

# Oxazoline chemistry IX. Synthesis and characterisation of the first Zinc oxazoline dialkyldithiocarbamate complexes; X-ray crystal structure determinations of $[\text{Zn}(\text{S}_2\text{CNR}_2-\kappa^2\text{S})_2(2\text{-R}'\text{-}4,4\text{-R}''\text{-}2\text{-oxazoline-}\kappa^1\text{N})]$ ( $\text{R} = \text{R}' = \text{Me}$ , $\text{R}'' = \text{H}$ ; $\text{R} = \text{Et}$ , $\text{R}' = \text{Me}$ , $\text{Et}$ or $\text{Ph}$ , $\text{R}'' = \text{H}$ ; $\text{R} = \text{Bz}$ ; $\text{R}' = \text{R}'' = \text{Me}$ )<sup>☆</sup>

Andreas Decken<sup>a,1</sup>, Charles R. Eisnor<sup>b</sup>, Robert A. Gossage<sup>b,\*</sup>, Sarah M. Jackson<sup>b,2</sup>

<sup>a</sup> Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

<sup>b</sup> The David Upton Hill Laboratory of Inorganic Chemistry, 6 University Avenue, Elliott Hall, Department of Chemistry, Acadia University, Wolfville, Nova Scotia, Canada B4P 2R6

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This manuscript is dedicated to a mentor and friend, Prof. Dr. Gerard van Koten, in recognition of his outstanding contributions to the chemistry of organic, organometallic and coordination compounds.

## Abstract

The synthesis and characterisation (NMR, IR, X-ray diffraction and elemental analysis) of a series of zinc dialkyldithiocarbamate complexes incorporating a monodentate oxazoline ligand are described. These compounds represent the first known examples of oxazolines that are bound to a  $[\text{Zn}(\text{S}_2\text{CNR}_2)_2]$  fragment. The syntheses of the title materials involves the treatment of solutions of  $[\text{Zn}(\text{S}_2\text{CNR}_2)_2]$ , ( $\text{R} = \text{Me}$ : **1**,  $\text{Et}$ : **2** or  $\text{benzyl (Bz)}$ : **3**) with oxazolines (**L**) of general formula 2- $\text{R}'$ -4,4- $\text{R}''$ -2-oxazoline ( $\text{R}' = \text{Me}$ ,  $\text{Et}$  or  $\text{Ph}$ ;  $\text{R}'' = \text{H}$  or  $\text{Me}$ ). The compounds can be isolated in yields ranging from 17% to 82% and all of the complexes are assumed to be mononuclear species of general formula  $[\text{Zn}(\text{S}_2\text{CNR}_2-\kappa^2\text{S})_2(\text{L})]$ . The nature of the bonding in several examples has been further elucidated in the solid-state by single crystal X-ray diffraction; specifically the cases of  $\text{R} = \text{Me}$ ,  $\text{L} = 2\text{-methyl-}2\text{-oxazoline}$ : **12**;  $\text{R} = \text{Et}$ ,  $\text{L} = 2\text{-R}'\text{-}2\text{-oxazoline}$ :  $\text{R}' = \text{Me}$ : **9**,  $\text{Et}$ : **10** or  $\text{Ph}$ : **11** and  $\text{R} = \text{Bz}$ ,  $\text{L} = 2,4,4\text{-trimethyl-}2\text{-oxazoline}$ : **16**. The structurally characterised materials contain two chelating dialkyldithiocarbamate groups and a single oxazoline ligand bound through the N-atom. The disposition of donor atoms around the formally Zn(II) metal centre is best described as distorted trigonal bipyramidal. Complex **16** is the first known N-donor complex of **3** to be fully characterised. In case of the common commercial oxazoline, viz. 4,4-dimethyl-2-phenyl-2-oxazoline, none of the zinc compounds tested forms a stable complex. Some aspects of the steric and electronic effects on oxazoline adduct formation within this series of complexes is discussed. The relationship of these new compounds to other structurally similar and industrially relevant zinc dialkyldithiocarbamate complexes is also detailed.

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**Keywords:** Oxazoline; Zinc complexes; Dithiocarbamate; X-ray crystal structures; 4,5-Dihydro-2-oxazole

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\* Corresponding author. Tel.: +1 902 5851109; fax: +1 902 5851114.  
E-mail addresses: [adecken@unb.ca](mailto:adecken@unb.ca) (A. Decken), [rgossage@acadiau.ca](mailto:rgossage@acadiau.ca) (R.A. Gossage).

<sup>1</sup> Direct queries regarding the crystallography to this author.

<sup>2</sup> Undergraduate Research Participant: 2003–2004.

## 1. Introduction

Group XII dithiocarbamates (DTC) represent a large and interesting class of inorganic compounds [1,2]. These materials are used in a wide number of diverse

applications which include their role as additives to pavement asphalt [3], in analytical determinations [4,5] and as potent biological pesticides and/or pharmaceuticals (e.g., Ziram™ [6–12]). Zinc DTC are also useful precursors to metal chalcogen thin films (e.g., ZnS [13–25]) and for the design of metal complexes for use as selective binding agents for the inclusion of “guest” species [26–31]. In addition, zinc DTC (in combination with amines) act as effective radical scavenging agents for high thermal stress industrial lubricants; an additional role of such complexes is to engender high thermal stability characteristics to the resulting lubricant composite [32,33]. It has been known for some time that zinc DTC can act as promoters of rubber vulcanisation [34–39] and can serve as antioxidants for increasing the longevity and photo-stability of a variety of polymers, oils and other materials [40–59]. Somewhat surprisingly, zinc DTC can also act as oxidants of organic molecules such as catechols [60]. Other uses of Group XII DTC include their applications in materials science [61]. The late Prof. Dr. van der Kerk played a pivotal role in the development of such DTC as biological agents [6,7,11]. Coincidentally, Prof. van der Kerk was the doctoral mentor of Prof. Dr. Gerard van Koten, to whom this special issue of *Inorganica Chimica Acta* is dedicated. In turn, Gerard has played an important part in fostering my own (i.e. R.A. Gossage’s) interests in these fascinating materials.

