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Adducts of Diethyldithiocarbamate Complexes of Zinc(II) and Copper(II) with Piperidine [M(Pip)$(Edtc)_2$] and Their Solvated Forms [M(Pip)$(Edtc)_2$] · L (L = C_6H_6, C_5H_5N, C_4H_9NO): Synthesis, EPR and Solid-State (^{13}C, ^{15}N) CP/MAS NMR Studies

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Abstract—Crystal adducts of diethyldithiocarbamate complexes of zinc(II) and copper(II) with piperidine (Pip) were synthesized, and their solvated forms with the outer-sphere molecules of benzene, pyridine (Py), and morpholine (Mf) were obtained. Adducts with composition [M(Pip)$(Edtc)_2$] · L (L = Py, Mf) were shown to be able, in principle, to give solvated isomers [M(L)$(Edtc)_2$] · Pip with the Pip molecule arranged in the outer sphere. The composition, structure, and properties of the obtained adducts were studied by EPR, high-resolution solid-state ^{13}C, ^{15}N NMR spectroscopy. Solvation of all three adducts with Pip, Mf, and Py was found to result in a substantial increase in the contribution of the trigonal–bipyramidal component to the geometry of a copper coordination pentahedron. In addition, for adducts with Mf and Py, a structural unification of two isomeric forms was observed at the molecular level to yield a qualitatively new (rather than intermediate) state. It was shown that in all solvated forms of the copper(II) adducts, the metal polyhedron is mainly a trigonal bipyramid, while the square–pyramidal contribution is insignificant. Results of (^{13}C, ^{15}N) NMR studies revealed a structural inequivalence of the $Edtc^-$ ligands in the zinc adducts under investigation.

According to data of three independent investigation methods (EPR, high-resolution solid-state (^{13}C, ^{15}N) NMR, and X-ray diffraction) carried out in [1, 2], it was shown that crystal adducts of dialkyldithiocarbamate complexes of zinc(II) and copper(II) with pyridine (Py) and morpholine (Mf) occur as two conformational isomers that differ in the spatial orientation of their coordinated heterocycles. Studies of their interaction with organic molecules of different nature (benzene [3], Py [4], methylene chloride and chloroform [5], dichloroethane [6], and carbon tetrachloride [7, 8]) made it possible to establish that even with an unchanged state of aggregation, the solvation of the above crystal adducts results in the formation of ordered molecular channels in their lattice, the channels being occupied with the solvated molecules, and the structure thus being rearranged into a clathrate. However, we believe that the deep structural rearrangement of the adducts observed simultaneously at the molecular level [3–8] is much more essential. This rearrangement involves structural unification of two conformers of initial nonsolvated adducts and transition into a qualitatively new (not intermediate) structural state. This state is distinguished by (a) changing M–N distance, (b) spatial reorientation of the coordinated heterocycle, and (c) a significant increase in the trigonal–bipyramidal (TB) contribution to the geometry of the metal coordination polyhedron.

Previously [9], we synthesized and characterized by EPR and thermographic methods isotope-substituted (^{63}Cu, ^{65}Cu) samples of bis(diethyldithiocarbamato)piperidinecopper(II) [$^{63/65}Cu$(Pip)$(Edtc)_2$] magnetically diluted with zinc.We established that unlike the respective adducts with Py [1], Mf [2], and trimethylphosphine [10], which at the molecular level occur in the form of two or even three isomers, an adduct with piperidine exists in one molecular form.

The aim of this work was to synthesize adducts of diethyldithiocarbamate complexes of zinc(II) and copper(II) with piperidine and their solvated forms, including outer-sphere cyclic molecules of the donor bases with different chemical nature (Py and Mf) and benzene, and to study their composition, structure, and spectra by using EPR and high-resolution solid-state (^{13}C, ^{15}N) NMR (with a natural abundance of isotopes).

EXPERIMENTAL

Bis(diethyldithiocarbamato)piperidinezinc(II) [Zn(Pip)$(Edtc)_2$] (**I**) was synthesized using the following two methodological procedures:

(1) by dissolving dimeric diethyldithiocarbamatozinc(II) complex $[Zn_2(Edtc)_4]$ in toluene containing piperidine in an amount exceeding the stoichiometric amount by ~10% and through further crystallization of the adduct at room temperature (by analogy with procedures described in [11–13]);

(2) by quantitative absorption of piperidine vapors from the gas phase with powdered $[Zn_2(Edtc)_4]$.

Solvates having composition $[Zn(Pip)(Edtc)_2] \cdot L$ with L = C_6H_6, Py, Mf (complexes **II**, **III**, and **IV**, respectively) were obtained via careful wetting of the crystal adduct **I** with the respective solvents without changing its state of aggregation. The degree of conversion of **I** into the solvated forms and stoichiometric ratios Zn : Pip : L were determined by jointly using data of ^{13}C NMR and gravimetry.

Compound **II** was also produced by crystallization from a solution, as in the case of **I**. However, this time, benzene was used instead of toluene. Crystals of **I** and **II** were separated from the mother liquor, washed with a small amount of the respective solvent, and dried in air until they became loose. The soichiometric ratios of M : Pip and M : Pip : C_6H_6 were determined in them from the loss of sample mass after the full desorption of piperidine and benzene (upon careful heating). To improve the accuracy of determination, we used samples with masses less than 1 g. Data of ^{13}C, ^{15}N NMR reveal the spectral identity of samples **I** and **II** obtained by different methods.

