Asian Journal of Chemistry; Vol. 28, No. 4 (2016), 825-829

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19530

Synthesis, Crystal, Molecular Structure and Theoretical Modeling of $[Fe(H_2O)_6]L_2·2H_2O$ and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2·2H_2O$ (L = 4-Nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion)

O. KOVALCHUKOVA[1,*], M. RYABOV[1], A. STASH[2] and T. BERIKASHVILI[3]

[1]Department of General Chemistry, Peoples' Friendship University of Russia, Moscow, Russia
[2]Karpov Institute of Physical Chemistry, Moscow, Russia
[3]Department of Physics, Georgian Technical University, Tbilisi, Georgia

*Corresponding author: Fax: +7 49 96195912; Tel: +7 49 59550860; E-mail: okovalchukova@mail.ru

Received: 28 July 2015; *Accepted*: 20 September 2015; *Published online*: 30 December 2015; AJC-17700

The crystal and molecular structures of $[Fe(H_2O)_6]L_2·2H_2O$ and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2·2H_2O$ (L = 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion) were detected by X-ray analysis. It was shown that the above mentioned organic anion cannot replace water molecules from the coordination sphere of transition metal complexes. According to the DFT/B3LYP calculations, the low complexing ability of 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion in comparison with its carbocyclic analogues is determined by the features of the electronic structure of 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion.

Keywords: 4-Nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion, Metal complexes, DFT/B3LYP modeling.

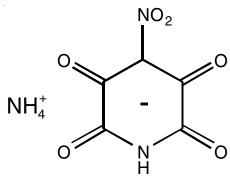
INTRODUCTION

Over the last decades, the efforts of synthetic inorganic chemists have been concentrated on the synthesis of self-assembling coordination polymers of an extended framework architecture [1] with oxalate- [2] or cyanometalates $[M(CN)_n]^{m-}$ [3] as monomer blocks. The above monomer complexes may act as bridging fragments to form 2-D and 3-D coordination polymers containing transition metal cations. In the case of bimetallic ($M^{2+}M^{3+}$) compounds, the possibility of electron and magnetic exchange appears which brings new properties and areas of application of the coordination polymers [4].

The oxalate- and cyano-anions in the polymeric complexes may be exchanged by polyoxo carbocyclic anions. The features of the structure of their monomeric and polymeric complexes containing transition metals was recently reviewed [5].

Previously we reported the synthesis and crystal structure of a new polyoxo heterocyclic organic anion – 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate (L) in the form of ammonium [6] and sodium salts [7] and its silver(I) [8] and barium complexes [9].

As it is evident from the crystal structure determination, the 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion is planar with the double bond character of the CO bonds (1.20-1.23 Å) and one elongated CC bond of particularly singular character (1.53-1.54 Å) which splits the 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion into two non-conjugated nitro-diketone and amide fragments. Similar structures were detected for carbocyclic 6-membered polyoxo anions [5].



(NH$_4$L)

Structure of 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate (L)

The coordination does not change significantly the C-O distances of 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion (L) comparing with its ammonium and sodium salts. The organic anion acts as bridging polydentate ligand which can form the 3D-lattice separately or in combination with the oxalate anion.

Here we report the synthesis, crystal structure determination, spectroscopic characteristics and some properties of $[Fe(H_2O)_6]L_2·2H_2O$ and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2·2H_2O$ (L is 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion) as well as the theoretical modeling of the complexing ability of the above mentioned anion in comparison with its carbocyclic polyoxo-analogues.

EXPERIMENTAL

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification.

