SUPPORTING INFORMATION

Exploring photoswitchable properties of two nitro nickel(II) complexes with (N,N,O)-donor ligands and their copper(II) analogues

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Scheme 1S. Schematic representation of the synthetic protocol applied to obtain the studied compounds (M = Ni or Cu). Bold red-color bonds denote that either 2-picolyamine (black only) or 8-aminoquinoline (black & red together) were used in the synthesis of the 1a or 1b ligands (and consequently – M-2a or M-2b complexes), respectively.

Figure 1S. DSC curves obtained for Ni-2b when scanning the 120–300 K temperature range. Green area shows the monoclinic-to-triclinic phase transition upon temperature decrease, while the purple circle indicates the reverse process.
Figure 2S. PXRD patterns obtained for the Ni-2a bulk sample (top panel – full pattern, bottom – selected range magnification). Black curve – experimental pattern, red – Le Bail-fitted model, green bars – reflection positions (taking into account both Kα1-Kα2 splitting), blue – residual.
**Figure 3S.** PXRD patterns obtained for the Ni-2b bulk sample (top panel – full pattern, bottom – selected range magnification). Black curve – experimental pattern, red – Le Bail-fitted model, green bars – reflection positions (taking into account both Kα1-Kα2 splitting), blue – residual.
Figure 4S. PXRD patterns obtained for the Cu-2a bulk sample (top panel – full pattern, bottom – selected range magnification). Black curve – experimental pattern, red – Le Bail-fitted model, green bars – reflection positions (taking into account both Kα1-Kα2 splitting), blue – residual.
Figure 5S. PXRD patterns obtained for the Cu-2b bulk sample (top panel – full pattern, bottom – selected range magnification). Black curve – experimental pattern, red – Le Bail-fitted model, green bars – reflection positions (taking into account both $K\alpha_1$-$K\alpha_2$ splitting), blue – residual.
**Table 1S.** Summary of all collected X-ray diffraction datasets.

| Complex | Crystal No. | Temperature, T / K | Data collection code | Remarks                  |
|---------|-------------|--------------------|----------------------|--------------------------|
| Ni-2a   | 1st         | 290                | Ni-2a-290K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 240                | Ni-2a-240K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 200                | Ni-2a-200K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 160                | Ni-2a-160K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 140                | Ni-2a-140K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 120                | Ni-2a-120K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 100                | Ni-2a-100K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 120                | Ni-2a-120K-dark-heating-xtal-1 | heating cycle          |
|         |             | 140                | Ni-2a-140K-dark-heating-xtal-1 | heating cycle          |
|         |             | 160                | Ni-2a-160K-dark-heating-xtal-1 | heating cycle          |
|         |             | 180                | Ni-2a-180K-dark-heating-xtal-1 | heating cycle          |
|         |             | 200                | Ni-2a-200K-dark-heating-xtal-1 | heating cycle          |
|         | 2nd         | 140                | Ni-2a-140K-dark-xtal-2       | light-OFF data collection |
|         |             | 140                | Ni-2a-140K-irr-140K-xtal-2  | after irradiation at 140 K |
|         |             | 160                | Ni-2a-160K-irr-140K-xtal-2  | after irradiation at 140 K |
|         |             | 180                | Ni-2a-180K-irr-140K-xtal-2  | after irradiation at 140 K |
|         |             | 200                | Ni-2a-200K-irr-140K-xtal-2  | after irradiation at 140 K |
| Ni-2b   | 1st         | 290                | Ni-2b-290K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 240                | Ni-2b-240K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 200                | Ni-2b-200K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 180                | Ni-2b-180K-dark-cooling-xtal-1 | cooling cycle           |
|         |             | 160                | Ni-2b-160K-dark-cooling-xtal-1 | cooling cycle           |
|         | 2nd         | room temp.         | Ni-2b-RT-dark-xtal-2       | light-OFF data collection |
|         |             | 160                | Ni-2b-160K-dark-xtal-2     | light-OFF data collection |
|         |             | 160                | Ni-2b-160K-irr-160K-xtal-2 | after irradiation at 160 K |
|         |             | 440                | Ni-2b-240K-irr-160K-xtal-2 | after irradiation at 240 K |
Table 2S. Selected X-ray data collection, processing and refinement parameters for all presented crystal structures.

