HETEROMETALLIC ZINC COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

Milan Melník[1], Katarina Györyová[2], Jān Skorsepa[2] and Clive E.Holloway[3]

[1] Department of Inorganic Chemistry, Slovak Technical University,Radlinského 9,
812 37 Bratislava, Slovakia
[2] Department of Inorganic Chemistry, P.J.Safarik's University,041 54 Kosice, Slovakia
[3] Department of Chemistry, York University, 4700 Keele St.,
North York, Ontario, M13J 1P3, Canada

This review covers the heterometallic complexes of zinc, and complements two previous reviews on the inorganic and organic complexes, respectively. There are nearly fifty of these heterometallic derivatives in which the heterometal atoms include both transition and non-transition metals, both hard (class A) and soft (class B). The most common geometry found around zinc is tetrahedral. The trinuclear and polynuclear are most common, followed by binuclear and somewhat fewer tetra- and hexanuclear examples. The compounds include both organic and coordination complexation around the zinc and heterometal atoms.

CONTENTS

0. ABBREVIATIONS

acen	N,N'-ethylenebis (acetylacetoneiminate)
(baa)$_2$en	[5,5'-(1,2-ethythanediyldinitrilo)bis(1-phenyl-1,3-hexanedionate)]
bpy	2,2'-bipyridyl
Bu	butyl
cdta	cyclohexane-1,2-diaminetetraacetate
C_6H_6	benzene
$C_{14}H_{35}N_6$	hexaazabicyclo [6,6,6] icosane

cp	cyclopentadienyl
crot	crotonate
cth	dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraarylcyclotetradecane
α-dik-tadMe$_4$	2,3-dioxo-5,6,13,14-dibenzo-7,12-dimenthyl-9,10-(4",5"-dimenthylbenzo)-1,4,8,11-tetraazacyclotetradeca-7,11-diene
dmf	dimethylformamide
edta	ethylenediaminetetraacetate
en	ethylenediamine
Et	ethyl
m	monoclinic
Me	methyl
Me$_3$P	trimethylphosphine
6Mequ	6-methylquinoline
or	orthorhombic
ph	phenyl
PPh$_3$	triphenylphosphine
py	pyridine
qu	quinoline
tg	tetragonal
thf	tetrahydrofuran
tr	triclinic
4-vipy	4-vinylpyridine

1. INTRODUCTION

Over the last twenty years, studies on the reactivity of various metal derivatives with zinc salts have been carried out. Some of these studies have resulted in isolable compounds that have been suitable for crystallographic structural studies. We have recently completed a classification and review of the structures of zinc coordination compounds [1] and of organozinc compounds [2]. This present review covers the structures of organic compounds of zinc which contain one or more other metals up to the end of 1992.

One of the aims of this review is to clarify the factors which govern the stereochemical interactions around zinc and other metal(s) in such compounds. Almost fifty heterometallic zinc compounds have been surveyed, and the structures have been classified according to nuclearity. Within in each subgroup, the derivatives are referenced in order of increasing zinc-metal distance.

2. HETEROBINUCLEAR ZINC COMPOUNDS

There are ten heterobinuclear zinc derivatives listed in Table 1. There are five distinct types of bridging, with two bridging ligands being the most common [5-10]. In [(cp)(CO)$_3$MoZnBr](thf)$_2$] [3] the ZnO$_2$Br moiety is combined with the MoC$_8$ moiety directly through Zn-Mo bonding, unsupported by covalent bridges. The Zn-Mo bond distance of 271.1(1) pm is the shortest found in the heterobinuclear zinc derivatives.

In yellow [(cp)$_2$(C))Nb(μ-H)Zn(BH$_4$)$_2$].½C$_6$H$_6$ [4] the bridging hydrogen atom brings the zinc and niobium atoms within 282.9(2) pm, with a Zn-H-Nb angle of 107.5^0. In another two species [6,7], two oxygen ligands are used for bridging, and in others [8,9] two chlorine atoms serve as the bridges. There is an example [10] where two sulphur ligands hold tetrahedral ZnS$_2$I$_2$ and pseudo-octahedral FeS$_4$C$_2$ moieties together.

In this series there are relationships between the Zn-M distance, the Zn-L-M and μL-Zn(M)-μL angles. The Zn-M distance elongates as the Zn-L-M angle opens and the μL-Zn-(M)-μL angle closes, and vice-versa. The values are: 279.3 pm, 118.1 and 61.8^0 (mean) [5]: 312.0 pm, 104.4 and 74.4° (mean) [6]; 360 pm, 92.6 and 87.2° (mean) [8]. There is also a correspondence between the bridge angles and the covalent radii of the bridging atoms. The Zn-L-M angle closes and the μL-Zn(M)-μL opens with increasing radii. The mean values are: 118.1 and 61.8^0 (H, 37 pm), 102 and 78^0 (0, 73 pm), 90 and 90^0 (C1, 99 pm).

The structure of red [ZnC1$_2${Ni(α-dik-tad-me$_4$)}] [11] is shown in Fig.1. As can be seen, the zinc atom is tetrahedrally coordinated, by the α-diketo portion of the macrocycle plus the two chloride ligands. The nickel is in a square-planar environment in the macrocycle cavity, with a Zn..Ni distance of about 514.0(3) pm.

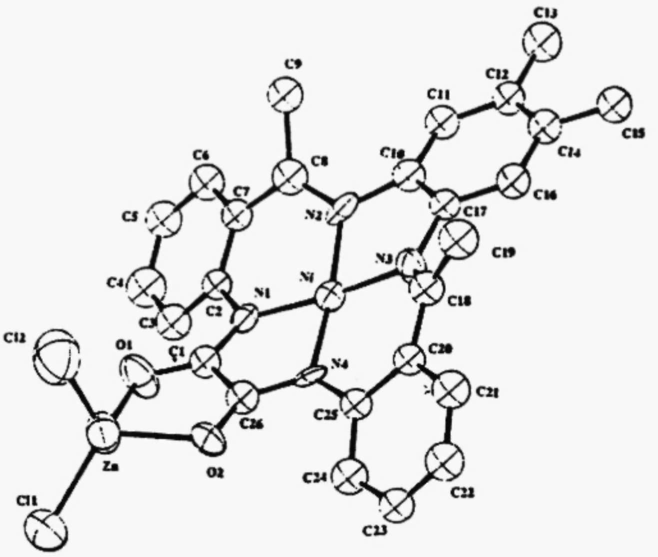

Fig.1 Structure of {ZnCl$_2$[Ni(α-dik-tad-Me$_4$)]} [11]