In order to increase the amount of information on EPR spectra, bis(diethyldithiocarbamato)piperidinecopper(II) $[Cu(Pip)(Edtc)_2]$ (**V**) and its solvated forms with C_6H_6, Py, and Mf (complexes **VI**, **VII**, and **VIII**, respectively) were obtained as isotope-substituted compounds magnetically diluted with zinc (Cu : Zn = 1 : 1000) by analogy with **I**–**IV**. Copper (II) salts with a concentration of ^{63}Cu 99.3(1) at. % and of ^{65}Cu 99.2(1) at. % were used. The ratios of Cu : Pip : L were determined in the same way as was done for zinc complexes, the only difference being that the degree of transformation of crystals **V** into solvated forms was estimated from EPR spectra.

All of the obtained compounds were kept in sealed tubes. The reagents used in the synthesis were made by NaEdtc · $3H_2O$ (Fluka), piperidine (BDH Chemicals Ltd), morpholine, and pyridine (Aldrich).

EPR spectra of magnetically diluted compounds **V**–**VIII** were recorded at room temperature on a 70-02 XD/1 (MP "SZ", Minsk) radiospectrometer at a working frequency of ~9.5 GHz. Frequency measurement was performed using a ChZ-46 frequency meter. *g*-Factors were calculated relative to DPPH. The accuracy of determination of the *g*-factor was ±0.002%, while that of the hiperfine structure (HFS) constants was ±2%. EPR spectra were simulated within the framework of a second approximation of the perturbation theory using WIN-EPR SimFonia software, version 1.2 (Bruker). In the course of approximating model spectra to experimental spectra, we varied the *g*-factors, HSF constants, resonance line widths, and percentage of the Lorentz and Gauss contribution to the line shape.

Zinc compounds **I**–**IV** were studied using high-resolution solid-state ^{13}C ($I = 1/2$, $\mu = 0.7021$) and ^{15}N ($I = 1/2$, $\mu = -0.2831$) pulse NMR spectroscopy with a natural abundance of isotopes. ^{13}C and ^{15}N NMR spectra were registered at room temperature on a CMX-360 radiospectrometer (Chemagnetics Infinity, USA) with working frequencies of 90.52 and 36.48 MHz, respectively, and a superconducting magnet (B_0 = 8.46 T) and Fourier transformation. ^{13}C spectra were obtained using the proton cross-polarization effect [14], the ^{1}H–^{13}C interaction time being 2 ms. Dipole–dipole ^{13}C–^{1}H interactions were suppressed by applying the proton decoupling effect with an rf field corresponding to the proton resonance frequency and $\omega_1^H/2\pi = 54.2$ kHz [14]. The duration of the $\pi/2$ proton pulses was 5.0 μs. Polycrystalline samples of the complexes under study weighing ~350 mg were pressed into standard rotors made from zirconium dioxide with a diameter of 7.5 mm. Due to the low natural abundance of the ^{13}C isotope (1.108 at. %), a signal acquisition procedure was used with the number of scans ranging from 1024 to 2048 and a scan time of 2 s. In order to average the anisotropy of chemical shift δ for investigated nuclei in the course of signal acquisition, the rotors with the samples were rotated by a stream of dry air at a magic angle ($\alpha = 54.75°$) to the magnetic field direction. The spinning frequencies were 4400, 5200, and 5500 (2) rps, respectively. The ^{13}C isotropic chemical shifts were measured relative to a low-field component of an external standard, i.e., crystal adamantane (δ = 38.56 ppm relative to tetramethylsilane [15]). The chemical shifts were corrected for drift of the magnetic field intensity during the experiments, the frequency equivalent of the drift for the ^{13}C nuclei being 0.051 Hz/h.

^{15}N NMR spectra were registered using proton cross-polarization with an ^{1}H–^{15}N interaction time equal to 1.2 ms. Proton frequency $\omega_1^H/2\pi = 58.3$ kHz was used for the purpose of suppression of the ^{15}N–^{1}H dipole–dipole interactions in decoupling. The duration of the $\pi/2$ pulses was 5.0 μs. The natural abundance of the ^{15}N isotope amounts to 0.365 at. %; therefore, 2500 to 18500 scans were used in the spectra acquisition, the scan time being 2 s. The spinning rate was 4400, 5500, and 6000(2) rps. The ^{15}N isotropic chemical shifts were measured relative to the crystal NH_4Cl used as an external standard (0 ppm, –341 ppm in an absolute scale [16, 17]). Drift of the magnetic field intensity for the ^{15}N nuclei in the frequency equivalent was 0.016 Hz/h.

RESULTS AND DISCUSSION

EPR Spectra. Experimental EPR spectra of compounds **V**–**VIII** exhibit a number of common features