| Data set               | Ni-2a-290K-dark-cooling-xtal-1 | Ni-2a-240K-dark-cooling-xtal-1 | Ni-2a-200K-dark-cooling-xtal-1 | Ni-2a-160K-dark-cooling-xtal-1 | Ni-2a-140K-dark-cooling-xtal-1 | Ni-2a-120K-dark-cooling-xtal-1 |
|------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Moiety formula         | C16H15N3Ni1O3                  |                                |                                |                                |                                |                                |
| Moiety formula mass, $M_r$ / a.u. | 356.00                      |                                |                                |                                |                                |                                |
| Crystal system         | triclinic                      |                                |                                |                                |                                |                                |
| Space group            | $P\bar{1}$ (no. 2)            |                                |                                |                                |                                |                                |
| $Z$                    | 2                              |                                |                                |                                |                                |                                |
| $F_{000}$              | 368                            |                                |                                |                                |                                |                                |
| Crystal colour & shape | orange plate                   |                                |                                |                                |                                |                                |
| Crystal size / mm³     | 0.05×0.15×0.19                 |                                |                                |                                |                                |                                |
| $T$ / K                | 290                            | 240                            | 200                            | 160                            | 140                            | 120                            |
| $a$ / Å                | 7.5324(3)                      | 7.4868(3)                      | 7.4560(4)                      | 7.4308(4)                      | 7.4166(4)                      | 7.4036(5)                      |
| $b$ / Å                | 8.1607(4)                      | 8.1511(3)                      | 8.1469(4)                      | 8.1474(4)                      | 8.1470(5)                      | 8.1485(6)                      |
| $c$ / Å                | 13.7040(7)                     | 13.6670(6)                     | 13.6490(7)                     | 13.6372(7)                     | 13.622(8)                      | 13.6104(9)                     |
| $\alpha$ / °          | 100.410(4)                     | 100.337(3)                     | 100.302(4)                     | 100.277(4)                     | 100.289(5)                     | 100.310(6)                     |
| $\beta$ / °           | 101.755(4)                     | 101.551(3)                     | 101.435(4)                     | 101.262(4)                     | 101.159(5)                     | 101.086(6)                     |
| $\gamma$ / °          | 102.921(4)                     | 102.899(3)                     | 102.851(4)                     | 102.891(5)                     | 102.899(5)                     | 102.899(6)                     |
| $V$ / Å³              | 780.91(7)                      | 774.28(6)                      | 770.41(7)                      | 767.74(8)                      | 765.69(8)                      | 764.01(10)                     |
| $d_{calc}$ / g·cm⁻³   | 1.5140                         | 1.5270                         | 1.5347                         | 1.5400                         | 1.5441                         | 1.5475                         |
| $\theta$ range        | 3.39° - 76.17°                 | 3.40° - 76.22°                 | 3.40° - 75.98°                 | 3.40° - 75.88°                 | 3.40° - 75.73°                 | 3.31° - 75.39°                 |
| Absorption coefficient, $\mu$ / mm⁻³ | 1.956                         | 1.973                          | 1.983                          | 1.990                          | 1.995                          | 2.000                          |
| No. of reflections collected / unique | 9116 / 3168                   | 9056 / 3145                    | 8926 / 3128                    | 8741 / 3112                    | 8623 / 3102                    | 8479 / 3083                    |
| $R_{int}$              | 3.00%                          | 2.88%                          | 3.29%                          | 5.00%                          | 5.40%                          | 5.97%                          |
| No. of reflections with $I > 3\sigma(I)$ | 2483                          | 2542                            | 2517                            | 2266                            | 2218                            | 2175                            |
| No. of parameters / restraints / constraints | 209 / 0 / 60                   | 209 / 0 / 60                    | 209 / 0 / 60                    | 216 / 2 / 70                    | 219 / 0 / 67                    | 219 / 0 / 67                    |
| $R[F]$ ($I > 3\sigma(I)$) | 3.71%                          | 3.51%                          | 3.54%                          | 4.31%                          | 4.48%                          | 4.78%                          |
| $R[F]$ (all data)      | 4.95%                          | 4.62%                          | 4.61%                          | 6.28%                          | 6.60%                          | 7.07%                          |
| $\phi_{res}$ / $e$·Å⁻³ | -0.28 / +0.34                  | -0.31 / +0.38                  | -0.28 / +0.40                  | -0.31 / +0.42                  | -0.31 / +0.49                  | -0.36 / +0.53                  |
| CCDC code              | 2110810                        | 2110811                        | 2110818                        | 2110820                        | 2110819                        | 2110812                        |
| Data set                     | Ni-2a-100K-dark - cooling-xtal-1 | Ni-2a-120K-dark - heating-xtal-1 | Ni-2a-140K-dark - heating-xtal-1 | Ni-2a-160K-dark - heating-xtal-1 | Ni-2a-180K-dark - heating-xtal-1 | Ni-2a-200K-dark - heating-xtal-1 |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Moiety formula              | $\text{C}_{16}\text{H}_{15}\text{N}_3\text{Ni}_1\text{O}_3$ |                                  |                                  |                                  |                                  |                                  |
| Moiety formula mass, $M_r$/ a.u. | 356.00                          |                                  |                                  |                                  |                                  |                                  |
| Crystal system              | triclinic                       |                                  |                                  |                                  |                                  |                                  |
| Space group                 | $\bar{P}1$ (no. 2)              |                                  |                                  |                                  |                                  |                                  |
| $Z$                         | 2                               |                                  |                                  |                                  |                                  |                                  |
| $F_{000}$                   | 368                             |                                  |                                  |                                  |                                  |                                  |
| Crystal colour & shape      | orange plate                    |                                  |                                  |                                  |                                  |                                  |
| Crystal size / mm$^3$        | 0.05×0.15×0.19                  |                                  |                                  |                                  |                                  |                                  |
| $T / K$                     | 100                             | 120                             | 140                             | 160                             | 180                             | 200                             |
| $a / \text{Å}$              | 7.4023(7)                       | 7.4081(5)                       | 7.4242(5)                       | 7.4449(4)                       | 7.4848(3)                       | 7.4553(4)                       |
| $b / \text{Å}$              | 8.1523(7)                       | 8.1507(6)                       | 8.1555(6)                       | 8.1616(5)                       | 8.1532(4)                       | 8.1473(4)                       |
| $c / \text{Å}$              | 13.6139(12)                     | 13.6011(9)                      | 13.6058(9)                      | 13.6166(10)                     | 13.6235(6)                      | 13.6521(7)                      |
| $\alpha / ^\circ$           | 100.305(7)                      | 100.336(6)                      | 100.383(6)                      | 100.413(6)                      | 100.394(4)                      | 100.286(4)                      |
| $\beta / ^\circ$            | 101.078(8)                      | 101.060(6)                      | 101.096(5)                      | 101.156(5)                      | 101.263(3)                      | 101.447(5)                      |
| $\gamma / ^\circ$           | 102.856(8)                      | 102.871(6)                      | 102.858(6)                      | 102.845(6)                      | 102.848(3)                      | 102.865(5)                      |
| $V / \text{Å}^3$            | 764.64(13)                      | 764.27(10)                      | 766.41(10)                      | 769.47(9)                       | 769.10(6)                       | 770.51(7)                       |
| $d_{\text{calc}} / \text{g·cm}^{-3}$ | 1.5462                        | 1.5470                          | 1.5427                          | 1.5365                          | 1.5373                          | 1.5345                          |
| $\theta$ range              | $3.40^\circ - 77.52^\circ$      | $3.40^\circ - 76.21^\circ$     | $3.40^\circ - 75.95^\circ$     | $3.40^\circ - 75.75^\circ$     | $3.40^\circ - 76.08^\circ$     | $3.40^\circ - 76.00^\circ$     |
| Absorption coefficient, $\mu / \text{mm}^{-1}$ | 1.998                         | 1.999                           | 1.994                           | 1.986                           | 1.987                           | 1.983                           |
| No. of reflections collected / unique | 8471 / 3080                   | 8479 / 3089                     | 8603 / 3107                     | 8705 / 3115                     | 8808 / 3122                     | 8912 / 3130                     |
| $R_{\text{int}}$            | 6.38%                           | 5.97%                           | 5.53%                           | 5.25%                           | 3.84%                           | 3.20%                           |
| No. of reflections with $I > 3\sigma(I)$ | 2068                        | 2173                           | 2215                           | 2173                           | 2215                           | 2508                           |
| No. of parameters / restraints / constraints | 219 / 0 / 67                     | 219 / 0 / 67                     | 219 / 0 / 67                     | 219 / 0 / 67                     | 219 / 0 / 67                     | 209 / 0 / 60                     |
| $R[F] (I > 3\sigma(I))$     | 5.07%                           | 4.83%                           | 4.57%                           | 4.55%                           | 3.77%                           | 3.64%                           |
| $R[F]$ (all data)           | 8.09%                           | 7.36%                           | 7.17%                           | 6.83%                           | 5.21%                           | 4.80%                           |
| $\varphi_{\text{min/max}} / \text{e·Å}^{-3}$ | -0.47 / +0.65                 | -0.39 / +0.47                   | -0.34 / +0.43                   | -0.25 / +0.45                   | -0.25 / +0.45                   | -0.32 / +0.35                   |
| CCDC code                   | 2110815                         | 2110821                         | 2110813                         | 2110814                         | 2110816                         | 2110817                         |
Table 2S (continued). Selected X-ray data collection, processing and refinement parameters for all presented crystal structures.

