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Synthesis and structures of nickel(II) complexes with thioether-containing β-aminovinyl ketones

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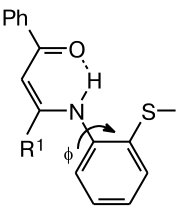
New ligands, *viz.*, thioether-containing β-aminovinyl ketones, and Ni^{II} complexes with these ligands were synthesized. The compounds were characterized by X-ray diffraction analysis, EXAFS, NMR, and IR spectroscopy, and magnetochemistry.

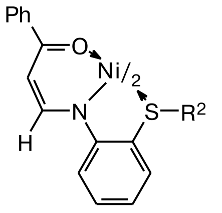
Key words: nickel-containing enzymes, β-aminovinyl ketones, metal chelates, X-ray diffraction analysis, EXAFS, NMR spectroscopy, magnetochemistry.

In biological systems, not only the deprotonated thiolate groups of cysteine but also the sulfide fragments of methionine can serve as S-donor centers.**[1—3]** Modeling of active sites of some important nickel-containing enzymes by simple complexes gave impetus to the development of the chemistry of nickel chelates with N,S- and N,O,S-ligands.**[4—7]**

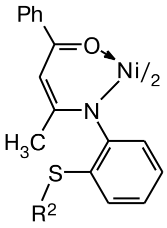
With the aim of studying the coordination ability of the sulfide group and its influence on the structures of metal chelates as well as for the purpose of modeling active sites of nickel-containing proteins, we synthesized new ligands **1** and Ni^{II} complexes **2** and **3** containing these ligands.



1a—d



2a,b



3a,b

φ is the degree of noncoplanarity.

	1a	1b	1c	1d	2a	2b	3a	3b
R^1	H	H	Me	Me				
R^2	Me	Ph	Me	Ph	Me	Ph	Me	Ph

Results and Discussion

The Claisen reaction of acetophenone with ethyl formate afforded a sodium salt of β-hydroxymethyleneacetophenone, which reacted with hydrochlorides of the corresponding amines in an aqueous medium to give β-aminovinyl ketones **1a,b**. Azomethines **1c,d** were synthesized by the reactions of benzoylacetone with the corresponding amines in toluene in the presence of catalytic amounts of toluenesulfonic acid.

For β-aminovinyl ketones **1a,b**, the ketamine form is more preferable than the imine-enol form, which is confirmed by the IR and ^{1}H NMR spectroscopic data. The IR spectra have absorption bands in the region of 1660—1579 cm^{-1}, which is undoubtedly associated with the involvement of the double bonds under consideration in conjugation. It is difficult to choose between two tautomeric forms based on the IR spectra. The ^{1}H NMR spectra show doublets of doublets for the α-methine proton at δ 7—8 and a doublet for the proton of the NH group at δ 12—13 with $^3J = 12$ Hz. The above-mentioned signals are indicative of the presence of the ketamine form of compounds **1a,b** in solutions. The replacement of the H atom in β-aminovinyl ketones by the Me group leads to substantial changes in the ^{1}H NMR spectra. Thus, the doublet for the proton of the NH group is transformed

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into a singlet and the spectra contain no doublets of doublets for the α-methine proton at δ 7—8. Such ^{1}H NMR spectral patterns and the data from IR spectroscopy did not allow us to unambiguously establish the tautomeric form of α-methyl-substituted β-aminovinyl ketones **1c,d**.

The *ab initio* quantum-chemical calculations[8] of the molecular structures of ligands **1** demonstrated that the ketamine form is more favorable for these ligands than the imine-enol form regardless of the nature of substituents. The conformational features of β-aminovinyl ketones **1**, in particular, the degree of noncoplanarity, are associated primarily with steric interactions and depend substantially on the nature of the substituent R^1 (H, CH_3) in the H-chelate ring. Thus, the following theoretical noncoplanarity angles were obtained: $\phi = 1°$ (**1a,b**) and 70° (**1c,d**) for β-aminovinyl ketones; $\phi = 1°$ (R^1 = H) and 69° (R^1 = Me) for the OR^2 analog. Based on the results of theoretical calculations,[8] planar structures were predicted for the ligands with R = H, whereas such structures are sterically forbidden for R = Me.

