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Conformational Influence of Dithiocarbazinic Acid Bishydrazone Ligands on the Structure of Zinc(II) Complexes: A Comparative XANES Study

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(1,2-Ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands **1a**−**g** form zinc chelates with [ZnN_2S_2] units, as shown by means of IR, NMR, XPS, X-ray crystal structure analysis, and Zn and N K-edge XANES. The conformation of ligands **1a**−**g** strongly determines the structure of the corresponding zinc complexes **2a**−**g**. Powder samples of these complexes were studied by Zn K-edge XANES. The Zn K-edge XANES results agree with those of X-ray crystal structure data, when available. A tetrahedral ligand environment was confirmed for only one complex (**2a**). The other zinc chelates (**2b**−**g**) show dimeric structures with square pyramidal complex geometry. With pyridine, five-coordinated zinc complexes **3a**−**c** form, as shown by Zn K-edge XANES in comparison with X-ray crystal structure data. XANES studies afford considerable advantage for obtaining structural information, in particular when crystals of sufficient quality cannot readily be obtained.

Introduction

Structural data of the [MN_2S_2] complex unit resulting from the coordination of bis(thiohydrazones) and bis(thiosemicarbazones) of 1,2-diketones and ketoaldehydes with copper(II) and nickel(II) as central ions are well-known.[1−3] The coordination sphere of these complexes shows *s-cis* ligand arrangement in mononuclear and *s-trans* conformation related to the C−C bond of the azadiene group (C-5/C-5’) in polynuclear species. Both central ions preferably form, however, mononuclear square planar complexes.[4−6] Because Zn(II) usually favors tetrahedral coordination, the question arises how the conformation of substituted (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands (**1a**−**g**) affects the structure of the corresponding zinc complexes. Iskander proposed *s-cis* arrangement of (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands in the appropriate zinc chelates.[7] Because that ligand conformation requires planar coordination, the formation of tetrahedrally coordinated zinc complexes should not occur. One expects, therefore, that zinc complexes with **1a**−**g** should be stabilized either through dimerization or by additional coordination of monodendate Lewis bases (Figure 1, B, C).

Iskander concluded from UV−vis and ^{1}H-NMR spectroscopic data of **2c** and **2d** that five-coordinated zinc complexes form with pyridine as additional ligand.[8] X-ray crystal structure data of Lewis base adducts of [ZnN_2S_2] complexes with *N*,*N*-diethylnicotinamide confirmed this conclusion.[9] Using X-ray crystal structure analysis, we found comparable structural effects involving the additional coordination of pyridine with [pyridine-(1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]-zinc(II) (**3a**).

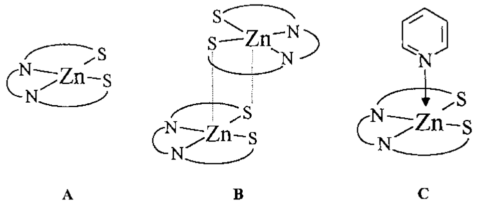

Figure 1. Scheme of the coordination sphere of (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands **1a**−**g** in [ZnN_2S_2] complexes **2a**−**g** (A, B) and **3a**−**c** (C).

Zn K-edge XANES studies were performed to gain insight into the structural influence of the (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands **1a**−**g** on the geometry of their Zn complexes **2a**−**g**. The results of these studies were compared with data on model zinc complexes of known structure distinguished by coordination number 4, 5, and 6, respectively. Zn K-edge XANES analysis of powder samples of **2a**−**g** was used because most of these complexes do not crystallize in sufficient quality, as required for conventional single-crystal X-ray diffraction structure determination. The insufficient quality of the *R* values ($R_1 > 10\%$) for **2a** (see Table 1) is due to the impossibility of obtaining suitable crystals. XANES results provide structural data on the local environment

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Table 1. Selected Distances (Å), Angles (deg), and Their Esd's for **3a** and **2a**[a]

3a		**2a**			
		Coordination Sphere			
Zn1−S2	2.367(1)	Zn1−S2	2.294(5)	Zn1−Zn2	6.183(4)
Zn1−S3	2.377(1)	Zn1−S11	2.259(5)	Zn1−Zn3	6.198(5)
Zn1−N2	2.156(2)	Zn1−N2	2.076(14)	Zn2−Zn3	6.328(5)
Zn1−N3	2.156(2)	Zn1−N11	2.097(14)		
Zn1−N5	2.081(2)				
S2−Zn1−S3	115.66(3)	S2−Zn1−S11	139.0(2)	Zn3−Zn1−Zn2	61.47(6)
S2−Zn1−N2	79.01(6)	S2−Zn1−N2	84.9(4)	Zn1−Zn2−Zn3	59.38(6)
N2−Zn1−N3	72.83(8)	N2−Zn1−N11	101.0(5)	Zn2−Zn3−Zn1	59.15(6)
N3−Zn1−S3	79.11(6)	N11−Zn1−S11	86.0(4)		
N2−Zn1−S3	146.29(6)	N2−Zn1−S11	125.0(4)		
N3−Zn1−S2	142.67(6)	N11−Zn1−S2	117.8(4)		
N5−Zn1−S2	106.43(6)				
N5−Zn1−N2	95.47(8)				
N5−Zn1−N3	100.27(7)				
N5−Zn1−S3	107.74(6)				
N2−C3−C4−N3	3.8(3)	N2−C3−C4−N3	162.5(14)		
		N6−C9−C10−N7	173.4(15)		
		N10−C15−C16−N11	171.6(16)		

[a] The relatively large standard deviations of the bonding data of **2a** are due to the quality of the very small crystals, which were all that could be obtained.

of the excited atoms, but they lack structural information on atoms far from the excited ones.

