ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 7, pp. 1263–1267. © Pleiades Publishing, Ltd., 2007.
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Quantum-Chemical Study of the Reaction of Pent-4-en-2-yn-1-ol with Copper, Zinc, and Nickel Sulfides

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Received February 6, 2007

Abstract — Complexes of metal sulfides MS (M = Cu, Zn, Ni) with pent-4-en-2-yn-1-ol modeling dimethyl(isopropenylethynyl)carbinol, a potent floating agent for benefication of nonferrous metal ores, were calculated by the B3LYP density functional theory method with the 6-31G** basis set. The adsorption mechanisms of vinylacetylenic and aliphatic alcohols were shown to vary depending on the nature of the metal sulfide. This fact can be taken into account on the flotation of mixed ores for selective metal extraction.
DOI: 10.1134/S1070363207070195

The use of dimethyl(isopropenylethynyl)carbinol (**I**) in the flotation of copper sulfide ores commonly results in a much more efficient copper extraction compared with aliphatic alcohols [1]. In the present research we made an attempt to explain this phenomenon and to predict, by quantum-chemical calculations, the behavior of vinylacetylenic alcohols in the flotation of polymetal ores.

It is known that the flotation properties of substances are mainly determined by the ability of the agents to form complexes with metal-containing molecules in the floated ore [2]. This reaction results in hydrophobization of the inorganic surface, which is prerequisite for successful extraction into the foam concentrate. However, special research by quantum-chemical methods which could give insight into the mechanism of these processes are almost lacking. A lot of papers have been published on quantum-chemical simulation of catalytic complex formation between metal catalysts and organic molecules, such as acetylene or ethylene [3–12], as well as chemical transformations involving metal ions [13–16]. The stage of complex formation, which plays an important role in reactions of organometallic compounds, too, has been studied by quntum-chemical methods [17–20].

Quantum-chemical calculations [3, 4] showed that the stabilization of metal–olefin π complexes is determined by the donor–acceptor transfer of the electron density of the olefin π MO on a vacant metal *sp* orbital (direct donation) and by the reverse dative electron transfer of an occupied metal *d* orbital on a vacant olefin π* MO (back donation). Acetylene (A) in π complexes can donate two pairs of π electrons to symmetry-appropriate metal orbitals to form two M←A donor–acceptor bonds and accept two pairs of *d* electrons from symmetry-appropriate metal *d* orbitals to form two M→A dative bonds [21].

In all alcoholic foaming agents, the center of metal sulfide adsorption is the hydroxyl oxygen atom. Vinylacetylenic alcohols can additionally coordinate metals by C≡C and C=C π orbitals.

The aim of the present work was to calculate and compare intermolecular interactions to gain insight into the difference in the mechanisms of adsorption of compound **I** and aliphatic alcohols and to correlate it with the nature of the metal sulfide. As reference we chose the simplest of vinylacetylenic alcohols $HOCH_2C–CCH=CH_2$ (pent-4-en-2-yn-1-ol) (**II**). Schematic structures of the calculated complexes of molecule **II** with metal sulfides MS (M = Cu, Zn, Ni) are given in Fig. 1. We focused on interactions of metal sulfide cations with all electronically unsaturated centers in molecule **II**: hydroxyl oxygen and C≡C bond in $\mathbf{C_1}$, C≡C π system in C_2, C=C π system in $\mathbf{C_3}$, and hydroxyl oxygen in $\mathbf{C_4}$. Complexes $\mathbf{C_4}$ (because of the similarity of alcohol and water hydroxyls) characterize, to a certain extent, the tendency of sulfides to hydrophilization.

