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Ligand Properties of Thioamides and Their *N*- and *N,N'*-Derivatives

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Abstract—A series of nonempirical calculations by the Hartree–Fock method with full geometry optimization for a number of *N*- and *N,N'*-derivatives of thioamides which are potential functional groups for sorbents for extraction of platinum metals from technological solutions. The ligands all prefer to coordinate to platinum metal ions by the sulfur atom (soft Lewis base) at an angle to the sulfur–oxygen bond.

Thiourea $SC(NH_2)_2$, thioacetamide $SC(NH_2)(CH_3)$, and their *N*- and *N,N'*-derivatives represent a class of thioamide ligands forming numerous coordination compounds with all platinum metals. Thiourea and thioacetamide are widely applied in analytical chemistry of platinum metals, first for group concentration of these metals. The high selectivity of thioamides with respect to platinum metals in solutions on a background of large excesses of non-ferrous metals and iron is also preserved in sorption materials obtained by grafting these molecules to various organic and inorganic polymer matrices. Such sorbents can be considered as polymeric ligands [1]. The prospective use of thioamide sorption materials for extraction of platinum metals from technological solutions and in analytical practice predetermine the interest in studying the effects of functional groups bound to nitrogen atoms on the properties of the above-mentioned organic compounds.

The aim of this work was to elucidate by quantum-chemical methods the features of the electronic structure of *N*- and *N,N'*-derivatives of thioamides, which may be responsible for their sorption capacity with respect to platinum metal ions.

For the objects for study we took thioacetamide and the following thiourea derivatives: 4-methylthiosemicarbazide, *N*-propyl-*N'*-allylthiourea, *N*-propyl-*N'*-phenylthiourea, and *N*-propyl-*N'*-benzoylthiourea. It should be noted that earlier we calculated the electronic structures of thiourea, a series of its simplest derivatives, and a Pt(II) thiourea complex by the CNDO method with a system of semiempirical parameters specially developed for sulfur compounds [2]. According to these calculations, the ligand capacities of these compounds depends primarily on the presence of lone electron pairs localized on the $3p_\pi$ orbitals of sulfur. The reactivity of lone electron pairs of nitrogen atoms ($2p_\pi$ orbitals) was correlated with bond arrangement (planar or pyramidal) around these atoms. In planar SCNN structures, the involvement of lone electron pairs of nitrogen atoms into the conjugation system resulted in weakening of the donor power of the ligands and made impossible their *N*-coordination to metal. In the case of a pyramidal immediate surrounding of nitrogen atoms, such coordination was not excluded. This conclusion was deduced from the calculations based on X-ray diffraction data for tetramethylthiourea $SC[N(CH_3)_2]_2$ [3], according to which nitrogen atoms in this compound deviate from the plane of surrounding carbon atoms by 0.75 Å. The CNDO calculations in [2] were performed with no geometry optimization, and this, in essence, predetermined that the calculations resulted in different electronic structures of tetramethylthiourea and thiourea. Later it was found that the X-ray diffraction geometry of tetramethylthiourea, reported in [3], involves an obvious inconsistency: The sum of the angles at the pyramid apex (nitrogen atom) is close to 358°, implying that this pyramid is very low (0.75 Å), which is improbable. In this connection it seemed reasonable to include again thiourea in the series of thiourea derivatives to be calculated in this work by the nonempirical Hartree–Fock (HF) method with full geometry optimization by the GAMESS program complex [4] in the 6–31G basis with polarizing *d* functions on the S atom [HF(a) calculations]. In addition, for thiourea and tetramethylthiourea we performed calculations by the density functional method (DFT) which usually adequately reproduces

Table 1. Atomic charges (*q*, *e*), dipole moments (μ, D), bond lengths (*R*, Å), and energies (E_{HOMO}, eV) in thiourea and its derivatives {Hartree–Fock [HF(a) and HF(b)] and density functional (DFT) calculations}

