Supporting Information

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Synthesis and Characterization of Redox-Active Charge-Transfer Complexes with 2,3,5,6-Tetracyanopyridine (TCNPy) for the Photogeneration of Pyridinium Radicals

Eva Wöß, Uwe Monkowius, and Günther Knör*[a]

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SUPPORTING INFORMATION

Synthesis and Characterization of Redox-Active Charge-Transfer Complexes with 2,3,5,6-Tetracyanopyridine (TCNPy) for the Photogeneration of Pyridinium Radicals

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1) Details on digital simulation of cyclic voltammograms:

Software used: DigiSim 3.03 (BAS Bioanalytical Systems)
Reference: A. W. Bott, Current Separations 1999, 18, 9

EC-mechanism: A + e = B and B = C
CV-parameters: E(start) 0.1385 V ; E(rev) -0.862 V ; E(end) 0.1385 V
V / mV s⁻¹ 0.02 ; 0.05 ; 0.10 ; 0.15 ; 0.20 ; 0.25
Cycles 1 ; T 298K ; area 0.02 cm² ; geometry: planar;
Chemical parameters: E° = -0.505 V ; α = 0.55 ; ks = 0.005 cm s⁻¹ ; D = 1.2 x 10⁻⁵ cm² s⁻¹
K(eq) = 1 ; kf = 0.1

2) Details on X-ray structural determinations:
checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0030 Å  Wavelength=0.71073

Cell:  
a=10.1454(13)  b=12.2525(17)  c=13.952(2)  
alpha=90  beta=90  gamma=90

Temperature:  
205 K

Volume:  
Calculated 1734.3(4)  Reported 1734.3(4)

Space group:  
P b c a  P b c a

Hall group:  
-P 2ac 2ab  -P 2ac 2ab

Moisety formula:  
C9 H N5

Sum formula:  
C9 H N5  C9 H N5

Mr:  
179.15  179.15

Dx, g cm$^{-3}$:  
1.372  1.372

Z:  
8  8

Mu (mm$^{-1}$):  
0.093  0.093

F000:  
720.0  720.0

F000':  
720.21

h,k,lmax:  
12,14,16  12,14,16

Nref:  
1542  1539

Tmin,Tmax:  
0.966,0.979  0.960,0.980

Tmin':  
0.956

Correction method= MULTI-SCAN

Data completeness= 0.998  Theta(max)= 25.060

R(reflections)= 0.0491(1137)  wr2(reflections)= 0.1102(1539)

S = 1.175  Npar= 128

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given ........................          ?
PLAT366_ALERT_2_C Short? C(sp?)--C(sp?) Bond  C1     --   C2     ...       1.39 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor      *N1B    --  *H3A    ...          ?
PLAT420_ALERT_2_C D-H Without Acceptor      *N1A    --  *H3B    ...          ?

Alert level G
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF ....          ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms ............          2
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum ....          ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max   datum ....          ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min   datum ....          ?
PLAT301_ALERT_3_G Note: Main Residue Disorder ...................         14 Perc.

ALERT level A = Most likely a serious problem - resolve or explain
ALERT level B = A potentially serious problem, consider carefully
ALERT level C = Check. Ensure it is not caused by an omission or oversight
ALERT level G = General information/check it is not something unexpected

ALERT type 1 CIF construction/syntax error, inconsistent or missing data
ALERT type 2 Indicator that the structure model may be wrong or deficient
ALERT type 3 Indicator that the structure quality may be low
ALERT type 4 Improvement, methodology, query or suggestion
ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A
PUBL006_ALERT_1_A  _publ_requested_journal is missing
e.g. 'Acta Crystallographica Section C'

ALERT level A = Data missing that is essential or data in wrong format
ALERT level G = General alerts. Data that may be required is missing
Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in Acta Crystallographica Section C or Section E, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. Your explanation will be considered as part of the review process.

If you intend to submit to another section of Acta Crystallographica or Journal of Applied Crystallography or Journal of Synchrotron Radiation, you should make sure that at least a basic structural check is run on the final version of your CIF prior to submission.

# start Validation Reply Form
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
# end Validation Reply Form

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 25/09/2012; check.def file version of 20/09/2012
checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found.  CIF dictionary  Interpreting this report

Datablock: I

Bond precision:  C-C = 0.0033 A  Wavelength=0.71073

Cell:  

| Calculated | Reported |
|------------|----------|
| a=6.6458(15) | b=6.5632(14) |
| alpha=90 | beta=101.630(8) |
| c=15.190(4) | gamma=90 |

Temperature: 200 K

Volume  649.0(3)  649.0(3)
Space group  P 21/n  P 1 21/n 1
Hall group  -P 2yn  -P 2yn
Moiety formula  C9 H N5, C6 H6 O2  ?
Sum formula  C15 H7 N5 O2  C15 H7 N5 O2
Mr  289.26  289.26
Dx, g cm\(^{-3}\)  1.480  1.480
Z  2  2
Mu (mm\(^{-1}\))  0.105  0.105
F000  296.0  296.0
F000’  296.12
h,k,lmax  7,7,18  7,7,18
Nref  1147  1142
Tmin,Tmax  0.952,0.985  0.950,0.990
Tmin’  0.945

Correction method= MULTI-SCAN

Data completeness= 0.996  Theta(max)= 25.040
R(reflections)= 0.0480( 880)  wR2(reflections)= 0.1179( 1142)
S = 1.102  Npar= 101

The following ALERTS were generated. Each ALERT has the format

**test-name_ALERT_alert-type_alert-level.**

Click on the hyperlinks for more details of the test.

- **Alert level C**
  - **ABSTY02_ALERT_1_C**  An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as multi-scan
| Alert Level    | Alert Type  | Description                                                                 |
|---------------|-------------|-----------------------------------------------------------------------------|
| Alert level G | Alert type 1| CIF construction/syntax error, inconsistent or missing data                |
|               | Alert type 2| Indicator that the structure model may be wrong or deficient                |
|               | Alert type 3| Indicator that the structure quality may be low                              |
|               | Alert type 4| Improvement, methodology, query or suggestion                               |
|               | Alert type 5| Informative message, check                                                  |

checkCIF publication errors

| Alert level A | _publ_requested_journal is missing | e.g. 'Acta Crystallographica Section C' |
|---------------|-----------------------------------|----------------------------------------|
| Alert level A | Data missing that is essential or data in wrong format |
| Alert level G | General alerts. Data that may be required is missing |
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PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
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# end Validation Reply Form

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PLATON version of 25/09/2012; check.def file version of 20/09/2012
