Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION SECTION

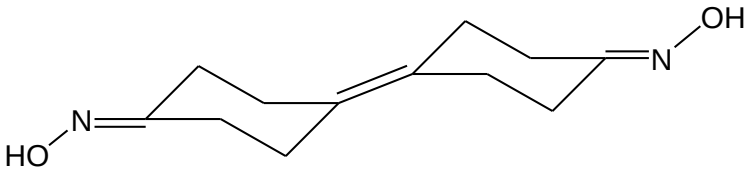
for the paper

First *bis*-cyanoxime: synthesis and properties of a new versatile and accessible polydentate bifunctional building block for coordination and supramolecular chemistry.

by

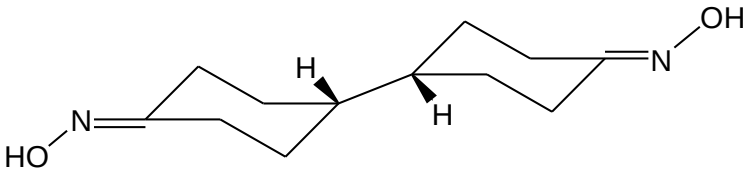
Carl Cheadle, Nikolay Gerasimchuk, Charles L. Barnes
Sergiy I. Tyukhtenko and Svitlana Silchenko

Some spectroscopically and structurally characterized non-chelating dioximes that, however, were never used as ligands in coordination chemistry. Appropriate citations and crystal data references are provided next to chemical structures.



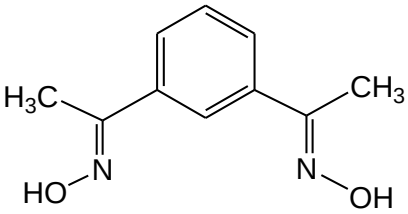
CCDC refcodes: **ZUKSON, ZUKSIH**

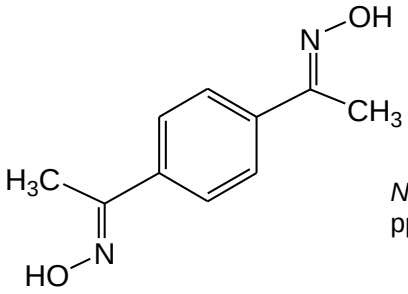
Tetrahedron, 1996, **52**, N°5, pp.1773-1784



CCDC refcodes: **XEXROH, XEXRIB**

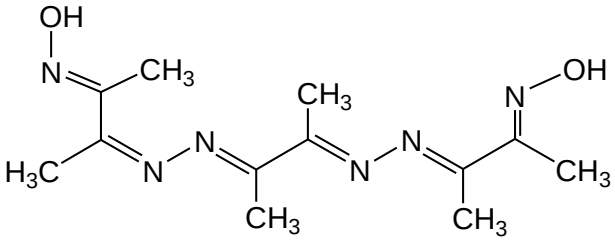
Chem. Mater., 1999, **11**, N°6, pp.1484-14912.





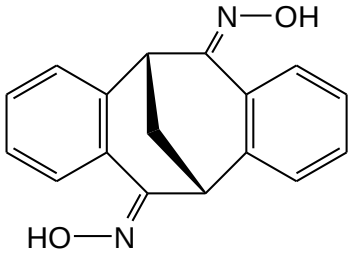
CCDC refcode: **UJUKIT**

New J. Chem., 2003, **27**, pp.1084-1094.



CCDC refcode: **XULMAS**

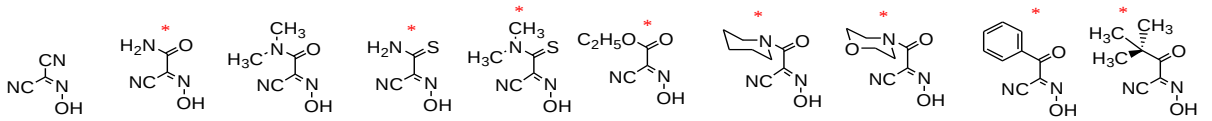
Y.Z. Voloshin, O.A.Varzatskii, I.I.Vorontsov, M.A.Antipin,, E. Yu. Tkachenko *Izv. Acad. Nauk SSSR (Russ. Chem. Bull*), 2002, p. 933.



CCDC refcode: **WUHGEL**

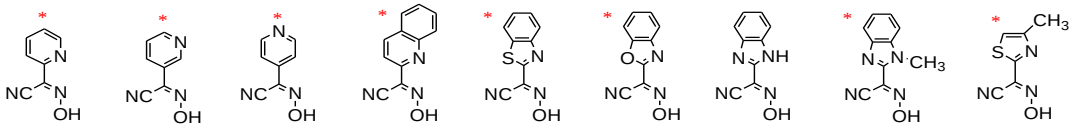
J.D.Field, P.Turner, M.M.Harding, T. Hatzikominus, L.Kim. *New J. Chem*. 2002, **26**, p.720-725.

The list of currently known and relatively well studied cyanoximes. Red asterisks indicate compounds for which crystal structures were determined.



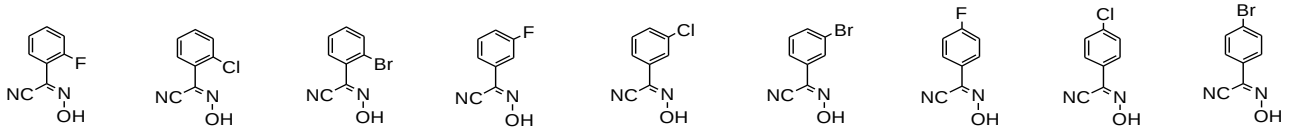
1 **CCO** | **2** **HACO** | **3** **HDCO** | **4** **HTCO** | **5** **HTDCO** | **6** **HECO** | **7** **HPiPCO** | **8** **HMCO** | **9** **HBCO** | **10** **HPiCO**

Amido- / ester- and keto- cyanoximes



11 **H2PCO** | **12** **H3PCO** | **13** **H4PCO** | **14** **HQCO** | **15** **HBTCO** | **16** **HBOCO** | **17** **HBIHCO** | **18** **HBIMCO** | **19** **HTLCO**

Heterocyclic cyanoximes

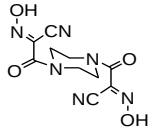


20 **H2F-PhCO** | **21** **H2Cl-PhCO** | **22** **H2Br-PhCO** | **23** **H3F-PhCO** | **24** **H3Cl-PhCO** | **25** **H3Br-PhCO** | **26** **H4F-PhCO** | **27** **H4Cl-PhCO** | **28** **H4Br-PhCO**

Monosubstituted arylcyanoximes

29 **H2,6-diF-PhCO** | **30** **H2F6Cl-PhCO** | **31** **H3,5-diF-PhCO** | **32** **H2,4-diF-PhCO** | **33** **H2,4-diCl-PhCO** | **34** **H2,6-diCl-PhCO**

Disubstituted arylcyanoximes

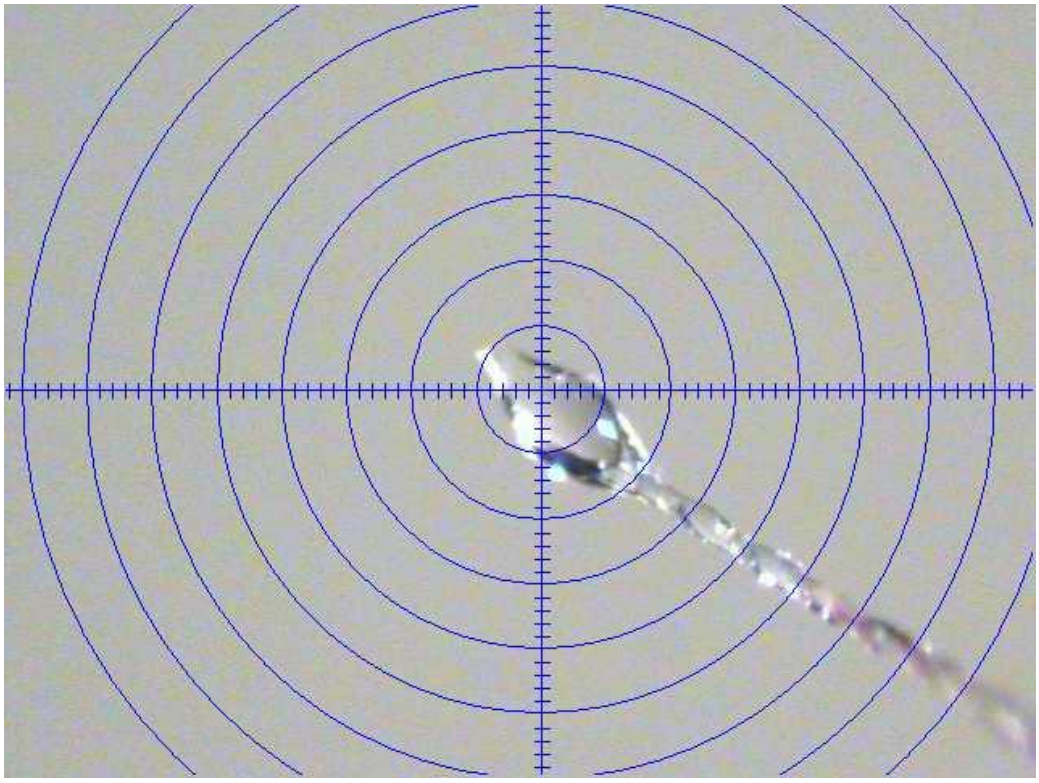


35

H_2BiPiPCO

Bis-cyanoxime

A video-microscope photograph of a single crystal of **2** used for the structure determination.



