Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION for the paper:

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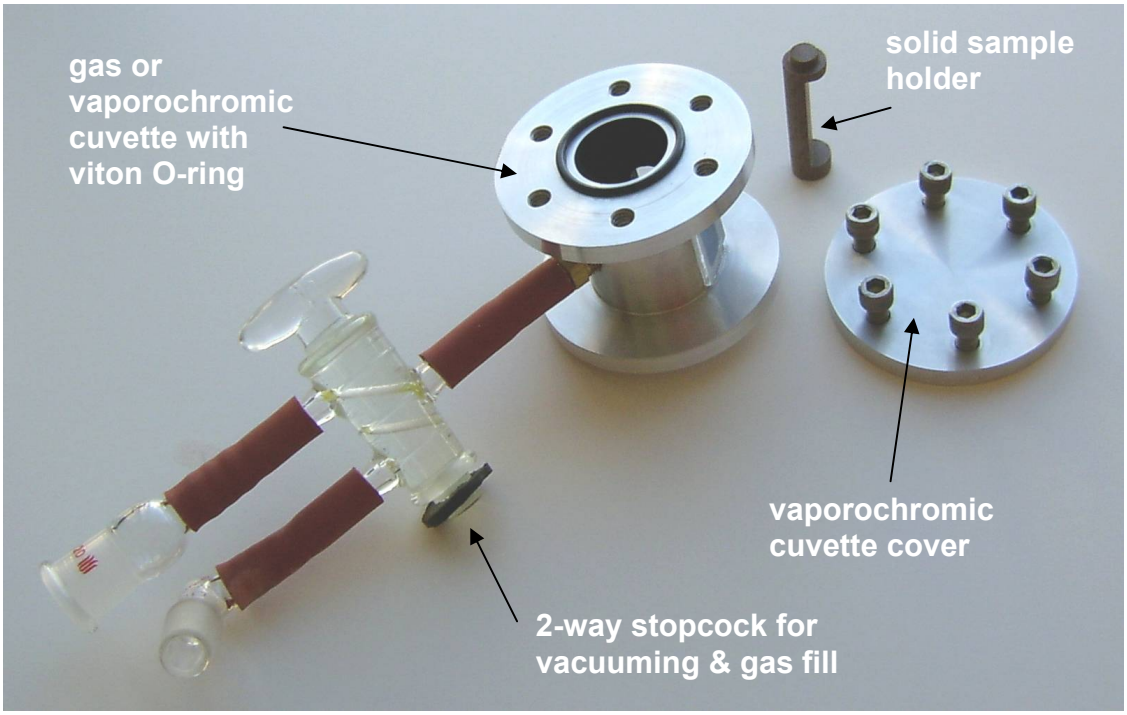
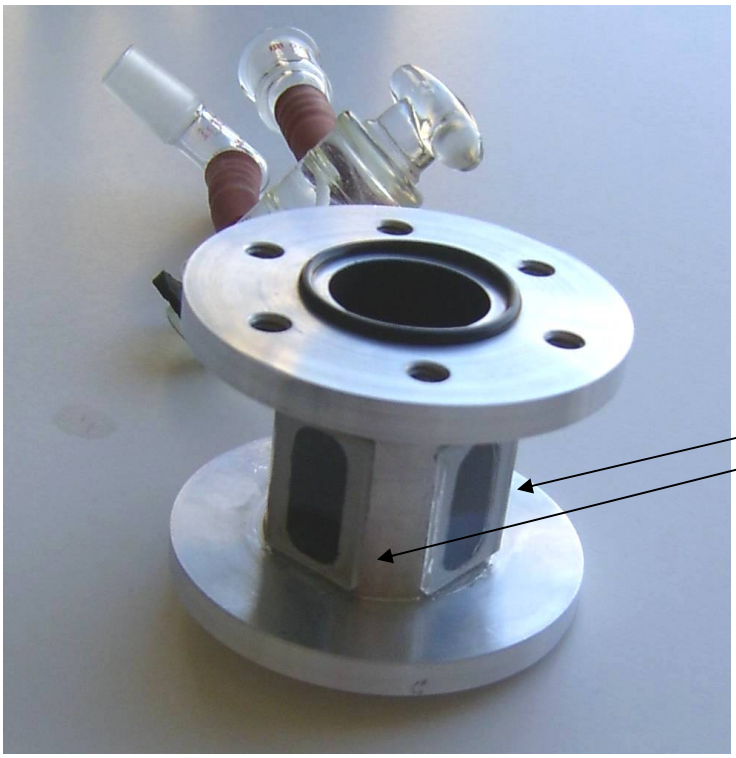
by Nikolay Gerasimchuk, Andrey N. Esaulenko, Kent N. Dalley and Curtis Moore

ESI S1 Designed cuvette for studies of influence of different gases on photoluminescence of solid metal complexes.





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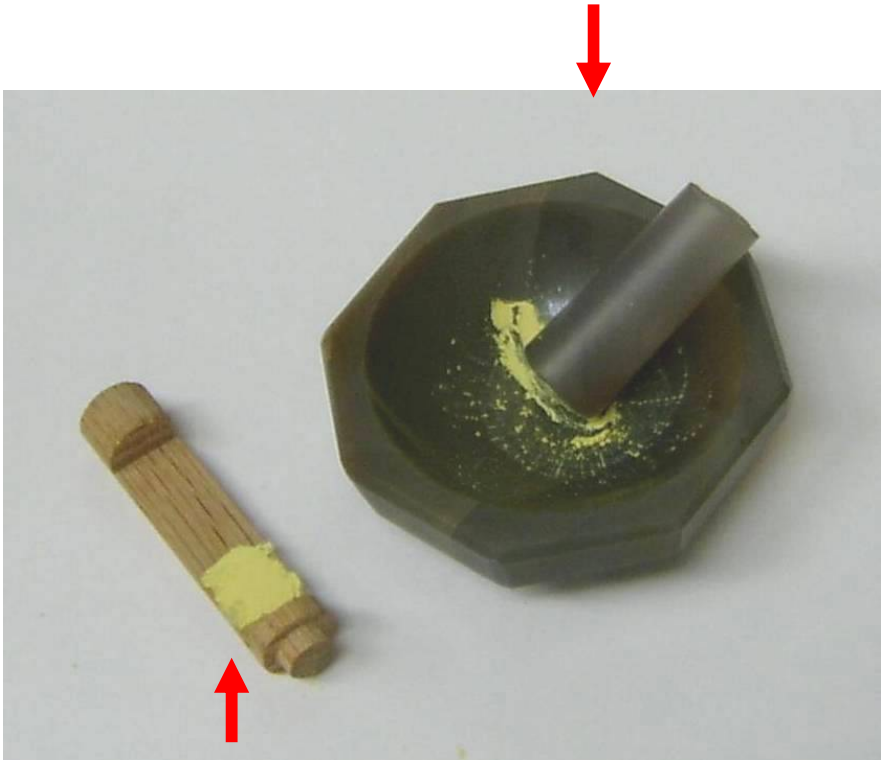
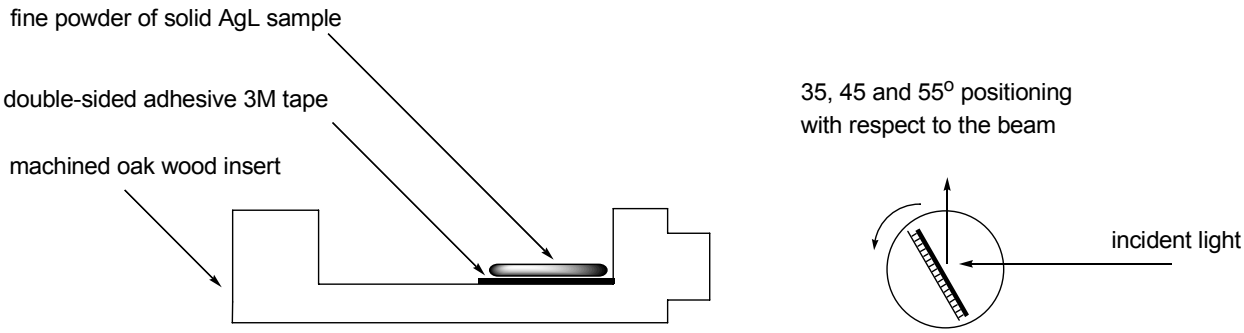
ESI S2 Experimental setup for room temperature solid state photoluminescence measurements.

Agate mortar and pestle used for fine grinding of solid Ag(I) 2-cyano-2-isonitroso-acetamide complex 6 prior to room temperature fluorescence measurements.



An insert (oak wood) that was placed into the cuvette holder for solid state fluorescence measurements. Oak wood was chosen because of its own low light reflectivity and good adhesion to the tape.



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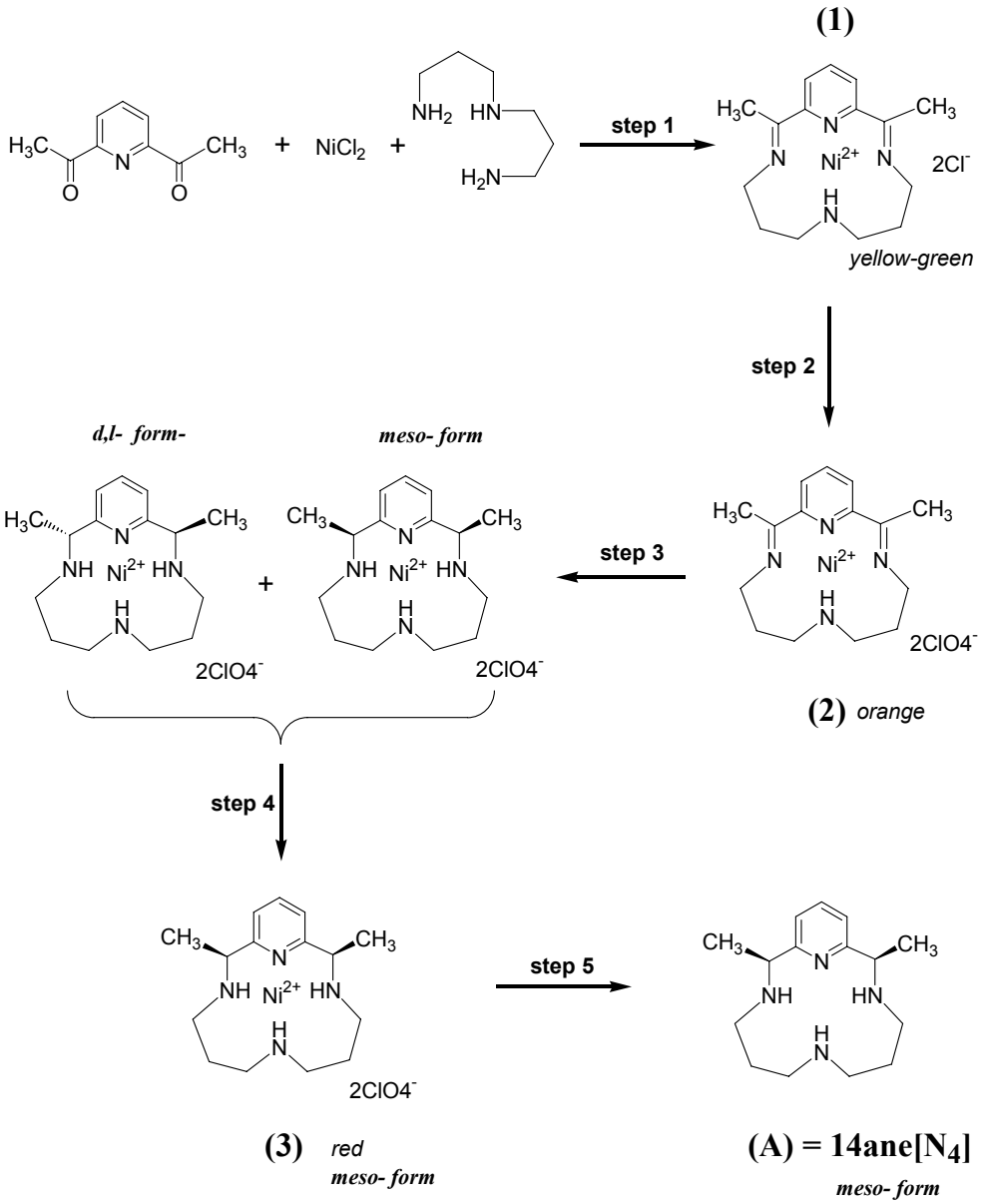
ESI S3 Scheme for synthesis of the macrocyclic ligand **2.**



