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Metastable States of Ruthenium Nitrosyl Complexes. Density Functional Quantum-Chemical Calculations

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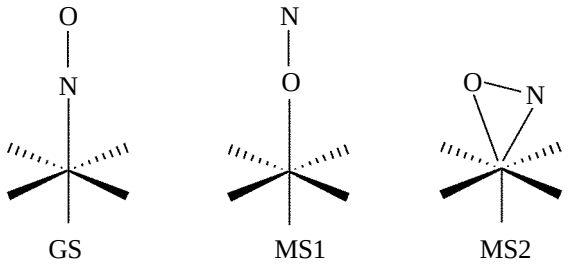
Abstract—Geometry optimization for the ground state and metastable isomers of the nitrosyl complexes *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ (L = imidazole, pyridine, pyrazine, nicotinamide), $[Ru(NO)(CN)_5]^{2-}$, and $[Ru(NO)Cl_5]^{2-}$ was performed in terms of the density functional theory (SVWN/LanL2DZ + 6-31G). The energy gap between the stable structure and the isomer with linear coordination of NO via the oxygen atom is practically independent of the nature of ligand L in the series of ammonia complexes with the same charge, and the energy gap between the stable structure and the isomer with side η^2 coordination of NO gets slightly smaller if ligand L possesses π-acceptor properties.

The discovery in 1977 by Mossbauer spectroscopy that irradiation of sodium nitroprusside dihydrate $Na_2[Fe(NO)(CN)_5NO]\cdot 2H_2O$ at low temperatures gives long-lived metastable states [1] has given impetus to search for photoinduced metastable isomers of transition metal complexes. Compounds whose optical or magnetic properties are affected by transformations induced on a molecular level can find industrial application as energy accumulators, switches, or display devices. Furthermore, the interest in metastable structures formed by nitrosyl complexes is explained by the assumed role such structures play in biological processes involving nitrogen(II) oxide [2]. An important characteristic of metastable states is the decomposition temperature (T_d) which correlates to a certain extent with the stretching vibration frequency ν(NO) of the ground state (GS) and the assumed π-donocity order of *trans*-ligands L: $OH^- < NH_3 < Cl^- < SCN^- < Br^- < I^-$ (the stronger π-donor is ligand L, the weaker N–O bond); the nature of equatorial ligands is less important but not negligible [2]. Photocrystallographic studies showed that these metastable compounds are isomers with linear coordination of NO via the oxygen atom (MS1) and with side η^2 coordination on NO (MS2).



First quantum-chemical calculations of metastable isomers of nitrosyl complexes were fulfilled for sodium nitroprusside [3]; they showed that the potential energy surface has local minima corresponding to side coordination (MS2) and to the isomer with the isonitrosyl Fe–ON bond (MS1). Latter calculations of ruthenium nitrosyl complexes were published [4–6]. Da Silva and Franco [4] made use of B3LYP/3-21G and ZINDO/S calculations to show that in $[Ru(NO)\cdot(NH_3)_5]^{3+}$ and *trans*-$[Ru(NO)(NH_3)_4(OH)]^{2+}$ the excitation preceding population of MS1 relates to the electronic transition $(d_{xz}d_{yz})^4(d_{xy})^2 \rightarrow (d_{xz}d_{yz})^4(d_{xy})^1(\pi^*NO)^1$ [4]. The complexes $[Ru(NO)\cdot(NH_3)_5]^{3+}$ and $[Ru(NO)(CN)_5]^{2-}$ were considered in detail in [5]. The results of calculations of the ground state (GS), MS1, and MS2 for *trans*-$[Ru(NO)(NH_3)_4\cdot(nc)]^{3+}$ (nc is nicotinamide) and of GS for *trans*-$[Ru(NO)(NH_3)_4(L)]^{q+}$ (L = NH_3, H_2O, OH^-, Cl^-, and NO_2^-) and the energy gaps between GS and MS1 for these compounds were given in [6]. The calculation results for $[Ru(NO)(NH_3)_5]^{3+}$, $[Ru(NO)(NH_3)_4(nc)]^{3+}$, and $[Ru(NO)(CN)_5]^{2-}$ suggest existence of both the metastable isomers MS1 and MS2[1] in all the complexes, but experimental evidence for the η^2-coordinated isomer was obtained for the last complex only. Gorelsky and Lever [5] explained the failure to detect the MS2 isomer for the ammonia complex by the absence of allowed electronic transitions in the visible region for MS1 and the resulting blocking of popula-

[1] The corresponding information for the rest *trans*-$[Ru(NO)\cdot(NH_3)_4(L)]^{q+}$ complexes was not given in [5].