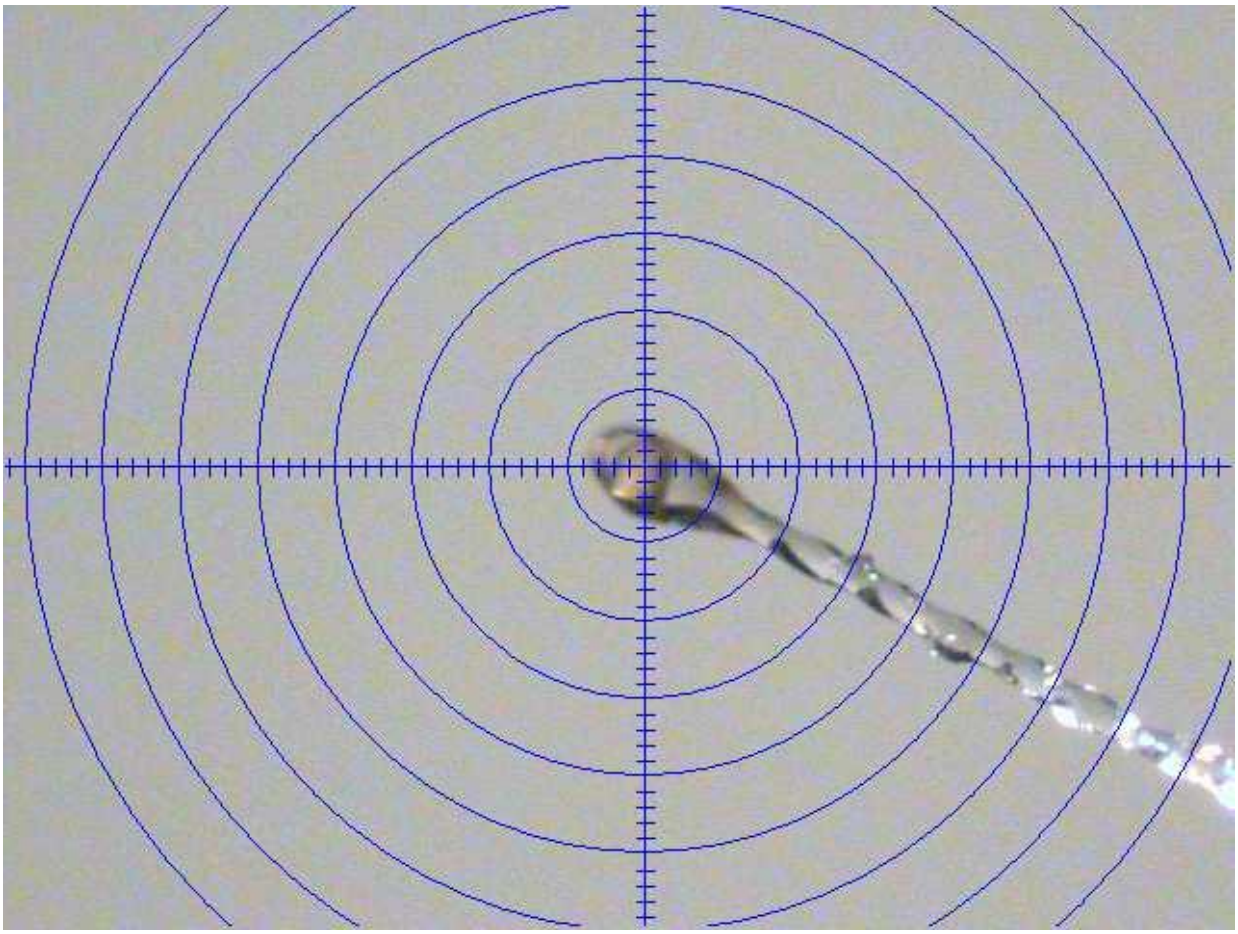
Selected for structural determination crystal of 2 represented a non-merohedral twin. A total of 2896 frames were collected (4 omega + 2 phi scans). The total exposure time was 48.27 hours. The integration of the data using a monoclinic unit cell yielded a total of 1201 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 1201 were independent (average redundancy 1.000, completeness = 99.7%, Rsig = 3.27%) and 853 (71.02%) were greater than $2\sigma(F^2)$.

Normal twined crystal workup procedure was applied. Specifically: 1) 4 runs with 360 frames were examined and 1592 reflections with I > or equal 20 sigma(I) were harvested; 2) two domains were selected that absorbed over 96% of these reflections; 3) domain #1 had 951 reflections, domain #2 had 634 reflections; 4) both domains generated monoclinic cells with the volume 611 A^3, and P2(1)/n space group, Z=2; 5) the TWIN law is 0.9970 -0.0003 -0.0129 0.00107 -1.0000 0.0052 -0.4608 -0.0008 -0.9970; both domains are related through 178.2 degrees rotation; 6) twin4.hkl and twin5.hkl files were generated in TWINABS; 7) the XPREP used for data conditioning 1309 reflections that gave mean I/sigma = 16.08; 8) |E x E(-1)| = 0.970, for centrosymmetric structures; 9) the structure has emerged using the twin4.hkl file and *_0m.p4p files.

Compound represents a co-crystallized mixture of syn- (51.24%) and anti- (48.76%) geometrical isomers with net occupancy 1.00. The respective line from the RES file output is:
FVAR 0.31390 0.51240

Electronic Supporting Materials: **4**

A video-microscope photograph of a single crystal of **4** in the Cryoloop used for the structure determination; inner circle represents 0.1 mm mark.

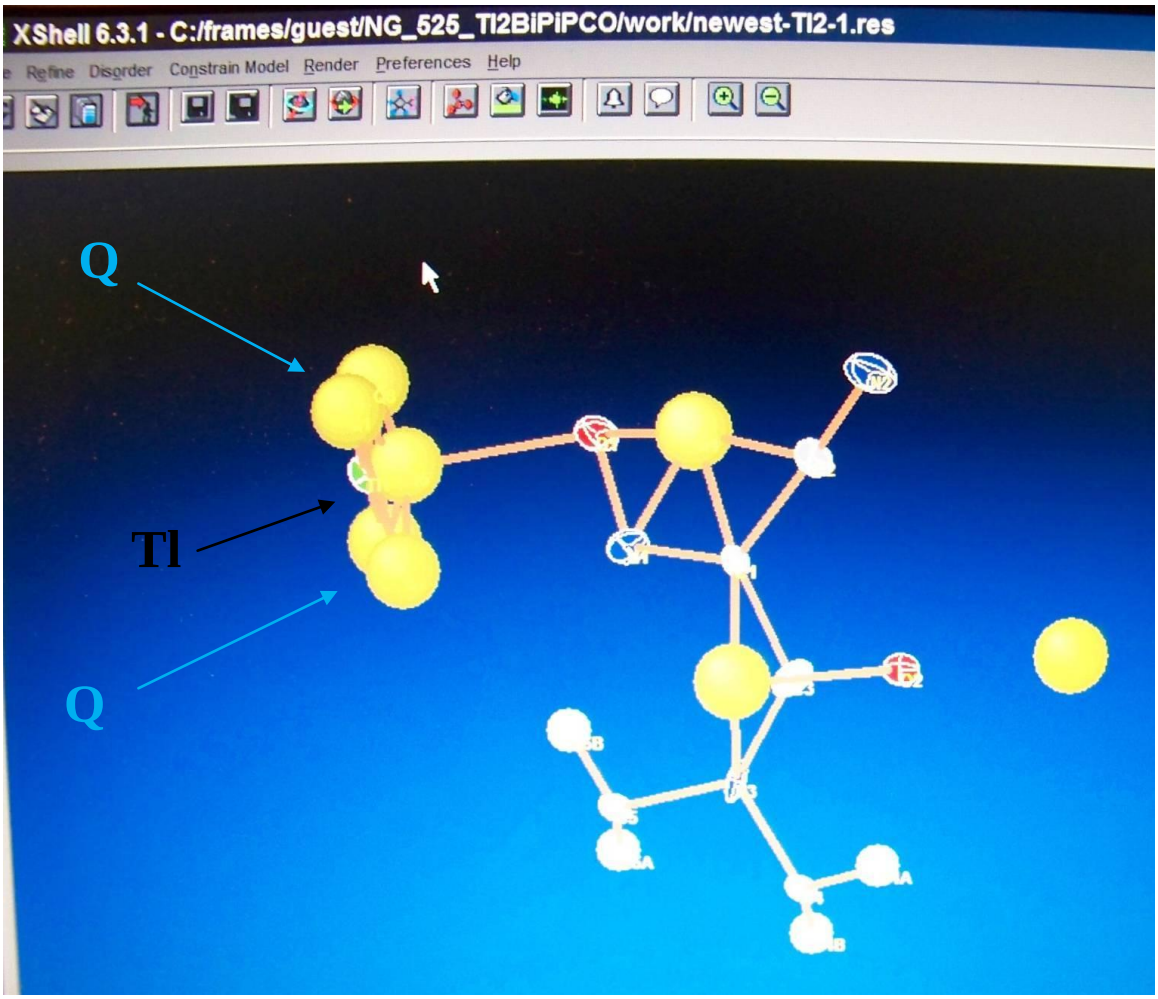


Unit cell determination for the crystal of dithallium complex **4** was done on a basis of 120 images from 4 different crystal/detector orientations that generated 264 strong reflections with $I>20\sigma(I)$. The crystal had 0.52^{o} mozaicity.

The CELL_NOW –t program was applied to investigate the possibility of presence of multiple domains or twinning. Results convincingly evidenced that the specimen is a single crystal, FOM=0.958, and all 264 reflections were indexed in one unit cell with reported in the paper metric dimensions. Thus, complex **4** crystallizes in the monoclinic centrosymmetric $P2_1/c$ space group (#14), which was unambiguously suggested by the XPREP program that used 8260 reflections, mean I/σ=10.91, with value of $\left| E \cdot E^{-1} \right| = 0.845$.

Data set, which covered a full sphere of reflections, was integrated to a 0.78 Å resolution leading to selected 8260 reflections (from 8447 total; 2.2% were rejected) with 1630 unique; $R_{int} = 0.041$, $R_{sym} = 0.023$. The multi-scan absorption correction was done using the SADABS program.

A photograph from the computer screen showing the ASU in the structure of Tl_2(BiPiPCO), **4**, and the most intense 7 Q-peaks. Five of those peaks of residual electron density are positioned close to the metal ion and represent typical for heavy metals “ripples”, have no reasonable chemical meaning. A black arrow points at Tl(I), while blue arrows are directed towards peaks of residual electron density around the central atom. The final printout of residual electron density peaks from the *.LST file is shown after the picture below.



Qn	x	y	z	sof	U	Peak,e	Distances to nearest atoms (with symmetry equivalents)			
Q1	0.0207	0.3677	0.4585	1.00000	0.05	2.78	0.93 TL1	2.21 O1	2.32 O2	2.71 O1
Q2	0.2978	0.6331	0.5431	1.00000	0.05	2.56	1.98 O1	1.99 TL1	2.00 O2	3.01 N1
Q3	0.4806	0.3667	0.4585	1.00000	0.05	2.36	1.04 TL1	2.29 O2	2.31 O1	2.91 O1
Q4	0.1936	0.6326	0.3819	1.00000	0.05	2.09	1.13 O1	1.48 N1	1.66 C2	1.66 C1
Q5	0.1181	0.3987	0.4206	1.00000	0.05	2.03	0.79 TL1	2.13 O1	2.61 N1	2.66 O1
Q6	0.2189	0.5962	0.1119	1.00000	0.05	1.55	0.83 C3	1.21 N3	1.66 C1	1.84 O2
Q7	0.2888	0.3913	0.5601	1.00000	0.05	1.31	1.22 TL1	2.18 O1	2.38 N1	2.88 O1

checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: I NG_521_H2BiPipCO_newest

```
Bond precision:      C-C = 0.0040 A              Wavelength=0.71073
Cell:         a=6.298(5)     b=15.488(12)     c=6.453(5)
              alpha=90       beta=102.648(13) gamma=90
Temperature: 120 K
                    Calculated                      Reported
Volume              614.2(8)                        614.2(8)
Space group         P 21/n                          P21/n
Hall group          -P 2yn                          -P 2yn
Moiety formula      C10 H10 N6 O4                   C10 H10 N6 O4
Sum formula         C10 H10 N6 O4                   C10 H10 N6 O4
Mr                  278.24                          278.24
Dx,g cm-3           1.505                           1.505
Z                   2                               2
Mu (mm-1)           0.120                           0.120
F000                288.0                           288.0
F000'               288.14
h,k,lmax            7,19,7                          7,19,7
Nref                1205                            1201
Tmin,Tmax           0.989,0.993                     0.662,0.745
Tmin'               0.985
Correction method= MULTI-SCAN
Data completeness= 0.997        Theta(max)= 26.000
R(reflections)= 0.0605( 853)       wR2(reflections)= 0.1859( 1201)
S = 1.096              Npar= 112
```

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

PLAT906_ALERT_3_C Large K value in the Analysis of Variance 8.066
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 4

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ?

