

Structural Organization of Nickel(II), Zinc(II), and Copper(II) Complexes with Diisobutyldithiocarbamate: EPR, ^{13}C and ^{15}N CP/MAS NMR, and X-Ray Diffraction Studies

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Abstract—The structures and spectroscopic properties of nickel(II), zinc(II), and copper(II) complexes with dibutyl- and diisobutyldithiocarbamate were studied by EPR and ^{13}C and ^{15}N CP/MAS NMR spectroscopy and X-ray diffraction analysis. According to the EPR data, copper(II) forms mononuclear $[\text{}^{63/65}\text{Cu}\{\text{S}_2\text{CNR}_2\}_2]$ and heterobinuclear complexes $[\text{}^{63/65}\text{CuZn}\{\text{S}_2\text{CNR}_2\}_4]$ under magnetic dilution conditions. The isomeric forms of nickel(II) and zinc(II) diisobutyldithiocarbamates were detected by ^{13}C and ^{15}N NMR spectroscopy. The crystalline zinc(II) diisobutyldithiocarbamate was found to have a unique structural organization with alternating mononuclear $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ and binuclear molecular forms $[\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$ in the 1 : 1 ratio.

Dithiocarbamate complexes of transition metals have found wide use in various areas of practical activity [1]. For coordination chemistry, dialkyldithiocarbamates are of interest as ligands with different structural functions (monodentate, terminal bidentate, bridging bidentate, and mixed), which allows their complexes to be structurally organized in a variety of types (mono-, bi-, tri-, and, in the general case, polynuclear).

Mononuclear centrosymmetric nickel(II) complexes with dithiocarbamate ligands $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ [2–18] contain the terminal dithiocarbamate groups coordinated by nickel in a bidentate manner through two sulfur atoms to give small planar four-membered chelate rings $[\text{NiS}_2\text{C}]$ ($\text{R} = \text{CH}_3$ [2], C_2H_5 [3–5], C_3H_7 [6, 7], $i\text{-C}_3\text{H}_7$ [8], C_4H_9 [9, 10], $i\text{-C}_4\text{H}_9$ [9, 11], and $\text{C}_2\text{H}_5\text{O}$ [12] or $\text{R}_2 = (\text{CH}_2)_4$ [13], $(\text{CH}_2)_5$ [14], $(\text{CH}_2)_6$ [7, 15, 16], C_6H_5 and CH_3CO [17], and CH_3 and C_6H_5 [18]). In contrast to nickel, zinc forms binuclear molecular structures $[\text{Zn}_2(\text{S}_2\text{CNR}_2)_4]$ [19–31] ($\text{R} = \text{CH}_3$ [19, 20], C_2H_5 [21–23], C_3H_7 [24], $i\text{-C}_3\text{H}_7$ [25], C_4H_9 [26], and $\text{CH}_2\text{CH} = \text{CH}_2$ [27] or $\text{R}_2 = (\text{CH}_2)_4$ [28], $(\text{CH}_2)_6$ [29], CH_3 and C_2H_5 , CH_3 and C_3H_7 , CH_3 and $i\text{-C}_3\text{H}_7$, CH_3 and C_4H_9 [30], and C_2H_5 and *cyclo*- C_6H_{11} [31]), in which the dithiocarbamate ligands are structurally non-equivalent in pairs. Two of them, namely, terminal bidentate ligands, form four-membered chelate rings $[\text{ZnS}_2\text{C}]$, while the other two (bridging ligands) connect the adjacent Zn atoms. The resulting dimer includes an

elongated nonplanar eight-membered chelate ring $[\text{Zn}_2\text{S}_4\text{C}_2]$ in the chair [21–25, 27–31] or tub conformation [19, 20, 26]. The coordination polyhedron of the zinc atom is a distorted tetrahedron or a trigonal bipyramid composed of sulfur atoms. The only exception is the mononuclear dicyclohexyldithiocarbamate complex $[\text{Zn}\{\text{S}_2\text{CN}(c\text{-C}_6\text{H}_{11})_2\}_2]$ with a tetrahedral structure [31]. (The presence of the two bulky cycloalkyl substituents in the ligand makes it sterically impossible to form a binuclear molecular structure.)

However, dithiocarbamate complexes containing ligands with long-chain alkyl substituents have been poorly studied to date, although they can be of the greatest practical interest (as molecular precursors of film metal sulfides) because the molecular volatility in a vacuum increases with a lengthening of the hydrocarbon chain of a substituent.

The goal of this study was to obtain nickel(II), zinc(II), and copper(II) complexes with diisobutyl- and dibutyldithiocarbamate and compare their structural organizations.

EXPERIMENTAL

Nickel(II) and zinc(II) complexes with dibutyl- (BDtc) and diisobutyldithiocarbamate (*i*-BDtc) **I–III** were obtained by reactions of aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 with the corresponding sodium dithio-

carbamates used in a stoichiometric excess (~10%). The resulting voluminous precipitates were washed by decanting, filtered off, and dried in air. The complexes were additionally purified by recrystallization from organic solvents.

Synthesis of bis(*N,N*-dibutyldithiocarbamato-*S,S'*)nickel(II) [Ni{S₂CN(C₄H₉)₂}₂] (I). A solution of Na{S₂CN(C₄H₉)₂} · H₂O (4.91 g, 0.02 mol) in water (100 ml) was added to a vigorously stirred solution of NiCl₂ · 6H₂O (2.38 g, 0.01 mol) in water (100 ml). The dark green precipitate was washed by decanting, filtered off, and dried in air. Recrystallization from a mixture of anhydrous ethanol and chloroform (1 : 1) gave long dark-green acicular crystals. The yield of complex I was 90%.

For NiS₄N₂C₁₈H₃₆, [Ni(BDtc)₂] (*M* = 467.45)

anal. calcd. (%): Ni, 12.56.

Found (%): Ni, 12.11/12.02
(data for the ⁵⁸Ni/⁶⁰Ni nuclides).

Synthesis of bis(*N,N*-diisobutyldithiocarbamato-*S,S'*)nickel(II) [Ni{S₂CN(*i*-C₄H₉)₂}₂] (II). A solution of Na{S₂CN(*i*-C₄H₉)₂} · 3H₂O (5.63 g, 0.02 mol) in water (100 ml) was added to a vigorously stirred solution of NiCl₂ · 6H₂O (2.38 g, 0.01 mol) in water (100 ml). The light green precipitate was washed by decanting, filtered off, and dried in air. Recrystallization from a mixture of anhydrous ethanol and chloroform (1 : 1) gave crystals as thin light green plates. The yield of complex II was 93%.

For NiS₄N₂C₁₈H₃₆, [Ni(*i*-BDtc)₂] (*M* = 467.45)

anal. calcd. (%): Ni, 12.56.

Found (%): Ni, 12.42/12.31 (⁵⁸Ni/⁶⁰Ni).

