UNUSUAL "ENTANGLED" MAGNETIC AND ELECTRONIC PROPERTIES OF POLYFUNCTIONAL NITROSYL IRON COMPLEXES

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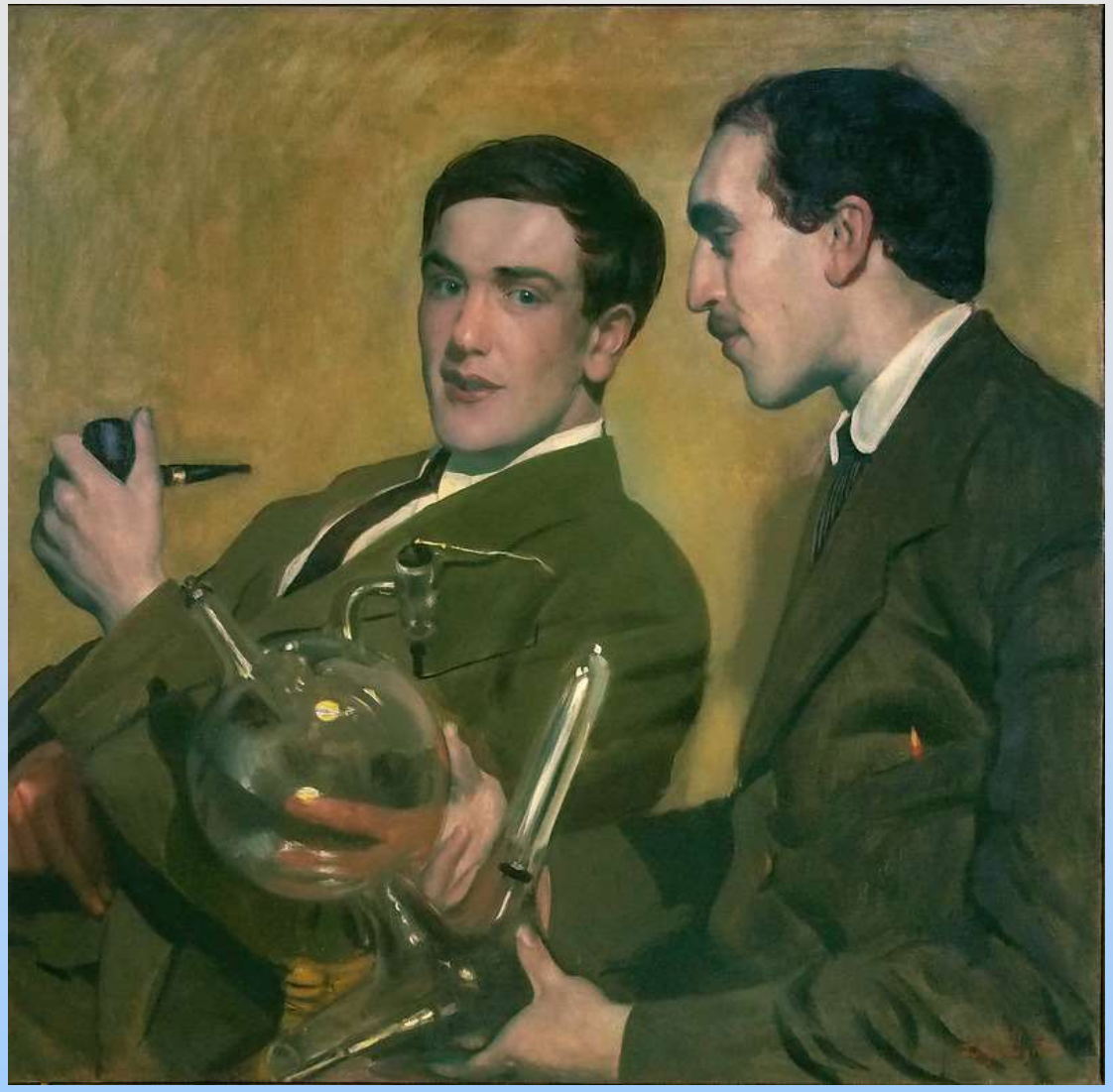


Portrait of Professors P.L.Kapitsa and N.N.Semenov
(1921г.)

Academician Nikolai M. Emanuel,
Professor Gennadii N. Bogdanov,
Professor Nina P. Konovalova

Academician Nikolai N.Semenov

Academician Nikolai M. Emanuel

Content

I. Biologic significance of nitric oxide molecule (NO)

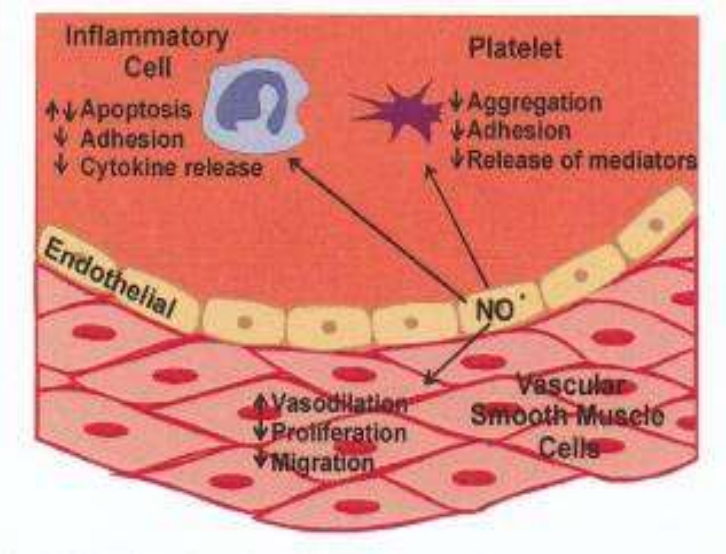
II. Specific features of DNIC structure

III. Unusual “entangled” magnetic properties of DNICs with thiocarbamide ligands

IV. Quantum entanglement in the dimer of DNIC of μ-S-C-N type

V. Conclusions

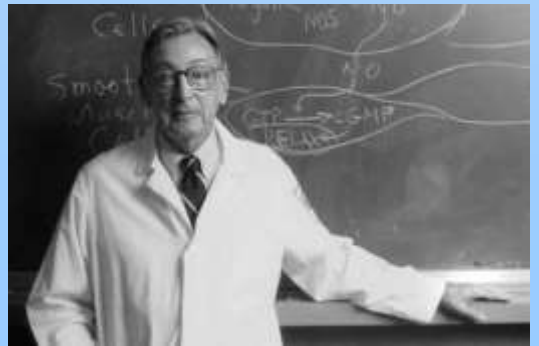
BREAKTHROUGH IN THE INVESTIGATION OF NO CHEMISTRY IN BIOLOGIC SYSTEMS



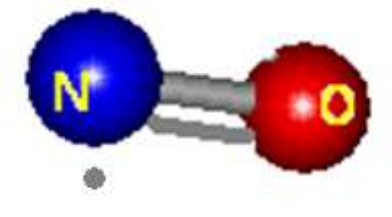
•**Eighties of XX century**: Discovered that NO can release from stimulated endothelial cells to induce vasodilatation.

•**1992:** NO molecule is called “molecule of the year”

•**1998:** F.Murad, R.F. Furchgott, L.J. Ignarro. Nobel prize for “the discovery of related to NO as a signaling molecule in cardio-vascular system



NITRIC OXIDE NO



A new type of messenger molecules in living organisms

Chemical properties

- gas
- free radical
- short life time
- highly reactive

- a signal molecule in various physiological and biochemical processes
- the integral component of cardiovascular system
- immune response to pathogens
- participates in the control of genetic apparatus at the level of mRNA transcription and translation

Biological value of nitric oxide

Regulating

NO low concentrations

< 150 nMol

Vascular permeability
Vascular tone
Cytoadherence
Inhibition of trombocytes
Control of the immune system
Neurotransmission
Metabolism in liver
Memory and learning
Synaptic adaptation
Kidney function
Erection

Protective

NO high concentrations

> 150 nMol

Cytotoxic protection
Inhibition of leucocytes
Reduction of blood pressure
Antitumor activity
Antioxidant activity
Antibacterial activity
Antimalarial activity

Pathologic

NO excess

1000 and more nMol

Increased susceptibility to metal toxicity, alkylation and radiation
Inhibition of mitochondrial breath
Peroxide oxidation of lipids
Damage of DNA
Inhibition of ferments
Reduction of antioxidants amount

K.Szacilowski, A. Chmura, Z. Stasicka**, Coord. Chem. Rev.(**2005) V.249, p.2408

Diseases and states caused by changes of the amount of endogenous NO

blood pressure	encephalopathy
ischemic heart-disease	epilepsia
myocardial infarction	neurotic depression
bronchial asthma	neurodegenerative diseases (Alzheimer's disease, Parkinson disease)
septic shock	impotence
acute respiratory pain syndrome	pancreatic diabetes;
thrombosis-embolic disease	immunodeficiency
renal failure	pulmonary hypertension
bronchospasm	cancer

The strategy for creation of NO drugs for therapy of socially relevant diseases :

- NO chemistry
- NO amount

anti –NO therapy

- traps for NO excess
- Inhibition of NOS activity

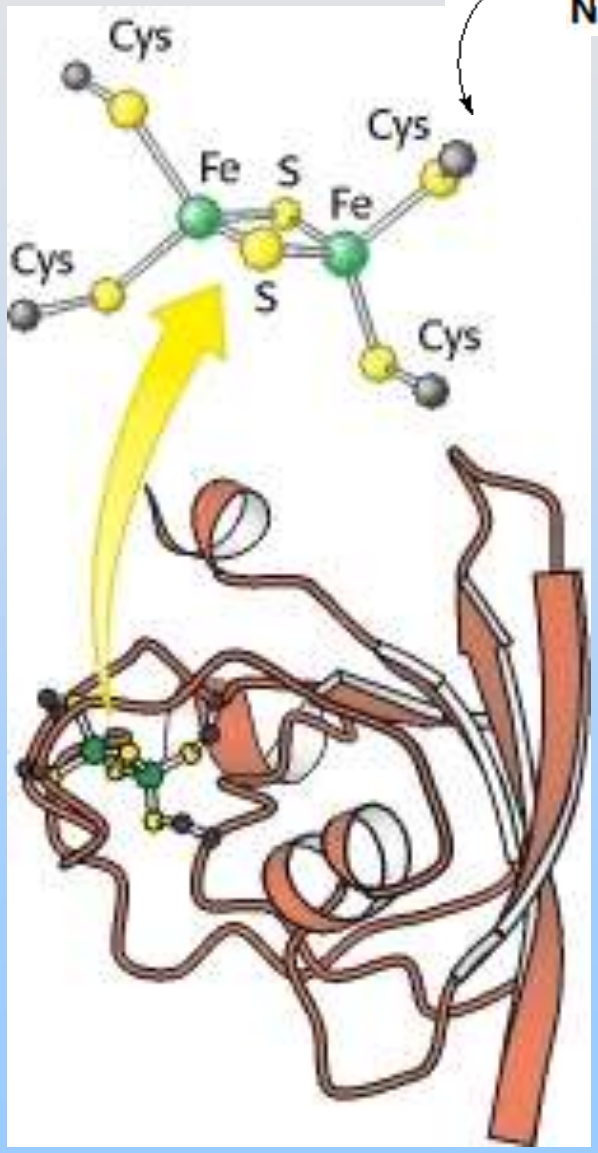
NO therapy

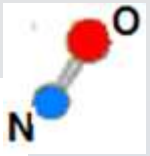
Basic requirements to NO donors :

- Target products of NO donors synthesis should be isolated in pure and solid state
- NO donors should decompose fast in aqueous solutions at physiological pH values without additional activation to release NO
- NO donors decomposition should occur with quantitative yield of nitric oxide

Biological cycle of decomposition and assembly of [2Fe-2S] ferredoxine

Structure of the active site: binuclear Fe complex with natural thiols

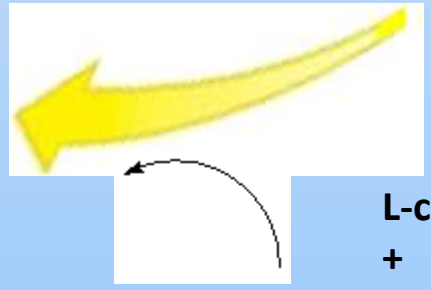




Modification of [2Fe-2S] cluster under the NO excess

Dinitrosyl iron complex (DNIC) g=2.03

Reparation of the active site structure



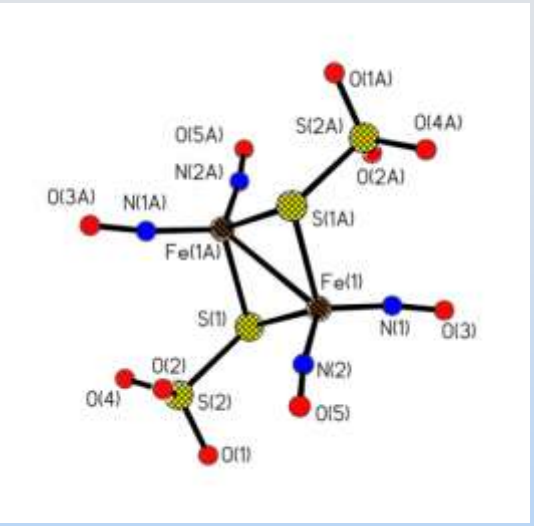
L-cysteine + Cysteine desulfurase

M.-L. Tsai, Ch.-Ch. Chen, I-J. Hsu et. al., *Inorg Chem*, (2004) 43, 5159

Structure of the obtained biomimetic models of the active sites of non-heme proteins