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Table 1. Bond lengths (R, Å) and RuNO bond angle (deg) in $[Ru(NH_3)_5(NO)]^{3+}$, calculated by various methods with the LanL2DZ(Ru), 6-31G*(N, O, H) (I), LanL2DZ(Ru), 6-31G(N, O, H) (II), DZVP (III), and SBK(Ru), 6-31G(N, O, H) basis sets (IV)

Parameter	Experiment [11]	Calculated [12]		This work			
		SVWN/III	B3LYP/III	SVWN5/I	SVWN5/II	SVWN5/IV	B3LYP/IV
R(N–O)	1.172(14)	1.146	1.129	1.139	1.164	1.164	1.153
R(Ru–N)	1.770(9)	1.763	1.819	1.782	1.782	1.784	1.815
$R(Ru–N_{trans})$	2.02(1)	2.136	2.194	2.127	2.126	2.141	2.200
$R(Ru–N_{cis})$	2.093(9)–2.100(8)	2.147–2.148	2.210	2.139–2.142	2.143–2.146	2.153–2.155	2.215–2.216
∠RuNO	172.8(9)	177	179	179.4	179.4	179.5	179.5

tion of MS2 via the channel proposed by Delley *et al.* [3].

$$MS1 \xrightarrow{h\nu} MS1^* \longrightarrow MS2.$$

Thus, the available published data show that quantum-chemical calculations for isolated complex ions make it possible to reveal metastable states of nitrosyl complexes, to obtain their geometric structures and vibration spectra, and to describe their electronic structures. This creates prerequisites for further, more systematic research into the mentioned states by quantum-chemical methods. The present work was fulfilled in the context of this problem.

We chose the complexes *trans*-$[Ru(NO)(NH_3)_4 \cdot (L)]^{3+}$ (L = NH_3, im is imidazole, py is pyridine, pyz is pyrazine, and nc), $[Ru(NO)(CN)_5]^{2-}$, and $[Ru(NO)Cl_5]^{2-}$ as objects for study. The choice of ligands L in the *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ series allows us to trace the dependence of characteristics of metastable states on the nature of the ligands in the *trans* position to NO: L = NH_3 is a medium-strength donor and exhibits no acceptor properties, whereas the rest ligands can be arranged, on the basis of stretching vibration frequencies ν(NO) and Lever electrochemical parameters ΣE_L, can be arranged in the order L = im > py > nc > pyz in terms of the Ru(II)→NO dative bond strength [7]. The three $[Ru(NO)(X)_5]^q$ complexes form a series of compounds, whose inner coordination sphere is formed by a σ-donor (X = NH_3, q = +3), a σ- and π-donor (X^- = Cl^-, q = –2), and a strong σ-donor and a weak π-acceptor (X^- = CN^-, q = –2). The complexes $[Ru(NO)(NH_3)_5]^{3+}$, $[Ru(NO) \cdot (CN)_5]^{2-}$ and *trans*-$[Ru(NO)(NH_3)_4(nc)]^{3+}$ were earlier considered in [2, 4–6], [5], and [2, 6], respectively; these published data were used to select the calculation technique and to control the resulting data.

