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CHEMISTRY

Single-Crystal X-ray Diffraction and CP/MAS ^{13}C and ^{15}N NMR Study of Zinc *N,N*-Di-*iso*-butyldithiocarbamate Complex: A Unique Structural Organization

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Most zinc dithiocarbamate complexes have binuclear molecular structures: $[Zn_2(S_2CNR_2)_4]$ (R = CH_3 [1], C_2H_5 [2], C_3H_7 [3], *iso*-C_3H_7 [4], C_4H_9 [5]; or R_2 = $(CH_2)_4$ [6]; R_2 = $(CH_2)_6$ [7]; R_2 = (CH_3, C_2H_5), (CH_3, C_3H_7), $(CH_3$, *iso*-$C_3H_7)$, (CH_3, C_4H_9) [8]; R_2 = $(C_2H_5$, *cyclo*-$C_6H_{11})$ [9]). In these compounds, pairs of ligands have different structural functions: bidentate chelating and bridging. The former ligands are involved in planar four-membered metallacycles ZnS_2C, whereas the other two ligands act as bridges that link neighboring zinc atoms into a dimer, which results in the formation of an extended nonplanar eight-membered $Zn_2S_4C_2$ metallacycle (a chair [2–10] or boat [1, 5] conformation). Therefore, each zinc atom has a distorted tetrahedral or trigonal-bipyramidal environment of four or five sulfur atoms. The only exception is the mononuclear dicyclohexyldithiocarbamate complex $[Zn\{S_2CN($*cyclo*-$C_6H_{11})_2\}_2]$, with a tetrahedral structure [9]. The presence of two bulky cyclic alkyl substituents in the ligand renders the formation of the binuclear molecular structure sterically impossible.

In this work, we pioneered the synthesis of a zinc dithiocarbamate complex with a unique structural organization. The latter was characterized by X-ray single-crystal diffraction and CP/MAS ^{13}C and ^{15}N NMR data. The unit cell of this complex concurrently contains mono- and binuclear molecular species in a 1 : 1 ratio. In both types of molecules, all six dithiocarbamate ligands are structurally and NMR nonequivalent.

The complex with the composition $Zn_3S_{12}N_6C_{54}H_{108}$ (compound **I**), composed of binuclear molecules of bis[μ-(*N,N*-di-*iso*-butyldithiocarbamato-*S,S*')(*N,N*-di-*iso*-butyldithiocarbamato-*S,s*')zinc(II)], $[Zn_2\{S_2CN($*iso*-$C_4H_9)_2\}_4]$, and mononuclear molecules of bis(*N,N*-di-*iso*-butyldithiocarbamato-*S,S*')zinc(II), $[Zn\{S_2CN($*iso*-$C_4H_9)_2\}_2]$, was prepared by reacting aqueous solutions of $ZnCl_2$ and $Na\{S_2CN($*iso*-$C_4H_9)_2\} \cdot 3H_2O$.[1] The resulting solid was recrystallized from absolute ethanol. ^{13}C and ^{15}N NMR spectra were recorded on a Chemagnetics Infinity CMX-360 spectrometer operating at 90.52 and 36.48 MHz, respectively, with a superconducting magnet (B_0 = 8.46 T) and Fourier transform. Proton cross polarization was used for recording the spectra. To suppress ^{13}C–^{1}H and ^{15}N–^{1}H dipole–dipole interactions, CW decoupling at the proton resonance frequency was used [10]. Samples of the complexes under study (~350 mg) were placed in a zirconia rotor 7.5 mm in diameter. In MAS ^{13}C/^{15}N NMR experiments, the spinning frequency was 5000/3000(1) Hz; the number of scans was 3000/20600; the proton $\pi/2$ pulse width was 5.0/5.0 μs; the ^{1}H–^{13}C/^{1}H–^{15}N contact time was 3.0/2.0 ms; and the repetition time was 2.0/2.0 s. Isotropic ^{13}C NMR chemical shifts were measured from tetramethylsilane. Isotropic ^{15}N NMR chemical shifts were measured from the signal of crystalline NH_4Cl (0 ppm; –341 ppm on the absolute scale [11]). The homogeneity of the magnetic field was monitored by measuring the width of the reference signal of crystalline adamantine with $\delta(^{13}C)$ = 38.56 ppm, which was 2.4 Hz. The ^{13}C/^{15}N chemical shifts were corrected for the magnetic field drift in the course of the experiments, which constituted 0.098/0.032 Hz/h on the frequency scale. To refine the chemical shifts and integrated intensity ratios for overlapping signals in the ^{13}C NMR spectra, spectra were simulated piecewise with allowance for the line position and width, as well as for the Lorentzian and Gaussian contributions to the line shape.

