ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 9, pp. 1476–1480. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © N.S. Panina, A.V. Eremin, L.S. Gerasimova, A.A. Nikiforov, A.N. Belyaev, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 9, pp. 1417–1421.

Quantum Chemical DFT Study of Two Types of Stable Structures of Ni(II) High-Spin Binuclear Carboxylate Complexes

N. S. Panina, A. V. Eremin, L. S. Gerasimova, A. A. Nikiforov, and A. N. Belyaev

St. Petersburg State Technological Institute, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: nataliepanina2707@gmail.com

Received November 25, 2010

Abstract—Quantum chemical calculations of the electronic structure of $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2]$ complex were performed using the DFT B3LYP method in the 6-31G(d,p) basis. The calculations made it possible to detect the existence of two types of stable structures of Ni(II) high-spin binuclear carboxylate complexes with different terminal ligands, i.e. with a relatively symmetrical metal-carboxylate $Ni_2(\mu\text{-}O_2CR)_4$ framework and with its significant distortion caused by the second-order Jahn-Teller effect.

DOI: 10.1134/S1070363212090034

Earlier we synthesized and studied $[Ni_2(\mu\text{-}O_2CCH_3)_4\cdot(O\text{-}DMSO)_2]$, a new complex of Ni(II) acetate of the "Chinese lantern" type with two molecules of dimethyl sulfoxide coordinated in terminal positions via the oxygen atom. The studies were based on the methods of X-ray diffraction, infrared and electron spectroscopy, and elemental analysis [1]. In the present work a quantum chemical study of the specified compound was performed in order to define the specific features of its electronic and geometrical structure. The electronic structure calculations were carried out in the basis of the GAMESS-09 program [2] using the DFT B3LYP method in the 6-31G(d,p) basis. The normal mode frequency analysis demonstrated that the structures of the compounds in the gas phase obtained as a result of geometry optimization corresponded to the minima on the potential energy surface.

The calculations of the electronic structure of the high-spin coordination compound $[Ni_2(\mu\text{-}O_2CCH_3)_4\cdot(O\text{-}DMSO)_2]$ in the gas phase led to two conformation isomers **I, II** (Fig. 1) corresponding to different minima on the potential energy surface. Taking into account the energies of zero vibrational levels structure **II** turned out to be by 126.3 kJ mol^{-1} more stable than structure **I**.

Electronic and geometry characteristics of the obtained conformation isomers are different. Charges on Ni atoms amount to 0.85 and 0.89 *e* for structures **I** and **II**, respectively. The spin density on each Ni atom in structure **II** (1.77 *e*) is slightly higher than the spin density on metal atoms in structure **I** (1.69 *e*). The latter is caused by its higher delocalization in carboxylate bridges of structure **I**: the presence of a minor share of spin density on the oxygen and carbon atoms. Both structures belong to the same C_i symmetry group; nevertheless, they differ significantly from each other by the Ni–Ni and Ni–O interatomic distances both in μ-carboxylate and in terminal ligands O(DMSO) and also by the NiNiO(DMSO) angles. In structure **I** the average values of Ni-μ-($OOCCH_3$) bond lengths are shorter (1.980 Å) than in structure **II** (2.046 Å). Due to the strengthening of bonds of bridging carboxylate ligands with metal atoms in structure **I**, the lengths of the Ni–O(DMSO) terminal bonds have slightly larger values (2.145 Å) as compared to structure **II** (2.023 Å). These results are in compliance with the variations of the DMSO bond energies in the complex calculated for the dissociation process $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2] \rightleftarrows [Ni_2(\mu\text{-}O_2CCH_3)_4] + 2DMSO$ by the difference in total energies of the compounds taking into account the energies of their zero vibrational levels. As per one ligand, DMSO bond energy in the complex amounts to 89.3 kJ mol^{-1} for structure **I** and 110.2 kJ mol^{-1} for structure **II**.