We earlier showed [8] that the Hartree–Fock approximation is unsuitable for nitrosyl complexes: The electron correlation effects in them are so significant that perturbative methods do not ensure stable results. Therefore, we resorted to the density functional theory (DFT) as the calculation scheme. The SVWN5 local exchange correlation functional [9] and LanL2DZ basis set with effective core potential for Ru [10] and 6-31G basis sets for H, C, N, and O were chosen on the basis of preliminary calculations for $[Ru(NO) \cdot (NH_3)_5]^{3+}$ with widely varied functionals and basis sets (selected results are given in Table 1). For $[Ru(NO)Cl_5]^{2-}$ we fulfilled DFT calculations with the SVWN5 functional and LanL2DZ (Ru, Cl) + 6-31G (N, O), LanL2DZ (Ru, Cl) + 6-31G (N, O), and DZVP (Ru, N, O, Cl) [13][2] basis sets and also with the B3LYP functional [14] and DZVP (Ru, N, O, Cl) basis set. The geometry of the complexes was optimized without imposing symmetry constraints. Two conformations were considered for $[Ru(NO)(NH_3)_4 \cdot (nc)]^{3+}$ (Fig. 1): **A** ($CONH_2$ group is directed to equatorial ligands by the oxygen atom) and **B** ($CONH_2$ is directed to equatorial ligands by the amino group). According to the calculations, the first structure is more energetically favorable for an isolated complex ion. Orbital populations were discussed on the basis of the results of the calculations in which the z axis is directed along the Ru–L bond and the xz plane passes through aromatic ring atoms (GS and MS1 structures) or through Ru–N atoms (MS2). All the calculations were fulfilled using the GAMESS program [15] (release 2002).

The calculation results for $[Ru(NO)Cl_5]^{2-}$ in GS, MS1, and MS2 are given in Table 2. Similar data for

[2] The basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database (Ver. 1.0), Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory (Pacific Northwest Laboratory, Richland, Washington, USA), created with the financial support of the United States Department of Energy.

Table 2. Bond lengths (R, Å), RuNO bond angle (deg), N–O stretching vibration frequency [ν(NO), cm^{-1}] in GS, MS1, and MS2, and changes in the N–O stretching vibration frequency [$\Delta\nu$(NO), cm^{-1}] and total energy (ΔE, eV) in going from the ground to metastable states in $[Ru(NO)Cl_5]^{2-}$, calculated with the LanL2DZ(Ru, Cl) (I), 6-31G*(N, O) LanL2DZ (Ru, Cl), 6-31G(N, O) (II), and DZVP basis sets (III)

Parameter	Experiment[a] [2, 16, 17]			SVWN5							B3LYP/III		
				I	II			III					
	1	2	3	GS	GS	MS1	MS2	GS	MS1	MS2	GS	MS1	MS2
R(N–O)	1.131	1.112	1.149	1.172	1.200	1.200	1.260	1.179	1.171	1.221	1.170	1.157	1.200
R(Ru–N)	1.738	1.747	1.775	1.725	1.737		1.912	1.731		1.899	1.746		1.966
R(Ru–O)						1.818	2.276		1.817	2.236		1.850	2.297
R(Ru–Cl_{trans})	2.357	2.359	2.331	2.373	2.374	2.343	2.367	2.344	2.302	2.302	2.404	2.355	2.357
R(Ru–Cl_{cis})	2.357	2.371	2.368	2.453	2.455	2.440	2.416	2.420	2.406	2.374	2.492	2.483	2.440
						2.438	2.433			2.374			2.440
							2.451			2.457			2.572
							2.494			2.472			2.573
∠RuNO							89.27	180	0	88.80	180	0	83.66
ν(NO)		1895		1927	1809	1709	1327	18951	832	1517	1894	1885	1614
ν(NO)						100	482		63	378		9	280
ΔE						1.73	1.70		1.69	1.42		1.77	1.30

[a] Experimental data for $(Cat)_2[Ru(NO)(Cl)_5]$ [Cat: NH_4^+ (1), K^+ (2), and $HNC_5H_3NH_2CONH_2^+$] (3).

the *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ series are presented in Table 3.

The calculations reveal two metastable states, MS1 and MS2, for all the complexes. This result is consistent with the available published calculation results for ruthenium nitrosyl complexes [2, 5, 6], even though MS2 with side coordination was experimentally detected only for $[Ru(NO)(CN)_5]^{2-}$.

