H), 1598 (s) v(C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta = 2.58$  (s, 3H, CH<sub>3</sub>) overlapped by DMSO- $d_6$  (s, 3H, CH<sub>3</sub>), 7.73–7.85 (s, 2H, Ar–H), 11.48 (s, 1H, OH), 14.16 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} (75.5 MHz, DMSO- $d_6$ ):  $\delta = 26.48$  (CH<sub>3</sub>), 31.32 (CH<sub>3</sub>), 110.16 (Ar–H), 114.16 (Ar–H), 116.13 (C=N), 135.21 (Ar– NH–N), 135.54 (Ar–NO<sub>2</sub>), 143.48 (Ar–NO<sub>2</sub>), 145.76 (Ar–OH), 196.49 (C=O), 197.36 (C=O) ppm.

Syntheses of 3 and 5. To 26.5 mg(0.1 mmol) of 1 in methanol (50 mL) were added 6.9 mg (0.1 mmol) NaNO<sub>2</sub> and 22.4 mg (0.4 mmol) KOH [or 16.0 mg (0.4 mmol) NaOH for the synthesis of 5]. The mixture was stirred for 5 min at r.t. and left for slow evaporation in air. Red X-ray quality crystals of 3 or dark red powder of 5 started to form in 1 d.

**Compound 3.** Yield: 64% (based on 1), dark red crystals, soluble in ethanol, acetone, methanol and water, insoluble in chloroform. Calcd for  $3.4H_2O$ ,  $C_{11}H_{17}KN_4O_{11}$  (M = 420.4): C 31.43, H 4.08, N 13.33%; found C 31.50, H 3.49, N 13.32%. MS (ESI): m/z: 348 [3-4H<sub>2</sub>O]. IR (KBr): 3453 (s, br) v(OH), 1676 (s) v(C=O), 1648 (s) v(C–O), 1570 (s) v(C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO, Me<sub>4</sub>Si):  $\delta = 2.41$  (s, 3H, CH<sub>3</sub>) overlapped by DMSO- $d_6$  (s, 3H, CH<sub>3</sub>), 6.96–7.39 (s, 2H, Ar–H). <sup>13</sup>C{<sup>1</sup>H} (75.5 MHz, DMSO- $d_6$ ):  $\delta = 26.56$  (CH<sub>3</sub>), 31.23 (CH<sub>3</sub>), 104.24 (Ar–H), 111.80 (Ar–H), 112.92 (C=N), 129.81 (Ar–N=N), 133.13 (Ar–NO<sub>2</sub>), 138.70 (Ar–NO<sub>2</sub>), 146.35 (Ar–OK), 161.51 (C–OK), 186.30 (C=O) ppm.

**Compound 5.** Yield: 48% (based on 1), dark red powder, soluble in ethanol, acetone, methanol and water, insoluble in chloroform. Calcd for **5**·4H<sub>2</sub>O, C<sub>11</sub>H<sub>17</sub>NaN<sub>4</sub>O<sub>11</sub> (M = 404.3): C 32.68, H 4.24, N 13.86%; found C 32.88, H 4.12, N 13.83%. MS (ESI): m/z: 354 [**5**-4H<sub>2</sub>O]. IR (KBr): 3432 (s, br) v(OH), 1676 (s) v(C=O), 1653 (s) v(C=O), 1559 (s) v(C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta = 2.39$  (s, 3H, CH<sub>3</sub>) overlapped by DMSO- $d_6$  (s, 3H, CH<sub>3</sub>), 6.95–7.38 (s, 2H, Ar–H). <sup>13</sup>C{<sup>1</sup>H} (75.5 MHz, DMSO- $d_6$ ):  $\delta = 28.10$  (CH<sub>3</sub>), 29.40 (CH<sub>3</sub>), 104.51 (Ar–H), 108.66 (Ar–H), 110.34 (C=N), 113.04 (Ar–N=N), 124.19

(Ar–NO<sub>2</sub>), 129.66 (Ar–NO<sub>2</sub>), 146.06 (Ar–ONa), 149.03 (C–ONa), 164.90 (C=O) ppm.

Synthesis of 4. Method 1. To 26.5 mg (0.1 mmol) of 1 in methanol (50 mL) were added 6.9 mg (0.1 mmol) NaNO<sub>2</sub> and 11.2 mg (0.2 mmol) KOH, and the resulting mixture was stirred for 10 min at r.t. Then 23.8 mg (0.1 mmol) NiCl<sub>2</sub>·6H<sub>2</sub>O was added, the mixture was stirred for 10 min and left for slow evaporation in air at r.t. Green X-ray quality crystals of 4 started to form in 3 d.