TABLE 1. Crystallographic and Structural Data for Heterobinuclear Zinc Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L	[pm]	Zn-M [pm] M-L-M [°] μL-M-μL [°]	L-M-L	[°]	Ref
[(cp)(CO)$_3$Mo-	m	1108.1(6)		ZnO_2Br_2	O^b	211.4(6,3)	271.1(1)	O,O^b	not given	3
	$P2_1/n$	1311.5(10)	102.63(4)		Br	243.3(2)		O,Br	not given	
ZnBr(thf)$_2$]	4	1414.1(6)		MoC_8	OC	200.0(13,39)		O,Mo	116.6(2,2.9)	
					C_{cp}	238.0(13,30)		Br,Mo	123.8(1)	
								C,Zn	68.0(3,2.3)	
									129.3(3)	
[(cp)$_2$(CO)Nb^{III}	tr	810.5(2)	89.65(1)	ZnH_5	BH_4	184.7(-,111)	282.9(2)	not given		4
	$P\bar{1}$	935.0(2)	95.49(1)		μH	176.6	107.5			
(μ-H)Zn(BH$_4$)$_2$]·½C_6H_6	2	1125.2(2)	94.33(2)	$NbC_{11}H$	C_{cp}	237.6(5,32)		μH,C	102.8	
(yellow)					OC	205.8(4)				
					μH	175				
[(cp)$_2$Mo(μ-H)$_2$	m	1318.9(4)		ZnH_2Br_2O	Br	242.0(3,10)	279.3(3)	O,Br	100.2(3,2.3)	5
	$P2_1c$	782.5(2)	99.55(2)		O	207.0(11)	118.1(-,4.4)	Br,Br	109.1(1)	
ZnBr$_2$(dmf)]		1653.1(4)			μH	169(-,10)	59.8	Br,Mo	117.9(1,2.8)	
				$MoC_{10}H_2$	C_{cp}	231.5(18,58)	-	not given		
					μH	158(-,18)	-			
							63.8			
NiZn(py){(baa)$_2$en}	m	2840.3(6)		ZnO_4N	O_{eq}	194.8(6,1)	312.0(2)	O,O	103.7(2)	6
	I2/c	846.5(3)	108.86(2)				104.4(3)	O,μO	88.9(2,2)^c	
(red brown)	8	3022.0(9)			μO_{eq}	209.2(6,11)	69.0(2)	O,N	102.7(3,1.5)	
								μO,N	100.6(3,2.2)	
				NiO_2N_2	pyN_{ap}	208.7(7)	-			
							-			
					μO	184.6(6,5)	79.8(2)	N,N	87.8(4)^d	
					N	185.1(8,7)		O,N	96.7(3,4)^d	
(thf)Fe(acen)ZnCl$_2$	tr	1400.6(3)	98.49(1)	ZnO_2Cl_2	μO	203.6(7,4)	not given	Cl,Cl	121.3(1)	7
	$P\bar{1}$	982.3(2)	90.90(1)		Cl	220.2(3,4)	99.5(3,6)	O,Cl	112.1(2,1.9)	
	2	807.7(2)	107.57(1)				79.6(3)			
				FeO_3N_2	μO_{eq}	199.7(7,12)	-	μO,N	92.1(3,6)	
					N_{eq}	201.9(9,10)	-		154.8(3,2.9)	
					thfO_{ap}	210.7(7)	81.5(3)	N,N	83.7(3)^d	

$(cth)Ni(\mu\text{-}Cl)_2ZnCl_2$	m	1904.8(3)		$ZnCl_4$	Cl	224(1,0)	360(3)	Cl,Cl	108.9(1)	8
	C2/c	954.0(3)	101.38(5)		μCl	231(3,0)	92.6(1)	Cl,μCl	113.2(2,5.9)	
	4	1285.3(3)					95.2(1)			
				NiN_4Cl_2	N	211(4,2)	-	N,N	87.1(1,1.9)^d	
					μCl	266(3)	-		100.0(1)	
							79.7(1)		170.8(1)	
								N,Cl	80.1(1)	
									163.2(1)	
$(thf)_4V(\mu\text{-}Cl)_2ZnCl_2$ (blue)	m	1473.2(5)		$ZnCl_4$	Cl	222.3(2,4)	335.4(1)	Cl,Cl	119.14(7)	9
	$P2_1/c$	968.0(3)	94.12(2)		μCl	234.1(2,3)	87.6(6,1)	Cl,μCl	110.1(1,2.7)	
	4	1620.7(6)					96.29(6)			
				VO_4Cl_2	O	214.5(4,20)	-	O,O	89.2(1,2.2)	
					μCl	250.2(2,3)	-		176.40(15)	
							88.39(6)	O,Cl	91.0(1,3.0)	
									177.0(1,1.0)	
$\{(p\text{-}ClC_6H_4)NC\}_2Fe$ $\mu\text{-}Et_2NCS_2)_2ZnI_2$ (deep red)	tg	1821.7(1)		ZnS_2I_2	μS	242.2(5,0)	not given	I,I	118.4(1)	10
	$P4_12_12$	-			I	255.2(3,0)	90.0(2)	I,S	110.2(1)	
	4	1925.5(8)					88.8(2)			
				FeS_4C_2	S	230.5(6)	-	S,S	166.2(2)	
					μS	237.4(5)	-	S,μS	85.1(2,10.0)	
					C	183.2(17)	91.2(2)	C,C	86.4(8)	
								C,S	95.1(1,2.0)	
								C,μS	91.9(5)	
$\{ZnCl_2[Ni^{II}(\alpha\text{-diktad-}Me_4)]\}.(dmf)$ (red)	m	1113.9(9)		ZnO_2Cl_2	O	202.9(11,6)	514.0(3)	O,O	81.8(5)^d	11
	$P2_1/c$	1619.2(19)	98.03(7)		Cl	217.2(7,9)		Cl,Cl	120.6(2)	
	4	1614.9(14)								
				NiN_4	N	187.3(14,21)		N,N	90.0(6,4.6)	
$[Co^{III}(C_{14}H_{35}N_6)ZnCl_3]Cl.2H_2O$	m	862.5(1)		$ZnCl_3C$	Cl	232.2(2,52)		not given		12
	$P2_1/c$	1627.3(5)	93.12(1)		C	204.9(4)				
	4	1538.1(4)								
				CoN_6	N	198.0(4,9)		N,N	86.0(2,4)^d	

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Six membered metallocyclic ring.

d. Five membered metallocyclic ring

Finally, in $[Co(C_{14}H_{35}N_6)ZnC1_3]C1.2H_20$, [12] $ZnC1_3C$ and CoN_6 moieties are held together through a carbon atom of the heptadentate macrocycle ligand with an extraordinarily stable Zn-C bond of 204.9(4) pm.

In the series of heterobinuclear zinc derivatives the zinc is mostly tetrahedrally coordinated and only in three examples is penta-coordinated. There are six different heterometal atoms in the zinc derivatives, of which the most common is nickel(II). The mean Zn-L bond distance increases in the order: 176 pm (H, 37 pm) < 208 7 pm (N, 75 pm < 209.2 pm (0, 73 pm) < 224 pm (C1, 99 pm) < 242.7 pm (Br, 118 pm) < 255.2 pm (I, 133 pm), which corresponds quite well with the covalent radius of the coordinated atom.