The calculations were performed by the RHF ab initio method for systems with closed shells and by the ROHF method for copper-containing molecules

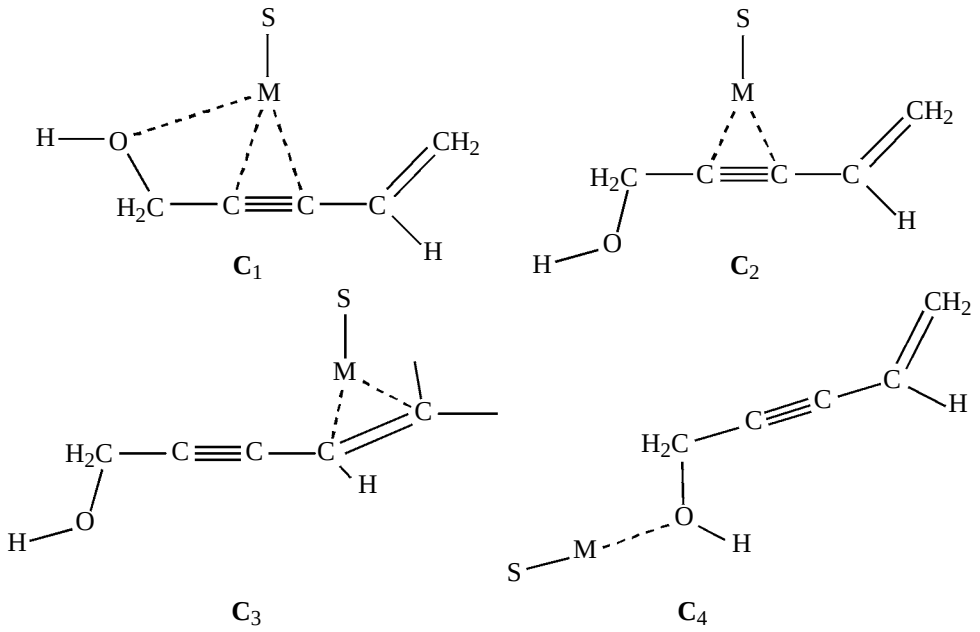

Fig. 1. Schematic structures of pent-4-en-2-yn-1-ol with metal sulfides MS.

Table 1. Energy characteristics, atomic charges, and bond lengths in metal sulfides MS

Parameters	CuS	ZnS	NiS
E_{tot}, au	–2038.229	–2177.084	–1906.043
ZPE, au	0.0012	0.0011	0.0013
R(M–S), Å	1.968	2.027	1.926
$R(M–S)_{exp}$, Å	2.051 [a]	–	–
q(M)	0.339	0.434	0.327
q(S)	–0.339	–0.434	–0.327
μ, D	4.723	5.413	4.439
ε(HOMO), au	–0.192 (SOMO) [b]	–0.225	–0.204
ε(LUMO), eV	–0.112	–0.151	–0.141
P(M–S)	1.778	1.880	2.118

[a] Estimated interatomic distances taken from [25]. [b] (SOMO) Singly occupied MO.

and complexes in ground doublet states using the 6-31G(*d,p*) [22] basis set and B3LYP hybrid density functional [23, 24] [B3LYP/6-31G(*d,p*)]. The same method was used to calculate force constant matrices for sulfides MS, vinylacetylenic alcohol, and complexes in the energy minima on potential energy surfaces (PES), lacking imaginary vibration frequencies. The calculated zero-point vibration energies (ZPE) were taken into account in the determination of the stabilization energies of intermolecular complexes. All calculations were performed using the GAMESS program [25] adapted for PC [26].

The principal calculated characteristics of molecules involved in complex formation are listed in Tables 1 and 2.

In all the metal sulfides (Table 1), the M–S bond length, ionic charges, and dipole moments μ increase in the order NiS < CuS < ZnS, which corresponds to the positions of the metals in the Periodic Table. The nature of HOMO and LUMO in the sulfides, too, is determined by their electronic structure: The HOMO in NiS is a doubly occupied sulfur *p* AO strongly contributed by nickel *d* AOs, in CuS this is a singly occupied [p_S + d_{Cu}] orbital (with a smaller contribution of copper *d* AOs), and ZnS, a virtually pure sulfur *p* AO with a small admixture of zinc *d* AOs, degenerate with the second sulfur *p* AO. The LUMO is a mixture of the [d_{Ni} + p_S] orbital in NiS and antibonding σ*(M–S) orbitals in CuS and ZnS. The stronger atomic interaction in NiS compared to CuS and ZnS is nicely fitted by the calculated bond orders P(M–S), which measure this bond strength (Table 1).