Method	*R*(S–C)	*R*(C–N)	h_N	*q*(S)	*q*(C)	*q*(N)	μ	E_{HOMO}
$SC(NH_2)_2$								
HF(a)	1.688	1.345	0.00	–0.35	0.61	–0.91	6.2	–8.509 –8.552 –11.984[a]
HF(b)	1.684	1.337	0.00	–0.37	0.47	–0.87	6.3	–8.487 –8.498 –11.940[a]
DFT	1.683	1.358	0.00	–0.32	0.35	–0.58		
$SC[N(CH_3)_2]_2$								
HF(a)	1.689	1.363	0.14	–0.35	0.63	–0.81	5.6	–8.122 –8.383 –9.831[a]
Experiment [3]	1.68	1.37						
DFT	1.686	1.379	0.19	–0.31	0.31	–0.45		
$SC(NH_2)(CH_3)$								
HF(a)	1.661	1.338	0.00	–0.30	0.31	–0.87	5.2	–8.645 –8.922 –13.902[a]
$SC(NHNH_2)(NHCH_3)$								
HF(a)	1.687	1.354 1.345	0.00 0.00 0.32	–0.35	0.67	–0.73 (N^1) –0.89 (N^2) –0.55 (N^3)	4.6	–8.617 –8.645 –10.955[a] –11.752[a]
$SC(NHCH_2CH_2CH_3)(NHCH_2CH{=}CH_2)$								
HF(b)	1.690	1.342 1.345	0.06 0.09	–0.37	0.52	–0.77 (N^1) –0.76 (N^2)	5.6	–8.381 –8.441 –10.660[a]
$SC(NHCH_2CH_2CH_3)(NHC_6H_5)$								
HF(b)	1.682	1.342 1.353	0.06 0.07	–0.35	0.51	–0.85 (N^1) –0.77 (N^2)	5.4	–8.187 –8.356 –10.960[a]
$SC(NHCH_2CH_2CH_3)(NHCOC_6H_5)$								
HF(b)	1.655	1.342 1.390	0.08 0.06	–0.25	0.51	–0.89 (N^1) –0.76 (N^2)	7.8	–8.470 –8.696 –11.208[a]

[a] Nitrogen lone electron pair.

molecular geometry. To characterize stationary points as energy minima, we calculated normal vibration frequencies for all the compounds. The calculated data are given in Tables 1 and 2, and the geometric structures of the molecules are shown in Figs. 1–7.

As follows from Table 1, both the sulfur and nitrogen atoms in all the compounds under consideration bear excess electron density. This suggests potential ambidentacity of these compounds. The coordination of thioamide ligands to platinum metal ions have most commonly been interpreted in terms of Pearson's principle of hard and soft acids and bases [5–7]. To assess the ligand capacities of the compounds under study on the basis of nonempirical calculations of their electronic structure, in this work we made use of Klopman's theoretical approach to the concept of hard and soft acids and bases [8]. According to Klopman, soft Lewis acids, such as platinum ion metals, interact with a potentially ambidentate ligand to coordinate the metal ion not to an atom bearing the highest negative charge but to a center having the greatest charge density on the highest occupied molecular orbital (HOMO). This orbital should have an energetically favorable high energy (in other words, a low molecular ionization energy). Such interaction is

Table 2. Bond lengths (*R*, Å) and bond angles (φ, deg) in thiourea and its derivatives