Step 1: Template condensation. Step 2: Ligand exchange reaction. Step 3: Reduction of the ligand in complex **3**. Step 4: Separation of the two reduced isomeric Ni(II) macrocyclic complexes by multistep crystallization. Step 5: Demetallation reaction.

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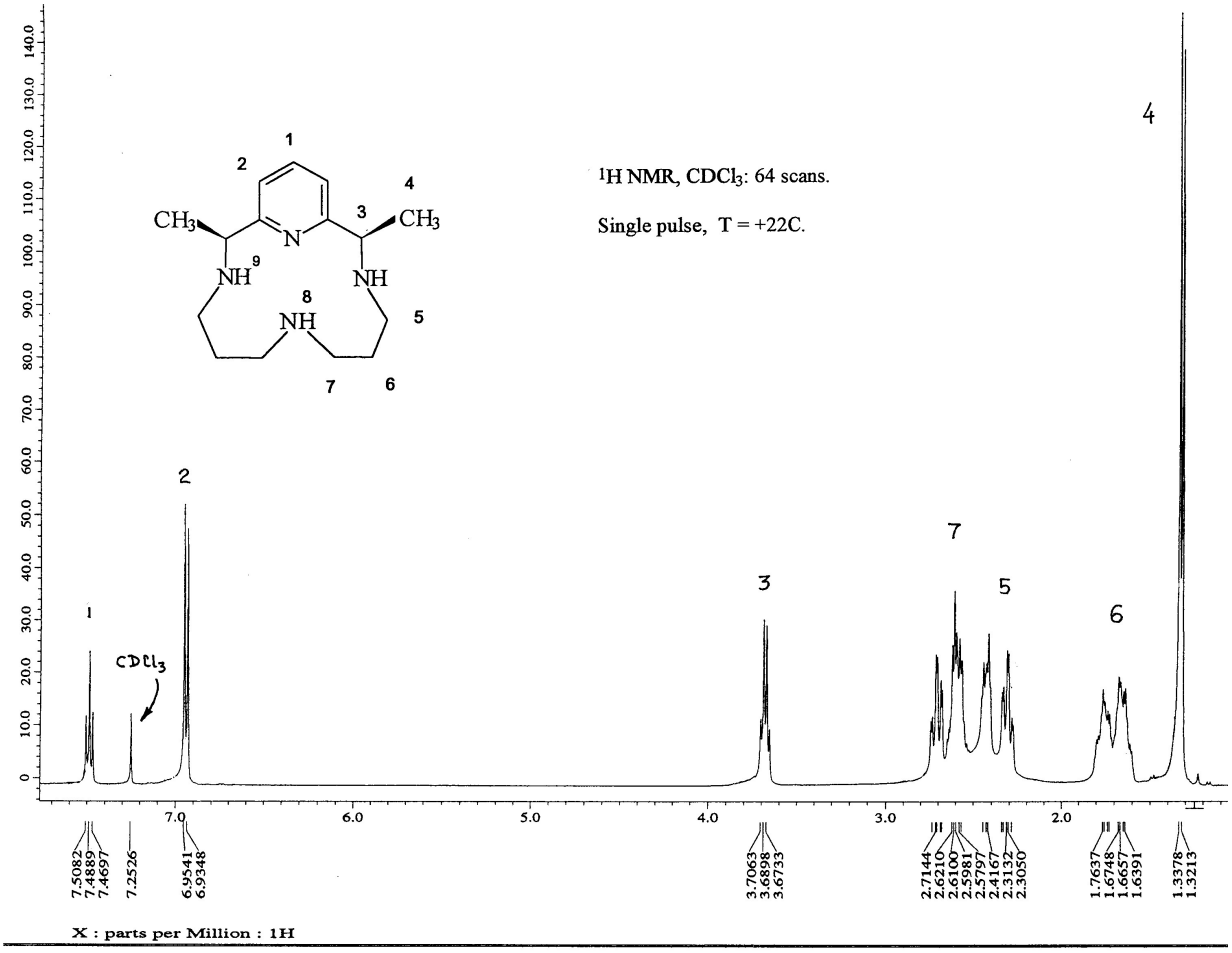
ESI S4 Fragment of ^{1}H NMR spectrum of pure *meso*-form of the macrocyclic ligand **2.** Signals of the amine protons *8* and *9* are broadened beyond detection at these conditions.



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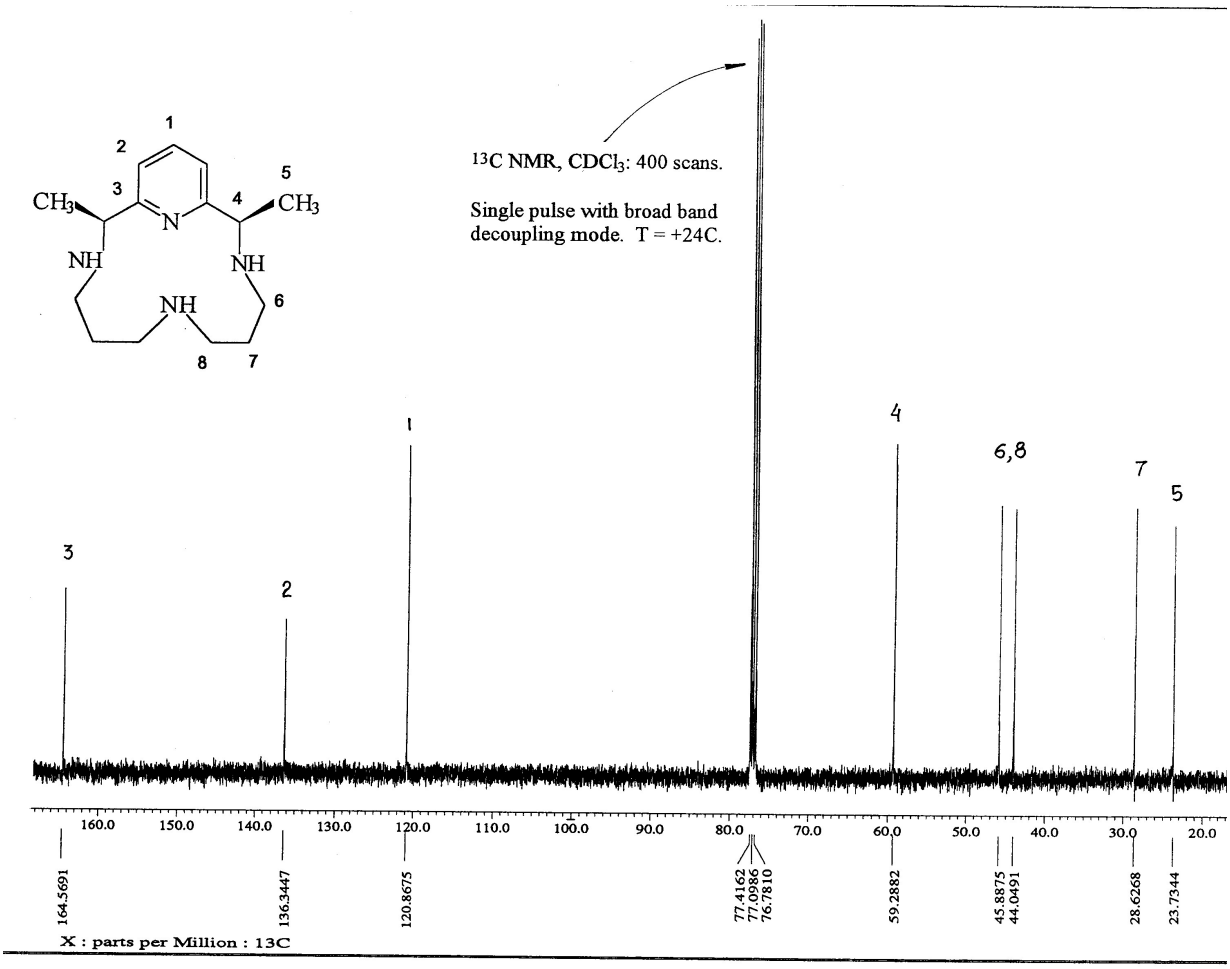
ESI S5 Fragment of $^{13}C\{^{1}H\}$ NMR spectrum of pure *meso*-form of the macrocyclic ligand **2.**