General procedure: Synthesis of $[Fe(H_2O)_6]L_2{\cdot}2H_2O$ (**I**) and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2{\cdot}2H_2O$ (**II**) was performed according to the following procedure. 5 mL of the aqueous solution of NH_4L (0.1 mol/L) was added to 5 mL of aqueous solutions containing $CrCl_3/MnCl_2$ or $FeCl_3/FeCl_2$ (0.05 mol/L for each of the salt). The formed mixtures were heated on a water bath at 60 °C for 3.5 h and then stored under room temperature for a week until the precipitation of single crystals of complexes started. The crystals were separated from the solution by filtration and dried until the constant mass in the dessicator over KOH under room temperature. Yield 60 % for **I** and 45 % for **II**. Anal. calcd. for $C_{10}H_{20}N_4O_{20}Fe$ (**I**): C, 20.99; H, 3.52; N, 9.79; Fe, 9.76. Found: C, 20.76; H, 3.48; N, 9.23; Fe, 9.55 %. IR (KBr, cm^{-1}): 3600-3450 $\nu(H_2O)$; 1742, 1723, 1714 $\nu(C=O)$; 1631 $\delta(H_2O)$; 1458 $\nu_{as}(NO_2)$; 1263 $\nu_s(NO_2)$. Anal. calcd. for $C_{10}H_{20}N_4O_{20}Cr_{0.14}Mn_{0.86}$ (**II**): C, 22.92; H, 3.82; N, 10.70. Found: C, 22.73; H, 3.56; N, 10.32 %. IR (KBr, cm^{-1}): 3600-3455 $\nu(H_2O)$; 1742, 1723, 1714 $\nu(C=O)$; 1628 $\delta(H_2O)$; 1457 $\nu_{as}(NO_2)$; 1262 $\nu_s(NO_2)$.

Detection method: Elemental analysis (C, N, H) was performed on a Flash 2000 instrument. The X-ray diffraction data were collected at 100(2) K with an Enraf Nonius CAD-4 diffractometer using Mo radiation ($\lambda = 0.71073$ Å) and w scans were used for the data collection. The structure was solved with direct methods using SHELXTL [10]. The refinement of the structure was performed by the full-matrix least square method on F2 for all the data with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were added using a riding model. CCDC reference numbers 1057146 and 1057134. The supplementary crystallographic data can be obtained free of charge from Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The crystallography details for the structures determination of the compounds are presented in Table-1.

Theoretical modeling of molecular and electronic structure of the L anion and its carbocyclic analogues was performed in the frames of the density functional theory (DFT) using a hybrid B3LYP functional [11,12] and the def2-SV(P) basis set [13]. Within the calculation, the full geometry optimization was performed. The analysis of the electronic structure was performed with the NBO approach [14]. All the calculations were performed with the Firefly 7.1.G program complex [15].

RESULTS AND DISCUSSION

According to the elemental analysis data, the isolated complexes can be formulated as $[Fe(H_2O)_6]L_2{\cdot}2H_2O$ (**I**) and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2{\cdot}2H_2O$ (**II**) where L is 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion. They are formed by replacement of two ammonium cations in NH_4L by the hexaaqua-cation of the corresponding metal. Structurally, they are built from the centrosymmetric complex cations $[M(H_2O)_6]^{2+}$, two 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anions and two lattice water molecules (Fig. 1).