The interatomic distance Ni–Ni in structure **I** (2.361 Å) is by 0.260 Å shorter than the analogous

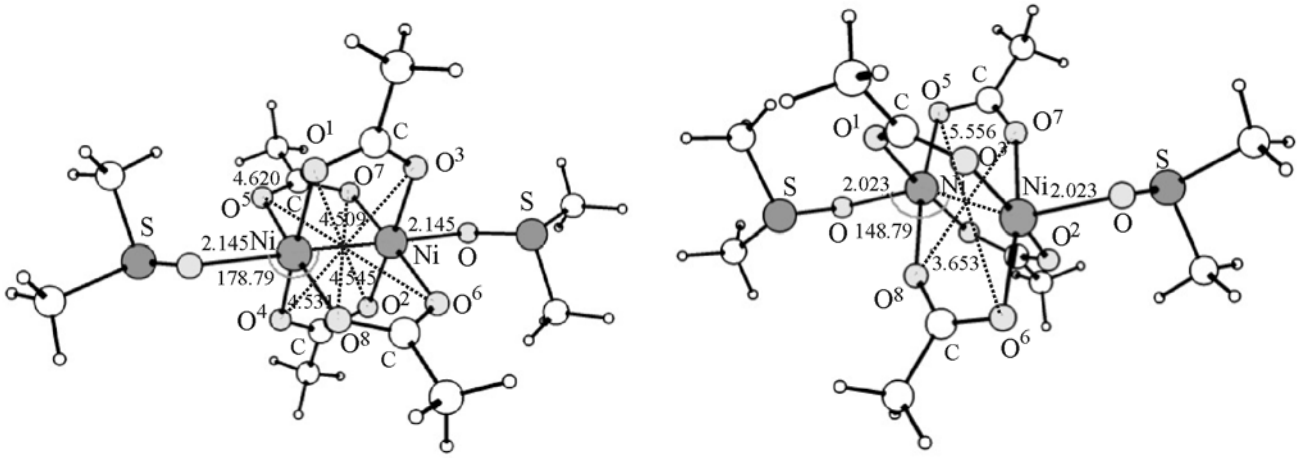

Fig. 1. Optimized structures of the $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2]$ complex.

distance in structure **II** (2.62 Å). The angle NiNiO (DMSO) in structure **I** is equal to 178.79°, whereas in structure **II** it is decreased to 148.79°. Due to the dissymmetrical arrangement of terminal ligands in structure **I** the distances between oxygen atoms belonging to different carboxylate bridges and located diagonally to each other differ as follows: $r_1(O^1–O^2)$ 4.545, $r_2(O^3–O^4)$ 4.531, $r_3(O^5–O^6)$ 4.620, and $r_4(O^7–O^8)$ 4.509 Å.

The values of interatomic distances in two pairs of μ-O-atoms located diagonally in structure **II** are rather close: $r_1(O^1–O^2)$ 4.604 and $r_2(O^3–O^4)$ 4.591 Å. At the same time, in the other two pairs of μ-O-atoms these distances are significantly different: $r_3(O^5–O^6)$ 5.556 and $r_4(O^7–O^8)$ 3.653 Å. In this context structure **II** appears much more distorted. For the sake of convenience from now on we will call more symmetrical structure **I** S-structure and much more distorted structure **II**, AS.

Despite the differences in absolute values of the experimental bond lengths and in the structures obtained as a result of geometry optimization (see the table), it is possible to conclude that according to the data of X-ray diffraction analysis the structure of the synthesized complex $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2]$ corresponds to the quantum chemical high-energy S-structure. At the same time, the published data on nickel(II) binuclear carboxylates with different terminal ligands [3–13] point to the fact that there are also numerous significantly distorted AS-structures.

Distortions of the compounds under consideration seem a natural consequence of the nature of terminal ligands. However, another reason of the specified effect is also possible, as it can be the result of vibronic interactions in the binuclear carboxylate framework. In this connection, the present work includes a calculation of the electronic structure of the bimetal carboxylate framework without terminal ligands, $[Ni_2(\mu\text{-}O_2CCH_3)_4]$. As it was previously done for the $[Ni_2(\mu\text{-}O_2CCH_3)_4 \cdot (O\text{-}DMSO)_2]$ complex, in this case we obtained two different optimized structures corresponding to S- and AS-conformation isomers (Fig. 2). Similarly to the coordination compound with terminal ligands, S-structure possessing C_{4h} symmetry in the absence of terminal ligands has a higher energy (by 83.7 kJ mol^{-1}) than AS-structure of C_i symmetry. In S-structure Ni–Ni interatomic distance is by 0.235 Å shorter than a similar distance in AS-structure. The difference in the distances between the diagonally located oxygen atoms in μ-carboxylate bridges found for the coordination compound $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DNMSO)_2]$ is also retained: in S-structure $r_1(O^1–O^2) = r_2(O^3–O^4) = 4.497$ and $r_3(O^5–O^6) = r_4(O^7–O^8) = 4.540$ Å; in AS-structure $r_1(O^1–O^2)$ 4.505, $r_2(O^3–O^4)$ 4.498, $r_3(O^5–O^6)$ 5.657, and $r_4(O^7–O^8)$ 3.549 Å. It should be noted that a significant distortion of the bimetal framework takes place in only one of the "Chinese lanterns" of AS-structure.

