

data_WO3-bpy-4Na

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_audit_creation_method          SHELXL-97
_chemical_name_systematic
;
?
;
_chemical_name_common           ?
_chemical_melting_point         ?
_chemical_formula_moiety        'C10 H8 N2 Na0.26 O4 W2'
_chemical_formula_sum            'C10 H8 N2 Na0.26 O4 W2'
_chemical_formula_weight        625.84
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```
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  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
  _atom_type_scatter_source
```

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C C 0.0181 0.0091 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
H H 0.0000 0.0000 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
N N 0.0311 0.0180 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
O O 0.0492 0.0322 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
W W -5.4734 5.5774 'International Tables Vol C Tables 4.2.6.8 and
6.1.1.4'
Na Na 0.1353 0.1239 'International Tables Vol C Tables 4.2.6.8 and
6.1.1.4'
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```
_symmetry_cell_setting          'Orthorhombic'
_symmetry_space_group_name_H-M  'P c a b'
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  '-x, -y+1/2, z+1/2'
  'x+1/2, -y, -z+1/2'
  '-x+1/2, y+1/2, -z'
  '-x, -y, -z'
  'x, y-1/2, -z-1/2'
  '-x-1/2, y, z-1/2'
  'x-1/2, -y-1/2, z'
```

```
_cell_length_a                  7.48501(14)
_cell_length_b                  7.40943(15)
_cell_length_c                  22.6257(4)
_cell_angle_alpha               90.00
_cell_angle_beta                90.00
_cell_angle_gamma               90.00
_cell_volume                    1254.81(4)
_cell_formula_units_Z           4
_cell_measurement_temperature   293(2)
_cell_measurement_reflns_used   8286
_cell_measurement_theta_min     14.2
_cell_measurement_theta_max     144.1
```

```
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_exptl_crystal_size_min        0.01
_exptl_crystal_density_meas    ?
_exptl_crystal_density_diffn   3.312
_exptl_crystal_density_method  'not measured'
_exptl_crystal_F_000           1123
_exptl_absorpt_coefficient_mu   33.777
_exptl_absorpt_correction_type  empirical
_exptl_absorpt_correction_T_min 0.1313
_exptl_absorpt_correction_T_max 1.0000
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;
data scaling includes absorption [ABSCOR, Higashi (1995)]
_exptl_special_details
;
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_diffn_radiation_wavelength     1.54178
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_diffn_radiation_monochromator  'confocal optics'
_diffn_measurement_device_type   'Rigaku Spider'
_diffn_measurement_device_details 'cureved image plate detector'
_diffn_measurement_method       \w-scans
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_diffn_reflns_av_sigmaI/netI    0.0972
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_diffn_reflns_limit_k_min       -9
_diffn_reflns_limit_k_max       6
_diffn_reflns_limit_l_min       -26
_diffn_reflns_limit_l_max       26
_diffn_reflns_theta_min         7.09
_diffn_reflns_theta_max         72.03
_reflns_number_total            1192
_reflns_number_gt               1018
_reflns_threshold_expression     >2sigma(I)

_computing_data_collection      'Crystal Clear (Rigaku, 2005)'
_computing_cell_refinement      'FS Process (Rigaku, 1998)'
_computing_data_reduction       'FS Process (Rigaku, 1998)'
_computing_structure_solution   'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics   'Mercury (Macrae et. al., 2006) and POV-RAY (Cason, 2003)'
_computing_publication_material 'SHELXL-97 (Sheldrick, 2008)'

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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Despite poor merging statistics for orthorhombic mmm symmetry and a number (19) of reflections that merged very poorly, the final values for R_1 (observed data) and wR_2 are satisfactory and comparable to other data sets with and without sodium implantation.

There is clear evidence of substantial disorder on the equatorial oxygen atoms of the W-O layer. This disorder appears also to extend, but to a lesser extent to the W atoms. Disorder of the W atoms has not been modelled. The pyridyl ring is well ordered. Despite the small, although highly significant, difference in the a and b cell lengths, there is no evidence for significant twinning.

A small number (16) of reflections with exceptionally poor agreement between F_{calc} and F_{obs} were eliminated from refinement, possibly because the small crystal was mounted against a 0.15 mm glass fibre, but also because of instabilities in the low temperature device.

After sodium implantation (4% w/w), crystal quality was noticeably deteriorated and more highly mosaic. The substantial number (22) of violations of systematic absences for space group $Pcab$ (non-standard setting of $Pbca$) is attributed to partial overlap of reflections.

A sodium ion is present in low occupancy (0.125), in part because of disorder across a centre of inversion. It sits just off the axial W-O3 axis in a small cavity bounded by the O3 and the 4,4'-bipyridyl groups.