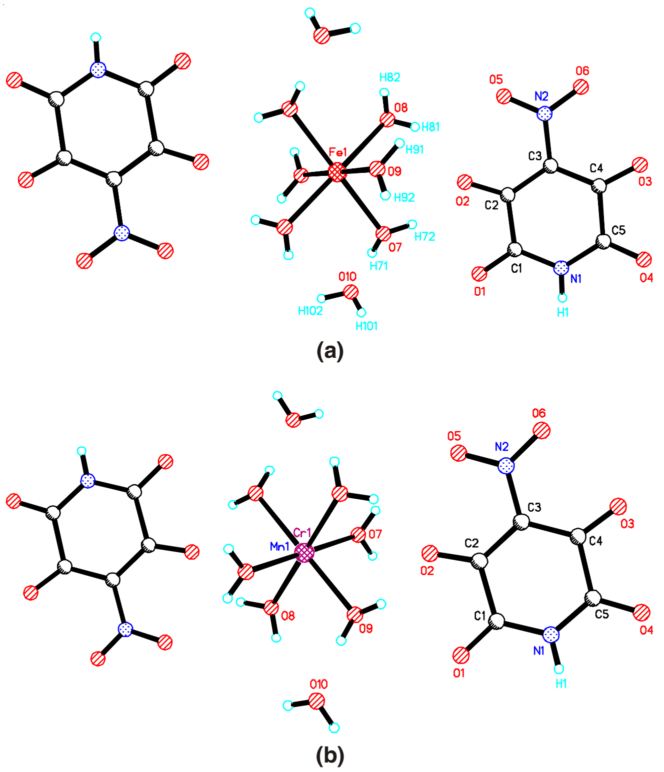
The structure **II** shows partial replacement of the manganese atoms by chromium ones (14 % in the lattice). In the complex cation (Fig. 1), the metal atom is coordinated by the O atoms of six water molecules arranged in an octahedral pattern. The MO bond lengths are 2.073-2.162 Å for **I** and 2.1341-2.2078 Å for **II**; the angles in the equatorial plane of the octahedron are 87-89°.

The nature of a metal in **I** and **II** does not change the general scheme of crystal formation, so the complexes are isostructural. In turn, they are isostructural to the complexes of similar composition $[M(H_2O)_6]L_2{\cdot}2H_2O$ (M = Ni, Co, Cd) which structures were previously reported [16,17].

The structure of the organic anions does not differ from that described previously [6-9,18,19]. The heterocyclic framework is nearly planar (the average deviation of the atoms

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT PARAMETERS FOR $[Fe(H_2O)_6]L_2$ (**I**) AND $[Cr_{0.18}Mn_{0.82}(H_2O)_6]L_2$ (**II**)

Parameters	Compound **I**	Compound **II**
Empirical formula	$C_{10}H_{20}N_4O_{20}Fe$	$C_{10}H_{20}N_4O_{20}Cr_{0.14}Mn_{0.86}$
Formula weight	570.13 g/mol	568.81 g/mol
Crystal colour	Yellow	Yellow
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a(Å) 5.694(1); b(Å) 9.845(2); c(Å) 9.891(2); α(°) 69.54(3); β(°) 78.74(3); γ(°) 84.90(3)	a(Å) 5.7350(1); b(Å) 9.864(2); c(Å) 9.890(2); α(°) 70.40(3); β(°) 85.32(3); γ(°) 79.00(3)
Volume	509.4(2) $Å^3$	517.3(2) $Å^3$
Z, calculated density	1, 1.859 Mg m^{-3}	1, 1.826 Mg m^{-3}
Absorption coefficient	0.853 mm^{-1}	0.737 mm^{-1}
F(000)	292	291
Crystal size	0.56 × 0.43 × 0.08 mm	0.70 × 0.35 × 0.20 mm
Theta range for data collection	2.91 to 29.98 deg.	2.91 to 29.98 deg.
Limiting indices	$-6 \le h \le 0$, $-11 \le k \le 11$, $-11 \le l \le 11$	$-6 \le h \le 0$, $-11 \le k \le 11$, $-11 \le l \le 11$
Reflections collected/unique	1889/1581 [R(int) = 0.0665]	1901/1722 [R(int) = 0.0130]
Completeness to θ = 29.98	100 %	100 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1889/0/196	1901/0/204
Goodness-of-fit on F2	1.218	1.086
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0396, wR2 = 0.1255	R1 = 0.0233, wR2 = 0.0667
R indices (all data)	R1 = 0.0665, wR2 = 0.1298	R1 = 0.0329, wR2 = 0.0681



(a)

(b)

Fig. 1. Molecular structures of **I** (a) and **II** (b)

from their mean_square plane is less than 0.01 Å). The ring is not aromatic: the imine (OC-NH-CO) and β-diketone fragments [OC-C(NO_2)-CO] are linked by the single CC bonds (1.538 and 1.557 Å for **I** and **II**, respectively). The CO bond lengths are in the interval from 1.200 to 1.228 Å that indicates their double bond character. The nitro groups of the ligands are not coplanar with the framework (the corresponding angle is 10.6°). The exocyclic N atoms show trigonal bond orientations (the sums of their bond angles are 360.9 and 359.78°, respectively).