Synthesis of zinc diisobutyldithiocarbamate III composed of binuclear molecules of bis[μ-(*N,N*-diisobutyldithiocarbamato-*S,S,S'*)(*N,N*-diisobutyldithiocarbamato-*S,S'*)zinc(II)] [Zn₂{S₂CN(*i*-C₄H₉)₂}₄] and mononuclear molecules of bis(*N,N*-diisobutyldithiocarbamato-*S,S'*)zinc(II) [Zn{S₂CN(*i*-C₄H₉)₂}₂]. A solution of Na{S₂CN(*i*-C₄H₉)₂} · 3H₂O (5.63 g, 0.02 mol) in water (50 ml) was added to a vigorously stirred solution of ZnCl₂ (1.36 g, 0.01 mol) in water (100 ml). The reaction mixture was stirred with a magnetic stirrer to give a light brown oily product that rapidly crystallized in air. The reaction mixture was left overnight. The resulting white finely crystalline precipitate was filtered off, washed with water, and dried in air. Both products were spectrally identical. The total yield of complex III was 79%. For X-ray diffraction

analysis, single crystals of complex III were obtained from anhydrous ethanol.

For Zn₃S₁₂N₆C₅₄H₁₀₈, [Zn(BDtc)₂][Zn₂(BDtc)₄]
(*M* = 1422.42)

anal. calcd. Zn, 13.79.

Found (%): Zn, 13.62/13.48 (⁶⁴Zn/⁶⁶Zn).

For EPR studies, isotope-substituted copper(II) complexes were obtained as described for complexes I–III but in a magnetically diluted state (Cu : M = 1 : 1000) from isotope-enriched cupric salts with a copper content of 99.3(1) at % for ⁶³Cu and 99.2(1) at % for ⁶⁵Cu.

EPR spectra were recorded on a 70-02 XD/1 radio spectrometer (~9.5 GHz; MP SZ, Minsk) at ~295 K. The operating frequency was measured with a ChZ-46 microwave frequency meter. *g* Factors were calculated with reference to DPPH. The error in the determination of *g* factors was ±0.002; hyperfine structure (HFS) constants are given in oersteds (Oe) to within ±2%. EPR spectra were modeled at the MP2 level with the WIN-EPR SimFonia program (Bruker Co. software, version 1.2). During the fitting of model spectra to experimental ones, *g* factors, HFS constants, resonance line widths, and contributions (in percent) from the Lorentz and Gauss components to the line shape were varied.

¹³C and ¹⁵N MAS NMR spectra were recorded on a CMX-360 pulse spectrometer (Chemagnetics Infinity Co.) operating at 90.52 and 36.48 MHz, respectively (superconducting magnet with *B*₀ = 8.46 T; Fourier transform). The ¹H–¹³C and ¹H–¹⁵N cross polarization techniques were used. The ¹³C–¹H and ¹⁵N–¹H dipolar interactions were suppressed via proton decoupling in a magnetic field with the corresponding proton resonance frequency [32]. Samples (~350 mg) of the complexes were packed into ZrO₂ rotors 7.5 mm in diameter. The spinning rates in ¹³C/¹⁵N MAS NMR experiments were 3400 to 5000/2600 to 3100(1) Hz; the excitation pulse duration was 4.5 to 5.0/5.0 μs; the pulses were spaced at 2.0/2.0 to 2.5 s. Because of the relatively low natural contents of the ¹³C/¹⁵N nuclides (1.108/0.365 at %), the spectra accumulation technique was used: the number of scans was 460 to 3000/2200 to 20 600.

Isotropic ¹³C and ¹⁵N chemical shifts δ (ppm) are referenced to a line of crystalline adamantane used as the external standard (δ 38.56 ppm relative to tetramethylsilane [33]) and crystalline NH₄Cl (δ 0 ppm; –341 ppm on the absolute scale [34, 35]). The width of a reference line (2.4 Hz) for crystalline adamantane was used to check the uniformity of the magnetic field. The δ values were corrected for drift of the magnetic field strength during the measurements (its frequency equivalent for ¹³C/¹⁵N nuclei was 0.050/0.017 Hz/h). Chemical shifts and integrated intensity ratios for overlapping signals in

Table 1. Selected crystallographic parameters and a summary of data collection and refinement for structure **III**

Parameter	Value
Empirical formula	C ₅₄ H ₁₀₈ N ₆ S ₁₂ Zn ₃
<i>M</i>	1422.29
Crystal system	Orthorhombic
<i>a</i> , <i>b</i> , <i>c</i> , Å	38.220(4), 9.341(1), 21.288(2)
$\alpha = \beta = \gamma$, deg	90°
<i>V</i> , Å ³	7600(1)
<i>Z</i>	4
Space group	<i>Pna</i> 2 ₁
ρ (calcd), g/cm ³	1.243
<i>T</i> , K	295(2)
Wave length (MoK α), Å	0.71073
Crystal size, mm	Prism (0.08 × 0.15 × 0.25)
θ scan range, deg	3.06–23.29
Ranges of <i>h</i> , <i>k</i> , <i>l</i> indices	–42 ≤ <i>h</i> ≤ 42, –5 ≤ <i>k</i> ≤ 10, –21 ≤ <i>l</i> ≤ 23
Number of measured reflections	28977
Number of independent reflections	10284
<i>R</i> _{int}	0.0933
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	4547
Refinement method	full-matrix least squares on <i>F</i> ²
Number of parameters refined	700
<i>R</i> factors for <i>F</i> ² > 2 σ (<i>F</i> ²)	<i>R</i> ₁ = 0.0408, <i>wR</i> ₂ = 0.0516
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.1160, <i>wR</i> ₂ = 0.0609
GOOF	0.649
Residual electron density (min/max), e/Å ³	–0.248/0.348

the ¹³C NMR spectra were additionally refined by fragment-by-fragment mathematical modeling with consideration of the line positions and widths and the contributions from the Lorentz and Gauss components to the line shapes.

X-ray diffraction analysis of complex **III** was performed on a SMART 1000 CCD diffractometer (MoK α radiation, graphite monochromator; crystal–detector distance 45 mm) with an edged single crystal. Reflections were collected in sets composed of 906, 660, and

345 frames for $\varphi = 0^\circ, 90^\circ, \text{ and } 180^\circ$, respectively; ω scanning was carried out at a scan step of 0.2° and a frame exposure time of 10 s. Absorption correction was applied from equivalent reflections. The structure was solved by the direct method and refined by the least-squares method in isotropic approximation for the C(17) and C(18) atoms and in anisotropic approximation for the rest of non-hydrogen atoms. The hydrogen atoms were located geometrically and refined in the rider model, except for the HC(17) and HC(18) protons