3. HETEROTRINUCLEAR ZINC COMPOUNDS

Structural information for heterotrinuclear zinc compounds are summarized in Table 2. There are five examples containing one zinc atom plus two heterometal atoms. In two of these [13,14] the molecules have linear M-Zn-M bonds with a mean Li-Zn distance of 245.3 pm [13] and Mo-Zn distance of 253.8 pm [14]. In pink-red [15] two $Ta{=}CCMe_3$ fragments are coordinated through bridged carbon atoms to one $ZnC1_2$ molecule, where both chlorine atoms also serve as the bridges. The mean Zn-Ta distance is 281.5(3) pm. In green [16] two cp_2TiC1 fragments are coordinated to one $ZnC1_2$ moiety. The geometry around the zinc atom is pseudotetrahedral with chlorine atoms bridging to the titanium atoms (Table 2).

The crystal structure of $[(Me_3P)PtC1(SOP(OPr^i)_2)_2Zn].CH_2C1_2$ [17] is shown in Fig.2. As can be seen, each square planar $[\{(Me_3P)PtC1(SOP(OPr^i)_2\}_2]^-$ group behaves as a

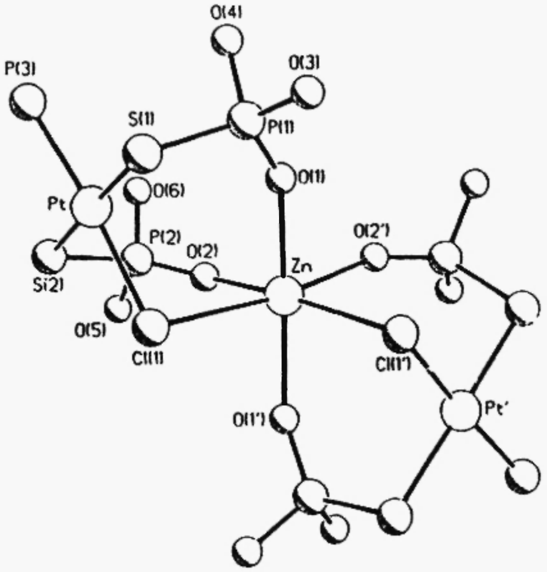

Fig.2 Structure of $[(Me_3P)PtCl(SOP(OPr^i)_2)_2Zn.CH_2Cl_2$ [17]

tridentate ligand facially coordinating the central zinc via one chlorine and two oxygen atoms. The transannular Zn..Pt distance is 388 pm and the Pt-Zn-Pt angle is 158^0.

The remaining ten examples [18-21] (Table 2) contain two zinc atoms plus a heterometal atom. The structure of a red derivative [18] consists of a central cobalt atom surrounded in a roughly tetrahedral fashion by two zinc atoms, a phosphorus atom, and a η^5-bound cyclopentadienyl group. The mean Zn-Pt distance of 228.9(1) pm is the shortest found in heterometallic zinc complexes. The Zn-C(cp-centroid) distances are 201.8(5) and 202.8(5) pm for Zn(1) and Zn(2) respectively. The Zn-cp binding is, however, definitely of the η^5 type [18] (Table 2).

In $[\{ZnC1_3(thf)(PPh_3)\}_2V]$ [19], the "central" atom is in fact vanadium, and the two zinc atoms are part of the ligand system around the zinc atom. Two zinc atoms, with a tetrahedral coordination of three chlorine atoms and one PPh_3 molecule, are each connected to the vanadium center via two chlorine bridges. Two molecules of tetrahydrofuran complete the octahedral coordination sphere of the vanadium atom.

There are eight examples, $[MZn^2(crotonate)_2L_2]$ where M is Mg, Cd, Ca, Sr, Co, Ni or Mn, and L is a unidentate N heterocyclic ligand [20,21]. The structure of colourless $MgZn_2(crotonate)_6(4\text{-vipy})_2$ [20] is shown in Fig.3 as an example. The molecule contains an exactly linear array of three metal atoms linked by six crotonate bridges. Four of the bridges are of the syn-syn type, coordinating to one metal atom through each of their two 0 atoms. The remaining two crotonates are simultaneously chelating to one Zn, and are also bridging through an 0 atom to Mg. The zinc atoms are five-coordinated, while the Mg is octahedrally coordinated (Table 2).

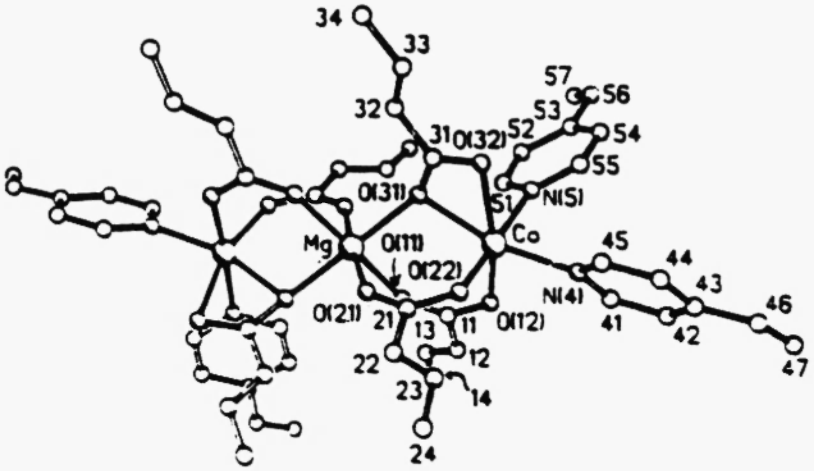

Fig.3 Structure of $MgZn_2(crot)_2(4\text{-vipy})_2$ [20]