Arguably the most simple examples of zinc DTC are the complexes [bis(*N,N*-dimethyldithiocarbamato)zinc] (**1**) and [bis(*N,N*-diethyldithiocarbamato)zinc] (**2**); both of these compounds are dimeric in the solid-state (i.e., they have the general formula  $[\text{Zn}(\text{S}_2\text{CNR}_2)_2]_2$ ), each containing structurally unique (two bridging and two chelating) dithiocarbamato ligands [1,2,62–67]. Freezing point depression and vapour pressure osmometry measurements have indicated that the dimeric nature of these two species is not retained in solution (**1**:  $\text{CHCl}_3$ ; **2**:  $\text{C}_6\text{H}_6$ ) and hence solvated zinc monomers of assumed formula  $[\text{Zn}(\text{S}_2\text{CNR}_2-\kappa^2\text{S})_2]$  are formed upon dissolution [62,63,65]. The related complex [bis(*N,N*-dibenzoyldithiocarbamato)zinc] (**3**) is a rare example of a (solid-state) monomeric Zn DTC [1,2,68–71]; presumably **3** is also a monomer [68,72,73] in solution.<sup>3</sup> (see Fig. 1).

The treatment of complexes such as **1–3** with N-donor ligands generally results [1,2,69–71,74–106] in the isolation of monometallic compounds of general formula  $[\text{Zn}(\text{S}_2\text{CNR}_2)_2(\text{N-donor})_x]$ , ( $x = 1$  or  $2$ ), in which both dithiocarbamate anions are bound in a chelating (i.e., in a  $-\kappa\text{S}^2$ ) fashion. Structurally characterised examples [74–106] of this chemistry include the five coordinate complexes  $[\text{Zn}(\text{S}_2\text{CNMeR})_2(\text{L})]$  ( $\text{L} = \text{pyridine [py]}$ ;



**1**:  $\text{R} = \text{Me}$ ,  $n = 2$ ;

**2**:  $\text{R} = \text{Et}$ ,  $n = 2$ ;

**3**:  $\text{R} = \text{benzyl}$ ,  $n = 1$

Fig. 1.

$\text{R} = \text{Me}$  or  $i\text{Pr}$ ),  $\{\mu\text{-}N,N'\text{-(Me}_2\text{N[CH}_2\text{]}_2\text{NMe}_2)[\text{Zn}(\text{S}_2\text{CNMe}^i\text{Pr}-\kappa^2\text{S})_2]_2\}$ , and  $[\text{Zn}(\text{S}_2\text{CNEt}_2-\kappa^2\text{S})_2(\text{L})]$  ( $\text{L} = \text{piperidine, morpholine or py}$ ). Conversely, five coordinate complexes are also known in which one or both of the dithiocarbamate ligands is found to bind in a monodentate fashion (e.g.,  $[\text{Zn}(\text{S}_2\text{CNHR}-\kappa^2\text{S})(\text{S}_2\text{CNHR}-\kappa^1\text{S})-(2,2'\text{-bipy}-\kappa^2\text{N})]$ ;  $\text{R} = -\text{CH}_2\text{CH}_2\text{OH}$  [104–106]). Structurally, the complex  $[\text{Zn}(\text{S}_2\text{CNEt}_2-\kappa^2\text{S})_2(\text{py})]$  exists in no less than three (polymorphic) solid-state forms. This solid material has been used to form inclusion adducts with N-atom donor molecules, aromatics (e.g., benzene) and a number of halocarbons (e.g.,  $\text{CCl}_4$ ).

Six coordinate compounds are also a structural possibility within the class of zinc dithiocarbamate N-donor complexes, such as the compound  $[\text{Zn}(\text{S}_2\text{Cpyr}-\kappa^2\text{S})_2(4,7\text{-diphenyl-1,10-phenanthroline}-\kappa^2\text{N})]$  ( $\text{pyr} = \text{pyrroline}$ , [1,2,107–117]). Group XII DTC are also known in which the  $\text{S}_2\text{CNR}_2^-$  containing fragments act simply as counterions [113–115], such as is found in the complexes  $[\text{Zn}(\text{en})_3]^{2+} \cdot [\text{L}^-]_2$  ( $\text{en} = \text{ethylenediamine}$ ;  $\text{L} = \text{S}_2\text{CNEt}_2$ ). Hence, the zinc DTC have been shown to adapt a wide variety of structural motifs depending on both the type of N-donor ligand(s) present and the nature of the dithiocarbamate ligands.

Our research interests are focussed on the coordination and medicinal inorganic chemistry of oxazolines (i.e., 4,5-dihydro-2-oxazoles) and related oxazole ligands [118–125] and includes the design of functional organic frameworks that contain an oxazoline (ox) unit [121–125]. As the ox coordination chemistry of the general class of Group XII DTC is a completely unexplored area [1,2,126,127], we felt that an investigation of the chemistry of this class of materials was a warranted endeavour. In this report, we detail some of our recent work involving the study of the coordination chemistry of zinc DTC with potentially monodentate ox ligands. Five coordinate zinc complexes can generally be isolated in good yield. However, we have found that in some cases subtle changes in the nature of the zinc-bound dithiocarbamate groups and/or properties of the ox hinders the isolation of a ligand adduct. Some plausible explanations for the observed reactivity trends are discussed. In addition, we present the X-ray diffraction data of five representatives of this structurally intriguing and important class of zinc containing materials [1,2,62–117]. These compounds represent the first examples of oxazolines coordinated to the general class of

<sup>3</sup> The unusual complex  $[\text{Zn}(\text{S}_2\text{CNR}_2)_2]_n$ , ( $\text{R} = i\text{-butyl}$ ) exists as both a monomer and dimer within the lattice of the solid-state crystalline unit cell [72,73].

[Zn(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>] compounds; to the best of our knowledge we are also disclosing the first structurally characterised N-donor ligand complex of **3**.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterisation

We began our investigations using five common and commercially available 2-oxazolines **4–8** (Fig. 2) and readily available and soluble zinc complex **2**. Treatment of dichloromethane solutions of **2** with 2 equiv of ox **4**, **5** or **6** leads to the facile isolation of colourless complexes **9**, **10** and **11**, respectively.