The LanL2DZ (Ru, Cl) + 6-31G (N, O) calculations underestimate ν(NO), but, however, they reproduce very well the tendency in this value in going from GS to MS1 and MS2: for *trans*-$[Ru(NO)\cdot(NH_3)_4(L)]^{3+}$ the GS→MS1 and GS→MS2 transitions decrease ν(NO) by 160 and 400 cm^{-1}, respectively; the respective values for $[Ru(NO)(Cl)_5]$ are 100 and 480 cm^{-1} and for $[Ru(NO)(CN)_5]^{2-}$, 77 and 426 cm^{-1}. According to the experimental data in [6], the decrease in ν(NO) upon the GS→MS1 transition is 148 cm^{-1} for $[Ru(NO)(NH_3)_4(nc)]^{3+}$, 125 cm^{-1} for $[Ru(NO)Cl_5]^{2-}$, 125–135 cm^{-1} for ethylene diamine derivatives, 114 cm^{-1} for $[Ru(NO)(NO_2)_4(OH)]^{2-}$, and 152 (or 127) [5] for $[Ru(NO)(NH_3)_5]^{3+}$. For $[Fe(NO)(CN)_5]^{2-}$, $\Delta\nu$(GS→MS1) is 116 cm^{-1} and $\Delta\nu$(GS→MS2) is 287 cm^{-1} [5]; for ruthenium nitrosyl porphyrins, $\Delta\nu$(GS→MS1) is 146 and 128 cm^{-1} and $\Delta\nu$(GS→MS2), 294 and 242 cm^{-1} [18]. The calculated ν(Ru-NO) values for GS are higher by about 100 cm^{-1} than those for MS1.

The extension of the basis sets for N and O to include polarization functions (transition from the 6-31G basis set to 6-31G* or DZVP) results in shortening of the N–O bond and increase in the ν(NO) frequency but sharply deteriorates $\Delta\nu$(GS→MS1) values. The choice of the B3LYP functional instead of SVWN5 results in equalization of ν(GS) and ν(MS1) (Table 2), while in the case of $[Ru(NO)\cdot(CN)_5]^{2-}$, in an incorrect ν(GS)/ν(MS1) ratio: the B3LYP/LanL2DZ estimate for $\Delta\nu$(GS→MS1) is 44 cm^{-1} and the B3LYP/DZVP estimate, 12 cm^{-1} [5]. Coppens *et al.* failed to reproduce the decrease in

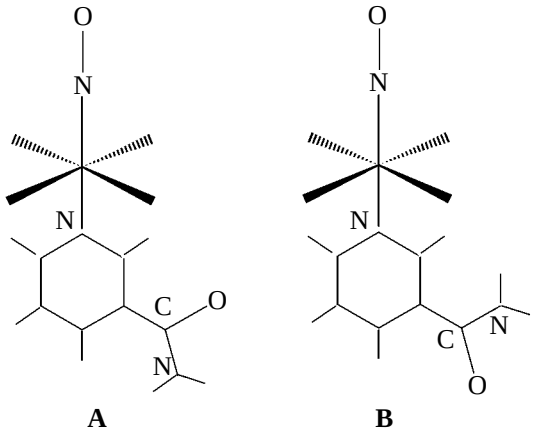


Fig. 1. Geometric structure of *trans*-$[Ru(NO)\cdot(NH_3)_4(nc)]^{3+}$.

Table 3. Energies of MS1 and MS2 with respect to GS (ΔE, eV), vibration frequencies [ν(NO), cm^{-1}], bond lengths (R, Å), angles (deg), atomic charges (q), orbital populations (n), and bond orders (B) for *trans*-$[Ru(NO)(NH_3)_4L]^{3+}$, calculated by the SVWN5/LanL2DZ (Ru, Cl), 6-31G (N, O) method

