Russian Journal of General Chemistry, Vol. 74, No. 4, 2004, pp. 481–485. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 4, 2004, pp. 529–534.

Electronic Spectra of Ruthenium Nitrosyl Complexes with Macrocyclic Ligands

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Received September 23, 2003

Abstract — Electronic spectra of ruthenium(II) nitrosyl complexes $[Ru(NO)(salen)(X)]^n$ (X = Cl, H_2O; n = 0, 1) and [Ru(NO)(P)(ONO)] with tetradentate π-conjugated ligands *N*,*N*'-ethylenebis(salicylideniminato) dianion (salen) and porphinate dianion (P) were calculated by the TD DFT and CINDO/CI methods. The data obtained were compared to the results of previous calculations of the spectra of *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ complexes with nitrogen-containing heterocyclic ligands L. It was found that charge-transfer transitions to π* orbitals of the RuNO group dominate in the long-wave part of the spectrum irrespective of the other ligands.

Incorporation of nitrosyl group in the inner coordination spheres of transition metal complexes results in essential modification of their spectral properties. In our previous work [1] we calculated and interpreted the electronic absorption spectra of ruthenium nitrosyl complexes with nitrogen-containing heterocyclic ligands L (L = pyridine, pyrazine, histidine, imidazole). We showed that charge-transfer transitions $\pi(L) \rightarrow \pi^*(RuNO)$ dominate in the spectra of such compounds owing to strong π-acceptor power of the nitrosyl group, whereas intensive charge-transfer transitions $d_\pi(Ru) \rightarrow \pi^*(L)$, characteristic of visible and UV regions of similar Ru(II) compounds without nitrosyl group, are absent from the spectra of the nitrosyl complexes. Continuing the systematic study of this problem, we have considered in this work ruthenium nitrosyl complexes [Ru(NO)(salen)(X)] (X = Cl, H_2O; n = 0, 1) and [Ru(NO)(P)(ONO)] with tetradentate π-conjugated ligands *N*,*N*'-ethylenebis-(salicylideniminato) dianion (salen) and porphinate dianion (P).

We have found earlier [2] that electron correlation effects should be taken into account to describe correctly the electronic structure of nitrosyl complexes containing $RuNO^{3+}$ groups. Therefore, to calculate the electronic spectra of the compounds under consideration, we chose two methods taking into account the correlation effects: a nonstationary density functional method (TD DFT) and a semiempirical configuration-interaction method (CINDO/CI) with double excitations to π orbitals of the $RuNO^{3+}$ groups in the CI basis. The TD DFT calculations were made using the GAUSSIAN 98 program with the B3LYP hybrid functional in the LANL2DZ basis for ruthenium and with the 6-31G basis for the other atoms [3]. The technique of the CINDO/CI calculations of the spectra of nitrosyl complexes has been described in [1]. As the compounds under consideration are uncharged molecules or singly charged cations, the interaction with solvent and counterions was assumed to be weak and was not taken into account in the calculations. The experimental geometric parameters of the compounds [4, 5] were used in the calculations.

Spectra of nitrosoruthenium salen complexes. The CINDO and DFT calculations give approximately equal orders of frontier molecular orbitals. In all the cases, five to seven higher occupied molecular orbitals (HOMO) are predominantly the molecular orbitals of salen, and the highest two of them are π orbitals of phenyl rings. The molecular orbitals with appreciable contributions of Ru d_{xz}, d_{yz}, and d_{xy} AOs (the *z* axis is directed along the bonds of the linear RuNO group) and NO π orbitals are located below in energy. The chlorine atomic orbitals in [Ru(NO)(salen)(Cl)] make the major contribution to the HOMO-3 and HOMO-4 orbitals (DFT method) and to the HOMO-6, HOMO-7, and HOMO-8 orbitals (CINDO method). Two lower unoccupied molecular orbitals are predominantly π* MOs of the RuNO group with a small admixture of salen orbitals. The molecular orbitals containing salen orbitals and ruthenium d_{z^2} and $d_{x^2-y^2}$ AOs are located higher. Nevertheless, despite similar compositions of the frontier molecular orbitals, the spectra calculated by the two methods differ essentially.

