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Note

Hexacoordinated complexes of bivalent zinc incorporating thioether binding ☆

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Abstract

The reaction of zinc(II) acetate dihydrate with dithiaalkyl-substituted triazene 1-oxides, $[RN(O)NNHC_6H_4S]_2(CH_2)_2$ (H_2RL; R = Me, Ph) has afforded light-yellow Zn(MeL) and light-green $Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$, the first hexacoordinated complexes of zinc bonded by acyclic ligands incorporating thioether sites. Spectral features of the complexes are briefly noted. Both the complexes have been structurally characterized revealing distorted octahedral binding of the metal ion in $ZnO_2N_2S_2$ coordination spheres; the Zn–O, Zn–N and Zn–S distances lie in the ranges 2.056(7)–2.105(8), 2.005(8)–2.029(8) and 2.649(4)–2.720(3) Å, respectively. Crystal data: Zn(MeL): monoclinic, space group $P2_1/c$, $a = 26.529(9)$, $b = 7.974(3)$, $c = 19.396(8)$ Å, $\beta = 110.57(3)°$, $V = 3842(3)$ Å^3, $Z = 8$, $R = 5.40\%$, $R_w = 5.73\%$; $Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$: orthorhombic, space group *Pbcb*, $a = 9.540(3)$, $b = 19.449(6)$, $c = 29.534(8)$ Å, $V = 5480(3)$ Å^3, $Z = 8$, $R = 5.65\%$, $R_w = 5.42\%$.

Keywords: Crystal structures; Zinc complexes; Hexacoordinate complexes; Thioether complexes

1. Introduction

In view of the importance of sulfur binding of zinc in life processes [1], the synthesis, structure and properties of new chelates incorporating such binding are of current interest [2]. Chelated zinc(II) is usually tetra- or penta-coordinated, the latter being less prevalent than the former [3]. Authentic examples of hexacoordinated zinc(II) species incorporating sulfur ligands are however very rare [3,4]. Indeed it has been argued that the maximum coordination number attainable in S,N ligated neutral zinc(II) complexes is five [2]. In the present work we report the successful synthesis and characterization of a pair of hexacoordinated zinc(II) complexes of coordination type $ZnO_2N_2S_2$ using suitably designed hexadentate acyclic ligands with thioether donor sites.

2. Experimental

2.1. Chemicals

The purification of dichloromethane for spectral work was done by a reported procedure [5]. All other chemicals and solvents were of analytical grade and used as received.

2.2. Physical measurements

Spectra were recorded on the following equipment: UV–Vis, Hitachi 330 spectrophotometer; IR spectra, Perkin-Elmer 783 IR spectrophotometer. A Perkin-Elmer 240C elemental analyzer was used to perform microanalytical data (CHN).

2.3. Preparation of ligands and complexes

The amine 1,2-bis((2-aminophenyl)thio)ethane was synthesized by following a reported method [6]. The ligands H_2MeL and H_2PhL were prepared by coupling diazotized solutions of the amine with *N*-methylhydroxylamine and *N*-phenylhydroxylamine, respectively

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Table 1
Crystallographic data

Compound	Zn(MeL)	Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$
Crystal system	monoclinic	orthorhombic
Chemical formula	$C_{16}H_{18}N_6O_2S_2Zn$	$C_{26.50}H_{23}N_6O_2S_2ClZn$
Formula weight	455.9	620.6
Space group	$P2_1/c$	$Pbcb$
a (Å)	26.529(9)	9.540(3)
b (Å)	7.974(3)	19.449(6)
c (Å)	19.396(8)	29.534(8)
β (°)	110.57(3)	
V (Å^3)	3842(3)	5480(3)
Z	8	8
T (K)	296	296
λ (Å)	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.576	1.505
μ (mm^{-1})	1.521	1.084
R [a] (%)	5.40	5.65
R_w [b] (%)	5.73	5.42
Goodness of fit indicator [c]	1.16	0.88

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0001$ for Zn(MeL) and 0.00007 for Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$.
[c] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

[7,8,11b]. The two complexes Zn(MeL) and Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$ were synthesized by similar procedures. Details of preparation are described below for Zn(MeL) only.