| Moiety formula | Ni-2a-140K-dark-xtal-2 | Ni-2a-140K-irr-140K-xtal-2 | Ni-2a-160K-irr-140K-xtal-2 | Ni-2a-180K-irr-140K-xtal-2 | Ni-2a-200K-irr-140K-xtal-2 |
|----------------|------------------------|----------------------------|---------------------------|---------------------------|---------------------------|
| Moiety formula mass, $M_r$/ a.u. | 356.00                 |                            |                           |                           |                           |
| Crystal system | triclinic              |                            |                           |                           |                           |
| Space group | $P\bar{1}$ (no. 2)   |                            |                           |                           |                           |
| $Z$ | 2                      |                            |                           |                           |                           |
| $F_{000}$ | 368                    |                            |                           |                           |                           |
| Crystal colour & shape | orange plate          |                            |                           |                           |                           |
| Crystal size / mm$^3$ | 0.05×0.15×0.25 |                            |                           |                           |                           |
| $T$ / K | 140                    | 140                        | 160                       | 180                       | 200                       |
| $a$ / Å | 7.4121(4)              | 7.4646(9)                  | 7.4870(15)                | 7.426(4)                  | 7.4497(3)                 |
| $b$ / Å | 8.1490(4)              | 8.1753(6)                  | 8.1749(12)                | 8.166(3)                  | 8.1435(3)                 |
| $c$ / Å | 13.6104(6)             | 13.5119(9)                 | 13.5286(19)               | 13.623(8)                 | 13.6386(5)               |
| $\alpha$ / $^\circ$ | 100.221(4)            | 100.600(6)                 | 100.684(12)               | 100.88(4)                 | 100.279(3)               |
| $\beta$ / $^\circ$ | 101.157(4)            | 100.480(8)                 | 100.490(14)               | 101.52(5)                 | 101.386(4)               |
| $\gamma$ / $^\circ$ | 102.885(5)           | 102.812(8)                 | 102.696(15)               | 102.76(4)                 | 102.913(4)               |
| $V$ / Å$^3$ | 764.28(7)             | 768.69(13)                 | 772.0(2)                  | 765.7(7)                  | 768.87(6)                |
| $d_{calc}$ / g·cm$^{-3}$ | 1.5470               | 1.5381                     | 1.5314                    | 1.5441                    | 1.5377                    |
| $\theta$ range | 3.40$^\circ$ – 72.88$^\circ$ | 3.42$^\circ$ – 72.96$^\circ$ | 3.42$^\circ$ – 73.52$^\circ$ | 3.41$^\circ$ – 73.45$^\circ$ | 3.40$^\circ$ – 73.04$^\circ$ |
| Absorption coefficient, $\mu$ / mm$^{-1}$ | 1.999                | 1.988                      | 1.979                     | 1.995                     | 1.987                     |
| No. of reflections collected / unique | 11924/2996            | 11792/3017                 | 10837/3028                | 10339/3004                | 11560/3021                |
| $R_{int}$ | 4.33%                  | 6.12%                      | 7.62%                     | 14.12%                    | 4.50%                     |
| No. of reflections with $I > 3\sigma(I)$ | 2356                 | 2078                       | 1780                      | 1037                      | 2385                      |
| No. of parameters / restraints / constraints | 209 / 0 / 60           | 219 / 0 / 67               | 216 / 0 / 70              | 208 / 0 / 60              | 208 / 0 / 60              |
| $R[F]$ (I > 3$\sigma(I)$) | 3.37%                  | 6.52%                      | 8.77%                     | 13.05%                    | 3.79%                     |
| $R[F]$ (all data) | 4.79%                  | 9.45%                      | 13.89%                    | 24.35%                    | 5.05%                     |
| $\sigma_{min/\max}$ / e·Å$^{-3}$ | $-0.25 / +0.35$        | $-0.49 / +0.87$            | $-0.73 / +1.06$           | $-1.20 / +3.14$           | $-0.28 / +0.42$           |
| CCDC code | 2110822               | 2110824                    | 2110825                   | 2110823                   | 2110826                   |
Table 2S (continued). Selected X-ray data collection, processing and refinement parameters for all presented crystal structures.