Unit cell parameters were determined and intensities of 28977 reflections (of them, 10284 unique reflections and 4547 reflections with $I > 2\sigma(I)$) were collected

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[1] Sodium di-*iso*-butyldithiocarbamate was obtained by reacting carbon disulfide with di-*iso*-butylamine in an alkaline medium. Thermal analysis shows that the solid is a crystal hydrate. The compound was additionally characterized by ^{13}C NMR (Table 1).

Table 1. ^{13}C and ^{15}N NMR chemical shifts δ (ppm) of zinc(II) complexes referenced to TMS and NH_4Cl, respectively

Complex	^{13}C				^{15}N
	–S_2CN=	=N–CH_2–	–CH=	–CH_3	=N–
[$Zn_2\{S_2CN(iso\text{-}C_4H_9)_2\}_4$]	204.3, 203.7 201.9 (34)*, 201.6 (1 : 1 : 1 : 1)	66.4, 66.2 65.4, 64.8 (1 : 1 : 1 : 1)	28.3, 28.0 27.9, 27.8	24.0, 23.5 22.8, 22.7 22.2, 22.1 22.0, 21.5 21.3, 21.0 20.8, 20.0	145.2, 143.5 125.8, 124.1 (1 : 1 : 1 : 1)
[$Zn\{S_2CN(iso\text{-}C_4H_9)_2\}_2$]	205.8 (40)*	62.3, 60.7 (1 : 3)	27.5, 26.8		133.4, 132.6 (1 : 1)
[$Ni\{S_2CN(iso\text{-}C_4H_9)_2\}_2$]	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)
[$Zn_2\{S_2CN(C_4H_9)_2\}_4$] [5]	203.4, 200.4 (34)* (1 : 1)				150.0, 131.6 (1 : 1)
$Na\{S_2CN(iso\text{-}C_4H_9)_2\} \cdot 3H_2O$ (1 : 2 : 2 : 4)	208.2	66.7	28.0, 27.1 (1 : 1)	23.0, 22.4, 20.8 (1 : 1 : 2)	

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

from a single crystal of **I** (0.08 × 0.15 × 0.25 mm) on a Bruker SMART 1000 CCD diffractometer (MoK_α radiation, graphite monochromator, crystal–detector distance 45 mm). Data were collected in series of 906, 660, and 345 frames at φ = 0, 90°, and 180°, respectively; ω scan with an increment of 0.2° and an exposure time of 10 s per frame was used. The θ range was 3.06°–23.29°. Intensity data were corrected for absorption based on equivalent reflections, $\mu(MoK_\alpha)$ = 1.304 mm^{-1}. The structure was solved by direct methods and refined by least-squares calculation in the isotropic approximation for the atoms C(17) and C(18) and in the anisotropic approximation for the remaining non-hydrogen atoms. Hydrogen atoms were introduced in geometrically calculated positions and were refined as riding on the C atoms, except for the hydrogen atoms at C(27) and C(18), which were not revealed from a difference electron-density synthesis. The refinement converged with $R1 = 0.0408$ and $wR2 = 0.0516$ ($F^2 > 2\sigma(F^2)$) at GOF = 0.649. The minimum and maximum residual electron densities were $\Delta\rho_{min}/\rho_{max}$ = –0.248/+0.348 e/Å^3. To correctly determine the absolute molecular configuration, the Flack parameter (0.06(1)) [12] was used. Data collection and editing, as well as refinement of unit cell parameters, were performed with the SMART and SAINT Plus program packages [13]. Structure solution and refinement were performed with the SHELXTL/PC program package [14]. Selected bond lengths and angles are listed in Table 2.

