Letters to the Editor

First X-ray diffraction study of nitrosonium complexes of nitrogen-containing organic compounds: a complex of 1,10-phenanthroline with $NO^+BF_4^-$

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X-ray diffraction data on nitrosonium complexes of N-bases are lacking in the literature.[1] However, information on the molecular structures of these complexes is necessary for a deeper insight into the mechanisms of various organic reactions, such as nitrosation of N-heterocyclic compounds, diazotization, the formation of nitrosoamines, *etc.*[1] The knowledge of the structures of nitrosonium complexes of N-heterocyclic compounds is essential to the understanding of a unique role of the NO molecule and the NO^+ cation in biochemical processes taking place *in vivo*.[1,2]

According to the results of quantum-chemical calculations and the experimental data for gaseous and liquid phases, N-bases exhibit rather high affinities for the NO^+ cation. It is assumed that the latter is bound to the N atom of the base to form the N—N σ-bond (*n*-complex).[1] When studying the nitrosonium complex of 1,10-phenanthroline (PL), we found a new type of binding of the NO^+ cation to a molecule of the N-heterocyclic compound, *viz.*, the N atom of the cation is bound simultaneously to two N atoms of the base.

The crystals of the salt $[PL—NO]^+BF_4^-$ were prepared by the reaction of PL with $NOBF_4$ in MeCN at 20 °C followed by keeping at −15 °C for 10 days. According to the X-ray diffraction data (a Bruker P4 diffractometer, Mo-Kα radiation, −35 °C, θ/2θ scanning technique, $2\theta < 45°$, Bruker-XTL and SHELXL-97 program packages), the crystals of $[C_{12}H_8N_3O]^+BF_4^-$ are monoclinic, space group $P2_1/n$, $a = 11.137(1)$, $b = 18.608(2)$, $c = 13.355(5)$ Å, $\beta = 112.62(2)°$, $V = 2555(1)$ Å^3, $Z = 8$, $d_{calc} = 1.544$ g cm^{-3}, $wR_2 = 0.4039$ for all 3158 F^2, $S = 1.578$, $R_1 = 0.1619$ for 1429 reflections with $F_0 > 4\sigma(F)$.* The unit cell contains two types of cations and anions characterized by close values of the bond lengths and bond angles. The NO groups of the complex are located at

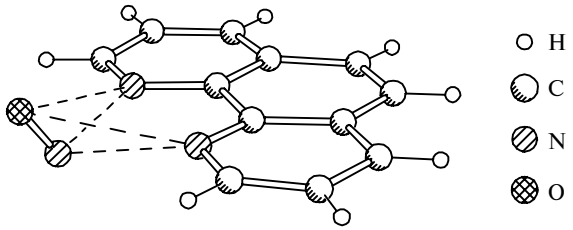

Fig. 1. Molecular structure of the complex of the nitrosonium cation with 1,10-phenanthroline (the anion is BF_4^-).

* Evidently, the high values of the R_1 and wR_2 factors resulted from the poor quality of the crystal (the presence of a satellite, probable twinning).

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angles of 54° and 61° to the phenanthroline core (Fig. 1). The distances from the N atom of the NO group to the N atoms of the core (2.34(2) and 2.34(2) Å; 2.25(2) and 2.28(2) Å for two crystallographically independent molecules) are much smaller than the average value for the intermolecular N...N contact (3.00 Å),[3] whereas the distances from the O atom of this group to the N atoms of the core (2.64(2) and 2.73(2) Å; 2.76(2) and 2.81(2) Å) are close to the corresponding value for the O...N pair (2.78 Å).[3] The N—O bond lengths in the complex (0.90(1) and 1.00(2) Å) are close to the corresponding value for the NO^+ cation (0.997 Å).[4]

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