2.3.1. *[1,2-Bis((o-(1-methyl-1-oxidotriazen-3-yl)-phenyl)thio)ethanato-N^3,S,O]zinc(II), Zn(MeL)*

To a light-yellow solution of the ligand H$_2$MeL (0.40 g, 1.02 mmol) in a mixture of dichloromethane (20 ml) and methanol (15 ml), 0.114 g (2.03 mmol) of potassium hydroxide was added. The resulting solution was stirred at room temperature (25 °C) for about 0.5 h. A methanolic solution (15 ml) of 0.224 g (1.02 mmol) of zinc(II) acetate dihydrate was added to the reaction mixture which was stirred for a further period of 1 h. The precipitate formed was washed with water and methanol. The crystalline pale brown product was finally dried in vacuo (yield 88%). *Anal.* Found: C, 42.32; H, 4.19; N, 18.75. Calc.: C, 42.28; H, 4.13; N, 18.72%.

The light-green complex Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$ was synthesized similarly from ligand H$_2$PhL; a recrystallization step from dichloromethane–hexane was added at the end (yield 89%). *Anal.* Found: C, 51.09; H, 3.69; N, 13.49. Calc.: C, 51.13; H, 3.64; N, 13.52%.

2.4. *X-ray diffraction analysis*

Unless otherwise indicated the same description applies to both the complexes. Cell parameters of Zn(MeL) (0.32×0.34×0.41 mm) and Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$ (0.12×0.32×0.36 mm) grown (298 K) by slow diffusion of hexane into dichloromethane solutions were determined by least-squares fits of 30 machine-centered reflections ($2\theta = 15$–$30°$). Systematic absences led to space group determination: $P2_1/c$ for Zn(MeL) and $Pbcb$ for Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$. Data were collected by the ω-scan method ($2\theta = 2$–$50°$) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Two check reflections measured after every 98 reflections showed no significant intensity reduction during ~76 h (Zn(MeL)) and ~52 h (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$) of exposure to X-rays. Data were corrected for Lorentz–polarization effects and absorption [9]. Of the 7507 (Zn(MeL)) and 5413 (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$) reflections collected, 6745 (Zn(MeL)) and 4790 (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$) were unique, of which 2933 (Zn(MeL)) and 1627 (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$) satisfying $I > 3\sigma(I)$ were used for structure solutions.

The structures were solved by direct methods. All non-hydrogen atoms of Zn(MeL) were made anisotropic. Due to the limited number of observed data, only the following atoms were made anisotropic for Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$: Zn, all O, N and S, Cl(1), C(1)–C(3), C(13), C(14) and C(27). Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. All refinements were done by full-matrix least-squares procedures. The highest residuals were 0.31 (Zn(MeL)) and 0.47 (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$) e Å^{-3}. All calculations were performed on a MicroVax II computer with the SHELXTL-PLUS programs [10]. Significant crystal data are summarized in Table 1. Atomic coordinates and isotropic thermal parameters are collected in Table 2 (Zn(MeL)) and Table 3 (Zn(PhL)·$\frac{1}{2}$CH$_2$Cl$_2$).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for Zn(MeL) [a]