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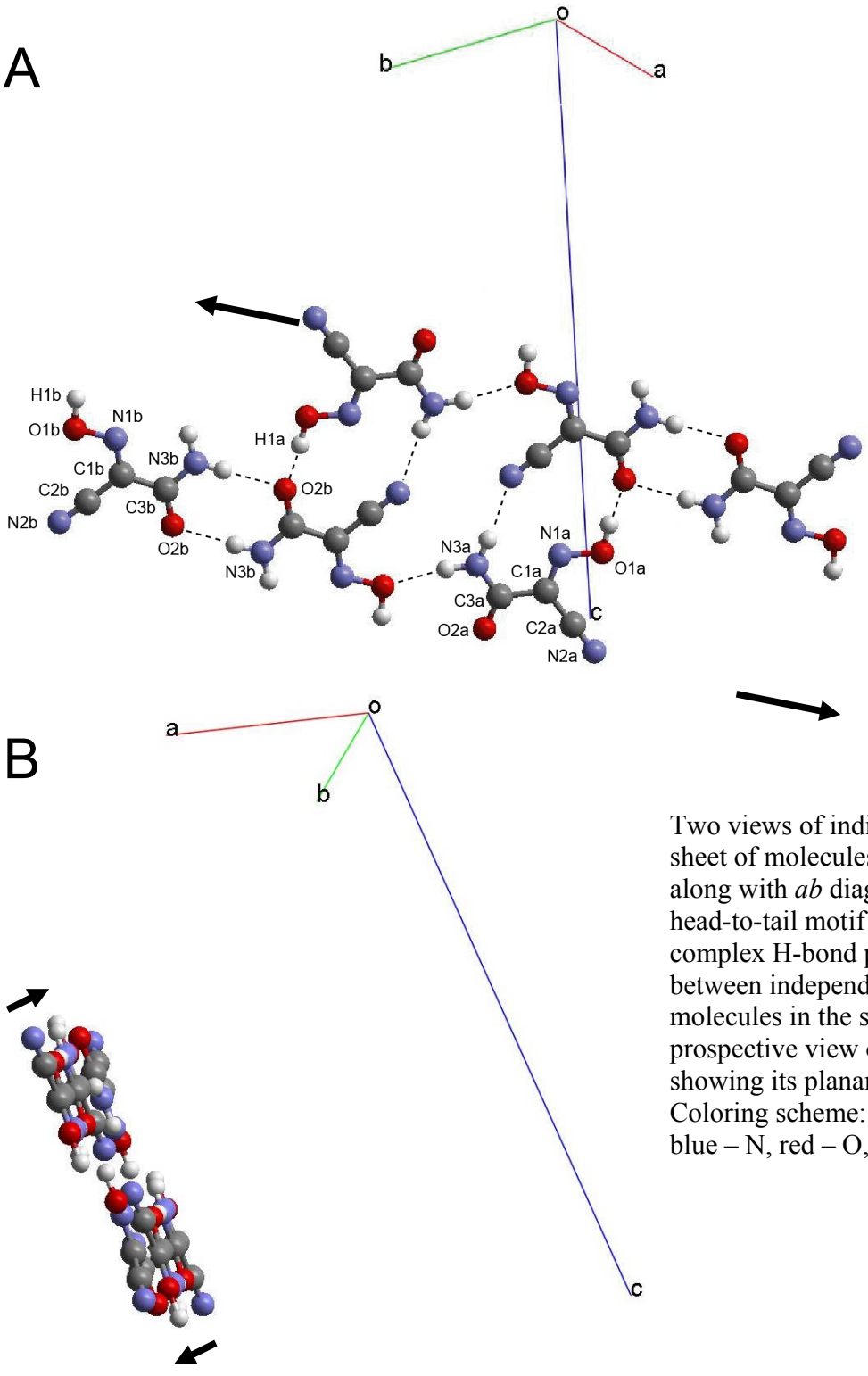
ESI S6 Fragment of crystal packing of **1.** Coloring scheme: red – O, blue – N, grey – C, white – H.



Two views of individual planar sheet of molecules running along with *ab* diagonal. **A** – head-to-tail motif showing a complex H-bond pattern between independent ***a*** and ***b*** molecules in the sheet; **B** – prospective view of the sheet showing its planarity. Coloring scheme: grey – C, blue – N, red – O, white – H.

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ESI S7 Details of crystal structure determination for **6**.

Now when the structure of **6** has been reliably determined, it is understandable why it was so difficult to gather structural information about this particular complex. Complex **6** always was crystallizing as very thin plates regardless of method of crystals growth, and this caused significant problems in selection of a suitable specimen for structural characterization. Eventually, after careful screening of six batches of crystalline material, somewhat satisfactory looking specimen was identified and data set for this crystal was collected at 120 K with 120 seconds of exposure time per image. However, despite all efforts selected crystal of **6** still turned out to be a non-merohedral twin. The crystal was indexed by harvesting reflections over the entire data collection, and with the use of the CELL_NOW program it was possible to determine the twin law: -0.9998 0.00030 0.00010 -0.00033 -1.0000 0.00007 0.36296 0.00014 0.99998. The data was integrated using both unit cells, and the TWINABS program was applied for absorption correction and refinement of reflections data. A total of 996 reflections (BASF = 0.374) were used for the successful structure solution of **6**.

The shear plane of the crystal is at *a/2* and that is where H-bonding between 2D sheets occurs (see S8 below). The analysis of the crystal structure of **6** and the identification of the shear plane explain why it was very difficult to grow single crystals suitable for the X-ray analysis: there is a significant degree of freedom in alignment of 2D sheets in the *0bc* plane that lead to: a) the formation of very thin plates impractical for the collection of a reliable data set, b) the greater possibility for twinning or formation of multidomain species.

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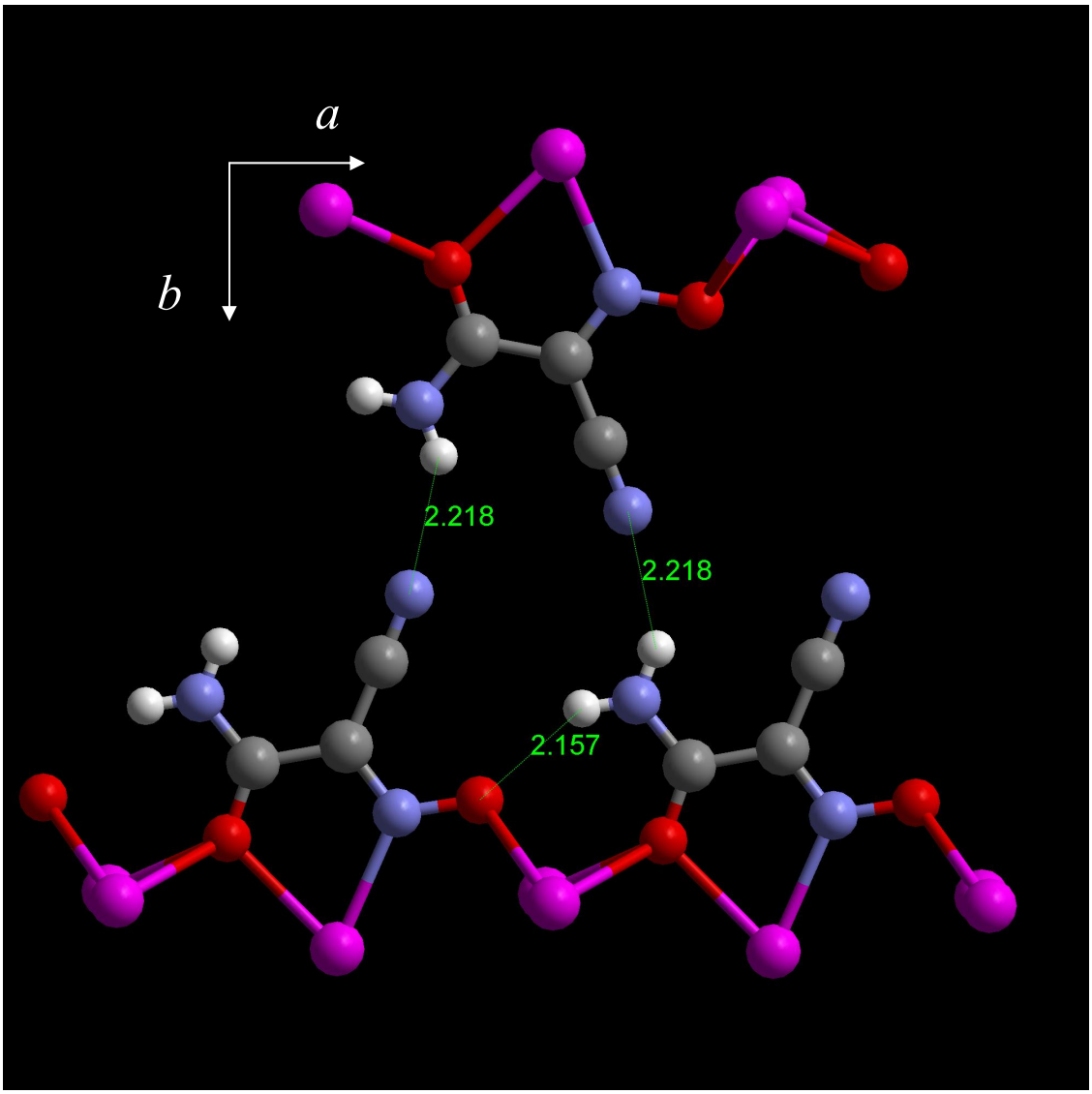
ESI S8 H-bonding in the structure of **6**. Fragment of the crystal structure viewed along ***c*** axis showing two sheets of 2D coordination polymer connected by an *inter-layer* hydrogen bond between only one proton of the amide group and nitrogen atom of the cyano-group. The second proton of the amide group is engaged into *intra-layer* hydrogen bonding with oxygen atom of the nitroso-group of neighboring cyanoxime anion.



Coloring scheme: magenta – Ag, red – O, blue – N, grey – C, white – H.

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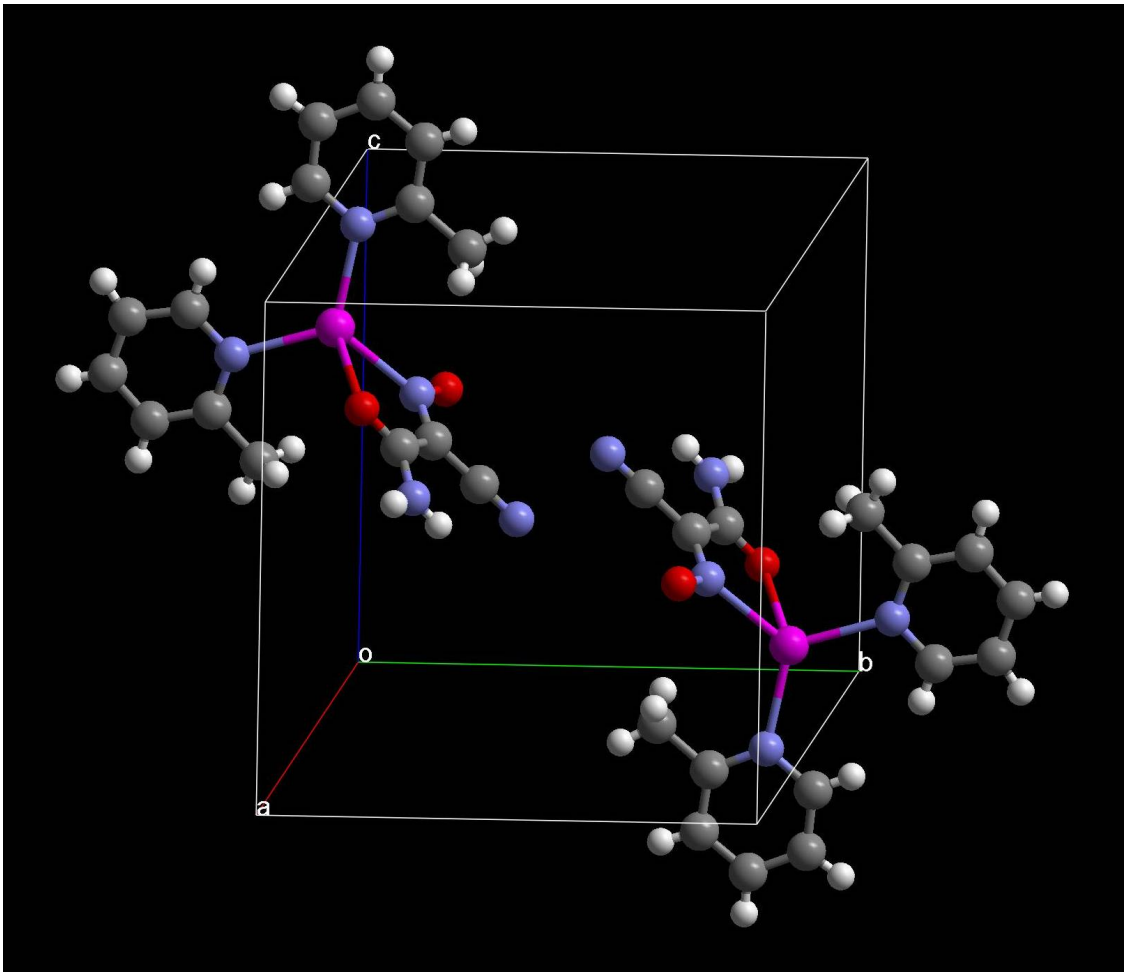
ESI S9 Unit cell content in the structure of **7**.