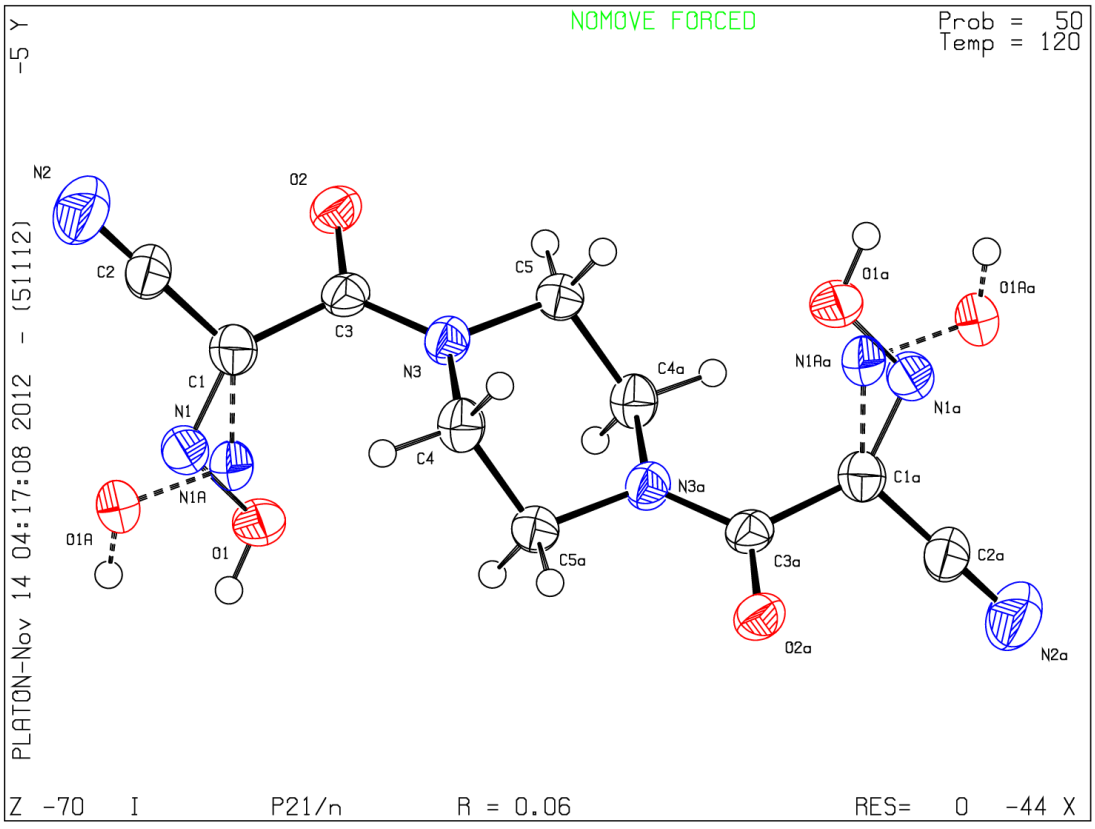
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 2
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.11
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 20 Perc.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 18
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... !

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

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

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock I - ellipsoid plot



checkCIF/PLATON (full publication check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: I $Tl_2BiPipCO$

```
Bond precision: C-C = 0.0167 A          Wavelength=0.71073
Cell:        a=4.2757(8) b=13.674(2)    c=12.009(2)
             alpha=90    beta=99.347(2) gamma=90
Temperature: 120 K
               Calculated                Reported
Volume         692.8(2)                  692.8(2)
Space group    P 21/c                    P 21/c
Hall group     -P 2ybc                   -P 2ybc
Moiety formula C5 H4 N3 O2 Tl            C10 H8 N6 O4 Tl2
Sum formula    C5 H4 N3 O2 Tl            C10 H8 N6 O4 Tl2
Mr             342.49                    684.96
Dx,g cm-3      3.284                     3.284
Z              4                         2
Mu (mm-1)      23.259                    23.258
F000           608.0                     608.0
F000'          597.82
h,k,lmax       5,17,15                   5,17,15
Nref           1561                      1555
Tmin,Tmax      0.058,0.156               0.189,0.293
Tmin'          0.010
Correction method= NUMERICAL
Data completeness= 0.996 Theta(max)= 27.210
R(reflections)= 0.0451(     wR2(reflections)= 0.1013(
1369)                       1555)
S = 1.272         Npar= 100
```

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

PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0167 Ang

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 3
PLAT004_ALERT_5_G Info: Polymeric Structure Found with Dimension . 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ ?
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 2.00 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 23.02
PLAT371_ALERT_2_G Long C(sp2)-C(sp1) Bond C1 - C2 ... 1.45 Ang.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 18

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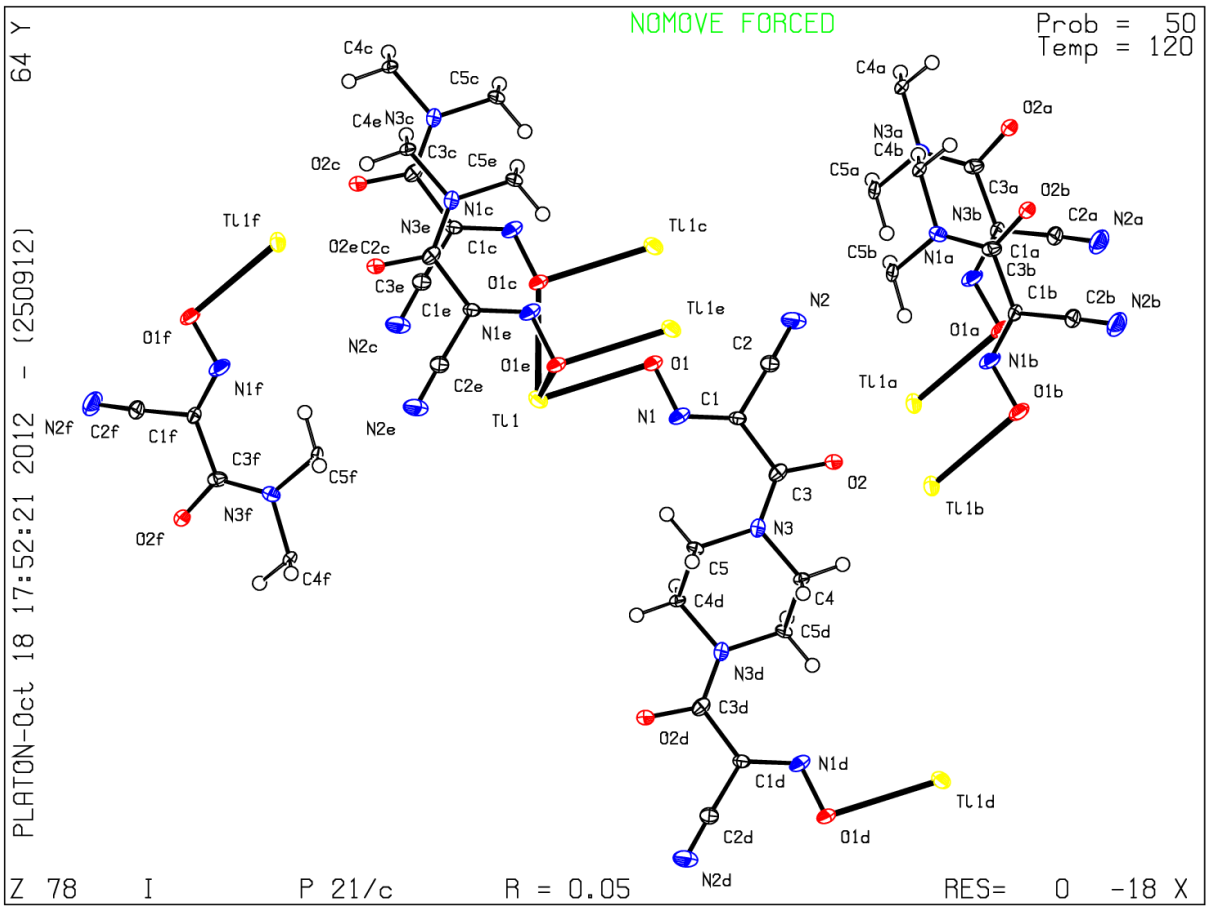
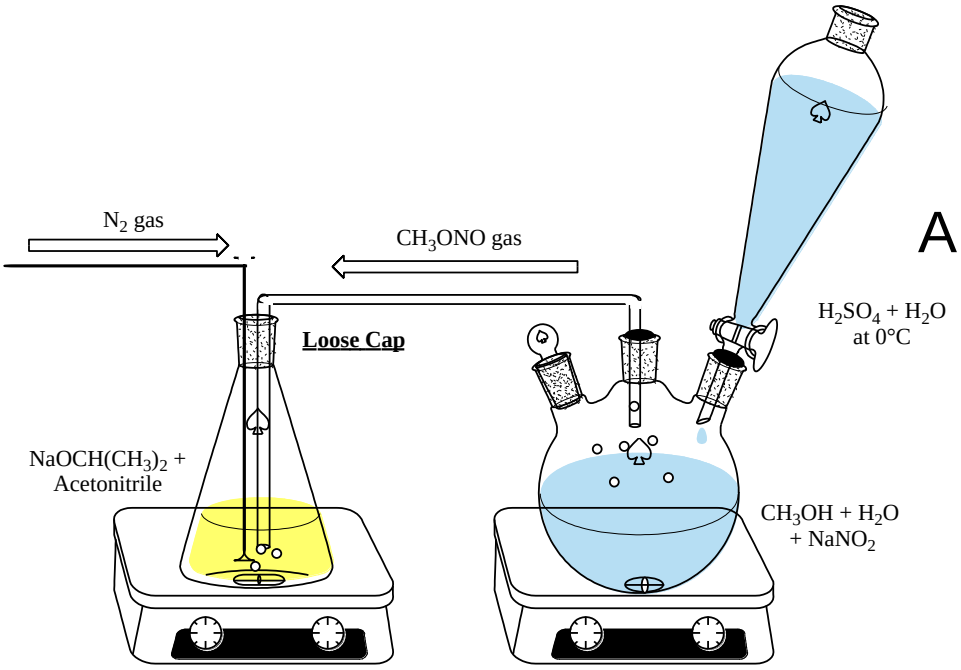
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