Bond	*R*	Angle	φ	Bond	*R*	Angle	φ
$\mathrm{SC(NH_2)_2}$				$\mathrm{SC(NHCH_2CH_2CH_3)(NHCOC_6H_5)}$			
$\mathrm{S{-}C}$	1.688	$\mathrm{N^1CN^2}$	116.032	$\mathrm{S{-}C^1}$	1.682	$\mathrm{SC^1N^1}$	123.458
$\mathrm{C{-}N}$	1.345			$\mathrm{C^1{-}N^1}$	1.342	$\mathrm{SC^1N^2}$	123.314
$\mathrm{SC[N(CH_3)_2]_2}$				$\mathrm{C^1{-}N^2}$	1.353	$\mathrm{N^1C^1N^2}$	113.227
$\mathrm{S{-}C^1}$	1.689	$\mathrm{SC^1N^1}$	122.081	$\mathrm{N^1{-}C^2}$	1.455	$\mathrm{C^1N^1C^2}$	126.250
$\mathrm{C^1{-}N^1}$	1.363	$\mathrm{SC^1N^2}$	122.114	$\mathrm{C^2{-}C^3}$	1.527	$\mathrm{C^1N^1H^1}$	117.418
$\mathrm{C^1{-}N^2}$	1.364	$\mathrm{C^1N^1C^2}$	122.336	$\mathrm{C^3{-}C^4}$	1.528	$\mathrm{C^2N^1H^1}$	115.740
$\mathrm{N^1{-}C^2}$	1.464	$\mathrm{C^1N^1C^3}$	120.912	$\mathrm{N^2{-}C^5}$	1.426	$\mathrm{N^1C^2C^3}$	113.245
$\mathrm{N^1{-}C^3}$	1.460	$\mathrm{C^2N^1C^3}$	114.128	$\mathrm{C^5{-}C^6}$	1.384	$\mathrm{C^2C^3C^4}$	111.796
$\mathrm{N^2{-}C^4}$	1.464	$\mathrm{C^1N^2C^4}$	122.247	$\mathrm{C^5{-}C^7}$	1.384	$\mathrm{C^1N^2H^2}$	116.994
$\mathrm{N^2{-}C^5}$	1.460	$\mathrm{C^1N^2C^5}$	120.701			$\mathrm{C^1N^2C^5}$	127.266
		$\mathrm{C^4N^2C^5}$	114.191			$\mathrm{C^5N^2H^2}$	114.829
$\mathrm{SC(NH_2)(CH_3)}$						$\mathrm{C^6C^5C^7}$	120.134
$\mathrm{S{-}C^1}$	1.661	$\mathrm{SC^1N}$	122.603	$\mathrm{SC(NHCH_2CH_2CH_3)(NHC_6H_5)}$			
$\mathrm{C^1{-}N}$	1.338	$\mathrm{SC^1C^2}$	122.448	$\mathrm{S{-}C^1}$	1.655	$\mathrm{SC^1N^1}$	124.181
$\mathrm{C^1{-}C^2}$	1.508	$\mathrm{N^1C^1C^2}$	114.926	$\mathrm{C^1{-}N^1}$	1.342	$\mathrm{SC^1N^2}$	125.375
$\mathrm{SC(NHNH_2)(NHCH_3)}$				$\mathrm{C^1{-}N^1}$	1.390	$\mathrm{N^1C^1N^2}$	110.369
$\mathrm{S{-}C^1}$	1.687	$\mathrm{SC^1N^1}$	122.402	$\mathrm{N^1{-}C^2}$	1.455	$\mathrm{C^1N^1C^2}$	125.860
$\mathrm{C^1{-}N^1}$	1.354	$\mathrm{SC^1N^2}$	123.301	$\mathrm{C^2{-}C^3}$	1.528	$\mathrm{N^1C^2C^3}$	113.328
$\mathrm{N^1{-}N^3}$	1.387	$\mathrm{C^1N^1N^3}$	124.756	$\mathrm{C^3{-}C^4}$	1.528	$\mathrm{C^2C^3C^4}$	111.777
$\mathrm{C^1{-}N^2}$	1.345	$\mathrm{C^1N^2C^2}$	124.260	$\mathrm{N^2{-}C^5}$	1.391	$\mathrm{C^1N^1H^1}$	117.003
$\mathrm{N^2{-}C^2}$	1.456	$\mathrm{N^1C^1N^2}$	114.297	$\mathrm{C^5{-}O}$	1.186	$\mathrm{H^1N^1C^2}$	115.793
$\mathrm{SC(NHCH_2CH_2CH_3)(NHCH_2CH{=}CH_2)}$				$\mathrm{C^5{-}C^6}$	1.505	$\mathrm{C^1N^2H^2}$	114.571
$\mathrm{S{-}C^1}$	1.690	$\mathrm{SC^1N^1}$	123.059	$\mathrm{C^6{-}C^7}$	1.390	$\mathrm{C^1N^2C^5}$	129.704
$\mathrm{C^1{-}N^1}$	1.342	$\mathrm{SC^1N^2}$	122.983	$\mathrm{C^6{-}C^8}$	1.390	$\mathrm{C^5N^2H^2}$	115.126
$\mathrm{C^1{-}N^2}$	1.345	$\mathrm{N^1C^1N^2}$	113.958			$\mathrm{N^2C^5O}$	124.592
$\mathrm{N^1{-}C^2}$	1.455	$\mathrm{C^1N^1C^2}$	126.394			$\mathrm{C^6C^5O}$	121.496
$\mathrm{N^2{-}C^5}$	1.456	$\mathrm{C^1N^1H^1}$	117.152			$\mathrm{N^2C^5C^6}$	113.913
$\mathrm{C^2{-}C^3}$	1.527	$\mathrm{C^2N^1H^1}$	115.764			$\mathrm{C^5C^6C^7}$	123.865
$\mathrm{C^5{-}C^6}$	1.505	$\mathrm{C^1N^2C^5}$	126.255			$\mathrm{C^5C^6C^8}$	116.825
$\mathrm{C^3{-}C^4}$	1.528	$\mathrm{C^1N^2H^2}$	117.083			$\mathrm{C^7C^6C^8}$	119.285
$\mathrm{C^6{-}C^7}$	1.318	$\mathrm{C^5N^2H^2}$	115.017				
		$\mathrm{N^1C^2C^3}$	113.243				
		$\mathrm{C^2C^3C^4}$	111.853				
		$\mathrm{N^2C^5C^6}$	112.388				
		$\mathrm{C^5C^6C^7}$	124.116				