Elemental analysis measurements suggest the general formula [Zn(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(ox)]<sub>n</sub> (i.e., a 1:1 Zn:ox complex). These data are further corroborated by <sup>1</sup>H NMR spectroscopy (see Section 4) and by single crystal X-ray diffraction studies (vide infra). Notably, there are distinct <sup>1</sup>H NMR chemical shifts differences for presumably ligated ox compounds **4–6** relative to the free ligand form<sup>4</sup> (see Section 4 and [118]). Both ligand **7** and its 2-phenyl congener **8** were found to be unreactive towards **2** under identical reaction conditions as described above for complexes **4–6**. The heating of a sample of **2** to reflux temperature (dichloromethane or toluene as solvent) in the presence of an excess of **7** or **8**, was likewise ineffective at facilitating complex formation; as was the slow evaporation of a mixture of **2** dissolved in (neat) liquid **7** that had been heated on a steam bath for 15 min. and then left to evaporate at RT. In all cases, complex **2** was recovered unchanged in virtually quantitative yields. Compound **7** also did not displace (reflux; CHCl<sub>3</sub>; 18 h) coordinated ligand **6** from complex **11**. We assume that steric effects (i.e., the methyl substituents on formal ox ring position-4) are the likely cause for these observations. Justification for this view comes from the fact that the presence of such bulky groups on this ox ring position has been used to explain why compounds **4–6** can be readily polymerized by Lewis acids (following complex formation via bonding at N) whereas compounds such as **8** are completely inert to such reactivity [128–131]. Electronic effects seem less likely to be the reason for these observations. This certainly seems to be the case with ligand **7**, since both **4** (which readily coordinates to **2**) and **7** have virtually identical electronic abilities as weak bases, as indicated by the very similar pK<sub>a</sub> values (**4**: 5.52; **7**: 5.59) of the corresponding protonated forms [132].

Similar reactions of ligands **4–8** with **1** were at first hampered by the notoriously poor solubility of this zinc

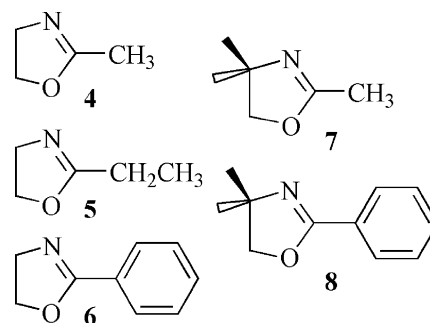


Fig. 2.

starting material [62,63]. It was also discovered that purifying the resulting complexes was often tedious as trace amounts of residual **1** were found to be difficult to extract from the products. Pure adducts were obtained with both oxazolines **4** and **5** (complexes **12** and **13**, respectively) by boiling the ox with **1** in toluene for an extended time period, followed by hot filtration. However, even under these forcing conditions, compounds **6**, **7** and **8** could not be induced to form a stable adduct with **1**. Steric effects are again invoked as a partial explanation for these observations, combined in the case of ox **6** with the electron withdrawing capacity of the Ph group that may render **6** insufficiently nucleophilic to coordinate to **1** [132,133].<sup>5</sup> This latter result is in obvious contrast to the above reaction of **6** with **2**.

In the case of similar reactions with the monomeric zinc complex **3**, *electronic* effects seem to be an important aspect of the coordination chemistry. This is rationalised by the observation that the stronger bases **4**, **5** and **7** [132,133] form stable adducts with **3** (complexes **14–16**) but both of the 2-phenyl-2-oxazolines (**6** and **8**) do not.<sup>6</sup> This suggests that the Lewis acidity of **3** (slightly enhanced by the electron withdrawing benzylic substituents relative to the alkyl groups found in complexes **1** and **2**) may be enough of a driving force for ox complex formation. However, the steric bulk of the phenyl group located on ox position-2 may also be partly responsible for these observations. As mentioned earlier, complex **3** is a rare example of a zinc DTC complex that is monomeric in both solution and the solid-state [1,2,62–67]; this observation has been attributed to the steric bulk of the organic substituents on the dithiocarbamate groups in this and the other four structurally related examples [68–73]. Such a hypothesis suggests that both steric and electronic components are important for stable adduct formation and that small changes in acidity of the metal and basicity of the ox

<sup>4</sup> For example: <sup>1</sup>H NMR data [118] of 2-methyl-2-oxazoline (**4**): 4.12 (t, *J* = 9.5), 3.73 (t), 1.86 (s) and complex **9**: 4.38 (t, *J* = 9.6), 3.99 (t), 2.12 (s).

<sup>5</sup> The pK<sub>a</sub> value (4.4) of protonated **6** indicates that this oxazoline is an order of magnitude less basic than **4** [132].

<sup>6</sup> The pK<sub>a</sub> value of protonated **8** has not, to our knowledge, been previously reported in the literature.

can have a drastic effect on adduct formation. This aspect will require further investigation.

None of the zinc materials tested here forms a stable, isolable complex with the common commercial ox **8**. This infers that the array of known (and easily synthesised) 4,4-dimethyl-2-phenyl-2-oxazoline derivatives are inappropriate ligands for coordination to zinc DTC. This may help to explain the hitherto dearth of examples of ox complexes within this collection of zinc materials, despite the large number of examples of stable N-donor complexes [1,2,13–31,62–67,69–71,74–106]. Since electronic effects may be a primary driving force in complex formation with zinc complex **3**, a more basic 2-phenyl-2-oxazoline, such as 4,4-dimethyl-2-(4'-*tert*-butylphenyl)-2-oxazoline, may form a stable coordination complex.

## 2.2. X-ray crystal structures

As there are no examples [1,2,126,127] of ox complexes of the Group XII DTC reported in the literature, we felt that a structural investigation of this class of compounds was in order. Elemental analyses and  $^1\text{H}$  NMR spectroscopy of the above isolated materials had suggested that mononuclear five coordinate zinc species were the likely structural motif for these materials. However, these analytical methods could not eliminate the possibility of a symmetrical (bridged) di- or multi-metallic species nor could these data unequivocally determine the binding mode(s) of the dithiocarbamate ligands. As mentioned earlier, the solid-state structural aspects of zinc DTC are quite diverse and includes many examples of four [104–106], five [74–106]