TABLE 2. Crystallographic and Structural Data for Heterotrinuclear Zinc Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	Zn-M [pm] Zn-Zn [pm M-L-M [°]	L-M-L [°]		Ref
[{Li(Me$_2$NC$_6$H$_4$NMe$_2$)}$_2$	m	1603.38(5)		ZnC$_4$	C^b	212.7(5,6)	245.3(7,7)	C,C^b	109.5(2,9.7)	13
	P2$_1$/c	1017.67(3)	107.015(1)					Li,Li	173.6(2)	
Zn[(CH$_2$)$_5$}$_2$]		1797.85(3)		LiN$_2$	N	213.0(8,8)		N,N	86.0(3,5)^c	
(colourless)										
{(cp)(CO)$_3$Mo}$_2$Zn	m	1110.1(4)		ZnC$_2$	C	254.2(6,20)	253.8(1)	Mo,Mo	180	14
	P2$_1$/n	754.2(2)	64.43(2)							
(white)	2	1172.6(4)		MoC$_8$	OC	197.4(6,8)		C,C	81.1(2,1.6)	
					C$_{cp}$	233.5(6,13)			103.9(2)	
								C,Zn	67.3(2,6)	
									126.7(1)	
[{Cl$_2$(MeOCH$_2$CH$_2$OMe)		951.9(2)		ZnC$_2$Cl$_2$	μC	212(2,2)	281.5(3,11)	μC,μC	147.0(6)	15
	or	1400.6(3)			μCl	251.6(6,20)	-	μCl,μCl	105.0(2)	
Ta(μ-CCMe$_3$)}$_2$	Pbca	4464.5(9)					90.1(7,2)			
	8			TaO$_2$Cl$_3$C	O	217.0(14,5)		not given		
Zn(μ-Cl)$_2$]						243.7(3,25)				
					Cl	238.0(4,10)				
(pink/red)					μCl	245.3(4,2)				
					μC	183(2,4)				
[(cp$_2$TiCl)$_2$ZnCl$_2$]·	or	1823.6(10)		ZnCl$_4$	μCl	225.2(2,3)	342.0(2)	Cl,Cl	115.9(8,1.2)	16
	Pbcn	1551.3(8)					-	Ti,Ti	173.4(1)	
2C$_6$H$_6$	4	1123.7(6)					90.0(6,1)			
				TiC$_{10}$Cl$_2$	C$_{cp}$	233.4(9,16)		Cl,Cl	82.09(6)	
(green)										
					μCl	258.0(2,10)	97.57(6)			
[(Me$_3$P)PtCl(SOP	m	2513(2)		ZnO$_4$Cl$_2$	O	229.8(9,21)	388	O,O	95.4(4,5.5)	17
	C2/c	1086.6(7)	119.83(5)		μCl	280.3(5)	-		164.5(5)	
(OPr^i)$_2$)$_2$Zn].CH$_2$Cl$_2$	4	2785(2)					96.3(3)	O,Cl	84.1(2,2.0)	
							103.0(2)		172.4(3)	
				PtS$_2$ClP	S	233.2(5,2)		S,Cl	89.0(2,1.7)	
					μCl	239.2(5)		S,P	91.1(2,3.0)	
					P	221.2(5)				

(cpZn)$_2$Co(cp)(PPh$_3$)	m	1510.8(3)		ZnC$_5$	C$_{cp}$	233.8(6,131)	228.9(1,1)	not given		18
	P2$_1$/n	1748.2(4)	91.46(4)				278.34(5)			
(red)	4	1066.8(6)					93.7(1,2.3)			
				PtC$_5$P	C$_{cp}$	206.9(3,16)		not given		
					Ph$_3$P	212.06(7)				
[{ZnCl$_3$(thf)	tr	1192.2(3)	107.47(1)	ZnCl$_3$P	Cl	219.7(1)	328.9(1)	Cl,μCl	113.5(1,1.4)	19
	P$\bar{1}$	1418.9(2)	108.03(1)		μCl	230.9(1,16)	-	μCl,μCl	97.22(5)	
(PPh$_3$)}$_2$V].2CH$_2$Cl$_2$	1	899.1(3)	86.16(1)		P	239.2(1)	89.9(4)	Cl,P	110.58(6)	
								μCl,P	110.7(1,1.1)	
				VCl$_4$O$_2$	μCl	251.4(1,13)		Cl,Cl	87.08(4)	
					O	212.0(3)			180.00	
								Cl,O	89.8(1,1.3)	
[MgZn$_2$(crot)$_6$	m	1035.1(1)		ZnO$_4$N	O	196.0(2,3)	338.5	O,O	101.9(1,2.7)	20
	P2$_1$/c	1431.5(2)	106.52(1)			232.0(3)	-		153.0(1)	
(4-vipy)$_2$]	2	1438.2(2)			μO	206.5(2)	108.7(1)	O,μO	58.6(1)	
					N	205.6(3)			102.6(1,8)	
(colourless)								O,N	98.2(1,14.3)	
								μO,N	135.5(1)	
				MgO$_6$	O	206.2(3,30)		O,O	98.1(1,6.5)	
					μO	200.0(2)		μO,O	88.3(1,3)	
[MgZn$_2$(crot)$_6$(qu)$_2$]	tr	1096.5(3)	104.85(1)	ZnO$_4$	O	194.5(2,5)	330	O,O	118.4(1,7.5)	21
	P$\bar{1}$	1097.7(3)	111.82(1)			206.1(3)	-	O,μO	56.5(1)	
(colourless)	1	1107.5(3)	101.86(1)		μO	237.6(3)	104.8(1)		97.8(1,2.3)	
					N	208.1(3)		O,N	97.1(1,1.4)	
								μO,N	151.7(1)	
				MgO$_6$	O	205.0(2,2)		O,O	90.1(1)	
					μO	205.7(3)		μO,O	90.8(1,2)	
[CdZn$_2$(crot)$_6$(qu)$_2$]	m	1074.02(5)		ZnO$_3$N	O	194.6(3,6)	330	O,O	108.2(1)	21
	P2$_1$/c	1187.31(5)	98.966(4)		μO	196.3(2)	-	O,μO	107.1(1,4.7)	
(colourlsss)	2	1783.51(7)			N	202.2(3)	103.2(1)	O,N	101.8(1,6)	
								μO,N	128.4(1)	
				CdO$_6$	O	224.2(3,30)		O,O	89.1(1)	
					μO	231.4(2)		O,μO	89.5(1,3)	
[CoZn$_2$(crot)$_6$(qu)$_2$]	m	1060.62(5)		ZnO$_3$N	O	194.3(7,1)	330	O,O	109.1(1)	21
	P2$_1$/c	1195.98(5)	98.203(5)		μO	199.3(3)	-	O,μO	103.4(1,3.2)	
(purple)	2	1777.79(8)			N	204.0(3)	107.4	O,N	100.9(1,7)	
								μO,N	137.4(1)	
				CoO$_5$				O,O	90.0(1,9)	