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

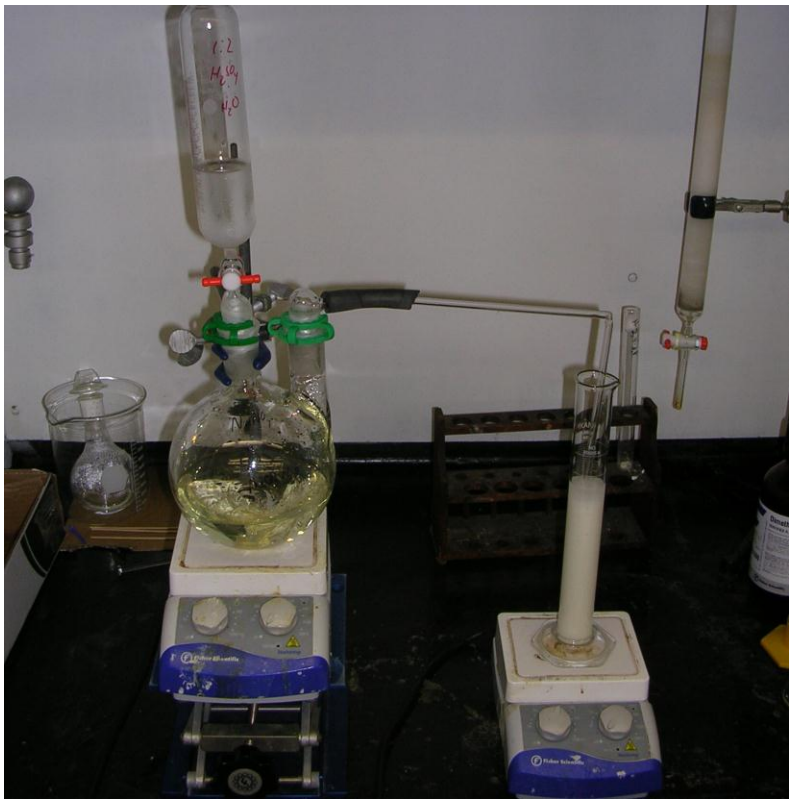
Datablock I - ellipsoid plot



Experimental scheme (**A**) and actual experimental setup used (**B**) for the generation of methyl nitrite for the oximation of deprotonated acetonitriles under basic conditions.



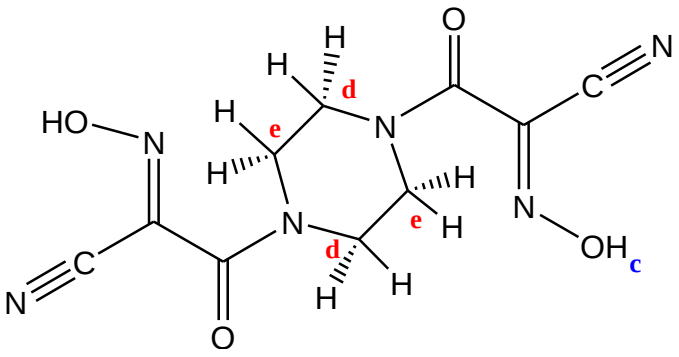
A



B

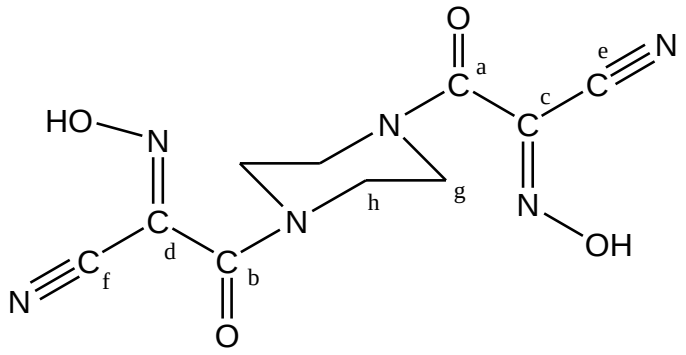
Chemical Shift Data (in ppm) of Variable Temperature ^{1}H NMR studies of the H_2BiPiPCO ligand **2** in dmso-d_6.

	Temperature						
Proton	**25°C**	**35°C**	**45°C**	**55°C**	**65°C**	**75°C**	**85°C**
d	3.728	3.725	3.689	3.701	3.700	3.703	3.705
e	3.657	3.664					
c	14.269	14.199	14.229				



Chemical Shift Data (in ppm) of Variable Temperature ^{13}C NMR studies of H_2BiPipCO (**2**) in dmso-d_6**.**

Carbon	Temperature							
atom	**25°C**	**35°C**	**45°C**	**55°C**	**65°C**	**75°C**	**85°C**	**95°C**
a	158.0	158.0	158.1	158.1	158.1	158.1	158.2	158.3
b	156.3	156.4	156.4	156.5	156.5	156.6	156.6	156.8
c	130.1	130.1	130.1	130.2	130.2	130.3	130.4	130.5
d	127.0	127.1	127.1	127.1	127.1	127.2	127.2	127.4
e	113.2	113.2	113.2	113.1	113.1	113.1	113.1	113.2
f	109.2	109.2	109.2	109.2	109.1	109.1	109.1	109.1
g	46.6							
g	46.4	46.3						
g	45.8	45.8	45.9	46.0	45.3	45.3	45.3	45.4
g	45.6							
g	45.0							44.1
h	42.5							
h	42.3	42.4	42.3	42.1	42.6	42.7		
h	41.7	41.7						41.5
h	41.4				41.3	41.3	41.3	41.4
h	40.9							41.1
h	40.7							40.9
h	40.3							



Actual microscope photographs of powdery samples of synthesized metal derivatives of the first bis-cyanoxime at 40x magnification:

$Na_2BiPipCO \times 4H_2O$, **3**

$Tl_2BiPipCO$, **4**

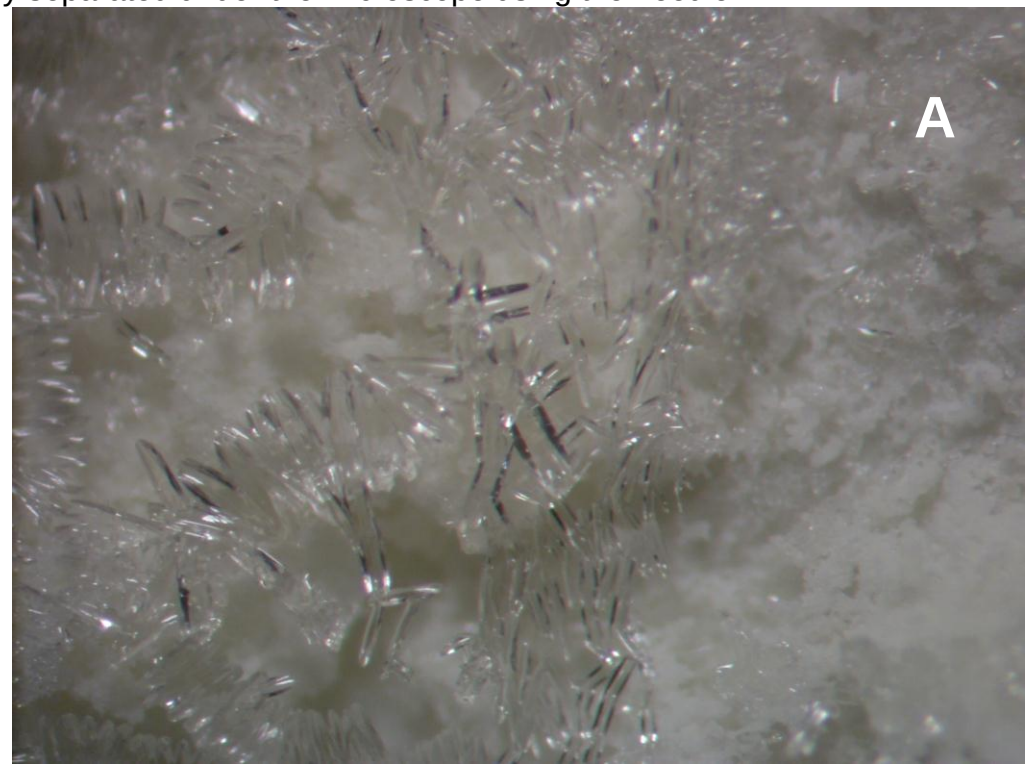
$Ag_2BiPipCO \times 2H_2O$, **5**

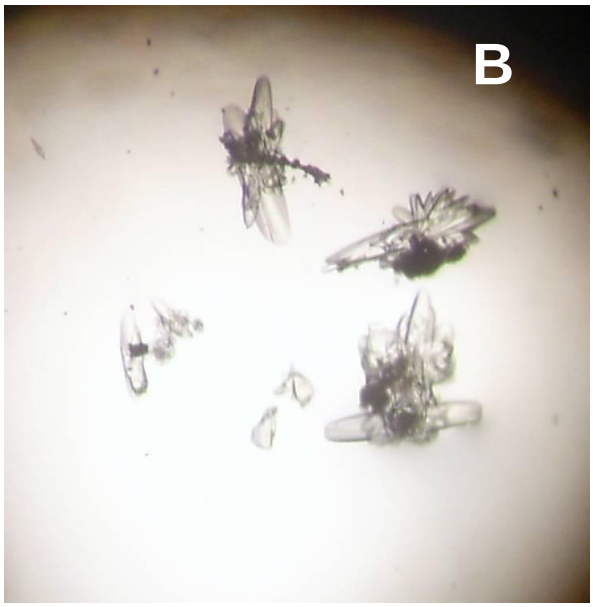
$NiBiPipCO \times 4H_2O$, **6**

$PdBiPipCO \times 4H_2O$, **7**

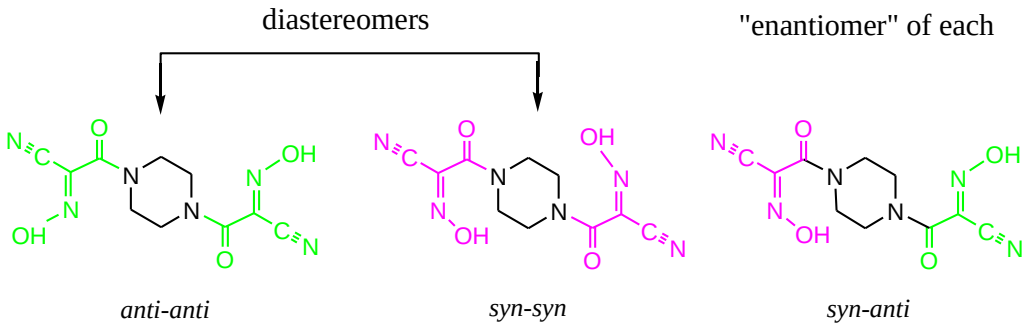
$PtBiPipCO \times 5H_2O$, **8**

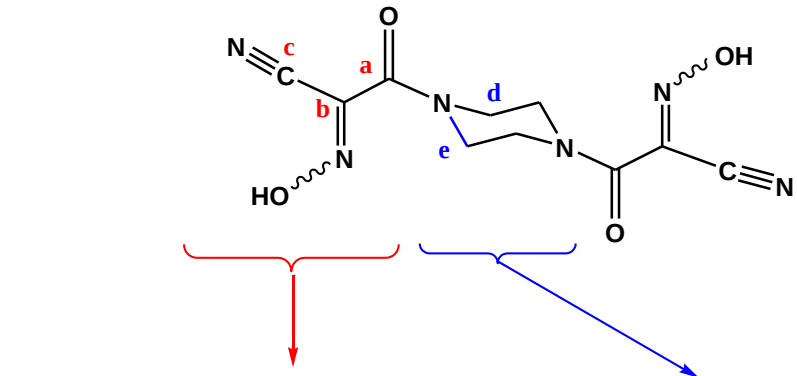
A - Solid mixture obtained after prolonged evaporation of solvent mixture (H_2O/EtOH) from solution of **2**. Actual photographs of crystals of the 51.2 % : 48.80% mixture of syn-/anti-geometrical isomers of **2** (**B**), and amorphous powder of almost pure anti- isomer (**C**). Both were easily separated under the microscope using the needle.