| Data set | Ni-2b-290K-dark-cooling-xtal-1 | Ni-2b-240K-dark-cooling-xtal-1 | Ni-2b-200K-dark-cooling-xtal-1 | Ni-2b-180K-dark-cooling-xtal-1 | Ni-2b-160K-dark-cooling-xtal-1 | Ni-2b-RT-dark-xtal-2 |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|----------------------|
| Moiety formula | C_{19}H_{15}N_{3}Ni_{1}O_{3} | C_{19}H_{15}N_{3}Ni_{1}O_{3} | C_{19}H_{15}N_{3}Ni_{1}O_{3} | C_{19}H_{15}N_{3}Ni_{1}O_{3} | C_{19}H_{15}N_{3}Ni_{1}O_{3} | C_{19}H_{15}N_{3}Ni_{1}O_{3} |
| Moiety formula mass, $M_r$ / a.u. | 392.04 | 392.04 | 392.04 | 392.04 | 392.04 | 392.04 |
| Crystal system | monoclinic | triclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P 2_1/c$ (no. 14) | $P 1$ (no. 2) | $P 1$ (no. 2) | $P 2_1/c$ (no. 14) | $P 1$ (no. 2) | $P 2_1/c$ (no. 14) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 |
| $F_{000}$ | 808 | 808 | 808 | 808 | 808 | 808 |
| Crystal colour & shape | brown plate | brown plate | brown plate | brown plate | brown plate | brown plate |
| Crystal size / mm$^3$ | 1.88×0.13×0.11 | 1.88×0.13×0.11 | 1.88×0.13×0.11 | 0.08×0.11×0.13 | 0.08×0.11×0.13 | 0.08×0.11×0.13 |
| $T$ / K | 290 | 240 | 200 | 180 | 160 | 290 |
| $a$ / Å | 14.1514(7) | 14.1275(4) | 14.1166(3) | 14.1196(6) | 14.1181(4) | 14.1146(7) |
| $b$ / Å | 6.8027(3) | 6.7861(12) | 6.7699(8) | 6.7595(13) | 6.7551(10) | 6.7593(13) |
| $c$ / Å | 17.9707(6) | 17.9317(9) | 17.8897(8) | 17.8685(11) | 17.8553(10) | 17.8675(7) |
| $\alpha$ / $^\circ$ | 90 | 89.017(6) | 88.801(4) | 88.760(7) | 88.714(5) | 90 |
| $\beta$ / $^\circ$ | 103.885(4) | 103.987(5) | 104.046(4) | 104.018(6) | 104.113(5) | 103.816(4) |
| $\gamma$ / $^\circ$ | 90 | 93.019(6) | 93.747(4) | 93.966(7) | 94.140(5) | 90 |
| $V$ / Å$^3$ | 1679.45(13) | 1665.8(3) | 1655.0(2) | 1650.6(3) | 1646.5(3) | 1678.78(13) |
| $d_{calc}$ / g·cm$^{-3}$ | 1.884 | 1.899 | 1.912 | 1.917 | 1.921 | 1.884 |
| Absorption coefficient, $\mu$ / mm$^{-1}$ | 3.22$^\circ$ - 75.55$^\circ$ | 2.54$^\circ$ - 75.56$^\circ$ | 2.55$^\circ$ - 75.59$^\circ$ | 2.55$^\circ$ - 80.79$^\circ$ | 2.55$^\circ$ - 75.77$^\circ$ | 3.22$^\circ$ - 75.61$^\circ$ |
| No. of reflections collected / unique | 12943 / 3428 | 13035 / 6230 | 13044 / 6192 | 12983 / 6182 | 12887 / 6140 | 13530 / 3452 |
| $R_{int}$ | 3.76% | 6.07% | 6.27% | 8.93% | 6.44% | 2.72% |
| No. of reflections with $I > 3\sigma(I)$ / restraints / constraints | 2309 / 0 / 60 | 469 / 0 / 120 | 469 / 0 / 120 | 469 / 0 / 120 | 469 / 0 / 120 | 235 / 0 / 60 |
| $R[F](I > 3\sigma(I))$ | 5.13% | 9.61% | 8.22% | 11.07% | 9.36% | 4.36% |
| $R[F]$ (all data) | 7.21% | 14.44% | 12.10% | 16.53% | 13.94% | 6.54% |
| $\varphi_{max}$ / $\varphi_{min}$ / $e$·Å$^{-3}$ | -0.66 / +0.65 | -0.72 / +1.98 | -0.64 / +1.95 | -1.41 / +2.07 | -0.91 / +2.27 | -0.53 / +0.42 |
| CCDC code | 2110831 | 2110833 | 2110832 | 2110835 | 2110834 | 2110827 |
| Data set          | Ni-2b-160K-darkxtal-2 | Ni-2b-160K-irr-160K-xtal-2 | Ni-2b-240K-irr-160K-xtal-2 | Cu-2a      | Cu-2b      |
|------------------|-----------------------|----------------------------|---------------------------|------------|------------|
| Moiety formula   | C_{19}H_{15}N_3NiO_3  | C_{19}H_{15}N_3NiO_3       | C_{19}H_{15}N_3NiO_3      |            |            |
| Moiety formula mass, M_r / a.u. | 392.04 | 360.86 | 396.89 |            |            |
| Crystal system   | triclinic             | triclinic                  | triclinic                 |            |            |
| Space group      | P̅1 (no. 2)           | P̅1 (no. 2)                 | P̅1 (no. 2)                |            |            |
| Z                | 4                     | 2                          | 2                          |            |            |
| F_000            | 808                   | 370                        | 406                        |            |            |
| Crystal colour & shape | brown plate       | brown plate             | green plate              |            |            |
| Crystal size / mm³ | 0.08×0.11×0.13 | 0.05×0.19×0.22 | 0.04×0.11×0.20 |            |            |
| T / K            | 160                   | 160                        | 240                        | 100        | 100        |
| a / Å            | 14.1083(10)           | 14.1508(14)                | 14.1382(13)                | 8.435(2)   | 6.804(2)   |
| b / Å            | 6.7505(3)             | 6.7652(5)                  | 6.8015(8)                  | 9.513(2)   | 9.080(2)   |
| c / Å            | 17.8681(8)            | 17.8650(9)                 | 17.9478(8)                 | 10.739(2)  | 13.866(3)  |
| α / °            | 88.724(3)             | 90.025(5)                  | 89.744(7)                  | 69.07(3)   | 75.87(3)   |
| β / °            | 104.156(5)            | 103.718(6)                 | 103.931(6)                 | 69.65(3)   | 83.43(3)   |
| γ / °            | 94.061(4)             | 90.165(7)                  | 90.193(9)                  | 72.48(3)   | 84.76(3)   |
| V / Å³           | 1645.88(16)           | 1661.5(2)                  | 1675.1(3)                  | 739.0(3)   | 824.2(4)   |
| d_calc / g·cm⁻³ | 1.5821                | 1.5673                     | 1.5545                     | 1.6216     | 1.5992     |
| θ range          | 2.55° - 75.75°        | 2.55° - 75.59°             | 2.54° - 77.80°             | 4.58° - 75.56° | 3.30° - 75.76° |
| Absorption coefficient, μ / mm⁻¹ | 1.922 | 1.904 | 1.889 | 2.260 | 2.091 |
| No. of reflections collected / unique | 18886 / 6654 | 10519 / 5836 | 19389 / 6800 | 17061 / 3031 | 17819 / 3393 |
| R_int            | 6.15%                 | 3.62%                      | 8.49%                      | 4.31%      | 10.28%     |
| No. of reflections with I > 3σ(I) | 3505 | 3136 | 2935 | 2791 | 2818 |
| No. of parameters / restraints / constraints | 469 / 0 / 120 | 459 / 0 / 196 | 469 / 0 / 120 | 208 / 0 / 60 | 235 / 0 / 60 |
| R[F] (I > 3σ(I)) | 11.73%                | 10.90%                     | 6.89%                      | 3.33%      | 5.46%      |
| R[F] (all data)  | 17.23%                | 16.51%                     | 12.63%                     | 3.60%      | 6.43%      |
| ϕ_max / e·Å⁻³    | -1.15 / +3.36          | -1.22 / +1.66              | -0.82 / +1.16              | -0.38 / +0.48 | -0.78 / +0.98 |
| CCD code         | 2110828               | 2110829                    | 2110830                    | 2110808    | 2110809    |
Table 3S. Selected interactions engaging the nitro group adopting both the nitro and endo-nitrito binding modes in the Ni-2a crystal structure (Ni-2a-140K-irr-140K-xtal-2 data set).