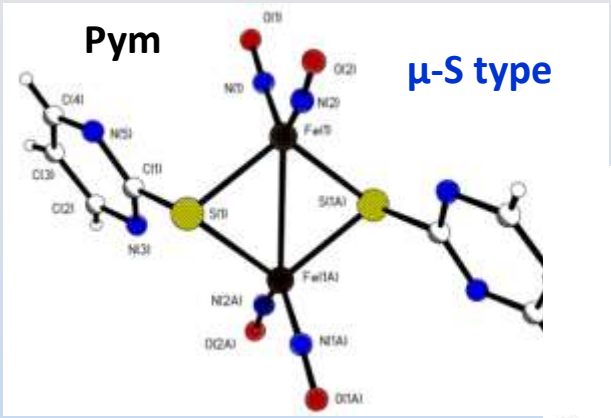
Binuclear thionitrosyl iron complexes

Anionic diamagnetic



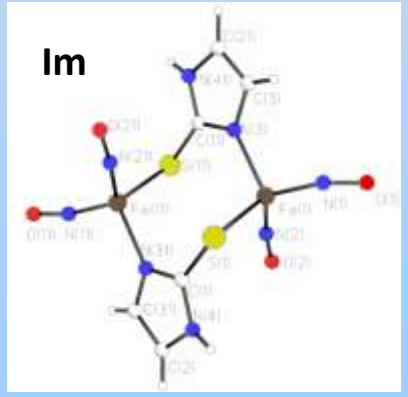
Neutral diamagnetic

Pym **μ-S type**



Neutral paramagnetic

Im

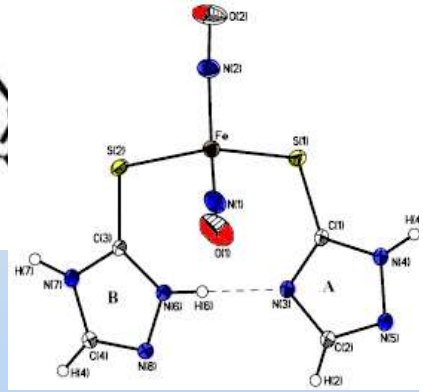


μ-N-C-S type

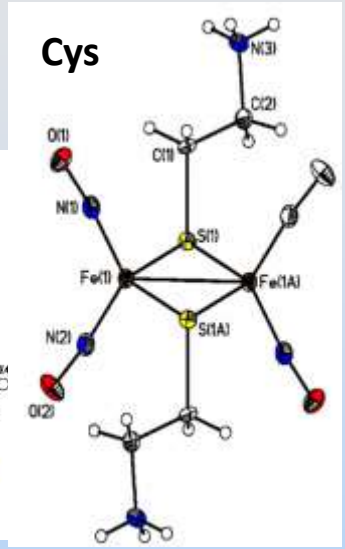
Mononuclear DNICs

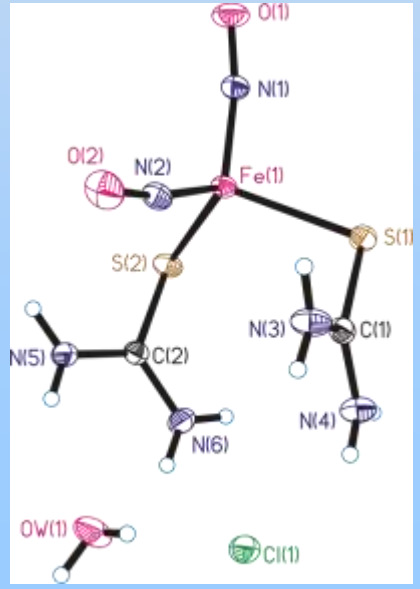
Cationic diamagnetic

Neutral

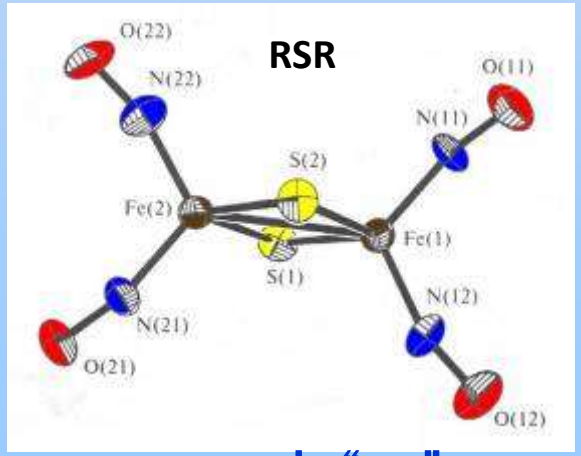


Cys



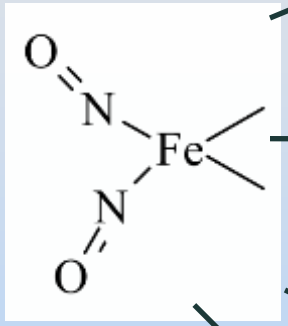


RSR



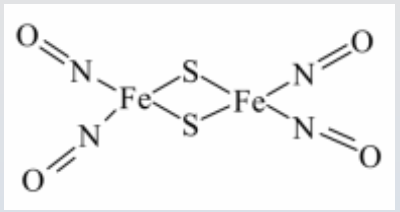
Binuclear Roussin's "red" salt

Structural principles for the formation of binuclear nitrosyl iron complexes DNICs



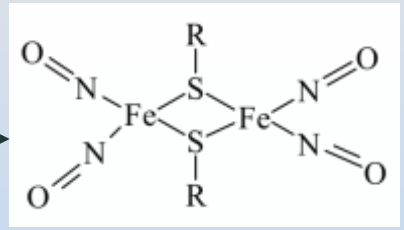
Main structural unit –dinitrosyl iron (DNI)

a)



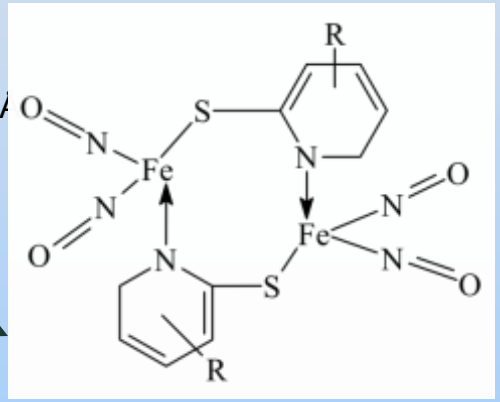
⌈-S type (anionic form), diamagnetic Fe…Fe 2.70 Å

b)



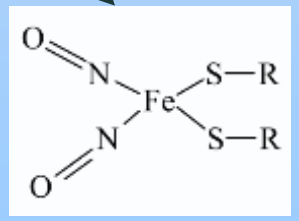
⌈-S type (neutral form), diamagnetic Fe…Fe 2.70 Å

c)



⌈-SCN type neutral paramagnetic, Fe…Fe 4.1 Å

d)



Neutral or cationic form, paramagnetic

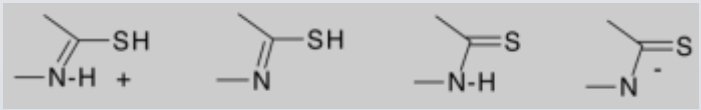
[Fe(NO)2] n
The DNIC fragment has charge +1

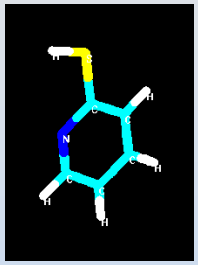
n=xπNO+(d-x)dFe=9

Nitrosyl iron fragments are linked through bidentate or tridentate bridges of bivalent sulfur atoms

Structures of functional S-ligands,

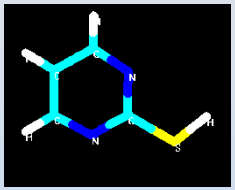
which are inhibitors for the growth of various tumors, antiinflammatory and antibacterial agents, and natural thiols





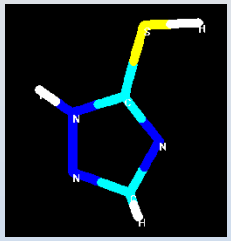
2-mercaptopiridine

Py



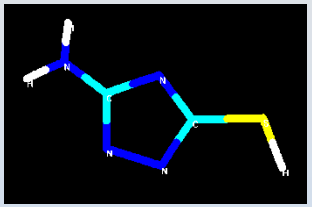
2 –mercapropirimidine

Pym



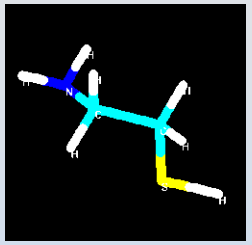
3-mercapto-1,2,4-triazole

Triaz



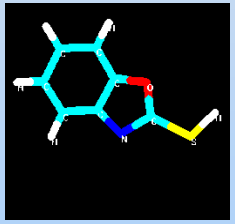
2-mercapto-5-amino-1,2,4-triazole

AmTriaz



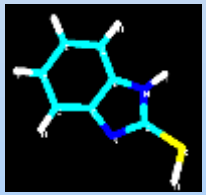
cysteamine

CysAm



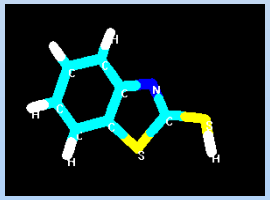
2-mercapto

Boz



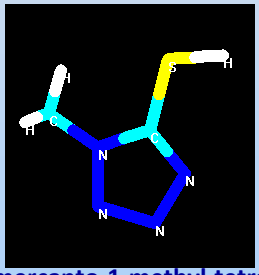
2-mercapto benzoxaazole

Bim



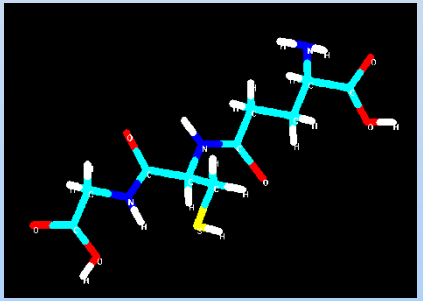
2-mercapto benzimidazole

Btz



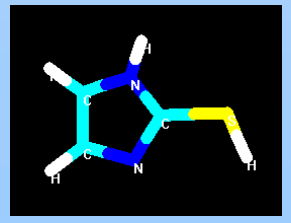
5-mercapto-1-methyl-tetrazole benzthiazole

Tetraz



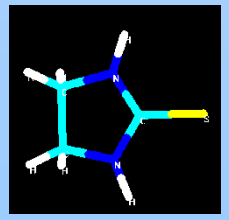
glutathione

Glu



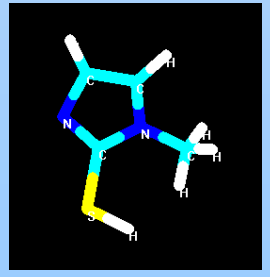
2-mercaptoimidazole

Im



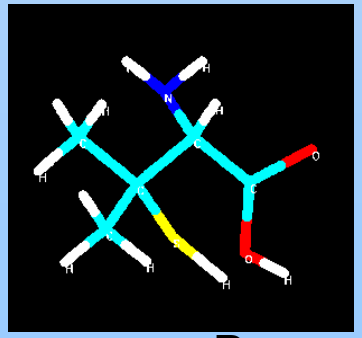
2 -mercaptoimidazoline

Imid



2-mercapto-1-methyl-imidazole

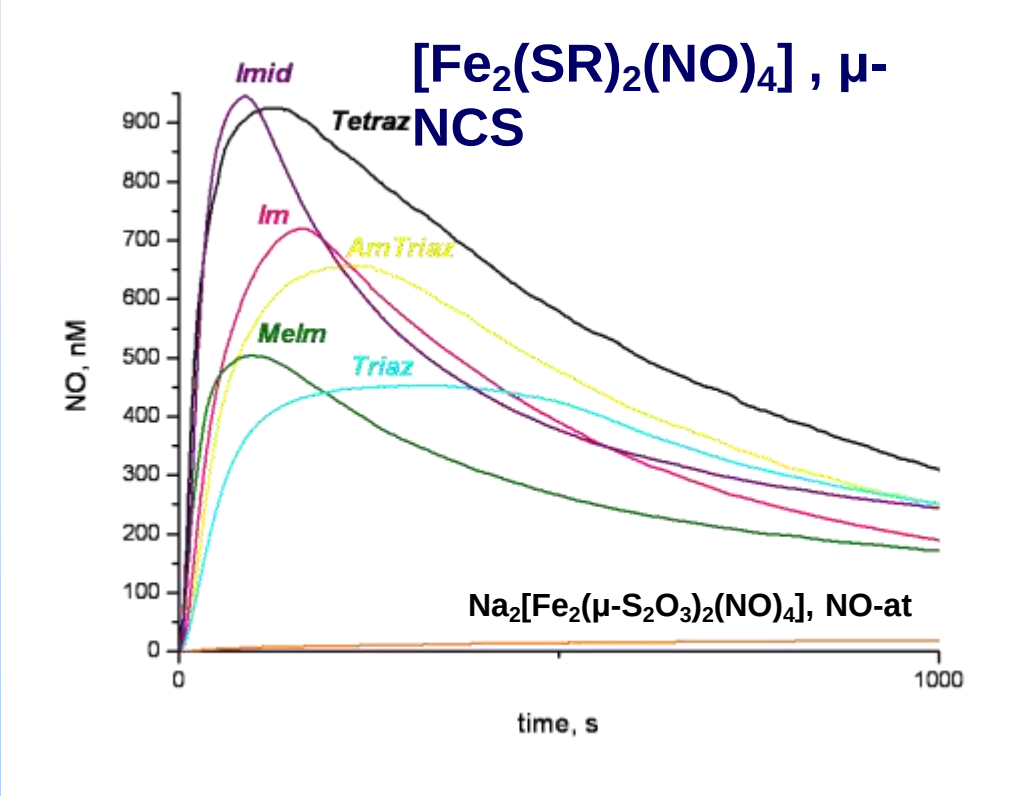
Mim



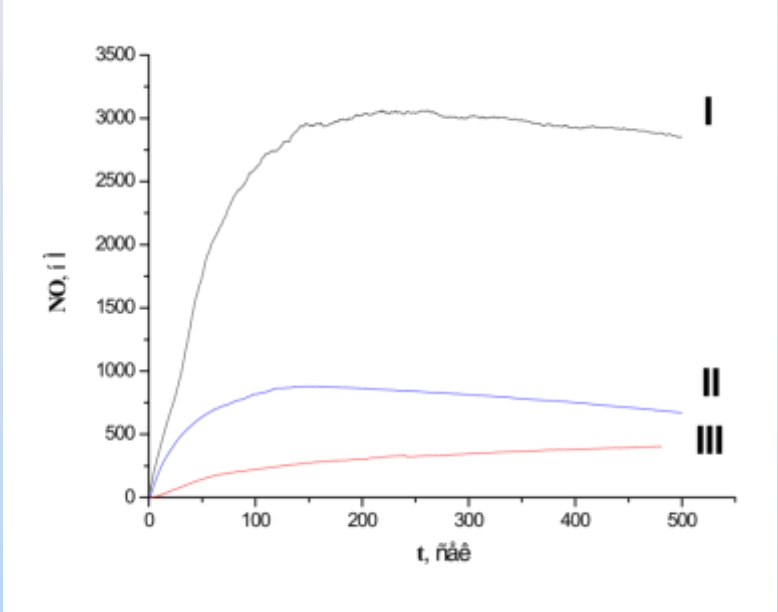
penicillamine

Pen

NO-donor activity of neutral and anionic nitrosyl iron complexes in 1% aqueous solution of DMSO



Dependence of amount of NO generated by neutral complexes with concentration $0.4 \cdot 10^{-5}$ M at pH 7.00 and T=25^{0}C on time in anaerobic conditions. In aerobic conditions NO amount increases.