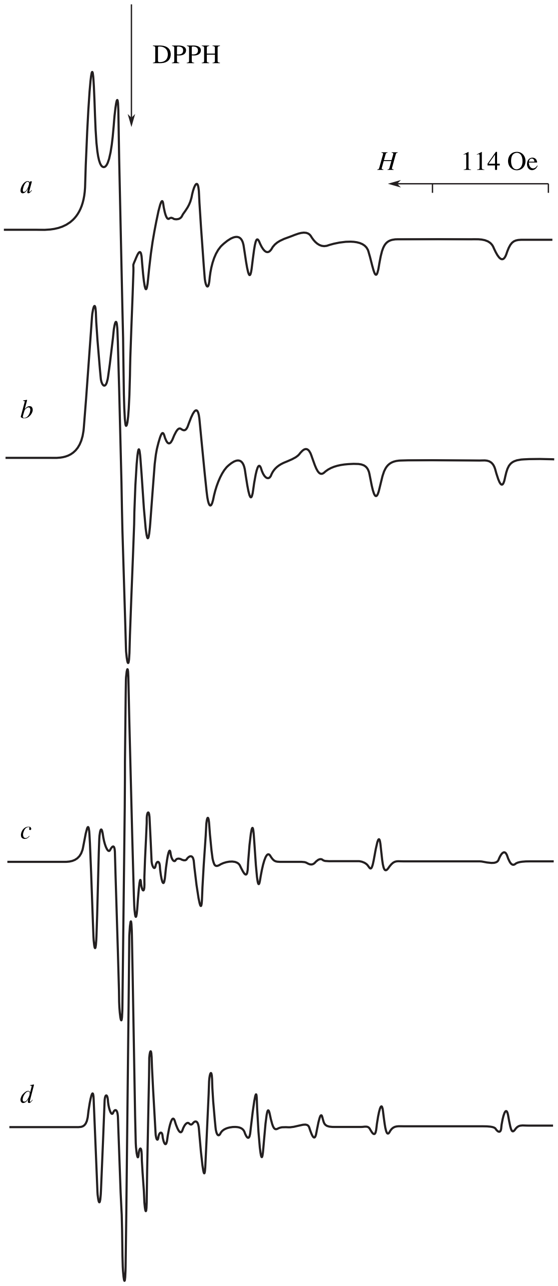

Fig. 1. (*a*, *c*) Experimental and (*b*, *d*) theoretical EPR spectra of solvated adduct $[^{63}Cu(Pip)(Edtc)_2] \cdot Py$ magnetically diluted with zinc in the form of (*a*, *b*) the first and (*c*, *d*) the third derivatives ($T = 295$ K).

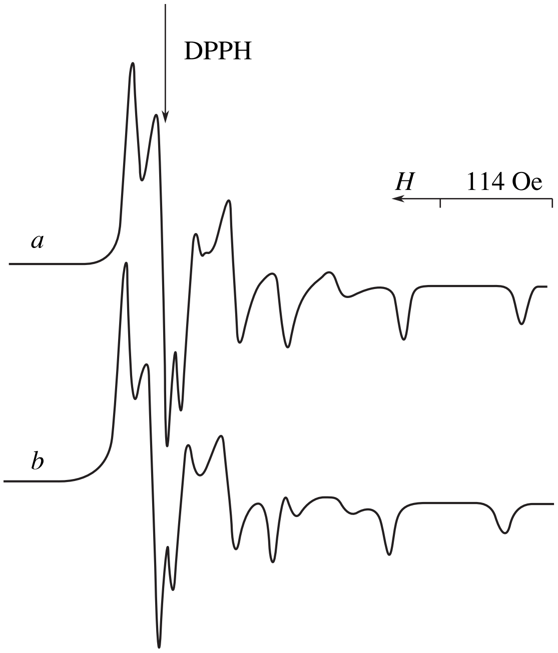

Fig. 2. EPR spectra of solvate isomers of (*a*) $[^{63}Cu(Pip)(Edtc)_2] \cdot Mf$ and (*b*) $[^{63}Cu(Mf)(Edtc)_2] \cdot Pip$ magnetically diluted with zinc(II).

(Figs. 1, 2). Thus, their high-field regions contain two high-intensity peaks due to additional absorption (AA) [18]. In this case, the close intensities of the HFS components in two quartets of the nonequidistant lines due to the interaction of an unpaired electron with nuclei of ^{63}Cu or ^{65}Cu ($I = 3/2$) are evidence of the three-axial anisotropy of the EPR parameters. In addition, simulation of a high-field AA peak having the shape of the adsorption line can only be performed under the assumption of the third orientation in the high-field region. However, of the four HFS components with the orientation being discussed, only one component can be observed in reality, the remaining three components having been overlapped by AA peaks and HFS components with intermediate orientation. Therefore, EPR parameters of this orientation were refined on the basis of the results of a computer simulation in two stages. First, model EPR spectra were properly constructed (Fig. 1b). Then, a double differentiation of the experimental spectra was made to result in a basic reduction of the HFS components and thus in an increase in the resolution level. At the second stage, the third derivatives of the model spectra (Fig. 1d) were approximated as closely as possible to the experimental spectra (Fig. 1c). The EPR parameters produced from the results of the best approximation are listed in Table 1.

It is evident that the solvated adducts $[Cu(Pip)(Edtc)_2] \cdot B$ (B = Py, Mf) containing two molecules of the donor bases with different chemical natures (Pip–Mf and Pip–Py) can have isomeric forms. These forms will differ in the manner of distribution of Pip and B (Mf, Py) molecules in the inner and outer coordination sphere and, hence, can be regarded as solvate isomers.

In so far as piperidine ($pK_a = 11.25$) is a donor base stronger than Mf (8.33) and Py (5.20) [19],[1] it was

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[1] The basicity of nondissociating organic bases is characterized by the value of pK_a (K_a is a dissociation constant for acid $[BH]^+$ conjugated with base B).

Table 1. EPR* parameters of compounds **V**–**X**

No.	Complex	g_1	A_1^{Cu}, Oe	g_2	A_2^{Cu}, Oe	g_3	A_3^{Cu}, Oe
V	$[Cu(Pip)(Edtc)_2]$	2.120	125/134	2.061	52/56	2.016	19/20
VI	$[Cu(Pip)(Edtc)_2] \cdot C_6H_6$	2.117	117/125	2.075	64/68	2.017	21/23
VII	$[Cu(Pip)(Edtc)_2] \cdot Py$	2.118	123/132	2.064	55/59	2.016	18/19
VIII	$[Cu(Pip)(Edtc)_2] \cdot Mf$	2.122	119/128	2.065	54/58	2.015	13/14
	$[Cu(Mf)(Edtc)_2]$** [2]	2.121	135/145	2.038	21/23	2.038	21/23
		2.120	133/143	2.038	21/23	2.038	21/23
X	$[Cu(Mf)(Edtc)_2] \cdot Pip$	2.120	119/127	2.068	59/63	2.015	13/14
	$[Cu(Py)(Edtc)_2]$** [1]	2.121	135/145	2.039	32/34	2.019	5.0/5.5
		2.118	137/147	2.039	32/34	2.019	5.0/5.5
IX	$[Cu(Py)(Edtc)_2] \cdot Pip$	2.120	120/128	2.069	61/65	2.015	13/14

* HFS constants are given for ^{63}Cu and ^{65}Cu isotopes.