Table 1  
Crystallographic data for compounds **9–12** and **16**

Complex	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>16</b>
Formula	$\text{C}_{14}\text{H}_{27}\text{N}_3\text{OS}_4\text{Zn}$	$\text{C}_{15}\text{H}_{29}\text{N}_3\text{OS}_4\text{Zn}$	$\text{C}_{19}\text{H}_{29}\text{N}_3\text{OS}_4\text{Zn}$	$\text{C}_{10}\text{H}_{19}\text{N}_3\text{OS}_4\text{Zn}$	$\text{C}_{36}\text{H}_{39}\text{N}_3\text{OS}_4\text{Zn}$
$M_w$ (g/mol)	447.00	461.02	509.06	390.89	723.31
Crystal size (mm <sup>3</sup> )	$0.35 \times 0.45 \times 0.5$	$0.125 \times 0.225 \times 0.3$	$0.15 \times 0.3 \times 0.4$	$0.1 \times 0.35 \times 0.55$	$0.45 \times 0.30 \times 0.225$
Habit	irregular	irregular	parallelepiped	plate	irregular
Crystal system	tetragonal	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P4_32_12$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1$
<i>Unit cell dimensions</i>					
$a$ (Å)	8.3924(6)	15.1710(8)	9.6580(12)	15.6018(6)	12.3365(10)
$b$ (Å)	8.3924(6)	8.5354(5)	9.8976(12)	7.3628(3)	12.5096(9)
$c$ (Å)	28.994(3)	16.6390(9)	14.7704(17)	14.6224(5)	12.8861(10)
$\alpha$ (°)			71.698(2)		
$\beta$ (°)		91.4080(10)	80.490(2)	96.824(1)	117.120(1)
$\gamma$ (°)			63.038(2)		
$V$ (Å <sup>3</sup> )	2042.1(3)	2153.9(2)	1194.4(2)	1667.82(11)	1770.0(2)
$Z$	4	4	2	4	2
Density (calc.: Mg/m <sup>3</sup> )	1.454	1.422	1.416	1.557	1.357
Absorption coefficient (mm <sup>-1</sup> )	1.617	1.536	1.393	1.968	0.962
$F(000)$	936	968	532	808	756
$\theta$ Range (°) data collection	2.53–27.49	1.34–27.49	2.37–25.00	2.63–27.50	1.78–24.99
Completeness to $\theta = 27.49^\circ$ (%)	99.8	98.2	93.1	97.9	95
Exposure time (s)	10	15	10	20	20
Index ranges	$-10 \leq h \leq +10$ $-10 \leq k \leq +10$ $-33 \leq l \leq +37$	$-19 \leq h \leq +17$ $-10 \leq k \leq +10$ $-21 \leq l \leq +21$	$-11 \leq h \leq +11$ $-10 \leq k \leq +11$ $-17 \leq l \leq +17$	$-19 \leq h \leq +20$ $-9 \leq k \leq +9$ $-17 \leq l \leq +18$	$-12 \leq h \leq +14$ $-14 \leq k \leq +14$ $-14 \leq l \leq +13$
Reflections collected	14211	14906	6172	11247	8751
Independent reflections	2341	4856	3915	3752	5175
$[R_{\text{int}}]$	0.0288	0.0221	0.0163	0.0271	0.0262
Min./max. transmission	0.892	0.842	0.819	0.753	0.810
Data/restraints/parameters	2341/0/128	4856/0/222	3915/0/369	3752/0/248	5175/1/409
GOF on $F^2$	1.099	1.063	1.262	1.066	1.001
Final $R$ indices [ $I > 2\sigma(I)$ ]					
$R_1$	0.0176	0.0282	0.0395	0.0270	0.0284
$wR_2$	0.0447	0.0733	0.1313	0.0763	0.0665
$R$ indices (all data)					
$R_1$	0.0181	0.0377	0.0414	0.0306	0.0307
$wR_2$	0.0448	0.0774	0.1319	0.0787	0.0672
Largest/mean shift/esd	0.000/0.000	0.002/0.000	0.000/0.000	0.001/0.000	0.001/0.000
Largest differential peak/hole <sup>a</sup>	0.277/−0.465	0.559/−0.365	0.739/−0.662	0.652/−0.236	0.759/−0.296

$$wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [F_o^4])^{1/2}$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum F_o$$

$$\text{Weight} = 1/[\sigma_o^2(F_o^2) + (A * P)^2 + (B * P)] \text{ where } P = (\max(F_o^2, 0) + 2 * F_c^2)/3$$

<sup>a</sup> Units of e Å<sup>-3</sup>.

and six coordinate [107–117] zinc species with a combination of both mono and/or bidentate dithiocarbamate ligands and/or mono, bidentate and/or bridging N-donor ligands (vide supra). The nature of the coordination sphere around the metal atom can therefore range from distorted tetrahedral to trigonal bipyramidal (or square pyramidal) and pseudo-octahedral. The (distorted) trigonal bipyramidal polyhedron seems to be the most frequently encountered structural form [69–117] and this is indeed the coordination environment observed in the solid-state form of all five derivatives described herein. The relevant X-ray data for the solid-state characterisation of complexes **9–12** and **16** can be found in Table 1. Molecular diagrams of these species are depicted in Figs. 3–7,

respectively. These are the first ox complexes of the zinc DTC to be structurally characterised; we also believe that **16** is the first N-donor complex of **3** to be structurally investigated. Selected bond lengths and angles can be found in Table 2. The most distinguishing features of all five of these materials is the distorted trigonal bipyramidal array of ligands (four S-donor atoms and a single N-donor atom) of the two chelating dialkyldithiocarbamate ligands and a single ox ligand, bound through the N-atom, as expected [118,126,127]. The latter binding atom occupies a formally equatorial site of the ligand polyhedron, as in related species [69–117]. Thus, two distinctly different sets of Zn–S bond lengths are observed, with the equatorial bonds being much