[NiZn$_2$(crot)$_6$(qu)$_2$]	m	1066.0(2)		ZnO$_3$N	O	195.8(3,17)	330	O,O	109.9(1)	21
	P2$_1$/c	1405.0(3)	104.50(2)		μO	197.4(2)	-	O,μO	103.3(1,1.8)	
(yellow)	2	1504.6(3)			N	202.6(3)	106.1(1)	O,N	100.2(1,9)	
								μO,N	138.4(1)	
				NiO$_6$	O	204.5(3,17)		O,O	90.0(1,3.0)	
					μO	211.4(3)				
[MnZn$_2$(crot)$_6$(qu)$_2$]	m	1091.26(5)		ZnO$_3$N	O	196.1(2,20)	330	O,O	106.5(1)	21
	P2$_1$/c	969.13(5)	100.527(5)		μO	196.0(2)	-	O,μO	108.3(1,2.2)	
(pink)	2	2075.05(9)			N	202.3(2)	103.8(1)	O,N	102.2(1,1.9)	
								μO,N	127.9(1)	
				MnO$_6$	O	214.5(2,20)		O,O	90.0(1,3.1)	
					μO	223.8(1)				
[CaZn$_2$(crot)$_6$	tr	1017.0(1)	93.230(5)	ZnO$_3$N	O	195.1(3,14)		O,O	117.7(1,6.5)	21
	$P\bar{1}$	1039.7(1)	90.666(6)		N	208.6(3)		O,N	98.7(1,1.3)	
(6-Mequ)$_2$]	1	1206.4(1)	113.518(5)							
				CaO$_6$	O	229.2(3,16)		O,O	86.8(1,1.1)	
(colourless)										
[SrZn$_2$(orot)$_6$	tr	969.5(2)	65.97(1)	ZnO$_3$N	O	193.1(3,9)		O,O	117.2(1,7.3)	21
	$P\bar{1}$	1118.6(2)	86.88(1)		N	209.0(4)		O,N	99.6(2,2.9)	
(6-Mequ)$_2$	1	1177.7(2)	86.80(1)							
				SrO$_6$	O	246.4(4,5)		O,O	87.7(1,6.7)	
(colourless)										

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

d. Five membered metallocyclic ring

4. HETEROOLIGONUCLEAR ZINC COMPOUNDS

The data for these compounds are given in Table 3 in order of increasing nuclearity. There are six examples of heterotetranuclear zinc compounds, three of them containing two zinc atoms plus two heterometal atoms [14,22,23], and the remaining three containing only one zinc atom plus three heterometal atoms [24-26]. In purple $[(bpy)ZnFe(CO)_4]_2$ [22], the four-membered metal-metal bonded ring is rigorously planar. Each zinc atom is pseudotetrahedrally bonded to the two nitrogen atoms in a bidentate 2,2' -bipydridyl ligand and to two adjacent iron atoms with Zn-Fe distances of 253.2(1) and 258.5(1) pm. The iron atoms are each bonded to the two adjacent zinc atoms and to four carbonyl groups in an extremely distorted cis octahedral geometry (Table 3).

In crystals of white $[(cp)(CO)_3MoZnC1(OEt_2)]_2$, [14] two zinc atoms are doubly bridged by two chlorine atoms. The coordination of zinc is completed by a π-$(cp)(CO)_3Mo$ moiety (Zn-MO = 263.2(1) pm) and a diethyl ether species (Zn-0 = 209.3(5) pm. The structure of dark red $[(H_4)(PMePh_2)_4V_2(\mu\text{-}BH_4)_2Zn_2]$ was described [23] as a diamond-shaped V_2Zn_2 aggregate (a squashed butterfly) with four edge-bridging hydrogens. The η^2-borohydride hydrogens and the hydrogens bridging V to Zn furnish a tetrahedral environment about zinc (Table 3).

The X-ray crystal structure of air-stable dark red $[ZnI_2Pt_3(\mu\text{-}CO)_3(PPh(Pr^i)_2)_3]$ [24] is shown in Fig.4. As can be seen, the structure consists of a Pt_3-triangle capped by a zinc atom. The $ZnPt_3$ tetrahedron is distorted, having two Zn-Pt distances of 265.0(5) pm and one of 275.5(5) pm. There are also slight differences in the Pt-Pt distances (267.9 - 268.6(2) pm).

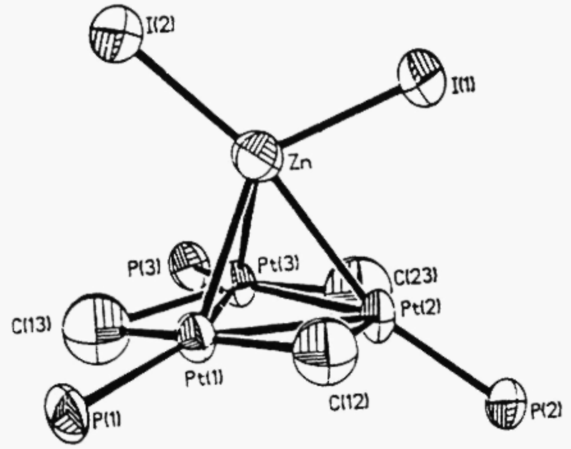

Fig.4 Structure of $ZnI_2Pt_3(\mu\text{-}CO)_3(PPh(Pr^i)_2)_3$ [23]

TABLE 3. Crystallographic and Structural Data for Heterooligonuclear Zinc Compounds[a]

COMPOUND (colour)	Crys-cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]		Zn-M [pm] Zn-L-M [°]	L-M-L [°]		Ref
$[(bpy)ZnFe(CO)_4]_2$	tr	854.1(2)	69.66(1)	ZnN_2	N^b	211.7(2,1)	255.9(1,27)	N,N^b	77.75(8)[c]	22
	$P\bar{1}$	871.2(2)	79.33(1)					Fe,Fe	113.98(2)	
(purple)	2	1051.8(2)	77.83(1)					N,Fe	114.9(1,7.1)	
								C,C	100.0(1,3.3)	
				FeC_4					150.05(4)	
					OC	176.3(3,9)		Zn,Zn	66.02(2)	
$[(cp)(CO)_3Mo-$	tr	852.4(3)	56.03(2)	$ZnCl_2O$	μCl	240.0(2,1)	263.2(1)	Cl,Cl	90.3(1)	14
	$P\bar{1}$	909.2(3)	110.13(2)		O	209.3(5)		Cl,O	98.4(1,1.5)	
$ZnCl(OEt_2)]_2$	1	1315.2(4)	103.96(2)				89.7(1)	Cl,Mo	122.1(1,1.1)	
								O,Mo	119.2(1)	
(white)				MoC_8	OC	195.1(8)		C,C	86.8(3,5)	
					C_{cp}	233.7(10)			107.3(3)	
								C,Zn	65.6(1,4)	
									122.0(2)	
$[(H_4)(PMePh_2)_4V^I_2$	tr	1267.8(3)	111.58(1)	ZnH_4	H	180(5,2)	264.5(2,12)			23
	$P\bar{1}$	1377.5(3)	110.70(1)		μH	165(5,5)				
$(\mu-BH_4)_2Zn_2$	1	1048.3(2)	111.53(1)	VH_4P_2	H	not given		μH,μH	159(2)	
					μH	183(5,3)		P,P	106.4(0)	
(dark red)					P	253.9(1,10)				
$[\{ZnI_2\}\{Pt_3(\mu-CO)_3$	m	1680(1)		ZnI_2	I	255.5(7,20)	267.6(5,79)	I,I	114.2(2)	24
	C_2	1397(1)	107.00(4)					Pt,Pt	60.1(1,1.0)	
$(PPh(Pr^i)_2)_3\}]$	4	2413(1)		PtC_2I	μOC	206(9)	268.3(2,4)[d]		not given	
					P	229(1)				
(red)										
$(NBu_4)[Zn\{Fe(cp)$	m	981.92(3)		$ZnFe_3$			254.1(2,22)	Fe,Fe	120.0(1,2.9)	25
	$P2_1/c$	2181.3(7)	106.93(2)							
$(CO)_2\}_3]$	4	1865.0(5)		FeC_7	OC	172.5(12,24)		C,C	91.2(6,5)	
					C_{cp}	173.2(13,2)			131.3(6,3.3)	
(red)										