Parameter	L = NH_3			L = im			L = py			L = pyz			L = nc[a]		
	GS	MS1	MS	GS	MS1	MS	GS	MS1	MS	GS	MS1	MS	GS	MS1	MS
ΔE, eV	–	1.681	1.911	–	1.687	1.816	–	1.671	1.802	–	1.671	1.669	–	1.627	1.638
ν(NO)	1920	1757	1520	1911	1753	1505	1908	1752	1508	1912	1756	1538	1892	1729	1485
R(N–O)	1.164	1.175	1.212	1.166	1.177	1.216	1.166	1.176	1.215	1.165	1.175	1.210	1.169	1.182	1.221
R(Ru–N)	1.782	–	1.979	1.788	–	1.976	1.790	–	1.975	1.789	–	1.979	1.793	–	1.991
R(Ru–O)	–	1.878	2.239	–	1.884	2.248	–	1.887	2.261	–	1.888	2.341	–	1.896	2.253
R(Ru–L)	2.126	2.083	2.073	2.054	2.012	2.011	2.081	2.037	2.036	2.091	2.048	2.059	2.076	2.034	2.037
R(Ru–NH_3)	2.146	2.140	2.141	2.129	2.128	2.137	2.129	2.129	2.140	2.139	2.132	2.146	2.127	2.126	2.141
	2.144	2.142	2.137	2.132	2.129	2.128	2.134	2.131	2.134	2.137	2.135	2.137	2.132	2.130	2.134
	2.143	2.140	2.173	2.131	2.132	2.125	2.131	2.131	2.127	2.137	2.133	2.139	2.130	2.131	2.132
∠RuNO	179.4	–	85.54	179.16	–	86.06	179.54	–	86.84	179.36	–	91.19	178.42	–	85.56
∠RuON	–	179.6	61.80	–	179.93	61.29	–	179.82	60.70	–	179.67	57.70	–	177.25	61.75
∠N$RuNH_3$	93.42	92.05	73.24	93.06	91.59	73.93	92.90	91.44	73.82	92.38	91.49	73.45	93.19	91.43	74.98
	91.62	92.04	114.58	93.09	92.21	116.58	92.93	91.88	116.34	92.74	91.76	113.11	93.22	92.04	113.95
	91.72	90.60	90.72	93.83	91.58	89.28	93.60	91.77	89.00	92.75	91.59	90.12	92.64	90.03	89.13
	93.27	91.42	90.40	92.44	92.05	91.65	92.34	91.42	90.26	92.25	91.20	89.14	91.08	91.22	89.74
q(Ru)	0.749	0.768	0.602	0.789	0.835	0.659	0.783	0.823	0.637	0.773	0.830	0.605	0.768	0.803	0.618
q(N)	0.078	0.378	0.155	0.098	0.351	0.149	0.090	0.353	0.144	0.095	0.367	0.133	0.083	0.325	0.124
q(O)	0.044	–0.215	0.008	0.021	–0.210	–0.004	0.022	–0.210	–0.006	0.033	–0.206	0.003	0.008	–0.221	–0.027
q(NO)	0.122	0.163	0.163	0.119	0.141	0.145	0.113	0.142	0.138	0.128	0.161	0.136	0.092	0.105	0.098
$q(N)_L$	–0.912	–0.904	–0.896	–0.588	–0.586	–0.592	–0.519	–0.522	–0.525	–0.517	–0.518	–0.506	–0.538	–0.536	–0.539
q(L)	0.413	0.433	0.463	0.489	0.503	0.522	0.500	0.511	0.552	0.459	0.465	0.608	0.556	0.607	0.667
ν_π(NO)	5.089	4.920	2.324	5.107	4.949	2.328	5.104	4.944	2.334	5.088	4.932	2.330	5.130	4.988	4.514
d_{xz}(Ru)	1.484	1.533	1.330	1.487	1.561	1.323	1.488	1.561	1.330	1.484	1.571	1.379	1.501	1.594	1.342
d_{yz}(Ru)	1.478	1.548	1.865	1.470	1.523	1.837	1.472	1.526	1.829	1.476	1.533	1.801	1.483	1.551	1.855
B(N–O)	1.719	1.671	1.457	1.706	1.655	1.439	1.708	1.659	1.441	1.718	1.671	1.460	1.689	1.627	1.404
B(Ru–L)	0.548	0.608	0.594	0.534	0.605	0.573	0.551	0.622	0.592	0.523	0.589	0.523	0.541	0.604	0.560

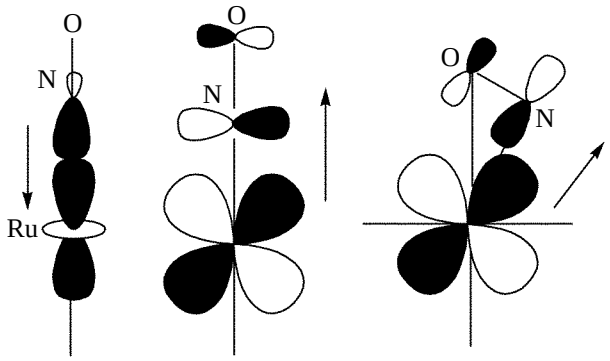
[a] Data for conformation **A** are given (Fig. 1).

ν(NO) on the transition of nitrosyl complexes from GS to the metastable state with linear NO coordination via the oxygen atom. In the case of $[Ru(NO)Cl_5]^{2-}$, all calculations, especially B3LYP/DZVP, overestimate the Ru–Cl_{cis} distance.