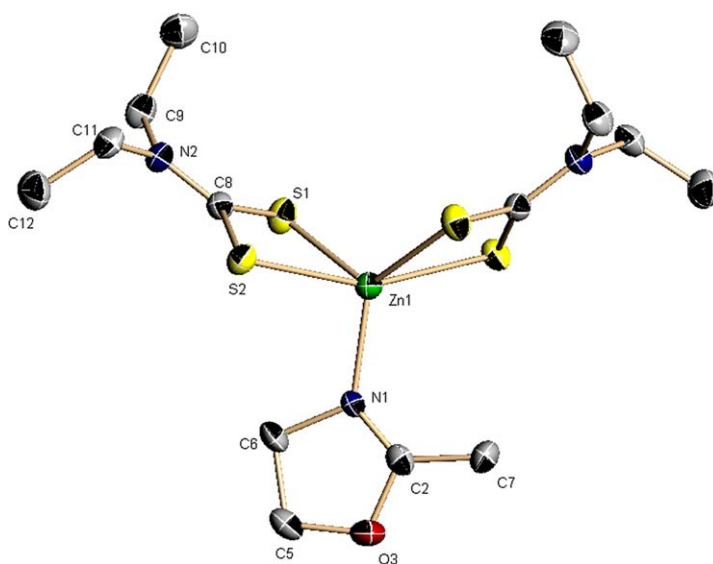


Fig. 3. Molecular diagram of complex **9** with thermal ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

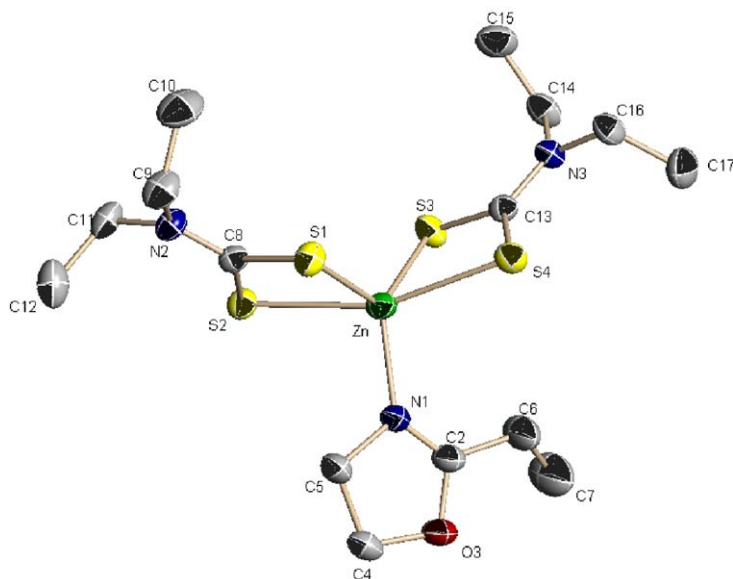


Fig. 4. Molecular diagram of complex **10** with thermal ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

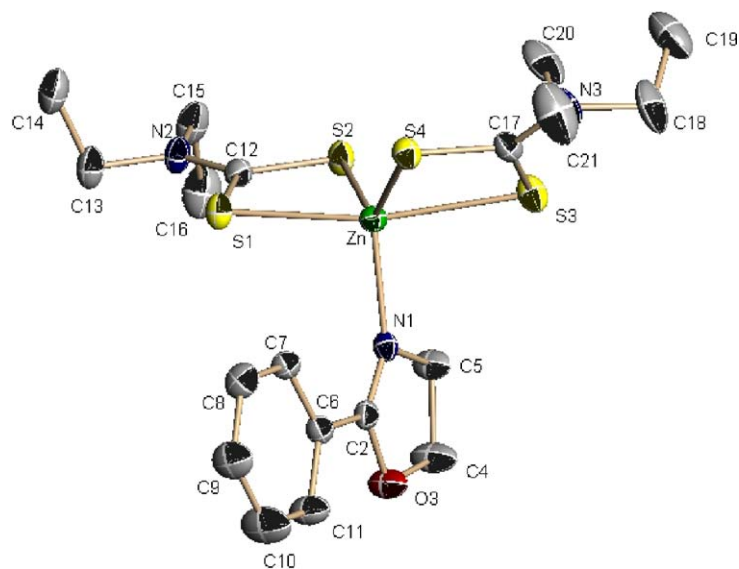


Fig. 5. Molecular diagram of complex **11** with thermal ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

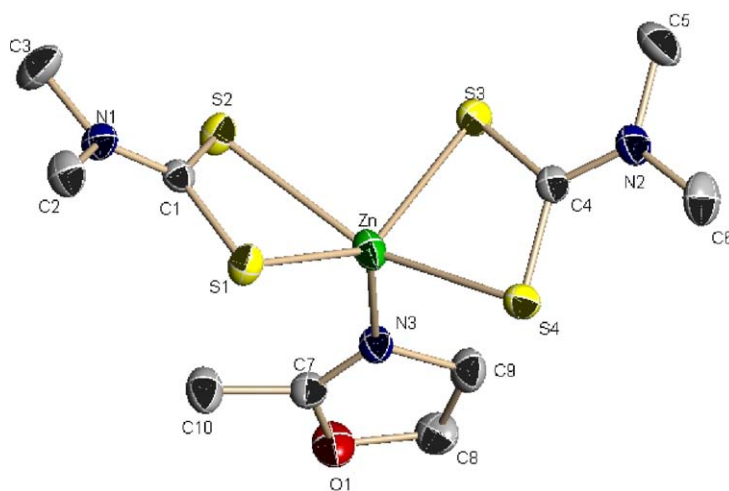


Fig. 6. Molecular diagram of complex **12** with thermal ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

longer than those occupying the axial sites [69–106]. Obviously, a result of this is that each chelating ligand occupies one equatorial and one axial site of the zinc's coordination sphere. The other bond lengths and angles are typical for this class of materials [13–31,62–117,119,126,127].

### 3. Conclusions

The first known examples of oxazolines coordinated to zinc dithiocarbamate complexes have been synthesised and fully characterised. Five coordinate distorted trigonal bipyramidal zinc complexes are formed with the ox in a (formally) equatorial position. In all of the examples that have been structurally characterised, both

dithiocarbamate ligands are bound in a chelating ( $\kappa^2S$ ) fashion that bridges equatorial and axial sites. The reactivity results reported herein are summarised in [Scheme 1](#). These data demonstrate that subtle changes in the steric and electronic components of *both* the ox and the DTC starting material can have a profound influence on the formation of stable adducts. As the latter compounds can exist in a plethora of structural forms (likely with a wide variety of Lewis acidities) and oxazolines are known with a vast array of differing steric and electronic characteristics, the precise requirements for stable complex formation will obviously require further scrutiny. Such experimentation could lead to a quantitative measure of the relative binding strengths of various zinc DTC and oxazolines. Future work is directed towards the testing of these new materials