Crystals of **I** ($Zn_3S_{12}N_6C_{54}H_{108}$, M = 1422.42) are orthorhombic; at 295 K, a = 38.220(4) Å, b = 9.341(1) Å, c = 21.288(2) Å, $\alpha = \beta = \gamma = 90°$, V = 7600(1) Å^3, Z = 4, d_{calc} = 1.243 g/cm^3, space group $Pna2_1$. Elemental analysis for zinc was carried out by the HR-ICP-MS method (high-resolution inductively coupled plasma mass spectrometry) in the medium resolution range, $\Delta m/m \approx 4500$ (Finnigan MAT ELEMENT, Bremen, Germany).

For $Zn_3S_{12}N_6C_{54}H_{108}$ anal. calcd. (wt %): Zn, 13.79. Found (wt %): Zn, 13.62/13.48 (measured for $^{64}Zn/^{66}Zn$ nuclides).

^{13}C and ^{15}N NMR spectra. The ^{13}C NMR spectrum of the zinc complex (Fig. 1a) shows sets of signals (1 : 2 : 2 : 4) that arise from the –S(S)CN=, =NCH_2–, =CH–, and –CH_3 groups. The most informative is the first set of signals. The pattern of this set (2 : 1 : 1 : 1 : 1) indicates the presence of six magnetically nonequivalent dithiocarbamate groups in **I**. The ^{15}N NMR spectrum of **I** (Fig. 1b) is consistent with this assignment and shows six signals of equal intensity (1 : 1 : 1 : 1 : 1 : 1). Note that recording the ^{15}N NMR spectra of the melt of **I** (prone to supercooling) in the course of slow crystallization allowed us to reveal different rates of accumulation of the outer doublets with respect to the central one. This fact is direct evidence of the presence of two types of structurally different molecular forms in **I**. From this standpoint, the experimental NMR spectra can be explained by the concurrent presence of binuclear and mononuclear forms of complex **I**, in which all ligands are structurally nonequivalent. The outer ^{15}N NMR doublets were assigned to the binuclear form of the complex. Previously [5], we found an analogous pattern of ^{15}N NMR spectral nonequivalence for [$Zn_2\{S_2CN(C_4H_9)_2\}_4$] (Table 1). That the central doublet arises from the mononuclear form is supported by

Table 2. Selected bond lengths *d* (Å) and bond angles ω (deg) in the structure of $[Zn_2\{S_2CN(iso\text{-}C_4H_9)_2\}_4][Zn\{S_2CN(iso\text{-}C_4H_9)_2\}_2]$