| Motif | $E_{\text{int}}$ / kJ·mol$^{-1}$ | Selected interactions | Motif | $E_{\text{int}}$ / kJ·mol$^{-1}$ | Selected interactions |
|-------|-----------------|----------------------|-------|-----------------|----------------------|
| Ni01  | -60.5           | C1-H1⋯O1a            | Ni01  | -48.4           | C1-H1⋯O1b            |
|       |                 | C2-H2⋯O1a            |       |                 | C2-H2⋯O1b            |
| Ni02  | -24.3           | C7-H7⋯O2a            |       |                 | -                   |
| NiS1  | -44.7           | C14-H14⋯O1a          | NiS1  | -45.9           | C14-H14⋯O1b          |
|       |                 | C11(π)⋯C14(π)        |       |                 | C11(π)⋯C14(π)        |
| NiS2  | -126.0          | C4-H4⋯O1a            | NiS2  | -132.4          | C4-H4⋯O1b            |
|       |                 | C6-H6b⋯O1a           |       |                 | C6-H6b⋯O1b           |
|       |                 | C1(π)⋯C8(π)          |       |                 | C1(π)⋯C8(π)          |
| NiS2' | -142.1          | C6-H6a⋯O2a           | NiS2' | -128.1          | C6-H6a⋯O2b           |
|       |                 | C1(π)⋯C8(π)          |       |                 | C1(π)⋯C8(π)          |

Table 3S (continued). Selected interactions engaging the nitro group adopting both the nitro and endo-nitrito binding modes in the Ni-2a crystal structure (Ni-2a-140K-irr-140K-xtal-2 data set).

| Motif | $E_{\text{int}}$ / kJ·mol$^{-1}$ | Selected interactions | Motif | $E_{\text{int}}$ / kJ·mol$^{-1}$ | Selected interactions |
|-------|-----------------|----------------------|-------|-----------------|----------------------|
| Ni01  | -54.3           | C1-H1⋯O1a            | Ni01  | -48.4           | C1-H1⋯O1b            |
|       |                 | C2-H2⋯O1a            |       |                 | C2-H2⋯O1b            |
| Ni02  | -23.9           | C7-H7⋯O2a            |       |                 | -                   |
| NiS1  | -45.3           | C14-H14⋯O1a          | NiS1  | -45.3           | C14-H14⋯O1b          |
|       |                 | C11(π)⋯C14(π)        |       |                 | C11(π)⋯C14(π)        |
| NiS2  | -129.2          | C4-H4⋯O1a            | NiS2  | -129.2          | C4-H4⋯O1b            |
|       |                 | C6-H6b⋯O1a           |       |                 | C6-H6b⋯O1b           |
|       |                 | C1(π)⋯C8(π)          |       |                 | C1(π)⋯C8(π)          |
| NiS2' | -129.2          | C6-H6a⋯O2a           | NiS2' | -128.1          | C6-H6a⋯O2b           |
|       |                 | C1(π)⋯C8(π)          |       |                 | C1(π)⋯C8(π)          |
Table 4S. Selected intermolecular interactions for both nitro and endo-nitrito isomers for the Ni-2b complex (Ni-2b-160K-irr-160K-xtal-2 data set).