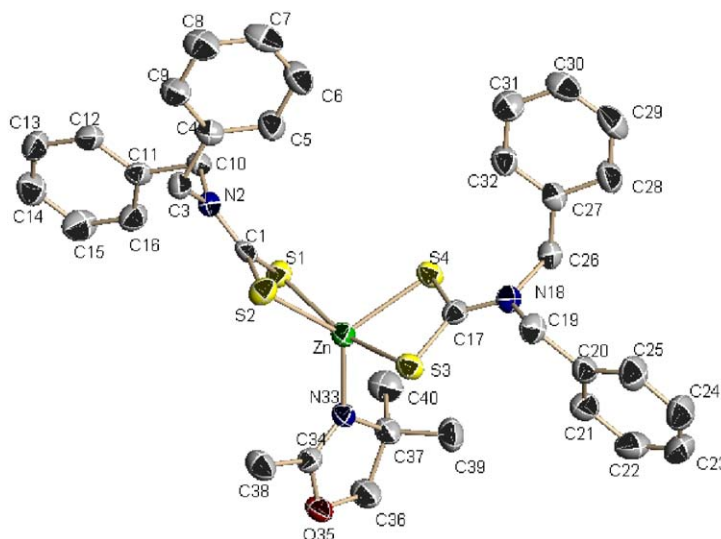


Fig. 7. Molecular diagram of complex **16** with thermal ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

Table 2  
Selected bond lengths (Å) and angles (°) for complexes **9–12** and **16**

Complex	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>16</b>
<i>Grouping</i>					
Zn–N <sub>ox</sub> <sup>a</sup>	2.042(2)	2.036(2)	2.082(4)	2.0270(13)	2.040(2)
Zn–S <sub>ax</sub>	2.3353(4)	2.3389(5) 2.3438(6)	2.3493(13) 2.3780(14)	2.3196(4) 2.3387(4)	2.3480(8) 2.3527(8)
Zn–S <sub>eq</sub>	2.6231(4)	2.6197(6) 2.6233(5)	2.5015(13) 2.5980(14)	2.5575(5) 2.7476(5)	2.5779(9) 2.5980(8)
C–N <sup>b</sup>	1.3282(2)	1.328(3) 1.328(2)	1.329(6) 1.324(7)	1.328(2) 1.319(2)	1.344(4) 1.333(4)
C–N <sub>ox</sub> <sup>c</sup>	1.258(3)	1.273(2)	1.260(6)	1.276(2)	1.270(4)
S <sub>ax</sub> –Zn–S <sub>ax</sub>	158.51(2)	159.90(2)	167.84(5)	158.20(2)	164.63(3)
S <sub>eq</sub> –Zn–S <sub>eq</sub>	121.66(2)	123.28(2)	128.86(5)	122.91(2)	114.40(3)
S <sub>eq</sub> –Zn–N <sub>eq</sub>	111.69(7)	119.89(5) 116.77(5)	108.36(11) 122.24(11)	118.92(4) 117.54(4)	118.44(7) 127.13(7)

<sup>a</sup> N<sub>ox</sub> = N-atom of oxazoline.

<sup>b</sup> C–N bond length of the dithiocarbamate groups.

<sup>c</sup> Formal C=N of the oxazoline ring.

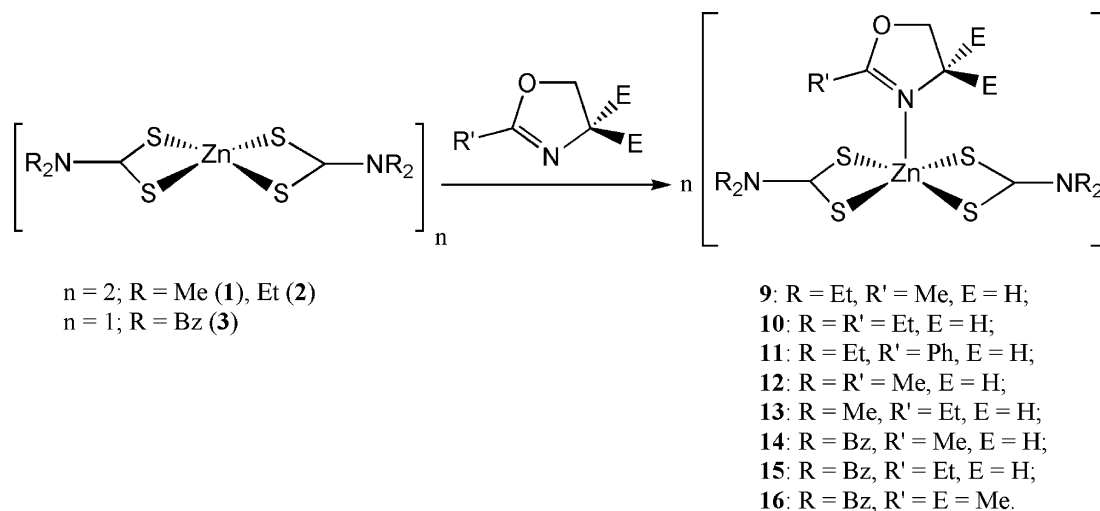
as polymer stabilising elements and as potential promoters of rubber vulcanisation processes [34–60]. In addition, their application as possible radical scavenging agents is a topic of current research. These results will be reported in due course.

## 4. Experimental

### 4.1. General

All reactions were carried out in air using standard bench-top synthetic techniques. All reagents were purchased from commercial suppliers (Sigma–Aldrich/

BDH/TCI) and used as received. Melting points were determined on a Mel-Temp II or Büchi melting point apparatus and are uncorrected. IR spectra were recorded from NaCl plates (thin films) or as KBr pellets using a Perkin–Elmer 683 IR spectrometer and frequency values are reported in units of cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> solutions at room temperature (RT) on a Bruker Avance 300 MHz NMR spectrometer located at ACMA (Wolfville, Canada). Spectra are referenced to TMS ( $\delta = 0.00$  ppm) as external standard. Elemental analyses measurements were performed the Lakehead University Centre for Analytical Services (LUCAS: Thunder Bay, Canada), The ANALEST Centre (Uni-



Scheme 1.

versity of Toronto, Canada), the analytical chemistry services department of the University of Windsor (Windsor, Canada) and in the laboratories of Prof. J. Roff (Dept. of Environmental Science, Acadia University, Wolfville, Canada).