XANES studies of zinc compounds are few in number. This may be due to the absence of any pre-edge structure. Thus far known Zn K-edge XANES investigations concern primarily tetrahedrally coordinated species such as catalytic active or superconducting metal oxides, semiconducting zinc chalcogenides, and diverse zinc complexes.[10]

XANES studies of **2a−g** are based on the monitoring of changes in the relative intensity of the white line and in the characteristic spectral features of the near edge structure. The findings obtained show that XANES may be considered as a reliable tool to elucidate the coordination environment of the central ions of diverse metal complexes.

Experimental Section

Instrumentation and Methods. Elemental analyses were obtained using a Heraeus CHN-O-RAPID analyzer. NMR spectra were recorded with a 400 MHz spectrometer (UNITY 400, VARIAN) using DMSO-d_6 or $CDCl_3$ at 299 K. The following frequencies were used: ^{1}H, 399.952 MHz; ^{13}C, 100.577 MHz. IR spectra were measured in KBr with a Perkin-Elmer FTIR 1725 spectrometer.

XPS measurements were carried out using a VG ESCALAB 220i XL spectrometer equipped with a monochromatized Al Kα X-ray source (10 kV, 20 mA) in the focusing magnetic lens mode and a pass energy of 10 eV. All binding energies obtained refer to the C1s signal of saturated hydrocarbon at 284.6 eV.

N K-edge XANES spectra were recorded using synchrotron radiation of the electron storage ring BESSY/Berlin (800 MeV and 250−700 mA). A high-energy plane grating monochromator PM 5[11] and a current channeltron in total electron yield mode were used. Calibration of photon energy was carried out using the N K-edge XANES main peak (N 1s^{-1}2pπ*) of KNO_3 at 405.12 eV. The spectra were normalized to the first σ* resonance in the continuum.

Zn K-edge XANES spectra were recorded in transmission mode, using synchrotron radiation from the electron storage ring DORIS III/Hamburg (3.5 GeV and 20−100 mA) and the double-crystal monochromator RÖMO II.[12] The photon energy was calibrated relative to the energy of the maximum in the derivative of the rising edge absorbance at 9660 eV of the Zn K edge of ZnO at 9660 eV, and the spectra were normalized at 9740 eV.

X-ray Crystallographic Data Collection. Single-crystal X-ray diffraction measurements were carried out with a Stoe Stadi4 four-circle diffractometer[13] for **3a** and with a Stoe image plate diffraction system,[14] IPDS, for **2a**. Both diffractometers were equipped with a flat graphite-crystal monochromator, using Mo Kα radiation (0.710 73 Å) at 25 °C. Selected bond distances and angles are listed in Table 1.

Full details of the structure determination have been deposited at the Fachinformationzentrum Karlsruhe, Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. This material may be obtained from there by quoting the depository numbers CSD 408525 (**3a**) and CSD 408524 (**2a**).

Syntheses. The (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) ligands **1a−g** were prepared according to the literature.[7,15] The complexes **2a−g** were prepared by dropwise addition of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.005 mol) to a stirred ethanolic solution (100 mL) of the corresponding ligands **1a−g** (0.005 mol). After the mixture had been refluxed for 1 h, a yellow powder was collected by filtration, recrystallized with $CHCl_3$, and dried under vacuum (see Scheme 1).

[(1,2-Ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2a). Yield: 91%. Anal. Calcd for $C_6H_8N_4S_4Zn$: C, 21.85; H, 2.45; N, 16.99; S, 38.89; Zn, 19.37. Found: C, 21.99; H, 2.60; N, 17.09; S, 38.10; Zn, 19.53. IR (KBr), cm^{-1}: ν(C=N) 1550; ν(C−S−Zn) 825. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.61$ (6H, s, H-1, H-1′), 8.17 (2H, s, H-5, H-5′). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 14.4$ (C-1, C-1′), 143.8 (C-5, C-5′), 191.0 (C-2, C-2′).