termed orbital-controlled. Hard Lewis acids will coordinate to the most negatively charged atom in the ligand, i.e. a charge-controlled reaction will take place. Our calculations for thiourea (Tables 1 and 2, Fig. 1), as well as earlier semiempirical calculations [2], showed that the two highest occupied MOs with close energies (E_1 –8.509 and E_2 –8.552 eV) are localized mainly on sulfur $3p_\pi$ AOs. The HOMO has a small contribution of the $2p_z$ orbitals of carbon and nitrogen atoms, perpendicular to the SCNN plane, i.e., it relates to the system of conjugated bonds. The second highest occupied MO includes a small contribution of the $2p_y$ AOs of carbon atoms, coplanar to the S–C bond. It is these two highest occupied MOs, which must be responsible for the fact that in orbital-controlled reactions acceptors would coordinate to the sulfur atom at an angle of about 90° to the S–C bond. In the thiourea molecule the $2p_\pi$ AOs of nitrogen atoms are mainly localized on a deeper MO (E_3 –11.984 eV), and, therefore, these atoms would be hard bases with respect to soft Lewis acids, such as platinum metal ions. The negative charge on the thiourea sulfur atom (–0.35 *e*) ranks much below the charge on nitrogen (–0.91 *e*), but the terminal position of the sulfur atom, along with the energy characteristics of HOMO, may make electron acceptor to prefer to approach this

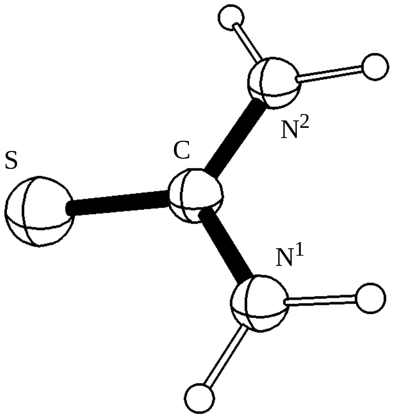

Fig. 1. Molecular geometry of thiourea $SC(NH_2)_2$.

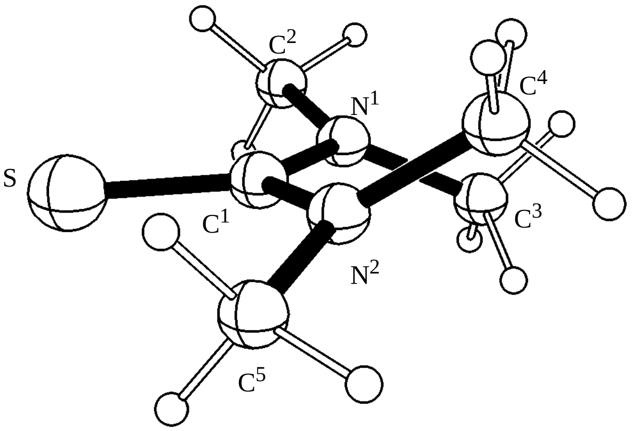

Fig. 2. Molecular geometry of tetramethylthiourea $SC[N(CH_3)_2][N(CH_3)_2]$.