## 4.2. Syntheses

### 4.2.1. Synthesis of $[\text{Zn}(\text{S}_2\text{CNEt}_2-\kappa^2\text{S})_2(2\text{-methyl-2-oxazoline-}\kappa^1\text{N})]$ (**9**)

A 5.5 g sample of **2** (7.6 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (~100 mL). Compound **4** (1.3 mL: 15 mmol) was added to the resulting mixture and the solution was stirred at RT for 12 h. The mixture was then filtered and volatile components removed in vacuo. The resulting crude off-white solid was re-crystallised in three crops from boiling acetone to yield a clear, colourless crystalline material (5.8 g: 86%); m.p. 113–114 °C (dec.). IR: 1655 (st).  $^1\text{H}$  NMR  $\delta = 4.38$  (t, 2H,  $J = 9.6$ ,  $\text{OCH}_2$ ), 3.99 (t, 2H,  $\text{NCH}_2$ ), 3.90 (q, 8H,  $J = 7.2$ ,  $\text{NCH}_2$ ), 2.12 (s, br, 3H,  $\text{CH}_3$ ), 1.33 (t, 12H,  $\text{CH}_2\text{CH}_3$ ). Anal. Calc. for  $(\text{C}_{14}\text{H}_{27}\text{N}_3\text{OS}_4\text{Zn}, 447.0)$ : C, 37.62; H, 6.09; N, 9.40. Found: C, 37.21; H, 6.16; N, 9.30%.

### 4.2.2. Synthesis of $[\text{Zn}(\text{S}_2\text{CNEt}_2-\kappa^2\text{S})_2(2\text{-ethyl-2-oxazoline-}\kappa^1\text{N})]$ (**10**)

A 6.2 g sample of **2** (8.6 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (~100 mL). To the mixture was added **5** (1.7 mL: 17 mmol) and the solution stirred at RT for 12 h. The mixture was then filtered and volatile components removed in vacuo. The resulting crude off-white solid was re-crystallised in three crops from boiling acetone to yield a clear, colourless crystalline product **10** (total mass: 5.39 g: 68%); m.p. 86–88 °C (dec.). IR: 1655 (st).  $^1\text{H}$  NMR  $\delta = 4.38$  (t, 2H,  $J = 9.9$ ,  $\text{OCH}_2$ ), 4.06 (t, 2H,  $\text{NCH}_2$ ), 3.89 (q, 8H,  $J = 7.2$ ,  $\text{NCH}_2$ ), 2.55 (q, 2H,  $\text{CH}_2$ ), 1.34 (t, 12H,  $\text{CH}_2\text{CH}_3$ ), 1.24 (t, 3H,

$\text{CH}_2\text{CH}_3$ ). Anal. Calc. for  $(\text{C}_{15}\text{H}_{29}\text{N}_3\text{OS}_4\text{Zn}, 461.0)$ : C, 39.08; H, 6.34; N, 9.11. Found: C, 39.05; H, 6.12; N, 9.01%.

### 4.2.3. Synthesis of $[\text{Zn}(\text{S}_2\text{CNEt}_2-\kappa^2\text{S})_2(2\text{-phenyl-2-oxazoline-}\kappa^1\text{N})]$ (**11**)

A 10.0 g sample of **2** (13.8 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (~200 mL) and  $\text{CHCl}_3$  (~100 mL). To the mixture was added **6** (3.8 mL: 26 mmol) and the solution was then stirred at RT for 12 h and then heated to reflux temperature for approximately 1 h. The mixture was then filtered and volatile components removed in vacuo. The resulting crude off-white solid complex **11** was isolated in a yield of 11.3 g (82%). An analytical sample, in the form of clear, colourless crystals, was obtained by the slow evaporation of a saturated acetone solution of crude **11**. mp 144–145 °C (dec.). IR: 1655 (st).  $^1\text{H}$  NMR  $\delta = 7.98$  (m, 2H, ArH), 7.42 (m, 3H, ArH), 4.47 (t, 2H,  $J = 10$  Hz,  $\text{OCH}_2$ ), 4.11 (t, 2H,  $\text{NCH}_2$ ), 3.87 (q, 8H,  $J = 7.0$  Hz,  $\text{CH}_2$ ), 1.33 (t, 12H,  $\text{CH}_3$ ). Anal. Calc. for  $(\text{C}_{18}\text{H}_{29}\text{N}_3\text{OS}_4\text{Zn}, 497.1)$ : C, 44.83; H, 5.74; N 8.25. Found: C, 45.10; H, 5.51; N 8.23%.

### 4.2.4. Synthesis of $[\text{Zn}(\text{S}_2\text{CNMe}_2-\kappa^2\text{S})_2(2\text{-methyl-2-oxazoline-}\kappa^1\text{N})]$ (**12**)

A 9.99 g sample of **1** (33 mmol) was suspended in toluene (300 mL) and compound **4** (3.0 mL: 36 mmol) was added to the suspension. The mixture was then heated to reflux temperature for a period of 18 h. The mixture was cooled to RT, filtered and the solution was then isolated. This mixture was then evaporated to dryness (rotary evaporator) to give an off-white slightly hygroscopic solid (approx. 11.2 g). The solid was washed with  $\text{Et}_2\text{O}$  (200 mL) and the fine white powder collected (yield: 10.4 g: 82%); m.p. 245–252 °C (dec.). IR: 1655 (st).  $^1\text{H}$  NMR  $\delta = 4.46$  (t, 2H,  $J = 10.2$ ,  $\text{OCH}_2$ ), 4.19 (t, br, 2H,  $\text{NCH}_2$ ), 3.49 (s, 12H,  $\text{NCH}_3$ ), 2.32 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calc. for  $(C_{10}H_{19}N_3OS_4Zn \cdot [H_2O])$ , 408.9): C, 29.37; H, 5.18; N, 10.28. Found: C, 29.94; H, 4.80; N, 10.29%.