The energies (eV) and molar extinction coefficients ($l\ mol^{-1}\ cm^{-1}$) of the absorption maxima in the experimental spectra of [Ru(NO)(salen)(Cl)] (a solution in acetonitrile) and $[Ru(salen)(NO)(H_2O)]^+$ (an

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Table 1. Energies (E, eV), oscillator strengths (f), and nature of transitions[a] in the complexes [Ru(NO)(salen)(Cl)] and $[Ru(NO)(salen)(H_2O)]^+$, calculated by the CINDO/CI method (in the range of $E > 4$ eV, only transitions with $f > 0.01$ are given)

[Ru(NO)(salen)(Cl)]			$[Ru(NO)(salen)(H_2O)]^+$		
E	f	transition	E	f	transition
2.33	0.0005	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)	2.30	0.0002	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)
2.52	0.0001	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)	3.50	0.0008	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)
2.55	0.0008	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)	2.55	0.0004	π(RuNO), π(salen) $\rightarrow \pi^*$(RuNO)
2.79	0	d_{xy}, π(salen) $\rightarrow \pi^*$(RuNO)	3.07	0.0017	d_{xy}, π(salen) $\rightarrow \pi^*$(RuNO)
2.86	0.0001	d_{xy}, π(salen) $\rightarrow \pi^*$(RuNO)	3.24	0.0015	d_{xy}, π(salen) $\rightarrow \pi^*$(RuNO)
3.56	0.011	π(salen), Cl $\rightarrow \pi^*$(RuNO)	3.33	0.016	π(salen) $\rightarrow \pi^*$(RuNO)
3.67	0.004	π(RuNO), π(salen) $\rightarrow d_{z^2}$	3.55	0.014	π(salen) $\rightarrow \pi^*$(RuNO)
3.90	0.006	π(salen) $\rightarrow \pi^*$(RuNO)	4.27	0.038	π(salen) $\rightarrow \pi^*$(RuNO)
3.97	0.006	π(salen) $\rightarrow \pi^*$(RuNO)	4.36	0.016	π(salen) $\rightarrow \pi^*$(RuNO)
4.14	0.008	π(salen) $\rightarrow \pi^*$(RuNO)	4.41	0.158	π(salen) $\rightarrow \pi^*$(RuNO)
4.20	0.009	π(RuNO), π(salen) $\rightarrow d_{z^2}$	4.56	0.175	π(salen) $\rightarrow \pi^*$(RuNO)
4.55	0.166	π(salen) $\rightarrow \pi^*$(salen), π^*(RuNO)	4.79	0.113	π(salen) $\rightarrow \pi^*$(RuNO)
4.60	0.095	π(salen), Cl $\rightarrow \pi^*$(RuNO)	4.91	0.060	π(salen) $\rightarrow \pi^*$(salen), π^*(RuNO)
4.68	0.036	π(salen), Cl $\rightarrow \pi^*$(RuNO)	5.05	0.070	salen $\rightarrow \pi^*$(RuNO)
4.73	0.134	π(salen), Cl $\rightarrow \pi^*$(RuNO)	5.31	1.073	π(salen) $\rightarrow \pi^*$(salen)
4.76	0.042	Cl, π(salen) $\rightarrow \pi^*$(RuNO)	5.49	0.125	π(salen) $\rightarrow \pi^*$(salen)
5.04	0.126	Cl $\rightarrow \pi^*$(RuNO)	5.50	0.015	π(salen) $\rightarrow \pi^*$(salen)
5.14	0.051	salen $\rightarrow$ RuNO	5.66	0.151	π(salen) $\rightarrow \pi^*$(RuNO)
5.39	0.269	π(salen) $\rightarrow \pi^*$(salen), π^*(RuNO)	5.75	0.018	salen $\rightarrow$ RuNO
5.45	0.374	π(salen) $\rightarrow \pi^*$(salen)	5.76	0.022	π(salen) $\rightarrow \pi^*$(salen)
5.55	0.120	π(salen) $\rightarrow \pi^*$(salen), d_{z^2}	6.03	0.019	π(salen) $\rightarrow \pi^*$(salen)
5.58	0.194	π(salen) $\rightarrow \pi^*$(salen), π^*(RuNO)			