Coloring scheme: magenta – Ag, red – O, blue – N, grey – C, white – H.



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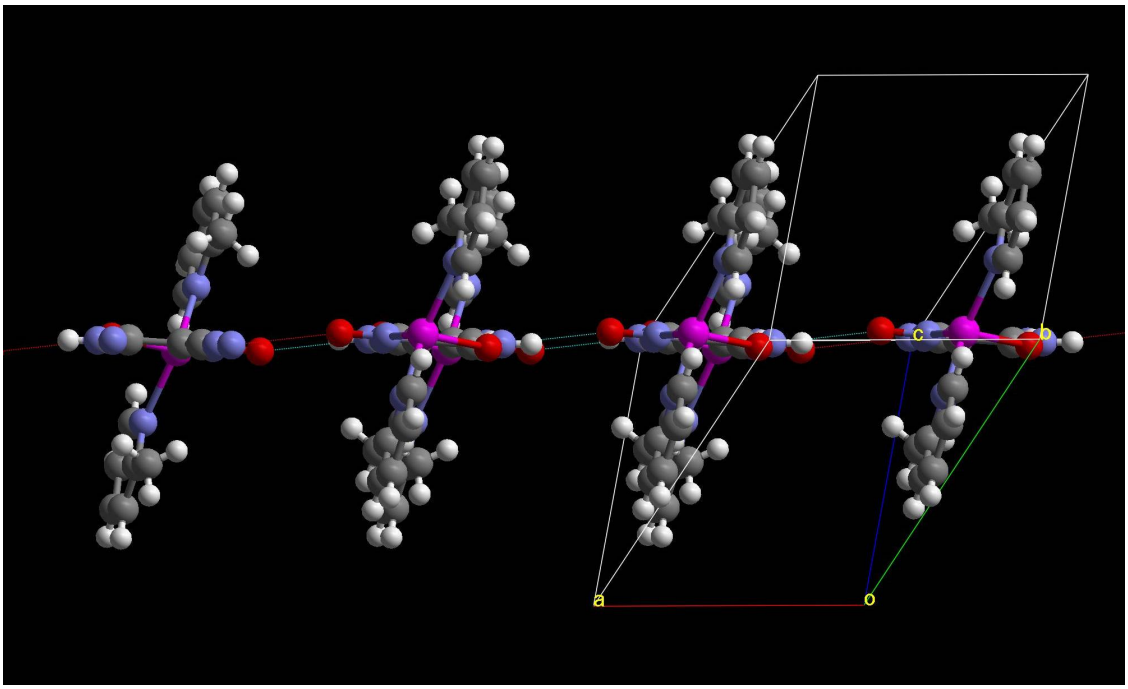
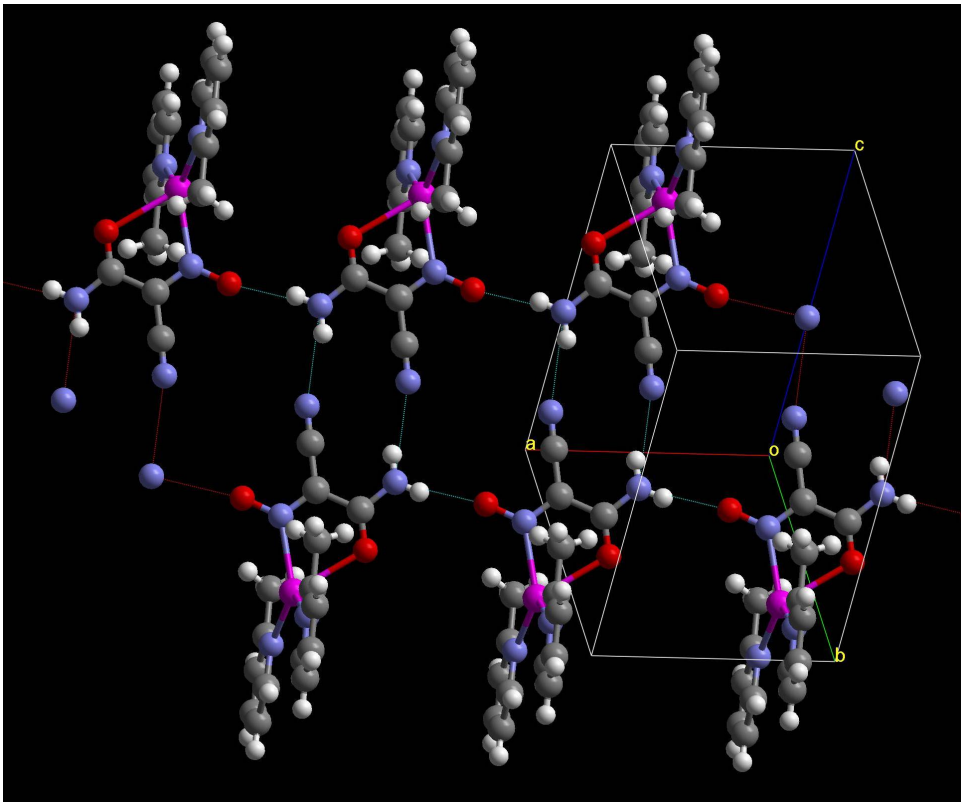
ESI S10 Crystal packing diagram for **7** showing extensive H-bonding: two views of the unit cell with neighboring molecules.





Coloring scheme: magenta – Ag, red – O, blue – N, grey – C, white – H.

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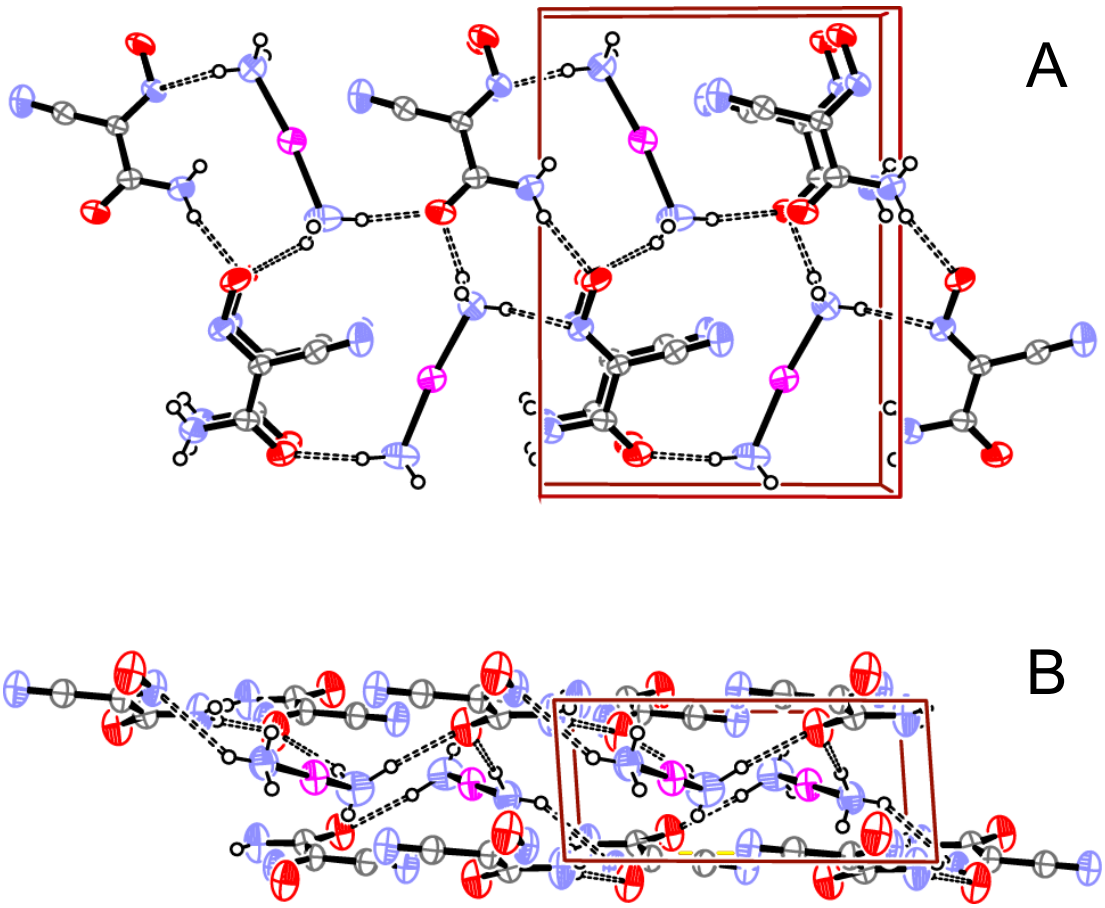
ESI S11 Fragments of crystal packing in the structure of **8**.



Two orthogonal projections of two adjacent unit cells in the structure of **8** showing extensive intermolecular H-bonding. **A** – side view, **B** – top view. An ORTEP representation at 50% thermal ellipsoids probability. Coloring scheme: magenta – Ag, red – O, blue – N, grey – C, white – H.