[(1-Methyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2b). Yield: 77%. Anal. Calcd for $C_7H_{10}N_4S_4Zn$: C, 24.45; H, 2.93; N, 16.30; S, 37.30; Zn, 19.02. Found: C, 24.82; H, 3.04; N, 16.21; S, 37.20; Zn, 18.65. IR (KBr), cm^{-1}: ν(C=N) 1570; ν(C−S−Zn) 870. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.42$ (3H, s, CH_3), 2.61 (3H, s, H-1), 2.62 (3H, s, H-1′), 8.20 (1H, s, H-5). ^{13}C

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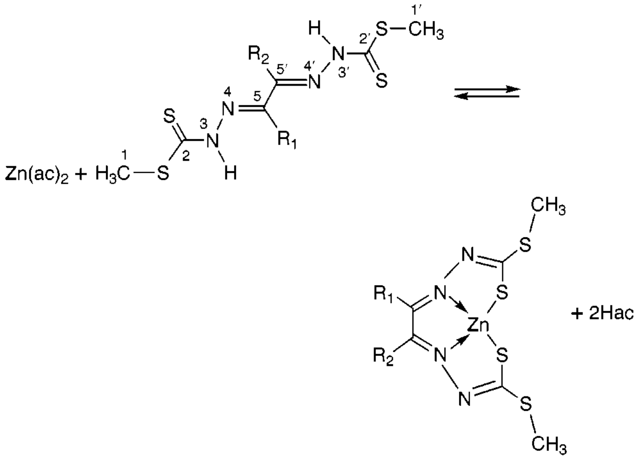
Scheme 1



1a–g

no.	R^1	R^2
a	H	H
b	H	CH$_3$
c	CH$_3$	CH$_3$
d	H	Ph

2a–g

no.	R^1	R^2
e	CH$_3$	Ph
f	Ph	Ph
g	1,2-cyclohexanediyliden	

NMR (DMSO-d_6, 100 MHz): $\delta = 14.4$ (C-1), 14.6 (C-1′), 16.3 (CH$_3$), 153.0 (C-5), 146.6 (C-5′), 187.4 (C-2), 190.8 (C-2′).

[(1,2-Dimethyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2c). Yield: ca. 67%. Anal. Calcd for $C_8H_{12}N_4S_4Zn$: C, 26.85; H, 3.38; N, 15.66; S, 35.84; Zn, 18.27. Found: C, 26.95; H, 3.61; N, 15.66; S, 35.67; Zn, 18.24. IR (KBr), cm^{-1}: ν(C=N) 1580; ν(C−S−Zn) 870. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.39$ (6H, s, CH$_3$), 2.62 (6H, s, H-1, H-1′). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 14.4$ (C-1, C-1′), 14.6 (CH$_3$), 154.9 (C-5, C-5′), 186.9 (C-2, C-2′).

[(1-Phenyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2d). Yield: ca. 75%. Anal. Calcd for $C_{12}H_{12}N_4S_4Zn$: C, 35.51; H, 2.98; N, 13.80; S, 31.60; Zn, 16.11. Found: C, 35.67; H, 3.13; N, 13.63; S, 31.21; Zn, 16.30. IR (KBr), cm^{-1}: ν(C=N) 1570; ν(C−S−Zn) 860. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.61$ (3H, s, H-1), 2.64 (3H, s, H-1′), 7.64, 7.65, 8.22 (5H, d, t, t, Ph), 8.70 (1H, s, H-5). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 14.7$ (C-1), 14.9 (C-1′), 131.0, 128.4, 129.9, 131.1 (Ph), 146.3 (C-5), 147.4 (C-5′), 190.3 (C-2), 191.0 (C-2′).

[(1-Phenyl-1,2-propanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2e). Yield: ca. 70%. Anal. Calcd for $C_{13}H_{14}N_4S_4Zn$: C, 37.18; H, 3.36; N, 13.34; S, 30.54; Zn, 15.57. Found: C, 37.30; H, 3.40; N, 13.60; S, 30.25; Zn, 15.30. IR (KBr), cm^{-1}: ν(C=N) 1570; ν(C−S−Zn) 860. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.40$ (3H, s, CH$_3$), 2.63 (3H, s, H-1), 2.64 (3H, s, H-1′), 7.43, 7.49, 7.60 (5H, d, t, t, Ph). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 14.38$ (C-1), 14.56 (C-1′), 16.64 (CH$_3$), 131.3, 128.0, 129.5, 130.0 (Ph), 153.4 (C-5), 155.0 (C-5′), 187.0 (C-2), 189.5 (C-2′).

[(1,2-Diphenyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2f). Yield: ca. 97%. Anal. Calcd for $C_{18}H_{16}N_4S_4Zn$: C, 44.85; H, 3.35; N, 11.62; S, 26.61; Zn, 13.56. Found: C, 44.65; H, 3.40; N, 11.32; S, 26.37; Zn, 16.50. IR (KBr), cm^{-1}: ν(C=N) 1570; ν(C−S−Zn) 880. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.62$ (6H, s, H-1, H-1′), 7.48, 7.50, 7.80 (10H, d, t, t, Ph). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 14.6$ (C-1, C-1′), 131.7, 127.4, 130.2, 129.7 (Ph), 153.8 (C-5, C-5′), 189.0 (C-2, C-2′).