In the lattice, the complexes **I** and **II** have layered crystal structures (Fig. 2). Each layer consists of alternating cation and anion containing stacks aligned with the *a* axis. In stacks, the complex cations are hydrogen bonded to form infinite chains (Tables 2 and 3). Thus, the crystal structure determination indicates that 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion cannot replace water molecules from the hydrated cations of transition elements. This is rather different from other carbocyclic polyoxo compounds for which a lot of transition metal complexes are reviewed [5].

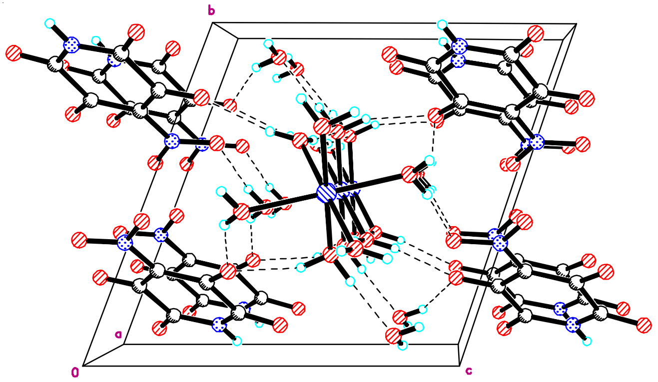


Fig. 2. Molecular packing in crystals of **I** (along the *a* axis)

TABLE-2
GEOMETRICAL PARAMETERS OF THE
HYDROGEN BONDS IN COMPLEX **I**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠DHA
N1-H1···O1	0.82(4)	2.07(4)	2.883(3)	170(3)
O7-H71···O10	0.86(4)	1.80(4)	2.655(3)	178(4)
O7-H72···O2	0.86(4)	1.90(4)	2.724(3)	159(3)
O8-H81···O2	0.77(4)	2.08(4)	2.760(3)	146(3)
O8-H82···O6	0.75(4)	2.14(4)	2.877(3)	170(4)
O9-H91···O3	0.87(4)	1.94(4)	2.781(3)	162(4) 2
O9-H92···O7	0.78(5)	2.13(5)	2.899(3)	170(4)
O10-H101···O4	0.65(4)	2.24(4)	2.873(3)	170(4)
O10-H102···O3	0.85(5)	2.15(4)	2.834(3)	138(4)

TABLE-3
GEOMETRICAL PARAMETERS OF THE
HYDROGEN BONDS IN COMPLEX **II**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠DHA
N1-H1···O1	0.86(2)	2.05(2)	2.905(2)	171.7(19)
O7-H71···O9	0.83(3)	2.07(3)	2.8951(18)	173(3)
O7-H72···O3	0.82(3)	2.03(3)	2.8054(19)	157(3)
O8-H81···O2	0.88(3)	2.01(3)	2.7824(19)	146(2)
O8-H82···O6	0.83(3)	2.07(3)	2.889(2)	166(2)
O9-H91···O10	0.87(3)	1.79(3)	2.660(2)	173(2)
O9-H92···O2	0.87(3)	1.90(3)	2.7257(18)	157(2)
O10-H101···O4	0.81(3)	2.09(3)	2.890(2)	166(3)
O10-H102···O3	0.79(3)	2.16(3)	2.863(2)	149(2)

In order to explain the unexpected behaviour of L in the reactions of complex formation, the theoretical modeling of the electronic structure of the above mentioned anion with comparison to some model structures (Fig. 3) was performed.