Atom	x	y	z	U_{eq}
Zn(1)	3689(1)	6988(2)	350(1)	51(1)
Zn(2)	1285(1)	5695(2)	6740(1)	54(1)
S(1)	4016(1)	5211(4)	1600(2)	57(1)
S(2)	3596(1)	3915(3)	−264(2)	54(1)
S(3)	1275(1)	2604(3)	6142(2)	61(1)
S(4)	816(1)	4069(4)	7543(2)	65(1)
O(1)	3799(3)	8299(9)	−506(4)	67(3)
O(2)	3404(3)	8996(9)	783(4)	61(3)
O(3)	1631(3)	7499(9)	7526(4)	61(3)
O(4)	1276(3)	7243(9)	5856(4)	63(3)
N(1)	4311(3)	8243(11)	−440(5)	57(4)
N(2)	4678(3)	7568(11)	117(5)	57(4)
N(3)	4493(3)	6937(10)	609(4)	48(3)
N(4)	2909(3)	6422(10)	126(4)	49(3)
N(5)	2625(3)	7467(11)	372(5)	53(3)
N(6)	2900(3)	8734(11)	696(5)	53(4)
N(7)	2135(3)	7097(11)	7889(4)	46(3)
N(8)	2359(3)	5743(12)	7803(4)	50(3)
N(9)	2023(3)	4763(10)	7288(4)	43(3)
N(10)	497(3)	6094(10)	6182(5)	50(3)
N(11)	366(3)	7156(11)	5615(5)	52(3)
N(12)	782(3)	7691(10)	5486(4)	52(3)
C(1)	4458(5)	9037(17)	−1014(6)	79(5)
C(2)	4874(4)	6110(12)	1194(6)	50(4)
C(3)	5429(4)	6072(14)	1293(6)	64(5)
C(4)	5778(4)	5275(16)	1892(8)	79(6)
C(5)	5613(4)	4496(15)	2409(7)	79(5)
C(6)	5078(4)	4475(13)	2317(6)	64(5)
C(7)	4711(4)	5261(12)	1717(6)	49(4)
C(8)	3827(4)	3133(15)	1223(7)	74(5)
C(9)	3945(4)	2673(14)	553(7)	66(5)
C(10)	2908(4)	3664(13)	−376(5)	45(4)
C(11)	2649(4)	2192(15)	−673(6)	61(5)
C(12)	2106(4)	1991(16)	−790(6)	68(5)
C(13)	1822(4)	3285(16)	−617(6)	66(5)
C(14)	2076(3)	4739(13)	−326(6)	54(4)
C(15)	2629(3)	4959(13)	−188(5)	42(4)
C(16)	2645(5)	9933(16)	1016(7)	80(6)
C(17)	2446(4)	8294(14)	8436(6)	66(5)
C(18)	2262(4)	3206(13)	7216(5)	44(4)
C(19)	2793(4)	2806(14)	7633(5)	53(4)
C(20)	2997(4)	1284(15)	7488(6)	59(5)
C(21)	2695(4)	223(15)	6953(6)	63(5)
C(22)	2172(4)	601(14)	6568(6)	58(4)
C(23)	1946(3)	2105(13)	6681(5)	47(4)
C(24)	900(4)	1453(13)	6621(8)	80(6)
C(25)	991(5)	1939(16)	7395(7)	80(6)
C(26)	153(4)	4277(14)	6892(5)	54(4)
C(27)	−279(4)	3440(14)	7021(6)	64(5)
C(28)	−790(4)	3604(16)	6525(8)	72(5)
C(29)	−883(4)	4614(16)	5919(7)	71(5)
C(30)	−470(4)	5487(14)	5796(6)	61(4)
C(31)	61(4)	5300(13)	6285(6)	50(4)
C(32)	691(4)	8947(13)	4909(6)	64(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $\text{Zn(PhL)} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ [a]