[a] Orbitals with greater contributions are listed first.

aqueous solution) are as follows: [Ru(NO)(salen)(Cl)]: 2.5–2.8 w, 3.35 (4000), 4.1 sh, 4.8 sh, 4.95 (23 000), 5.65 (24 000) [4]; 3.30 (5700) 5.00 (36 000), 5.54 (39 000) [6]; $[Ru(NO)(salen)(H_2O)]^+$: 2.5–2.8 w, 3.4 (2500), 4.2 sh, 4.5 sh, 5.2 (23 000), 5.8 sh [4].

The spectral data for the complexes under study, calculated by the CINDO/CI method, are given in Table 1. The calculated transition energies and intensities reasonably agree with the experimental data. According to Table 1, the low-intensity absorption in the long-wave region of the spectrum (2.5–3.0 eV) is caused by transitions inside the RuNO group with a small admixture of the charge transfer from RuNO to the π^* MO of salen. All the other bands in the spectrum are mixed, with various relative contributions of the charge transfer from salen to π^*(RuNO) and intraligand $\pi \rightarrow \pi^*$(salen) transitions, the intraligand contribution dominating only in certain transitions with energies higher than 4.5 eV. In particular, intensive bands in the near UV region (3.3–3.4 eV, ~270 nm) should be attributed to the charge transfer salen $\rightarrow \pi$(RuNO), which agrees with the opinion of Works *et al*. [6].

The TD DFT calculations of the electronic spectra of [Ru(NO)(salen)(X)] complexes are shown in Table 2. The agreement between the calculated and experimental energies and intensities of transitions is somewhat worse than in the CINDO/CI calculations: the energies of the first transitions are underestimated by ~1 eV; high-intensity transitions with energies greater than 5 eV are absent in the case of the aqua complex. The main differences in the assignment in comparison with the CINDO/CI calculations concern the long-wave part of the spectrum. According to the TD DFT calculations, the first transitions represent the charge transfer salen $\rightarrow \pi^*$(RuNO), and the experimental bands with the energies of 3.35 (chloride complex) and 3.40 eV (aqua complex) are caused mainly by $\pi \rightarrow \pi^*$(salen) transitions.

The assignment [4] of the spectrum of [Ru(NO)·(salen)(Cl)], based on INDO/S calculations [7], is similar to our assignment, presumably due to the fact

Table 2. Energies (E, eV), oscillator strengths (f), and nature of transitions in the complexes [Ru(NO)(salen)(Cl)] and $[Ru(NO)(salen)(H_2O)]^+$, calculated by the TD DFT method (for transitions with $f > 0.01$)