Nickel(II) chelates were synthesized by the reactions of the corresponding β-aminovinyl ketones **1** with nickel(II) acetate. According to the results of elemental analysis, the compositions of the complexes thus prepared correspond to the formula NiL_2.

The complexes prepared from aminoketones **1a,b** are paramagnetic (μ_{eff} = 2.9—3.14 μB) due to which they are substantially different from the known diamagnetic chelate complexes with β-aminovinyl ketones containing the *N*-aryl substituents.[9,10] The coordination units in the latter complexes are planar. As follows from the magnetochemical measurements, these complexes can have octahedral or tetrahedral structures. The results of X-ray diffraction analysis of the metal chelate prepared from aminoketone **1b** demonstrated that this compound has distorted *cis*-octahedral structure **2b** (Fig. 1). The Ni(1)—S(1) distances (2.4634(9) and 2.4723(9) Å) are somewhat longer that those in the thioether nickel complexes studied previously.[11—14]

The ligands form two virtually coplanar mutually orthogonal planes. Two five-membered and two six-membered metallocycles are folded along the N(1)...S(1) and N(1)...O(1) lines (the folding angles are 16—19°) due to asymmetry of the ligand. The presence of two five-membered metallocycles, which are sterically more strained than six-membered metallocycles, leads to a distortion of the octahedral symmetry of the coordination polyhedron.[11—14]

The Ni(1)—N and Ni(1)—O bond lengths are 2.002(2), 2.009(2) Å and 2.009(2), 2.024(2) Å, respectively. The