| Motif  | $E_{int}$ / kJ·mol$^{-1}$ | Selected interactions | Motif  | $E_{int}$ / kJ·mol$^{-1}$ | Selected interactions |
|--------|--------------------------|-----------------------|--------|--------------------------|-----------------------|
| Ni$_{01}$ | -39.6                    | C2-H2⋯O4             | Ni$_{01}$ | -37.0                    | C2-H2⋯O4             |
|        |                          | C2'-H2'⋯O2           |        |                          | C2'-H2'⋯O2           |
| Ni$_{03}$ | -44.6                    | C13-H13⋯O3'          | Ni$_{03}$ | -43.5                    | C13-H13⋯O3'          |
|        |                          | C15-H15⋯O4           |        |                          | C15-H15⋯O4           |
| Ni$_{52}$ | -95.1                    | C5(π)⋯C6(π)          | Ni$_{52}$ | -93.1                    | C5(π)⋯C6(π)          |
| Ni$_{52'}$ | -94.6                   | C5'(π)⋯C6'(π)        | Ni$_{52'}$ | -91.0                    | C5'(π)⋯C6'(π)        |

Table 4S (continued). Selected intermolecular interactions for both nitro and endo-nitrito isomers for the Ni-2b complex (Ni-2b-160K-irr-160K-xtal-2 data set).

| Motif  | $E_{int}$ / kJ·mol$^{-1}$ | Selected interactions | Motif  | $E_{int}$ / kJ·mol$^{-1}$ | Selected interactions |
|--------|--------------------------|-----------------------|--------|--------------------------|-----------------------|
| Ni$_{01}$ | -38.2                    | C2-H2⋯O4             | Ni$_{01}$ | -38.1                    | C2-H2⋯O4             |
|        |                          | C2'-H2'⋯O2           |        |                          | C2'-H2'⋯O2           |
| Ni$_{03}$ | -44.3                    | C13-H13⋯O3'          | Ni$_{03}$ | -43.8                    | C13-H13⋯O3'          |
|        |                          | C15-H15⋯O4           |        |                          | C15-H15⋯O4           |
| Ni$_{52}$ | -94.1                    | C5(π)⋯C6(π)          | Ni$_{52}$ | -94.1                    | C5(π)⋯C6(π)          |
| Ni$_{52'}$ | -92.8                   | C5'(π)⋯C6'(π)        | Ni$_{52'}$ | -87.7                    | C5'(π)⋯C6'(π)        |

Table 5S. Selected intermolecular interactions for the Ni-2b complex at RT (i.e. before phase transition; Ni-2b-RT-dark-xtal-2 data set).

| Motif  | $E_{int}$ / kJ·mol$^{-1}$ | Selected interactions |
|--------|--------------------------|-----------------------|
| Ni$_{01}$ | -41.3                    | C2-H2⋯O1             |
| Ni$_{03}$ | -43.1                    | C13-H13⋯O1           |
|        |                          | C15-H15⋯O3           |
| Ni$_{52}$ | -95.9                    | C5(π)⋯C6(π)          |

Table 6S. Percentage contribution of selected interatomic contacts to the generated Hirshfeld surface.

| Compound | Temperature / K | O-H | C-H | N-H | H-O | H-C | H-N | C-C | H-H |
|----------|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Ni-2a$^a$ | 100            | 11.3| 7.3 | 2.5 | 10.1| 5.6 | 2.5 | 5.4 | 46.3|
| Cu-2a    | 100            | 10.0| 14.1| 6.7 | 8.1 | 11.9| 5.3 | 1.9 | 37.6|
| Ni-2b (high $T$) $^b$ | 290            | 13.5| 9.5 | 0.3 | 11.5| 8.1 | 0.2 | 4.9 | 41.7|
| Ni-2b (mol. A) (low $T$) $^c$ | 160            | 13.3| 9.4 | 0.4 | 11.2| 8.0 | 0.3 | 5.2 | 41.4|
| Ni-2b (mol. B) (low $T$) $^c$ | 160            | 13.4| 9.6 | 0.5 | 11.4| 8.0 | 0.5 | 5.4 | 41.0|
| Cu-2b    | 100            | 10.3| 8.2 | 4.3 | 8.2 | 6.5 | 3.9 | 7.0 | 41.7|

$^a$ Ni-2a-100K-dark-cooling-xtal-1 data set. $^b$ Ni-2b-290K-dark-cooling-xtal-1 data set. $^c$ Ni-2b-160K-dark-cooling-xtal-1.
Table 7S. Hirshfeld surface fingerprint plots generated for the Ni-2b complex; all and selected X⋯H contacts (data sets the same as in Table 6S).

| Molecule                      | all⋯all | O⋯H   | N⋯H   | C⋯H   |
|-------------------------------|---------|-------|-------|-------|
| Ni-2b (high $T$)              | ![Plot](image1) | ![Plot](image2) | ![Plot](image3) | ![Plot](image4) |
| Ni-2b (mol. A) (low $T$)      | ![Plot](image5) | ![Plot](image6) | ![Plot](image7) | ![Plot](image8) |
| Ni-2b (mol. B) (low $T$)      | ![Plot](image9) | ![Plot](image10) | ![Plot](image11) | ![Plot](image12) |
Figure 6S. Theoretical IR spectra computed at the DFT(B3LYP)/6-311++G** level of theory for the analysed Ni-2a linkage isomers plotted using the GAUSSSUM program (full width at half maximum set to 10).
Figure 7S. Theoretical IR spectrum computed at the DFT(B3LYP)/6-311++G** level of theory for the analysed Ni-2b linkage isomers plotted using the GAUSSSUM program (full width at half maximum set to 10).
**Table 8S.** Key vibrational modes characteristic for the examined linkage isomers of the nitro group based on the theoretical data. Visualization of selected modes is attached in the form of GIF files.