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_refine_ls_weighting_scheme       calc
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'calc w=1/[\s^2^(Fo^2^)+(0.0654P)^2+1.8147P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      SHELXL
_refine_ls_extinction_coef        0.00011(5)
_refine_ls_extinction_expression
'Fc^*=kFc[1+0.001xFc^2^l^3^/sin(2\q)]^-1/4^'
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_refine_ls_number_parameters      115
_refine_ls_number_restraints      84
_refine_ls_R_factor_all           0.0607
_refine_ls_R_factor_gt            0.0531
_refine_ls_wR_factor_ref          0.1308
_refine_ls_wR_factor_gt           0.1221
_refine_ls_goodness_of_fit_ref    1.053
_refine_ls_restrained_S_all       1.023
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loop_

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_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group

O3 O 1.0484(7) 0.0110(7) 0.3383(4) 0.0174(13) Uani 1 1 d U . .
Na1 Na 0.031(12) 0.015(9) 0.469(6) 0.13(3) Uiso 0.13 1 d P . .
C6 C 0.9211(11) 0.1234(13) 0.1272(3) 0.0297(13) Uani 1 1 d U . .
H6 H 0.8516 0.2024 0.1493 0.036 Uiso 1 1 calc R A 2
W1 W 1.04605(6) 0.02026(7) 0.263542(15) 0.0158(3) Uani 1 1 d U . .
O1A O 0.786(2) 0.038(3) 0.2523(7) 0.018(3) Uani 0.52(2) 1 d PU . 1
O2A O 1.076(3) 0.2601(19) 0.2508(5) 0.019(3) Uani 0.52(2) 1 d PU . 1
O2B O 1.005(4) 0.259(2) 0.2522(5) 0.019(3) Uani 0.48(2) 1 d PU . 2
O1B O 0.789(2) -0.037(3) 0.2532(7) 0.016(3) Uani 0.48(2) 1 d PU . 2
N1 N 1.0361(11) 0.0157(10) 0.1551(5) 0.0299(14) Uani 1 1 d U . 2
C1 C 0.9021(10) 0.1210(13) 0.0668(3) 0.0298(13) Uani 1 1 d U . 2
H1 H 0.8196 0.1972 0.0488 0.036 Uiso 1 1 calc R . 2
C2 C 1.1356(11) -0.0975(12) 0.1242(3) 0.0292(13) Uani 1 1 d U . 2
H2 H 1.2145 -0.1729 0.1442 0.035 Uiso 1 1 calc R . 2
C3 C 1.1265(10) -0.1076(12) 0.0640(3) 0.0298(13) Uani 1 1 d U . 2
H3 H 1.1996 -0.1883 0.0439 0.036 Uiso 1 1 calc R . 2
C4 C 1.007(2) 0.0038(13) 0.0318(5) 0.0297(14) Uani 1 1 d U . 2

loop_

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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12

O3 0.017(2) 0.014(2) 0.022(2) -0.0009(17) -0.0007(18) 0.0021(15)
C6 0.031(3) 0.028(3) 0.030(3) 0.001(2) -0.003(2) 0.007(2)
W1 0.0173(4) 0.0125(4) 0.0175(4) -0.00012(12) -0.00049(12) 0.00013(14)
O1A 0.014(4) 0.017(5) 0.022(3) 0.000(4) 0.001(3) 0.001(4)
O2A 0.017(5) 0.017(4) 0.022(3) 0.001(3) 0.007(3) -0.001(4)
O2B 0.018(5) 0.017(4) 0.022(3) 0.000(3) 0.003(3) 0.000(4)
O1B 0.012(4) 0.015(5) 0.021(3) 0.001(4) -0.003(3) 0.001(4)
N1 0.031(3) 0.030(3) 0.029(3) 0.002(2) -0.004(2) 0.003(2)
C1 0.032(3) 0.028(3) 0.030(3) 0.000(2) -0.002(2) 0.008(2)
C2 0.030(3) 0.029(3) 0.029(3) 0.000(2) -0.004(2) 0.006(2)
C3 0.030(3) 0.028(3) 0.031(3) 0.000(2) -0.003(2) 0.007(2)
C4 0.030(3) 0.028(3) 0.031(3) 0.000(2) -0.002(3) 0.007(2)

_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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  _geom_bond_atom_site_label_2
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  _geom_bond_site_symmetry_2
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O3 W1 1.693(8) . ?
O3 Na1 2.97(14) 1_655 ?
Na1 Na1 1.5(3) 5_556 ?
Na1 O3 2.97(14) 1_455 ?
Na1 C3 3.01(7) 6_466 ?
Na1 C1 3.04(9) 3_455 ?
C6 N1 1.331(12) . ?
C6 C1 1.375(10) . ?
W1 O2B 1.829(16) . ?
W1 O2A 1.832(14) . ?
W1 O1B 1.848(16) 3 ?
W1 O1A 1.866(16) 3 ?
W1 O1A 1.947(16) . ?
W1 O1B 1.963(17) . ?