Similar results were obtained for the forms of the trifluoroacetate compound $[Ni_2(\mu\text{-}O_2CCF_3)_4]$. The S-structure also has a higher energy than the AS-structure (ΔE = 87.1 kJ mol^{-1} taking into account ΔZPE). In the S-structure the Ni–Ni interatomic distance is by 0.352 Å shorter than a similar distance in the AS-structure. Like in AS-acetate structure, in one of the "Chinese lanterns" of AS-trifluoroacetate

Types of Ni(II) binuclear carboxylate complexes $[Ni_2(\mu\text{-}O_2CX)_4L_2]$ and their main geometry parameters

No.	Type	X	L	r(Ni–Ni)	$r_1(O^1–O^2)$, $r_2(O^3–O^4)$	$r_3(O^5–O^6)$, $r_4(O^7–O^8)$	$\Delta r_{1–2}$, $\Delta r_{3–4}$	NiNiL angle	Reference
1	S	$(CH_3)_3C$	Triethylamine	2.728	4.558, 4.556	4.644, 4.504	0.002, 0.140	177.72	[3]
2	S	$(CH_3)_3C$	(*N*-Phenyl)-*n*-phenylenediamine	2.497	4.639, 4.466	4.666, 4.454	0.173, 0.212	177.56	[4]
3	S	CH_3	O-DMSO	2.610	4.539, 4.488	4.531, 4.447	0.051, 0.084	177.46	[1]
(calculation)				2.361	4.545, 4.531	4.620, 4.509	0.014, 0.111	178.79	This work
4	S	2-Naphthyl	4,4'- Bipyridine	2.654	4.585, 4.533	4.625, 4.494	0.052, 0.131	176.89	[5]
5	S	$(CH_3)_3C$	Pyridine	2.604	4.561, 4.554	4.636, 4.460	0.007, 0.176	176.74	[3]
6	S	2-Naphthyl	4,4'- Bipyridine	2.635	4.620, 4.550	4.650, 4.510	0.070, 0.140	176.22	[6]
7	S	$(CH_3)_3C$	3,5-Dimethylpyrazole	2.693	4.643, 4.464	4.699, 4.418	0.179, 0.281	175.72	[7]
8	S	2,6-Di(*n*-tolyl)-phenyl	Pyridine	2.575	4.534, 4.459	4.657, 4.430	0.075, 0.227	175.39	[8]
9	S	C_2H_5	Water	2.623	4.490, 4.480	4.534, 4.499	0.010, 0.035	173.09	[9]
10	S	CH_3	Hexamethylenete-tramine	2.622	4.584, 4.429	4.584, 4.429	0.155, 0.155	172.07	[10]
11	S	2-Methyl-2-phenylpropionate	Triphenylphosphine	2.572	4.579, 4.498	4.622, 4.463	0.081, 0.159	172.42	[11]
12	AS	$(CH_3)_3C$	2-Methylpyridine	2.717	4.724, 4.392	4.799, 4.311	0.332, 0.488	169.46	[12]
13	AS	$(CH_3)_3C$	2,3-Dimethylpyridine	2.726	4.627, 4.462	4.827, 4.277	0.165, 0.550	168.30	[3]
14	AS	$(CH_3)_3C$	2,4-Dimethylpyridine	2.708	4.579, 4.524	4.847, 4.238	0.055, 0.609	166.65	[13]
15	AS	$(CH_3)_3C$	2- Ethylpyridine	2.723	4.696, 4.444	4.903, 4.205	0.252, 0.698	166.00	[12]
16	AS	2- Phenyl-isopropyl	Quinoline	2.734	4.610, 4.537	5.141, 3.953	0.073, 1.188	165.70	″
17	AS	1,1-Diphenylethyl	Quinoline	2.765	4.637, 4.531	4.997, 4.160	0.106, 0.837	165.01	″
18	AS	$(CH_3)_3C$	2,5-Dimethylpyridine	2.720	4.567, 4.554	5.103, 4.028	0.013, 1.075	160.84	″

structure it is possible to detect two pairs of μ-O-atoms located diagonally with significantly different interatomic distances: long (5.647 Å) and short (3.497 Å).