A – The relationship between three geometrical isomers of **2**.
B – A guide to the explanation of complexity and interpretation of the $^{13}C\{^{1}H\}$ NMR spectra of the new dioxime.





3 carbon atoms: amide, oxime, nitrile

6 lines in ^{13}C NMR spectra due to the presence of two geometrical isomers: anti- (major) and syn- (minor)

these carbon atoms are NOT sensitive to the boat/chair conformational changes on the piperazine ring

2 non-equivalent carbon atoms due to different positions relatively to the >C=O group

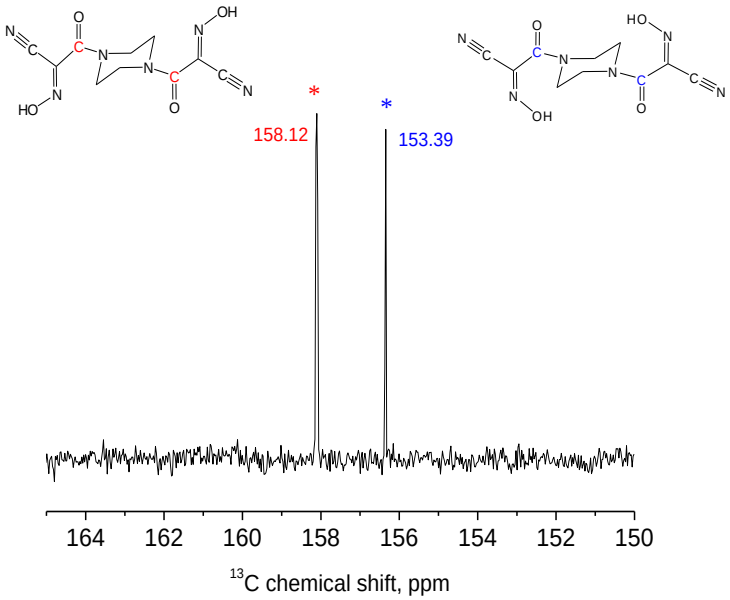
12 lines at room temperature due to 6 possible conformations of the piperazine ring (boat/chair) in 3 geometrical isomers:syn-syn, anti-anti and syn-anti. as depicted in Scheme 6

these carbon atoms ARE sensitive to syn-/anti-isomers because "swinging" oxime group comes in proximity of the piperazine ring.

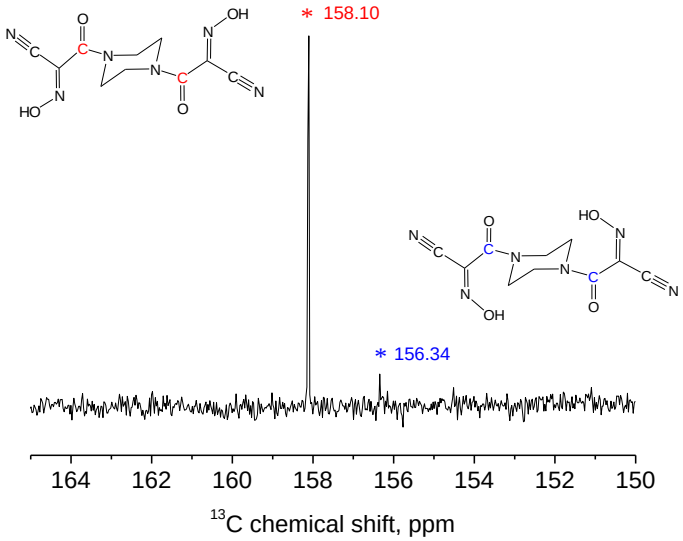
not very sensitive to the temperature change since the energy barrier between two isomers is too high

sensitive to the temperature change due to attainable energy barrier between boat/chair ring conformations

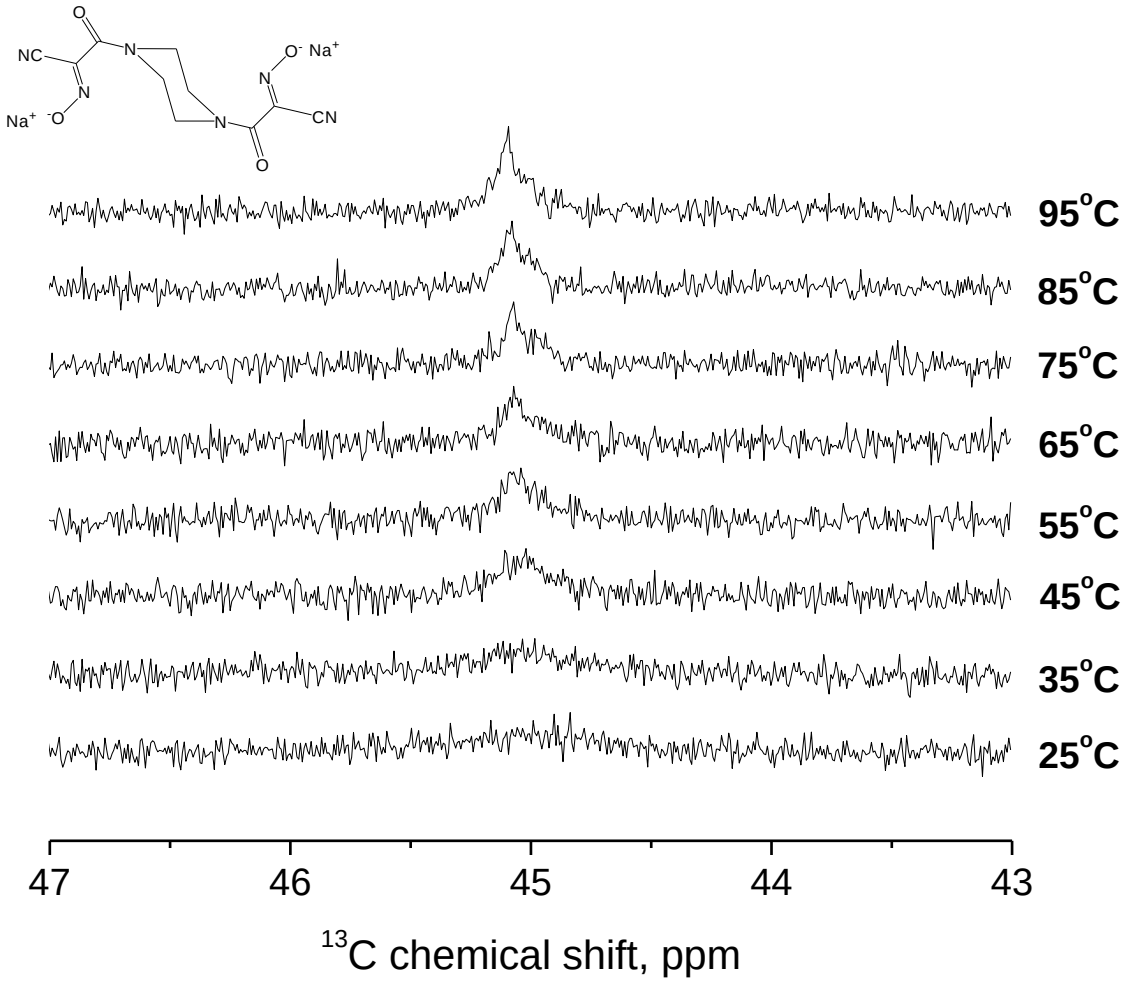
A - fragment of $^{13}C\{^{1}H\}$ NMR spectra of dmso-d_6 solution of clear crystals of **2,** that represent spontaneously crystallized 51.2 % : 48.80% mixture of syn-/anti- geometrical isomers; NT = 72,000 repetitions. *The area of the amide sp^2 carbon atom is shown in both spectra.*



B - fragment of $^{13}C\{^{1}H\}$ NMR spectra of dmso-d_6 solution of amorphous white powder of predominantly anti- isomer of **2**. A small “impurity” of the syn- isomer (blue), perhaps, is due to the inclusion of microcrystals of the enriched (syn-51.8 % : anti-48.2 %) mixture into the white powder; 70,000 accumulations (repetitions).