Table 2. Coordinates and isotropic equivalent thermal parameters U_{equiv} of the non-hydrogen atoms for structure **III**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}, \text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}, \text{\AA}^2$
Zn(1)	0.83641(1)	0.86993(6)	0.59880(2)	0.0617(2)	C(18)	0.9914(1)	1.1330(6)	0.5488(2)	0.139(3)
Zn(2)	0.91623(1)	0.69746(6)	0.64503(2)	0.0617(2)	C(19)	0.8520(1)	0.5310(4)	0.6094(2)	0.053(2)
Zn(3)	0.62494(2)	0.29711(7)	0.62096(3)	0.0722(2)	C(20)	0.8169(1)	0.3314(4)	0.6462(2)	0.066(2)
S(1)	0.79186(3)	0.8245(2)	0.67148(5)	0.0699(5)	C(21)	0.7972(1)	0.3796(5)	0.7055(2)	0.071(2)
S(2)	0.78173(3)	0.9109(2)	0.53999(6)	0.0735(5)	C(22)	0.7979(1)	0.2570(5)	0.7529(2)	0.107(2)
S(3)	0.87367(3)	0.10558(1)	0.57079(5)	0.0668(5)	C(23)	0.7595(1)	0.4255(5)	0.6920(2)	0.110(2)
S(4)	0.89083(3)	0.9070(1)	0.68967(5)	0.0626(4)	C(24)	0.8003(1)	0.4576(5)	0.5475(2)	0.067(2)
S(5)	0.87846(3)	0.5126(1)	0.67336(5)	0.0654(5)	C(25)	0.8048(1)	0.3378(5)	0.4982(2)	0.077(2)
S(6)	0.86301(3)	0.6626(1)	0.55453(5)	0.0603(4)	C(26)	0.7732(1)	0.3405(6)	0.4555(2)	0.126(3)
S(7)	0.96981(3)	0.6450(1)	0.70487(6)	0.0733(5)	C(27)	0.8382(1)	0.3491(5)	0.4611(2)	0.098(2)
S(8)	0.96202(3)	0.7359(2)	0.57409(5)	0.0737(5)	C(28)	0.9889(1)	0.7002(5)	0.6362(2)	0.057(2)
S(9)	0.65108(3)	0.4230(1)	0.70371(5)	0.0711(5)	C(29)	1.0469(1)	0.6813(5)	0.6860(2)	0.074(2)
S(10)	0.60253(3)	0.1794(1)	0.70978(6)	0.0778(5)	C(30)	1.0596(2)	0.8059(7)	0.7203(3)	0.200(4)
S(11)	0.59362(3)	0.3951(1)	0.53712(5)	0.0705(5)	C(31)	1.0818(2)	0.7612(7)	0.7724(3)	0.179(3)
S(12)	0.65260(3)	0.1933(2)	0.53413(6)	0.0762(5)	C(32)	1.0471(1)	0.9387(6)	0.7176(3)	0.142(3)
N(1)	0.7299(1)	0.8287(3)	0.6151(1)	0.053(1)	C(33)	1.0413(1)	0.7546(5)	0.5707(2)	0.076(2)
N(2)	0.9280(1)	0.11262(3)	0.6410(2)	0.056(1)	C(34)	1.0565(2)	0.6361(6)	0.5354(3)	0.231(4)
N(3)	0.8243(1)	0.4443(3)	0.6012(2)	0.051(1)	C(35)	1.0540(2)	0.5055(6)	0.5402(3)	0.190(4)
N(4)	1.0239(1)	0.7112(4)	0.6329(2)	0.062(1)	C(36)	1.0699(2)	0.7052(7)	0.4727(3)	0.229(4)
N(5)	0.6303(1)	0.3030(4)	0.8113(1)	0.059(1)	C(37)	0.6283(1)	0.3026(5)	0.7478(2)	0.058(2)
N(6)	0.6196(1)	0.2864(4)	0.4310(2)	0.054(1)	C(38)	0.6103(1)	0.1985(5)	0.8484(2)	0.066(2)
C(1)	0.7635(1)	0.8525(4)	0.6092(2)	0.055(2)	C(39)	0.5732(1)	0.2488(5)	0.8622(2)	0.086(2)
C(2)	0.7133(1)	0.7880(5)	0.6743(2)	0.068(2)	C(40)	0.5537(1)	0.1266(6)	0.8938(2)	0.128(2)
C(3)	0.6913(1)	0.9085(5)	0.7047(2)	0.098(2)	C(41)	0.5715(1)	0.3849(6)	0.9026(2)	0.126(2)
C(4)	0.7071(1)	1.0462(5)	0.7054(3)	0.138(3)	C(42)	0.6536(1)	0.4002(5)	0.8423(2)	0.068(2)
C(5)	0.6791(1)	0.8573(6)	0.7683(2)	0.135(3)	C(43)	0.6922(1)	0.3584(5)	0.8437(2)	0.081(2)
C(6)	0.7059(1)	0.8611(5)	0.5605(2)	0.070(2)	C(44)	0.6983(1)	0.2217(5)	0.8775(2)	0.103(2)
C(7)	0.7018(2)	0.7219(7)	0.5173(3)	0.164(3)	C(45)	0.7148(1)	0.4834(6)	0.8678(2)	0.131(2)
C(8)	0.6924(2)	0.5912(6)	0.5402(3)	0.150(3)	C(46)	0.6220(1)	0.2922(5)	0.4952(2)	0.052(2)
C(9)	0.6842(2)	0.7724(7)	0.4563(3)	0.182(3)	C(47)	0.5919(1)	0.3618(5)	0.3973(2)	0.064(2)
C(10)	0.9009(1)	1.0388(4)	0.6348(2)	0.050(2)	C(48)	0.5567(1)	0.2828(5)	0.3971(2)	0.077(2)
C(11)	0.9520(1)	1.1196(5)	0.6944(2)	0.072(2)	C(49)	0.5297(1)	0.3772(6)	0.3648(2)	0.111(2)
C(12)	0.9471(1)	1.2429(5)	0.7414(2)	0.082(2)	C(50)	0.5592(2)	0.1357(6)	0.3646(2)	0.125(3)
C(13)	0.9138(1)	1.2262(5)	0.7786(2)	0.105(2)	C(51)	0.6441(1)	0.2013(5)	0.3935(2)	0.074(2)
C(14)	0.9799(1)	1.2555(6)	0.7836(2)	0.130(2)	C(52)	0.6782(1)	0.2799(6)	0.3776(2)	0.094(2)
C(15)	0.9355(1)	1.2371(4)	0.5923(2)	0.063(2)	C(53)	0.6753(1)	0.4223(6)	0.3485(2)	0.117(3)
C(16)	0.9548(1)	1.1830(5)	0.5362(2)	0.082(2)	C(54)	0.7020(2)	0.1793(7)	0.3431(2)	0.143(3)
C(17)	0.9532(1)	1.3032(5)	0.4855(2)	0.133(3)					