According to Table 2, the energetically close conformations a, b, and c in molecule **II** differ considerably in the arrangement of the O atom ($OC^5C^2C^1$ torsion angle) and the hydroxyl hydrogen (HOC^5C^4 torsion angle). The HOMO in molecule **II** in all the conformations is a bonding π_z orbital almost equally contributed by the two unsaturated bonds, while the LUMO is antibonding π_z^*-MO.

The calculated characteristics of the intermolecular complexes (Table 3) allow us to analyze how sub-

Table 2. Calculated molecular characteristics of pent-4-en-2-yn-1-ol in various conformations [a]

Parameters	a	b	c
E_{tot}, au	–269.111	–269.108	–269.111
ZPE, au	0.0951	0.0946	0.0950
$R(C_1{=}C_2)$, Å	1.342	1.341	1.342
$R(C_2{-}C_3)$, Å	1.424	1.423	1.424
$R(C_3{\equiv}C_4)$, Å	1.214	1.213	1.214
$R(C_4{-}C_5)$, Å	1.466	1.460	1.466
$R(C_5{-}O)$, Å	1.424	1.425	1.424
R(O–H), Å	0.967	0.967	0.967
$\angle OC_5C_2C_1$	–29.0	180.0	–142.1
$\angle HOC_5C_4$	–53.8	180.0	53.8
$q(C_1)$	–0.209	–0.213	–0.208
$q(C_2)$	–0.152	–0.150	–0.153
$q(C_3)$	0.036	0.032	0.037
$q(C_4)$	–0.011	0.043	–0.014
q(O)	–0.522	–0.523	–0.522
μ, D	1.626	1.698	1.676
ε(HOMO), eV	–0.233	–0.226	–0.233
ε(LUMO), eV	–0.025	–0.017	–0.026

[a] The carbon atoms are numbered beginning with the C=C bond.

strate parameters change on complex formulation and compare the structures of complexes with different metal sulfides.

The differences in the electronic structure of metal cations strongly affect the complex formation of MS with molecule **II**. The following structural features can be mentioned. In complexes $\mathbf{C_1}$ with CuS and NiS, coordination primarily involves the metal cation and C≡C bond, which is reflects upon the $R(M\cdots C^3)$ and $R(M\cdots C^4)$ distances (Table 3). The strongest effect on the C≡C bond is from Ni^{2+}, as evidenced by the fact that its elongation (by 0.081 Å) compared with alcohol **II** in the nickel complex is stronger than in the copper complex (0.042 A). The C≡C elongation in complex $\mathbf{C_1}$ with ZnS is as small as 0.003 Å, and the $R(Zn\cdots C^3)$ and $R(Zn\cdots C^4)$ distances are much longer than in the CuS and NiS complexes. However, Zn^{2+} in this complex stronger interacts with the hydroxyl oxygen, as readily seen in Fig. 2a. At the same time, in complex $\mathbf{C_2}$ (Fig. 1), where the hydroxy group in molecule **II** is turned by 180° (conformation b), the interaction of Zn^{2+} with the acetylenic π system is stronger (this bond length increases by 0.027 Å) but weaker than in complexes $\mathbf{C_2}$ with CuS and NiS. The latter fact is explained by the presence in the copper and nickel cations of partly occupied d orbitals whose interaction with π orbitals is more favorable.

In complexes $\mathbf{C_3}$ with copper and zinc sulfides, the coordination interaction of the metal cations with π orbitals of the C=C bond is slightly weaker than with those of the C≡C bond. This is evidenced by the stabilization energies (E_{stab}) of these complexes (Table 3), calculated relative to the energy levels of individual molecules with ZPE corrections. Unlike what is observed in the CuS and ZnS complexes, the nickel cation interacts with π orbitals of the C≡C and C=C bonds (Fig. 2b), so that the stabilization energy of complex $\mathbf{C_3}$ with NiS is close those of complexes $\mathbf{C_1}$ and $\mathbf{C_2}$, where the interaction with the C≡C bond is prevailing.