** Data for two isomeric forms of adducts are given.

interesting to study, in principle, the possibility of synthesizing solvated adducts $[Cu(Py)(Edtc)_2] \cdot Pip$ (**IX**) and $[Cu(Mf)(Edtc)_2]$ (**X**). In this case, despite their strong basic nature, Pip molecules will be located in the outer coordination sphere, while the molecules of N-organic less strong bases will be coordinated to the central atom. Solvated forms of the adducts under discussion were obtained by quantitative absorption of Pip with crystals of $[Cu(B)(Edtc)_2]$, which were carefully wetted with piperidine (taken in stoichiometric ratio) without changing the state of aggregation. Unfortunately, the attempt to produce adducts **IX** and **X** by traditional methods of crystallization from the solutions failed.

EPR spectra of solvated forms $[Cu(Pip)(Edtc)_2] \cdot Mf$ (**VIII**) and $[Cu(Mf)(Edtc)_2] \cdot Pip$ (**X**) can be compared in Fig. 2. Despite the similar shapes of their spectra and close values of their EPR parameters, these compounds are spectrally nonidentical (Table 1). The individual spectral pattern of compound **X** (Fig. 2b) does not reveal any redistribution of the base molecules between the inner and outer coordination spheres, since not even a trace of adduct **VIII** can be detected in the sample composition.

In isotropic liquids, due to the coordination unsaturation, copper dithiocarbamate complexes form adducts having a square-pyramidal (SP) structure (C_{4v} symmetry) with N-donor organic bases. In these adducts, molecules B have an axial coordination and the copper(II) unpaired electron is mainly localized on $3d_{x^2-y^2}$ AO. In our case, the manifestation of rhombic nature in experimental EPR spectra of solvated and nonsolvated forms of crystal adducts suggests that the copper coordination polyhedron is significantly distorted toward trigonal bipyramid (D_{3h} symmetry) [1–9] when the ground state of the copper unpaired electron is considered to be the result of a combination of $3d_{x^2-y^2}$ and $3d_{z^2}$-AO.

Qualitatively, the predominate transition from the SP to the TB configuration is accompanied by the appearance in the experimental EPR spectra of a third (high-field) orientation with $g_3 \approx 2.00$. In this case, a gradual increase in the TB contribution to the geometry of the copper coordination polyhedron leads to an antibate change in A_1^{Cu} and A_2^{Cu}, such that the constants of the hiperfine structures of low-field orientation decrease, while those of an intermediate orientation increase (i.e., they become close in absolute values). With this point in view, let us consider the possibility of applying the difference $\Delta = A_1^{Cu} - A_2^{Cu}$ in practice for the purpose of estimating the TB contribution to the geometry of the copper polyhedron with CN = 5.

Experimental EPR spectra qualitatively similar to those discussed above were previously observed by us in [3, 4], for example, for magnetically diluted forms of $[Cu(Py)(Edtc)_2]$ solvated with benzene and pyridine (Table 1). Analysis of X-ray diffraction data for the above coordination compounds, performed as described in [20], made it possible to establish the predominate (above 80%) contribution of the TB component to the geometry of the metal coordination polyhedron. In the case of an initial nonsolvated adduct whose crystals have two isomeric forms (α and β), this contribution only slightly exceeds 50% [1]. It is noteworthy that the TB contribution for two isomeric forms of $[Cu(Mf)(Edtc)_2]$ calculated in the same manner turned out to be 7.5% and 22.7% [2]. Solvation of $[Cu(Py)(Edtc)_2]$ with molecules of different chlorohydrocarbons, whose sizes are smaller than those of the cyclic benzene or Py molecules, is also followed by distortion of the copper polyhedron geometry toward TB, but to a significantly lesser extent (64–71%) [5–8].

Data in Table 2 indicate that for eight solvated and nonsolvated molecular forms of magnetically diluted adduct $[Cu(Py)(Edtc)_2]$, with a gradual increase in TB

Table 2. Trigonal–bipyramidal contribution to the geometry of Cu(II) coordination polyhedron in adduct $[Cu(Py)(Edtc)_2]$ and its solvated forms $[Cu(Py)(Edtc)_2] \cdot L$

Complex	TB, %	Δ, Oe
[β-Cu(Py)(Edtc)$_2$]	55.0	105
[α-Cu(Py)(Edtc)$_2$]	55.6	103
$[Cu(Py)(Edtc)_2] \cdot 2CCl_4$	64.0	86
$[Cu(Py)(Edtc)_2] \cdot CHCl_3$	67.0	84
$[Cu(Py)(Edtc)_2] \cdot C_2H_4Cl_2$	67.8	83
$[Cu(Py)(Edtc)_2] \cdot CH_2Cl_2$	71.0	80
$[Cu(Py)(Edtc)_2] \cdot C_6H_6$	82.1	62
$[Cu(Py)(Edtc)_2] \cdot Py$	84.6	64

contribution to the geometry of the copper coordination pentahedron, parameter Δ shows a tendency to decrease monotonically.