[(1,2-Cyclohexanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2g). Yield: ca. 85%. Anal. Calcd for $C_{10}H_{14}N_4S_4Zn$: C, 31.28; H, 3.70; N, 14.59; S, 33.40; Zn, 17.03. Found: C, 31.53; H, 3.79; N, 14.52; S, 33.20; Zn, 16.75. IR (KBr), cm^{-1}: ν(C=N) 1575; ν(C−S−Zn) 870. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.58$ (6H, s, H-1, H-1′), 1.86, 3.09, (8H, m, −CH$_2$−). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 17.1$ (C-1, C-1′), 21.1, 29.2 (−CH$_2$−), 156.1 (C-5, C-5′), 191.9 (C-2, C-2′).

The pyridine adducts **3a**−**c** were obtained by dropwise addition of an excess of pyridine (0.02 mol) to a stirred solution of **2a**−**c** (0.005 mol) in dry benzene (150 cm^3).[8] After being refluxed for 2 h, the solution was confined to the half its volume. Cooling for 48 h at 5 °C led to red crystals, which were filtered off and recrystallized from benzene.

[Pyridine-(1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (3a). Yield: ca. 50%. Anal. Calcd (for **3a**·$0.5C_6H_6$) for $C_{14}H_{16}N_5S_4Zn$: C, 37.54; H, 3.60; N, 15.63; S, 28.63; Zn, 14.60. Found: C, 37.28; H, 3.79; N, 15.44; S, 28.85; Zn, 14.35. IR (KBr), cm^{-1}: ν(C=N) 1570; ν(C−S−Zn) 880. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 2.64$ (6H, s, H-1, H-1′), 8.31 (2H, s, H-5, H-5′), 8.50, 7.46, 7.86 (5H, d, t, t, pyH). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 14.6$ (C-1, C-1′), 149.4, 124.2, 136.6 (py), 144.0 (C-5, C-5′), 191.0 (C-2, C-2′).

[Pyridine-(1-methyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (3b). Yield: ca. 35%. Anal. Calcd for $C_{12}H_{15}N_5S_4Zn$: C, 34.08; H, 3.58; N, 16.56; S, 30.22; Zn, 15.46. Found: C, 33.82; H, 3.64; N, 16.68; S, 29.88; Zn, 15.70. IR (KBr), cm^{-1}: ν(C=N) 1590; ν(C−S−Zn) 880. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 2.32$ (3H, s, CH$_3$), 2.61 (3H, s, H-1), 2.62 (3H, s, H-1′), 7.83 (1H, s, H-5), 8.44, 7.47, 7.87 (5H, d, t, t, pyH). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 15.3$ (C-1), 15.4 (C-1′), 16.7 (CH$_3$), 148.5, 125.4, 139.3 (py), 144.6 (C-5), 151.5 (C-5′), 190.6 (C-2), 195.3 (C-2′).

[Pyridine-(1,2-dimethyl-1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (3c). Yield: ca. 40%. Anal. Calcd for $C_{13}H_{17}N_5S_4Zn$: C, 35.73; H, 3.92; N, 16.03; S, 29.35; Zn, 14.96. Found: C, 35.59; H, 4.22; N, 15.86; S, 29.00; Zn, 15.20. IR (KBr), cm^{-1}: ν(C=N) 1595; ν(C−S−Zn) 870. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 2.38$ (6H, s, CH$_3$), 2.61 (6H, s, H-1, H-1′), 8.45, 7.38, 7.84 (5H, d, t, t, pyH). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 14.8$ (C-1, C-1′), 15.3 (CH$_3$), 148.7, 125.2, 138.9 (py), 153.7 (C-5, C-5′), 190.4 (C-2, C-2′).

The model complexes **4**, **5**, and **6** were prepared according to the literature.[17]

Bis[(*N*′-(2,2′-dipyridylmethyliden)-*S*-methylhydrazonecarbodithionato)]zinc(II) (4). Yield: ca. 88%. Anal. Calcd for $C_{26}H_{22}N_8S_4Zn$: C, 48.78; H, 3.48; N, 17.50; S, 20.03; Zn, 10.21. Found: C, 48.92; H, 3.70; N, 17.66; S, 20.45; Zn, 10.50. IR (KBr), cm^{-1}: ν(C=N) 1585; ν(C−S−Zn) 855. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 2.39$ (6H, s, H-1), 7.40, 7.66, 7.26, 8.17 (8H, d, t, t, d, py-cis), 7.94, 7.90, 7.44, 7.80 (8H, d, t, t, d, py-trans). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 15.6$ (C-1), 148.9, 125.5, 138.3, 125.7, 149.2 (py-cis), 151.9, 127.9, 136.0, 124.1, 147.4 (py-trans) 150.9 (C-5), 195.4 (C-2).