[Ru(NO)(salen)(Cl)]			$[Ru(NO)(salen)(H_2O)]^+$		
E	f	transition	E	f	transition
1.49	<0.001	π(salen) → π*(RuNO)	1.66	0.001	π(salen) → π*(RuNO)
1.84	0.002	π(salen) → π*(RuNO)	1.90	0.003	π(salen) → π*(RuNO)
2.00	0.001	π(salen) → π*(RuNO)	2.06	0.017	π(salen) → π*(RuNO)
2.06	0.030	π(salen) → π*(RuNO)	2.88	0.029	π(salen) → π*(RuNO)
3.07	0.030	π(salen) → π*(salen)	3.12	0.056	π(salen) → π*(salen) + Ru + NO
3.22	0.022	π(salen) → π*(RuNO)	3.22	0.021	π(salen) → π*(salen) + Ru + NO
3.37	0.017	π(salen) → π*(salen)	3.44	0.023	salen + π*(salen) + π*(RuNO)
3.38	0.026	salen + Ru → Ru + NO + salen	3.88	0.042	salen → π*(salen)
3.50	0.041	π(salen) → π*(salen)	4.22	0.022	salen + Ru → Ru + NO + salen
3.52	0.018	salen → π*(RuNO)	4.36	0.022	salen + Ru → Ru + NO + salen
3.75	0.013	salen → Ru + NO	4.44	0.034	salen + Ru → Ru + NO + salen
4.49	0.022	Cl + salen → Ru + NO	4.54	0.210	salen + Ru → salen + NO + Ru
4.60	0.062	π(salen) → π*(salen)	4.66	0.224	salen → salen + NO + Ru
4.63	0.148	π(salen) → π*(salen)	4.74	0.106	π(salen) → salen + Ru
4.78	0.101	π(salen) → π*(salen) + Ru + NO	4.85	0.142	salen → π*(salen) + Ru + NO
4.82	0.035	π(salen) + Cl → π*(salen) + Ru + NO	5.29	0.026	π(salen) → salen + Ru
5.21	0.032	Ru + NO + Cl + salen → π*(RuNO)	5.46	0.035	salen + Ru → π*(salen) + Ru + NO
5.28	0.130	π(salen) → π*(salen)	5.56	0.056	salen + Ru → salen + NO + Ru
5.34	0.038	π(salen) → π*(salen)	5.60	0.059	π(salen) → π*(salen) + π*(RuNO)
5.52	0.078	salen → π*(salen) + Ru + NO	5.64	0.026	salen + Ru → π*(salen) + π*(RuNO)
			5.73	0.026	π(salen) → π*(salen)
			5.74	0.033	salen + Ru → salen + NO + Ru
			5.80	0.037	salen → π*(salen) + π*(RuNO)
			5.82	0.078	π(salen) → π*(salen)

that in both cases the CIS approximation was used, whereas in the above-described semiempirical CINDO calculations double-excited configurations involving two bonding and two antibonding π MOs of RuNO groups were included in the basis. This assumption can be confirmed by the fact that the exclusion of double excitations from the CI basis led to a decrease in the energies of the first transitions by ~0.5 eV and to an increase in the salen → π*(RuNO) contribution to these transitions, i.e., it made our results closer to the data of [4].

A common feature of the CINDO and TD DFT calculations of the spectra of nitrosyl complexes with salen is the absence of the characteristic charge-transfer transitions from Ru d AOs to π* orbitals of organic ligands observed in the spectra of Ru(II) complexes. For example, these intense transitions appear at 378 and 295 nm in the spectrum of $[Ru(salen)(H_2O)_2]$ calculated by the CINDO method (Table 3). However, the calculation for the similar Ru(III) complex as well as for the nitrosyl complex $[Ru(NO)(salen)(H_2O)]^+$ gives no high-intensity transitions in the range 300–400 nm. Earlier, when studying complexes $[Ru(NO)(NH_3)_4(L)]^{n+}$ (L is a heterocyclic ligand) [1], we have noted this feature of the spectra of nitrosyl complexes, allowing us to treat the oxidation state of ruthenium in such compounds as Ru(III).