The adducts of copper(II) obtained in this work can be arranged in the following order of increasing TB contribution: $[Cu(Pip)(Edtc)_2]$ (**V**), $[Cu(Pip)(Edtc)_2] \cdot Py$ (**VII**), $[Cu(Pip)(Edtc)_2] \cdot Mf$ (**VIII**), $[Cu(Mf)(Edtc)_2] \cdot Pip$ (**X**), $[Cu(Py)(Edtc)_2] \cdot Pip$ (**IX**), $[Cu(Pip)(Edtc)_2] \cdot C_6H_6$ (**VI**). In this series, parameter Δ has the following values: 73, 68, 65, 60, 55, and 53 Oe, respectively. This allows us to suggest that the TB contribution for compound **V** equals ~75%, that for **VII** and **VIII** is ~80%, and that for the remaining adducts (**IX**, **X**, and **VI**) significantly exceeds 85%.

Thus, data of EPR spectroscopy make it possible to state that, in a general case, solvation of all three crystal adducts with Pip, Mf, and Py results in an increase in the TB contribution to the copper pentahedron geometry. However, solvation of $[Cu(Mf)(Edtc)_2]$ and $[Cu(Py)(Edtc)_2]$ is characterized by one more essential feature: in the cases under consideration, structural unification of two isomeric forms of the adducts is observed at the molecular level, as well as a transition to a qualitatively new (but not intermediate) structural state.

High-resolution solid-state ^{13}C and ^{15}N NMR spectra. The patterns of experimental EPR spectra of copper(II) adducts depend both on the composition and structure of the nearest environment of the central atom. Therefore, it was reasonable to study the respective nonparamagnetic zinc mixed-ligand compounds using solid-state multinuclear NMR spectroscopy, since in this case, the structural state of the ligands can be characterized as a whole.

^{13}C NMR spectra of zinc adducts **I**–**IV** (Fig. 3) exhibit three groups of signals due to diethyldithiocarbamate ligands, coordinated Pip molecules, and to outer-sphere solvate molecules of benzene, Py, and Mf (Table 3). The authors of [21, 24] assigned the resonances of the ^{13}C atoms of the Edtc$^-$ ligands to the methyl, methylene, and dithiocarbamate groups. The $NC(S)S^-$ groups produce singlet (compounds **III**, **IV**)

Table 3. Chemical shifts (ppm) of ^{13}C and ^{15}N NMR signals for adducts $[Zn(Pip)(Edtc)_2] \cdot L$ (relative to TMS and NH_4Cl)

Compound	Edtc			Edtc	Pip, Py			Pip, Py	Mf		Mf	C_6H_6
	=NCS$_2$–	–CH$_2$–	–CH$_3$	=N–	*o*-	*m*-	*p*-	–N=	=N–CH$_2$–	–O–CH$_2$–	–N=	=CH–
[Zn(Pip)(Edtc)$_2$]	205.9	49.7	13.3	133.7	47.3	28.8	25.2	7.0				
	204.4(37)*	48.6	12.7	129.1								
$[Zn(Pip)(Edtc)_2] \cdot C_6H_6$	203.4 (46)*	49.3	12.5	135.8	46.9	28.2	25.2	7.5				128.7
	202.6		12.0	132.6								
			11.0									
$[Zn(Pip)(Edtc)_2] \cdot Py$	202.8 (44)*	48.8	13.1	135.0	46.8	27.1	25.8	−3.7				
			12.6	132.1	150.3	124.3	136.8	271.5				
			12.0									
			10.5									
$[Zn(Pip)(Edtc)_2] \cdot Mf$	203.4	49.0	12.6	135.4	47.3	28.6	26.3	−4.9	49.0	68.8	−1.0	
			12.2	131.0						67.6		
			11.6									
			11.0									
$NaEdtc \cdot 3H_2O$ [21]	206.5 (51)*	48.6 (71)*	13.2	139.1								
C_6H_6, Pip [22]					47.9	27.8	25.9					128.5
Py [24], Mf [23]					149.8	123.6	135.7	258.0	46.7	68.1		

* Asymmetric ^{13}C–^{14}N doublets (Hz).