Dependence of amount of NO generated by complex $Fe_2(\mu\text{-}SPym)_2(NO)_4$ ($0.4 \cdot 10^{-5}$M) on time in aqueous solutions in anaerobic conditions at T=25°C and various pH values: *I* – pH=6.00; *II* – pH=7.43; *III* – pH=7.00

The average maximum amount of NO generated by nitrosyl iron complexes I-VI in anaerobic water solutions at pH 7 and T=25^{0}C as compared to the commercial compound VII

Complex	I	II	III	IV	V	VI	VII
NO amount, nM	10.0 4NO	23.2 8NO	3.3 4NO	10.3 4NO	4.5 4NO	6.8 4NO	4.0 2NO

I – $[Fe(SC(NH_2)_2)_2(NO)_2]_2SO_4 \oplus H_2O$: 4NO groups in the cation

II – $[Fe(SC(NH_2)_2)_2(NO)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$: 4 NO groups in the cation and 4 NO groups in the anion

III – $Q_2[Fe_2(S_2O_3)_2(NO)_4]$, Q= Na^+: 4 NO groups in the anion

IV – $(CH_3)_4N^+$

V – $(C_3H_{7)4}N^+$

VI – $(C_4H_9)_4N^+$

VII – NONO- ate, diethylene triamine

Conclusion: DNICs are effective NO donors

Study of cardiotropic activity of water soluble nitrosyl iron complexes using the models of ischemic and reperfusion damage of myocardium in vitro and in vivo

NO role in regulation of vascular tone and metabolism of myocardium

Deficiency in NO formation

⇩

Development of endothelial disfunction

⇩

Increase of coronary vessels tone

⇩

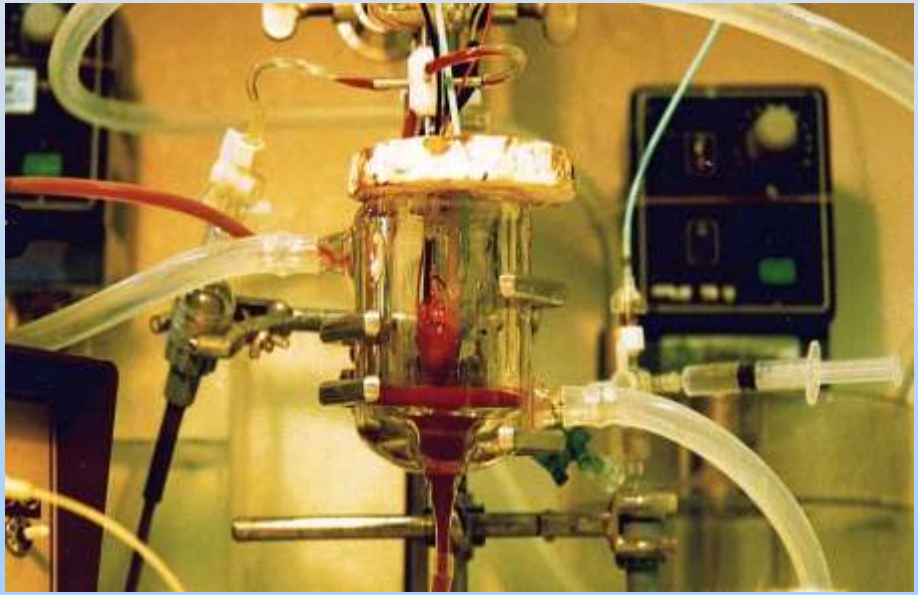
Growth of aggregation and adhesive ability of thrombocytes

If there is ischemic and reperfusion heart damage, syndrome “no reflow” develops, which leads to blood flow deterioration and death of cardiac histiocytes

Jones S.P., Bolli R. ***J. Mol. Cell. Cardiol.*** 2006; 40 (1): 16-23;
Jugdutt B.I. ***Heart Fail. Rev.*** 2002; 7(4): 391-405

Study of cardiotropic activity of water soluble nitrosyl iron complexes

Isolated perfused rat's heart *in vitro*



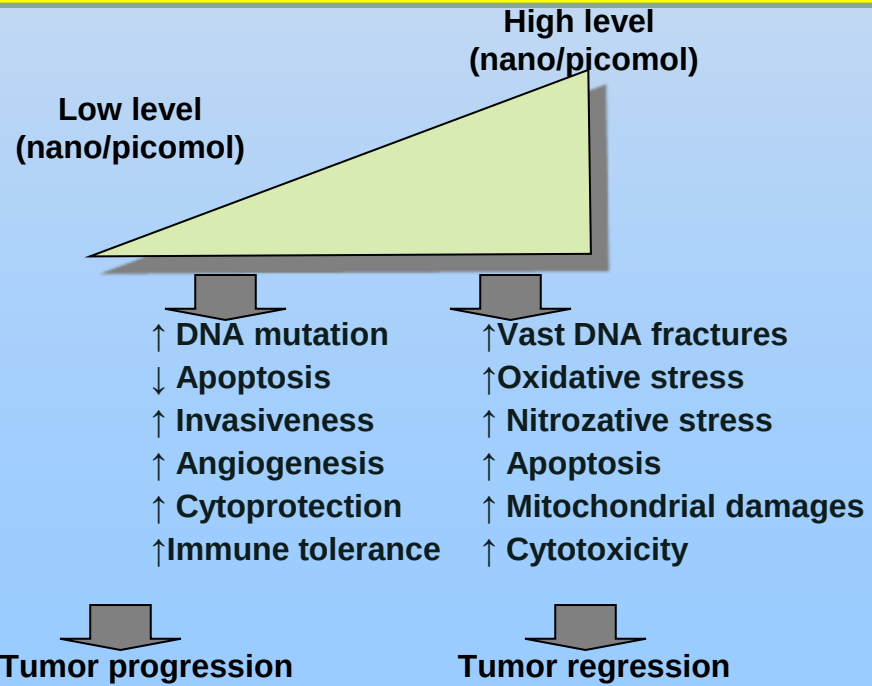
Model of regional ischemia of rats heart *in vivo*

Cardiotropic activity of nitrosyl iron complexes of anionic and cationic structural types has been first discovered on the models of ischemic and reperfusion miocardial infarction in vitro and in vivo. More effective influence on vasorelaxation has been found for the compounds under study than for the reference NO donors (nitroglycerin and sodium nitroprusside).

A.W.Carpenter & M.H.Schoenfish. ***Chem. Soc. Reviews .*** DOI:10.1039/c2cs15273h (2012)

Search for new approaches to the synthesis of effective and non-toxic "non-platinum" chemotherapeutic drugs

NO donors are promising substances for chemotherapy of tumor diseases (NO-therapy)



ИБХФ РАН им. Н.М. Эмануэля

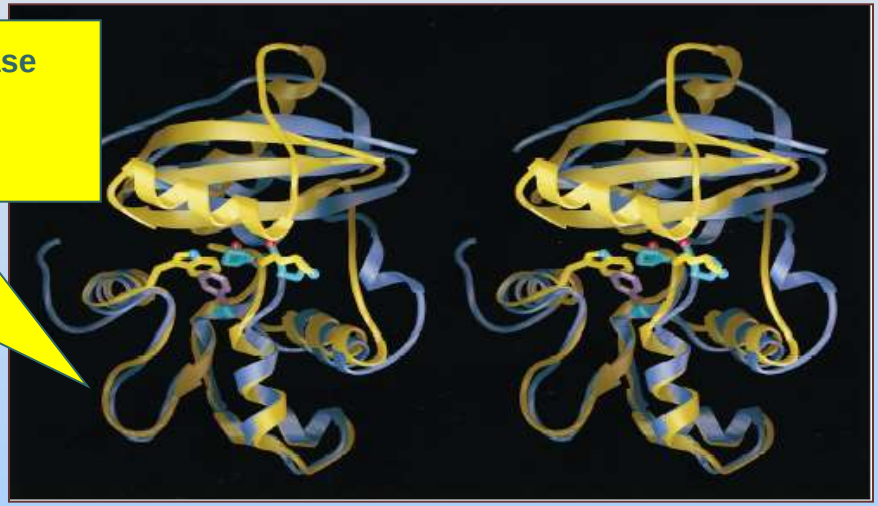
Molecular genetic mechanisms of carcinolytic activity of NO donors

- binding of NO with SH groups of proteins and ferments and their inhibition;
- induction of single-strand and double-strand DNA breaks that cause apoptosis;

DNA-DNA and DNA-protein cross-links formation

- inhibition of the protein of DNA repair of human tumor cells - O-6-methyl-guanine-DNA methyltransferase

Structure of O-6-methyl-guanine-DNA methyltransferase
метилтрансферазы
- human (blue)
- *E. coli* (yellow)



in *E.coli* model system, molecular-genetic mechanisms of cytotoxic and mutagenic activity of crystalline sulfur-nitrosyl iron complexes, a new class of NO-ates, have been studied for the first time: genes expression of DNA repair responses and mutation activity:

- SOS- and SoxRS-regulons genes (oxidative stress)
- Ada-repair response genes (cell resistance to alkylating compounds)

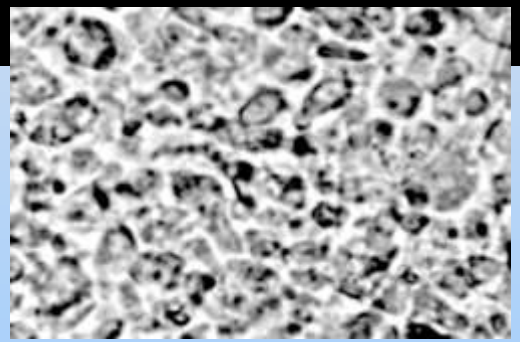
S.V. Vasil'eva, E.Yu. Moshkovskaya, N.A. Sanina, S.M.Aldoshin, A.F. Vanin//Biokhimiya (2004) 69, 8, 1088;
S.V. Vasil'eva, E.Yu. Moshkovskaya, N.A. Saninau et al // Dokl. Akad. Nauk. (2005) 402, 705;
S.V.Vasilieva, E.Ju. Moschkovskaya, A.S. Terekhov, N.A. Sanina, S.M. Aldoshin// Russian Journal of Genetics(2006)7, 737

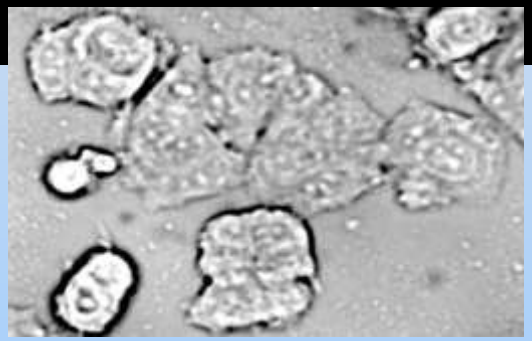
РОНЦ РАМН им. Н.Н. Блохина

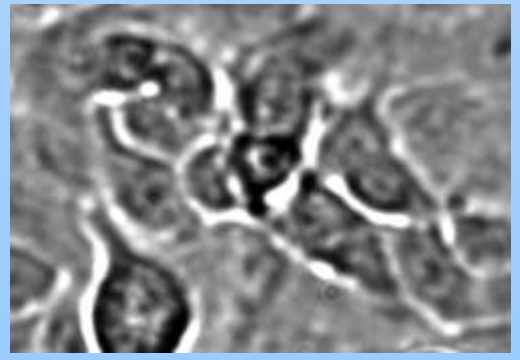
Investigation of anticancer activity of nitrosyl iron complexes in vitro

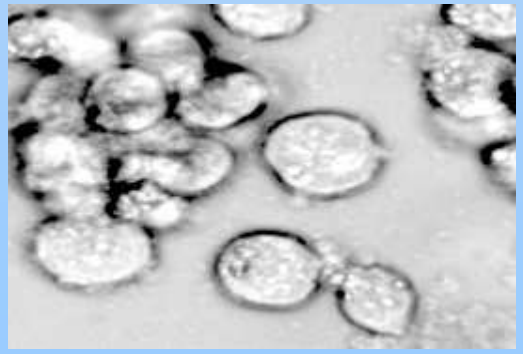
15 NO donors have been tested on lines of human tumor cells of various genesis :

- **Ovarian carcinoma SKOV-3**
- **Breast cancer MCF-7**
- **Non-small cell carcinoma of lung A549**
- **Myeloblast leucosis K562.**

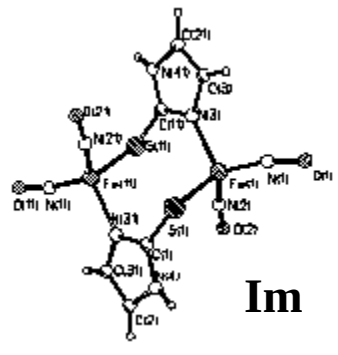


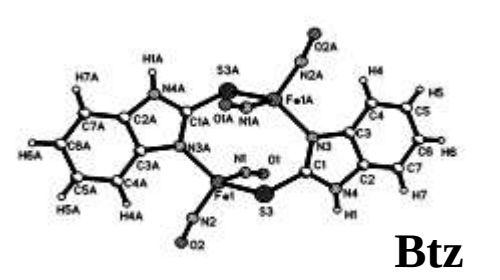


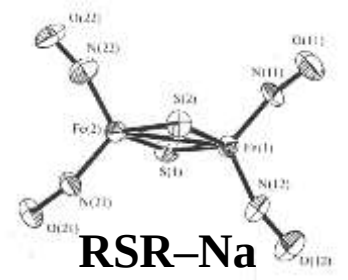


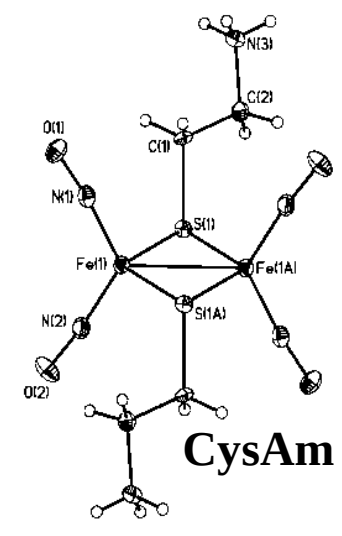


Anticancer activity of nitrosyl iron complexes *in vivo*







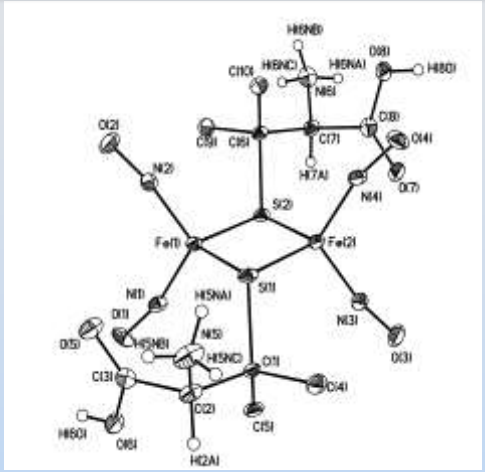


Anticancer activity of the compounds was studied on 4 models of mice's tumors, which are compulsory for the selection of new anticancer drugs:

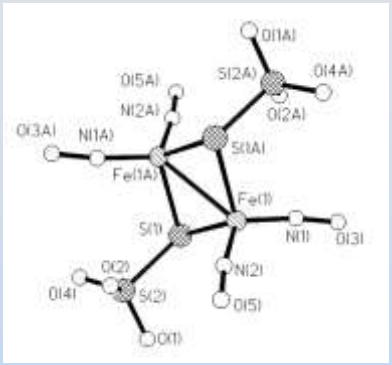
- melqanoma B-16
- epidermoid Lewis lung carcinoma (LLC)
- adenocarcinoma of mammary gland Ca-755
- lymphocytic leucaemia P-388

THE MOST ACTIVE NITROSYL BINUCLEAR WATER SOLUBLE IRON COMPLEXES AS PROMISING MEDICINES

for the therapy of acute coronary heart diseases:

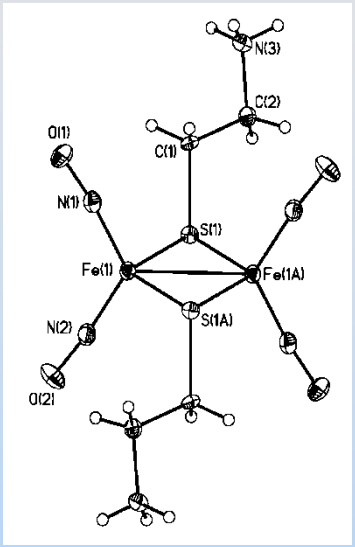


$[Fe_2(SR)_2(NO)_4]SO_4 \cdot H_2O$ with R=penicillamine



$Na_2[Fe_2(SR)_2(NO)_4]4 \cdot H_2O$ with R= thiosulfate

for antitumor therapy:



$Fe_2(SR)_2(NO)_4]SO_4 \cdot 2{,}5H_2O$ with R= cysteamine

Models of isolated perfused and regional ischemia of rat's heart

N.A. Sanina, L.I. Serebryakova et.al.,
Patents RF No. 2460531 (2012) ; No. 2437667(2012).

Experimental models of mice:

- colon adenocarcinoma AKATOL
- melanoma B16
- adenocarcinoma Ca-755
- LL-carcinoma (LLC)

N.A. Sanina, K.A.Lysenko et.al.
Patent US No. 8,067,628; B2 (2011)
Patent RF No. 2441873 (2012)

Specific features of DNIC structure

Unusual structure of nitrosyl {Fe(NO)x}n unit

Determination of Enemark-Feltham :

$\{Fe(NO)_x\}^n$, $n = x\pi^*_{NO} + (n-x)d_{Fe}$

Readiness of direct and reverse dative interaction

IR-spectra of the NO group:

NO^+ 1650-1985 cm^{-1}

NO^- 1525-1720 cm^{-1}

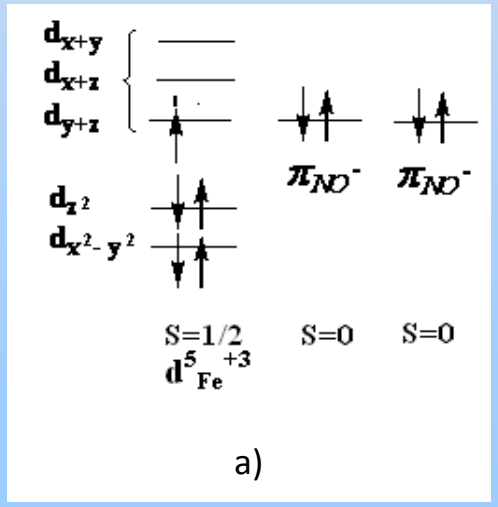
Strong overlapping of frequencies

Structure of the dinitrosyl unit $[Fe(NO)_2]$ for $Fe^+(d^7)$:

(a) Direct dative interaction $d^7_{Fe} \rightarrow \pi^*_{N-O}$
(b) no $d^7_{Fe} \rightarrow \pi^*_{N-O}$ dative interaction
(c) reverse $d^7_{Fe} \leftarrow \pi^*_{N-O}$ dative interaction

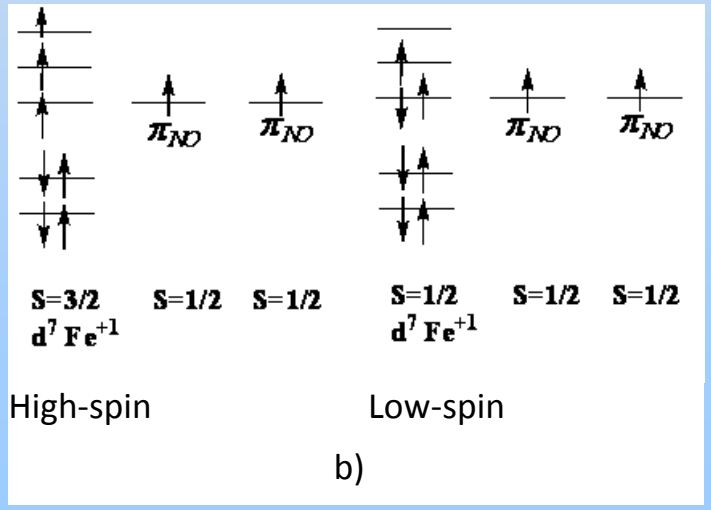
NO^- nitroxyl anion
$\cdot NO$ radical form
NO^+ nitrosonium cation

$[Fe^{+3}(NO^-)_2]^9$



a)

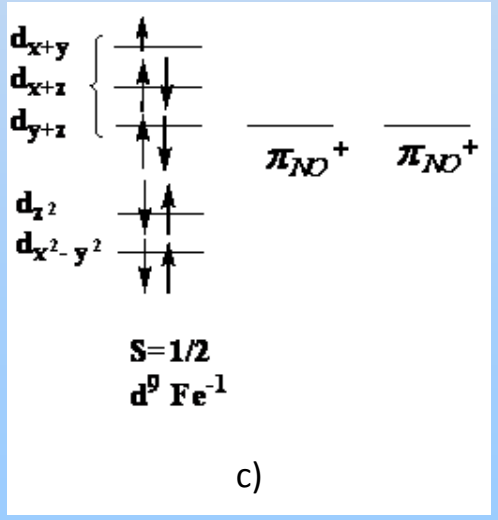
$[Fe^{+1}(\cdot NO)_2]^9$



High-spin Low-spin

b)

$[Fe^{-1}(NO^+)_2]^9$



c)

Oxidation state of Fe +3

Oxidation state of Fe +1

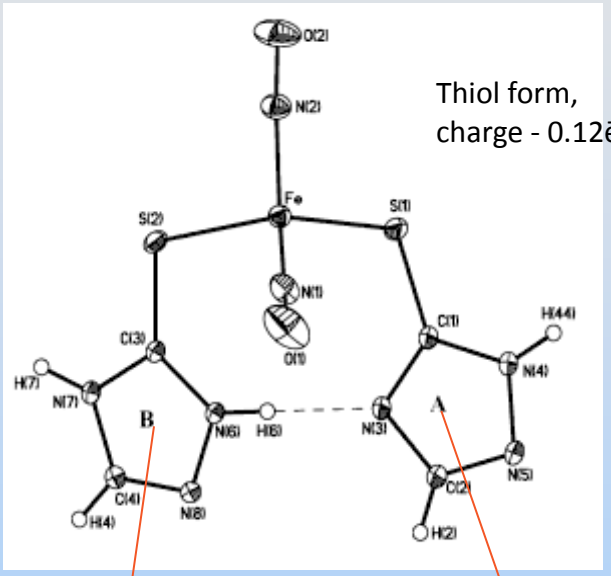
Oxidation state of Fe -1

Precision X-ray studies of nitrosyl iron complex with 2-mercaptotriazole

Values of bond lengths and angles

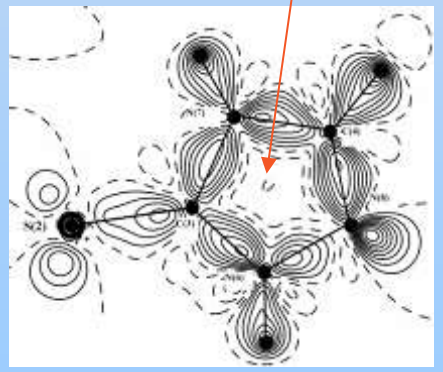
Fe-S, Å	2.302-2.322
Fe-N, Å	1.669-1.677
N-O, Å	1.164-1.163
Fe-N-O, º	169.0-172.8
C-S, Å	1.731, 1.707
(C=S 1.684 Å), C-S	1.720-1.740

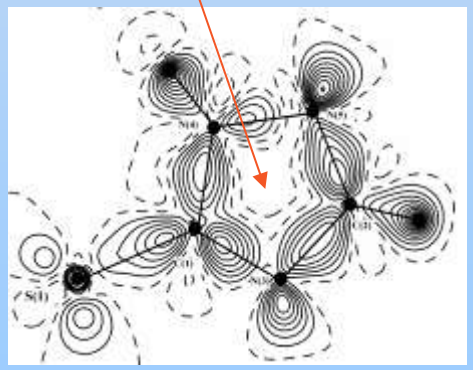
Thione form, charge of the cycle 0.08 ē



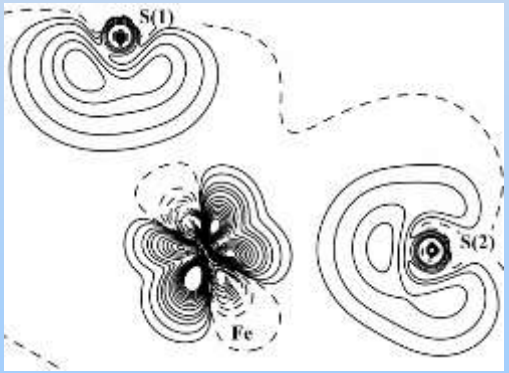
Thiol form, charge - 0.12ē

Charge on N-O ligands (-0.25) – (-0.37) ē.
Charge on S <(-0.20ē)





DED section in the plane of five-membered rings B and A.



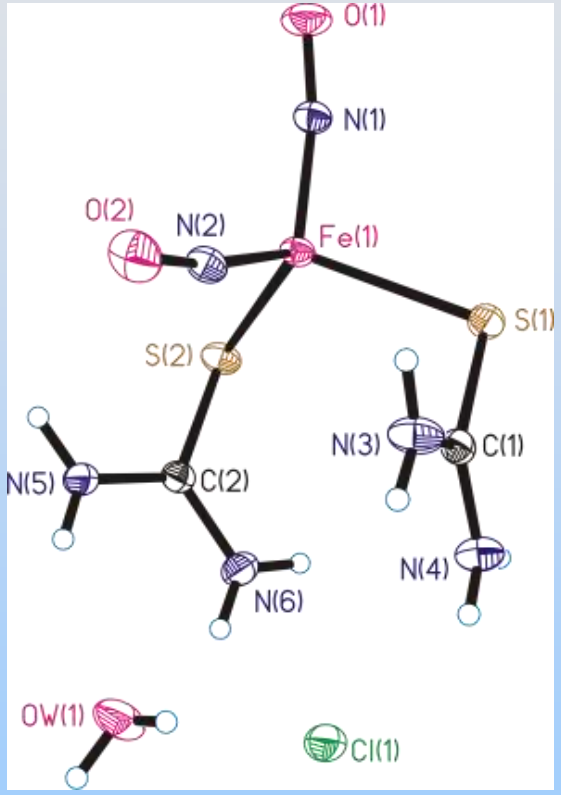
DED sections in FeS(1)S(2) plane "peak-hole" and "peak-peak" interaction types

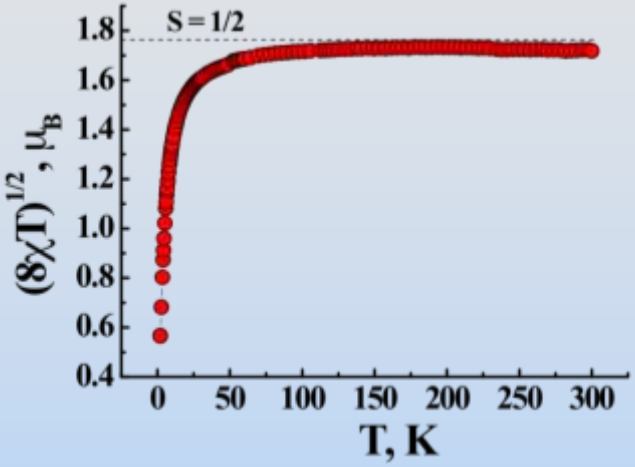
The lines are drawn with pace 0.1 eÅ^{-3}. Negative values are shown in dash line.

S. M. Aldoshin, K. A. Lysenko, M. Yu. Antipin, N. A. Sanina, V. V. Gritsenko , J. Mol. Structure.- 2008.- V.875.- P.309-315

Magnetic properties of mononuclear cationic DNIC with thiocarbamide ligand

Fe…Fe =5.81, 5.90, 6.04 Å





The temperature dependence of the effective magnetic moment of the sample. The dotted line – the expected value of the effective moment at room temperature for spin S = ½.

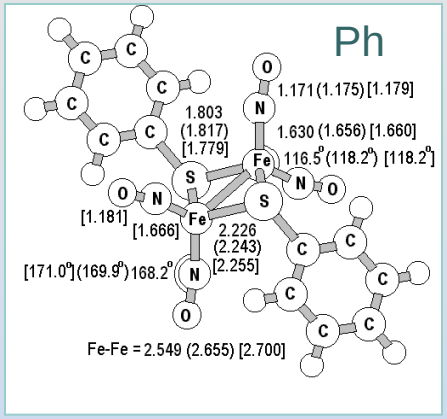
Conclusions:

-[$Fe(NO)_2]^9$ – fragment has one unpaired electron

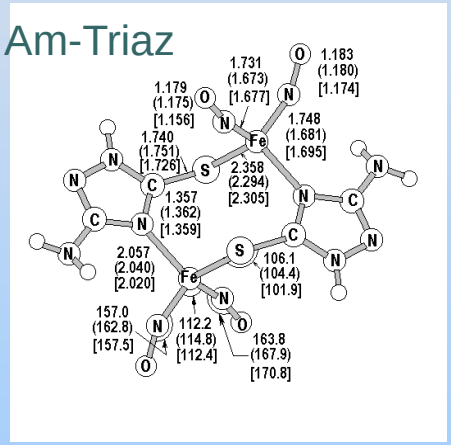
Sergey M. Aldoshin, Roman B. Morgunov, Andrei V. Palii, Natal'ya Yu. Shmatko, Nataliya A. Sanina, Study of Magnetic Behavior of Salts of Cationic Dinitrosyl Iron Complexes with Thiocarbamide and its Derivatives, Applied Magnetic Resonance (2015) 46, 12, 1383-1393.