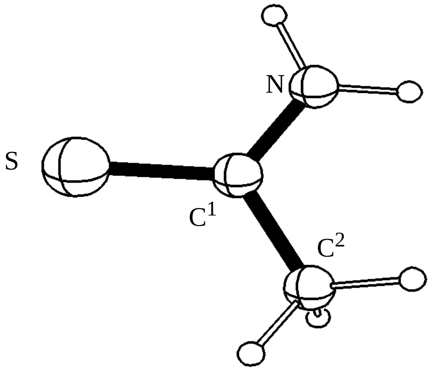

Fig. 3. Molecular geometry of thioacetamide $SC(NH_2)(CH_3)$.

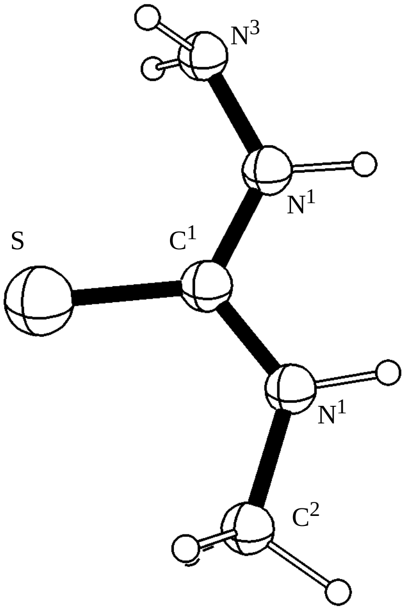

Fig. 4. Molecular geometry of 4-methylthiosemicarbazide $SC(NHNH_2)(NHCH_3)$.

atom. The above assumptions are confirmed by the X-ray diffraction data for the Pd(II) thiourea complex [9], according to which the S–C bonds are at an angle of 110° to the plane of the PdS_4 coordination polyhedron.

As follows from the calculations with full geometry optimization, the coplanarity of the bond system in the tetramethylthiourea molecule is actually disturbed (Tables 1 and 2, Fig. 2). The sum of bond angles at the vertex of the pyramid formed by one nitrogen atom and three its surrounding carbon atoms is ~357°, which corresponds to data of [3]. However, the height of this pyramid (h_N) is as small as 0.14 (HF) or 0.19 Å (DFT) instead of 0.75 Å, as indicated in [3]. The carbon atoms of the methyl groups in the base of the pyramid deviate from the plane of the S=C bond. As a result, the C_{2v} symmetry in thiourea is lowered to C_2 in tetramethylthiourea. Such geometry of $SC[N(CH_3)_2]_2$ sharply weakens π conjugation, with the result that C–N bonds in this molecule are longer [1.363 (HF) and 1.379 Å (DFT)] than in thiourea [1.345 (HF) and 1.358 Å (DFT)]. As noted above, the MO in thiourea, containg nitrogen p_z orbitals, has a rather low energy (E_3 –11.984 eV). The similar MO in tetramethylthiourea is also contributed by other AOs which have higher energies compared to nitrogen; as a result, the gap between this MO (E_3 –9.831 eV) and the two highest occupied MOs (E_1 –8.122 and E_2 –8.383 eV) localized predominantly on sulfur $3p_\pi$ AOs is decreased. In terms of the concept of hard and soft acids and bases, this suggests that nitrogen atoms