The E_{stab} of complex $\mathbf{C_4}$ with NiS, in which Ni^{2+} is coordinated to the hydroxyl oxygen in molecule **II**, is almost half those of the other Ni complexes. This is explained by a weak interaction of nickel *d* orbitals with oxygen lone electron pairs. According to the calculations, complex $\mathbf{C_4}$ with CuS should also be much less stable than complexes $\mathbf{C_1}$–$\mathbf{C_3}$. At the same time, the stabilizing effect of the interaction of Zn^{2+} with oxygen lone electron pairs on complex $\mathbf{C_4}$ is

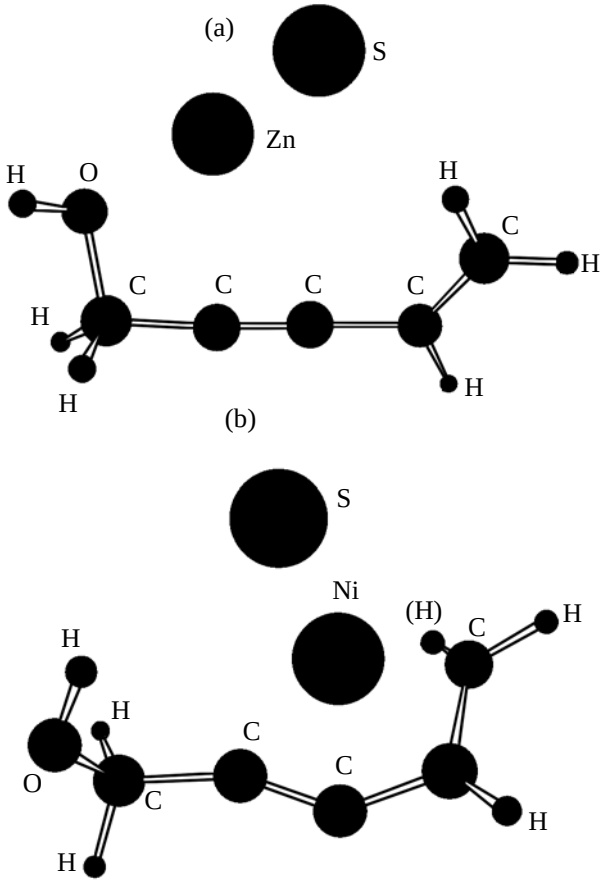

Fig. 2. Spatial arrangement of complexes (a) $\mathbf{C_1}$ with ZnS and (b) $\mathbf{C_3}$ with NiS.

Table 3. Geometric, energetic, and electronic parameters of complexes **II**–MS, calculated in the B3LYP/6-31G(*d,p*) approximation