The GS→MS1 transition in *trans*-$[Ru(NO)\cdot(NH_3)_4L]^{3+}$ is accompanied by a slight elongation of the N–O bond (Table 3) and shortening of the Ru–L bond (Tables 2 and 3). The Ru–N bond in GS is shorter by 0.1 Å than the Ru–O bond in MS1. Deviations of ruthenium populations $n(d_{xz})$ and $n(d_{yz})$ from 2 and of n_π(NO) from 4 can serve as measures of π-electron density delocalization within the RuNO group. In GS and MS1, the $n(d_{xz} + d_{yz})$ and n_π(NO) populations are about 3 and 5, respectively, which corresponds to the formal description of nitrosyl complexes as compounds of Ru(III) and NO^0 (Table 3). Although the isonitrosyl group is a weaker σ-donor compared to the nitrosyl group, the charge of the latter in MS1 is made a slightly more positive by weakening Ru→ON π-dative interaction (Table 3). For example, in $[Ru(NO)(NH_3)_5]^{3+}$, the total populations of NO σ orbitals [n_σ(NO)] are 9.79 (GS) and 9.92 (MS1), and the total populations of π orbitals [n_π(NO)] are 5.09 (GS) and 4.92 (MS1).

The weakened π-acceptor and σ-donor interactions also manifest themselves in higher populations of $d_{7\pi}$ AOs (d_{xz} and d_{yz}) and lower population of the metal d_{z^2} AO in MS1 compared to GS. These changes in charge distribution are accompanied by an essential decrease in the Ru–NO bond order (B): B(Ru–O) in MS1 is half B(Ru–N) in GS. According to calcula-

tions with the SVWN5 functional,[3] B(N–O) in MS1 slightly decreases, which agrees with the decrease in ν(NO). The Ru–L bond in MS1 is somewhat strengthened, as evidenced by the decreased length and increased multiplicity of this bond (Table 3). The π-acceptor power of ligands L is attenuated in the presence of the nitrosyl group: The π-orbital populations of L [n_π(L)] in none of the complexes are higher than those in the free ligands.



GS MS2

The d_{xz} and d_{yz} orbitals in MS2 with side η^2 coordination of NO are nonequivalent with respect to the Ru–NO bond: The d_{xz}–π*(NO) interaction gains features of σ bonding, and the charge transfer from this metal AO essentially increases and from the d_{yz} AO decreases (Table 3).

When the side coordination involves both atoms of the nitrosyl group, the N–O is weakened, as evidenced by its greater length, smaller bond order, and lower ν(NO) vibration frequency.

According to the calculations in [5] for $[Ru(NO)\cdot(NH_3)_5]^{3+}$ and $[Ru(NO)(CN)_5]^{2-}$, the calculated ΔE(GS→MS) values depend on the basis set. The same conclusion follows from our calculations for $[Ru(NO)Cl_5]^{2-}$ (Table 2). The energies (eV) of MS1 and MS2 relative to GS are compared below (for B3LYP [5] we give ΔH values which are very close to ΔE). In [6], the calculated ΔE values were treated as overestimated, whereas ΔE(MS1) and ΔE(MS2), as very close to each other.

	B3LYP [5]				VWN [6]		This work	
	DZVP		LanL2DZ					
	MS1	MS2	MS1	MS2	MS1	MS2	MS1	MS2
$[Ru(NO)(NH_3)_5]^{3+}$	1.53	1.44	1.51	1.77			1.68	1.91
$[Ru(NO)(NH_3)_4(nc)]^{3+}$					1.79	1.54	1.63	1.64
$[Ru(NO)(CN)_5]_2^-$	1.77	1.14	1.82	1.43			1.77	1.41

The ΔE(MS1) and ΔE(MS2) values for $[Ru(NO)\cdot(X)_5]^q$ (X = NH_3, Cl^-, CN^-) are given in Fig. 2. In spite of the fact that the results of various calculations essentially differ from each other, we can note that the energy of MS1 increases and the energy of MS2 decreases along the series X = NH_3, Cl^-, CN^-. If GS, MS2, and MS1 are considered as successive points in the coordinate of a model reaction of the isomerization of a nitrosyl complex into isonitrosyl through side η^2 coordination, the behavior of these three complexes should be qualitatively different. For $[Ru(NO)(NH_3)_5]^{3+}$ and $[Ru(NO)Cl_5]^{2-}$, only one metastable state with isonitrosyl coordination was experimentally detected. From the thermodynamic point of view, should be characteristic of $[Ru(NO)\cdot(CN)_5]^{2-}$ for which all calculations give ΔE(MS2) < ΔE(MS1) the most stable MS2, and experimental evidence is available that MS2 decomposes at a higher temperature than MS1 [19].