The experimental spectra of nitrosyl complexed considered in this work are compared to the spectra of certain salen-containing Ru(III) complexes in Table 3. The main distinction consists in the occurrence of a strong band in the visible region of the spectra of complexes without NO. According to our calculations of the complex $[Ru(salen)(H_2O)_2]^+$, this band can be attributed to the charge transfer from the π MO of salen to the d_π AO of ruthenium occupied with a single electron. Such transitions are impossible in nitrosyl complexes having no unpaired electrons [we can accept formally that an unpaired electron of Ru(III) on d_π AO forms a covalent bond with an unpaired electron of NO]. In other respects, the nitrosyl complexes behave as Ru(III) complexes, showing

Table 3. Positions of absorption maxima and band intensities in the spectra of salen-containing complexes

Compound	λ_{max}, nm (ε)						
	Experiment [2, 8]						
$[Ru(salen)(H_2O)_2]^+$	620 (2×10^3)	490 (10^3)	380 (8×10^3)	340 (9×10^3)		240 (2×10^4)	
[Ru(salen)(CO)(Cl)]	607 (785)		390 (8×10^3)	349 (4×10^3)	268 (7×10^3)	240 (10^4)	
[Ru(NO)(salen)(Cl)]		400–500	370 (4×10^3)	~300	~260	250 (2×10^4)	220 (10^4)
$Ru(NO)(salen)(H_2O)]^+$		~500	360	~300	~270	240	220
	CINDO/CI calculation						
$[Ru(salen)(H_2O)_2]$	400–430 (0.01–0.05)	378 (0.23)	295 (0.26)	240 (0.13)	233 (0.27)		
$[Ru(salen)(H_2O)_2]^+$	450 (0.10)	340 (0.03)	320 (0.02)	255 (0.56)	235 (0.22)	215 (0.07)	
$[Ru(NO)(salen)(H_2O)]^+$	440–520 (~0)	335 (0.01)	320 (0.01)	275 (0.19)	235 (0.78)	225 (0.21)	

characteristic transitions from the ligand orbitals to π*(RuNO) orbitals [as a result of the interaction with π*(NO), the vacancy on d_π AO is distributed now over two molecular orbitals] and to unoccupied ligand orbitals.

Spectra of nitrosoruthenium porphyrin complexes. As follows from numerous works devoted to the study of porphyrins and their complexes with transition and nontransition metals, the electronic spectra of these compounds in the visible and near UV ranges are determined by two bands caused by $\pi\rightarrow\pi^*$ transitions inside porphyrins, namely, by a relatively weak *Q* band with an absorption maximum about 2 eV and a very strong *B* band or Soret band (3.0–3.2 eV). In the shorter-wave region, there is an *N* band (3.6–3.8 eV), which is assigned to the transitions from the p_π orbital of nitrogen atoms to π* MO of porphyrin [9]. The structure of the spectrum of the free porphyrin is preserved in the complexes and does not depend on the metal to which porphyrin is coordinated and on the others ligands, including the nitrosyl group. In particular, the following energies (eV) and intensities (log ε) of the absorption maxima were obtained for a solution of [Ru(NO)(TTP)(ONO)] (TTP is tetra-*p*-tolylporphinate dianion) in toluene [10]: *Q* 2.16 (3.92), 2.28 (3.88); *B* 3.13 (5.08); *N* 3.52 (4.50).

In our calculations of the spectrum of this complex, we have replaced tolyl groups by the hydrogen atoms. Preliminary calculations of the spectra of free porphyrins have shown that introduction of substituents affects the position of the Soret band to the greatest extent, shifting it by ~0.2 eV toward lower energies. The results of CINDO/CI and TD DFT calculations of the spectrum of [Ru(NO)(P)(ONO)] are given in Table 4. Both calculation methods give overestimated transition energies, especially for the *B* and *N* bands: the values of 3.88 and 3.98 (CINDO) and 3.57 eV (TD DFT) correspond to the experimental energy of the *B* band of 3.13 eV; transitions with the energies of 4.12 and 4.14 eV calculated by the TD DFT method correspond to the *N* band of the experimental spectrum (3.52 eV). In the CINDO calculations, the transitions corresponding to the *N* band did not fall into the region under consideration (E < 4.4 eV). A similar extent of agreement with the experimental spectrum was attained in the calculations of porphyrin complexes with Mg, Fe, Ni, and Zn by the INDO/S [11, 12] (the position of the Soret band was overestimated by 0.5–0.7 eV) and TD DFT/B3LYP methods [13].