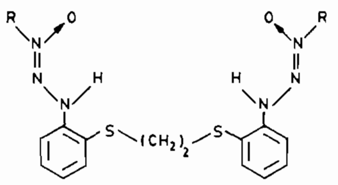
Atom	x	y	z	U_{eq}
Zn	3471(1)	996(1)	5771(1)	51(1)
Cl(1)	6432(12)	−3387(5)	7556(4)	324(6)
S(1)	5764(3)	1567(2)	6136(1)	67(1)
S(2)	2797(3)	2320(2)	5615(1)	65(1)
O(1)	2320(8)	603(4)	5242(2)	64(3)
O(2)	3505(8)	124(3)	6176(2)	63(3)
N(1)	3100(11)	587(4)	4873(3)	48(3)
N(2)	4399(10)	779(4)	4860(3)	49(4)
N(3)	4850(9)	990(4)	5257(2)	47(3)
N(4)	2242(9)	1241(4)	6306(3)	47(3)
N(5)	2089(9)	784(4)	6634(3)	47(3)
N(6)	2787(10)	219(4)	6544(3)	48(3)
C(1)	1027(11)	236(5)	4461(3)	52(4)
C(2)	433(12)	11(6)	4072(4)	68(5)
C(3)	1164(14)	−87(6)	3686(4)	70(5)
C(4)	2593(13)	41(6)	3694(4)	60(3)
C(5)	3228(11)	264(5)	4075(3)	49(3)
C(6)	2459(11)	360(5)	4468(3)	44(3)
C(7)	6247(12)	1223(5)	5246(3)	49(3)
C(8)	7075(11)	1186(5)	4854(3)	57(3)
C(9)	8450(13)	1432(6)	4878(3)	69(3)
C(10)	8970(14)	1711(6)	5259(4)	80(4)
C(11)	8186(13)	1755(6)	5642(4)	72(4)
C(12)	6761(12)	1519(5)	5634(3)	56(3)
C(13)	5213(15)	2464(7)	6152(5)	85(5)
C(14)	4459(13)	2738(5)	5756(5)	74(5)
C(15)	1775(11)	2418(5)	6106(3)	49(3)
C(16)	1055(12)	3044(6)	6179(3)	61(3)
C(17)	157(13)	3112(6)	6530(4)	73(3)
C(18)	−99(15)	2581(6)	6827(4)	74(3)
C(19)	591(12)	1953(5)	6763(3)	60(3)
C(20)	1514(12)	1860(5)	6401(3)	47(2)
C(21)	2742(11)	−324(5)	6874(3)	45(3)
C(22)	1910(12)	−264(6)	7248(3)	64(3)
C(23)	1917(12)	−803(6)	7561(4)	70(3)
C(24)	2710(13)	−1378(6)	7496(5)	75(3)
C(25)	3514(14)	−1424(6)	7111(4)	82(4)
C(26)	3549(13)	−896(6)	6792(3)	65(3)
C(27)	5000	−3942(19)	7500	279(27)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Synthesis and characterization

The two ligands used in the present work are of type I, abbreviated as H_2RL. We were prompted to choose these triazene 1-oxide thioether ligands on the basis of our recent experience that they act as reliable hexadentate $O_2N_2S_2$ donors towards a number of 3d ions [11–14].



H_2RL
R = Me,Ph
I

The stoichiometric reaction of H_2RL with zinc(II) acetate dihydrate proceeded smoothly in a mixed dichloromethane–methanol solution affording Zn(RL) complexes in excellent yields. The Zn(MeL) chelate

Table 4
Electronic [a] and IR [b] spectral data

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	ν(NO) (cm^{-1})	$\nu(N_3)$ (cm^{-1})
Zn(MeL)	670	37	1220	1460
	425	130sh [c]		
$Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$	870	25	1180	1450
	510	90sh [c]		

[a] Solvent is dichloromethane.
[b] KBr disk.
[c] sh = shoulder.

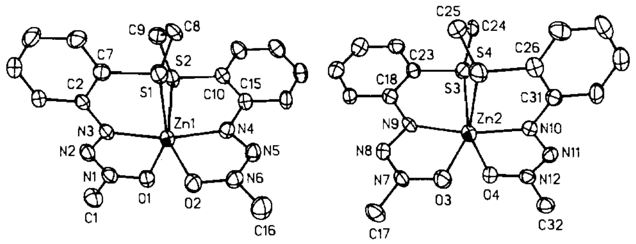


Fig. 1. ORTEP plot and atom-labeling scheme for Zn(MeL) with all atoms represented by their 30% probability ellipsoids.

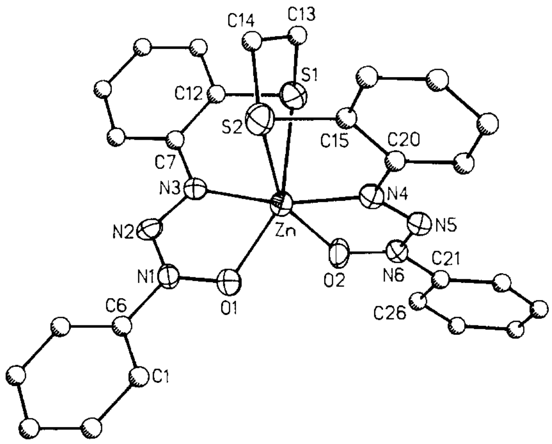


Fig. 2. Perspective view and atom-labeling scheme for Zn(PhL) with atoms other than carbon represented by their 30% probability ellipsoids.

