

data_WO3-bpy-2Na

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_audit_creation_method          SHELXL-97
_chemical_name_systematic
;
?
;
_chemical_name_common           ?
_chemical_melting_point         ?
_chemical_formula_moiety        'C5 H4 N1 Na0.13 O3 W1'
_chemical_formula_sum           'C5 H4 N1 Na0.13 O3 W1'
_chemical_formula_weight        312.80
```

```
loop_
  _atom_type_symbol
  _atom_type_description
  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
  _atom_type_scatter_source
```

```
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 b c a'
```

```
loop_
  _symmetry_equiv_pos_as_xyz
  'x, y, z'
  '-x+1/2, -y, z+1/2'
  '-x, y+1/2, -z+1/2'
  'x+1/2, -y+1/2, -z'
  '-x, -y, -z'
  'x-1/2, y, -z-1/2'
  'x, -y-1/2, z-1/2'
  '-x-1/2, y-1/2, z'
```

```
_cell_length_a                  7.4683(3)
_cell_length_b                  7.3910(3)
_cell_length_c                  22.5781(6)
_cell_angle_alpha               90.00
_cell_angle_beta                90.00
_cell_angle_gamma               90.00
_cell_volume                    1246.27(8)
_cell_formula_units_Z           8
_cell_measurement_temperature   100(5)
_cell_measurement_reflns_used   1187
_cell_measurement_theta_min     17.33
_cell_measurement_theta_max     143.02
```

```
_exptl_crystal_description      plate
_exptl_crystal_colour           yellow-green
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_exptl_crystal_size_max      0.080
_exptl_crystal_size_mid      0.080
_exptl_crystal_size_min      0.010
_exptl_crystal_density_meas  ?
_exptl_crystal_density_diffn 3.334
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000         1123
_exptl_absorpt_coefficient_mu 34.008
_exptl_absorpt_correction_type empirical
_exptl_absorpt_correction_T_min 0.008
_exptl_absorpt_correction_T_max 1.000
_exptl_absorpt_process_details

;
data scaling includes absorption [ABSCOR, Higashi (1995)]
_exptl_special_details
;
_diffn_ambient_temperature    100(5)
_diffn_radiation_wavelength    1.54178
_diffn_radiation_type          CuK\alpha
_diffn_radiation_source         'rotating anode'
_diffn_radiation_monochromator  'confocal optics'
_diffn_measurement_device_type  'Rigaku Spider'
_diffn_measurement_device_details 'cureved image plate detector'
_diffn_measurement_method       \w-scans
_diffn_detector_area_resol_mean 10
_diffn_standards_number         0
_diffn_standards_interval_count ?
_diffn_standards_interval_time  ?
_diffn_standards_decay_%        0
_diffn_reflns_number            6727
_diffn_reflns_av_R_equivalents  0.0936
_diffn_reflns_av_sigmaI/netI    0.0790
_diffn_reflns_limit_h_min       -9
_diffn_reflns_limit_h_max       8
_diffn_reflns_limit_k_min       -6
_diffn_reflns_limit_k_max       8
_diffn_reflns_limit_l_min       -26
_diffn_reflns_limit_l_max       23
_diffn_reflns_theta_min         7.11
_diffn_reflns_theta_max         69.93
_reflns_number_total            1125
_reflns_number_gt               1015
_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)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics   'Mercury (Macrae et. al., 2006) and POV-RAY (Cason, 2003)'
_computing_publication_material 'SHELXL-97 (Sheldrick, 2008)'

_refine_special_details
;
Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based

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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.

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 (31) 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, crystal quality was noticeably deteriorated and more highly mosaic.

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_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.0000P)^2^+146.9178P]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        0.00008(3)
_refine_ls_extinction_expression
'Fc^*=kFc[1+0.001xFc^2^l^3^/sin(2\q)]^-1/4^'
_refine_ls_number_reflns         1125
_refine_ls_number_parameters      115
_refine_ls_number_restraints      120
_refine_ls_R_factor_all           0.0570
_refine_ls_R_factor_gt            0.0536
_refine_ls_wR_factor_ref          0.1279
_refine_ls_wR_factor_gt          0.1251
_refine_ls_goodness_of_fit_ref    0.865
_refine_ls_restrained_S_all       0.820
_refine_ls_shift/su_max           0.002
_refine_ls_shift/su_mean          0.000