The examination of long-wave transitions is of the greatest interest from the chemical point of view, because they do not affect appreciably the appearance of the experimentally observed spectrum owing to their small intensity, but can play an important role in chemical processes occurring upon photoexcitation of the complexes. According to both calculation methods, in the region of 2–3 eV (the region of the *Q* band of free porphyrin), along with intraligand $\pi\rightarrow\pi^*$ transitions, there are several transitions to π* antibonding orbitals of the RuNO group. In the TD DFT calculations, this is the charge transfer from the ligands P and ONO, and, to a lesser extent, from the metal, whereas in the CINDO calculations these transitions correspond to the electronic excitation inside the RuNO group, leaving the charges of the complex fragments almost unchanged. The charge transfer to π*(RuNO) is admixed also to intense intraligand transitions (to a lesser extent in the case of the *B* band calculated by the CINDO method). Thus, in spite of the lack of apparent changes in positions and intensities of observable bands, the spectrum of the nitrosyl complex with porphyrin

Table 4. Energies (E, eV), oscillator strengths (f), and nature of transitions in [Ru(NO)(P)(ONO)], calculated by the CINDO/CI and TD DFT methods (for E > 2.5 eV, transitions with f > 0.01 are given)

CINDO/CI			TD DFT		
E	f	transition	E	f	transition
2.04	0	$\pi \rightarrow \pi^*$(RuNO)	1.94	0.001	ONO $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.17	0.001	$\pi \rightarrow \pi^*$(RuNO)	2.06	0.002	ONO $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.21	0	$\pi \rightarrow \pi^*$(RuNO)	2.29	0.001	TTP, ONO $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.23	0.027	π(TTP) $\rightarrow \pi^*$(RuNO)	2.52	0.010	TTP $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.24	0.028	π(TTP) $\rightarrow \pi^*$(RuNO)	2.54	0.013	TTP, ONO $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.46	0.025	π(TTP) $\rightarrow \pi^*$(TTP), π^*(RuNO)	3.57	0.518	TTP, ONO $\rightarrow \pi^*$(RuNO), π^*(TTP)
2.46	0.028	π(TTP) $\rightarrow \pi^*$(TTP), π^*(RuNO)	3.57	0.607	TTP, ONO $\rightarrow \pi^*$(RuNO), π^*(TTP), ONO
2.64	0.053	π(TTP) $\rightarrow \pi^*$(RuNO), π^*(TTP)	3.60	0.103	ONO $\rightarrow$ ONO
2.65	0.047	π(TTP) $\rightarrow \pi^*$(RuNO), π^*(TTP)	4.09	0.074	TTP, ONO $\rightarrow \pi^*$(RuNO), ONO
3.88	2.372	$\pi \rightarrow \pi^*$(TTP)	4.12	0.179	TTP $\rightarrow \pi^*$(RuNO), π^*(TTP)
3.98	2.724	$\pi \rightarrow \pi^*$(TTP)	4.14	0.201	TTP $\rightarrow \pi^*$(RuNO), π^*(TTP)
			4.20	0.036	TTP $\rightarrow \pi^*$(RuNO), ONO
			4.45	0.080	TTP $\rightarrow \pi^*$(RuNO), ONO

essentially differs from the spectrum of the free porphyrin in the nature of transitions.

The results of this work confirm our previous conclusion that the nitrosyl group exerts a dominating influence on the spectra, irerespective of the ligands surrounding the $RuNO^{3+}$ group.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 02-03-32715) and the Program "Universities of Russia" (project no. UR.05.01.025). The calculations with the GAUSSIAN 98 program were carried out at the Institute of Organic Chemistry, Russian Academy of Sciences, under financial support of the Russian Foundation for Basic Research (project no. 01-07-90072).

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