W1 O2A 1.987(15) 6_556 ?
W1 O2B 2.013(16) 6_556 ?
W1 N1 2.456(12) . ?
O1A W1 1.866(16) 3_455 ?
O2A W1 1.987(14) 6_566 ?
O2B W1 2.013(16) 6_566 ?
O1B W1 1.848(16) 3_455 ?
N1 C2 1.323(12) . ?
C1 C4 1.412(15) . ?
C1 Na1 3.04(9) 3 ?
C2 C3 1.366(11) . ?
C3 C4 1.420(15) . ?
C3 Na1 3.01(7) 6_656 ?
C4 C4 1.44(2) 5_755 ?

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W1 O3 Na1 175.8(17) . 1_655 ?
Na1 Na1 O3 162(9) 5_556 1_455 ?
Na1 Na1 C3 117(7) 5_556 6_466 ?
O3 Na1 C3 75(3) 1_455 6_466 ?
Na1 Na1 C1 119(9) 5_556 3_455 ?
O3 Na1 C1 72(3) 1_455 3_455 ?

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C3 Na1 C1 92(2) 6_466 3_455 ?
 N1 C6 C1 121.9(9) . . ?
 O3 W1 O2B 100.5(4) . . ?
 O3 W1 O2A 101.3(4) . . ?
 O2B W1 O2A 16.7(8) . . ?
 O3 W1 O1B 101.4(5) . 3 ?
 O2B W1 O1B 93.8(8) . 3 ?
 O2A W1 O1B 77.3(7) . 3 ?
 O3 W1 O1A 100.0(5) . 3 ?
 O2B W1 O1A 111.1(8) . 3 ?
 O2A W1 O1A 94.7(7) . 3 ?
 O1B W1 O1A 17.5(7) 3 3 ?
 O3 W1 O1A 98.2(5) . . ?
 O2B W1 O1A 75.5(8) . . ?
 O2A W1 O1A 92.0(7) . . ?
 O1B W1 O1A 159.1(8) 3 . ?
 O1A W1 O1A 159.00(10) 3 . ?
 O3 W1 O1B 96.9(5) . . ?
 O2B W1 O1B 92.1(8) . . ?
 O2A W1 O1B 108.4(7) . . ?
 O1B W1 O1B 159.41(6) 3 . ?
 O1A W1 O1B 148.1(7) 3 . ?
 O1A W1 O1B 16.6(6) . . ?
 O3 W1 O2A 97.0(4) . 6_556 ?
 O2B W1 O2A 162.2(6) . 6_556 ?
 O2A W1 O2A 157.1(8) . 6_556 ?
 O1B W1 O2A 85.7(11) 3 6_556 ?
 O1A W1 O2A 68.4(11) 3 6_556 ?
 O1A W1 O2A 99.0(10) . 6_556 ?
 O1B W1 O2A 82.8(11) . 6_556 ?
 O3 W1 O2B 97.9(4) . 6_556 ?
 O2B W1 O2B 154.0(11) . 6_556 ?
 O2A W1 O2B 160.7(6) . 6_556 ?
 O1B W1 O2B 100.4(11) 3 6_556 ?
 O1A W1 O2B 83.3(11) 3 6_556 ?
 O1A W1 O2B 83.8(11) . 6_556 ?
 O1B W1 O2B 67.5(11) . 6_556 ?
 O2A W1 O2B 15.2(8) 6_556 6_556 ?
 O3 W1 N1 176.7(3) . . ?
 O2B W1 N1 82.4(4) . . ?
 O2A W1 N1 82.0(4) . . ?
 O1B W1 N1 79.9(5) 3 . ?
 O1A W1 N1 80.4(5) 3 . ?
 O1A W1 N1 80.9(5) . . ?
 O1B W1 N1 81.3(5) . . ?
 O2A W1 N1 80.0(4) 6_556 . ?
 O2B W1 N1 78.8(4) 6_556 . ?
 W1 O1A W1 162.2(11) 3_455 . ?
 W1 O2A W1 166.5(14) . 6_566 ?
 W1 O2B W1 161.5(15) . 6_566 ?
 W1 O1B W1 162.6(12) 3_455 . ?
 C2 N1 C6 119.7(10) . . ?
 C2 N1 W1 121.3(7) . . ?
 C6 N1 W1 118.9(7) . . ?
 C6 C1 C4 120.6(9) . . ?
 C6 C1 Na1 111(3) . 3 ?
 C4 C1 Na1 98(2) . 3 ?
 N1 C2 C3 122.3(9) . . ?

C2 C3 C4 120.6(9) . . ?
C2 C3 Na1 108(3) . 6_656 ?
C4 C3 Na1 106(2) . 6_656 ?
C1 C4 C3 114.9(10) . . ?
C1 C4 C4 123.1(14) . 5_755 ?
C3 C4 C4 122.0(14) . 5_755 ?

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