$[Zn\{OH\}_2Co^{III}(en)_2\}_3$	m	1246.0(3)		ZnO_6	μO	210(1,2)	301(2,2)	O,O	77.9(3,2)^e	26
$(ClO_4)_4Cl.3H_2O$	$P2_1/c$	2324.4(6)	108.48(2)				97.2(4,5)			
	4	1590.4(4)		CoN_4O_2	N	not given		O,O	87.6(3,1)^e	
(deep red)					μO	191(1,1)				
$Zn_4Ni_2(cp)_6$	tg	935.2(5)		ZnC	C_{cp}	not given	240^{f1}		not given	27
	$P4_2/mnm$	-					256^{f1}			
	2	1632(1)					279^{f2}			
				NiC_5	C_{cp}	not given				
$ZnN_4Ni_2(C_5H_4Bu^t)_6$	m	1200(1)		ZnC (2)	C_{cp}	208(2)			not given	28
	$P2_1/c$	1743(1)	112.81(5)							
(green)	2	1344(2)		ZnC_5 (2)	C_{cp}	208(2)				
$Zn_4Ni_2(C_5H_4SiMe_3)_6$	m	1245.5(5)		ZnC (2)	C_{cp}	206(2)			not given	28
	$P2_1/c$	1853.9(5)	112.21(5)							
(green)	2	1350.4(5)		ZnC_3 (2)	C_{cp}	306(2)				
$[Zn_4O\{(CO)_9Co_3$	tr	1514.4(4)	62.13(2)	ZnO_4	O	not given				29
	$P\bar{1}$	1514.5(4)	62.10(2)		μ_4O	not given				
$(\mu_3-CCO_2)\}_6]$	1	1616.4(4)	60.00(2)	CoC_4	OC	not given				
					C	not given				
(purple-brown)										
$\{Li_2Zn(Me)_4\}_n$	tg	531.4(10)		ZnC_4	C	207(15)	388(2,13)	C,C	105,2(2)	30
	I4	-							111.7(2)	
(colourless)		1198.9(20)		LiC_4	C	268(4,16)		C,C	109.5(2,10.4)	
$\{NaZn(p-H_2NSO_2$	m	1851.9(6)		ZnO_4	μO	200.5(10,1)		O,O	95.6(5)	31
	$P2_1/c$	1489.7(10)	97.98(6)		O	202.7(13,24)	101.8(5,1.7)	O,μO	110.9(5,10.1)	
$C_6H_4COO)_3.H_2O\}_n$	4	1036.3(8)						μO,μO	114.8(5)	
				NaO_6	O	235.7(13,62)		O,O	79.5-175.3(4)	
(colourless)					μO	255.7(13,66)				

$[Na_2Zn_2\{C_6H_5(COO)_3\}_2$	tr	710(1)	66.94(2)	ZnO_5	μO_{eq}	197.2(3)	O_{eq},O_{eq}	119.8(1,14.6)	32
	$P\bar{1}$	979.3(2)	73.86(1)		O_{eq}	200.0(2)	O_{eq},O_{ap}	90.0(1,7.3)	
$11H_2O]_n$	1	1120.2(2)	84.76(1)		μH_2O_{eq}	201.5(2)	O_{ap},O_{ap}	176.73(10)	
					H_2O_{ap}	206.0(3)			
(colourless)					μH_2O_{ap}	223.2(3)			
				NaO_6	μO	249.1(2)			
					μH_2O	246.0(3,65)			
					O	236.3(3,29)			
					H_2O	244.6(4)			
$\{K_2Zn(OOCCH_2COO)_2$	m	943.1(5)		ZnO_6	O	202.0(5)	O,O	62.9(1)	33
	B2/m	772.2(4)			μH_2O	216.6(8)		119.4(2)	
$4H_2O\}_n$	2	1091.4(4)	115.7	KO_6	O	278.7(48)			
					μH_2O	300.0(9)			
(colourless)									
$[(H_2O)_4Mg(edta)Zn]_n$	or	1447.6(4)		ZnO_4N_2	O	199.1(5,26)	not given		34
	$Pn2_1a$	1323.7(4)				225.2(4,37)			
$2n.H_2O$	4	974.6(3)			N	204.3(5,1)			
				MgO_6	O	214.9(7,13)	not given		
(colourless)					H_2O	217.0(9,76)			
$[(H_2O)_4Mg(edta)Zn]_n$	or	1444(2)		ZnO_4N_2	O	210(4)	not given		35
	$Pna2_1$	976(1)			H	224(4)			
$2n.H_2O$	4	1310(5)		MgO_6	O	208(5)	not given		
(colourless)									
$[(H_2O)_4Zn(edta)Cu]_n$	or	1454.9(4)		ZnO_6	O	212(2,4)	O,O	90(1,4)	36
	$Pna2_1$	980.7(2)			H_2O	211(2,2)		174(1,6)	
$2n.H_2O$	4	1300.9(3)		CuO_4N_2	O	212(2,12)	O,O	97(1,13)	
					N	207(3,2)	O,H	84(1)	
(blue)								162(1)	
$[(H_2O)_4Zn(edta)Ni]_n$	or	1448.1(4)		ZnO_6	O	209(1,1)	O,O	90.0(3,9.4)	36
	$Pna2_1$	966.8(3)			H_2O	211(1,4)		173.5(3,5.1)	
$2n.H_2O$	4	1315.8(4)		NiO_4N_2	O	205(1,4)	O,O	98.6(3,16.7)	
					N	210(1,0)	O,N	81.6(3)	
(blue)								161.6(3)	