#### 4.2.5. Synthesis of $[Zn(S_2CNMe_2-\kappa^2S)_2(2\text{-ethyl-2-oxazoline-}\kappa^1N)]$ (**13**)

A 10.0 g sample of **1** (33 mmol) was suspended in toluene (300 mL) and compound **5** (3.6 mL: 36 mmol) was added to the suspension. The mixture was then heated to reflux temperature for a period of 23 h. The solution was cooled to RT, filtered and the solution was then isolated and evaporated. The resulting solids were then digested in dichloromethane (100 mL), filtered and then the solution was evaporated again to dryness (rotary evaporator) to give a white slightly hygroscopic solid (yield: 5.2 g: 40%); m.p. 196–197 °C (dec.). IR: 1653 (st).  $^1H$  NMR  $\delta$  = 4.44 (t, 2H,  $J$  = 9.6,  $OCH_2$ ), 4.14 (t, 2H,  $J$  = 7.7,  $NCH_2$ ), 3.49 (s, 12H,  $NCH_3$ ), 2.66 (q, 2H,  $CCH_2$ ), 1.24 (t, 3H,  $J$  = 7.5,  $CH_3$ ). *Anal.* Calc. for  $(C_{11}H_{21}N_3OS_4Zn)$ , 404.9): C, 32.63; H, 5.23; N, 10.38: the acquisition of an acceptable and reproducible combustion analysis could not be obtained. Found (example): C, 28.46; H, 5.36; N, 9.87%.

#### 4.2.6. Synthesis of $[Zn(S_2CNBz_2-\kappa^2S)_2(2\text{-methyl-2-oxazoline-}\kappa^1N)]$ (**14**)

A 0.99 g sample of **3** (1.6 mmol) was dissolved in toluene (~100 mL). Compound **4** (1.6 g: 1.9 mmol) was thereafter added to the resulting mixture. The solution was stirred and heated to reflux temperature for a period of 26 h. The mixture was then filtered and volatile components removed in vacuo. The resulting crude off-white solid was washed with  $Et_2O$  (50 mL). The residual solids were then re-dissolved in dichloromethane, filtered and all volatile components were then removed by rotary evaporation; this procedure resulted in the isolation of a white solid (0.66 g: 59%); m.p. 155–159 °C (dec.). IR: 1663 (st).  $^1H$  NMR  $\delta$  = 7.39 (m, 20H, ArH), 5.10 (s, 8H,  $CH_2Ph$ ), 4.37 (t, 2H,  $J$  = 9.4,  $OCH_2$ ), 4.04 (t, 2H,  $NCH_2$ ), 2.18 (s, 3H,  $CH_3$ ). *Anal.* Calc. for  $(C_{34}H_{35}N_3OS_4Zn)$ , 695.3): C, 58.73; H, 5.07; N, 6.04. Found: C 58.93; H 5.24; N, 4.83%.

#### 4.2.7. Synthesis of $[Zn(S_2CNBz_2-\kappa^2S)_2(2\text{-ethyl-2-oxazoline-}\kappa^1N)]$ (**15**)

A 1.0 g sample of **3** (1.7 mmol) was dissolved in  $EtOH$  (~100 mL). To the mixture was added **5** (0.2 g: 2 mmol) and the solution stirred and heated to reflux temperature for 48 h. The mixture was then filtered and volatile components removed in vacuo. The resulting crude off-white solid was washed with  $Et_2O$  (75 mL) and the residual solids dissolved in dichloromethane (25 mL), filtered and evaporated to give 0.35 g of a white solid. The ether washings, upon evaporation, gave a further 0.63 g of product. Both of the above solids were found to be identical by NMR spec-

troscopy. The combined yield was re-crystallized from boiling (wet) acetone to yield a clear, colourless, slightly hygroscopic product **15** (total mass: 0.83 g: 70%); m.p. 98–105 °C (dec.). IR: 1655 (st).  $^1H$  NMR  $\delta$  = 7.39 (m, 20H, ArH), 5.11 (s, 8H,  $CH_2$ ), 4.38 (t, 2H,  $J$  = 9.5,  $OCH_2$ ), 4.05 (t, 2H,  $NCH_2$ ), 2.54 (q, 2H,  $J$  = 7.7,  $CCH_2$ ), 1.26 (t, 3H,  $CH_3$ ). *Anal.* Calc. for  $(C_{35}H_{37}N_3OS_4Zn \cdot [H_2O]_{1.5})$ , 720.3): C, 57.09; H, 5.48; N 5.71. Found: C, 57.20; H, 5.45; N, 5.32%.

#### 4.2.8. Synthesis of $[Zn(S_2CNBz_2-\kappa^2S)_2(2,4,4\text{-trimethyl-2-oxazoline-}\kappa^1N)]$ (**16**)

Synthesised and isolated as described above for complex **15** using **3** (1.7 mmol) and 1.1 equiv of **7**. Yield: 17%; m.p. 181–183 °C (dec.). IR: 1650 (st).  $^1H$  NMR  $\delta$ : 7.40 (m, 20H, ArH), 5.09 (s, 8H,  $CH_2$ ), 3.94 (s, 2H,  $OCH_2$ ), 2.00 (s, 3H,  $N=CCH_3$ ), 1.31 (s, 6H,  $CH_3$ ). *Anal.* Calc. for  $(C_{36}H_{39}N_3OS_4Zn)$ , 723.3): C, 59.78; H, 5.43; N 5.81. Found: C, 60.52; H, 5.54; N, 5.95%.

### 4.3. X-ray crystallography

Colourless crystals of compounds **9–12** were grown from the slow cooling of a boiling saturated acetone solution of each of the complexes. Crystals of **16** (like-wise colourless) were grown from a dichloromethane solution of the complex that was thereafter layered with and diethylether and left to stand at RT. All crystals were colourless. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer (Mo  $K\alpha$  [ $\lambda$  = 0.71073 Å] radiation) using  $\omega$  and  $\theta$  scans with a scan width of 0.3°. The detector distance was 5 (**9**, **10** and **12**) or 6 (**11** and **16**) cm. Data was collected at a temperature of  $198 \pm 1$  K and no decay of the crystals qualities was observed. The data were reduced (SAINT) [134] and corrected for absorption (SADABS) [135]. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  (SHELXTL) [136]. Hydrogen atoms were included in calculated positions and refined using a riding model except for **11** and **12** in which the H atoms were found and refined isotropically.

### 5. Supplementary data

CCDC datasets numbered 267554–267558 (inclusive) contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). In addition, cif files of

the structures reported here have been deposited with the journal.

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