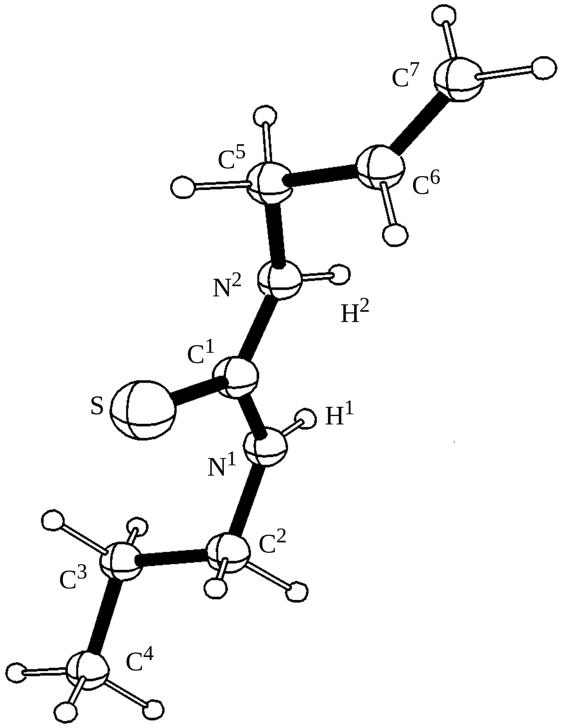

Fig. 5. Molecular geometry of *N*-propyl-*N'*-allylthiourea $SC(NHCH_2CH_2CH_3)(NHCH_2CH=CH_2)$.

in $SC[N(CH_3)_2]_2$ are less hard bases than similar atoms in $SC(NH_2)_2$ and thus more reactive toward soft Lewis acids.

According to the Hartree–Fock calculations, the positive inductive effect of the methyl group in thioacetamide mainly affects the charge on the carbon atom bound to sulfur. This charge has a lower positive value (0.31 *e*) in this compound compared to thiourea (0.61 *e*) and tetramethylthiourea (0.63 *e*) (Tables 1 and 2, Fig. 3). In the fully optimized geometry of thioacetamide the $SC(NH_2)$ fragment is planar. The S–C (1.661 Å) and C–N (1.338 Å) distances proved to be shorter than in thiourea, which is connected to stronger conjugation involving only one CNH_2 group. The HOMO (E_1 –8.645 eV) is a π-bonding orbital localized predominantly on sulfur $3p_y$ AO with an admixture of carbon $2p_y$ AO. The second MO (E_2 –8.922) is responsible for the S=C–N conjugation system, since it consists basically of sulfur $3p_z$ AO with admixtures of carbon and nitrogen $2p_z$ AOs. As in thiourea, the two highest occupied MOs in thioacetamide make the ligand to coordinate to electron acceptor by the sulfur atom in a direction perpendicular to the S–C bond. The $2p_z$ AO of the nitrogen atom in $SC(NH_2)(CH_3)$ can hardly interact with a soft Lewis acid, as it is localized on an even deeper MO (E_4 –13.902 eV) that the corresponding orbitals in thiourea, and thus it is the hardest Lewis basis in the series of compounds under consideration.

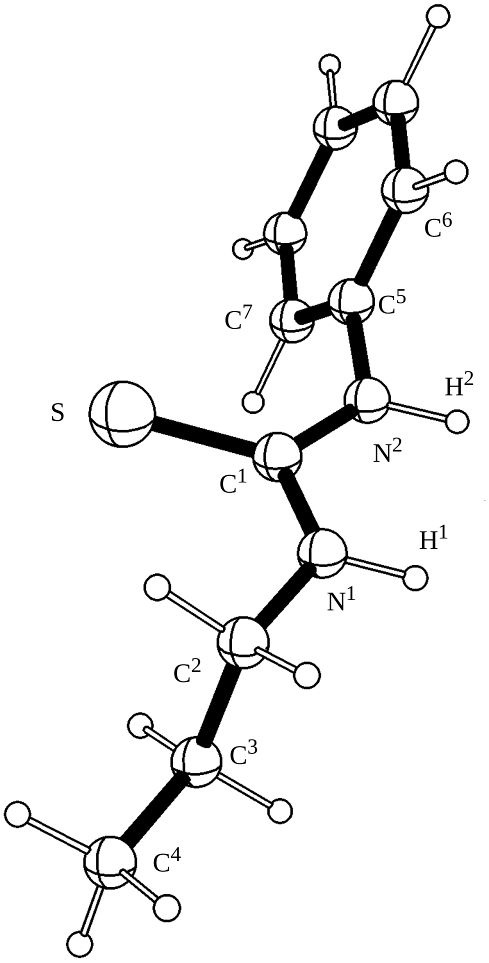

Fig. 6. Molecular geometry of *N*-propyl-*N'*-phenylthiourea $SC(NHCH_2CH_2CH_3)(NHC_6H_5)$.