Bond	*d*	Bond	*d*
Binuclear molecule			
Bridging ligands		Terminal ligands	
Zn(1)–S(3)	2.323(1)	Zn(1)–S(1)	2.340(1)
Zn(1)–S(4)	2.862(1)	Zn(1)–S(2)	2.466(1)
Zn(1)–S(6)	2.382(1)	Zn(2)–S(7)	2.461(1)
Zn(2)–S(4)	2.382(1)	Zn(2)–S(8)	2.339(1)
Zn(2)–S(5)	2.330(1)	S(1)–C(1)	1.734(4)
Zn(2)–S(6)	2.821(1)	S(2)–C(1)	1.718(4)
S(3)–C(10)	1.721(4)	S(7)–C(28)	1.713(4)
S(4)–C(10	1.740(4)	S(8)–C(28)	1.709(4)
S(5)–C(19)	1.704(4)	N(1)–C(1)	1.309(4)
S(6)–C(19)	1.747(4)	N(1)–C(2)	1.461(5)
N(2)–C(10)	1.327(4)	N(1)–C(6)	1.497(5)
N(2)–C(11)	1.462(5)	N(4)–C(28)	1.340(5)
N(2)–C(15)	1.493(5)	N(4)–C(29)	1.457(5)
N(3)–C(19)	1.345(4)	N(4)–C(33)	1.539(5)
N(3)–C(20)	1.452(5)		
N(3)–C(24)	1.470(5)		
Mononuclear molecule			
Zn(3)S(9)	2.342(1)	S(12)C(46)	1.706(4)
Zn(3)S(10)	2.349(1)	N(5)C(37)	1.352(5)
Zn(3)S(11)	2.336(1)	N(5)C(38)	1.471(5)
Zn(3)S(12)	2.340(1)	N(5)C(42)	1.433(5)
S(9)C(37)	1.703(4)	N(6)C(46)	1.370(5)
S(10)C(37)	1.719(4)	N(6)C(47)	1.461(5)
S(11)C(46)	1.702(4)	N(6)C(51)	1.465(5)

Angle	ω	Angle	ω
Binuclear molecule			
S(1)Zn(1)S(3)	138.71(5)	S(4)Zn(2)S(7)	107.22(5)
S(1)Zn(1)S(4)	95.96(4)	S(4)Zn(2)S(8)	115.87(5)
S(1)Zn(1)S(6)	115.14(5)	S(5)Zn(2)S(7)	103.53(5)
S(2)Zn(1)S(3)	105.87(5)	S(5)Zn(2)S(8)	138.11(5)
S(2)Zn(1)S(4	160.15(5)	S(6)Zn(2)S(7)	158.54(5)
S(2)Zn(1)S(6)	106.67(5)	S(6)Zn(2)S(8)	96.69(4)

Angle	ω	Angle	ω
Bridging ligands		Terminal ligands	
S(3)Zn(1)S(4)	68.75(4)	S(1)Zn(1)S(2)	75.35(4)
S(3)Zn(1)S(6)	104.15(5)	S(8)Zn(2)S(7)	75.06(4)
S(4)Zn(1)S(6)	93.18(4)	C(1)S(1)Zn(1)	85.5(1)
S(4)Zn(2)S(6)	94.22(4)	C(1)S(2)Zn(1)	82.0(1)
S(5)Zn(2)S(4)	104.65(5)	C(28)S(7)Zn(2)	81.6(2)
S(5)Zn(2)S(6)	69.17(4)	C(28)S(8)Zn(2)	85.5(2)
C(10)S(3)Zn(1)	95.6(1)	C(1)N(1)C(2)	123.6(3)
C(19)S(6)Zn(1)	101.8(1)	C(1)N(1)C(6)	120.1(3)
C(10)S(4)Zn(2)	102.9(1)	C(2)N(1)C(6)	116.2(3)
C(19)S(5)Zn(2)	94.9(2)	C(28)N(4)C(29)	123.0(4)
C(19)S(6)Zn(2)	78.3(1)	C(28)N(4)C(33)	119.8(4)
Zn(1)S(6)Zn(2)	86.77(4)	C(29)N(4)C(33)	117.1(3)
C(10)N(2)C(11)	122.8(3)	N(1)C(1)S(1)	120.9(3)
C(10)N(2)C(15)	120.5(3)	N(1)C(1)S(2)	122.4(3)
C(11)N(2)C(15)	116.7(3)	N(4)C(28)S(7)	119.5(3)
C(19)N(3)C(20)	120.3(3)	N(4)C(28)S(8)	122.9(3)
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)
N(2)C(10)S(3)	119.6(3)		
N(2)C(10)S(4)	122.7(3)		
N(3)C(19)S(5)	120.7(3)		
N(3)C(19)S(6)	121.7(3)		
S(3)C(10)S(4)	117.6(2)		
S(5)C(19)S(6)	117.5(2)		
Mononuclear molecule			
S(9)Zn(3)S(10)	77.59(5)	C(37)N(5)C(42)	119.8(3)
S(11)Zn(3)S(9)	126.63(5)	C(42)N(5)C(38)	119.8(3)
S(11)Zn(3)S(10)	127.71(5)	C(46)N(6)C(47)	121.2(3)
S(11)Zn(3)S(12)	77.89(5)	C(46)N(6)C(51)	121.4(4)
S(12)Zn(3)S(9)	127.56(5)	C(47)N(6)C(51)	117.3(3)
S(12)Zn(3)S(10)	127.35(5)	N(5)C(37)S(9)	121.3(3)
C(37)S(9)Zn(3)	82.3(2)	N(5)C(37)S(10)	120.3(3)
C(37)S(10)Zn(3)	81.8(2)	N(6)C(4)6S(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)