Table 3. Bond lengths d and angles ω in structure **III***

Bond	d , Å	Bond	d , Å	Angle	ω , deg	Angle	ω , deg
Binuclear molecule				Bridging ligands		Terminal ligands	
Bridging ligands		Terminal ligands		S(3)Zn(1)S(4)	68.75(4)	S(1)Zn(1)S(2)	75.35(4)
Zn(1)–S(3)	2.323(1)	Zn(1)–S(1)	2.340(1)	S(3)Zn(1)S(6)	104.15(5)	S(8)Zn(2)S(7)	75.06(4)
Zn(1)–S(4)	2.862(1)	Zn(1)–S(2)	2.466(1)	S(4)Zn(1)S(6)	93.18(4)	C(1)S(1)Zn(1)	85.5(1)
Zn(1)–S(6)	2.382(1)	Zn(2)–S(7)	2.461(1)	S(4)Zn(2)S(6)	94.22(4)	C(1)S(2)Zn(1)	82.0(1)
Zn(2)–S(4)	2.382(1)	Zn(2)–S(8)	2.339(1)	S(5)Zn(2)S(4)	104.65(5)	C(28)S(7)Zn(2)	81.6(2)
Zn(2)–S(5)	2.330(1)	S(1)–C(1)	1.734(4)	S(5)Zn(2)S(6)	69.17(4)	C(28)S(8)Zn(2)	85.5(2)
Zn(2)–S(6)	2.821(1)	S(2)–C(1)	1.718(4)	C(10)S(3)Zn(1)	95.6(1)	C(1)N(1)C(2)	123.6(3)
S(3)–C(10)	1.721(4)	S(7)–C(28)	1.713(4)	C(19)S(6)Zn(1)	101.8(1)	C(1)N(1)C(6)	120.1(3)
S(4)–C(10)	1.740(4)	S(8)–C(28)	1.709(4)	C(10)S(4)Zn(2)	102.9(1)	C(2)N(1)C(6)	116.2(3)
S(5)–C(19)	1.704(4)	N(1)–C(1)	1.309(4)	C(19)S(5)Zn(2)	94.9(2)	C(28)N(4)C(29)	123.0(4)
S(6)–C(19)	1.747(4)	N(1)–C(2)	1.461(5)	C(19)S(6)Zn(2)	78.3(1)	C(28)N(4)C(33)	119.8(4)
N(2)–C(10)	1.327(4)	N(1)–C(6)	1.497(5)	Zn(1)S(6)Zn(2)	86.77(4)	C(29)N(4)C(33)	117.1(3)
N(2)–C(11)	1.462(5)	N(4)–C(28)	1.340(5)	C(10)N(2)C(11)	122.8(3)	N(1)C(1)S(1)	120.9(3)
N(2)–C(15)	1.493(5)	N(4)–C(29)	1.457(5)	C(10)N(2)C(15)	120.5(3)	N(1)C(1)S(2)	122.4(3)
N(3)–C(19)	1.345(4)	N(4)–C(33)	1.539(5)	C(11)N(2)C(15)	116.7(3)	N(4)C(28)S(7)	119.5(3)
N(3)–C(20)	1.452(5)			C(19)N(3)C(20)	120.3(3)	N(4)C(28)S(8)	122.9(3)
N(3)–C(24)	1.470(5)			C(19)N(3)C(24)	122.8(3)	S(2)C(1)S(1)	116.7(2)
				C(20)N(3)C(24)	116.9(3)	S(8)C(28)S(7)	117.5(2)
Mononuclear molecule							
Zn(3)–S(9)	2.342(1)	S(12)–C(46)	1.706(4)	N(2)C(10)S(3)	119.6(3)		
Zn(3)–S(10)	2.349(1)	N(5)–C(37)	1.352(5)	N(2)C(10)S(4)	122.7(3)		
Zn(3)–S(11)	2.336(1)	N(5)–C(38)	1.471(5)	N(3)C(19)S(5)	120.7(3)		
Zn(3)–S(12)	2.340(1)	N(5)–C(42)	1.433(5)	N(3)C(19)S(6)	121.7(3)		
S(9)–C(37)	1.703(4)	N(6)–C(46)	1.370(5)	S(3)C(10)S(4)	117.6(2)		
S(10)–C(37)	1.719(4)	N(6)–C(47)	1.461(5)	S(5)C(19)S(6)	117.5(2)		
S(11)–C(46)	1.702(4)	N(6)–C(51)	1.465(5)				
				Mononuclear molecule			
Angle	ω , deg	Angle	ω , deg	S(9)Zn(3)S(10)	77.59(5)	C(37)N(5)C(42)	119.8(3)
Binuclear molecule				S(11)Zn(3)S(9)	126.63(5)	C(42)N(5)C(38)	119.8(3)
S(1)Zn(1)S(3)	138.71(5)	S(4)Zn(2)S(7)	107.22(5)	S(11)Zn(3)S(10)	127.71(5)	C(46)N(6)C(47)	121.2(3)
S(1)Zn(1)S(4)	95.96(4)	S(4)Zn(2)S(8)	115.87(5)	S(11)Zn(3)S(12)	77.89(5)	C(46)N(6)C(51)	121.4(4)
S(1)Zn(1)S(6)	115.14(5)	S(5)Zn(2)S(7)	103.53(5)	S(12)Zn(3)S(9)	127.56(5)	C(47)N(6)C(51)	117.3(3)
S(2)Zn(1)S(3)	105.87(5)	S(5)Zn(2)S(8)	138.11(5)	S(12)Zn(3)S(10)	127.35(5)	N(5)C(37)S(9)	121.3(3)
S(2)Zn(1)S(4)	160.15(5)	S(6)Zn(2)S(7)	158.54(5)	C(37)S(9)Zn(3)	82.3(2)	N(5)C(37)S(10)	120.3(3)
S(2)Zn(1)S(6)	106.67(5)	S(6)Zn(2)S(8)	96.69(4)	C(37)S(10)Zn(3)	81.8(2)	N(6)C(46)S(11)	120.2(3)
				C(46)S(11)Zn(3)	81.6(2)	N(6)C(46)S(12)	120.6(3)
				C(46)S(12)Zn(3)	81.4(2)	S(9)C(37)S(10)	118.4(2)
				C(37)N(5)C(38)	120.4(3)	S(11)C(46)S(12)	119.2(2)

* The symmetry operation code is $-x + 1, y, -z + 1/2$.

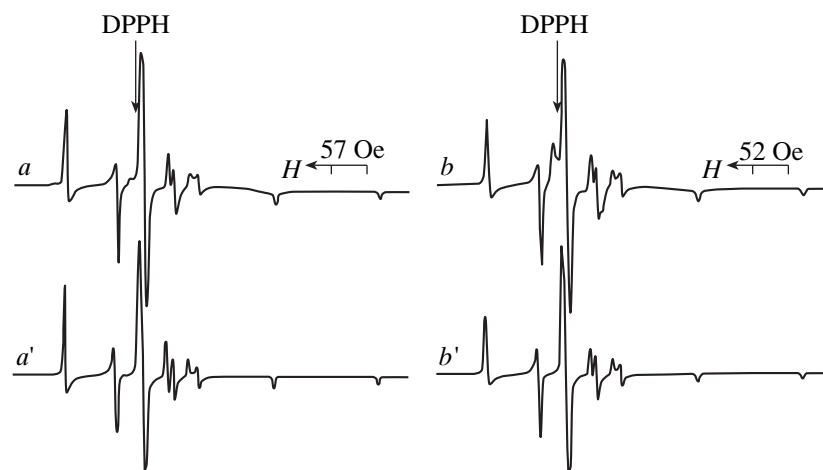


Fig. 1. (*a, b*) Experimental and (*a', b'*) simulated EPR spectra of the polycrystalline complexes (*a, a'*) $[\text{Cu}\{\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_2]$ and (*b, b'*) $[\text{Cu}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ magnetically diluted with nickel(II).

not detected from the electron-density difference map. The absolute molecular configurations were determined with the use of the Flack parameter (0.06(1)) [36]. The collected data were edited and the unit cell parameters were refined with the SMART and SAINT Plus programs [37]. All calculations for structure determination and refinement were performed with the SHELXTL/PC programs [38]. Selected crystallographic parameters and a summary of data collection are given in Table 1. Atomic coordinates are listed in Table 2. Bond lengths and angles are given in Table 3.