$[Zn_{0.7}Co_{0.3}(H_2O)_4]$	m	973.1(9)		ZnO_6	O	210.1(4,27)	O,O	90.0(2,7.2)	37
	$P2_1/n$	1178.3(2)	95.40(6)		H_2O	206.3(5,17)		173.2(2,2.2)	
$[Zn_{0.3}Co_{0.7}(edta)H_2O]$	4	2103.1(9)				217.3(4,16)	O,O	84.7(1,7)^c	
				CoO_4N_2	O	213.9(4,62)		95.5(1,8.0)	
$4H_2O$					H_2O	203.6(4)	N,N	82.3(2)	
					N	218.5(4,17)	O,N	76.3-157.4(2)	
$Zn_{0.5}Cu_{0.5}(HCOO)_2$	m	877(3)		ZnO_6	O	219(1)	not given		38
	$P2_1/c$	725(2)	98.0(5)		H_2O	207(1,3)			
$(H_2O)_2$	4	917(2)		CuO_6	O	206(2,4)			
						222(1)			
$Au_2Zn(EtCOO)_8(H_2O)_2$	tg	909.2(2)		ZnO_6	O	214.0(5)	O,O	90.0(1,6.6)	39
	I4	-			H_2O	201.7(7)		165.8(3)	
(colourless)	2	2254.0(8)						180.0(1)	
				AuO_4	O	197.8(6,7)	O,O	90.0(3,2.2)	
$Tl_2Zn(CN)_4$	c_ F43c	2494.6(13)		ZnC_4	NC	200.5(6,56)	C,C	109.5(4,1.5)	40
(colourless)				TlN_6	CN	298.5(7,341)	N,N	74.5-166.5(2)	
$Zn(en)Ni(CN)_4$	or	887.6(3)		ZnN_6	N_{en}	214.2(5)	N,N	82.6(2)^c	41
	Pbcn	991.1(3)			CN	216.0(5)		90.3(2,10.7)	
(yellow)	4	1110.6(5)				227.1(5)		170.3(2,1.5)	
				NiC_4	NC	187.5(5,5)	C,C	90.1(2)	
$Zn(en)_2Ag_2(CN)_4$	m	915.0(3)		ZnN_6	N_{en}	213.7(2)	N,N	82.1(7)^c	42
	I2/m	1330.8(4)	95.80(3)		CN	230.5(4)		89.0(1)	
(colourless)	2	644.2(2)						180.0	
				AgC_2	NC	205.4(4)	C,C	180.0	

Footnotes:

- a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
- b. The chemical identity of the coordinated atom or ligand is specified in these columns.
- c. Five membered metallocyclic ring
- d. The Pt-Pt distance.
- e. Four membered metallocyclic ring.
- f_1. The Ni-Ni distance.
- f_2. The Zn-Zn distance.

The geometry around zinc in $[Zn\{Fe(cp)(CO)_2\}_3]^-$ [25] is trigonal planar with the zinc atom 2.4 pm from the plane of the three iron atoms. All of the trigonal angles are 120 ± 3^0, and the mean Zn-Fe distance is 254.1(2) pm (Table 3). In another example [26] the central zinc(II) atom is surrounded octahedrally by three $[\mu\text{-OH})_2Co(en)_2]^+$ moieties with the ZnO_6 chromophore. The mean Zn..Co distance of 301 pm, with Zn-O-Co angles of 97.2^0, ruled out a metal-metal bond.

There are three examples of heterohexanuclear zinc compounds of the general formula $Zn_4Ni_2L_6$ [27,28]. The structure of $Zn_4Ni_2\ (C_5H_4SiMe_3)_6$ [28] is shown in Fig.5 as an example. These structures are unprecedented in showing examples of η^1-, η^3- and η^5- coordination of the cyclopentadienyl groups to a main group metal (Table 3).

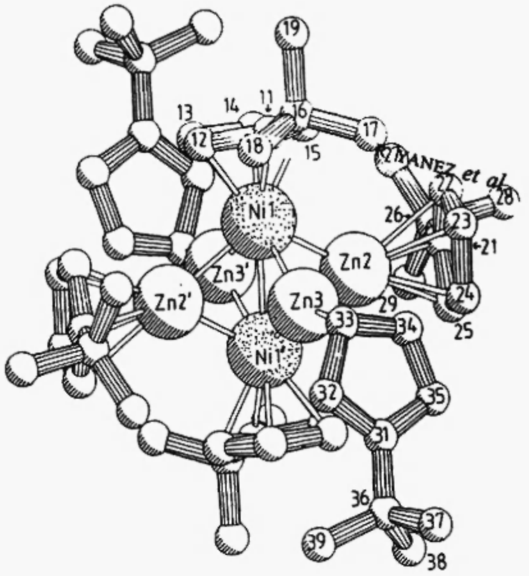

Fig.5 Structure of $Zn_4Ni_2(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^3\text{-}C_5H_4SiMe_3)_2(\eta^1\text{-}C_5H_4SiMe_3)_2$ [28]

The structure of a heterooligonuclear cluster, containing four zinc atoms plus eighteen cobalt atoms, is shown in Fig.6. The cluster has a diameter of 1,500 - 1,600 pm. It is the central metal cluster (the Zn tetrahedron) that determines the octahedral spatial distribution of the transition-metal clusters. The six $[(CO)_9Co_3(CCO_2)]^-$ moieties are located around the oxo-tetrazinc core [29].

The remaining fourteen species in Table 3 are polynuclear in structure [30-42]. The coordination geometry of the metal is predicated by the structures of the polymers and there is no straight-forward classification of types as in the previous cases. In the polynuclear examples the zinc(II) atoms are four- [30,31,40], five- [32] and six-coordinated [33-42]. The other heterometals are

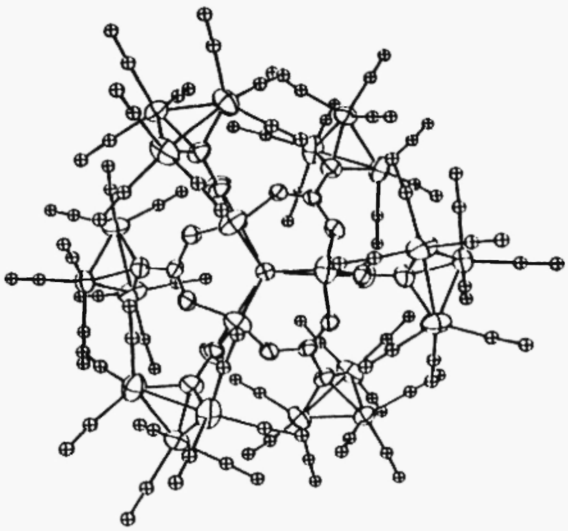

Fig.6 Structure of $Zn_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6$ [29]

two- [42], four- [30,39,41] and six-coordinated [31-40]. The most common bridging ligands are 0-donors and cyanide groups. There is no example in which the metal-metal distance was less than 300 pm.

5. CONCLUSIONS

Almost fifty heterometallic zinc compounds have been characterized by X-ray diffraction. Of these the number of examples by nuclearity increases in the order: Heterotri- < poly- < bi- < tetra- < hexa- < oligonuclear. While for zinc the tetrahedral geometry is most common, the heterometal atom usually has pseudooctahedral geometry. The shortest Zn-M bond distances are 228.8(1) pm (M = Co) in heterotrinuclear [27], 253.1(1) pm (M = Fe) in heterotetranuclear [22], and 271.1(3) pm (M = Mo) in heterobinuclear derivatives.