^{15}N NMR data on the specially synthesized nickel complex $[Ni\{S_2CN(iso\text{-}C_4H_9)_2\}_2]$ (Table 1), which contains only terminal ligands. Therefore, our NMR findings allow us to conclude that complex **I** at the molecular level concurrently exists as mono- and binuclear species in a 1 : 1 ratio. To verify this conclusion, the structure of complex **I** was determined by single-crystal X-ray diffraction.

Molecular structure of I. Selected bond lengths and bond angles are listed in Table 2. A specific feature of the structural organization of zinc di-*iso*-butyldithiocarbamate is that the structure at the molecular level

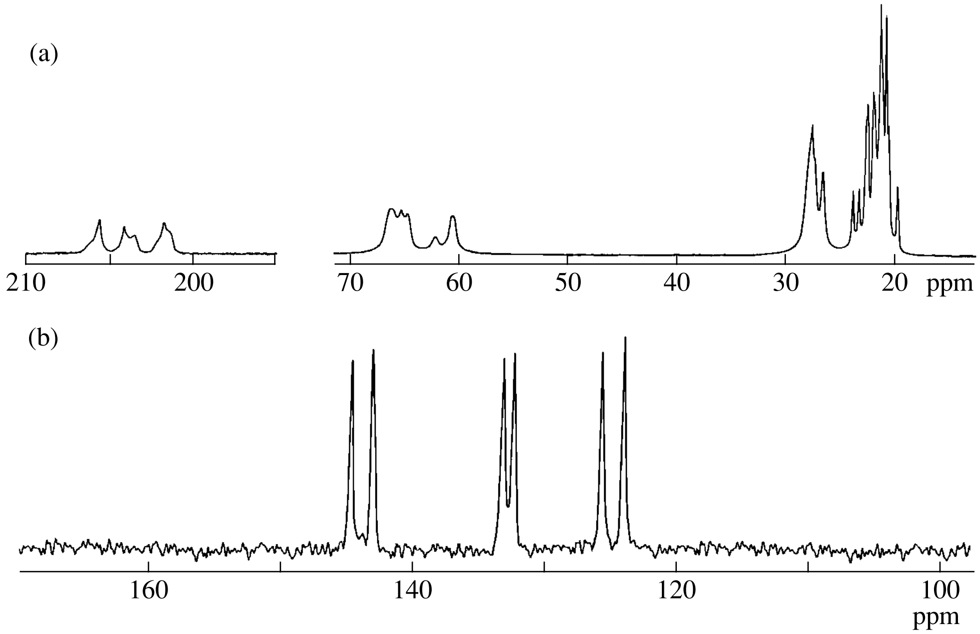

Fig. 1. CP/MAS ^{13}C and ^{15}N NMR spectra (295 K) of the polycrystalline zinc di-*iso*-butyldithiocarbamate complex $[Zn_2\{S_2CN(iso\text{-}C_4H_9)_2\}_4][Zn\{S_2CN(iso\text{-}C_4H_9)_2\}_2]$: (a) ^{13}C, 3000/5000; (b) ^{15}N, 20600/3000 (number of scans/spinning frequency, Hz).