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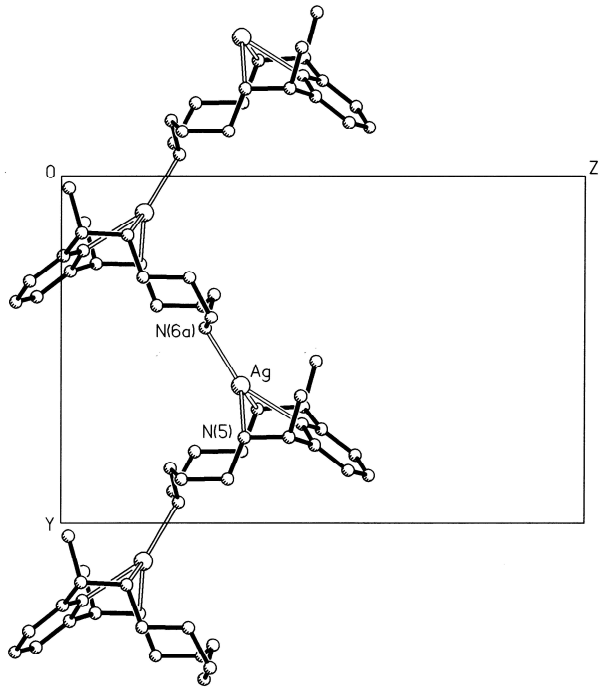
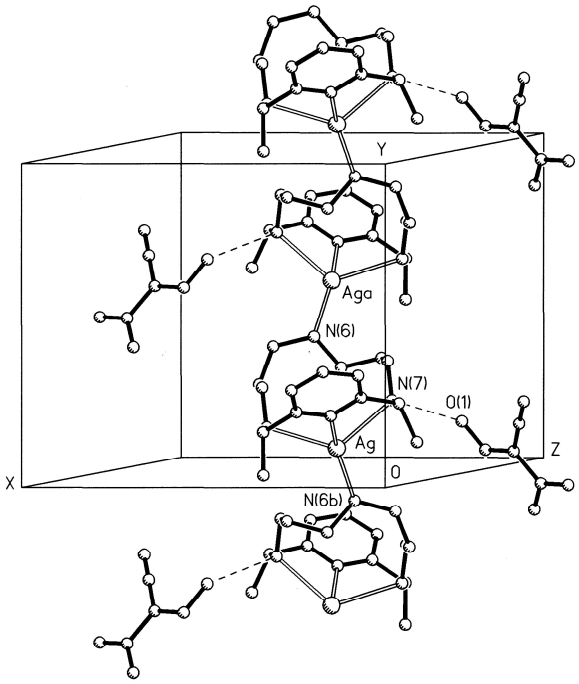
ESI S12 Fragments of crystal packing for **9**.

A – projection of a zigzag polymeric chain of cations $[Ag(N_4)]^+$ on *yz* plane;
B – view along of the unit cell diagonal showing the same chain and closest cyanoxime anions H-bonded to the macrocyclic molecules. H-atoms and CH_3CN solvent molecule are omitted for clarity.

A



B



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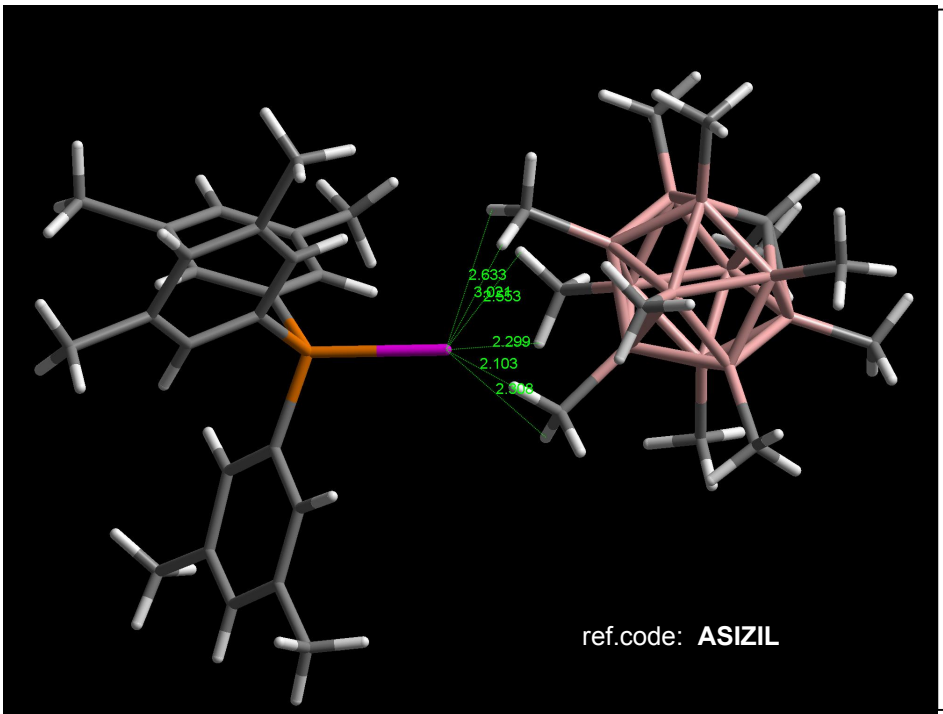
ESI S13 Results of the Cambridge Structural Data Base search for Ag---CH_2 or (CH_3) contacts.

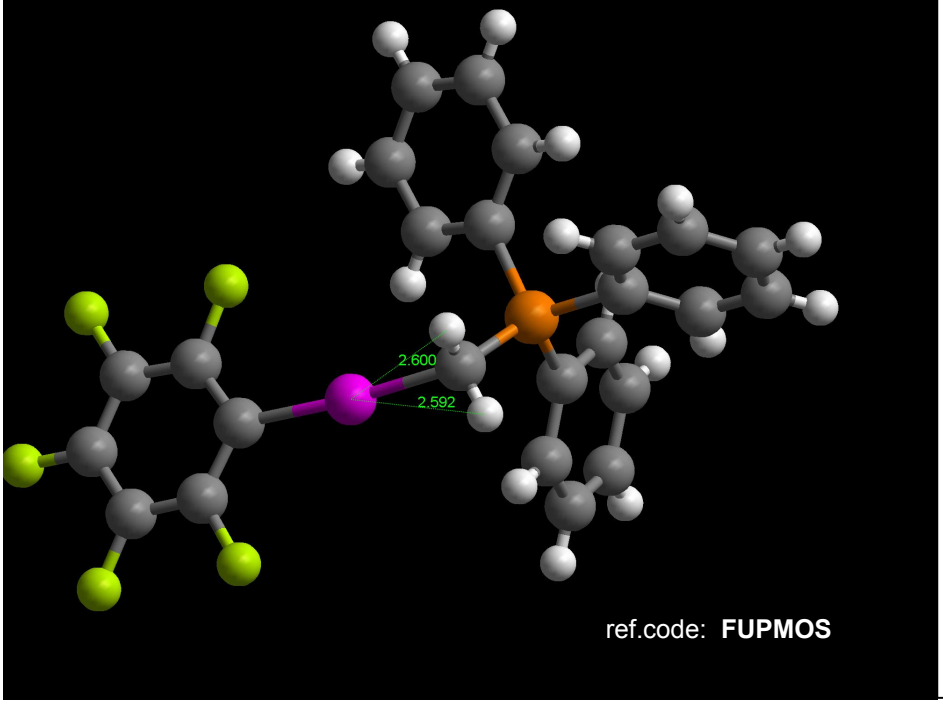


A.J.Clarke, M.J.Ingleson, G.Kociok-Kohn, M.F.Mahon, N.J.Patmore, J.P.Rourke, G.D.Ruggiero, A.S.Weller

J. Am. Chem. Soc., *126*, p. 1503, **2004**

C_{36} H_{61} Ag B_{11} P_1

(undecamethyl-1H-1-carba-closo-dodecaborate)-(tris(3,5-dimethyl phenyl)phosphine)-silver(I)



R.Uson, A.Laguna, A.Uson, P.G.Jones, K.Meyer-Base

J. Chem. Soc., Dalton Trans., p. 341, **1988**

C_{25} H_{17} Ag F_5 P

Pentafluorophenyl-triphenylphosphinomethylide-silver(I)

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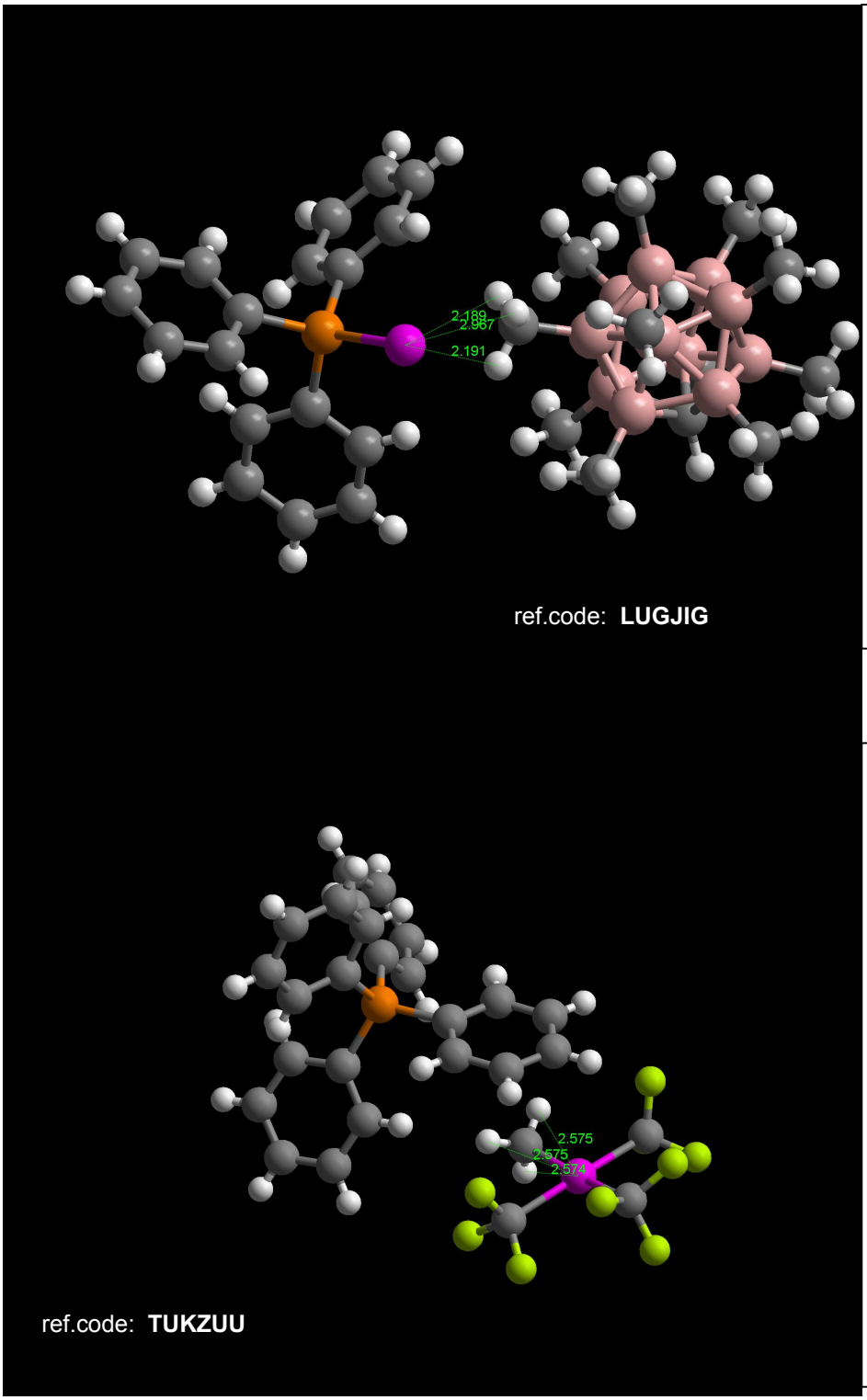
ESI S14 Results of the Cambridge Structural Data Base search for Ag---CH_2 or (CH_3) contacts (continued).