Parameters	Complexes with CuS				Complexes with ZnS				Complexes with NiS			
	C$_1$	**C**$_2$	**C**$_3$	**C**$_4$	**C**$_1$	**C**$_2$	**C**$_3$	**C**$_4$	**C**$_1$	**C**$_2$	**C**$_3$	**C**$_4$
E_{tot}, au	–2307.436	–2307.432	–2307.423	–2307.405	–2307.405	–2446.246	–2446.243	–2446.250	–2175.287	–2175.282	–2175.288	–2175.227
ZPE, au	0.0974	0.0968	0.0978	0.0989	0.0976	0.0962	0.0971	0.0985	0.0981	0.0975	0.0987	0.0989
E_{stab}, kcal mol^{-1}	–59.471	–58.951	–52.746	–38.618	–35.360	–34.158	–31.582	–32.989	–82.406	–81.671	–82.392	–44.333
R(M···C$_1$)	3.564	3.430	1.941	–	3.926	3.361	2.073	–	3.618	3.591	1.965	–
R(M···C$_2$)	3.112	3.031	1.964	–	3.882	3.098	2.180	–	3.088	3.063	1.991	–
R(M···C$_3$)	1.946	1.904	2.820	–	2.998	2.111	2.919	–	1.831	1.811	1.984	–
R(M···C$_4$)	1.883	1.892	3.804	–	2.695	2.048	3.881	–	1.793	1.802	1.9726	–
R(M···O)	3.073	–	–	1.896	1.985	–	–	1.947	3.273	–	–	1.846
R(M–S)	2.056	2.052	2.072	2.006	2.038	2.021	2.025	2.021	1.961	1.961	1.987	1.958
R(C$_3$≡C$_4$)	1.256	1.258	1.213	1.213	1.217	1.240	1.214	1.214	1.295	1.299	1.265	1.214
R(C$_2$–C$_3$)	1.437	1.436	1.425	1.423	1.424	1.431	1.413	1.423	1.439	1.437	1.405	1.423
R(C$_1$=C$_2$)	1.339	1.339	1.402	1.341	1.342	1.339	1.391	1.342	1.340	1.340	1.424	1.341
R(C$_5$–O)	1.412	1.420	1.422	1.471	1.474	1.417	1.419	1.479	1.411	1.421	1.410	1.483
∠OC^{5}C^{2}C^1	44.7	180.0	179.7	–106.4	28.5	–179.9	165.8	–102.9	22.4	–162.2	–94.4	–110.4
∠HOC^{5}C^4	–48.5	180.0	178.6	45.8	–155.0	180.0	174.2	43.9	–50.7	179.4	54.3	48.8
q(M)	0.395	0.422	0.467	0.294	0.403	0.365	0.397	0.347	0.388	0.390	0.402	0.261
q(S)	–0.377	–0.377	–0.358	–0.431	–0.589	–0.503	–0.485	–0.521	–0.376	–0.363	–0.391	–0.443
q(C$_1$)	–0.235	–0.240	–0.365	–0.195	–0.197	–0.225	–0.368	–0.193	–0.218	–0.220	–0.349	–0.194
q(C$_2$)	–0.072	–0.081	–0.410	–0.156	–0.172	–0.124	–0.379	–0.154	–0.074	–0.078	–0.169	–0.156
q(C$_3$)	–0.151	–0.031	0.134	0.015	0.159	0.090	0.172	0.043	–0.114	–0.058	–0.054	0.018
q(C$_4$)	–0.045	–0.140	0.059	0.028	–0.117	–0.155	0.083	0.008	–0.085	–0.105	–0.018	0.028
q(O)	–0.521	–0.521	–0.519	–0.571	–0.588	–0.516	–0.517	–0.589	–0.521	–0.527	–0.515	–0.559
Σq(M, S)	0.018	0.045	0.109	–0.137	–0.186	–0.138	–0.088	–0.174	0.012	0.027	0.011	–0.182

almost equal to that exerted by the interaction of Zn^{2+} with ethylenic and acetylenic π orbitals.

A characteristic feature of the ZnS complexes, as well as complexes **C$_4$** with all the metal sulfides is that the electron density in them is transferred from alcohol **II** to MS, reverse to the situation in complexes **C$_1$**–**C$_3$** with CuS and NiS. Evidence for this conclusion is provided by the total partial atomic charges on M and S in the complexes (Σq[M, S], Table 3). In complexes **C$_1$**–**C$_3$** with CuS and NiS, both direct electron donation from occupied π orbitals of the C=C and C–C bonds of molecule **II** to vacant *sp* orbitals of the metal cation and a stronger back electron donation from metal *d* orbitals to π* orbitals of the unsaturated bonds of **II**, as evidenced by the Malliken population analysis of localized MOs of the interacting molecules. In complexes **C$_1$**–**C$_3$** with ZnS, the back electron donatiton is much weaker because of the weaker interaction of fully occupied zinc *d* orbitals with untibonding π* orbitals of the vinylacetylenic system.

Thus, the calculations showed that compound **I** can be adsorbed on the sulfide cation not only by the OH group, but also by the unsaturated bonds and, consequently, this compound can better extract copper, zinc, and nickel than aliphatic alcohols, which is consistent with experimental data [1]. Therewith, according to the E_{stab} values of the complexes, nickel and copper should be extracted more effectively, which can be taken into account for their selective extraction in the flotation of mixed ores.

To conclude, the stabilization energies of the complexes, obtained in the present work, are appropriate for comparative analysis only, since for more correct values once should account for basis set superposition errors [28].

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