concurrently contains the mononuclear, $[Zn\{S_2CN(iso\text{-}C_4H_9)_2\}_2]$, and binuclear, $[Zn_2\{S_2CN(iso\text{-}C_4H_9)_2\}_4]$, forms of the complex. The unit cell of **I** includes four alternating structurally equivalent mononuclear and binuclear molecules (Fig. 2; Table 2). In the mononuclear molecule, the zinc atom is bidentately coordinated by two dithiocarbamate ligands to produce planar four-membered metallacycles $[ZnS_2C]$. The central atom is bound to a distorted tetrahedral array of sulfur atoms: the planes of the corresponding metallacycles form a roughly right angle (89.36°). The binuclear molecule results from bridging of neighboring zinc atoms by two ligands. The remaining two ligands in the dimer have a terminal function and form four-membered rings with the metal, as in the mononuclear molecule. In both types of molecules, the dithiocarbamate ligands are structurally nonequivalent, as might be expected from the ^{13}C and ^{15}N NMR spectra. All the ligands are anisobidentate: for each of the ligands, one of the Zn–S bonds is noticeably shorter than the other. However, the bridging ligands form noticeably stronger bonds with the metal than do the terminal ligands (Table 2). The $C_2NC(S)S$ moieties in all ligands are roughly planar. This fact, in combination with a noticeably higher strength of the N–C(S)S bonds (compared to N–CH_2), points to a significant contribution of double bonding to the formally ordinary bond (or, what is the same, indicates admixing of sp^2 to the sp^3 hybrid state of the nitrogen atom).

In the binuclear molecule, the zinc atoms (to a first approximation) are in a distorted tetrahedral environment of four relatively strongly bonded sulfur atoms (2.323–2.466 Å). The distances to the next, more distant, atoms S(6) and S(4) are already 2.821 and 2.862 Å, respectively. However, these values are noticeably smaller than the sum of the van der Waals radii of the zinc and sulfur atoms, 3.1 Å [15], which points to the existence of the fifth, relatively weak, Zn–S bond (i.e., the zinc coordination number is 5). The geometry of the zinc polyhedra is intermediate between a square pyramid and a trigonal bipyramid (TB). In the distorted TBs, the three most strongly bonded sulfur atoms form the equatorial plane and the more distant sulfur atoms are in axial positions. The bond angles in the equatorial planes of the TB (Zn(1): 138.71°, 115.14°, 104.15°; Zn(2): 138.11°, 115.87°, 104.65°) noticeably differ from 120°. At the same time, the axial $S_{ax}ZnS_{ax}$ angles are 160.14° (Zn(1)) and 158.54° (Zn(2)). The binuclear molecule is centrosymmetric. The Zn–Zn distance in this molecule is 3.5876(7) Å.

In both types of molecules, the four-membered metallacycles $[ZnS_2C]$ are characterized by rather short Zn–C distances (2.681–2.802 Å), which are only ~15% longer than the Zn–S bonds. The distance between opposite sulfur atoms is 2.926–2.939 Å and dictates the axis of rhombic distortion of the ring. This configuration of the four-membered metallacycle renders the *trans*-annular effect possible; i.e., the electron system of the metal and that of the *trans* carbon atom can interact directly through the space of the small four-membered ring rather than through the system of chemical bonds. By contrast, the geometry of the extended eight-membered metallacycle $[Zn_2S_4C_2]$, with a nonplanar