Theoretical study of binuclear complexes of μ-S and μ-N-C-S types and mononuclear iron complexes with aromatic ligands

μ-S



μ-N-C-S

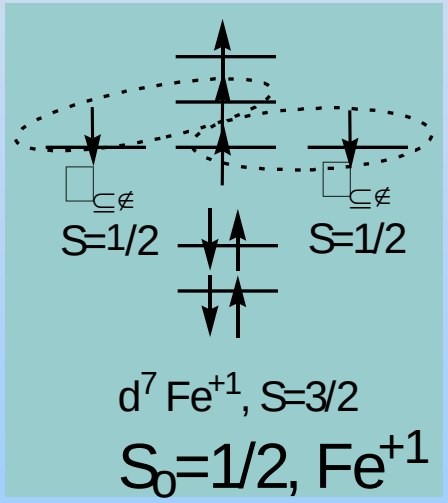


The calculations have been performed using density functional method B3LYP

RS	"multipleticity	Charge on Fe	Spin density on Fe	Charge on NO	Spin density on NO
Ph	1*	0.62	±2.41	-0.23	±0.77
Py	1*	0.63	±2.43	-0.22	±0.86
Pym	1*	0.61	±2.41	-0.21	±0.85

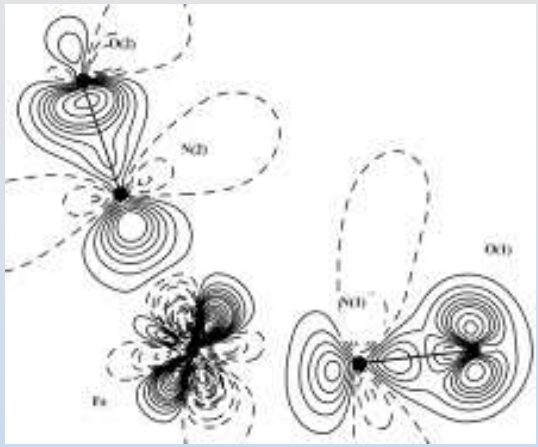
*** States with "broken" symmetry**

- **Fe(NO)2 –unit has one unpaired electron**
- **Pairing of opposite-oriented spins of NO and Fe(3+)**
- **Fe-NO bond is homeopolar.**



The singlet state with "broken" symmetry is lower than the triplet one. The calculation yields diamagnetic ground state of the complexes of ⌠-S and paramagnetic state for mononuclear complexes and binuclear complexes of ⌠-S-C-N-type

Fe-(N=O) bond: topological analysis of electron density function distribution $\rho(r)$, electron density gradient $\nabla\rho(r)$ and Laplacian $\nabla^2\rho(r)$ in the bond critical points



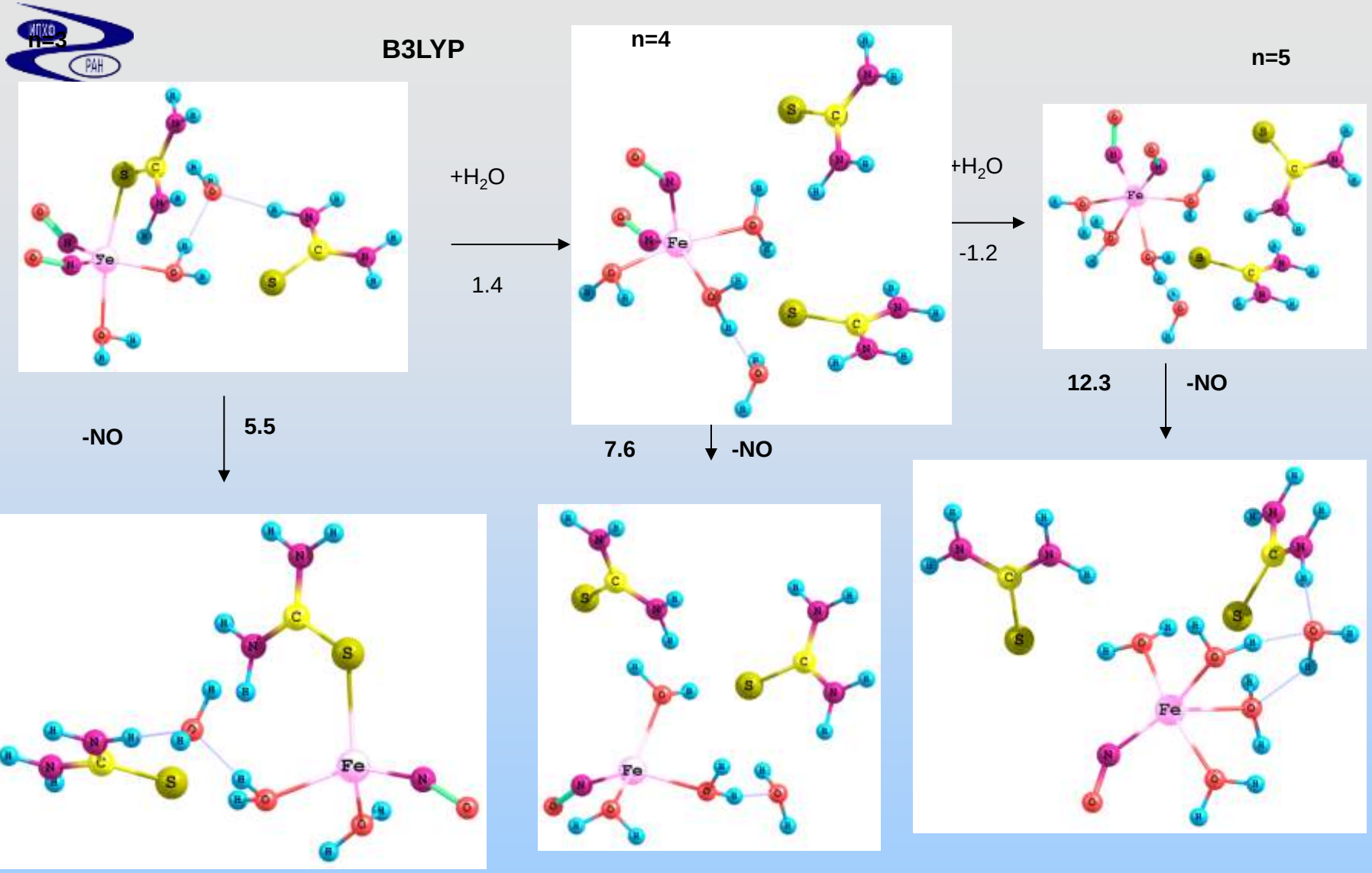
DED sections in FeN(1)N(2) plane. "peak-hole" interaction type

Structure of $Fe(SC(NH_2)_2)_2(NO)_2]^+$ cation

N.Emel'yanova, N. Shmatko, N. Sanina, S.Aldoshin. Comput. Theor. Chem., 1060 (2015), 1-9

Critical point (-3,1) $\nabla\rho(r) = 0$

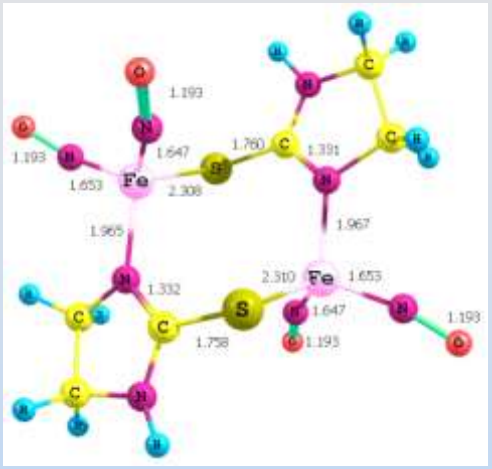
	Fe – N	N - O
$\rho(r)$, ē	0.185	0.530
$\nabla^2\rho(r)$	> 0	< 0
	Ionic or high-polar bond	covalent bond
$h_e(r)$	< 0	<0
local electron energy	covalent	bond
E of the bond kcal/mol	30-40	
The bond nature:	intermediate homeopolar	covalent



Optimized geometries of possible aqua-complexes with n water molecules, and of complexes forming after NO removal. All reactions are exothermal. The energies are shown in kcal/mol.

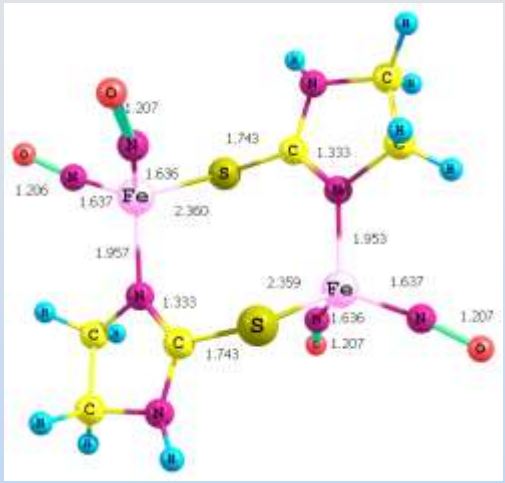
N.S. Emel'yanova, N.Yu. Shmatko, N.A. Sanina, S.M. Aldoshin. Izv. AN, Ser. Khim. (2015) N 10, 2344-2350.

Quantum-chemical modeling and experimental studies of insoluble neutral DNICs transfer into water-soluble reduced salt forms, and methods of their stabilization

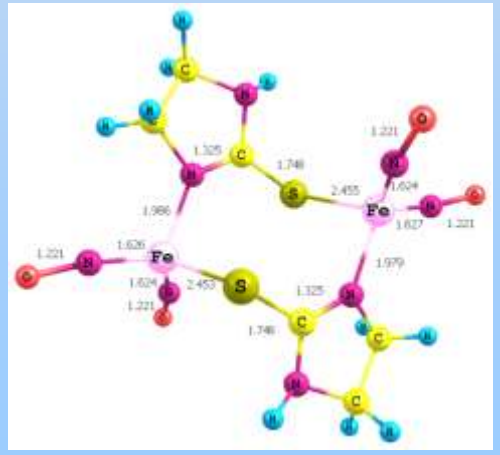


+e

-e



+e



2^-

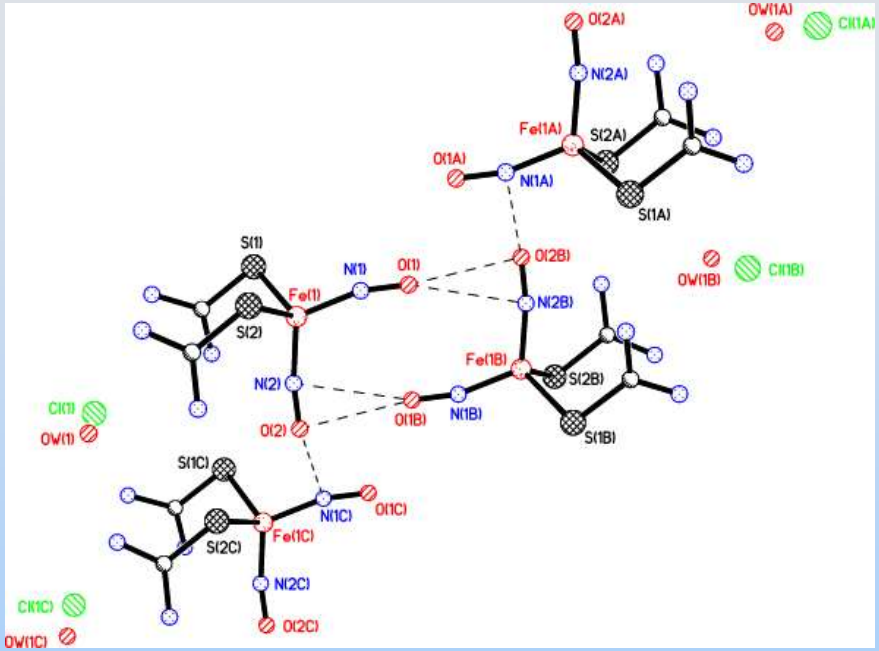
1.N.A. Sanina, A.G. Krivenko, R.A. Manzhos, N.S. Emel'yanova, G.I. Kozub, D.V. Korchagin, G.V. Shilov, T.A. Kondrat'eva, N.S. Ovanesyan, S.M. Aldoshin, New Journal of Chemistry (2014), **38**, 292-301;

2.N.S. Emel'yanova, N.A. Sanina, E.V. Knyaz'kina, A.G. Krivenko, R.A. Manzhos, S.M. Aldoshin. Izv. AN, Ser.Khim., 2014, 6 , 1265-1269.