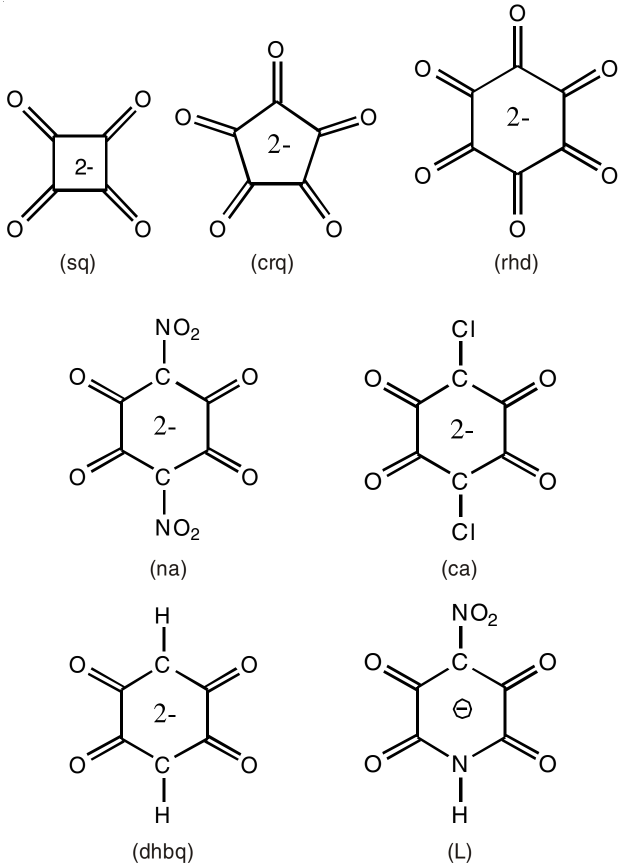


Fig. 3. Models for calculation

The optimized model structures were compared with the experimentally determined structural parameters (Table-4). As it is evident, the calculated bond lengths are in good accordance with the experimental data, so the applied method of modeling can be used for the description of the electronic structures of the models.

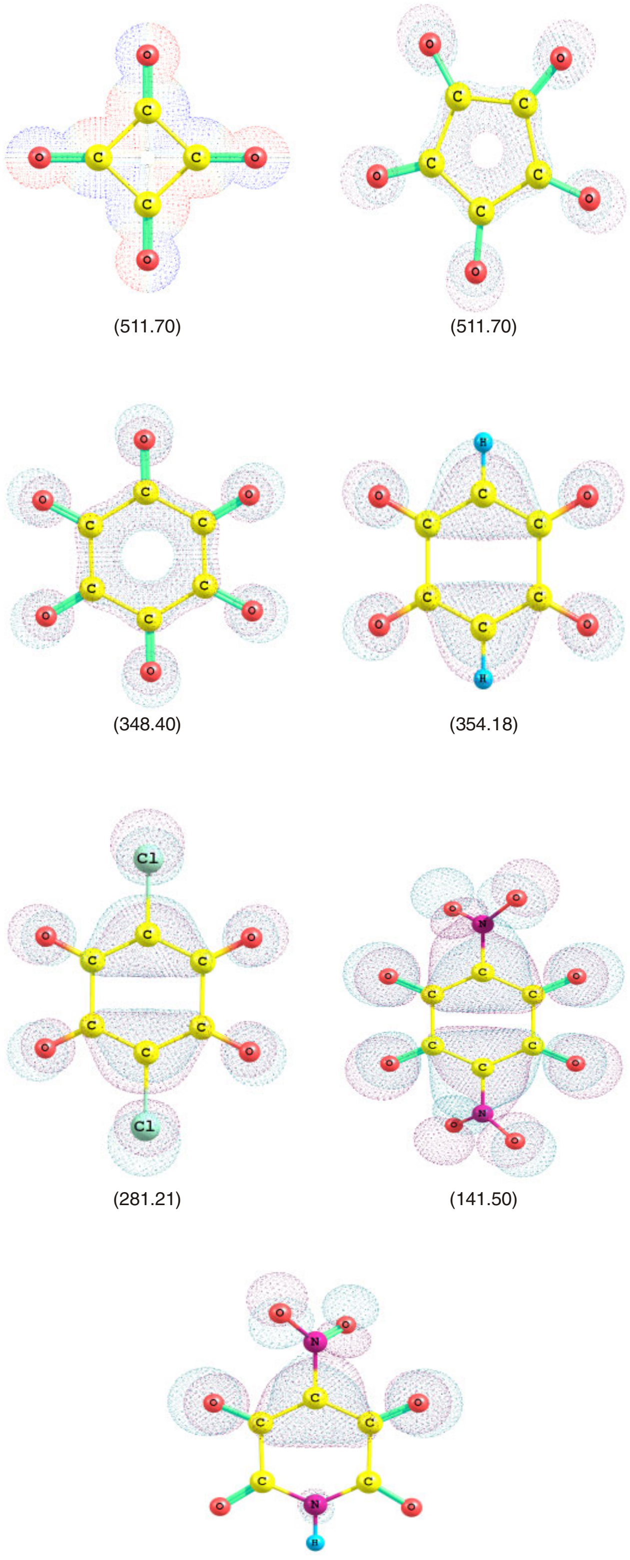
TABLE-4
EXPERIMENTAL AND THEORETICAL BOND LENGTHS IN L AND SOME MODEL STRUCTURES