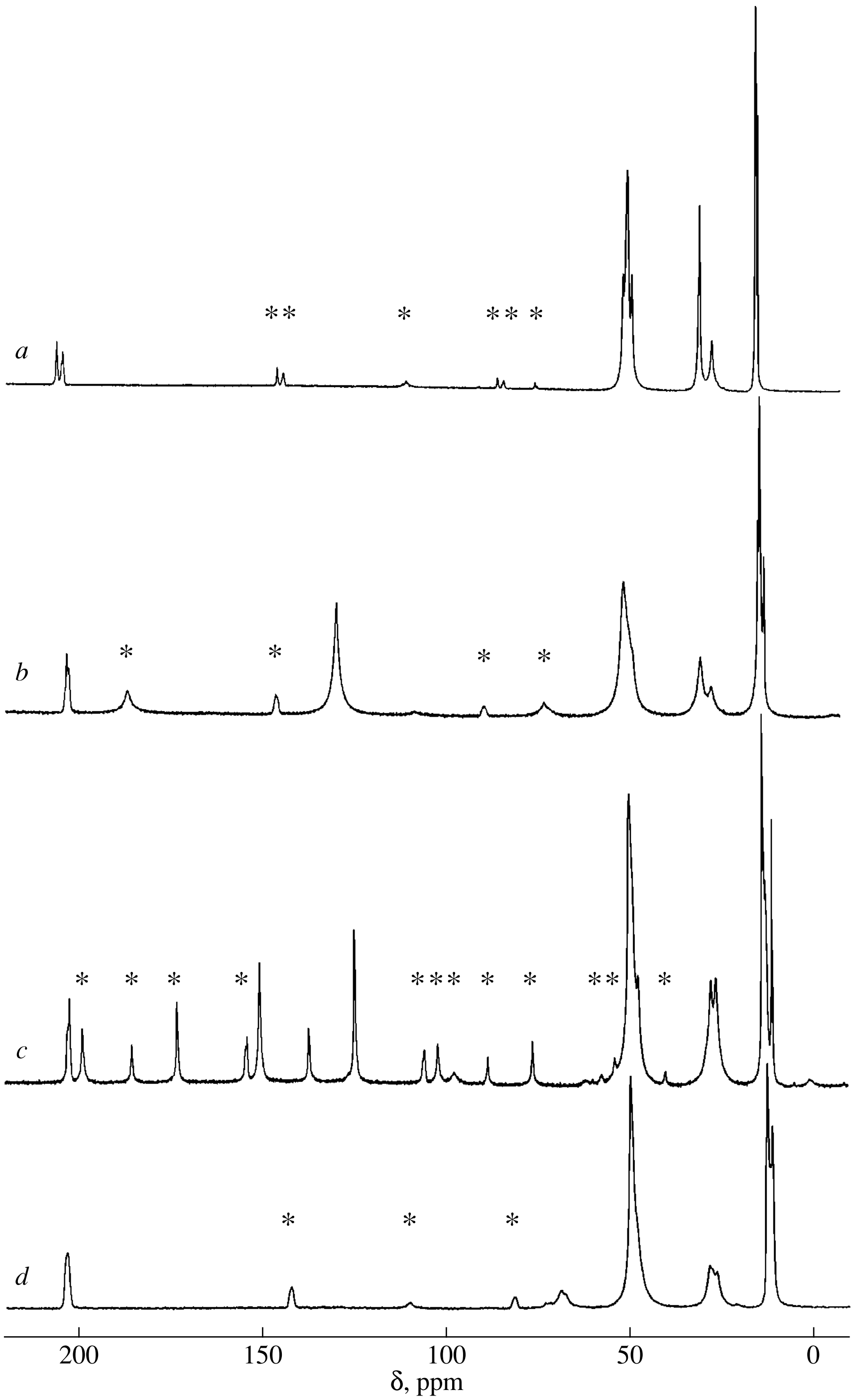

Fig. 3. ^{13}C NMR spectra (T = 295 K) of (*a*) adduct [Zn(Pip)(Edtc)$_2$] and its solvated forms: (*b*) [Zn(Pip)(Edtc)$_2$] · C_6H_6, (*c*) [Zn(Pip)(Edtc)$_2$] · Py, and (*d*) [Zn(Pip)(Edtc)$_2$] · Mf. Components that are formed as a result of incomplete averaging of ^{13}C chemical shift anisotropy are marked with an asterisk. Number of scans/spinning frequency of samples (rps): (*a*) 2048/5500; (*b*) 2048/5200; (*c*) 1024/4400; (*d*) 1024/5500.

or doublet (1 : 1) signals (compounds **I**, **II**) in the spectra. The doublet nature of the signals reflects some structural inequivalence of the Edtc$^-$ ligands in compounds **I** and **II**. In addition, the terminal methylene groups also turn out to be inequivalent, which can be explained by their distribution over two, three, or even four structural positions (Fig. 3, Table 3). The observed additional asymmetric splitting of the signals of the Edtc$^-$ group is due to incomplete suppression of the ^{13}C dipole–dipole interaction with the quadrupole ^{14}N nucleus (I = 1) under the conditions of the MAS experiment [25, 26].