M.J.Ingelson, M.F.Mahon, N.J.Patmore, G.D.Ruggiero, A.S.Weller

Angew. Chem., Int. Ed., *41*, p. 3694, **2002**

$(C_{30}H_{49}AgB_{11}P)_n$

catena-((μ3$-undecamethyl-1H-1-carba-closo-dodecaborate)-(triphenylphosphine)-silver(I))

R.Eujen, B.Hoge, D.J.Brauer

Inorg.Chem., *36*, p.1464, **1997**

$C_4H_3AgF_9^{1-}$, $C_{24}H_{20}P^{1+}$

Tetraphenyl phosphonium *tris*(trifluoromethyl)-methyl-silver(III)

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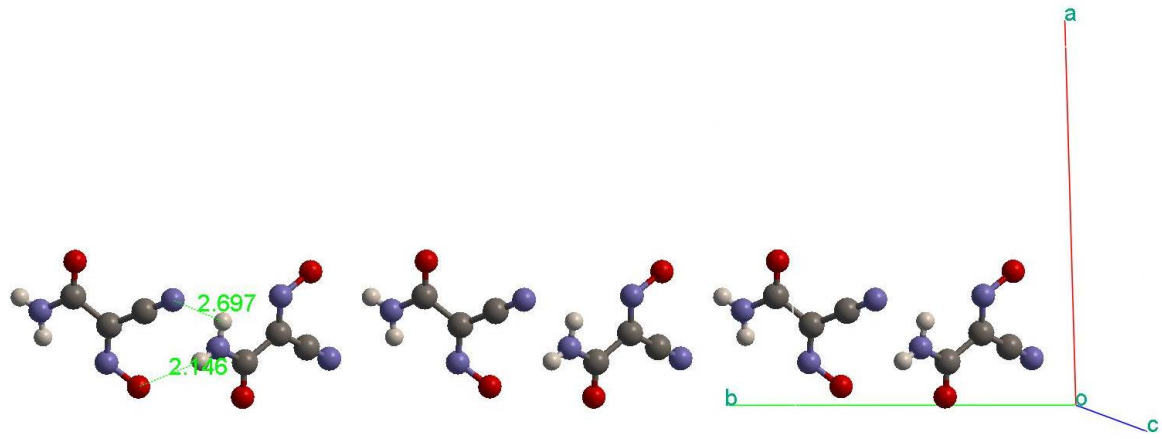
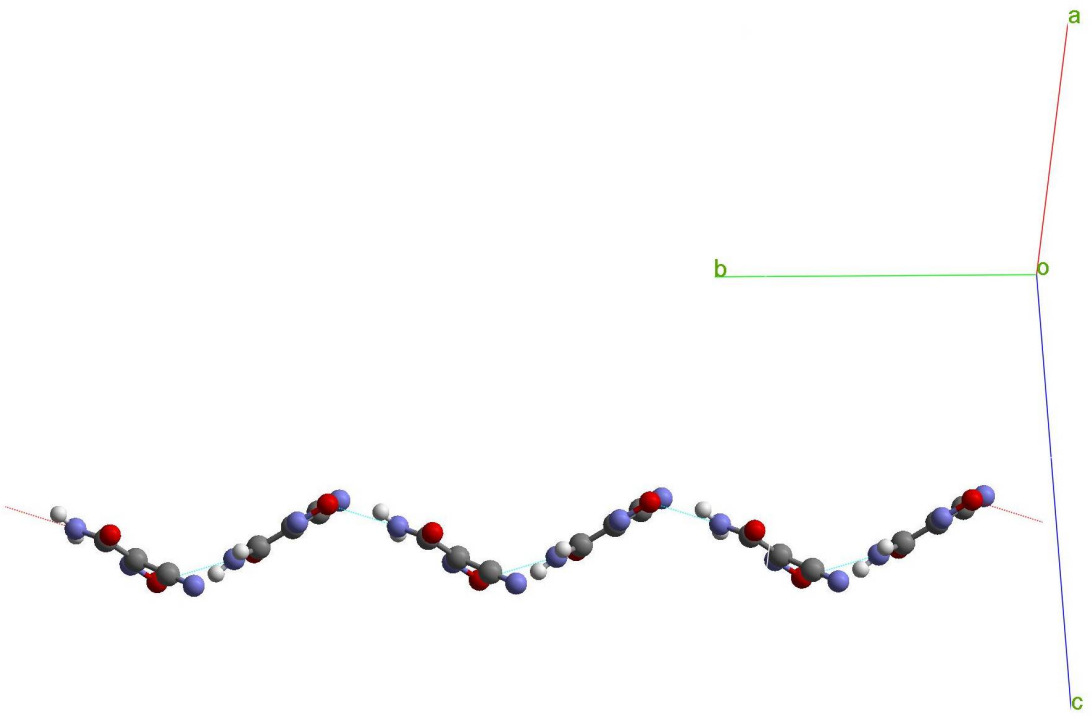
ESI S15 Fragment of crystal structure of **9** showing H-bonding between non-coordinated to silver(I) cyanoxime anions. Cationic part of complex and solvate molecule of acetonitrile are not displayed. Two views of a zigzag chain of $\mathbf{1}^-$ ions.

Coloring scheme: red – O, blue – N, grey – C, white – H.





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ESI S16 Hydrogen bonds in the structures of **1**, **6**, **7**, **8** and **9** with H..A < r(Å) + 2.000 Å and <DHA > 110°.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Sym. code
			1			
N(3A)-H(31A)	0.952	2.265	174.46	3.214	N(2B)	[x, y-1, z]
N(3A)-H(32A)	1.002	2.166	166.44	3.148	O(1B)	[-x+1, -y+2, -z+1]
N(3B)-H(31B)	0.967	2.167	153.11	3.061	N(2A)	[x, -y+½, z-½]
N(3B)-H(32B)	0.908	2.082	176.28	2.988	O(2B)	[-x+2, -y+1, -z+1]
O(1A)-H(1A)	0.988	1.692	174.26	2.677	O(2B)	[x, y-1, z]
O(1B)-H(1B)	1.049	1.529	169.13	2.567	O(2A)	[x, -y+3/2, z-½]
			6			
O(1)-H(2A)	0.860	2.157	146.99	2.916	O1	[x, y-1, z]
N(2)-H(2B)	0.860	2.217	147.44	2.978	N3	[-x+1, y-½, -z+½]
			7			
N(3)-H(1N3)	0.794	2.141	166.69	2.919	O(1)	[x-1, y, z]
N(3)-H(2N3)	0.837	2.276	161.85	3.083	N(2)	[-x, -y+1, -z+1]
			8			
N(3)-H(3A)	0.803	2.019	165.68	2.803	O1	[-x+2, y-1/2, -z]
N(4)-H(4A)	0.914	2.159	157.78	3.024	O1	[-x+1, y-1/2, -z+1]
N(5)-H(5A)	0.962	2.108	172.03	3.064	O2	[-x+2, y+1/2, -z+1]
N(3)-H(3B)	0.754	2.348	110.09	2.702	N1	
N(5)-H(5B)	0.830	2.443	147.19	3.173	O2	[-x+1, y+1/2, -z+1]
N(4)-H(4C)	1.066	2.155	171.87	3.213	O2	[x-1, y, z]
N(5)-H(5C)	0.870	2.560	148.12	3.331	N1	[x-1, y, z+1]
			9			
N(9)-H(9)	0.901	2.127	151.85	2.952	O(21)	[x-1, y, z]
N(13)-H(13)	0.965	2.355	158.55	3.272	N(33)	[-x+½, y+½, -z+½]
N(17)-H(17)	1.041	2.121	145.35	3.036	O(27)	
N(28)-H(28A)	0.821	2.146	148.77	2.880	O(21)	[-x+3/2, y-½, -z+½]
N(28)-H(28B)	0.888	2.233	112.66	2.703	N(22)	

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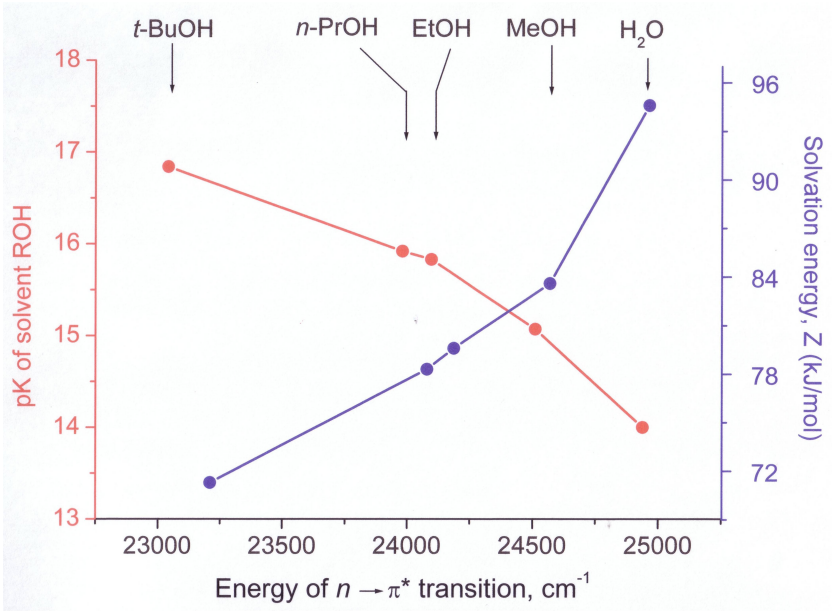
ESI S17 Solvatochromic studies:

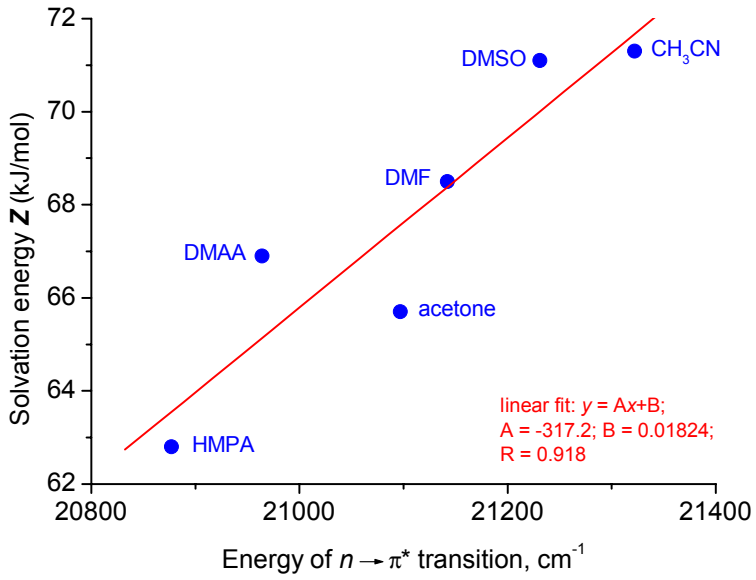
Non-linear relationships between energies of $n \rightarrow \pi^*$ transition in visible spectra of **1**$^-$ anion and solvent ROH parameters: acidity (red) and specific Kosover's solvation energy *Z* (dark blue).