Comp.	Bond length (Å)				
	Experimetnal (XRD)		Ref.	Theoretical (DFT)	
	CO	CC		CO	CC
(sq)	1.26	1.47	[18]	1.257	1.497
(crq)	1.259(6) 1.248(4)	1.471(9) 1.468(2)	[19]	1.248	1.494
(rhd)	1.234(4) 1.247(4) 1.252(4) 1.251(4) 1.258(4) 1.250(4)	1.449(5) 1.458(5) 1.443(5) 1.421(5) 1.424(5) 1.447(5)	[20]	1.241	1.501
(na)	1.236(3) 1.222(3)	1.409(3) 1.553(3) 1.433(3) 1.440(3)	[21]	1.229	1.444 1.572
(ca)	1.250(2) 1.260(3) 1.246(2) 1.248(3)	1.401(3) 1.538(3) 1.396(3) 1.400(3) 1.403(3) 1.535(3)	[22]	1.239	1.578 1.424
(dhbq)	1.264	1.543 1.395	[23]	1.250	1.424 1.569
(L)	1.209(3) 1.223(3)	1.535(4) 1.412(3)	[6]	1.221 1.222 1.222 1.222	1.499 1.498 1.536

According to the experimental and theoretical results (Table-4), the CO exocyclic bond lengths increase as following series: L < na < ca < rhd < crq < dhbq < sq. As the shortening of the CO bond length can be explained by the increase in the degree of its conjugation with the cycle and the decrease in the electron donating properties, we can suppose that the strongest complex forming ability belongs to the oxalate anion as L has the weakest ability of complex formation.

The process of formation of a coordinate bond may be described as interaction of the electrons of the highest occupied molecular orbital (HOMO) of the ligand with the vacant orbitals of a metal ion. In this occasion, such parameters as HOMO energy and input of the orbitals of different atoms in its formation are of a significant interest.

Fig. 4 represents the inputs of different atoms in formation of HOMOs of L and its carbocyclic analogues. The values of HOMO energies (in kJ/mol) are given in brackets. As it is evident, in the case of L only O atoms of the β-diketone fragment [OC-C(NO_2)-CO] are involved in the HOMO formation as in the case of the carbocyclic analogues all the O atoms of the keto groups contribute almost same amount of the electron density in the HOMO formation. The non-symmetricity of the HOMO of the 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion may be the reason of weak complexing abilities of L. On the other hand, for all the model compounds exept L, the HOMO energies are positive that indicates their non-bonding character. The negative HOMO energy value for L (-241.29 kJ/mol) may relate with its bonding nature and, thus, low electron donating ability.