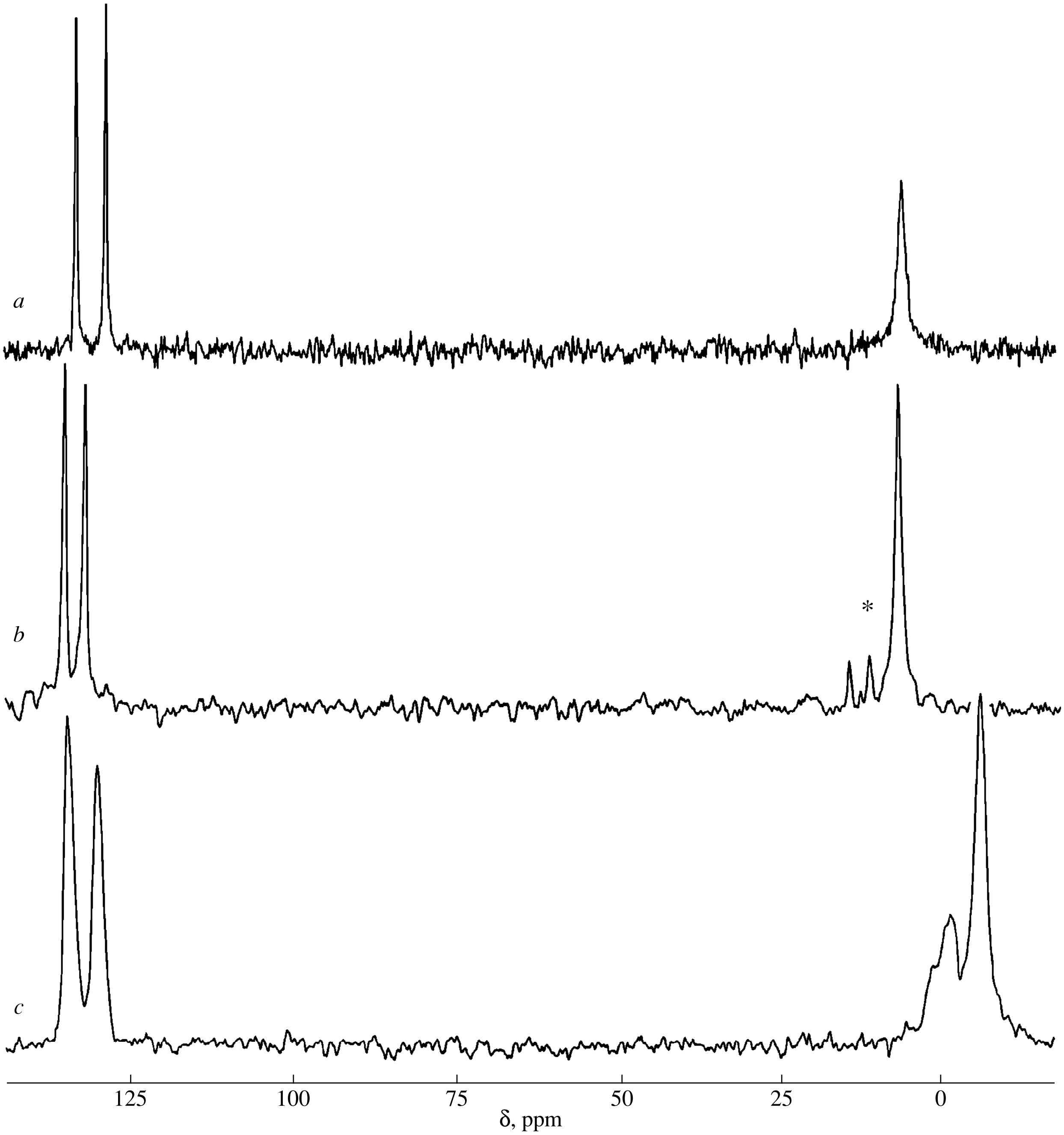

Fig. 4. ^{15}N NMR spectra (T = 295 K) of (*a*) [Zn(Pip)(Edtc)$_2$], (*b*) [Cu(Pip)(Edtc)$_2$] · C_6H_6, and (*c*) [Zn(Pip)(Edtc)$_2$] · Mf. Components that are formed as a result of incomplete averaging of ^{15}N chemical shift anisotropy are marked with an asterisk. Number of scans/spinning frequency of samples (rps): (*a*) 6000/6000; (*b*) 2500/4400; (*c*) 18500/5500.

Comparison of the ^{13}C chemical shifts listed in Table 3 for group NC(S)S$^-$ contained in NaEdtc · $3H_2O$ in nonsolvated (**I**) and solvated forms of adducts (**II**–**IV**) allows one to note that the ionic form of the ligand corresponds to the maximum value δ^{13}C. Covalent binding of the ligands in adduct **I** results in a chemical shift decrease. Further lowering of δ after adduct solvation can be explained by the strengthening of Zn–S bonds in the solvated forms. From this point of view, the doublet nature of the dithiocarbamate group signals in the ^{13}C spectra of compounds **I** and **II** suggests that the two Edtc$^-$ ligands in these complexes have different strengths of binding.

Chemical shifts in Table 3 and data in [22] make it possible to assign a triplet signal in a high-field region of the ^{13}C spectra to CH_2 groups in the *o*-, *m*-, and

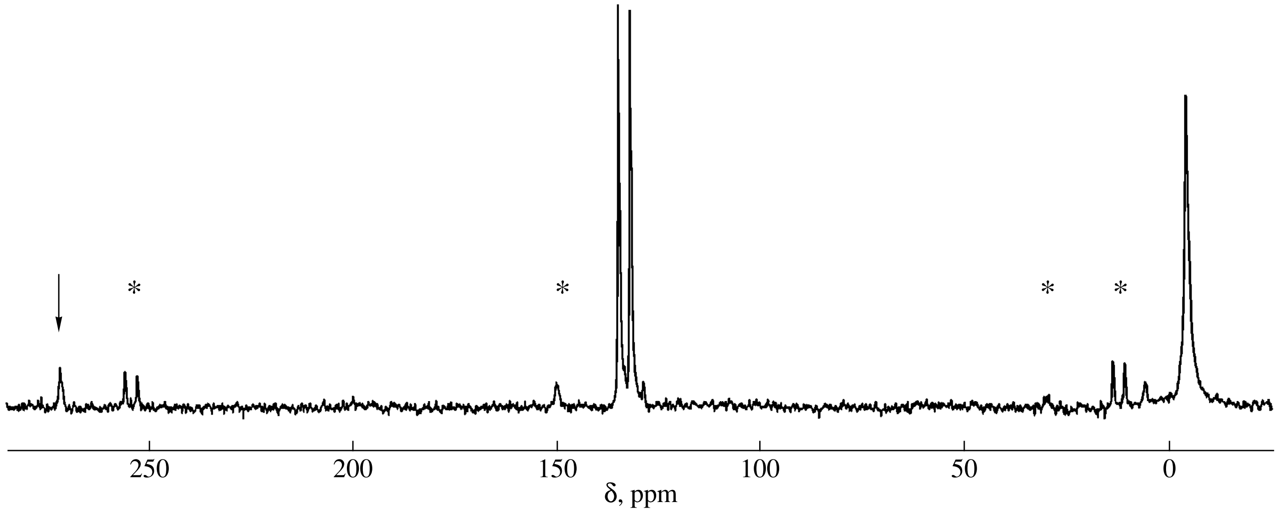

Fig. 5. ^{15}N NMR spectrum (T = 295 K) of [Zn(Pip)(Edtc)$_2$] · Py (11000 scans, sample spinning frequency is 4400 rps). Components that are formed as a result of incomplete averaging of ^{15}N chemical shift anisotropy are marked with an asterisk. Vertical arrow indicates the signal from the Py solvate molecule. The sample contains an admixture of a nonsolvated form of the adduct (~3%).

p-positions of coordinated Pip molecules. The main difference in the patterns of the ^{13}C NMR spectra of compounds **II**–**IV** and **I** consists in the availability of signals due to different solvate molecules (benzene, Py, or Mf). The benzene molecule is represented in the ^{13}C NMR spectrum (Fig. 3b) by a singlet signal in order to indicate that all six carbon atoms are structurally equivalent. The observed broadening of the signal resulting from the chemical shift dispersion can be explained by molecular dynamics or (within the framework of a steady-state model) by the random disordering of carbon atoms in the crystal lattice of compound **II** over several close structural positions. The chemical shift of benzene incorporated in **II** coincides with a characteristic of individual C_6H_6 [22] to prove its solvate nature.