Table 5
Selected bond distances (Å) and bond angles (°) and their e.s.d.s for Zn(MeL)

Bond distances			
Zn(1)–S(1)	2.675(3)	Zn(2)–S(3)	2.720(3)
Zn(1)–S(2)	2.698(3)	Zn(2)–S(4)	2.649(4)
Zn(1)–O(1)	2.070(8)	Zn(2)–O(3)	2.063(7)
Zn(1)–O(2)	2.070(8)	Zn(2)–O(4)	2.105(8)
Zn(1)–N(3)	2.014(8)	Zn(2)–N(9)	2.012(7)
Zn(1)–N(4)	2.008(8)	Zn(2)–N(10)	2.014(7)
O(1)–N(1)	1.318(12)	O(3)–N(7)	1.313(9)
O(2)–N(6)	1.303(11)	O(4)–N(12)	1.304(10)
N(1)–N(2)	1.290(11)	N(7)–N(8)	1.271(13)
N(2)–N(3)	1.315(14)	N(8)–N(9)	1.333(10)
N(4)–N(5)	1.320(13)	N(10)–N(11)	1.334(12)
N(5)–N(6)	1.275(12)	N(11)–N(12)	1.286(14)
Bond angles			
O(1)–Zn(1)–O(2)	96.3(3)	O(3)–Zn(2)–O(4)	93.9(3)
O(1)–Zn(1)–N(3)	76.9(3)	O(3)–Zn(2)–N(9)	76.7(3)
O(1)–Zn(1)–N(4)	111.4(3)	O(3)–Zn(2)–N(10)	113.3(3)
O(1)–Zn(1)–S(1)	154.5(2)	O(3)–Zn(2)–S(3)	152.0(2)
O(1)–Zn(1)–S(2)	96.9(2)	O(3)–Zn(2)–S(4)	94.9(2)
O(2)–Zn(1)–N(3)	114.9(3)	O(4)–Zn(2)–N(9)	112.2(3)
O(2)–Zn(1)–N(4)	76.5(3)	O(4)–Zn(2)–N(10)	75.9(3)
O(2)–Zn(1)–S(1)	95.2(2)	O(4)–Zn(2)–S(3)	100.9(2)
O(2)–Zn(1)–S(2)	153.1(2)	O(4)–Zn(2)–S(4)	153.1(2)
N(3)–Zn(1)–N(4)	165.8(3)	N(9)–Zn(2)–N(10)	167.4(3)
N(3)–Zn(1)–S(1)	77.6(3)	N(9)–Zn(2)–S(3)	75.7(2)
N(3)–Zn(1)–S(2)	90.9(2)	N(9)–Zn(2)–S(4)	94.5(3)
N(4)–Zn(1)–S(1)	93.4(2)	N(10)–Zn(2)–S(3)	93.5(2)
N(4)–Zn(1)–S(2)	76.9(2)	N(10)–Zn(2)–S(4)	77.3(3)
S(1)–Zn(1)–S(2)	82.5(1)	S(3)–Zn(2)–S(4)	82.6(1)

Table 6
Selected bond distances (Å) and bond angles (°) and their e.s.d.s for $Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$

Bond distances			
Zn–S(1)	2.688(3)	O(1)–N(1)	1.297(11)
Zn–S(2)	2.680(4)	O(2)–N(6)	1.324(11)
Zn–O(1)	2.078(6)	N(1)–N(2)	1.309(12)
Zn–O(2)	2.056(7)	N(2)–N(3)	1.319(11)
Zn–N(3)	2.029(8)	N(4)–N(5)	1.310(11)
Zn–N(4)	2.005(8)	N(5)–N(6)	1.295(14)
Bond angles			
O(1)–Zn–O(2)	98.2(3)	O(2)–Zn–S(2)	153.9(2)
O(1)–Zn–N(3)	75.4(3)	N(3)–Zn–N(4)	166.3(3)
O(1)–Zn–N(4)	114.8(3)	N(3)–Zn–S(1)	76.9(2)
O(1)–Zn–S(1)	152.0(2)	N(3)–Zn–S(2)	93.5(2)
O(1)–Zn–S(2)	95.2(2)	N(4)–Zn–S(1)	91.9(3)
O(2)–Zn–N(3)	111.5(3)	N(4)–Zn–S(2)	76.8(2)
O(2)–Zn–N(4)	77.2(3)	S(1)–Zn–S(2)	82.4(1)
O(2)–Zn–S(1)	95.7(2)		

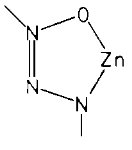
crystallizes as is, while the other complex forms as the crystalline dichloromethane adduct, $Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$.