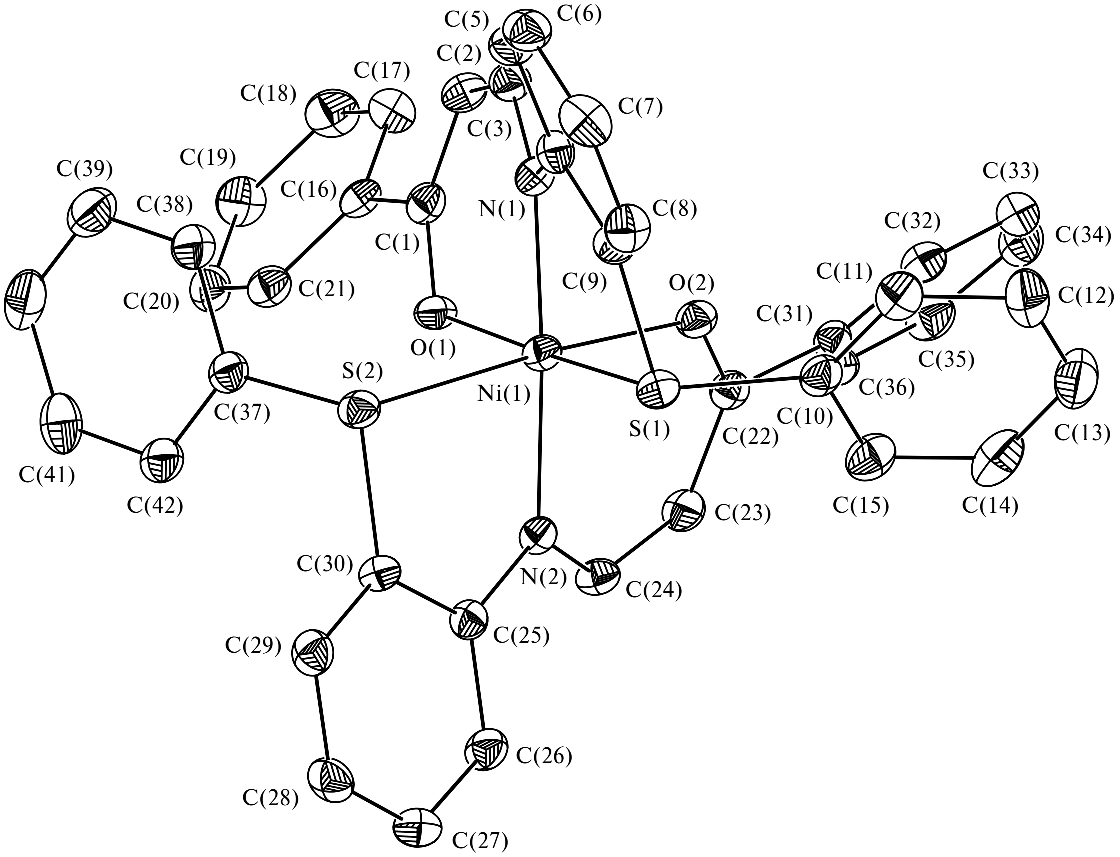

Fig. 1. Overall view of complex **2**.

Table 1. Structural data obtained by the multiple-shell fitting of the EXAFS data

Compound	R^2	R/Å	N	σ^2/Å^2	Atomic type	Q (%)
2b	Ph	2.05 (2.009, 2.024, 2.002, 2.009)	4	0.0020	N/O	2.8
		2.47 (2.4634, 2.4723)	2	0.0039	S	
3b	Ph	1.88	4	0.0026	N/O	1.6
		2.89	6	0.0056	C/N	
3a	CH_3	1.88	4	0.0025	N/O	3.0
		2.26	2	0.0043	C	

Note. R are interatomic distances, *N* is the coordination number, σ^2 is the Debye—Waller factor, Q is the target function. The values in parentheses were determined from the X-ray diffraction data for nickel complex **2**.

structural characteristics determined by EXAFS (Ni—N and Ni—O, 2.05 Å; Ni—S, 2.47 Å) are in good agreement with the results of X-ray diffraction analysis (Table 1).

Conceivably, metal chelates **2a,b** retain their octahedral structures in solution. At room temperature, complexes **2a,b** dissolved in $CDCl_3$ are paramagnetic as evidenced by the expansion of the chemical shift scale (δ = −16—30) in the ^{1}H NMR spectra and paramagnetic broadening of the proton signals.

The replacement of the α-methine H atom in the ligand by the Me group leads to a radical change in the properties of the metal chelates. The complexes prepared from ligands **1c,d** are diamagnetic both in the solid phase and solution. Their ^{1}H NMR spectra have no singlets for the proton of the NH group at δ 12—13, whereas the signals for the protons of all groups are shifted upfield.

According to the EXAFS results, the S atoms of the sulfide groups are uncoordinated and these complexes are, apparently, planar and have structure **3** (Ni—O and Ni—N distances are 1.99 Å).

Hence, the structures of complexes **2** and **3** depend substantially on the nature of the substituents in the ligands. This is the difference between the above compounds and the paramagnetic octahedral Ni^{II} chelates containing the quinoline ring as the substituent at the N atom studied by us earlier.[15]

Experimental

The IR spectra of all compounds were recorded on a Specord 75-IR instrument in Nujol mulls. The ^{1}H NMR spectra were measured on a Varian UNITY-300 spectrometer (300 MHz) in $CDCl_3$. The magnetic susceptibilites of the complexes in the crystalline state were measured at 299 K by the Faraday method. The effective magnetic moments were calculated by the formula $\mu_{eff} = (8\lambda_m T)^{1/2}$, where λ_m is the molar magnetic susceptibility taking into account the Pascal magnetic corrections.