Method 2. To 31.0 mg (0.1 mmol) of **2** in methanol (50 mL) were added 11.2 mg (0.2 mmol) KOH, and the resulting mixture was stirred for 10 min at r.t. Then 23.8 mg (0.1 mmol) NiCl<sub>2</sub>· $6H_2O$  was added, the mixture was stirred for 10 min and left for slow evaporation in air at r.t. The product started to form in 3 d, it was then filtered off and dried in air to give **4**.

**Compound 4.** Yield: 53% (based on 1), green crystals, soluble in ethanol, acetone, methanol and water, insoluble in chloroform. Calcd for  $C_{11}H_{16}NiN_4O_{11}$  (M = 439.0): C 30.10, H 3.67, N 13.37%; found C 29.99, H 3.28, N 12.98%. MS (ESI): m/z: 366 [4-4H<sub>2</sub>O]. IR (KBr): 3449 (s, br) v(OH), 1629 (s) v(C=O), 1594 (s) v(C=N) cm<sup>-1</sup>.

Synthesis of 6. To 26.5 mg (0.1 mmol) of 1 in methanol (50 mL) were added 11.2 mg (0.2 mmol) KOH. The resulting mixture was stirred for 10 min and left for slow evaporation in air at r.t. A dark red powder started to precipitate in 2 d, which was filtered off after 7 d and dried in air to give 6.

**Compound 6.** Yield: 61% (based on 1), dark red crystals, soluble in ethanol, acetone, methanol and water, insoluble in chloroform. Calcd for  $C_{11}H_{15}K_2N_3O_8$  (M = 395.0): C 33.41, H 3.82, N 10.63%; found C 33.75, H 3.53, N 9.97%. MS (ESI): m/z: 341 [6-3H<sub>2</sub>O]. IR (KBr): 3411 (s, br) v(OH), 1678 (s) v(C=O), 1650 (s) v(C=O), 1614 (s) v(C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta = 2.41$  (s, 3H, CH<sub>3</sub>) overlapped by DMSO- $d_6$  (s, 3H, CH<sub>3</sub>), 6.95–7.37 (s, 3H, Ar–H). <sup>13</sup>C{<sup>1</sup>H} (75.5 MHz, DMSO- $d_6$ ):  $\delta = 26.47$  (CH<sub>3</sub>), 31.19 (CH<sub>3</sub>), 103.86 (Ar–H), 111.57 (Ar–H), 112.94 (Ar–H), 133.06 (C=N), 138.89 (Ar–NH–N), 146.29 (Ar–NO<sub>2</sub>), 161.52 (Ar–OK), 194.85 (C–OK), 195.76 (C=O) ppm.

#### X-ray crystal structure determinations

The X-ray quality single crystals of compounds 3 and 4 were grown by slow evaporation in air at r.t. of their methanol solutions. They were immersed in a cryo-oil, mounted in a Nylon loop and measured at 150 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$ ) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT<sup>13a</sup> on all the observed reflections. Absorption corrections were applied using SADABS.<sup>13a</sup> Structures were solved by direct methods by using the SIR-9713b (3) or SHELXS-9713c (4) packages and refined with SHELXL-97.13c Calculations were performed using the WinGX System-Version 1.80.03.13d All hydrogen atoms were inserted in calculated positions. In 4, the O61 and O62 atoms of the nitro group are disordered over two sites with occupancies 0.53 and 0.47. Crystal data and details of data collection for 3 and 4 are reported in Table 1.

 Table 1
 Crystal data and structure refinement details for 3 and 4

	3	4
Formula unit	$C_{11}H_8KN_4O_7$	C <sub>11</sub> H <sub>16</sub> N <sub>4</sub> NiO <sub>11</sub>
Formula weight	348.32	438.99
T/K	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	P21/c	$P\overline{1}$
a/Å	5.6530(16)	8.2053(2)
b/Å	13.404(4)	10.2393(3)
c/Å	19.2441(18)	10.9106(2)
$\alpha /^{\circ}$	90	67.0990(10)
β/°	102.459(5)	73.6950(10)
γ/°	90	85.8660(10)
Ż	4	2
Volume/Å <sup>3</sup>	1423.8(6)	809.74(4)
$D_{\rm c}/{\rm g~cm^{-3}}$	1.625	1.800
$\mu/\mathrm{mm}^{-1}$	0.418	1.270
Independent reflections	8721	9045
Observed reflections	2598	2777
R <sub>int</sub>	0.1620	0.0181
Final $R1^a$ , $wR2^b$ $(I \ge 2\sigma)$	0.0889, 0.2053	0.0495, 0.1283
GOF	0.963	1.082
$^{a}R1 = \sum   F_{o}  -  F_{c}   / \sum  F_{c}  $	$F_{o} .^{b} wR2 = [\sum [w(F_{o}^{2} - R_{o})]^{2} + R^{2} = [\sum [w(F_{o})^{2} - R_{o})]^{2}$	$(F_{\rm c}^{2})^{2}]/\sum [w(F_{\rm o}^{2})^{2}]]^{1/2}$

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