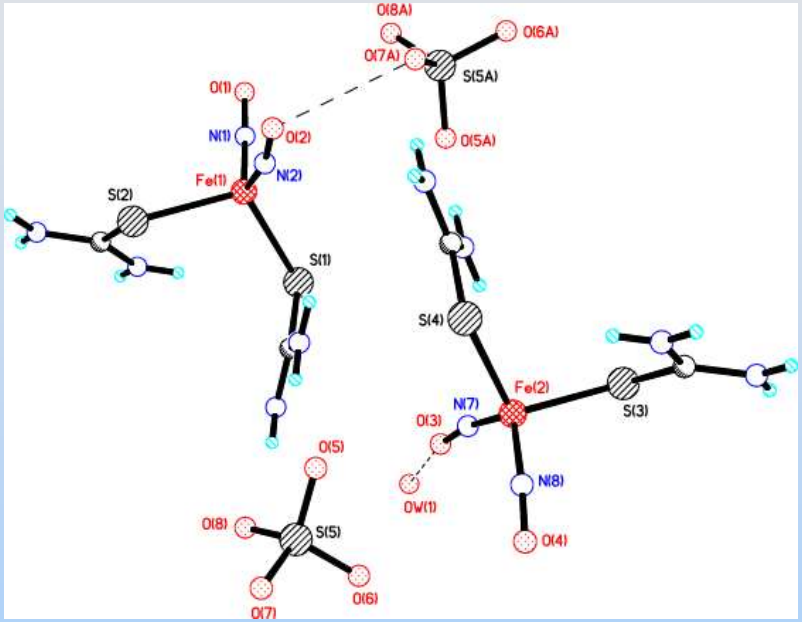
Unusual “entangled” magnetic properties of DNICs with thiocarbamide ligands

THE ROLE OF NO…NO INTERMOLECULAR INTERACTIONS IN THE DNIC CRYSTALLINE STRUCTURE

Packing type A



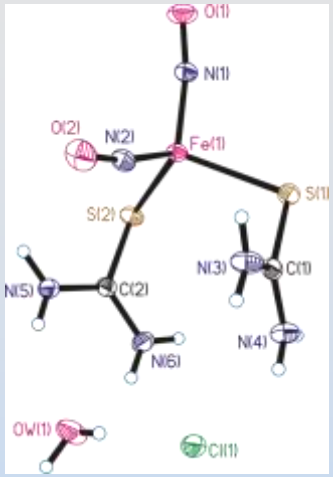
Packing type B



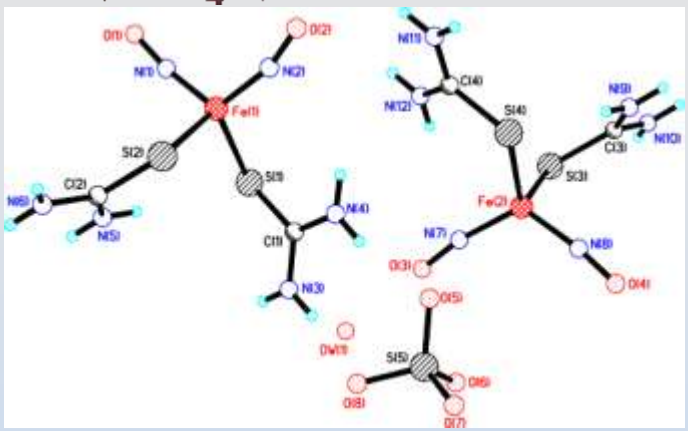
There are shortened van der Waals contacts
With the NO groups participation
O…O, O…N ~ 3Å

No shortened NO…NO contacts

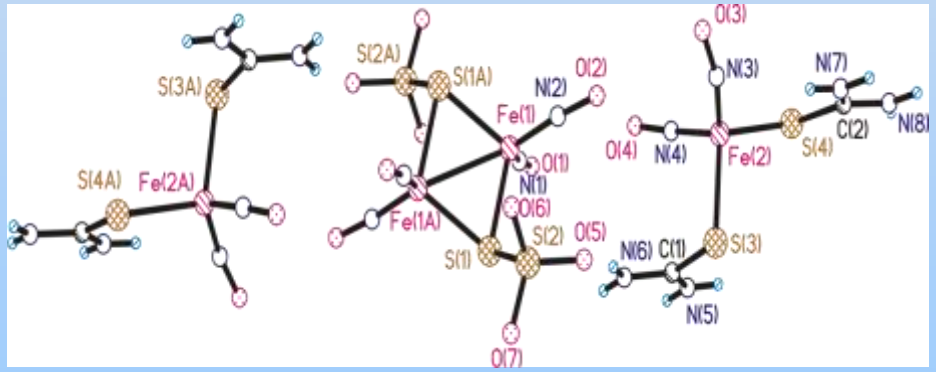
The studied cationic nitrosyl thiocarbamide iron complexes with various anions: Cl^-, SO_4^{2-}, $DNIC^{2-}$



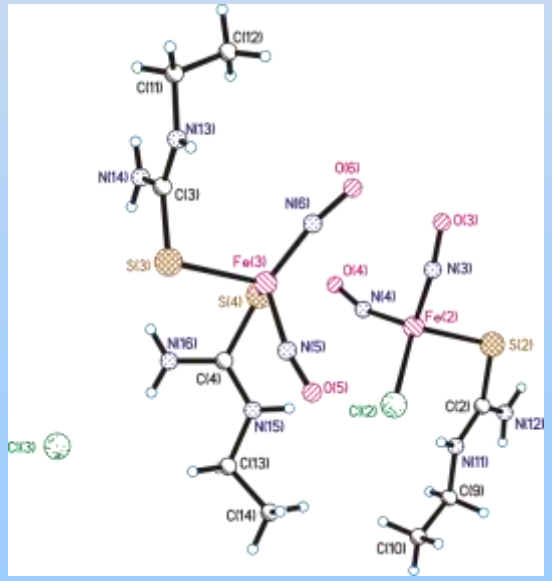
Complex 1
Fe…Fe 5.82; 5.90 Å
packing type A



Complex 2
Fe…Fe 5.06; 5.73 Å
packing type B

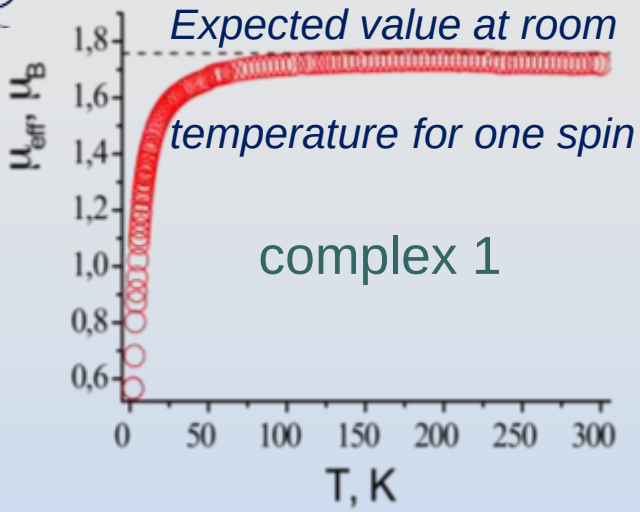


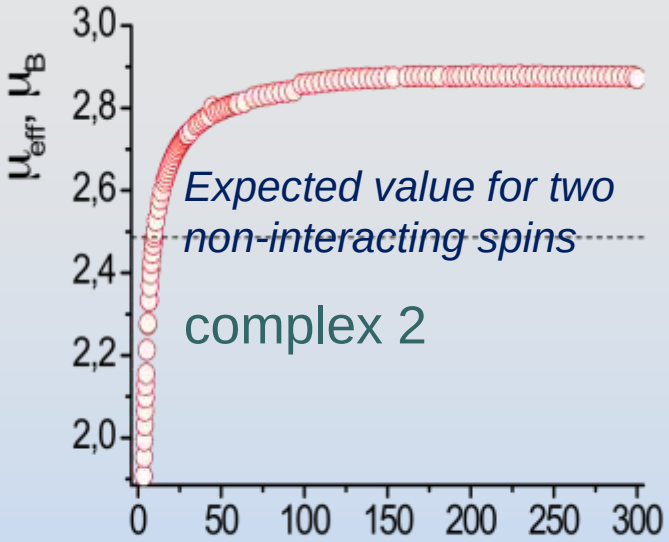
Complex 3
Fe(2)…Fe(2) 5.86; 5.91 Å
Fe(1)…Fe(2) 5.57; 5.87 Å
Packing type is intermediate between A and B

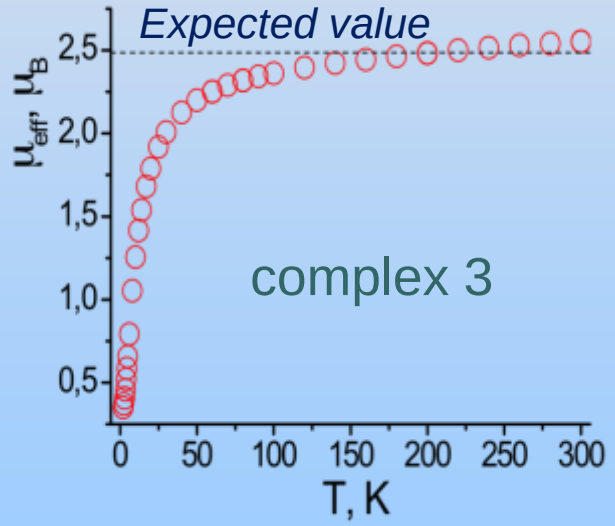


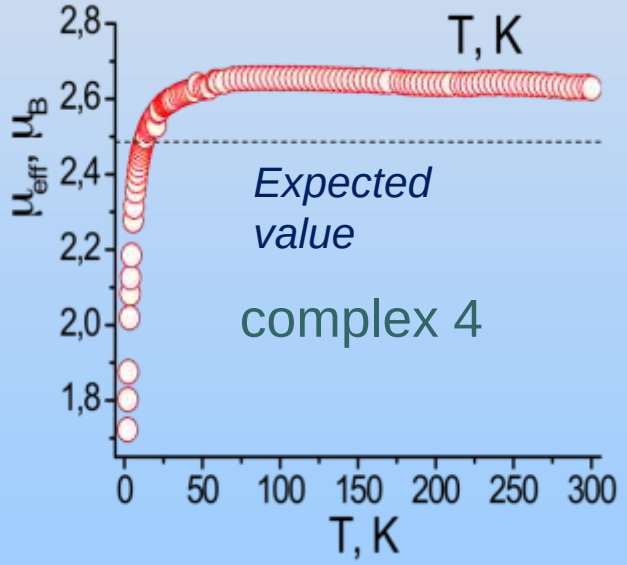
Complex 4
Fe…Fe 5.20; 5.29 Å
Packing type B

Magnetic properties of the complexes





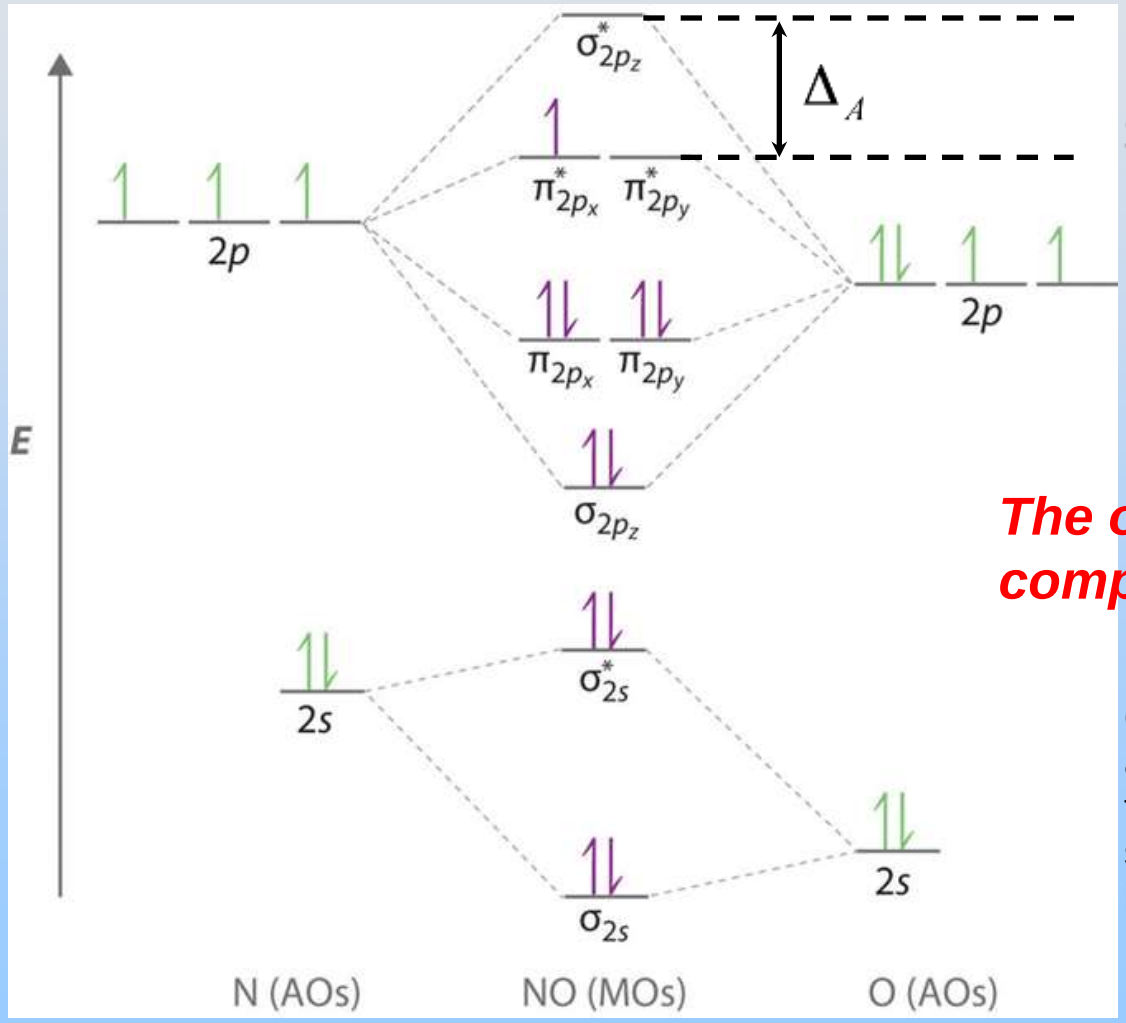




Complexes 2, 3, 4 show properties that are different from the expected ones

Free NO molecule has an axial symmetry

Основной $^2\Pi$ - терм - орбитальный дублет



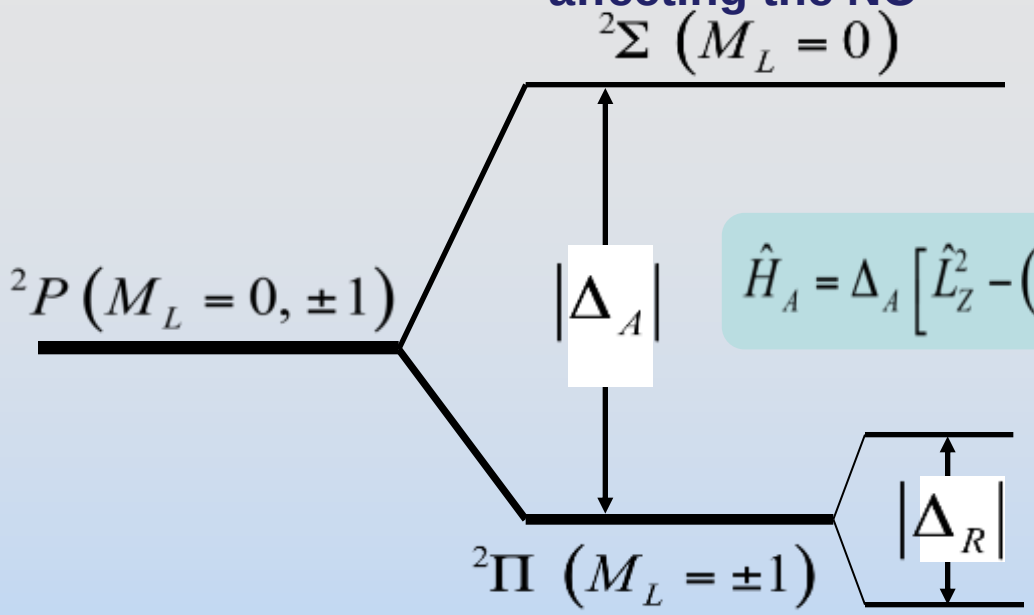
$^2\Sigma\ (M_L = 0)$

$^2\Pi\ (M_L = \pm 1)$

The orbital moment is not completely quenched

Coordination of NO with Fe is accompanied by quenching of the orbital moment due to the symmetry loss and intermolecular interactions