The nickel K-edge EXAFS spectra were recorded on a laboratory EXAFS spectrometer[16] constructed on the basis of a DRON-3 diffractometer. X-ray radiation was decomposed into a spectrum using a (1340) quartz crystal monochromator. The extended fine structure of the X-ray absorption spectrum $\chi(k)$ was resolved according to a standard procedure.[17] The Fourier transformation of the EXAFS spectra was performed in the range of photoelectron wave vectors k = 3.5—13.0 Å^{-1} with the weighting function k = 2. The scattering phases and amplitudes of the photoelectron wave necessary for the construction of the model spectrum were calculated with the use of the FEFF5 program.[18]

X-ray diffraction study of complex 2b. The crystals are triclinic, at 110 K: a = 12.543(2) Å, b = 12.592(2) Å, c = 13.530(2) Å, α = 112.134(4)°, β = 116.032(4)°, γ = 92.298(4)°, V = 1723.6(5) Å^3, d_{calc} = 1.386 g cm^{-1}, space group $P\bar{1}$, Z = 2. The intensities of 16724 reflections were measured on a Smart 1000 CCD diffractometer at 110 K (Mo-Kα radiation, graphite monochromator, ω scan technique, ω scan step was 0.3°, frames were exposed for 10 s, $2\theta_{max}$ = 55°) of which 7805 independent reflections (R_{int} = 0.0424) were used in subsequent calculations. The semiempirical absorption correction was applied using equivalent reflections. The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation based on F^2. The hydrogen atoms were located from difference electron density syntheses and refined isotropically. The final reliability factors were as follows: wR_2 = 0.1165, GOOF = 0.985 for all reflections (R_1 = 0.0504 for 5367 reflections with $I > 2\sigma(I)$). All calculations were carried out with the use of the SHELXTL PLUS program package.

β-Aminovinyl ketones 1a,b were synthesized according to a procedure analogous to that used in the previous studies.[9,15] Compounds **1a,b** were prepared by the reactions of aqueous-alcoholic solutions of hydrochlorides of the corresponding amines and an aqueous solution of a sodium salt of β-oxymethyleneacetophenone taken in equimolar amounts. The reaction mixture was kept for 12 h. The precipitate that formed was filtered off, washed with water, and recrystallized from isopropyl alcohol. The yields were 40—60%.

3-(2-Methylsulfanylphenylamino)-1-phenylpropen-1-one (1a). Found (%): C, 71.17; H, 5.39; N, 5.03. $C_{16}H_{15}NOS$. Calculated (%): C, 71.35; H, 5.61; N, 5.20. ^{1}H NMR ($CDCl_3$), δ: 2.50 (s, 3 H, S—CH_3); 6.09 (d, 1 H, CH, ^3J(CH=CH) = 8 Hz); 7.00—8.00 (m, 5 H, C_6H_5; 4 H, C_6H_4; 1 H, CH=CH—NH); 12.50 (d, 1 H, NH, ^3J(NH—CH) = 12 Hz). IR (Nujol mulls), ν(C=O)/cm^{-1}: 1660.

1-Phenyl-3-(2-phenylsulfanylphenylamino)propen-1-one (1b). Found (%): C, 75.85; H, 5.01; N, 4.01, $C_{21}H_{17}NOS$. Calculated (%): C, 76.10; H, 5.17; N, 4.23. ^{1}H NMR ($CDCl_3$), δ: 6.02 (d, 1 H, —C$\underline{H}$=CH—, J = 8.0 Hz); 7.00—7.93 (m, 10 H, 2 Ph; 4 H, C_6H_4); 7.45 (dd, 1 H, —CH=C$\underline{H}$—NH, J = 12.0 Hz, J = 8.0 Hz); 12.56 (d, 1 H, =CH—N$\underline{H}$, J = 12.0 Hz). IR (Nujol mulls), ν(C=O)/cm^{-1}: 1630.

β-Aminovinyl ketones 1c,d were prepared by refluxing equimolar amounts of benzoylacetone and the corresponding amines in toluene in the presence of catalytic amounts *p*-toluenesulfonic acid for 1 h. After cooling, the precipitate that formed was filtered off, washed with benzene, and recrystallized from toluene. The yields were 30—60%.