A



Graph of dependence between values of energy of $n \rightarrow \pi^*$ transitions in visible spectra of **1**$^-$ anion and solvent parameter for polar aprotic solvents.

B



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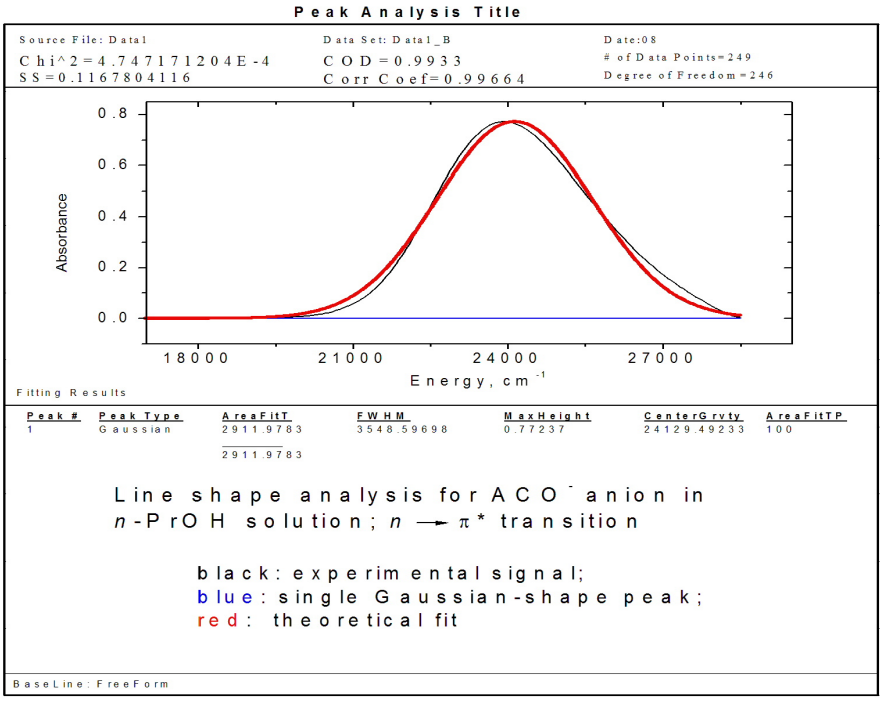
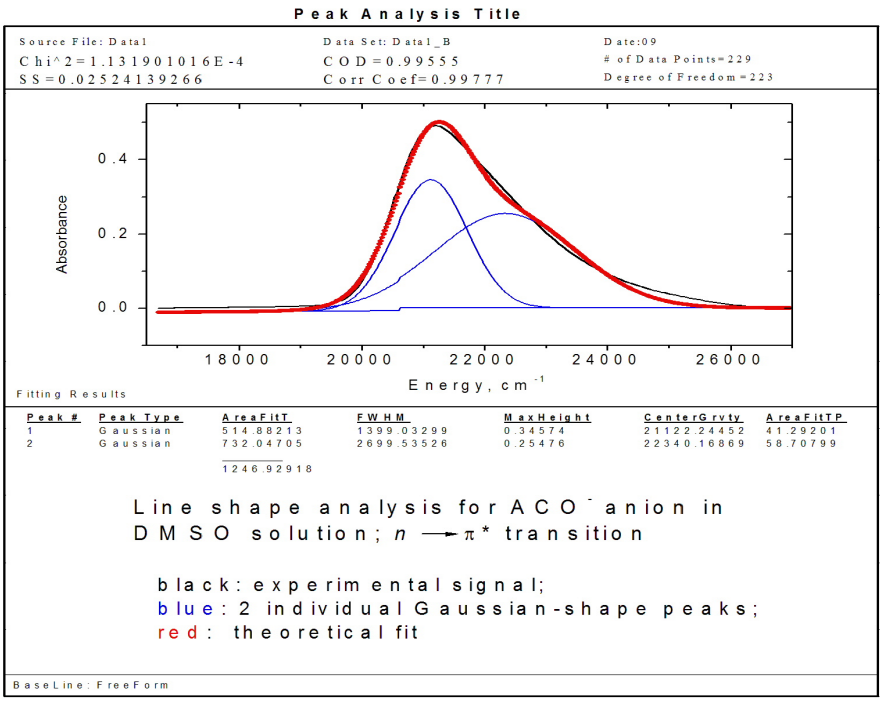
ESI S18 Line shape analysis of $n \rightarrow \pi^*$ transitions in visible spectra of $\mathbf{1}^-$ anion in polar protic solvent (**A**) and aprotic solvent (**B**).



A



B

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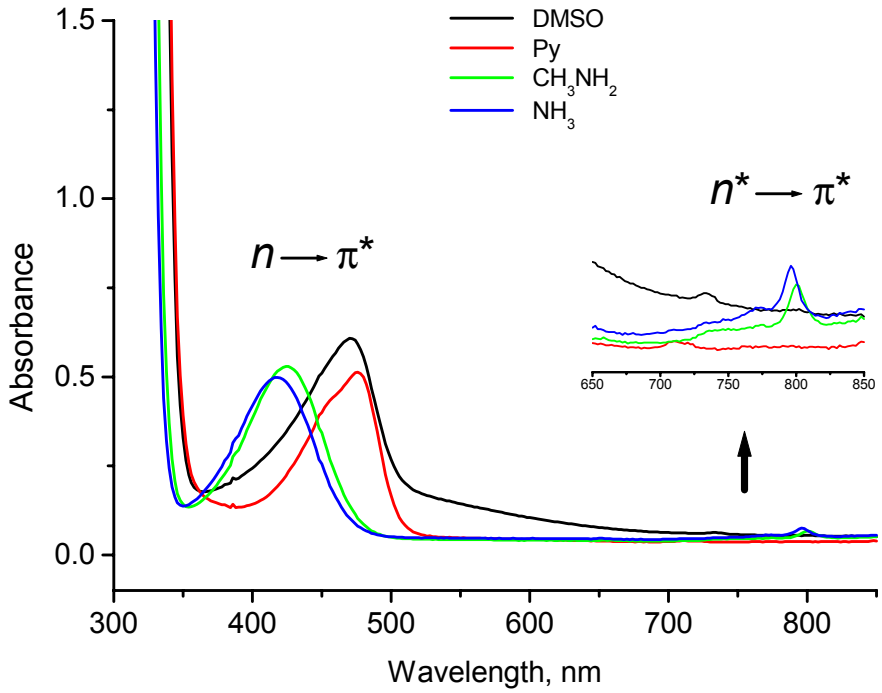
ESI S19 Room temperature visible spectra of **6** in different solvents. Clearly visible solvatochromic shift between polar protic solvents (NH_3, CH_3NH_2) and aprotic solvents (DMSO, Py).



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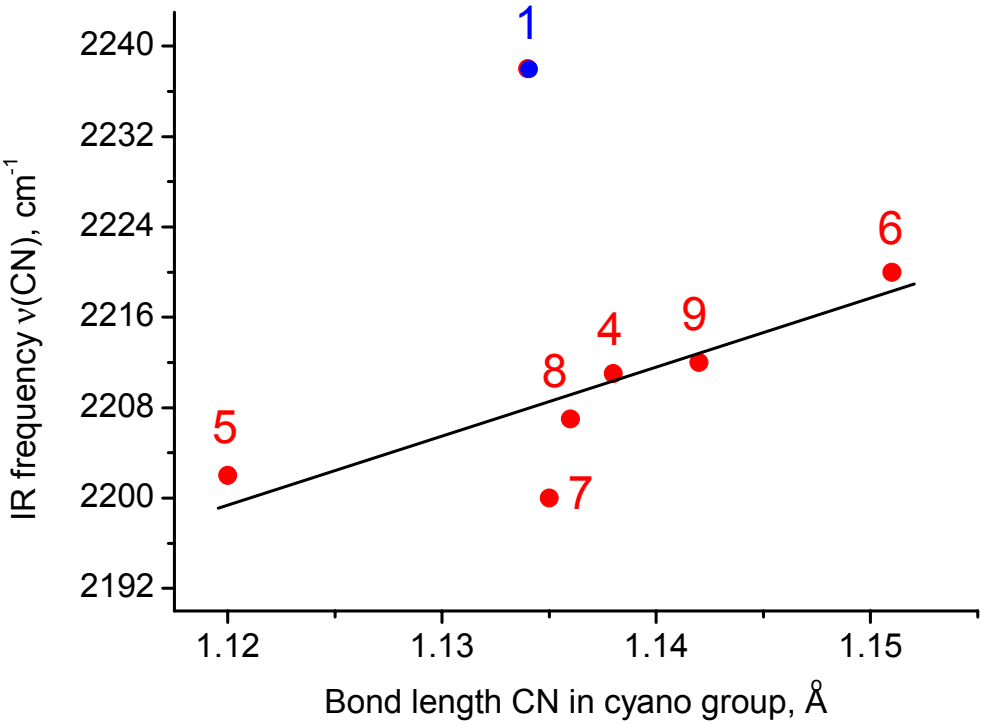
ESI S20 Correlation between IR frequency of ν(C≡N) and bond length of the cyano group in synthesized compounds; for linear fit results in R = 0.91. Data for **4** and **5** were taken from references [x] and [x].



