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Coordination chemistry with pyrazole-based chelating ligands: molecular structural aspects

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Abstract

Pyrazole-based chelating ligands form a variety of coordination complexes with a number of metal ions, providing varying coordination geometry and nuclearity. Recent years have seen considerable interest in the designing of various pyrazole-based ligands and to study their structural properties to serve specific stereochemical requirement of a particular metal-binding site. Using over 120 pyrazole-based chelating ligands, the stereochemical properties of over 110 discrete coordination complexes, studied by single-crystal X-ray crystallography were analysed. Various bonding modes for a given chelating ligand are involved, and are reviewed with reference to ligand structure and the resulting coordination complexes. It is shown that the metal coordination number of the resulting complexes varies from two to eight. The ligands are introduced systematically as a function of their denticity, making easy access to information on specific type of ligands and coordination complexes thereof. X-ray crystallographically-determined bond lengths of various donor atoms/groups are collected in a table, thus providing an accessible source for reference purposes. Source material for the review amounts to about 130 references.

Keywords: Pyrazole-based ligands; Coordination complexes; Bonding properties

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1. Introduction: purpose and scope of the review

The properties of metal-coordinated compounds, whether in classical inorganic coordination complexes or in organometallic compounds or in bioinorganic model compounds, are determined in large measure by the nature of ligands bound to the metal ion [1,2].

Bidentate and tridentate nitrogen heterocyclic compounds containing six-membered rings such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and 2,2′:6′,2″-terpyridine (terpy) have been extensively used in transition metal chemistry [3–5]. The key feature of these heterocycles is their π-electron deficiency. Hence they behave as excellent π-acceptors and in turn they provide soft sites for metal coordination. On the other hand, the π-excessive five-membered nitrogen heterocycle, pyrazole is a poorer π-acceptor. In fact, it is a better π-donor and hence acts as hard donor site.

Since their introduction in 1966 by Trofimenko, anionic tripodal ligands poly(pyrazolyl)borates [6] have found wide application in transition metal chemistry in general and bioinorganic and organometallic chemistry in particular. A number of excellent review articles are now available in the literature [7–10]. Synthesis and studies of coordinating ability of neutral analogues, poly(1-pyrazolyl)methanes, [11] which were also introduced by Trofimenko in 1970, have developed a rich coordination chemistry. Recently, a review article has appeared on the organometallic chemistry of palladium and platinum with poly(pyrazol-1-yl)alkanes and poly(pyrazol-1-yl)borates [12]. In 1987 Reedijk in his article *Heterocyclic Nitrogen Donor Ligands* provided a survey of the coordination chemistry of various kinds of nitrogen heterocyclic ligand systems [13]. The ease of synthesis of variously substituted pyrazoles is the most interesting feature in the incorporation of pyrazole groups in the design of new ligands and hence offers the opportunity of both electronic and steric control of the properties of the metal complexes.

An interesting situation arises when a six-membered heterocycle such as pyridine and a five-membered heterocycle such as pyrazole are directly linked in a single ligand system. In fact, the complexes of such ligands give rise to significantly different electronic properties. A survey of this category has been done in 1989 by Constable and Steel [14]. An even more interesting situation arises when the electronic communication between these two heterocycles is prevented. This has been done by incorporation of an 'insulating spacer' such as a methylene group between the rings. A number of other pyrazole-based chelating ligands, which consist of pyrazole heterocycles linked by NR ($R = H$ or alkyl or benzyl), O or S group(s), with incorporation of 'insulating spacer(s)' between the coordinating sites have also been synthesized and their coordination chemistry well-developed. Interestingly, reports of such systems have started appearing only during the last decade. There is an increasing interest in pursuing the study of pyrazole-containing chelating ligands, the subject of this review. The structural characterization of a large number of coordination complexes with such ligands has been done, giving rise to an opportunity to look into their structural varieties in a systematic manner. During the last 10 years three review articles on biological model systems containing pyrazole chelates have appeared [15–17].

Although there has been much interest in the variety of bonding possibilities associated with pyrazole-based chelating ligands and the amount of structural data on their coordination complexes, so far there is no review article on the present theme. In the last few years, many coordination compounds with 2,6-bis(pyrazol-1-ylmethyl)pyridine and 2-(pyrazol-1-ylmethyl)pyridine ligands and their substituted derivatives, and their structures and properties have been published by our group. Therefore we now undertake an attempt to present an overview of these compounds.

The purpose of this review is to update the progress made (i) in the design of pyrazole-based chelating ligands and (ii) in the development of systematic coordination chemistry thereof. Here an attempt has been made on a critical analysis of the molecular structural aspects of the resulting complexes. However, a fair amount of electronic structural aspects and reactivity studies has also been included. To reduce the scope of this review, the following categories of ligands (i) the poly(pyrazol-1-yl)borates and poly(pyrazol-1-yl)alkanes, [7–10,12] (ii) the ligands formed by the direct linkage of two heterocycles, such as, pyridine and pyrazole, [14], and (iii) the coordination complexes with alkali metals and polymeric structures are excluded.