3-(2-Methylsulfanylphenylamino)-1-phenylbut-2-en-1-one (1c). Found (%): C, 71.91; H, 5.83; N, 4.72. $C_{17}H_{17}NOS$. Calculated (%): C, 72.05; H, 6.05; N, 4.94. ^{1}H NMR, ($CDCl_3$), δ: 2.00 (s, 3 H, S—CH_3); 2.44 (s, 3 H, CH_3—C); 5.93 (s, 1 H, CH=C); 7.11—7.93 (m, 5 H, Ph; 4 H, C_6H_4); 12.82 (s, 1 H, NH). IR (Nujol mulls), ν(C=O)/cm^{-1}: 1620.

1-Phenyl-3-(2-phenylsulfanylphenylamino)but-2-en-1-one (1d). Found (%): C, 76.34; H, 5.38; N, 3.92. $C_{22}H_{19}NOS$. Calculated (%): C, 76.49; H, 5.54; N, 4.05. ^{1}H NMR ($CDCl_3$), δ: 1.93 (s, 1 H, CH_3); 5.82 (s, 1 H, CH=C); 7.10—7.92 (m, 10 H, 2 Ph; 4 H, C_6H_4); 12.89 (s, 1 H, NH). IR (Nujol mull), ν(C=O)/cm^{-1}: 1597.

Nickel(II) complexes 2 and 3 were prepared by heating a methanolic solution of the corresponding β-aminovinyl ketone (0.1 mmol) and nickel acetate (0.05 mmol) for 30—40 min. The precipitates that formed were filtered off, washed with methanol, and recrystallized from toluene.

Bis[3-(2-methylsulfanylphenylaminato)-1-phenylpropenone]nickel(II) (2a). The yield was 68% of the stoichiometric value. Found (%): C, 64.38; H, 4.51; N, 4.58. $C_{32}H_{28}N_2NiO_2S_2$. Calculated (%): C, 64.55; H, 4.74; N, 4.70. IR (Nujol mull), ν(C=O)/cm^{-1}: 1606. The magnetic moment (μ/μB) is 3.16.

Bis[1-phenyl-3-(2-phenylsulfanylphenylaminato)propenone]nickel(II) (2b). The yield was 60% of the stoichiometric value. Found (%): C, 69.85; H, 4.21; N, 3.67. $C_{42}H_{32}N_2NiO_2S_2$. Calculated (%): C, 70.11; H, 4.48; N, 3.89. IR (Nujol mull), ν(C=O)/cm^{-1}: 1592. The magnetic moment (μ/μB) is 3.32.

Bis[3-(2-methylsulfanylphenylaminato)-1-phenylbut-2-en-1-one]nickel(II) (3a). The yield was 56% of the stoichiometric value. Found (%): C, 65.35; H, 5.32; N, 4.40. $C_{34}H_{32}N_2NiO_2S_2$. Calculated (%): C, 65.50; H, 5.17; N, 4.49. IR (Nujol mull), ν(C=O)/cm^{-1}: 1590. The compound is diamagnetic.

Bis[1-phenyl-3-(2-phenylsulfanylphenylaminato)but-2-en-1-one]nickel(II) (3b). The yield was 58% of the stoichiometric value. Found (%): C, 70.56; H, 4.62; N, 3.54. $C_{44}H_{36}N_2NiO_2S_2$. Calculated (%): C, 70.69; H, 4.85; N, 3.75. ^{1}H NMR, ($CDCl_3$), δ: 1.30 (s, 6 H, 2 CH_3); 4.93 (s, 2 H, 2 CH—C); 6.61—7.30 (m, 20 H, 4 C_6H_5; 8 H, 2 C_6H_4). IR (Nujol mull), ν(C=O)/cm^{-1}: 1579. The compound is diamagnetic.

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