Bis[2-((2-methylmercaptothiocarbonyl)-hydrazone)propionato]zinc(II) (5). Yield: ca. 60%. Anal. Calcd for $C_{10}H_{14}N_4O_4S_4Zn$: C, 26.82; H, 3.15; N, 12.51; O, 14.29; S, 28.63; Zn, 14.60. Found: C, 26.70; H, 3.40; N, 12.28; O, 14.49; S, 28.22; Zn, 14.25. IR (KBr), cm^{-1}: ν(COO−Zn) 1630; ν(C=N) 1590; ν(C−S−Zn) 875. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.32$ (6H, s, CH$_3$), 2.55 (6H, s, C-1), 12.53 (2H, s, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 13.7$ (CH$_3$), 17.4 (C-1), 143.8 (C-5), 164.2 (COO-M), 201.0 (C-2).

Bis[(*N*′-(phenylmethyliden)-*S*-methylhydrazonecarbodithionato)]zinc(II) (6). Yield: ca. 92%. Anal. Calcd for $C_{18}H_{18}N_4S_4Zn$: C, 44.67; H, 3.75; N, 11.58; S, 26.50; Zn, 13.51. Found: C, 44.87; H, 3.64; N, 11.57; S, 26.30; Zn, 15.57. IR (KBr), cm^{-1}: ν(C=N) 1595; ν(C−S−Zn) 850. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 2.66$ (6H, s, H-1), 7.53 (2H, s, H-5), 8.42, 7.62, 7.64 (10H, d, t, t, Ph). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 15.3$ (C-1), 131.5, 132.6, 128.7, 131.8 (Ph), 152.2 (C-5), 183.6 (C-2).

Results and Discussion

Investigation in Solution. The conformational and coordination behavior of **1a**−**g** was studied by ^{1}H- and ^{13}C-NMR. NMR spectra of the bulky ligand **1d** indicate the presence of *s-trans* and *s-cis* (referred to C-5/C-5’) conformers (Table 2). The activation energy of the rotation around the C−C bond amounts to 60−62 kJ/mol. The high-field shift of C-2/C-2′ to 10−15

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Table 2. ^{1}H- and ^{13}C-NMR Chemical Shifts (ppm) of **1d** and **2d** in DMSO-d_6 at 299 K

	H-1	H-1′	H-5′	C-1	C-1′	C-2	C-2′	C-5	C-5′	N-4/N4′
1d										
s-cis	2.67	2.65	8.51	18.3	18.0	201.7	201.5	145.2	145.4	−67.2/−68.8
s-trans	2.48	2.63	8.15	17.7	17.8	199.9	200.1	139.3	139.5	−67.2/−68.8
2d	2.67	2.64	8.24	18.4	18.0	190.3	191.0	147.4	146.3	−64.2/−59.4

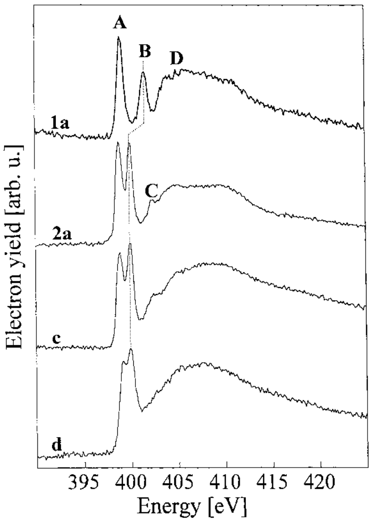

Figure 2. N K-edge XANES of (1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionate) (**1a**) and its metal complexes with Zn(II) (**2a**), Cu(II) (**c**), and Ni(II) (**d**) (A = N1s^{-1}2pπ* resonance from N-4; B = N1s^{-1}2pπ* resonance from N-3; C = N1s^{-1}2pπ* resonance (conjugated); D = N1s$^{-1}\sigma$* resonance).

ppm in **2a**−**g** indicates the coordination of thiolate sulfur within the [ZnN$_2$S$_2$] units. Nitrogen N-4/N-4′ coordination is confirmed by a 10 ppm high-field shift, when compared with the free ligands. The temperature and concentration independence of the NMR data agrees with the proposed monomeric complex units in solution (DMSO-d_6). The NMR data and 1D-NOE difference spectra of **2d** point to *s-cis* arrangement of the ligand upon the formation of a tricyclic four-dendate complex (Table 2).

Investigations in the Solid State. The absence of ν(N−H) and coupled δ(N−H) frequencies in the IR data of **2a**−**g** confirm the deprotonation of the NH groups. Furthermore, the ν(C=N) and the ν(C=S) frequencies shift to lower frequencies ($\Delta\nu$(C=N) = 10−35 cm^{-1}, $\Delta\nu$(C=S) = 40−100 cm^{-1}). These results establish a N$_2$S$_2$ environment of the central ion in **2a**−**g**.