The ΔE(MS1) and ΔE(MS2) values for the $[Ru(NO)(NH_3)_4(L)]^{3+}$ series are given in Fig. 3. It is clearly seen that the energies of MS1 are practically identical for all the complexes. The energies of MS2 are close to each other, but ΔE(MS2) regularly decreases with enhancing π-acceptor properties of *trans* ligand L. This effect is not so marked as that produced by the replacement of all the five ligands in the coordination sphere in the series $[Ru(NO)(NH_3)_5]^{3+}$, $[Ru(NO)Cl_5]^{2-}$, and $[Ru(NO)(CN)_5]^{2-}$, but it gives the basis to assume that the state with side η^2 coordination of NO can be stabilized by introducing π-acceptor ligands in nitrosyl complexes.

[3] The results of population analysis and calculated B(X–Y) values depend both on the calculation method and on the basis set. Therefore, only general tendencies are considered unless a special mention is given.

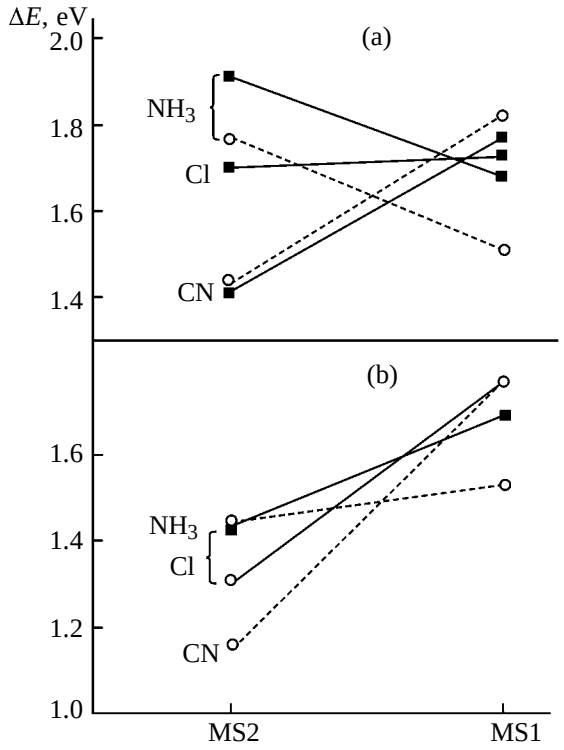


Fig. 2. Energies ΔE of MS1 and MS2 relative to GS for $Ru(NO)(X)_5]^q$. Basis set: (a) LanL2DZ(Ru, Cl) + 6-31G(C, N, O, H) and (b) DZVP. (Squares) SVWN5 functional, (circles) B3LYP functional, (broken line) data of [5], and (continuous lines) this work.

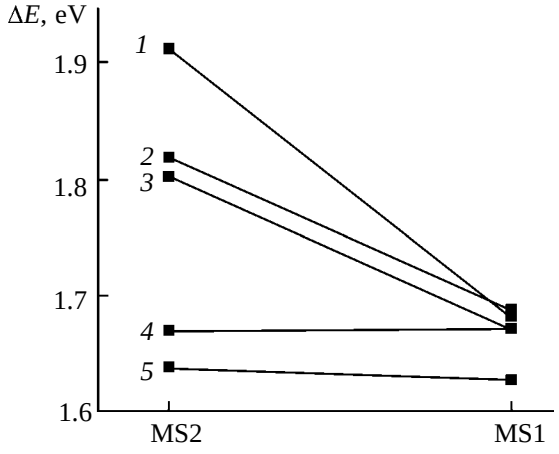


Fig. 3. Energies ΔE of MS1 and MS2 relative GS for *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$. Ligand L: (*1*) NH_3, (*2*) im, (*3*) py, (*4*) pyz, and (*5*) nc.

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