RESULTS AND DISCUSSION

The EPR spectra of copper(II) dibutyl- and diisobutyldithiocarbamates magnetically diluted with nickel(II) are nearly axially symmetric (Fig. 1; Table 4). However, computer modeling revealed some anisotropy of the g and A tensors in the xy plane. The spectra

show a well-resolved HFS due to ^{63}Cu or ^{65}Cu ($I = 3/2$) nuclei ($I = 3/2$) in all the three orientations and an additional high-field peak of a high intensity [39, 40] (Fig. 1). The spectral shape and the totality of the EPR parameters suggest that the nickel(II) complexes contain square-planar chromophores $[\text{CuS}_4]$ (sp^2d -hybridization state of copper(II): $s - + p_x - + p_y - + d_{x^2-y^2}$ AOs). From this viewpoint, the observed anisotropy of the EPR parameters in the xy plane suggests some rhombic distortion of the planar square because of diagonal non-equivalence of the M–S bonds.

Thus, copper(II) in the lattices of the corresponding nickel(II) complexes forms mononuclear dithiocarbamate complexes $[\text{Cu}(\text{Dtc})_2]$, although individual copper(II) dithiocarbamates are usually binuclear [41–43] or polynuclear [44]. (Mononuclear copper(II) dithiocarbamates can be obtained in the individual state only when dithiocarbamate ligands contain bulky alkyl sub-

Table 4. EPR parameters of magnetically diluted copper(II) dithiocarbamates

Complex	g_1	$A_1^{\text{Cu}*}$	g_2	$A_2^{\text{Cu}*}$	g_3	$A_3^{\text{Cu}*}$
$[\text{Cu}/\text{Ni}\{\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_2]$	2.086	159/170	2.023	41/44	2.020	38/41
$[\text{Cu}/\text{Ni}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$	2.086	161/172	2.024	41/44	2.019	38/41
$[\text{CuZn}\{\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_4]$	2.109	136/146	2.039	33/35	2.027	18/19
$[\text{Cu}/\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$	2.087	157/168	2.026	44/47	2.019	29/31
$[\text{CuZn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$	2.107	140/150	2.032	27/29	2.030	18/19

* The HFS constants are given for the $^{63}\text{Cu}/^{65}\text{Cu}$ nuclei.

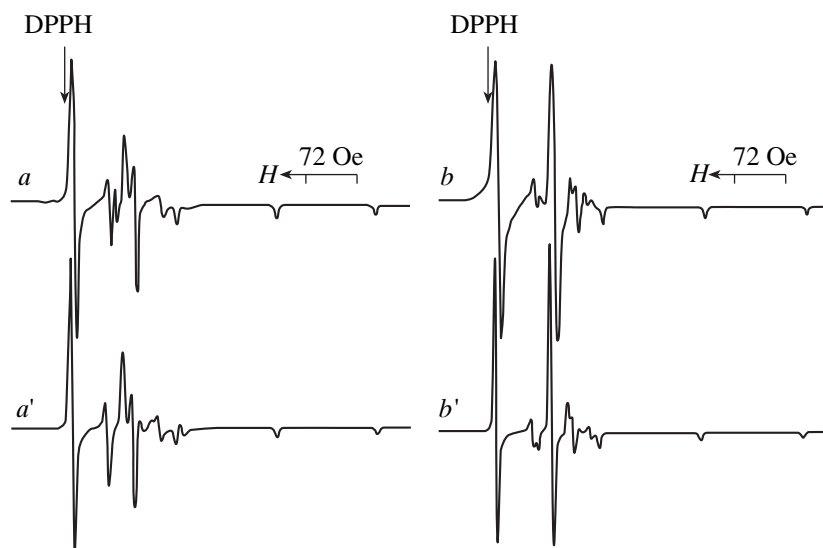


Fig. 2. (a, b) Experimental and (a', b') simulated EPR spectra of the complexes (a, a') $[\text{}^{63}\text{CuZn}\{\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_4]$ and (b, b') $[\text{}^{63}\text{CuZn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$ magnetically diluted with zinc.

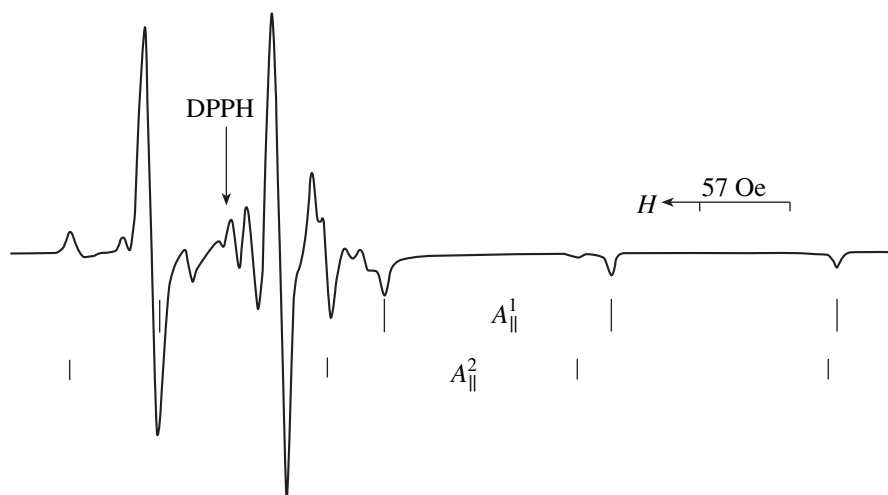


Fig. 3. The EPR spectrum of bis(diisobutyldithiocarbamato)copper(II) magnetically diluted with zinc and freshly precipitated from water.

stituents [18].) In our case, the formation and stabilization of the mononuclear complexes $[\text{Cu}(\text{Dtc})_2]$ is due to the 1000-fold dilution of the paramagnetic component with nickel(II) ($\text{Cu} : \text{Ni} = 1 : 1000$), under which the formation of complexes of any other structural types is *a fortiori* impossible for copper.

The EPR spectra of crystalline copper(II) dibutyl- and diisobutyldithiocarbamates magnetically diluted with zinc and precipitated from organic solvents show triaxial anisotropy of the EPR parameters (Fig. 2; Table 4). In addition, the spectra of samples precipi-

tated from an aqueous phase contain a set of low-intensity signals (Fig. 3) suggesting the presence of copper(II) in two magnetically nonequivalent positions. The EPR parameters were refined by computer simulation (Fig. 2; Table 4). In the former case, the pronounced triaxial anisotropy of the EPR parameters reflects the nonplanar structure of the copper(II) polyhedron as the result of the formation of heterobinuclear complexes $[\text{CuZn}(\text{Dtc})_4]$ in magnetically diluted systems. According to [45–52], such dimers are formed in the reaction of a paramagnetic component with a dia-