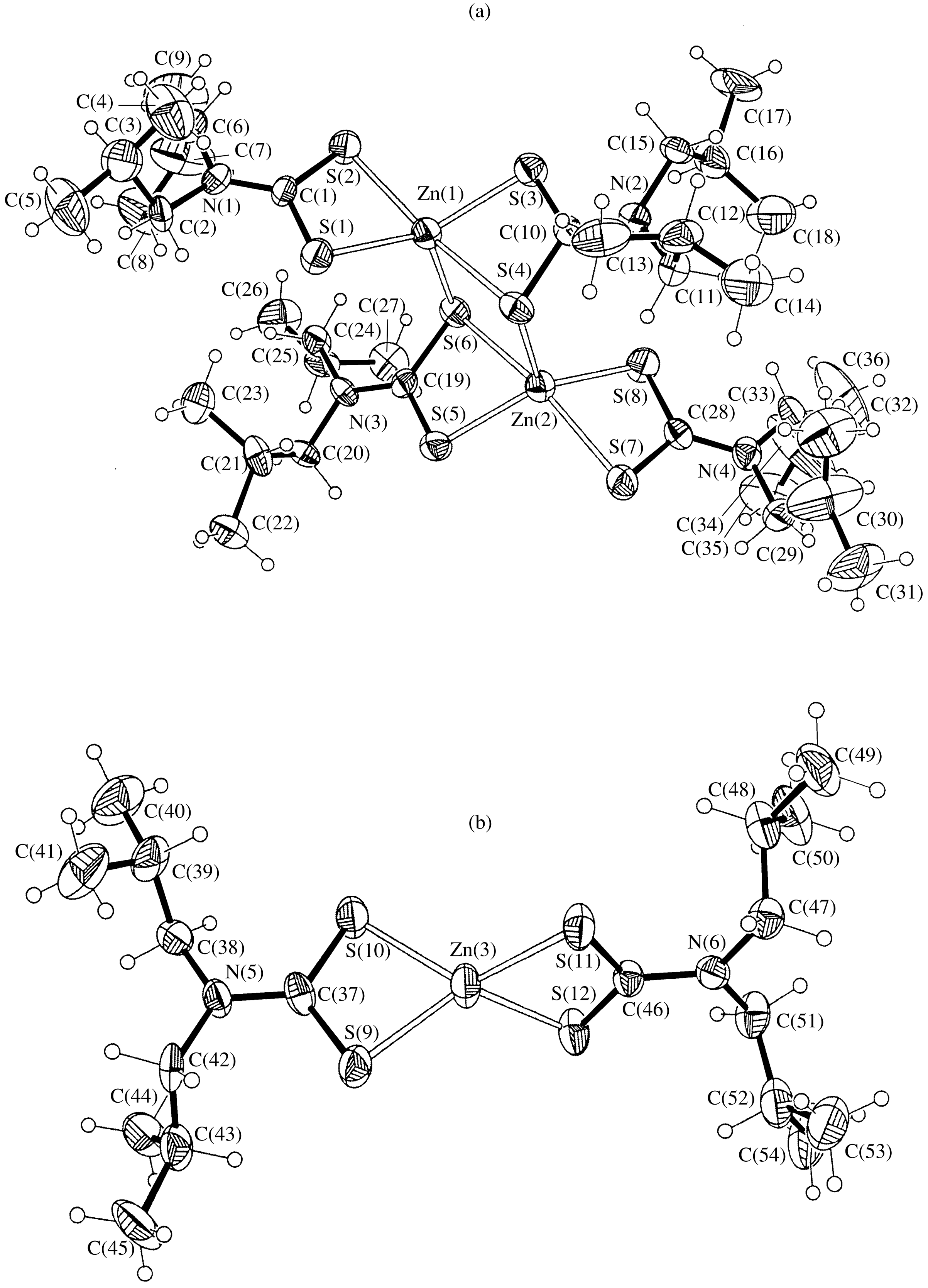

Fig. 2. Molecular structures of the (a) binuclear and (b) mononuclear complex forms. Thermal ellipsoids are shown at the 30% probability level.

structure, can be approximated by a chair conformation, as in the majority of dithiocarbamate complexes.

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