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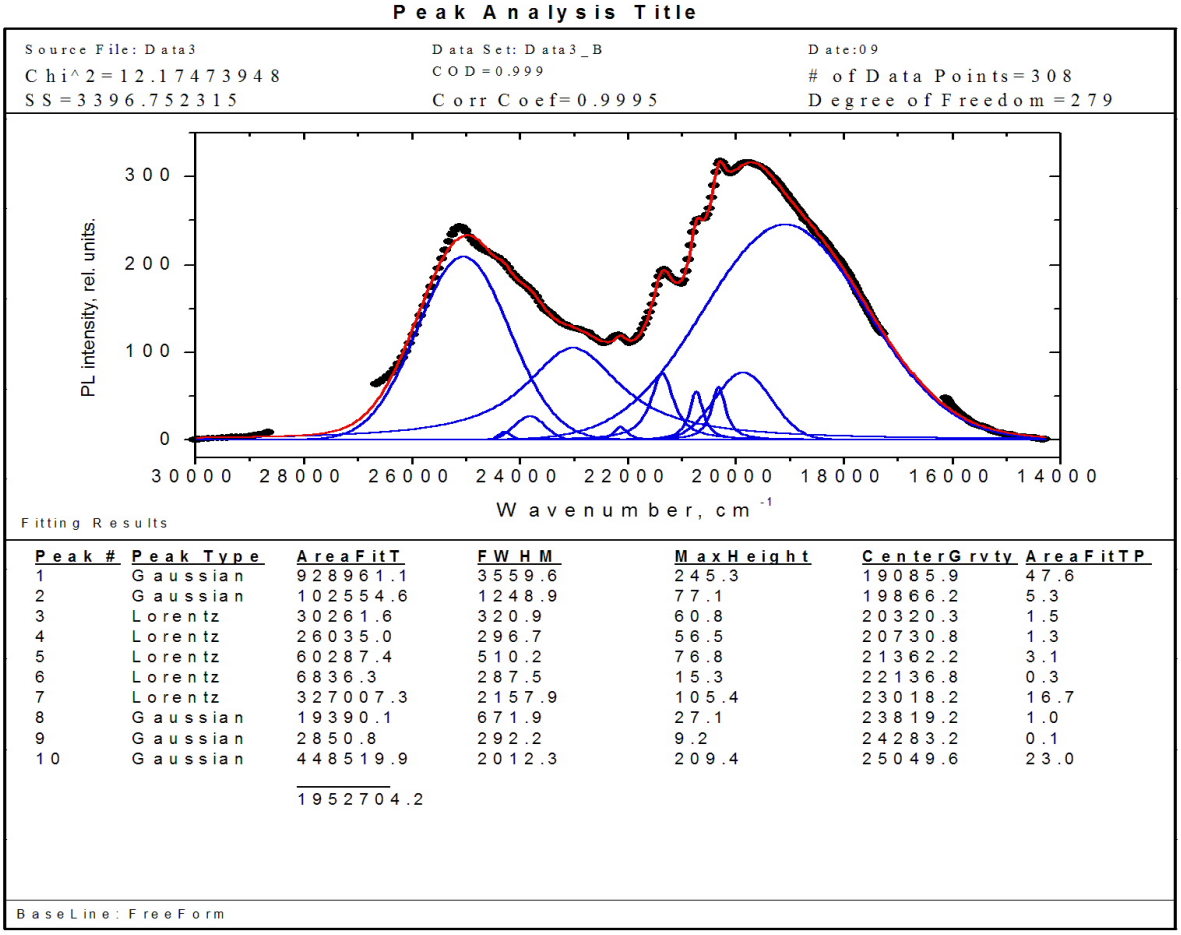
by Nikolay Gerasimchuk, Andrey N. Esaulenko, Kent N. Dalley and Curtis Moore

ESI S21 Full line shape analysis of the emission profile of **6** at 300 nm excitation wavelength. Minimum ten lines are sufficient for a good fitting of the experimental signal.

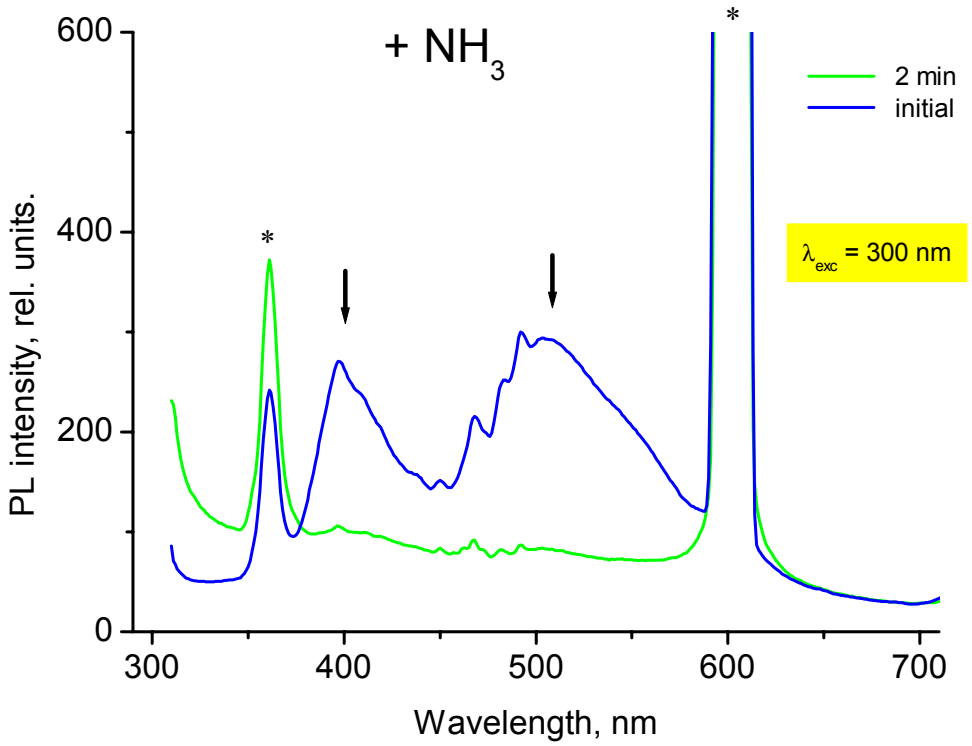


Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	928961.1	3559.6	245.3	19085.9	47.6
2	Gaussian	102554.6	1248.9	77.1	19866.2	5.3
3	Lorentz	30261.6	320.9	60.8	20320.3	1.5
4	Lorentz	26035.0	296.7	56.5	20730.8	1.3
5	Lorentz	60287.4	510.2	76.8	21362.2	3.1
6	Lorentz	6836.3	287.5	15.3	22136.8	0.3
7	Lorentz	327007.3	2157.9	105.4	23018.2	16.7
8	Gaussian	19390.1	671.9	27.1	23819.2	1.0
9	Gaussian	2850.8	292.2	9.2	24283.2	0.1
10	Gaussian	448519.9	2012.3	209.4	25049.6	23.0
		1952704.2				

Black: experimental signal;
red – theoretical fit;
blue – individual peaks in the spectroscopic envelope.

SUPPORTING INFORMATION for the paper:
2-Cyano-2-isonitroso acetamide and its Ag(I) complexes. Silver(I) cyanoximate as nonelectric gas sensor.
by Nikolay Gerasimchuk, Andrey N. Esaulenko, Kent N. Dalley and Curtis Moore

ESI S22 Rapid quench of photoluminescence of solid sample of **6** in the presence of NH_3. Asterisks indicate instrument artifacts.



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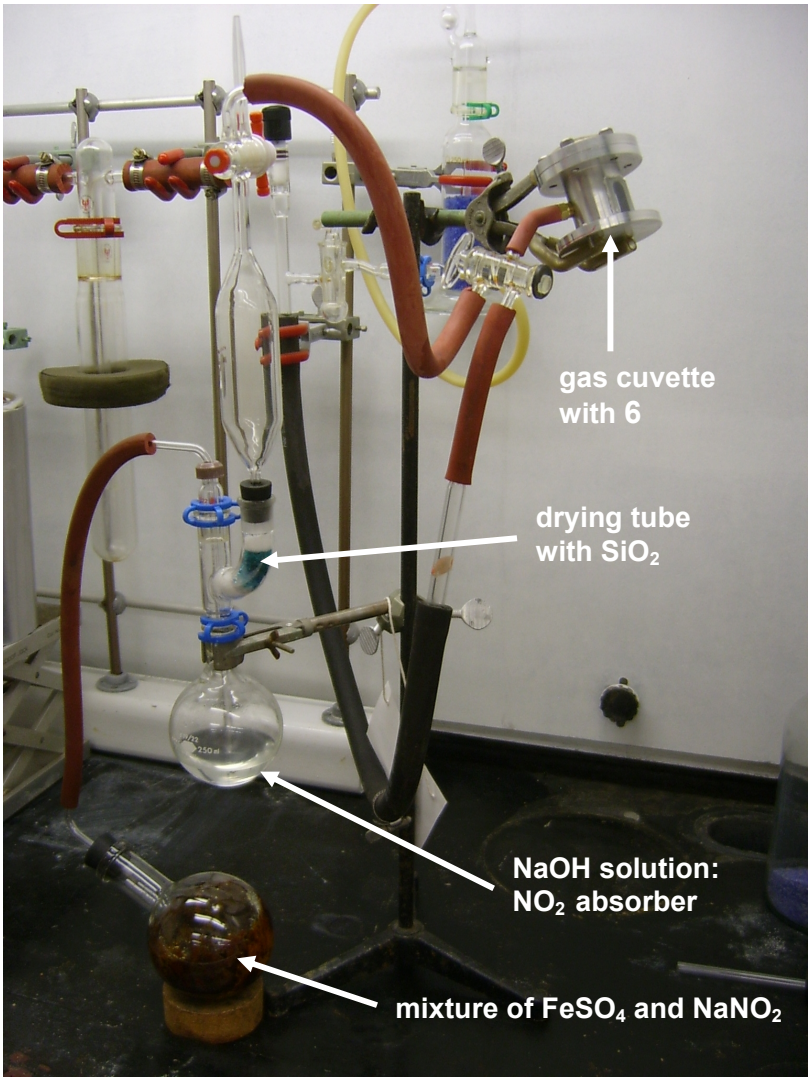
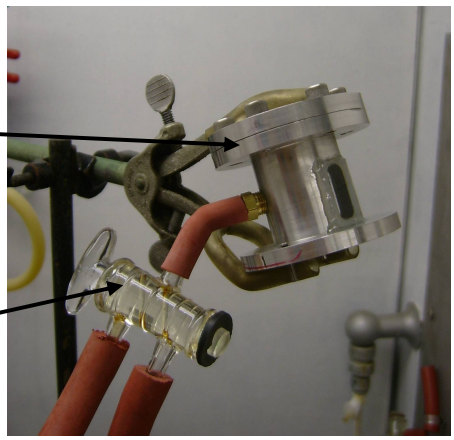
ESI S23 Generation of small quantities of dry and pure nitrous oxide, NO.



gas cuvette with sample of powdery **6**

2-way stopcock for gas fill / vacuum



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ESI S24 Chemical methods of generation of small quantities of dry and pure gases.

NH_3.
Ammonia was generated from 38% solution of ammonium hydroxide upon dropwise addition to pellets of solid KOH according to the equation below:

$NH_4OH \rightarrow NH_3 + H_2O$

SO_2
Sulfur dioxide was generated from hot mixture of concentrated H_2SO_4 and Cu ingots. Gas was bubbled through 96% sulfuric acid and then passed through the column filled with granulated SiO_2.

$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$

From: Suryaraman, M.G.; Viswanathan, A. *J. Chem. Ed*. **1949**, 594 – an excellent prep!

NO
Nitrous oxide was produced from solid mixture of $FeSO_4 \cdot 7H_2O$ and KNO_2 in 1 L flask upon slow gentle heating using a heat gun. This method allows preparation up to 5 liters of ~98% pure NO which comes as a steady flow of colorless gas.