Selected spectral data are listed in Table 4. Two characteristic vibrations [15] of the triazene 1-oxide chelate ring corresponding to N_3 and NO moieties are observed. It is remarkable that the complexes display a relatively weak band which shifts from 670 to 870 nm on going from Zn(MeL) to Zn(PhL). This band along with the associated shoulder in the region 400–550 nm (Table 4) is believed to represent forbidden intraligand transition(s).

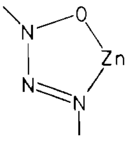
3.2. *Crystal structure*

The X-ray structures of both the complexes have been determined. The asymmetric unit of Zn(MeL) consists of two crystallographically distinct but metrically similar molecules (Fig. 1). In $Zn(PhL)\cdot\frac{1}{2}CH_2Cl_2$ there is only one type of molecule in the lattice (Fig. 2). Selected bond parameters are listed in Tables 5 and 6.

In both complexes the thioether functions are coordinated to the metal and the ligands behave in a hexadentate fashion affording $ZnO_2N_2S_2$ coordination octahedra with severe angular distortions from formal octahedral symmetry, see Tables 5 and 6. All the five-membered chelate rings incorporating N,O and N,S chelation are approximately planar. The dimethylene bridges constituting the five-membered ZnS_2C_2 rings are gauche in configuration. The N–N bond lengths are in conformity with the triazene 1-oxide, II and opposed to the hydroxytriazene, III formulation.



II



III

In the present complexes we have the first examples of structurally characterized acyclic zinc–thioether complexes in a pseudooctahedral environment. The Zn–S bond lengths lie within the range 2.649(4)–2.720(3) Å. The only other hexacoordinated complex of known structure incorporating zinc–thioether binding is the macrocyclic $[Zn(9S3)_2]^{2+}$ [4] where 9S3 is 1,4,7-trithiacyclononane. In the compact ZnS_6 core the Zn–S bond (~ 2.50 Å) is stronger than those in our complexes. On the other hand the Zn–O and Zn–N lengths of our complexes lying in the ranges 2.056(7)–2.105(8) and 2.005(8)–2.029(8) Å, respectively, are shorter than those of a pseudooctahedral pyruvic acid semithiocarbazone complex having a $ZnO_2N_2S_2$ coordination sphere (Zn–O, 2.167(6); Zn–N, 2.120(4) Å) [16].

Lastly we note that structure determination [11–14] of distorted octahedral 3d M(RL) type complexes including the present species has revealed the following average M–S(thioether) distances: Mn–S, 2.72; Co–S, 2.53; Ni–S, 2.51; Zn–S, 2.68 Å. These lengths do not show any correlation with the ionic radii (Mn^{2+}, 0.97; Co^{2+}, 0.89; Ni^{2+}, 0.83; Zn^{2+}, 0.88 Å) [17]. In the d^{10} Zn(RL) and d^5 Mn(RL) the M–S lengths are unusually long showing that the metal–thioether linkage is inherently weak in these cases.

4. Conclusions

Using the H_2RL ligands it has been possible to obtain for the first time hexacoordinated zinc(II) complexes of acyclic ligands with thioether binding. The unusual spectral features of the complexes in the visible region are noted.

5. Supplementary material

For Zn(MeL) and Zn(PhL)·$\frac{1}{2}CH_2Cl_2$, tables of complete bond distances (Tables 7 and 11) and angles (Tables 8 and 12), anisotropic thermal parameters (Tables 9 and 13), hydrogen atom positional parameters (Tables 10 and 14) and lists of the F_o–F_c values are available from author A.C.

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