(511.70) (511.70)

(348.40) (354.18)

(281.21) (141.50)

(-241.29)

Fig. 4. Incomes of different atoms in HOMO formation (HOMO energies, kJ/mol)

Conclusions

- Two new complex compounds $[Fe(H_2O)_6]L_2·2H_2O$ and $[Cr_{0.14}Mn_{0.86}(H_2O)_6]L_2·2H_2O$ (L is 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion) were isolated from aqueous solutions and detected by X-ray analysis.
- According to the crystal structure determination, it was indicated that the organic anion does not replace water molecules from the hydrated coordination sphere of transition metal cations.
- The low complexing ability of 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate anion in comparison with its carbocyclic analogues is determined by the features of the electronic structure of L.

ACKNOWLEDGEMENTS

This research was supported by the Russian Foundation for Basic Research (grant 13-03-00079).

REFERENCES

1. C.C. Wang, M.J. Ke, C.H. Tsai, I.H. Chen, S.I. Lin, T.Y. Lin, L.M. Wu, G.H. Lee, H.S. Sheu and V.E. Fedorov, *Cryst. Growth Des.*, **9**, 1013 (2009).
2. R. Clement, S. Decurtins, M. Gruselle and C. Train, *Monatsh. Chem.*, **134**, 117 (2003).
3. M. Ohba and H. Okawa, *Coord. Chem. Rev.*, **198**, 313 (2000).
4. S.M. Aldoshin, *J. Photochem. Photobiol.*, **200**, 19 (2008).
5. O. Kovalchukova and S. Strashnova, *Rev. Inorg. Chem.*, **34**, 1 (2014).
6. K.K. Palkina, N.E. Kuzmina, O.V. Kovalchukova, S.B. Strashnova and B.E. Zaitsev, *Dokl. Russ. Akad. Nauk*, **370**, 361 (2000).
7. N.E. Kuz’mina, O.V. Koval’chukova, S.B. Strashnova, K.K. Palkina, B.E. Zaitsev and N.Y. Isaeva, *Crystallogr. Rep.*, **49**, 758 (2004).
8. N.D. Do, O. Kovalchukova, A. Stash and S. Strashnova, *Acta Crystallogr.*, **69E**, m477 (2013).
9. R. Alabada, O. Kovalchukova, I. Polyakova, S. Strashnova and V. Sergienko, *Acta Crystallogr.*, **71E**, 459 (2015).
10. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
11. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
12. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
13. A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, **100**, 5829 (1994).
14. http://www.chem.wisc.edu/~nbo5
15. http://classic.chem.msu.su/gran/firefly/index.html.
16. O.V. Kovalchukova, N.E. Kuz'mina, K.K. Palkina, S.B. Strashnova, B.E. Zaitsev and M.A. Ryabov, *Russ. J. Inorg. Chem.*, **48**, 194 (2003).
17. O.V. Kovalchukova, A.I. Stash, D.D. Nguyen, S.B. Strashnova and V.K. Bel’skii, *Russ. J. Coord. Chem.*, **39**, 234 (2013).
18. L.R. Martins, M.C.C. Ribeiro and M.S. Skaf, *J. Phys. Chem. B*, **106**, 5492 (2002).
19. A. Ranganathan and G.U. Kulkarni, *J. Phys. Chem. A*, **106**, 7813 (2002).
20. C.-K. Lam and T.C.W. Mak, *Chem. Commun.*, 1568 (2001).
21. E.K. Andersen and I.G.K. Andersen, *Acta Crystallogr. B*, **31**, 379 (1975).
22. R. Benchekroun and J.M. Savariault, *Acta Crystallogr. C*, **51**, 186 (1995).
23. S. Kulpe, *J. Prakt. Chem.*, **316**, 353 (1974).