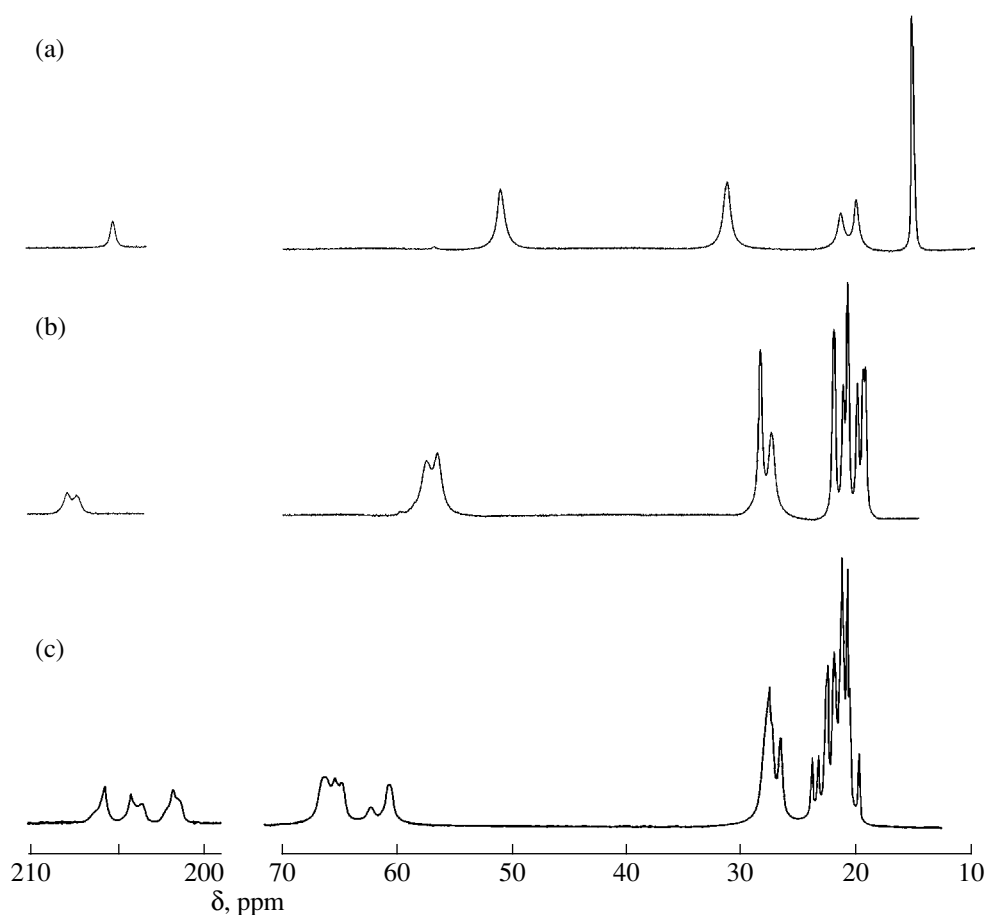


Fig. 4. The ^{13}C CP/MAS NMR spectra (295 K) of the polycrystalline nickel $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} =$ (a) C_4H_9 and (b) $i\text{-C}_4\text{H}_9$) and (c) zinc complexes $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2][\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$; the number of scans/spinning rate (Hz) is (a) 460/3700, (b) 1504/3400, and (c) 3000/5000.

magnetic matrix. In this case, the geometry of the nearest environment $[\text{S}_5]$ of the complexing metal is intermediate between a tetragonal pyramid and a trigonal bipyramid. The EPR parameters of the second paramagnetic center correspond to axial symmetry (Table 4) and are numerically close to those for mononuclear copper(II) dithiocarbamates in the nickel(II) lattice. The slight increase in the g factors and the simultaneous decrease in the HFS constants can be explained by some distortion of the chromophore $[\text{CuS}_4]$.

Thus, in the magnetically diluted complexes studied, copper(II) forms both mononuclear $[\text{Cu}(\text{Dtc})_2]$ and particularly heterobinuclear $[\text{CuZn}(\text{Dtc})_4]$ molecules (Table 4), as is evident from the substantially higher intensity of the former set of resonance signals.

The experimental ^{13}C and ^{15}N CP/MAS NMR spectra of complexes **I–III** suggest their individualities (Figs. 4, 5). In the ^{13}C and ^{15}N NMR spectra of complex **I**, the $=\text{NC}(\text{S})\text{S}-$ groups appear as single reso-

nance signals (Figs. 4a, 5a; Table 5) because of the centrosymmetric character of the molecular structure $[\text{Ni}\{\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2\}_2]$ [10]. On the contrary, the respective signals in the ^{13}C and ^{15}N NMR spectra of complex **II** are 1 : 1 doublets, which is due to the structural nonequivalence of the $=\text{NC}(\text{S})\text{S}-$ groups in $[\text{Ni}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ (Figs. 4b, 5b). According to the X-ray diffraction data, the unit cell of complex **II** includes two types of structurally nonequivalent centrosymmetric molecules $[\text{Ni}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ [11] and the ligand nonequivalence is of the intermolecular character.

Among the zinc complexes studied by us in [26], zinc diisobutyldithiocarbamate is characterized by an unusual ^{13}C NMR spectrum (Fig. 4c) containing resonance signals for the $=\text{NC}(\text{S})\text{S}-$, $=\text{NCH}_2-$, $=\text{CH}-$, and $-\text{CH}_3$ groups (Table 5). The first set of signals with the intensity ratio 2 : 1 : 1 : 1 is most informative, which suggests the presence of six nonequivalent dithiocarbamate groups in that complex. For this reason, the character of the ^{15}N NMR spectrum (Fig. 5c) showing

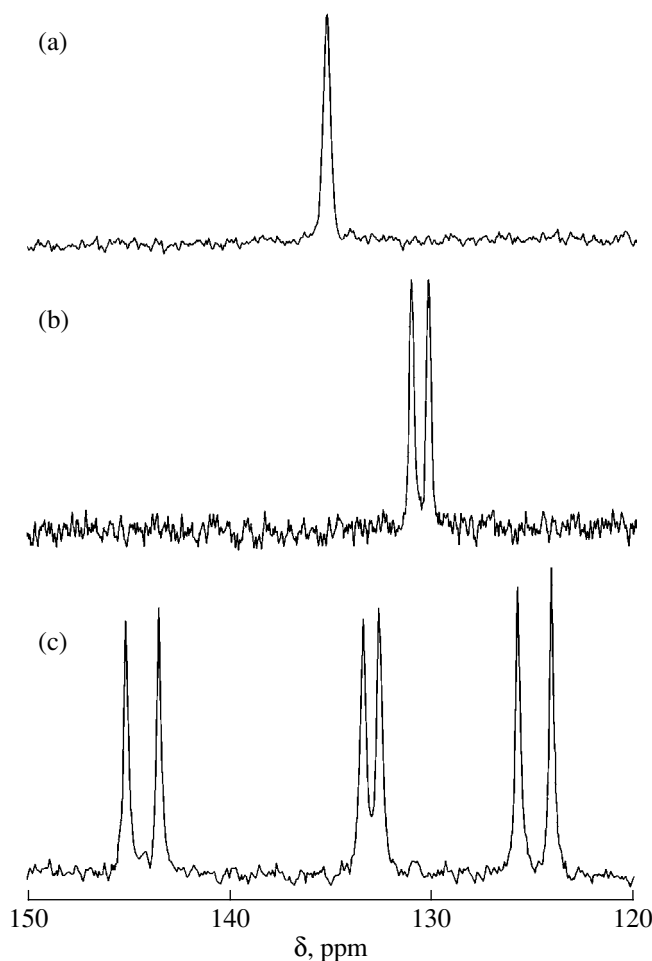


Fig. 5. The ^{15}N CP/MAS NMR spectra (295 K) of the polycrystalline nickel $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} =$ (a) C_4H_9 and (b) $i\text{-C}_4\text{H}_9$) and (c) zinc complexes $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2][\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$; the number of scans/spinning rate (Hz) is (a) 2200/2600, (b) 2500/3100, and (c) 20 600/3000.

six resonance signals (1 : 1 : 1 : 1 : 1 : 1) is quite expected. It is worth noting that recording of ^{15}N NMR spectra of melted complex **III** (tending to be overcooled) during slow crystallization revealed different accumulation rates of two terminal doublets with respect to the intermediate doublet.