Hamiltonians describing the influence of the crystalline field affecting the NO



$$\hat{H}_A = \Delta_A \left[\hat{L}_Z^2 - (1/3)L(L+1)\right]$$

$$\hat{H}_R = \Delta_R \left(\hat{L}_X^2 - \hat{L}_Y^2\right)$$

Spin-orbital interaction on NO

$$\hat{H}_{SO} = \kappa\,\lambda\,\hat{\boldsymbol{L}}\,\hat{\boldsymbol{S}}$$

$\lambda \sim 120$ cm^{-1} is parameter of spin-orbital interaction
κ is a factor of orbital reduction

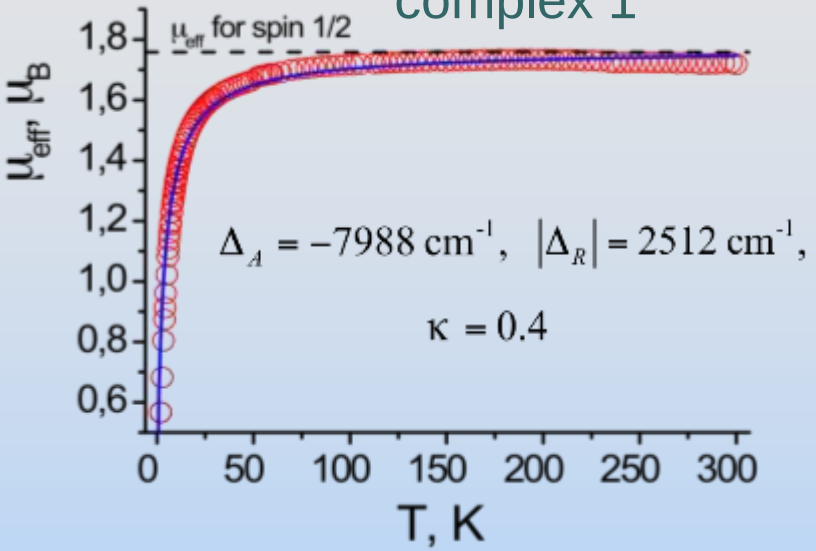
Zeeman interaction for NO

$$\hat{H}_{ZEEM}(\mathrm{NO}) = \mu_B\,\boldsymbol{H}\left(g\,\hat{\boldsymbol{S}} + \kappa\,\hat{\boldsymbol{L}}\right)$$

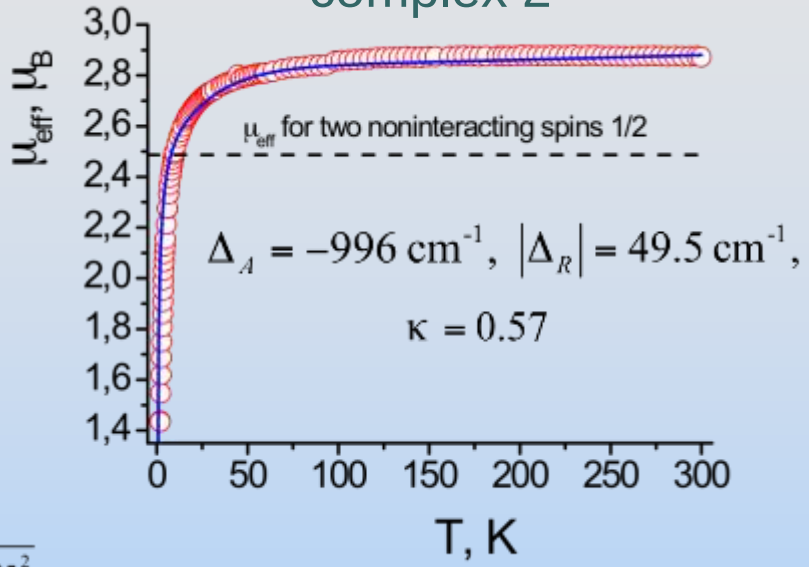
ΔR is a parameter of rhombic splitting in the cryst

Experimental $\mu_{eff}(T)$ dependence for complexes 1-4 (red circles) and theoretical dependence (blue solid lines) calculated with reasonable Δ_A, Δ_R, K and λ parameters

complex 1

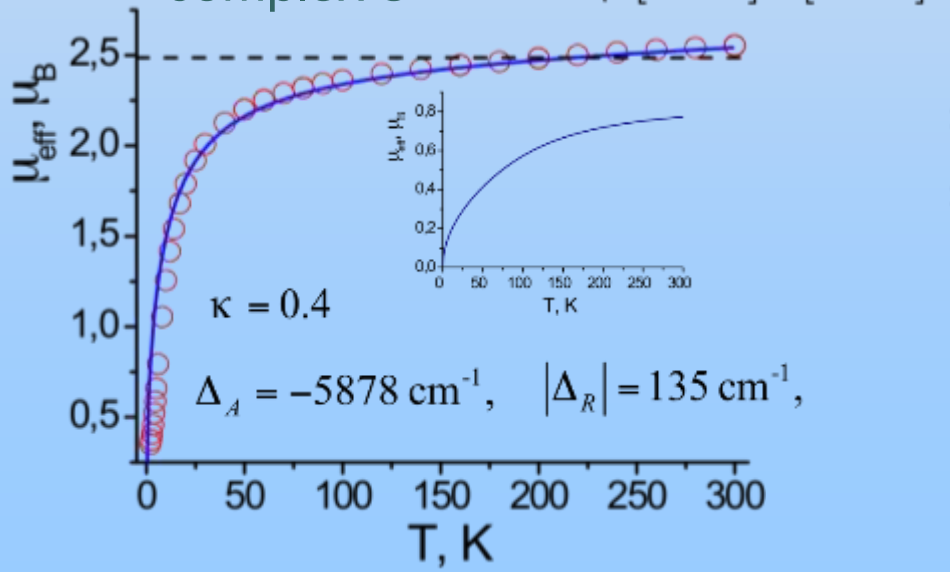


complex 2

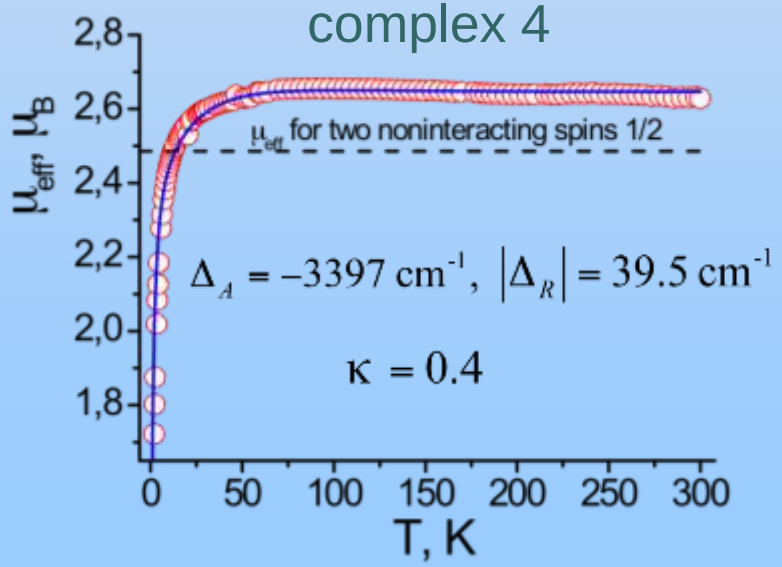


complex 3

$$\mu_{eff}(T) = \sqrt{2\left[\mu_{eff}^{K}(T)\right]^2 + \left[\mu_{eff}^{A}(T)\right]^2}$$



complex 4



Conclusions

- Structural data point to the possibility of the existence of non-quenched orbital moments on the nitrosyl groups, this being due to incomplete splitting of the ground terms of these groups and their Zeeman mixing with the excited terms;

- The contribution of the orbital moment to the resulting magnetic properties is determined by the parameter of axial splitting, the parameter of rhombic splitting, as well as by the factor of orbital reduction;

- By varying the above parameters in a reasonable range for each structure, magnetic properties of the complexes can be described;

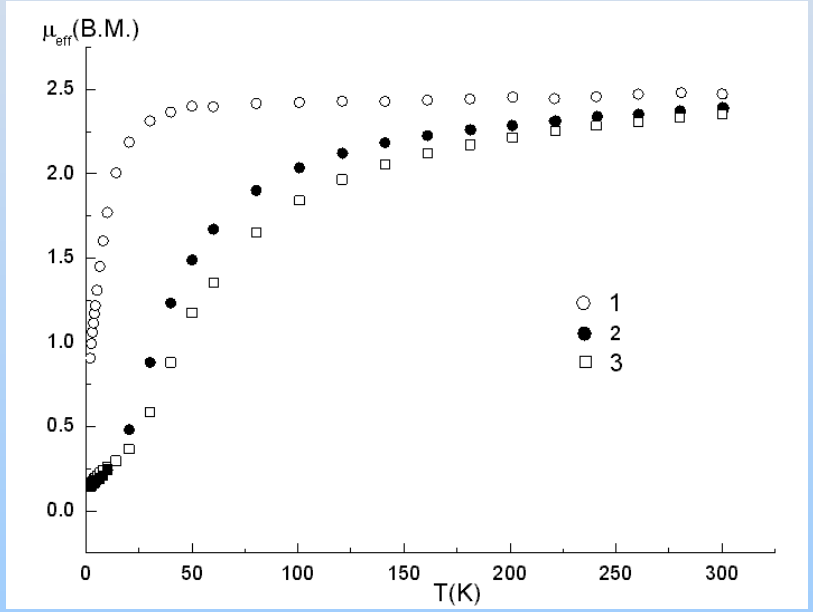
- Anionic paramagnetism has an orbital nature;

- To confirm the hypothesis and to reduce the number of adjusting parameters, the further investigations are necessary, which include quantum-chemical computations and additional experimental investigations using various resonance methods.

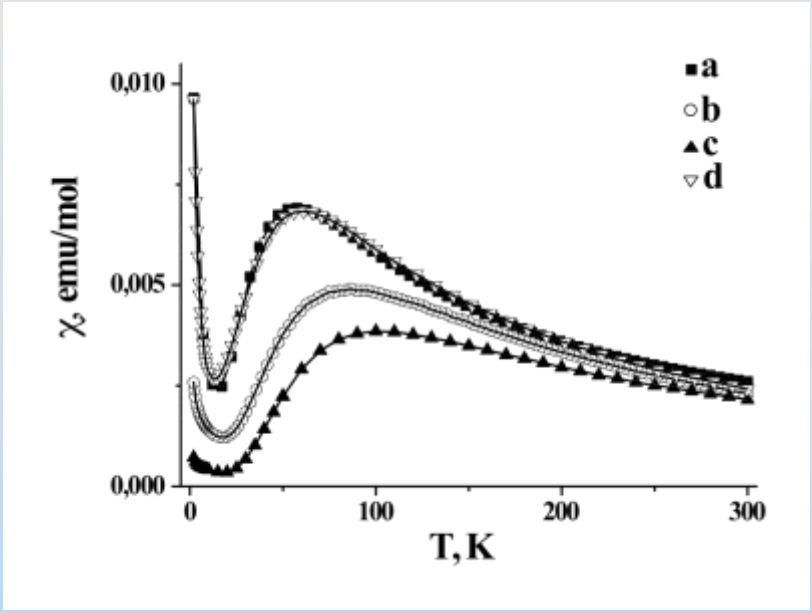
Quantum entanglement in the dimer of DNIC of μ-S-C-N type

Magnetic properties of neutral nitrosyl binuclear iron complexes of -N-C-S type $Fe_2(\mu\text{-}SR)_2(NO)_4$

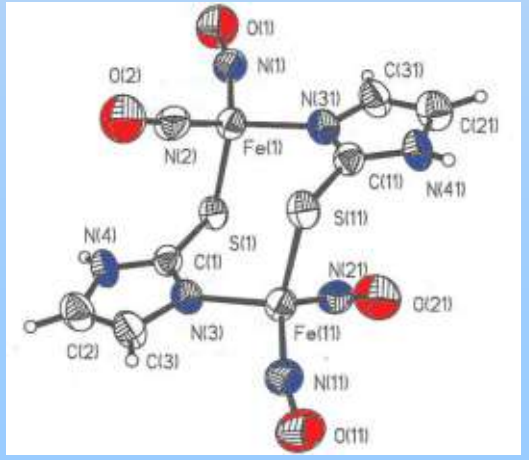
Heisenberg dimer with two non-interacting paramagnetic centers with one unpaired electron (s=1/2) on each center.
μ_{total}=2.44 μB



Temperature dependences of the effective magnetic moment for complexes AmTriaz (1), Im (2), Mim (3) in the constant magnetic field 1 кOe.

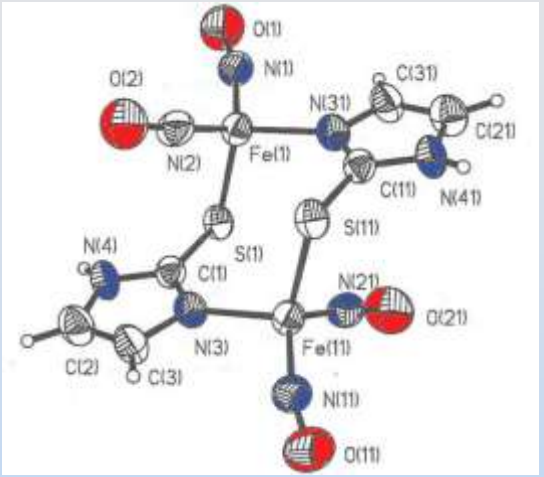


Temperature dependences of magnetic susceptibility for complexes Bim (a), Mim (b), Imid (c) and Im (d) in constant magnetic field 1 кOe.



