SUPPORTING INFORMATION

Synthesis and crystallization of $[Co(NH_3)_5NO_2]_2I_3Cl$

0.475 g of $[Co(NH_3)_5NO_2]Cl_2$ were added to 17 ml of distilled water, the mixture was stirred and heated to 50 °C until all $[Co(NH_3)_5NO_2]Cl_2$ was dissolved. 1.692 g of NH_4I was then added and the mixture was stirred without heating. After approximately 30 minutes of stirring the solution was cooled to room temperature and placed into the refrigerator and kept overnight at 4 °C. The next day dark red octahedral crystals of approximately 0.5 mm × 0.3 mm × 0.3 mm were observed which were later confirmed as $[Co(NH_3)_5NO_2]_2I_3Cl$.

Table S1. Experimental details

For all structures: $2(CoH_{15}N_6O_2)\cdot 3(I)\cdot Cl$, M_r = 796.37, triclinic, *P*-1, *Z* = 2. Experiments were carried out at 293 K with Mo *K*a radiation using an Esperanto-CrysAlisPro-abstract goniometer imported esperanto images. Absorption was corrected for by multi-scan methods, *CrysAlis PRO* 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. H-atom parameters were constrained. Computer programs: *CrysAlis PRO* 1.171.42.49 (Rigaku OD, 2022), *SHELXS2013*/1 (Sheldrick, 2015), *SHELXL2019*/2 (Sheldrick, 2019).

	$[Co(NH_3)_5NO_2]_2I_3Cl$	$[Co(NH_3)_5NO_2]_{1,38}[Co(NH_3)_5ONO]_{0,62}I_3Cl$
Crystal data		
a, *b*, *c* (Å)	7.1840 (3), 12.5765 (4), 12.7925 (4)	7.1863 (6), 12.5930 (11), 12.7172 (8)
a, b, g (°)	72.667 (3), 88.833 (3), 82.125 (3)	73.565 (7), 88.489 (6), 82.365 (7)
V (Å^3)	1092.64 (6)	1093.98 (16)
m (mm^{-1})	5.91	5.90
Crystal size (mm)	0.3 × 0.25 × 0.25	0.3 × 0.25 × 0.25
Data collection		
T_{min}, T_{max}	0.378, 1.000	0.369, 1.000
No. of measured, independent and observed reflections	9443, 4424, 3761 {$I > 2\sigma(I)$}	9215, 4440, 3415 {$I > 2\sigma(I)$}
R_{int}	0.021	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.627
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.027, 0.071, 1.11	0.042, 0.104, 1.03
No. of reflections	4424	4440
No. of parameters	209	219
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.94, -0.62	1.19, -0.89

Table S2. Deformation tensor coefficients multiplied by 10^6. For more information on coefficients see R. S. Bubnova *et al.*, 2013.

α_{11}	268.0439(0)
α_{22}	12118.48(0)
α_{33}	-8174.515(0)
μ_{a1}	20.6
μ_{b2}	51.7
μ_{c3}	28.2
α_a	848.5079(0)
α_b	1502.689(0)
α_c	-3714.787(0)
α_α	12694.39(0)
α_β	-4063.928(0)
α_γ	1547.156(0)
α_V	4212.009(0)

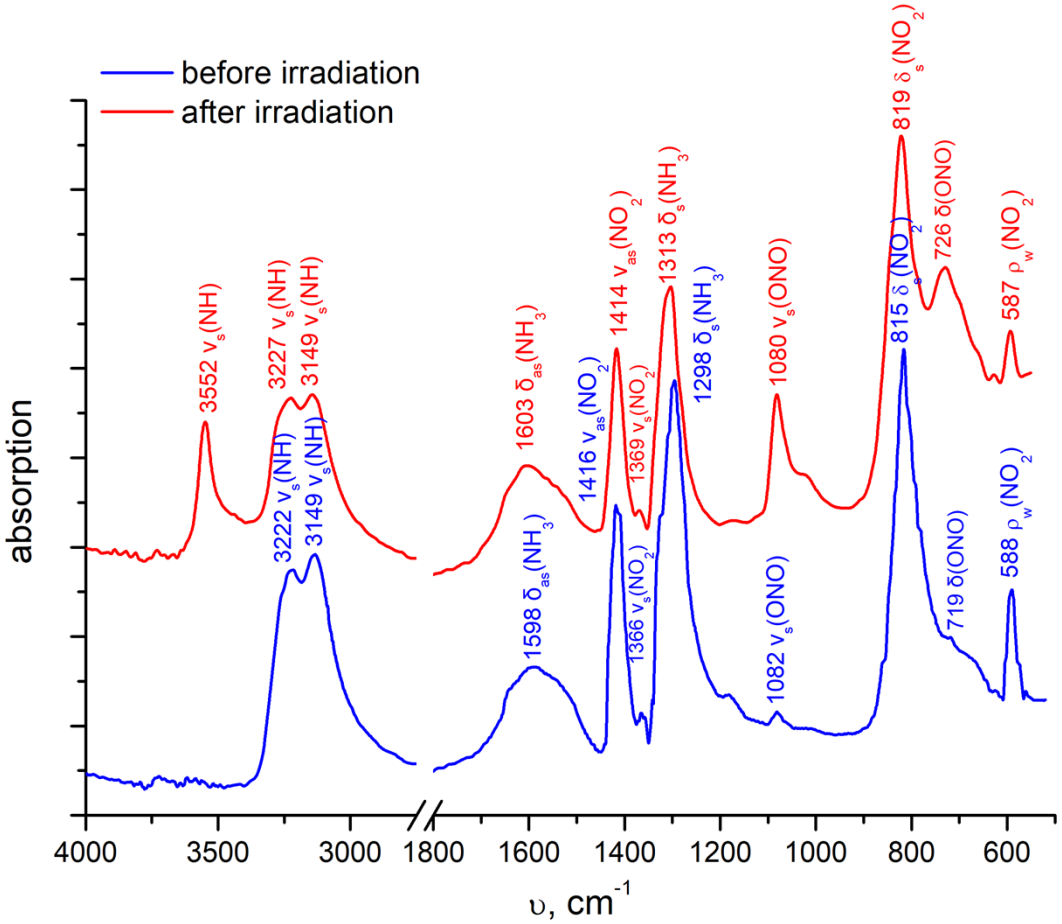

Figure S1. IR spectra of $[Co(NH_3)_5NO_2]_2I_3Cl$ before and after irradiation.

Table S3. Intermolecular contacts with oxygen atoms in CP2 for nitro- and nitrito-forms.

Intermolecular contacts in nitro-form (N-O distance, Å / N-H···O angle, ˚)			
N1-H1a···O3$^{1-x,1-y,1-z}$	N8-H8a···O3$^{1-x,1-y,1-z}$	N12-H12c···O3$^{1-x,1-y,1-z}$	N4-H4c···O4$^{1-x,2-y,-z}$
3.206(6) / 148.9	2.972(6) / 105.8	2.962(5) / 112.9	3.131(8) / 121.7
Intermolecular contacts in nitrito-form (N-O distance, Å / N-H···O angle, ˚)			
N1-H1a···O3$^{1-x,1-y,1-z}$	N8-H8a···O3$^{1-x,1-y,1-z}$	N12-H12c···O3$^{1-x,1-y,1-z}$	N4-H4c···O4$^{1-x,2-y,-z}$
3.267(10) / 142.0	2.916(11) / 117.2	2.943(9) / 121.5	3.143(7) / 123.8