Difference Hirshfeld fingerprint plots: A tool for studying polymorphs

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Supplementary Information

Synthesis and structure determination of $[Ni(L\text{-}NO_2)_2(dmso)_2]$

Synthesis

$Ni(NO_3)_2.6H_2O$ (0.0321 g, 0.11 mmol) was dissolved in ethyl acetate (10 mL) with dibutylphosphate (40 μL, 0.20 mmol). The yellow-green solution was examined using UV-Vis spectroscopy. Ketoxime **L**H (0.7452 g, 4.5 mmol) was dissolved in ethyl acetate (25 mL). The ketoxime solution 2.5 mL 0.18 M 0.45 mmol) was added to the metal/acid solution and mixed and the resulting green solution was re-examined via UV-Vis spectroscopy. After 24 hours the solution had darkened to dark yellow and a green jelly-like precipitate had formed. The precipitate was isolated and was found to be insoluble in dichloromethane, methanol, water, chloroform, acetone and ethyl acetate. The green precipitate was eventually dissolved in DMSO to give a yellow solution which was left to sit for several days and afforded red diamond shaped crystals.

Crystallography

The crystal data for $[Ni(\mathbf{L}\text{-}NO_2)_2(dmso)_2]$ are summarized in Table S1 with the structure depicted in Fig. S1 where ellipsoids have been drawn at the 50% probability level. Hydrogen bonding geometries are given in Table S2. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer using Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97 [1]. The hydroxyl hydrogen atom was clearly observed in later difference maps and was refined without restraints. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model. The isotropic displacement parameters were based on the equivalent parameter of the parent atom. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Results

The results of the structure determination were consistent with the formulation [Ni(L-NO_2)$_2$(dmso)$_2$]. The ketoxime ligand H**L** is presumed to have been nitrated as a result of strong heating in DMSO in the presence of nickel nitrate, converting the ligand to 2-hydroxy-5-methyl-3-nitroacetophenoneoxime (H**L**-NO_2). The molecule is situated on a crystallographic inversion centre. The oxime hydroxyl hydrogen atom is involved in bifurcated hydrogen bonds to the coordinated phenolic oxygen atom and to one of the oxygen atoms of the nitro group of the other ligand.

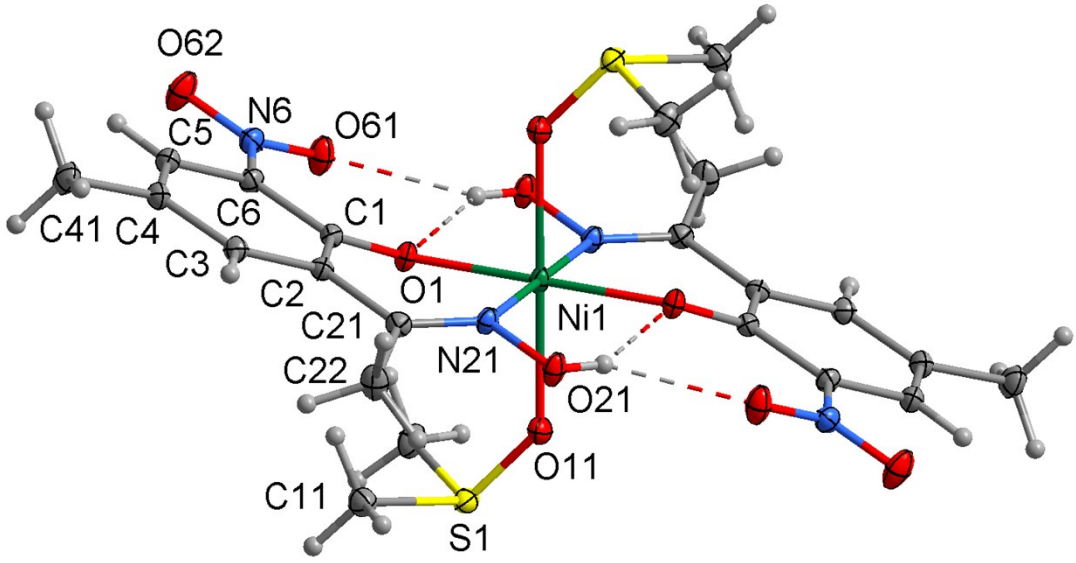

Fig. S1 Structure of the molecule of [Ni(**L**-NO_2)$_2$(dmso)$_2$] showing the numbering scheme and the intramolecular hydrogen bonding.

Table S1. Crystal data and structure refinement for [Ni(**L**-NO_2)$_2$(dmso)$_2$] CCDC = 1526949.

Empirical formula	$C_{22}H_{30}N_4NiO_{10}S_2$
Formula weight	633.33
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.8252(10) Å
	b = 7.7396(3) Å
	c = 15.3660(6) Å
	β= 95.439(5)°
Volume	1281.61(14) Å^3
Z	2
Density (calculated)	1.641 Mg/m^3
Absorption coefficient	0.985 mm^{-1}
F(000)	660
Crystal size	0.37 x 0.25 x 0.18 mm^3
θ range for data collection	2.95 to 34.55°.
Index ranges	-16<=h<=15, -12<=k<=11, -23<=l<=23
Reflections collected	16842
Independent reflections	5188 [R(int) = 0.0263]
Completeness to θ = 33.50°	99.7 %
Absorption correction	Analytical
Max. and min. transmission	0.890 and 0.809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5188 / 0 / 186
Goodness-of-fit on F^2	1.062
Final R indices [I>2σ(I)]	R1 = 0.0323, wR2 = 0.0827
R indices (all data)	R1 = 0.0380, wR2 = 0.0870
Largest diff. peak and hole	0.538 and -0.346 e.Å^{-3}

Table S2. Hydrogen bonds for mojvj9 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(21)-H(21)...O(1) [a]	0.78(2)	2.03(2)	2.7184(12)	147(2)
O(21)-H(21)...O(61) [a]	0.78(2)	2.22(2)	2.8438(13)	137(2)

Symmetry transformations used to generate equivalent atoms:

[a] 1-x,1-y,1-z

References

1 G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122.