For **1a** the XPS S2p$_{3/2}$ binding energy of the thione sulfur (C=S) appears at about 161.7 eV and that of the *S*-methyl group (−S−CH$_3$) at 163.8 eV. A turnover due to a dative Zn−S binding in **2a** was indicated by a S2p energy shift for the C=S group of ΔS2p = +0.6 to +0.8 eV. The S2p binding energy of the *S*-methyl group remains unchanged. The azomethine nitrogen (N-4) N1s binding energy at 399.7 eV differs from the value of the protonated nitrogen at the dithiocarbamide group (N-3) at 400.4 eV. After complex formation, the dithiocarbamide nitrogen (N-3) is deprotonated, shown by the coincidence of the N1s energies at 399.9 eV; a distinction between both nitrogen atoms is not possible. N K-edge XANES measurements enable a distinction between N-3 and N-4, because the energy splitting of the antibonding π* states leads to an energy shift of the corresponding resonances. The N1s^{-1}2pπ* resonances are dipole allowed and yield intensive sharp lines. N K-edge XANES of azomethine nitrogen of the noncoordinated ligand shows a N1s^{-1}2pπ* resonance A at 399.2 eV and a second π* resonance B due to the thioamide nitrogen (N-3) at 401.6 eV (Figure 2, **1a**).

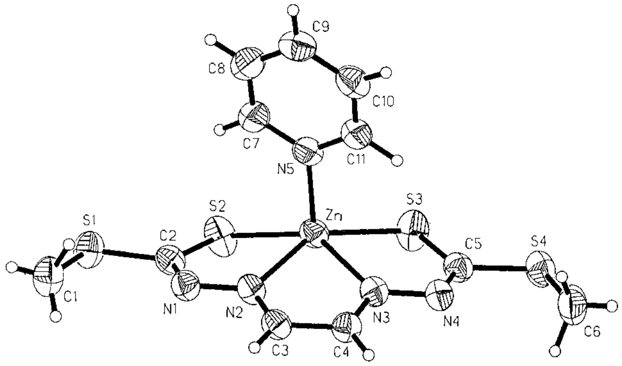

Figure 3. Molecular structure of [pyridine-(1,2-ethanediyliden)-bis-(*S*-methylhydrazone-carbodithionato)]zinc(II) (**3a**).

The broad peaks at higher energies D (Figure 2, **1a**) might be due to σ* resonances. The coordination with Cu(II), Ni(II) (used as reference compounds[17]), and Zn(II) leads to stronger double-bond character of the nitrogen−carbon bond of the dithiocarbamide group. This leads to both a low-energy shift of the resonance B with 1.5 eV and an increase in the oscillator strength (Figure 2, **2a**, **c**, **d**). These energy values are independent of the kind of central ions coordinated. The modification of the dative bond on the azomethine nitrogen (N-4) by changing the central ion shifts the N1s^{-1}2pπ* resonance A to 398.9 eV for Zn(II), 399.0 eV for Cu(II), and 399.1 eV for Ni(II) (Figure 2, **2a**, **c**, **d**). This shift is associated with a decrease in the intensity of peak A in the same order. This can be explained by the strong acceptor function of the dithiocarbamide group, leading to an increase of free d states in the corresponding central atoms. The low intensive small peak C (Figure 2) originates from conjugation effects as shown by means of Hartree−Fock calculations.[18]

Crystal Structure of [Pyridine-(1,2-ethanediyliden)-bis-(*S*-methylhydrazonecarbodithionato)]zinc(II) (3a). Figure 3 displays the molecular structure of the pyridine adduct **3a**.

3a exhibits a distorted square pyramidal structure. The conformation of the dianionic ligand points to a *s-cis* (C-5/C-5’) arrangement. The pyridine ligand coordinates in an axial position and stabilizes the approximately planar [ZnN$_2$S$_2$] unit. The zinc ion is shifted about 0.538(1) Å out of the [N$_2$S$_2$] plane in the direction of the pyridine ligand. The bonding angles between the pyridine nitrogen N-5 and the donating atoms in the coordination plane lie between 95° and 108° and correspond with the distortedly pyramidal arrangement with bonding angles of 104°, as postulated by Zeemann.[19] Within experimental error the tricyclic chelate ring appears as nearly planar. The maximum deviation of the nondonor atoms (C, N) from the chelate ring plane corresponds to ±(0.10−0.32) Å. The torsion angle determined for the diimine group is 3.8(3)°. Because of the steric influence of the ligand, the Zn−S distance (2.37 Å) is significantly larger than those of tetrahedral [ZnN$_2$S$_2$] chelates (2.15−2.26 Å).[20]

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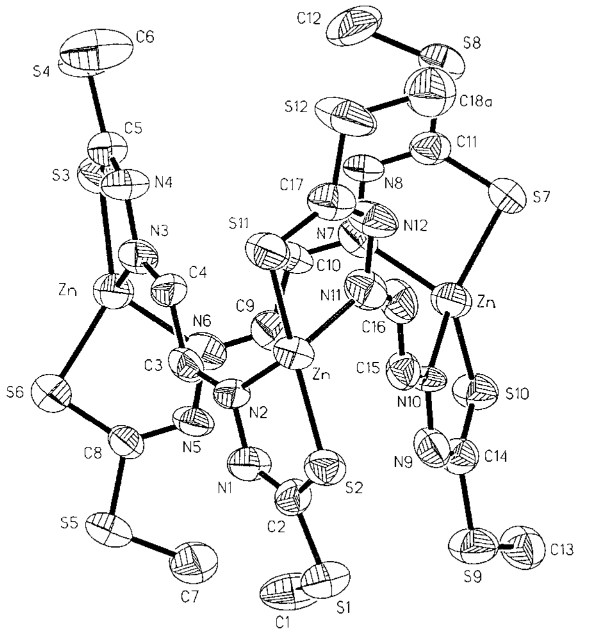


Figure 4. Molecular structure of [(1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) **(2a)**.