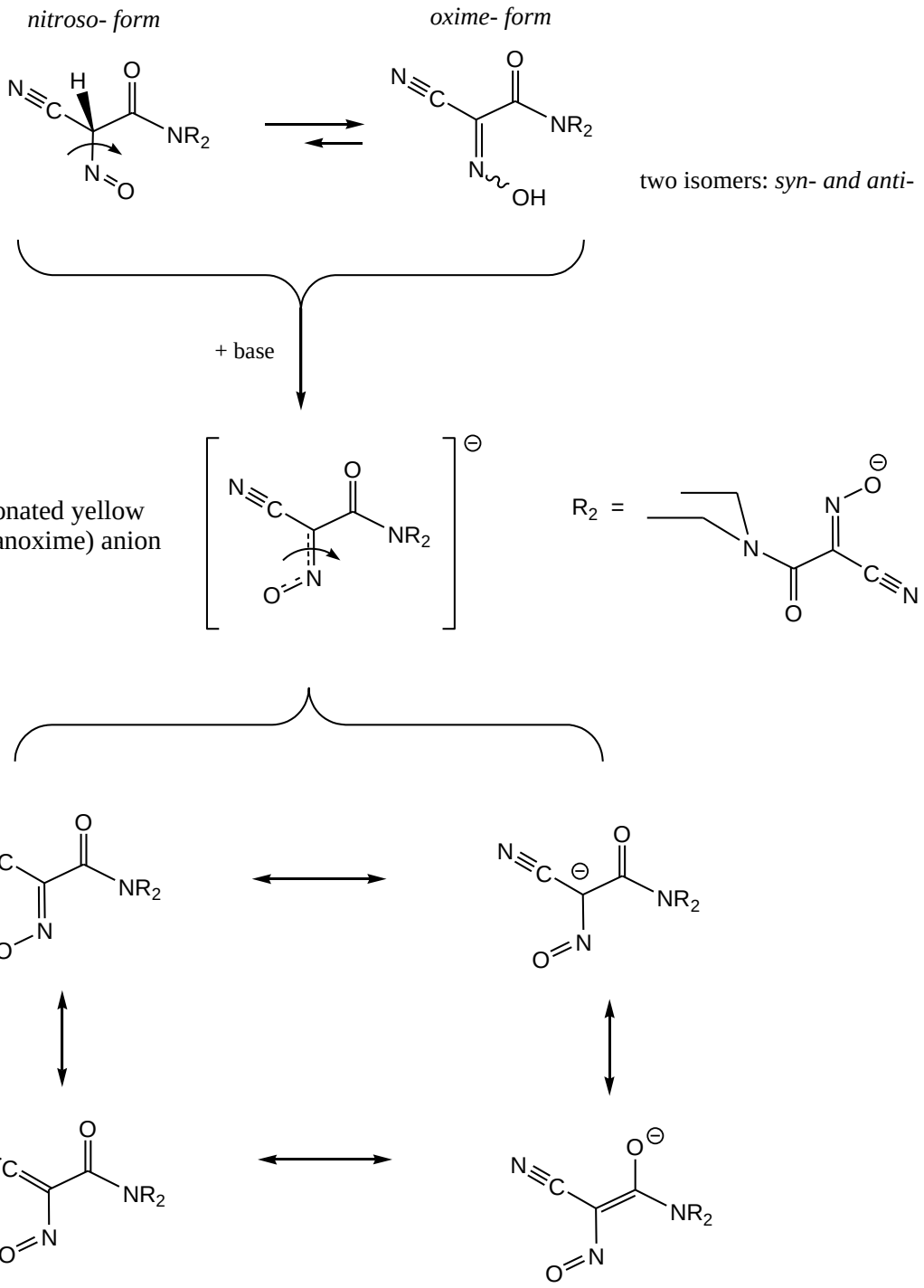
Stacked plot of fragments of $^{13}C\{^{1}H\}$ NMR spectra of **3** in the region of -CH_2- groups in DMSO-d_6 solution at variable temperatures.



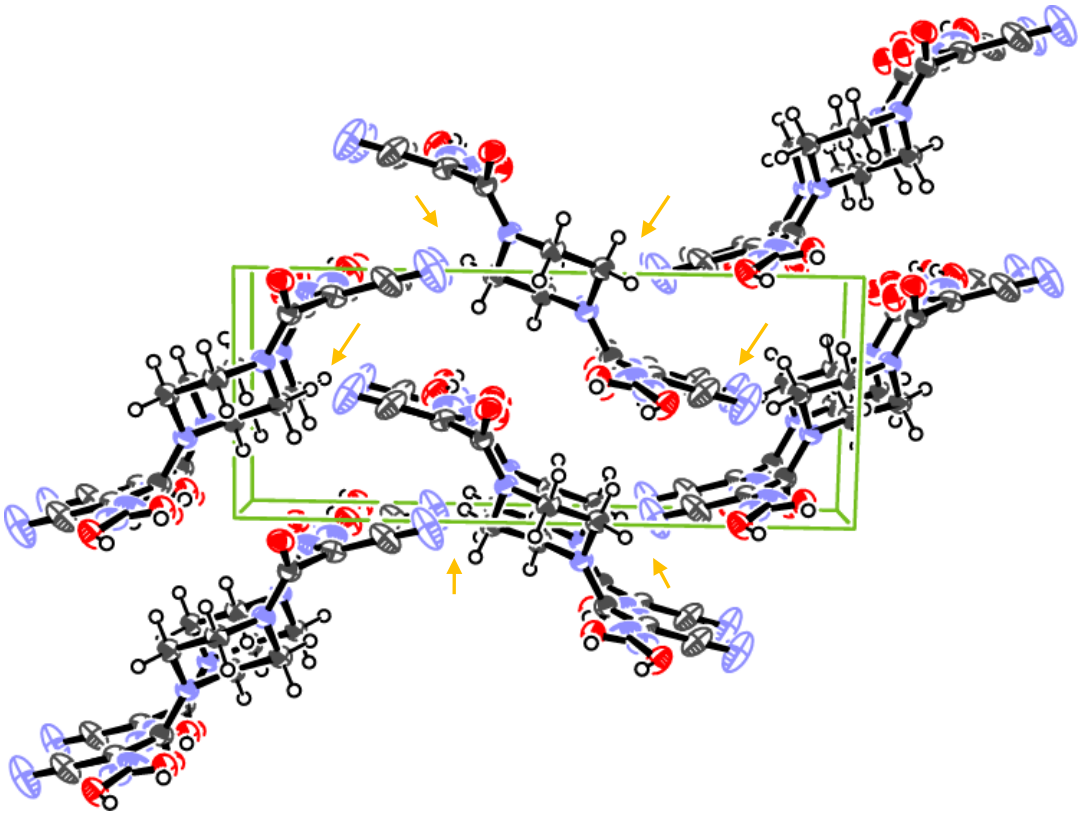
The disodium salt 3 generates 13C{1H} NMR spectra that suggest that the piperazine-ring in the dianion is much more flexible. At lower temperatures, the molecule's 'ring-flips' occur at a rate slower than the instrument's sampling time (a slow exchange region), giving a broad peak of a low intensity. At higher temperatures the exchange rate of ring-flipping is faster than the instrument's sampling time, and an increasingly sharp peak is observed (fast exchange region). Because the oxime group in the anion has a significantly different redistribution of electron density and exists also in the nitroso- form, it can freely rotate with minimal interaction with the piperazine ring. This causes the piperazine group to be very fluxional in 3 in contrast to the more rigid structure in 2, with steric interactions between the protonated oxime group in syn- and anti- isomers in the ligand 2.

Complete deprotonation of the compound and delocalization of negative charge in the dianion formed.

Protonated colorless *bis*-(cyanoxime), **2**:



Packing diagram in the structure of H_2BiPipCO: perspective view along *a*-axis. A system of puckered stacked ribbons (for example **I**, **II** and **III**) of molecules with intermolecular H-bonding is interconnected by means of van-der-Waals forces and electrostatic contacts between nitrogen atoms of the cyano-groups and methylene hydrogen atoms of the piperazine fragments at 2.550 and 2.747 Å (indicated by yellow arrows).



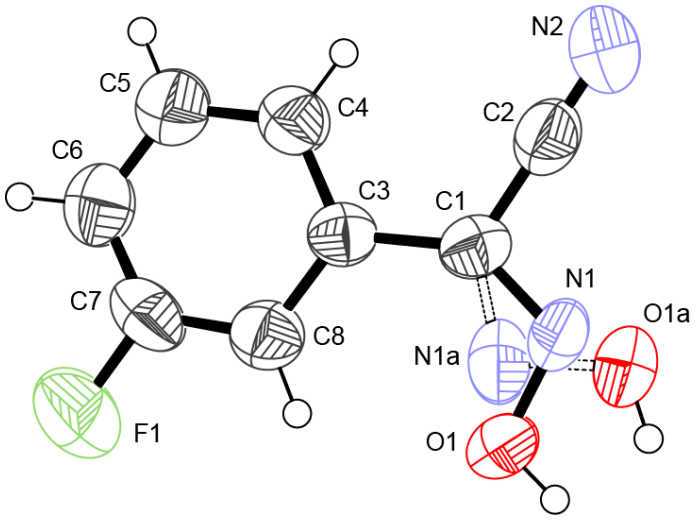
Hydrogen bonds for H_2BiPiPCO [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#2	0.84	1.85	2.680(5)	170.0
O(1A)-H(1A)...O(2)#2	0.84	1.86	2.648(6)	155.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2 #2 x-1,y,z

Molecular structure and numbering scheme for H(3F-PhCO) (**A**). An ORTEP drawing at 50% thermal ellipsoids probability level. Data from: *Inorganic Chemistry*. **2005**, *44* (23), 8326-8342.

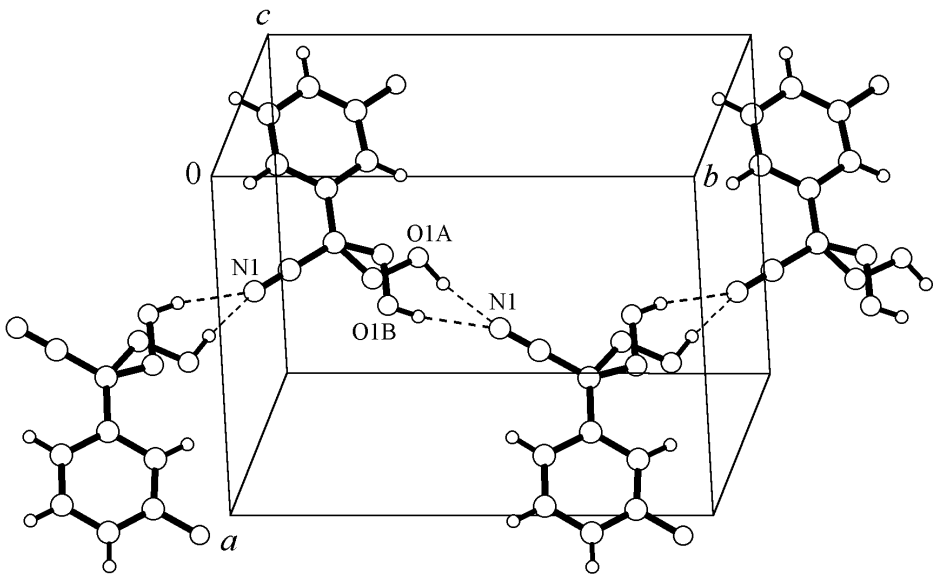
A



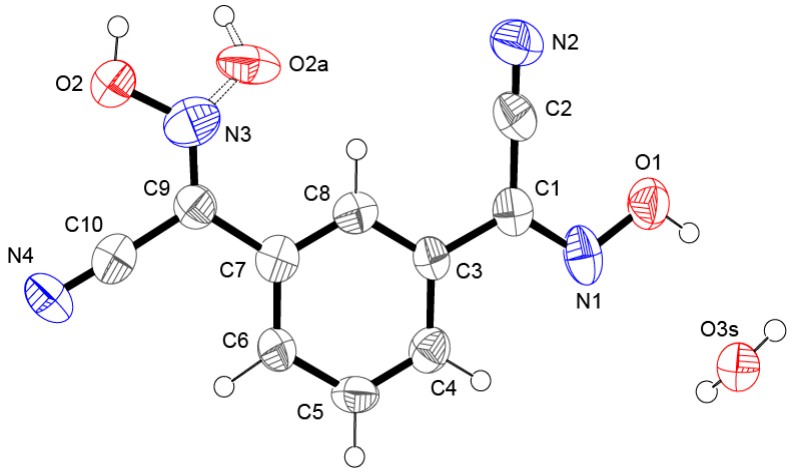
Parameters: P2(1)/c, #14; T=296 K; R1=0.0668, wR2=0.1345; GOF=1.008

There are two geometrical isomers *syn*- (58.4 %) and *anti*- (41.6%) that co-crystallized in the same lattice due to practically identical H-bonding pattern between the oxime fragment and cyano-group of neighboring molecule in the chain that dictates packing in the crystal (**B**).