^{13}C NMR spectra of solvated adduct **IV** are peculiar in that they exhibit signals assigned in accordance with data of [23] to OCH_2 and NCH_2 groups of solvated Mf molecules. In a spectrum of compound **III** (Fig. 3c), the Py molecule produces a triplet (2 : 1 : 2) signal due to the CH groups in the *o*-, *p*-, and *m*-positions. The ratio of the component intensities in the triplet suggests that the frequently observed molecular dynamics of the coordinated Py, as well as the structural disordering of the carbon atoms, are lacking in this case. According to data of [1, 4], the most sensitive to the structural state of the Py molecule are the signals of the carbon atoms in the *p*- and *m*-positions. (Although, one should note that the sensitivity of the latter is lower.) On the one hand, the respective values of δ^{13}C for the Py molecule in compound **III** (136.8 and 124.3 ppm) are close to the characteristics of the solvated Py molecule in adduct [Zn(Py)(Edtc)$_2$] · Py [4] (δ = 135.3 and 123.9 ppm) and also to the characteristics of Py as an individual substance [24] (Table 3), but on the other hand, they differ from the chemical shifts of coordinated Py molecules (δ = 140.2–144.0 and 125.5–127.2 ppm) [1, 3–8]. These data fully agree with the assumption on the outer-sphere location of the Py molecule in compound **III**.

^{15}N NMR spectra of compounds **I**–**IV** (Figs. 4, 5) contain a singlet signal due to the Pip coordinated molecule and a symmetric doublet signal (1 : 1) due to the Edtc$^-$ ligands. The latter fact reflects the structural inequivalence of the ligands incorporated in the adducts under study. It should be noted that in some cases (compounds **III**, **IV**), the ^{15}N NMR doublet signal from the NC(S)S$^-$ groups corresponds to a singlet signal from the ^{13}C nuclei of these groups (Figs. 3c, 3d). Thus, the structural equivalence of the carbon atoms directly interacting with the central atom through a low-size four-membered metal cycle (*trans*-annular effect) can be combined with the inequivalence of more distant nitrogen atoms in the periphery part of the ligand. Another explanation can be the higher sensitivity of the ^{15}N chemical shift (as compared to ^{13}C) to small structural perturbations.

In addition, ^{15}N NMR spectra of solvated forms **III** and **IV** contain signals from the outer-sphere Py (Fig. 5) and Mf molecules (Fig. 4c). According to data of [1, 3–8], the ^{15}N chemical shifts of coordinated Py molecules lie within the range of 225.2–231.5 ppm, whereas for solvate Py molecules, δ^{15}N = 279.4 ppm. Thus, the ^{15}N chemical shift is characterized by high sensitivity to the structural functions of the Py molecule contained in the adducts under study, which makes it possible to unambiguously interpret the ^{15}N NMR data. In the case of compound **III**, the signal from the Py molecule has δ^{15}N = 275.1 ppm, which indicates that pyridine is in the outer sphere. This conclusion complies with ^{13}C NMR data.

One should also note that with a long (above one day) period of ^{15}N NMR spectra acquisition for compound **III**, in addition to the main group of signals, signals of relatively low intensity appear due to solvate Py molecules (272.1 ppm), Edtc$^-$ ligands (135.0 and 131.1 ppm), and coordinated Pip molecules (2.5 ppm). This can be explained by the appearance of one more impurity form of solvated adduct. The values of δ^{15}N for the Edtc$^-$ ligands and Pip molecules of this impurity form are intermediate between the corresponding characteristics for $[Zn(Pip)(Edtc)_2]$ and $[Zn(Pip)(Edtc)_2] \cdot Py$. This is evidently due to the fact that the impurity form of the adduct contains less Py. Slight desorption of Py from compound **III** in the course of a long period of spectra acquisition also favors this assumption.

Attempts to apply the NMR method to study the zinc adduct with composition $[Zn(B)(Edtc)_2] \cdot Pip$ containing outer-sphere Pip molecules proved unsuccessful. Under high-frequency conditions of the MAS experiment and the considerable pressures being developed, redistribution of the base molecules between the inner and outer coordination spheres occurs very quickly.

Thus, data of EPR, high-resolution solid-state (^{13}C, ^{15}N) NMR spectroscopy, and of a stoichiometric study reveal that crystal adducts of diethyldithiocarbamate complexes of zinc(II) and copper(II) with Pip are liable to produce solvated forms with outer-sphere molecules of benzene, Py, and Mf. In this case, solvate isomers were obtained for forms solvated with Py and Mf. It was shown that solvation of crystal adducts of Cu(II) with Pip, Mf, and Py leads to a substantial increase in the TB contribution to the geometry of the Cu(II) coordination polyhedron. Adducts with Mf and Py were found to exhibit polyhedron distortion together with structural unification of two isomeric forms at a molecular level with transition to a qualitatively new state. The structural inequivalence of the Edtc$^-$ ligands in the zinc adducts under study was established on the basis of ^{13}C, ^{15}N NMR data.

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