loop_
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  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
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_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
W1 W 0.51977(8) 1.04669(11) 0.26376(2) 0.0146(3) Uani 1 1 d . . .
N1 N 0.5138(15) 1.0339(18) 0.1567(5) 0.0188(16) Uani 1 1 d U . .
O3 O 0.5089(11) 1.0501(14) 0.3396(4) 0.014(2) Uani 1 1 d U . .
C2 C 0.6251(19) 0.922(2) 0.1280(6) 0.0196(17) Uani 1 1 d U . .
H2 H 0.7060 0.8532 0.1498 0.024 Uiso 1 1 calc R . .
C3 C 0.4034(18) 1.142(2) 0.1250(6) 0.0195(16) Uani 1 1 d U . .
H3 H 0.3334 1.2277 0.1444 0.023 Uiso 1 1 calc R . .
C4 C 0.6234(19) 0.905(2) 0.0665(6) 0.0201(17) Uani 1 1 d U . .
H4 H 0.7019 0.8254 0.0479 0.024 Uiso 1 1 calc R . .
C5 C 0.5027(18) 1.008(2) 0.0326(6) 0.0195(17) Uani 1 1 d U . .
C6 C 0.3941(18) 1.126(2) 0.0636(6) 0.0199(16) Uani 1 1 d U . .
H6 H 0.3125 1.1973 0.0429 0.024 Uiso 1 1 calc R . .
O1A O 0.461(4) 0.783(3) 0.2523(8) 0.012(3) Uani 0.48(3) 1 d PU . 1
O2A O 0.760(3) 1.002(4) 0.2516(10) 0.024(3) Uani 0.48(3) 1 d PU . 1
O1B O 0.539(3) 0.778(3) 0.2517(8) 0.011(3) Uani 0.52(3) 1 d PU . 2
O2B O 0.759(3) 1.076(4) 0.2513(9) 0.024(3) Uani 0.52(3) 1 d PU . 2
Na1 Na 0.50(2) 1.03(2) 0.473(7) 0.18(7) Uiso 0.13 1 d P . .

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_atom_site_aniso_U_11
_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
W1 0.0157(4) 0.0168(5) 0.0114(4) -0.0010(2) -0.0002(2) 0.0036(3)
N1 0.019(2) 0.019(2) 0.018(2) -0.0002(19) 0.0001(18) -0.0003(18)
O3 0.015(2) 0.014(2) 0.015(2) 0.0001(15) -0.0003(15) -0.0003(15)
C2 0.020(2) 0.019(2) 0.019(2) -0.0001(19) 0.0003(18) 0.0003(19)
C3 0.020(2) 0.019(2) 0.019(2) -0.0006(19) 0.0002(18) 0.0000(19)
C4 0.020(2) 0.020(2) 0.020(2) 0.0000(19) 0.0004(19) 0.0003(19)
C5 0.020(2) 0.019(2) 0.019(2) -0.0002(19) 0.0002(19) 0.0000(19)
C6 0.020(2) 0.020(2) 0.019(2) -0.0003(19) -0.0002(18) 0.0002(19)
O1A 0.011(4) 0.011(3) 0.012(3) 0.003(2) 0.000(2) -0.001(2)
O2A 0.025(4) 0.024(4) 0.023(4) 0.000(2) -0.001(2) 0.000(2)
O1B 0.011(4) 0.011(3) 0.012(3) 0.003(2) 0.000(2) 0.001(2)
O2B 0.024(4) 0.025(4) 0.023(4) 0.000(2) -0.001(2) 0.000(2)

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_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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loop_
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  _geom_bond_atom_site_label_2
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  _geom_bond_site_symmetry_2
  _geom_bond_publ_flag

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W1 O3 1.715(9) . ?
W1 O1A 1.79(2) 3_655 ?
W1 O1B 1.80(2) 3_655 ?
W1 O2B 1.82(2) . ?
W1 O2A 1.85(3) . ?
W1 O2B 1.99(2) 6_556 ?
W1 O2A 2.00(3) 6_556 ?
W1 O1B 2.01(2) . ?
W1 O1A 2.01(2) . ?
W1 N1 2.419(12) . ?
N1 C2 1.340(18) . ?
N1 C3 1.353(18) . ?
O3 Na1 3.02(17) . ?
C2 C4 1.395(19) . ?
C3 C6 1.393(18) . ?
C4 C5 1.41(2) . ?
C4 Na1 3.07(17) 3_645 ?
C4 Na1 3.10(18) 6_656 ?
C5 C6 1.38(2) . ?
C5 C5 1.48(3) 5_675 ?
C6 Na1 3.13(17) 6_556 ?
O1A W1 1.79(2) 3_645 ?
O2A W1 2.00(3) 6_656 ?
O1B W1 1.80(2) 3_645 ?
O2B W1 1.99(2) 6_656 ?
Na1 Na1 1.3(3) 5_676 ?
Na1 C4 3.07(17) 3_655 ?
Na1 C4 3.10(18) 6_556 ?
Na1 C6 3.13(17) 6_656 ?