The presence of Lewis bases such as pyridine leads to a preference of five-coordination in the solid state. Therefore, complexes with coordination number 5 (**3a**−**c**) were used as reference compounds for the Zn K-edge XANES studies to simulate coordination spheres similar to the postulated dimeric structures **2a**−**g**.

Crystal Structure of [(1,2-Ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) (2a). According to the structure determination, **2a** exhibits a rather surprising geometric arrangement (Figure 4).

The less bulky substituents on C-5/C-5′ in **1a** lead to the formation of tetrahedrally distorted trimeric units with three ligands in an *s-trans* arrangement. Each ligand is coordinated to two different Zn ions. The Zn−S (2.259(5), 2.294(5) Å) and Zn−N bond distances (2.076(14), 2.097(14) Å) are significantly shorter than those of **3a** (Zn−S, 2.367(1), 2.377(1) Å; Zn−N, 2.156(2) Å) with a distorted square pyramidal structure (Table 2). **2a** shows distortions particularly reflected by N-2−C-3−C-4−N-3 torsion angles of 162.5(14)° (ideal 180°) and the geometry of the environment of each Zn ion. Bond distances and angles of the other Zn ions and ligands are equal within the error limit.

Zn K-Edge XANES Results of Reference Compounds. To obtain structural data of those Zn complexes, from which no single crystals could be obtained, at first X-ray absorption spectra of reference powder samples were recorded. Bis[(*N*′-(2,2′-dipyridyl-methyliden)-*S*-methylhydrazonecarbodithionato)]-zinc(II) (**4**) and bis[2-((2-methylmercaptothiocarbonyl)-hydrazone)propionato]zinc(II) (**5**) (coordination number 6, see Scheme 2), the pyridine adducts **3a** and **3c** (coordination number 5), and bis[(*N*′-(phenylmethyliden)-*S*-methylhydrazone-carbodithionato)]zinc(II) (**6**)[20] and **2a** (coordination number 4) were used as model compounds.

Modulation of the photoabsorption coefficient between 0 and 50 eV above the absorption edge (XANES) arises from core level excitation of electrons into empty valence levels, quasi-bound states, and also multiple scattering processes. The K-edge spectra of 3d transition elements show a pre-edge absorption feature, usually explained by electric dipole transitions to p-like states admixed to 3d states. Completely filled 3d shells in zinc compounds, however, prevent Zn1s^{-1}3d transitions. Instead, the Zn1s^{-1}4p transition leads to an intensive absorption structure, the white line.[21] The white line intensity changes with transition probability, which is partly dependent on the complex geometry. Empirical rules were established to assign resonance structures to appropriate types of coordination units.[22] A useful evaluation of the coordination geometry of zinc complexes is based on the relative intensity of the white line referred to normalization of the spectra at 9740 eV. The white line intensity changes, depending on the space filling within the first coordination sphere, and is influenced differently by octahedral coordination geometry than by tetrahedral or square planar structures, as illustrated in Figure 5.

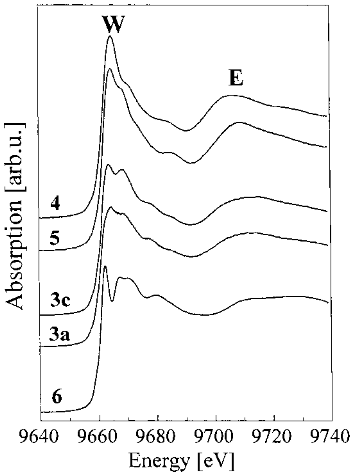
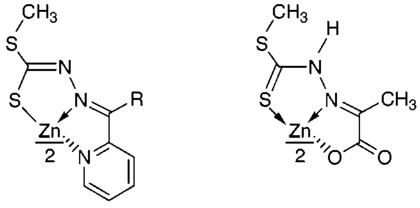


Figure 5. Zn K-edge XANES of reference compounds **4**, **5**, **3c**, **3a**, and **6** (W, white line; E: beginning of the EXAFS range).