This review is part of a series which includes inorganic zinc(II) coordination compounds [1] and zinc organometallic compounds [2]. Despite the increasing availability of data retrieval systems, the collection of such data is not always straightforward. Some examples remain effectively invisible due to their associated keywords and others do not include full structural information. Some authors do not include bonding parameters about the central atom, or M-M distances, bridge angles or adequate description of ligands used. It is hoped that this review will serve to concentrate the available material, highlight areas of particular interest and point out areas where more attention is warranted.

6. ACKNOWLEDGEMENTS

The authors wish to thank those who gave permission for reproduction of original figures, and the Ministry of Education of the Slovak Republic for financial support.

7. REFERENCES

1. M. Melnik, K. Györyová, J. Skoršepa and C.E. Holloway, Polyhedron, in press.
2. M. Melnik, K. Györyová, J. Skoršepa and C.E. Holloway, J. Organometal. Chem., in press.
3. D.E. Crotty, E.R. Corey, T.J. Anderson, M.D. Glick and J.P. Oliver, Inorg. Chem., 16 (1977) 920.
4. M.A. Poraj-Koshits, A.S. Ancyshitina, A.A. Pasynskij, G.G. Saditov, Y.V. Skrintin and V.N. Ostritova, Koord.Khim., 5 (1979) 1103.
5. D.E. Crotty, T.J. Anderson, M.D. Glick and J.P. Oliver, Inorg. Chem., 16 (1977) 2346.
6. M.D. Glick, R.L. Lintvedi, D.P. Gavel and B. Tomlonovic, Inorg. Chem., 15 (1976) 1654.
7. E. Solari, F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc., Dalton Trans., (1990) 1345.
8. A. Bencini, A. Caneschi, A. Dei, D. Gatteschi, C. Zanchini and O. Kahn, Inorg. Chem., 25, (1986) 1374.
9. P.D. Smith, J.L. Martin, J.C. Huffman, R.I. Bansemer and K.G. Caulton, Inorg. Chem., 24 (1985) 2997.
10. J.A. Mc Cleverty, S. McLuckie, N.J. Morrison, N.A. Bailey and J.W. Walter, J. Chem. Soc., Dalton Trans., (1977) 359.
11. D. Christodoulou, M.G. Kanatzidis and D. Coucouvanis, Inorg. Chem., 29 (1990) 191.
12. I.I. Creaser, J.D. Lyndon, A.M. Sargeson, E. Horn and M.R. Snow, J. Amer. Chem. Soc., 106 (1984) 5729.
13. H.O. Fröhlich, B. Kosan, B. Müller and W. Hiller, J. Organometal. Chem., 441 (1992) 177.
14. J.S. Denis, W. Butler, M.D. Glick and J.P. Oliver, J. Amer. Chem. Soc., 96 (1974) 5427.
15. A.W. Gal and H. van der Heijden, J. Chem. Soc., Chem. Commun., (1983) 420.
16. D.G. Sekutowski and G.D. Stucky, Inorg. Chem., 14 (1975) 2192.
17. J.C. Poat, A.M.Z. Slawin, D.J. Williams and J.D. Woolins, Polyhedron, 11 (1992) 2125.
18. P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, Inorg. Chem., 21 (1982) 3777.
19. F.A. Cotton, S.A. Duraj, W.J. Roth and C.D. Schmulback, Inorg. Chem., 24 (1985) 525.
20. W. Clegg, D.R. Harbron and B.P. Straughan, Acta Crystallogr., Sect. C, 47 (1991) 267.
21. V. Clegg, I.R. Little and B.P. Straughan, Inorg. Chem., 27 (1988) 1916.
22. R.J. Neustadt, T.H. Cymbaluk, R.D. Ernst and F.W. Cagle, Jr., Inorg. Chem., 19 (1980) 2375.
23. R.L. Bansemer, J.C. Huffman and K.G. Caulton, J. Amer. Chem. Soc., 105 (1982) 6163.
24. A. Stockhammer, K.H. Dahmen, T.Gerfin, L.M. Vanensi, V. Gramlich and W. Petter, Helv.

Chim. Acta, 74 (1991) 989.

25. R.B. Petersen, J.M. Ragosta, G.E. Whitwell, II., and J.M. Burlitch, Inorg. Chem., 22 (1983) 3407.
26. S. Müller and W. Thewalt, Z. Naturforsch., 44b (1989) 257.
27. P.H.M. Budzelaar, J. Boersma and G.J.M. van der Kerk, Angew. Chem., 95 (1983) 335.
28. B. Fischer, J. Boersma, G. Van Koten and A.L. Spek, New. J. Chem., 12 (1988) 613.
29. W. Cen, K.J. Haller and T.P. Tehlner, Inorg. Chem., 30 (1991) 3120.
30. E. Weiss and R. Wolfrum, Chem. Ber., 101 (1968) 35.
31. G.A. Gusejnov, F.N. Musaev, B.T. Usubaliev, I.R. Amiraslanov and H.S. Mamedov, Koord. Khim., 10 (1984) 1108.
32. C. Robl, Z. Anorg. Allg. Chem., 561 (1988) 57.
33. G.A. Kiosse, I.G. Filippova, A. Y. Leontiev, G.A. Popovich, T.I. Malinovskij, Y.V. Yablotov and N.V. Berbeleu, Dokl. Akad. Nauk SSSR, 304 (1989) 607.
34. X. Solans, M. Font-Altaba, J. Oliva and J. Herrera, Acta Crystallogr., Sect. C, 39 (1983) 435.
35. A.I. Pozhidaev, N.N. Neronova, T.I. Polypova, M.A. Poraj-Koshits and V.A. Logvinenko, Zh. Struct. Khim., 13 (1972) 738.
36. M.V. Leontieva, A. Y. Fridman, N. M. Djatlova, V.M. Agre and T.F. Sysoeva, Zh. Neorg. Khim., 32 (1987) 2494.
37. A. Fuertes, C. Miravitlles, E. Eseriva, E. Coronado, D. Beitrán and L. Padel, J. Chem. Soc., Dalton Trans., (1989) 863.
38. T. Ogata, T. Taga and K. Osaki, Bull. Chem. Soc. Jpn., 50 (1977) 1680.
39. P.G. Jones, R. Schelbach, E. Schwarzmann and C. Thöne, Acta Crystallogr., Sec.C, 44 (1988) 1196.
40. L. Wiehl, P. Klüfers, B.P. Schweiss, and H. Fuess, Z. Kristallogr., 184 (1988) 281.
41. J. Cěrnák, I. Potočňák, J. Chomič and M. Dunaj-Jurčo, Acta Crystallogr. Sect. C, 47 (1991) 1088.
42. C. Kappenstein, A. Qualli, M. Guerin, J. Černák and J. Chomič, Inorg. Chim. Acta, 147 (1988) 189.

Received: November 9, 1994 - Accepted: December 26, 1994 - Received revised camera-ready manuscript: January 16, 1995