| Mode       | Ni-2a (nitro) | Ni-2b (nitro) |
|------------|---------------|---------------|
| $\omega$(NO$_2$) | 581.02        | 566.70        |
| $\delta$(NO$_2$) | 835.94        | 838.41        |
| $\nu$(NO$_2$) | 1391.62       | 1391.96       |
| $\nu_\omega$(NO$_2$) | 1493.96       | 1495.36       |
| Ni-2a (endo-nitrito) | Ni-2b (endo-nitrito) |
| $\delta$(ONO) | 845.05        | 845.04        |
| $\nu$(N–O) | 1094.74       | 1080.76       |
| $\nu$(N=O) | 1507.30       | 1513.02       |
| Cu-2a (κ-nitrito) | Cu-2b (κ-nitrito) |
| $\omega$(ONO) | 347.65        | 350.89        |
| $\delta$(ONO) | 855.42        | 856.02        |
| $\nu$(N–O) | 1154.95       | 1150.47       |
| $\nu$(N=O) | 1454.98       | 1454.97       |
| Cu-2a (nitro) | Cu-2b (nitro) |
| $\delta$(NO$_2$) | 820.15        | 820.36        |
| $\nu$(NO$_2$) | 1366.82       | 1369.82       |
| $\nu_\omega$(NO$_2$) | 1481.48       | 1487.37       |
### Table 9S

IR spectral features characteristic for selected binding modes of the NO$_2$ group assigned based on the literature-reports of nickel(II) and copper(II) compounds. Note no information about ω(NO$_2$) were given.

| Compound | Isomer | $\nu_3$(NO$_2$) | $\nu_4$(NO$_2$) | $\rho_w$(ONO) | $\nu$(N=O) | $\nu$(N-O) |
|----------|--------|-----------------|-----------------|---------------|------------|------------|
| [Ni(py)$_4$(ONO)$_2$] | ONO | 1393 | 1114 | 825 | - | - |
| NiL$_2$(NO$_2$)$_2$L=4-(2-aminoethyl)morpholine | NO$_2$ | 1333 | 1310 | 808 | - | - |
| [NiL$_2$(ONOO)$_2$L=4-(2-aminoethyl)morpholine] | ONO | 1365, 1331 | 1318, 1304 | 828 | - | - |
| Ni[1-(2-aminoethyl)piperidine]$_2$(NO$_2$)$_2$ | NO$_2$ | 1360 | 1285 | 815 | - | - |
| Ni[1-(2-aminoethyl)piperidine]$_2$(ONO)$_2$ | ONO | 1385 | 1138 | 820 | - | - |
| Ni(C$_8$H$_{18}$N$_4$O$_2$)(NO$_2$)$_2$·H$_2$O | NO$_2$ | 1395 | 1274 | 814 | - | - |
| Ni(C$_8$H$_{18}$N$_4$O$_2$)(ONO)$_2$·H$_2$O | ONO | 1270 | 1269 | 798 | 1412 | 1208 |
| [Cu(ONO)(tpa)]PF$_6$ tpa= tris[[2-pyridyl]methyl]amine | ONO | - | - | - | 1426 | 1082 |
| [Cu(NO$_2$)(tpa)]PF$_6$ tpa = tris[(2-pyridyl)methyl]amine | NO$_2$ | 1387 | 1333 | - | - | - |
| (Pr-TPM)Cu(NO$_2$) TPM= tris(3,5-diisopropyl-1-pyrazolyl)methane | NO$_2$ | 1311 | 1282 | 814 | - | - |
| (Et-TPM)Cu(NO$_2$) TPM= tris(3,5-diethyl-1-pyrazolyl)methane | NO$_2$ | 1310 | 1283 | 813 | - | - |
| (Me-TPM)Cu(NO$_2$) TPM= tris(3,5-dimethyl-1-pyrazolyl)methane | NO$_2$ | 1314 | 1280 | 822 | - | - |
| (Pr-TACN)Cu(NO$_2$) TAC= 1,4,7-triisopropyl-1,4,7-triazacyclononane | NO$_2$ | 1306 | 1268 | 809 | - | - |

**References**

[1] D. M. L. Goodgame, L. M. Venanzi, *J. Chem. Soc.* 1963, 616-627.

[2] T. Chattopadhyay, M. Ghosh, A. Majee, M. Nethaji, D. Das, *Polyhedron* 2005, 24, 1677-1681.

[3] D. Das, I. R. Laskar, A. Ghosh, A. Mondal, K-I. Okamoto, N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.* 1998, 3987-3990.

[4] M. S. Chao, H. H. Lu, M. L. Tsai, C. M. Lin, M. P. Wu, *Inorg. Chem. Comm.* 2012, 24, 254–258.

[5] K. Nobutoshi, N. Hirotaka, K. Yoshinori, A. Gin-ya, S. Masatatsu, U. Akira, T. Koji, *Bull. Chem. Soc. Jpn* 1995, 68, 581-589.