Effective charges on nickel atoms in trifluoroacetate compounds in the absence of terminal ligands are 0.89 and 0.94 *e* for S- and AS-structures, whereas the values of these charges in acetate analogs amount to 0.85 and 0.89 *e*, respec-tively. Such effect can be caused either by a slightly lower σ-donor power of trifluoroacetate ligands or by implementation of their weak acceptor properties by means of vacant low-lying π*(O–C–O) molecular orbitals advantageous for π-dative interaction of metal ions [14]. In any case, an increase in positive charges on nickel atoms can contribute to the growth in Ni–Ni interatomic distances in trifluoroacetate compounds as follows: 2.249 (S) and 2.601 Å (AS) as compared to their acetate analogs, for which the distances are 2.202 and 2.437 Å, respectively.

The reason for a higher stability of distorted AS-structures can be attributed to the second-order Jahn-Teller effect, in compliance with which even in non-degenerate ground electronic state vibronic interactions can manifest themselves displacing the minimum on the potential surface from a more to a less symmetrical configuration [15]. A specific feature of the studied distorted AS-structures of Ni(II) binuclear carboxylate high-spin complexes (see the table) is the

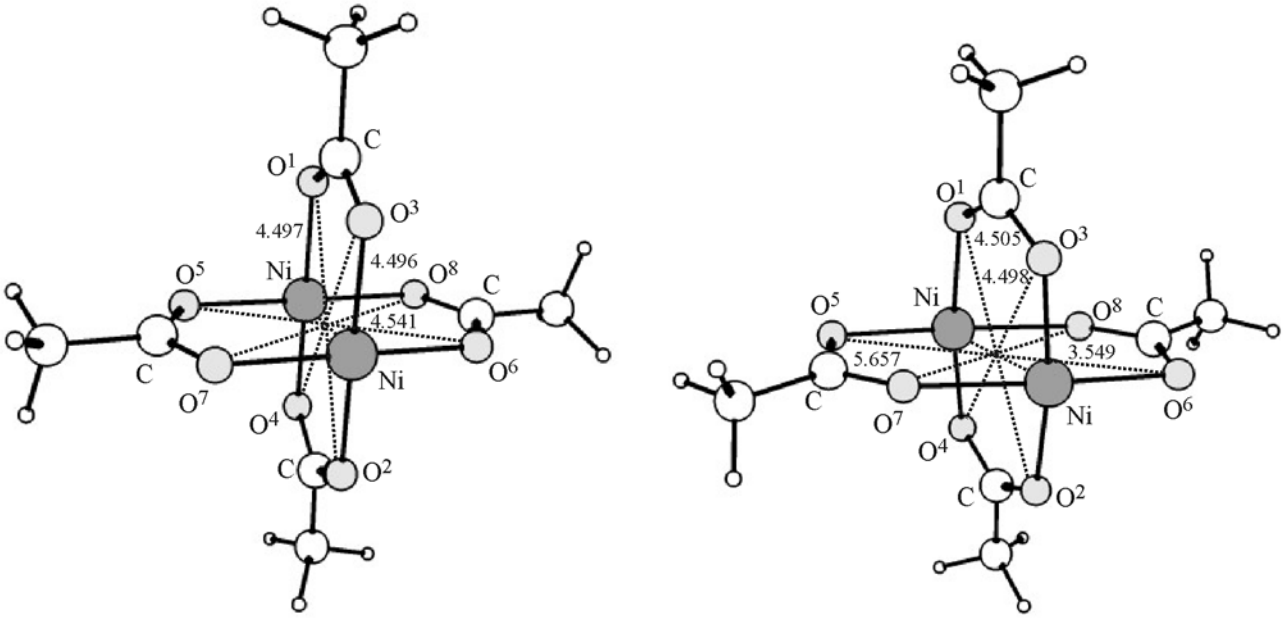

Fig. 2. Optimized structures of $[Ni_2(\mu\text{-}O_2CCH_3)_4]$ binuclear carboxylate framework.

presence of two pairs of μ-O-atoms located diagonally with significantly different interatomic distances, long (r_3) and short (r_4) in one of carboxylate "Chinese lanterns", which results in a significant distortion of the bridging carboxylate structure. It is natural that the presence of branched terminal ligands has an influence on the structure of real complexes. However, the obtained data make it possible to conclude that the effect of significant distortion of Ni(II) high-spin binuclear carboxylate complexes survives even in the absence of terminal ligands, i.e. it is associated by nature with vibronic interactions in the metal-containing carboxylate framework.