The latter fact is direct evidence of molecular entities of two types of structure in the complex under consideration. Hence, its ^{13}C and ^{15}N NMR spectra can be interpreted as a combination of the binuclear and mononuclear forms with six structurally nonequivalent ligands. The terminal doublets in the ^{15}N NMR spectrum were assigned to the binuclear form because an analogous spectral nonequivalence of the terminal and bridging ligands was observed in [26] for $[\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$ (Table 5). The assignment of the intermediate doublet in the ^{15}N NMR spectrum of zinc diisobutyldithiocarbamate to the mononuclear form was confirmed by ^{15}N NMR data for the complex

$[\text{Ni}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ including only terminal ligands (Table 5). Thus, according to the NMR data, the mononuclear and binuclear forms of complex **III** coexist in the 1 : 1 ratio.

To verify the correctness of our structural conclusions, the structure of complex **III** was determined from X-ray diffraction data.

Description of the molecular structures of $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ and $[\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$. The structural organization of zinc diisobutyldithiocarbamate is determined by the coexistence of its mononuclear $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$ and binuclear forms $[\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$ (Fig. 6; Table 3). In the unit cell of complex **III**, four structurally equivalent mononuclear molecules alternate with four binuclear ones (Fig. 7). In $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2]$, zinc coordinates two Dtc ligands in a bidentate manner to form planar four-membered chelate rings $[\text{ZnS}_2\text{C}]$. The coordination polyhedron of the zinc atom is a distorted tetrahe-

Table 5. Isotropic ^{13}C and ^{15}N chemical shifts δ (ppm) for nickel(II) and zinc(II) complexes with reference to TMS (^{13}C) and NH_4Cl (^{15}N)

Complex	^{13}C					^{15}N
	–S(S)CN=	=N–CH ₂ –	–CH ₂ –	–CH=	–CH ₃	=N–
[Ni{S ₂ CN(C ₄ H ₉) ₂ }] ₂	205.6	51.2	31.4, 21.6, 20.3		15.3	135.2
Na{S ₂ CN(C ₄ H ₉) ₂ } · H ₂ O	208.3	55.2	30.0 21.0		15.6, 14.9, 14.5 (2 : 1 : 1)	
[Zn ₂ {S ₂ CN(<i>i</i> -C ₄ H ₉) ₂ }] ₄	204.3, 203.7, 201.9 (34)*, 201.6	66.4, 66.2, 65.4, 64.8		28.3, 28.0 27.9, 27.8	24.0, 23.5 22.8, 22.7 22.2, 22.1 22.0, 21.5	145.2, 143.5, 125.8, 124.1 (1 : 1 : 1 : 1)
[Zn{S ₂ CN(<i>i</i> -C ₄ H ₉) ₂ }] ₂	205.8 (40)*	62.3, 60.7 (1 : 3)		27.5, 26.8	21.3, 21.0 20.8, 20.0	133.4, 132.6 (1 : 1)
[Ni{S ₂ CN(<i>i</i> -C ₄ H ₉) ₂ }] ₂	208.1, 207.5 (1 : 1)	57.6, 56.7 (1 : 1)		28.6, 27.6 (1 : 1)	22.2, 21.4 21.0, 20.2 19.7, 19.5 (2 : 1 : 2 : 1 : 1 : 1)	131.1, 130.3 (1 : 1)
Na{S ₂ CN(<i>i</i> -C ₄ H ₉) ₂ } · 3H ₂ O	208.2	66.7		28.0, 27.1 (1 : 1)	23.0, 22.4, 20.8 (1 : 1 : 2)	

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

dron made up of four S atoms. The angle between the chelate ring planes is nearly right (89.36°). The binuclear molecule is formed when adjacent Zn atoms are connected by two bridging ligands. Two other (terminal) ligands in the dimer form the same four-membered chelate rings as in the monomer molecule. As expected from the ^{13}C and ^{15}N NMR data, the Dtc ligands in both molecules are structurally nonequivalent. In all cases, the coordination is anisobidentate since one Zn–S bond is noticeably shorter than the other (although, on the whole, the bridging ligands are bound to zinc more strongly than are the terminal ligands (Table 3)).

In all ligands, the C₂NC(S)S groups are virtually planar, which suggests a substantial contribution from the double bond to the formally single N–C(S)S bond. In the binuclear molecule, the Zn atoms are surrounded by four relatively strongly bound S atoms (2.323–2.466 Å) forming, to a first approximation, a distorted tetrahedron. The distances between the Zn

atoms and the more distant S(6) and S(4) atoms are 2.821 and 2.862 Å, respectively. Insofar as these values are lower than the sum of the van der Waals radii of the Zn and S atoms [53], there exists a fifth, relatively weak Zn–S bond (C.N.(Zn) 5). The coordination polyhedra of zinc are intermediate between a tetragonal pyramid (TP) and a trigonal bipyramid (TBP). For quantitative characterization of the polyhedral geometry in metal complexes with C.N. 5, the parameter $\tau = (\alpha - \beta)/60$ was proposed in [54]; in our case, α and β are the values of the two largest SZnS angles ($\alpha > \beta$). For an idealized TP (C_{4v}) τ is zero since $\alpha = \beta$. In a regular TBP (C_{3v}), the axial SZnS angle (α) equals 180°, while the equatorial $\beta = 120^\circ$; i.e., $\tau = 1$. Any distorted polyhedra are described by $0 < \tau < 1$. For the Zn(1) and Zn(2) atoms, $\tau = 0.357$ and 0.341, respectively. Thus, the contribution from the TBP to the polyhedral geometry is somewhat more appreciable for Zn(1) than for Zn(2): in these cases, the ratios of the contributions of TBP (TP) are 35.7 (64.3) and 34.1 (65.9%), respectively.