B

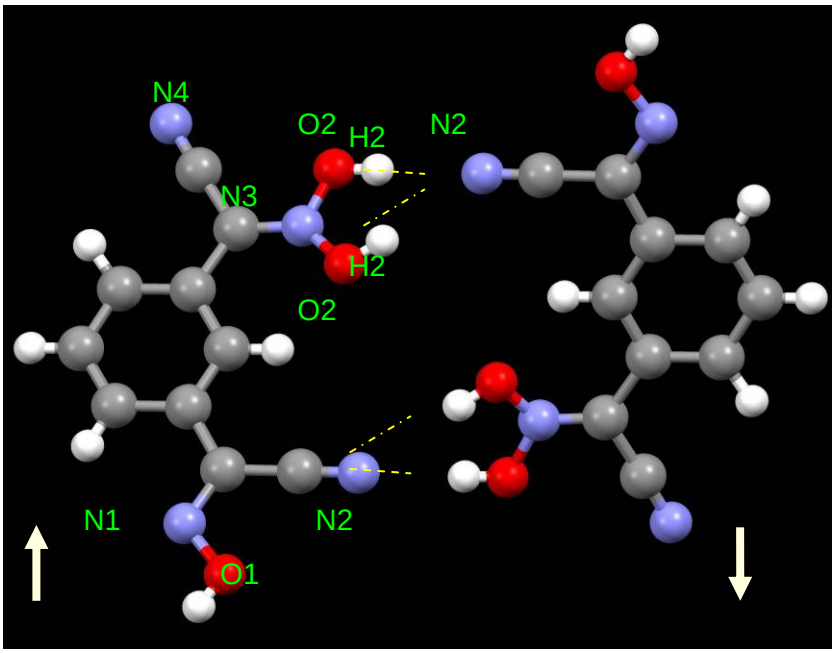


Molecular structure and numbering scheme for H_2(1,3-BCO), monohydrate (**A**). An ORTEP drawing at 50% thermal ellipsoids probability level. Data from: *Crystal Engineering Communications*. **2012**, DOI 10.1039/c2ce26395e.

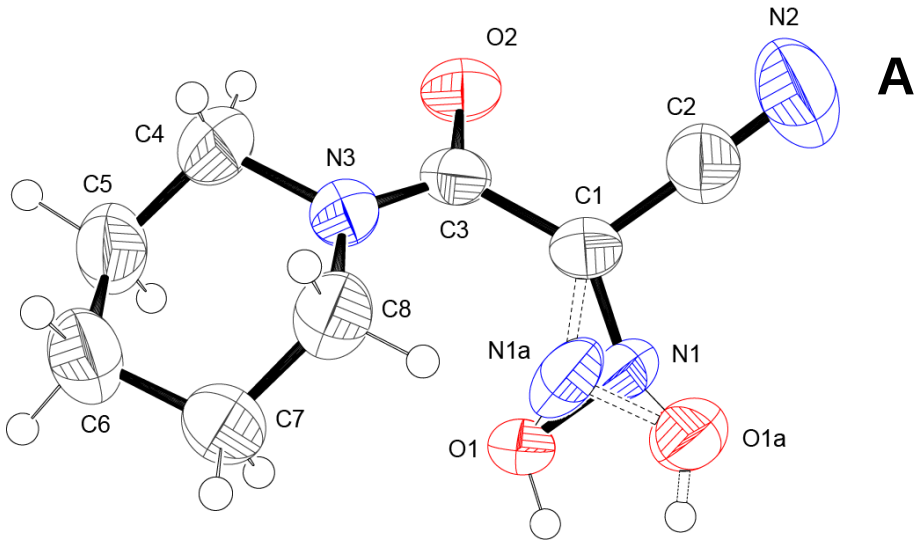


Parameters: Fdd2, #43; T=150 K; R1=0.0600, wR2=0.1413; GOF=1.037

Again, there are two geometrical isomers *syn*- (14.1 %, dashed line) and *anti*- (85.9 %, solid line) that co-crystallized in the same lattice due to similar H-bonding pattern between the oxime fragment and cyano-group of neighboring molecule in the adjacent layer that defines the packing in the crystal (**B**).

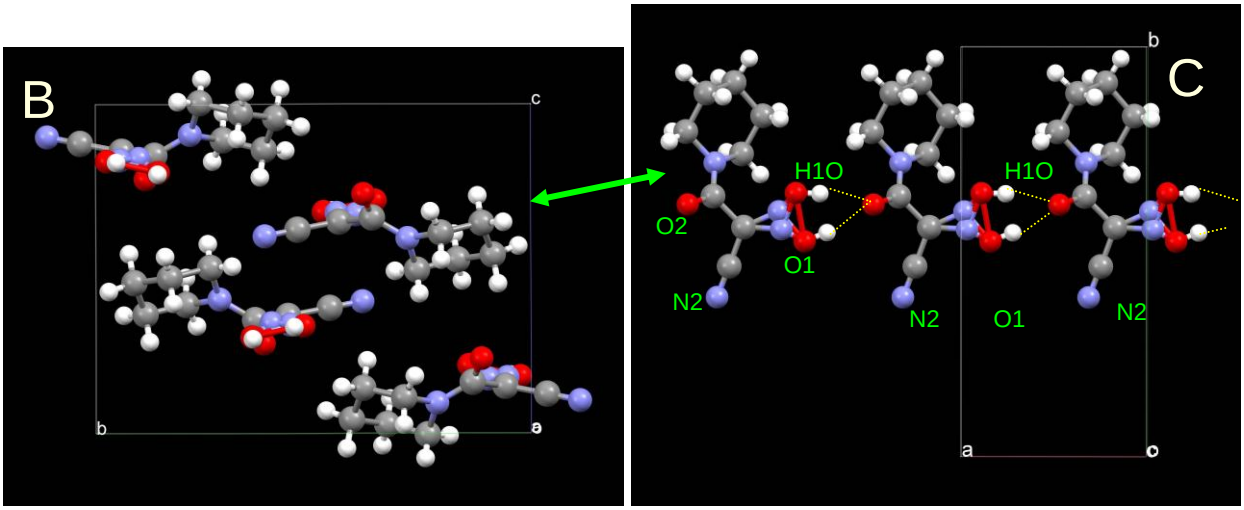


Molecular structure and numbering for "totally disordered" H(PipCO) (**A**). An ORTEP drawing at 50% thermal ellipsoids probability level. Two isomers – *syn*- (62.4%, solid lines) and *anti*- (37.6%, dashed lines) co-crystallized in the same lattice. The CCDC # is 910552.



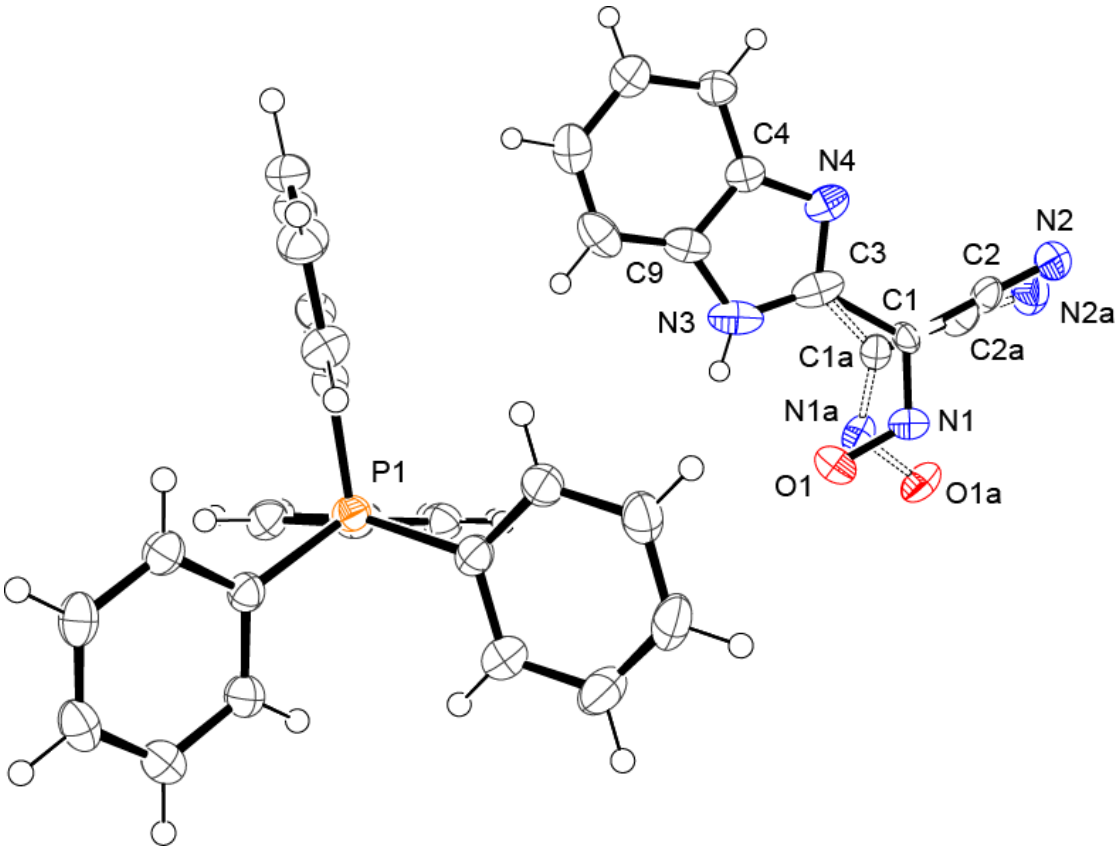
Parameters: P2(1)/c, #14; T=296 K; R1=0.0490, wR2=0.1176; GOF=1.012

Two orthogonal views of the structure of H(PiPCO): **B** – prospective view of the unit cell content along *a*; **C** - top view (along *c)* of one of the layers (indicated by green arrow) in the structure; yellow dots show almost identical for both geometrical isomers H-bonding responsible for crystal packing.



Molecular structure and numbering scheme for $P(C_6H_5)_4^+$ $BIHCO^-$. An ORTEP drawing at 50% thermal ellipsoids probability level. The ligand in this tetraphenyl-phosphonium salt is 2-cyanoxime-benzimidazole abbreviated as BIHCO (see Ilkun, O.T.; Archibald, S.; Barnes, C.L.; Gerasimchuk, N.; Biagioni, R.; Silchenko, S.; Gerasimchuk, O.A.; Nemykin, V. "Benz(2-heteroaryl)cyanoximes and their Tl(I) complexes: new room temperature blue emitters.", *Dalton Transactions*, **2008**, p.5715-5729).