The existence of a large number of both S- and AS-structures is probably related to conditions of coordination compounds synthesis. The results of the experimental study of the $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2]$ complex [1] demonstrate that it seems to be impossible to trace the influence of the temperature factor on the transition from the S-structure to the more stable AS-structure, as the compound disintegrates when heated, being unable to overcome a significant energy barrier, which exceeds 100 kJ mol^{-1} according to the data of the present work.

Therefore, the performed quantum chemical study makes it possible to explain the existence of different stable conformation isomers of Ni(II) high-spin binuclear carboxylate complexes and to divide them conventionally into two types (see the table). Coordination compounds of the first S-type are genetically originated from high-energy relatively symmetrical framework $Ni_2(\mu\text{-}O_2CR)_4$. Differences in the interatomic distances between diagonally located oxygen atoms of the "Chinese lantern" type in S-isomers can be significant due to the influence of terminal ligands; however, in cases under study they do not exceed 0.3 Å. The second AS-type of nickel binuclear carboxylates is genetically related to the low-energy distorted framework $Ni_2(\mu\text{-}O_2CR)_4$. The AS-type embraces complexes, where in one of the "Chinese lanterns" the inequality in distances between diagonally located oxygen atoms in bridging carboxylate ligands is much greater. The specified distortion primarily stems from the manifestation of the second-order Jahn-Teller effect. The influence of terminal ligands can only increase the distortion. According to the analysis of the experimental data [1, 3–13], an additional characteristic distinguishing feature of AS-complexes are NiNiL bond angle, which is notably different from 180° and also, as a rule, increased interatomic distances Ni–Ni.

REFERENCES

1. Eremin, A.V. and Belyaev, A.N., *Zh. Obshch. Khim.*, 2011, vol. 81, no. 2, p. 330.
2. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, G.A.,

Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347.

3. Eremenko, L.I., Nefedov, S.E., Sidorov, A.A., Golubnichaya, M.A., Danilov, P.V., Ikorskii, V.N., Shvedenkov, Y.G., Novotortsev, V.M., and Moiseev, I.I., *Inorg. Chem.*, 1999, vol. 38, p. 3764.
4. Chipanina, N.N., Stepanova, Z.V., Gavrilova, G.A., Sobenina, L.N., and Mikhaleva, A.I., *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 11, p. 1914.
5. Soon, W. Lee, Hye Jin Kim, Yeon Kyoung Lee, Kyungsoo Park, Jung-Ho Son, and Young-Uk Kwon, *Inorg. Chim. Acta*., 2003, vol. 353, p. 151.
6. Liang-Ping Hsu, Jing-Yun Wu, and Kuang-Lieh Lu, *J. Inorg. Organomet. Polym. Mater.,* 2007, vol. 17, p. 259.
7. Titov, L.V., *Zh. Neorg. Khim*., 2003, vol. 48, no. 9, p. 1476.
8. Lee, D., Hung, P.-L., Spingler, B., and Lippard, S.J., *Inorg. Chem.*, 2002, vol. 41, p. 521.
9. Meenakshi, D. and Rao, C.N.R., *Angew. Chem. Int. Ed.,* 2005, vol. 45, no. 2, p. 281.
10. Wang Shun, Hu Mao-Lin, and Seik Weng Ng, *Acta Cryst.*, 2002, vol. 58, p. 242.
11. Husebye, S., Kato, M., Maartmann-Moe, K., Muto, Y., Nakashima, M., and Tokii, T., *Acta Chem. Scand*., 1994, vol. 48, p. 628.
12. Morooka, M., Ohba, S., Nakashima, M., Tokii, T., Muto, Y., Kato, M., and Steward, O.W., *Acta Cryst*., 1992, vol. 48, p. 1888.
13. Hirashima, N., Husebye, S., Kato, M., Maartmann-Moe, K., Muto, Y., Nakashima, M., and Tokii, T., *Acta Chem. Scand.,* 1990, vol. 44, p. 984.
14. Panina, N.S., Belyaev, A.N., and Simanova, S.A., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 1, p. 98.
15. Bersuker, I.B., *Effekt Yana-Tellera i vibronnye vzaimodeistviya v khimii* (Jahn-Teller Effect and Vibronic Interactions in Chemistry), Moscow: Nauka, 1987.