Scheme 2



4: R = 2-pyridyl **5**

Maximum intensities for the white line typical for octahedrally coordinated compounds such as **4** and **5** are shown in Figure 5. Relative peak heights greater than 2 (related to the beginning EXAFS region at 9740 eV) were observed at the absorption maximum. The zinc complexes **3c** and **3a** (Figure 5) distinguished by coordination number 5 show relative white line peak heights of 1.63 and 1.52, respectively. These values are similar to those of tetrahedrally coordinated zinc complexes. The values of the relative peak height at the absorption maximum are summarized in Table 3. Characteristic features of the spectra of tetrahedrally coordinated compounds such as **6** are depicted in Figure 5. This spectrum shows pronounced splitting of the white line. Similar splitting is generally observed for tetrahedrally coordinated zinc ions, such as Zn[B(3-isopropylpyrazol-1-yl)$_4$]$_2$[10d] and ZnO.[23]

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Table 3. Results of Zn K-Edge XANES: Relative Peak Height at the Absorption Maximum (Normalized at 9740 eV)

	Zn K-edge XANES	
sample	coord no.	peak height
4	6	2.03
5	6	2.05
3c	5	1.63
3a	5	1.52
6	4	1.58
2d	5	1.58
2f	5	1.62
2b	5	1.55
2a	4	1.36

Photon energies greater than 50 eV above the absorption edge are dominated by single scattering processes. The extended X-ray absorption fine structure (EXAFS) may provide further structure data. The EXAFS amplitude usually is significantly influenced by the coordination number and the relative intensity of the amplitude at the beginning of the EXAFS region (E in Figure 5) and may normally serve as a useful criterion to distinguish between coordination numbers 4, 5, and 6. However, unfortunately, the zinc complexes under discussion show no definite EXAFS results because several bond distances to the central ion are not resolved. Compared with that, XANES findings are very valuable when different coordination numbers are concerned, because of the sensitivity of this method with respect to changes in the bond angles.

Zn K-Edge XANES Spectra of Zinc(II) Complexes 2a, 2b, 2d, and 2f. Since the complexes **2b**, **2d**, and **2f** do not crystallize in sufficient quality for X-ray crystal structure determination, Zn K-edge XANES was used to study the coordination geometry of **2b**, **2d**, and **2f** using powder samples of these complexes. Analysis of XANES data was performed to confirm the proposed square pyramidal coordination of these complexes. Relative white line intensities between 1.55 and 1.62 are observed. These values are lower than those for complexes with octahedral coordination. Furthermore, no splitting of the first absorption maximum typical for tetrahedral coordination was found. The intensity and shape of the white line of these compounds are in reasonable agreement with the Zn K-edge XANES results of the corresponding pyridine adducts (Figure 5, **3a**, **3c**). Thus, 5-fold coordination seems to be reasonable for **2b**, **2d**, and **2f**. Square pyramidal coordination is only possible for **2b**, **2d**, and **2f**, if the formation of sulfur-bridged dimers is assumed (Figure 1, B). The small fine structure variations at the near edge region are interpreted to be related to the differences in the zinc complex constitution of the five-coordinated pyridine adducts [ZnN_3S_2] and the sulfur-bridged dimeric zinc complexes **2b**, **2d**, and **2f** [ZnN_2S_3].

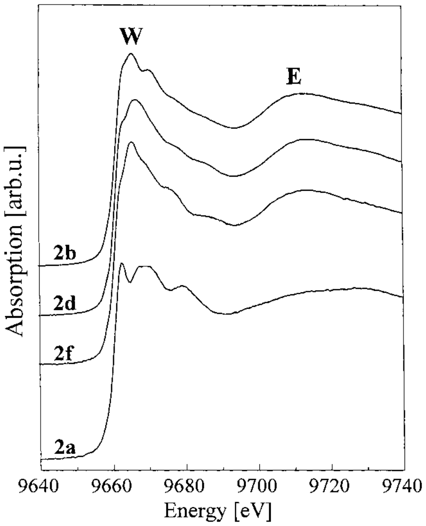

Figure 6. Zn K-edge XANES of selected substituted [(1,2-ethanediyliden)-bis(*S*-methyl-hydrazonecarbodithionato)]zinc(II) complexes **2b**, **2d**, **2f**, and **2a** (W, white line; E, begin of the EXAFS range).

The structural differences between complex **2a** and the other zinc complexes **2b**, **2d**, and **2f** of the same kind (Figure 6) are clearly demonstrated by Zn K-edge XANES. Zn K-edge XANES shows significant white line splitting (Figure 6, **2a**) indicative of tetrahedral complex geometry. This was confirmed by the X-ray structure analysis of **2a** and by comparison with the tetrahedral complex **6** (see Figure 5).

Conclusions

Zn K-edge XANES studies permit the distinction between different coordination geometries by means of the analysis of intensity proportions in the multiple scattering range. Zn K-edge XANES clearly indicates square pyramidal coordination for [(1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]-zinc(II) complexes **2b**−**g**, whereas [(1,2-ethanediyliden)-bis(*S*-methylhydrazonecarbodithionato)]zinc(II) **2a** is tetrahedrally coordinated. Due to the ligand conformation, the usually favored tetrahedral coordination geometry of zinc complexes can only be observed with *s-trans* (C-5/C-5’) conformed ligands upon formation of polynuclear complexes. On the other hand, *s-cis* (C-5/C-5’) conformation of the ligands leads to square pyramidal arrangement. The coordination geometry of the zinc complexes **2a** and **2b**−**g** is different when compared with that of corresponding Cu(II) and Ni(II) complexes distinguished by square planar coordination spheres.

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