Quantum-information correlations in DNIC dimeric molecules of μ-S-C-N type

Features of crystal chemical structure :



- there are no shortened intermolecular contacts;
- intermolecular Fe…Fe contacts exceed 5 Å;
- intramolecular Fe…Fe contacts are 4.0-4.1 Å

Magnetic and electronic properties :

- typical Heisenberg dimers with antiferromagnetic intramolecular exchange;
- T=0, the singlet state of the dimer is described by a wave function

$|\Psi\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ (1)

- Quantum state (1):

a) is entangled (the given state of the system Ψ does not define unambiguously a state of subsystems, however, if a state of one subsystem is defined, a state of the other is defined unambiguously);

b) describes a coherent superposition of two qubits of information (the register of the quantum computer);

Complexes of μ-S-C-N type can have quantum correlations at low temperatures, which are promising for quantum devices

Quantum entanglement (E) and magnetic susceptibility of DNIC of μ-S-C-N type

Hill and Wootters have defined values of quantum entanglement E via concurrence C in two-qubit systems

$$\tilde{C} = |\langle \psi | \tilde{\psi} \rangle|, where\ |\tilde{\psi}\rangle\ function, orthogonal\ |\psi\rangle \qquad (2)$$

$$\tilde{C} = |ad - bc|\ \ a,b,c,d - coefficients\ of\ basis\ functions \qquad (2a)$$

$$E = -\frac{1+\sqrt{1-\tilde{C}^2}}{2}\log_2\left(\frac{1+\sqrt{1-\tilde{C}^2}}{2}\right) - \frac{1-\sqrt{1-\tilde{C}^2}}{2}\log_2\left(\frac{1-\sqrt{1-\tilde{C}^2}}{2}\right) \qquad (3)$$

S.Hill, W.K.Wootters. Phys.Rev.Lett 78,5022 (1977); 80, 2245 (1988)

For Heisenberg dimer:

$$\tilde{C}(T) = \begin{cases} -1 + \dfrac{2}{1+3\exp\left[-2|J|/(kT)\right]}, & T < T_e \\ 0, & T \geq T_e \end{cases} \qquad (4)$$

E.B. Fel'dman, M.A. Yurischev. Pis'ma ZhETF, 90, 70 (2009)

$$where\ T_e = \frac{2}{\ln 3}|J|/k_B \qquad (5)$$

–In the dimer with ferromagnetic exchange (J≥0) , at T=0, C=0, E=0

–In the dimer with antiferromagnetic exchange (J<0), at T=0, C=1, E=1

–Upon T growth entanglement E in the dimer decreases, and at $T=T_E$ disappears completely

ENTANGLEMENT AND MAGNETIC SUSCEPTIBILITY

S.M. Aldoshin, A.I. Zenchuk, E.B. Fel'dman, M.A. Yurischev.
Russ.Chem.Rev. 81 (2), 91, 2012

- Entanglement in the dimer exists when:

$$\chi(T) < \frac{2}{3}\chi^{Curie}(T) \qquad (6)$$

$$\chi^{Curie}(T) = N_A g^2 \mu_B^2 / (2k_B T) \qquad (6a)$$

Curie law for two spins

Or when $\mu_{эфф}(T) < g\sqrt{nS}$ $(for\ Heisenberg\ \dim er\ DNIC\ n=2, g=2, s=1/2)$

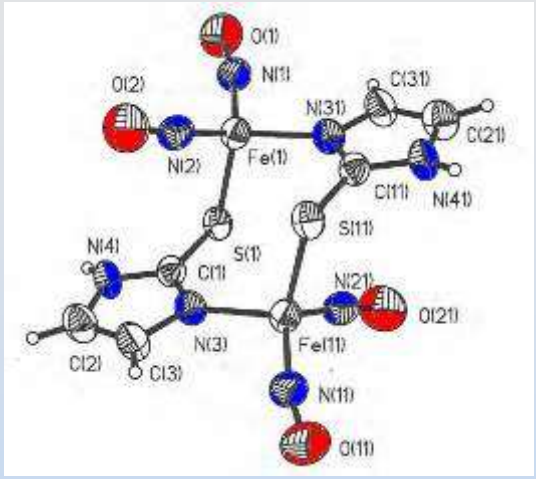
- The temperature above which entanglement disappears (T_e), and the temperature at which $\chi(T)$ has the maximum ($T\chi_{max}$), for Heisenberg dimer are related by the following equation:

$$T_e / T_{\max}^{\chi} = 1.4596 \qquad (7)$$

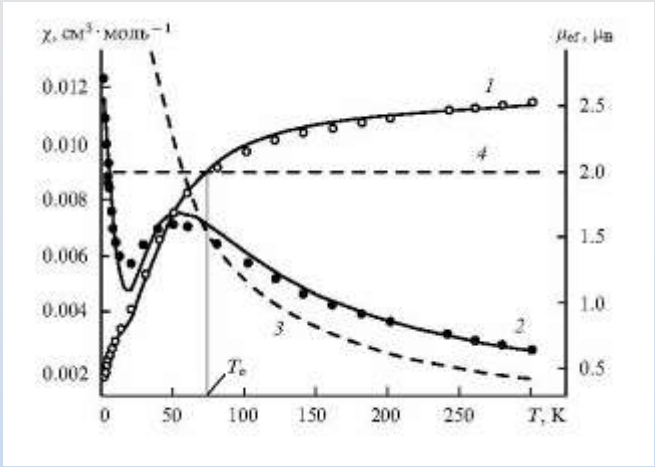
- T_e and the temperature of entanglement fluctuation T_f above which fluctuations become higher than the entanglement value E are related by the following equation:

$$T_f / T_e = 0.311771 \qquad (8)$$

QUANTUM ENTANGLEMENT IN BINUCLEAR DNIC (1) WITH IMIDAZOLE-2-YL LIGAND



Molecular structure of complex (1)
Fe(1)…Fe(11) = 4.102(7)Å;

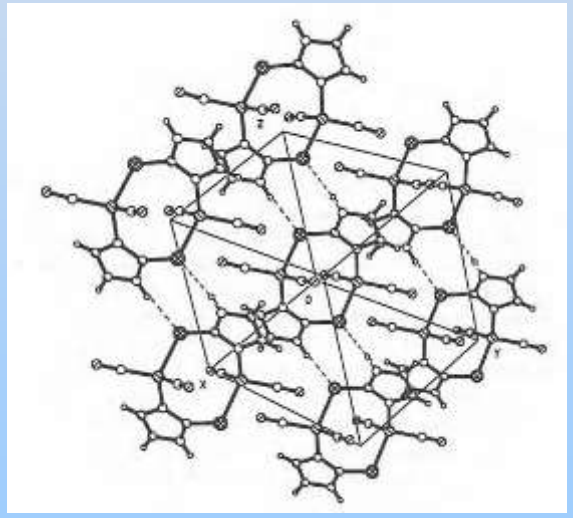


Temperature dependences of effective magnetic moment (1) and magnetic susceptibility for complex 1

Dotted line 3 – deformed Curie hyperbola at g=2

Horizontal dotted line 4 is plotted at level $g\sqrt{ns} = 2$

S.M. Aldoshin, A.I. Zenchuk, E.B. Fel'dman, M.A. Yurischev. Russ.Chem.Rev. 81 (2), 91, 2012



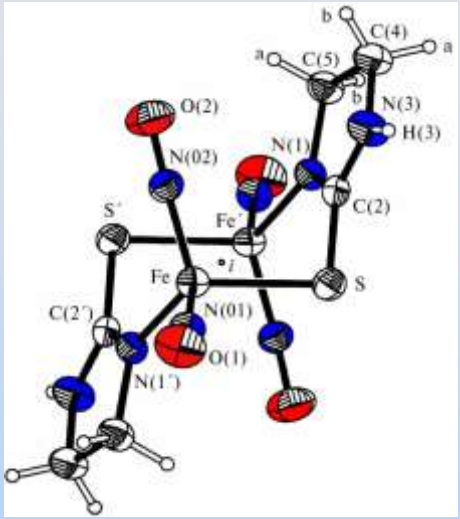
Crystalline structure of complex (1)

Intermolecular Fe…Fe distances are equal to 5.593 and 6.603Å;

–The sample contains ~2.3% of admixture, thus resulting in the increase of susceptibility near zero temperature
–Intersection point for curves 2 and 3 yields T_e=80K
–$T_e = T^x_{max}$ x 1.4596=90K
–Entanglement in complex (1) arises at the temperature below 80-90 K

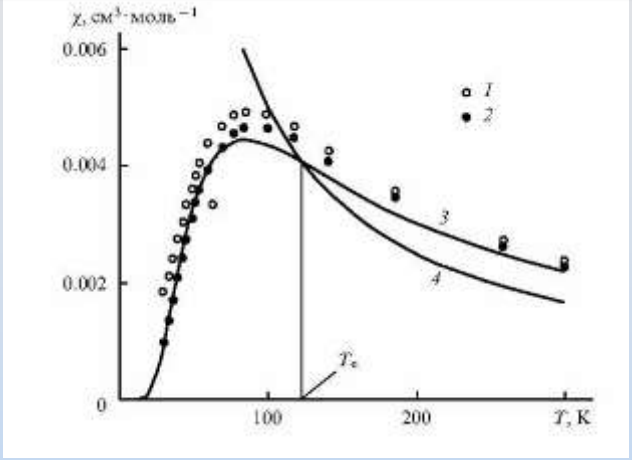
N.A.Sanina, S.M.Aldoshin et al J.Mol.Struct. 752,110,2005

QUANTUM ENTANGLEMENT AND ENTANGLEMENT FLUCTUATIONS IN BINUCLEAR DIMERIC DNIC (2) WITH IMIDAZOLIDEN-2-YL LIGAND



Molecular structure of complex (2)

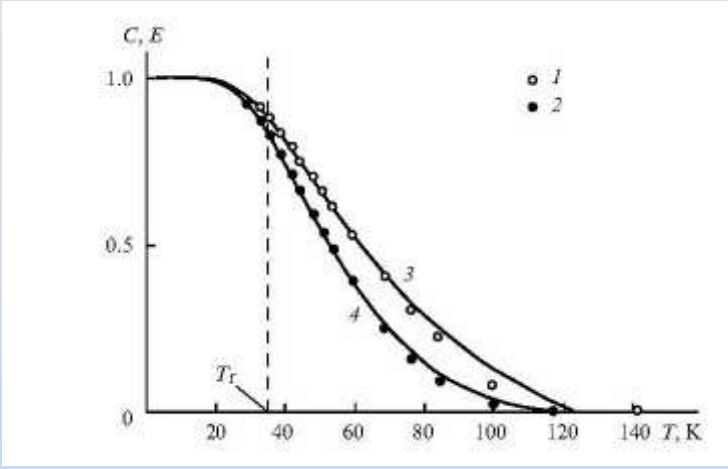
Fe…Fe = 4.030Å;



Temperature dependences of magnetic susceptibility for complex (2) taking into account the contribution of admixture (1) and after deducting this contribution (2)

3- theoretical dependence of Bleaney Bowers with J/k=-68K and g=2;

4- dependence $\chi(T) \propto \frac{2}{3}\chi^{Curie}(T)$ with g=2.



Temperature dependences of concurrence (1) and entanglement (2) for complex 2

Solid curves 3 and 4 – theoretical temperature dependences for C and E, respectively

- For complex (2) entanglement arises at T_e below 110-120 K

-at T=25 K entanglement is 0.90-0.95 of the maximal E=1

-at T_f =0.31776 x T_e =38K entanglement fluctuation becomes equal to the entanglement

N.A. Sanina, T.N. Rudneva, S.M. Aldoshin, et al. Russian Chemical Bulletin 56, 1, 28 , 2007

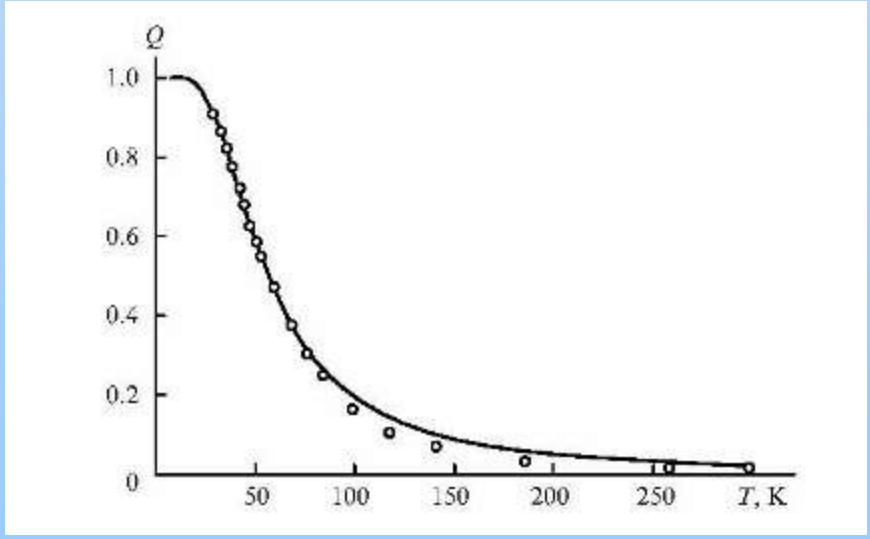
Conclusion: For dimeric binuclear DNIC, entanglement sufficient for their application as materials for quantum computers is achieved at T_f =38 K

S.M. Aldoshin, A.I. Zenchuk, E.B. Fel'dman, M.A. Yurischev. Russ.Chem.Rev. 81 (2), 91, 2012

QUANTUM CORRELATIONS FOR CREATION OF QUANTUM DEVICES

1. The presence of entanglement of quantum states in the system at rather high temperatures
2. Inconsiderable fluctuations
3. Long time of quantum decoherence (spin-lattice relaxation, interaction of a spin with ligands)
4. Entanglement can be a part of general quantum correlations, i.e., quantum discord

   $I = C + Q$ C-classical, Q – all quantum correlations (discord)
5. In DNIC quantum discord remains up to room temperature, and can appear in complexes with ferromagnetic exchange



Temperature dependence of quantum discord for complex 2

Circles – experimental data obtained from the measurements of magnetic susceptibility, solid curve – theoretical dependence

CONCLUSIONS

1. The basic structural unit of DNIC – $[Fe(NO)_2]^9$ is paramagnetic and has one unpaired electron S=1/2.

2. The structural data point to the possibility of existence of not completely quenched orbital moments on the nitrosyl groups due to incomplete splitting of the ground terms of these groups and their Zeeman mixing with the excited terms;

3. In spite of short Fe…Fe intramolecular distance ~2.72 Å, DNIC of μ-S-type have a residual paramagnetism. Anionic paramagnetism is of purely orbital origin;

4. In DNIC of μ-S-C-N type quantum-chemical correlations exist at low temperatures, this being promising for the development of quantum computers.

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- Program of basic research of RAS “Theoretical and experimental study of the chemical bond and mechanisms of basic chemical reactions and processes”
- Program of basic research of RAS “ Medical chemistry: molecular design of physiologically active compounds and medicines”
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