According to the Hartree–Fock calculations, in 4-methylthiosemicarbazide $SC(NHNH_2)(NHCH_3)$ the charge on the sulfur atom (–0.35 *e*) is the same as in thiourea (Tables 1 and 2, Fig. 4). However, this density is little more displaced to NHR fragments from the central carbon atom to create a little higher positive charge on the central atom (0.67 *e*) in $SC(NHNH_2)(NHCH_3)$ than in $SC(NH_2)_2$. The highest negative charge (–0.89 *e*), almost equal to the charge of nitrogen in thiourea (–0.91 *e*), is concentrated on the N^2 atom of the $NHCH_3$ group. The $SC^1N^1N^2N^3$ fragment is almost planar, but the N^3 atom of the terminal NH_2 group forms pyramidal bonds with its surrounding hydrogen atoms and the N^1 atom (h_N 0.32 Å). The negative charge on the N^3 atom is –0.55 *e*. The mutual arrangement of the two close-in-energy π-type highest occupied MOs (E_1 –8.617 and E_2 –8.645 eV) is reverse compared with that in

$SC(NH_2)_2$: The HOMO consists of sulfur $3p_y$ AO with an admixture of the carbon $2p_y$ AO oriented perpendicularly to the S–C bond, and the second MO is sulfur $3p_z$ AO involved in conjugation with the $2p_z$ AOs of carbon and nearest nitrogen atoms. Nitrogen $2p_\pi$ orbitals of the central planar fragment are localized on a deeper MO (E_3 –10.955 eV). The lone electron pair of the pyramidal N^3 atom of the terminal NH_2 group is even lower in energy (E_4 –11.752 eV). Thus, the calculation results show that this molecular system, too, prefer to coordinate to a soft Lewis acid by its sulfur atom at an angle to the forming metal–sulfur bond.

Earlier we performed for the last three compounds of the series under consideration Hartree–Fock calculations in the 6–31G basis with polarizing *d* functions on all the atoms, except for hydrogen [HF(b)]. In *N*-propyl-*N'*-allylthiourea $SC(NHCH_2–CH_2CH_3)\cdot(NHCH_2CH=CH_2)$ the charge distribution in the central fragment SCNN' in principle does not differ from that in thiourea [Table 1, HF(b)]. The pyramids at nitrogen atoms proved to be very low: 0.06 and 0.09 Å for the propyl (N^1) and allyl (N^2) nitrogen atoms, respectively. The optimized S–C (1.690 Å) and C–N (1.342 and 1.345 Å) bond lengths are slightly larger than in thiourea (1.684 and 1.337 Å, respectively). The two close-in-energy highest occupied MOs (E_1 –8.381 and E_2 –8.441 eV) are mostly localized on sulfur $3p_\pi$ AOs, but they include an admixture of $2p_\pi$ orbitals of carbon and nitrogen atoms of the central thiourea fragment. The MO with E_3 –10.098 eV relates to the π system of the allyl group. The MO consisting basically of nitrogen $2p_z$ orbitals includes a certain contribution of AOs of the $C=CH_2$ group is higher in energy (E_4 –10.660 eV) than the MO contributed by nitrogen $2p_\pi$ orbitals in thiourea. Thus, nitrogen atoms in *N*-propyl-*N'*-allylthiourea can be considered as less hard bases than similar atoms in thiourea.

The electron density distribution in *N*-propyl-*N'*-phenylthiourea $SC(NHCH_2–CH_2CH_3)(NHC_6H_5)$ is close to that in *N*-propyl-*N'*-allylthiourea, but, by the results of full optimization of molecular geometry, the S–C bond proved a little shorter (1.682 Å), and the C–N^2(phenyl) bond longer (1.353 Å) than the C–N^2(allyl) bond in the previous compound (Tables 1 and 2, Fig. 6). The two highest occupied MOs (E_1 –8.187 and E_2 –8.356 eV) are basically sulfur $3p_\pi$ AOs with small admixtures of $2p_\pi$ AOs of the central carbon atom and the nitrogen atoms. Nitrogen $2p_\pi$ AOs are localized on the MO with E_5 –10.960 eV, above which there are two phenyl MOs (E_3 –9.096 and E_4 –9.238 eV).