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  _geom_angle_atom_site_label_3
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  _geom_angle_site_symmetry_3
  _geom_angle_publ_flag

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O3 W1 O1A 101.0(7) . 3_655 ?
O3 W1 O1B 99.7(6) . 3_655 ?
O1A W1 O1B 18.8(7) 3_655 3_655 ?
O3 W1 O2B 101.4(7) . . ?
O1A W1 O2B 76.9(9) 3_655 . ?
O1B W1 O2B 95.6(9) 3_655 . ?
O3 W1 O2A 101.4(7) . . ?
O1A W1 O2A 93.8(10) 3_655 . ?
O1B W1 O2A 112.2(10) 3_655 . ?
O2B W1 O2A 17.1(10) . . ?
O3 W1 O2B 97.1(7) . 6_556 ?
O1A W1 O2B 86.6(14) 3_655 6_556 ?
O1B W1 O2B 68.0(14) 3_655 6_556 ?
O2B W1 O2B 157.2(10) . 6_556 ?

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O2A W1 O2B 161.1(12) . 6_556 ?
 O3 W1 O2A 97.5(7) . 6_556 ?
 O1A W1 O2A 101.9(15) 3_655 6_556 ?
 O1B W1 O2A 83.6(14) 3_655 6_556 ?
 O2B W1 O2A 160.9(11) . 6_556 ?
 O2A W1 O2A 152.7(13) . 6_556 ?
 O2B W1 O2A 15.7(9) 6_556 6_556 ?
 O3 W1 O1B 98.8(6) . . ?
 O1A W1 O1B 158.6(8) 3_655 . ?
 O1B W1 O1B 158.45(14) 3_655 . ?
 O2B W1 O1B 91.5(9) . . ?
 O2A W1 O1B 74.6(9) . . ?
 O2B W1 O1B 98.8(13) 6_556 . ?
 O2A W1 O1B 83.2(14) 6_556 . ?
 O3 W1 O1A 97.6(6) . . ?
 O1A W1 O1A 159.35(10) 3_655 . ?
 O1B W1 O1A 147.2(7) 3_655 . ?
 O2B W1 O1A 108.0(9) . . ?
 O2A W1 O1A 91.2(10) . . ?
 O2B W1 O1A 82.4(14) 6_556 . ?
 O2A W1 O1A 66.7(14) 6_556 . ?
 O1B W1 O1A 16.7(6) . . ?
 O3 W1 N1 176.0(4) . . ?
 O1A W1 N1 80.6(7) 3_655 . ?
 O1B W1 N1 80.7(6) 3_655 . ?
 O2B W1 N1 82.5(7) . . ?
 O2A W1 N1 82.1(7) . . ?
 O2B W1 N1 79.3(7) 6_556 . ?
 O2A W1 N1 78.6(7) 6_556 . ?
 O1B W1 N1 80.1(6) . . ?
 O1A W1 N1 80.2(6) . . ?
 C2 N1 C3 119.2(13) . . ?
 C2 N1 W1 119.7(9) . . ?
 C3 N1 W1 121.1(9) . . ?
 W1 O3 Na1 176(4) . . ?
 N1 C2 C4 122.1(13) . . ?
 N1 C3 C6 120.5(13) . . ?
 C2 C4 C5 119.9(13) . . ?
 C2 C4 Na1 112(3) . 3_645 ?
 C5 C4 Na1 98(3) . 3_645 ?
 C2 C4 Na1 105(3) . 6_656 ?
 C5 C4 Na1 105(4) . 6_656 ?
 Na1 C4 Na1 117(5) 3_645 6_656 ?
 C6 C5 C4 116.2(13) . . ?
 C6 C5 C5 122.8(17) . 5_675 ?
 C4 C5 C5 121.0(16) . 5_675 ?
 C5 C6 C3 121.9(14) . . ?
 C5 C6 Na1 106(3) . 6_556 ?
 C3 C6 Na1 109(3) . 6_556 ?
 W1 O1A W1 162.1(16) 3_645 . ?
 W1 O2A W1 160.0(18) . 6_656 ?
 W1 O1B W1 161.5(15) 3_645 . ?
 W1 O2B W1 167.0(17) . 6_656 ?
 Na1 Na1 O3 164(10) 5_676 . ?
 Na1 Na1 C4 125(10) 5_676 3_655 ?
 O3 Na1 C4 71(3) . 3_655 ?
 Na1 Na1 C4 99(10) 5_676 6_556 ?
 O3 Na1 C4 75(4) . 6_556 ?

C4 Na1 C4 85(4) 3_655 6_556 ?
Na1 Na1 C6 110(10) 5_676 6_656 ?
O3 Na1 C6 73(4) . 6_656 ?
C4 Na1 C6 90(4) 3_655 6_656 ?
C4 Na1 C6 148(6) 6_556 6_656 ?

_diffraction_measured_fraction_theta_max	0.956
_diffraction_reflns_theta_full	69.93
_diffraction_measured_fraction_theta_full	0.956
_refine_diff_density_max	3.252
_refine_diff_density_min	-3.223
_refine_diff_density_rms	0.399