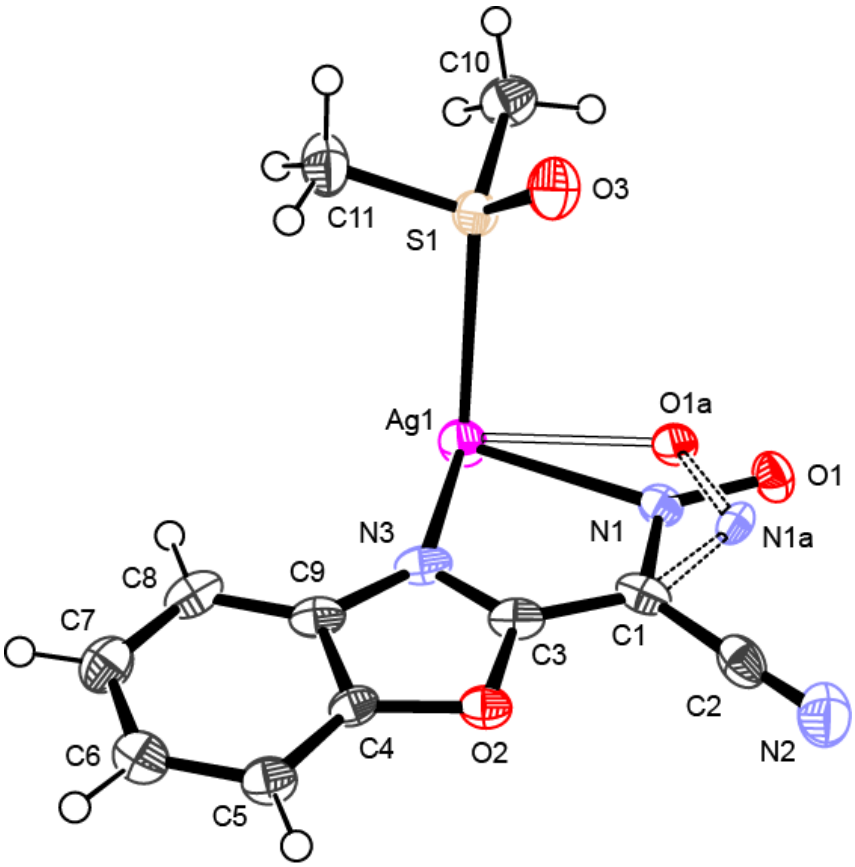
Two geometrical isomers of the deprotonated cyanoxime anion – $BIHCO^-$ - are shown: 58.3 % belong to the *syn*- isomer, while 41.7 % contributed from the *anti*- isomer. The CCDC # is 910553.



Parameters: P2(1)/n, #14; T=120 K; R1=0.0478, wR2=0.0981; GOF=1.015

ASU in the structure of Ag(BOCO)x(DMSO) showing “disordered” NO-group in the complex, which in reality represents two geometrical isomers of the complex that co-crystallized in one lattice. Thus, the cyanoxime anion here present as *anti*- and *syn*- isomers (83% and 17% respectively). An ORTEP drawing at 50% thermal ellipsoids probability level.

Data from: **Jeffrey Morton**, MS Thesis “*Further Investigations of Silver(I) Cyanoximates*”, 138 pp., Department of Chemistry, Missouri State University, 2010. The CCDC # is 910555.



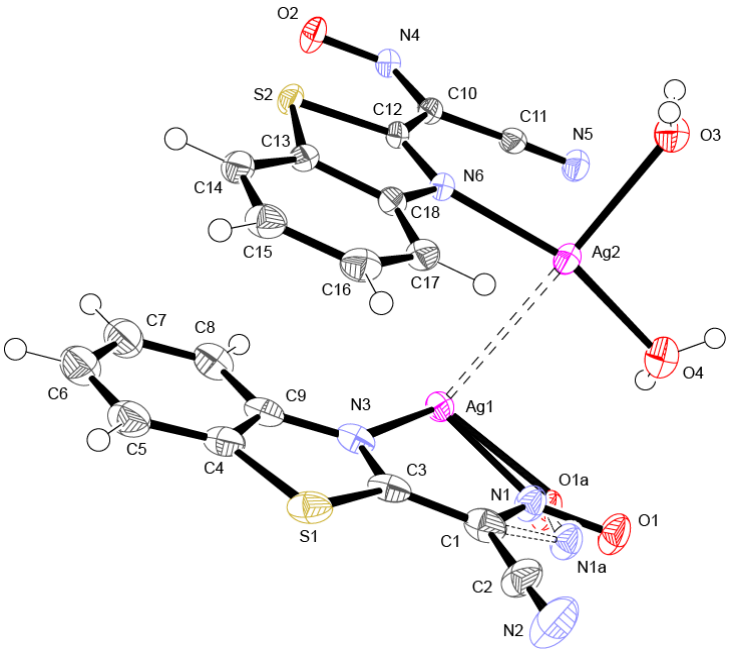
Parameters: P-1, #2; T=120 K; R1=0.0354, wR2=0.0607; GOF=1.018

The ASU in the structure of Ag(BTCO)x(H_2O) showing atomic numbering scheme (A). "Disordered" nitroso-group of one of the anions is displayed in dashed lines. The "disorder" is related to coexistence of *anti*- (70.3 %) and s*yn*- (29.7 %) isomers of one of the anions. The second anion is *ordered* and adopts exclusively *syn*- geometry. There is also a short intermetallic Ag---Ag distance of 3.055 Å.

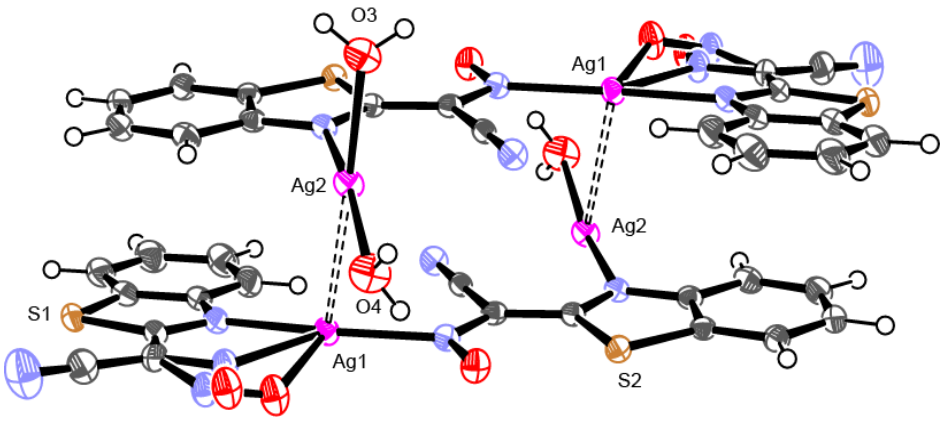
Data from: **Jeffrey Morton**, MS Thesis "*Further Investigations of Silver(I) Cyanoximates*", 138 pp., Department of Chemistry, Missouri State University, 2010.

Parameters: P-1, #2; T=163 K; R1=0.0421, wR2=0.1077; GOF=1.041.

The CCDC # is 910554.



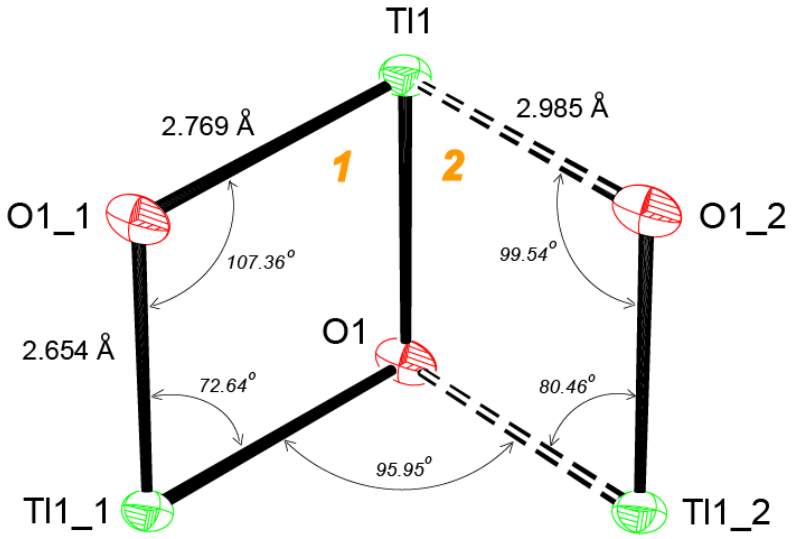
The "building block" of the crystal structure of [Ag(BTCO)· Ag(BTCO) · 2H_2O]: tetrameric unit. An ORTEP drawing at 50% thermal ellipsoids probability level.



Large Dewar flask filled with 4.5 L of hot water at +95^{o}C. Solution of Tl_2BiPipCO (**4**) was filtered hot into the large-mouth test tubes immersed into hot water and left for slow cooling within 5-6 days. The tube was suspended inside the Dewar all the time. Needle-like crystals appeared on the wall of the tube. Some of the crystals were suitable for the X-ray analysis.

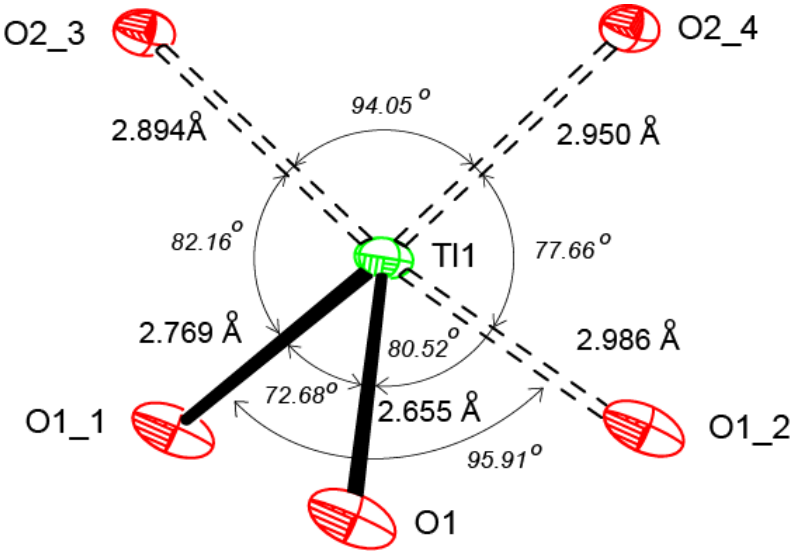
Details of geometry of two adjacent and slightly different Tl_2O_2 rhombs in the structure of **4** (**A**), and geometry of coordination polyhedron of Tl(I) in the structure of **4** (**B**).

A



Tl1 - Tl_1 = 4.369 Å
Tl1 - Tl_2 = 4.310 Å
Tl1_1 Tl1_2 = 4.276 Å

B



Symmetry operations for #1: 2-x, 1-y, 1-z; for #2: 1-x, 1-y, 1-z;
#3: 2-x, ½+y, 3/2-z; #4: 1-x, ½+y, 3/2-z.