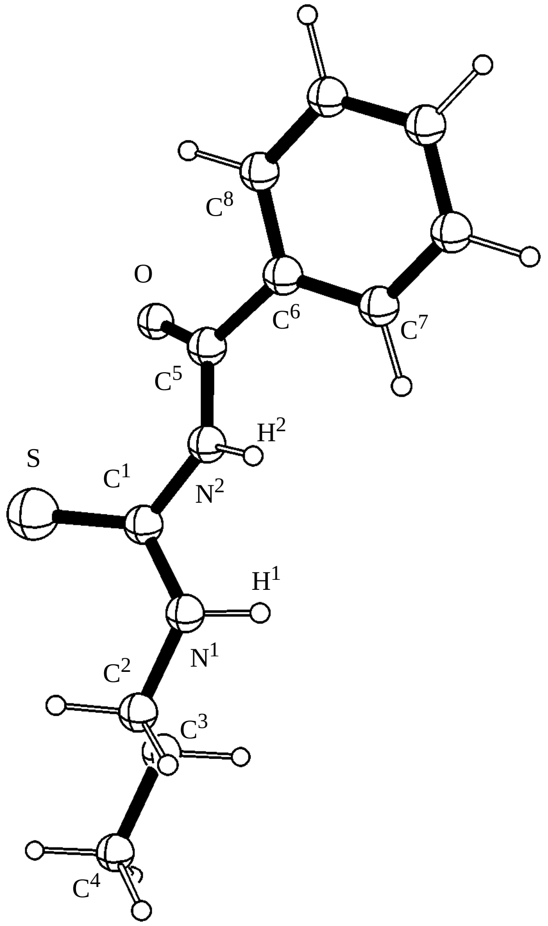

Fig. 7. Molecular geometry of *N*-propyl-*N'*-benzoylthiourea $SC(NHCH_2CH_2CH_3)(NHCOC_6H_5)$.

N-propyl-*N'*-benzoylthiourea $SC(NHCH_2–CH_2\cdot CH_3)(NHCOC_6H_5)$ differs from the above-considered *N,N'*-derivatives of thiourea by a smaller electron density on the sulfur atom (–0.25 e), an even shorter S–C distance (1.655 Å), and an elongated C–N^2(benzoyl) bond (1.390 Å) (Tables 1 and 2, and Fig. 7). The two highest MOs (E_1 –8.470 and E_2 –8.696 eV) are also sulfur $3p_\pi$ AOs with small admixtures of $2p_\pi$ AOs of the central carbon atom and the nitrogen atoms. The MOs with E_3 –9.570 and E_4 –9.706 eV are localized on the phenyl group. Nitrogen $2p_\pi$ AOs are involved in a low-energy MO (E_5 –11.208 eV), predetermining hardness of these atoms in donor–acceptor reactions.

Note that for three latter compounds, while having an energetically favorable HOMO localized on sulfur $3p_y$ AOs and arranged in the plane of the central fragment perpendicularly to the S–C bond, are more difficult to approach electron acceptor because of the branched substituents on nitrogen atoms (Figs. 5–7). In this case, an approach perpendicular to the plane of the central fragment of the ligand and involving sulfur $3p_z$ AO and nitrogen $2p_z$ AOs is possible.

Thus, our research showed that thioamides and their *N*- and *N,N*'-derivatives prefer to coordinate to platinum ion metals by the sulfur atom (soft Lewis basis) at an angle to the sulfur–carbon bond. Nitrogen atoms in these compounds are hard Lewis bases. However, the Lewis basicity of nitrogen atoms in certain thioamide compounds can be increased compared to thiourea. In this connection search for such potentially polydentate ligands and sorbents on their basis, for extraction of platinum metals from technological solutions seems to be promising.

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