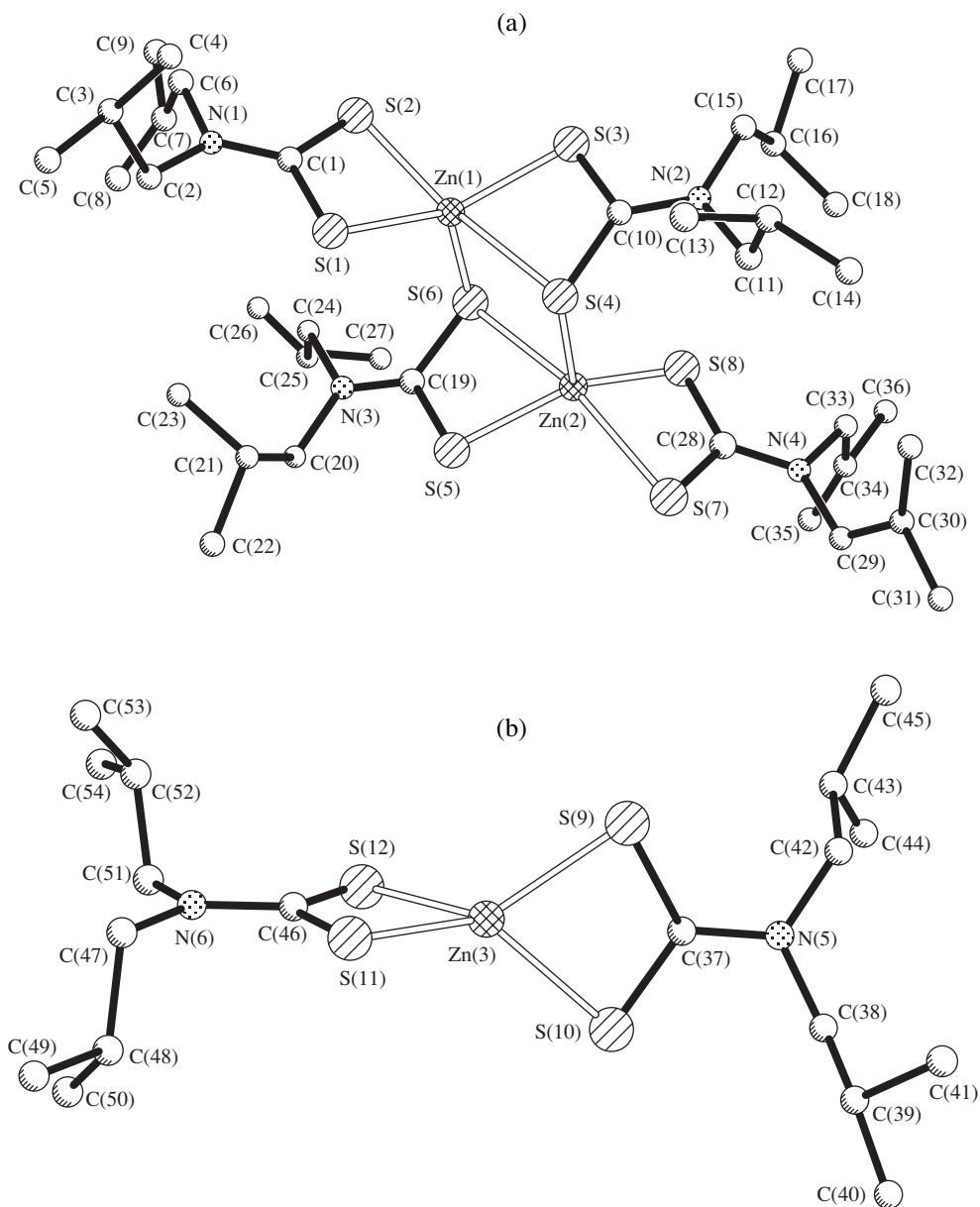


Fig. 6. Molecular structures of (a) the binuclear and (b) mononuclear forms of the complex $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2][\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$.

In the distorted TBPs, the three most strongly bound S atoms lie in the equatorial plane, while the more distant S atoms are in the axial positions. The SZnS bond angles in the equatorial planes of the TBP (Zn(1): 138.71° , 115.14° , and 104.15° ; Zn(2): 138.11° , 115.87° , and 104.65°) differ noticeably from 120° ; the axial $\text{S}_{\text{ax}}\text{ZnS}_{\text{ax}}$ angles are 160.14° for Zn(1) and 158.54° for Zn(2). To a first approximation, the binuclear molecule is centrosymmetric; the Zn–Zn distance is $3.5876(7)$ Å.

In the molecules of both structural types, the four-membered chelate rings $[\text{ZnS}_2\text{C}]$ are characterized by short Zn–C distances (2.681 – 2.802 Å), which are

longer than the Zn–S bonds only by $\sim 15\%$. In turn, the distance between the opposite S atoms is 2.926 to 2.939 Å, thus forming the longer axis of the rhombus. The configuration of the four-membered chelate ring allows the *trans*-annular effect to appear. In contrast, the geometry of the elongated eight-membered chelate ring $[\text{Zn}_2\text{S}_4\text{C}_2]$, which is nonplanar as most dithiocarbamate complexes, can be approximately described by the chair conformation.

A comparison of the data obtained for nickel(II) and zinc(II) dibutyl- and diisobutyldithiocarbamates makes it possible to conclude that branched alkyl substituents

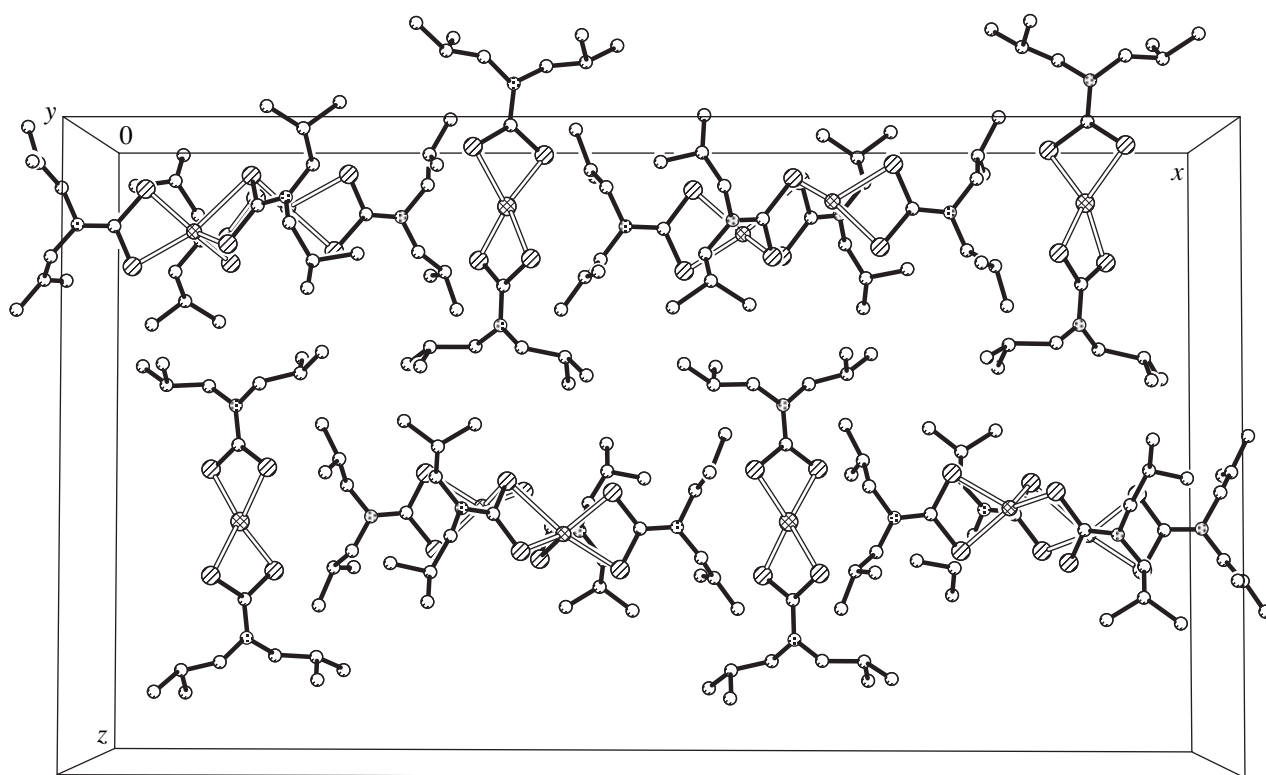


Fig. 7. Crystal structure of $[\text{Zn}\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_2][\text{Zn}_2\{\text{S}_2\text{CN}(i\text{-C}_4\text{H}_9)_2\}_4]$ (projection onto the xz plane).

at the N atom favor isomerism in coordination compounds.

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