[6] M. Kujime, C. Izumi, M. Tomura, M. Hada, H. Fujii, *J. Am. Chem. Soc.* 2008, 130, 6088-6098.
Figure 8S. IR absorption spectra for the Ni-2a complex in the solid state recorded while cooling from 295 K to 10 K. As indicated in the legend the black solid line denotes the 295 K measurement, while red lines present spectra recorded after sample cooling down to 10 K.
Figure 9S. IR absorption spectra for the Ni-2b complex in the solid state recorded while cooling from 295 K to 10 K. As indicted in the legend the black solid line denotes the 295 K measurement, while red lines present spectra recorded after sample cooling down to 10 K.
Figure 10S. IR absorption spectra for the (a) Ni-2a and (b) Ni-2b complexes in the solid state recorded at 10 K after irradiation with the LED light (405–735 nm).
**Figure 11S.** Multi-temperature IR spectrum recorded after irradiation at 530 nm at 10 K and at selected temperature points during heating of the Ni-2a sample; intensity changes of the 567 cm\(^{-1}\) peak are shown.
Figure 12S. Expansion of the 400–1000 cm\(^{-1}\) region of the Ni-2a complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to the computational results (Table 8S): decrease of the bands at 569/578 cm\(^{-1}\) and 822/870 cm\(^{-1}\) corresponding to the \(\omega(\text{NO}_2)\) and \(\delta(\text{NO}_2)\) modes of the nitro configuration. Identification of genuinely new bands due to the endo-nitrito form is not obvious, as many bands might simply shift as a consequence of the NO\(_2\) isomerisation, \textit{e.g.} from 518 cm\(^{-1}\) to 529 cm\(^{-1}\).
Figure 13S. Expansion of the 1000−1550 cm$^{-1}$ region of the Ni-2a complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to the computational results (Table 8S): decrease of the bands at 1342 and 1378 cm$^{-1}$ corresponding to the $v_s$(NO$_2$) and $v_{as}$(NO$_2$) modes of the nitro configuration. Appearance of a new band at 1104 cm$^{-1}$ corresponding to the $v$(N−O) mode of the endo-nitrito configuration.
Figure 14S. Expansion of the 400–1000 cm$^{-1}$ region of the IR for Ni-2b complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to computational results (Table 8S): decrease of the bands at 553/597 cm$^{-1}$ and 824 cm$^{-1}$ corresponding to the $\omega$(NO$_2$) and $\delta$(NO$_2$) modes of the nitro configuration. Identification of genuinely new bands due to the endo-nitrito form is not obvious, as many bands might simply shift as a consequence of the NO$_2$ isomerisation, e.g. from 771 cm$^{-1}$ to 778 cm$^{-1}$. 
Figure 15S. Expansion of the 1000–1550 cm\(^{-1}\) region of the Ni-2b complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum.

Observations with respect to the computational results (Table 8S): decrease of the bands at 1333 and 1384 cm\(^{-1}\) corresponding to the \(\nu_s(\text{NO}_2)\) and \(\nu_{as}(\text{NO}_2)\) modes of the nitro configuration. Appearance of a new band at 1102 cm\(^{-1}\) corresponding to the \(\nu(\text{N–O})\) mode of the endo-nitrito configuration.
Figure 16S. Expansion of the 400–1000 cm$^{-1}$ region of the Cu-2a complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum.

Observations with respect to the computational results (Table 8S): decrease of the bands at 837 and 854 cm$^{-1}$ corresponding to the $\delta$(ONO) mode of the $\kappa$-nitrito configuration and appearance of a new band at 820 cm$^{-1}$ corresponding to the $\delta$(NO$_2$) mode of the nitro configuration. The other observable changes correspond to shifts induced by the ONO isomerisation on the other ligand groups.
Figure 17S. Expansion of the 1000–1550 cm$^{-1}$ region of the Cu-2a complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to the computational results (Table 8S): decrease of the bands at 1118 and 1402 cm$^{-1}$ corresponding to the $\nu$(N-O) and $\nu$(N=O) mode of the $\kappa$-nitrito configuration, respectively, and appearance of a new band at 1082 cm$^{-1}$ which might correspond to the $\nu$(N-O) mode of an endo-nitrito configuration, for which also the increase around 1430 cm$^{-1}$ could be a signature ($\nu$(N=O)).
**Figure 18S.** Expansion of the 400–1000 cm$^{-1}$ region of the Cu-2b complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to the computational results (Table 8S): decrease of the band at 837 cm$^{-1}$ corresponding to the $\delta$(ONO) mode of the $\kappa$-nitrito configuration and appearance of a new band at 814 cm$^{-1}$ corresponding to the $\delta$(NO$_2$) mode of the nitro configuration.
Figure 19S. Expansion of the 1000–1550 cm\(^{-1}\) region of the Cu-2b complex IR absorption spectra. Black solid line denotes the ground state spectrum, red line presents the spectrum collected after 10 min of LED irradiation, while blue line shows the difference spectrum. Observations with respect to the computational results (Table 8S): decrease of the band at 1134 cm\(^{-1}\) corresponding to the \(\nu\)(N–O) mode of the \(\kappa\)-nitrito configuration and appearance of a new band at 1363 cm\(^{-1}\) corresponding to the \(\nu_s\)(N–O) mode of the nitro configuration. The new band at 1080 cm\(^{-1}\) might correspond to the \(\nu\)(N–O) mode of an endo-nitrito configuration.
Figure 20S. Solid-state UV-Vis spectra collected for all studied samples at ambient conditions.

Table 10S. Energy differences ($\Delta E_{rel}$) between the ground-state $\kappa$-nitrito and metastable nitro linkage isomers computed based on the optimized isolated-molecule geometries. Computations were performed at the DFT(B3LYP)/6-311++G** level of theory.

| Complex | Form          | Isolated mol. | $\Delta E_{rel}$ / kJ·mol⁻¹ |
|---------|---------------|---------------|-----------------------------|
| Cu-2a   | $\kappa$-nitrito | 0.0           |                              |
|         | nitro         |               | +12.6                       |
| Cu-2b   | $\kappa$-nitrito | 0.0           |                              |
|         | nitro         |               | +7.8                        |