The treatment of the principal theme of the subject has been done according to the ligand types in different sections. In each of the main categories, subgroups of ligands will be discussed, divided according to ring size, ring substituents and nature of donor atoms. For each subgroup of ligands the following facts will be presented: the types of coordination compounds; molecular structural aspects; and selected properties. This review concentrates on recent work, with coverage until mid-May, 1998, and it is hoped that it will make workers in this area aware of a wider range of available ligands and aid them in selecting appropriate ligands for their specific requirements.

2. Bidentate ligands

In all the complexes described in this section the metal ion is bound to a bidentate ligand having only one pyrazole ring. Fig. 1 shows the ligands **1**–**17** discussed in this section. The metric parameters for all the structurally characterized complexes of pyrazole-based chelating ligands considered in this article, are collected in Table 1.

2.1. One pyrazole and one aliphatic amine

The ligands **1** and **2** were synthesized; however, attempts to prepare their palladium(II) and copper(II) complexes resulted in the decomposition of the ligands [18].

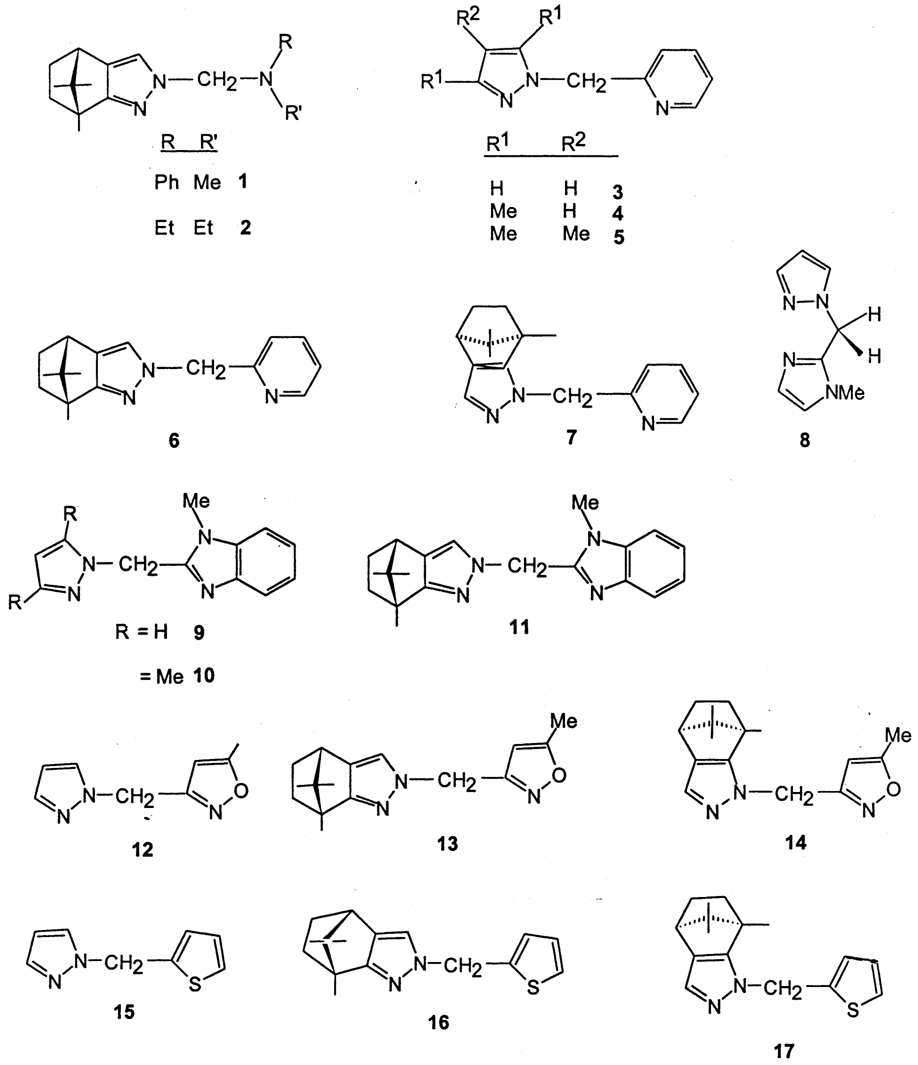

Fig. 1. Ligand structures (bidentate: **1**–**17**).

Table 1
Selected average bond distances (Å) of the structurally characterized complexes [a]

	M–N(pz)	M–N(am)/py/ bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/ CH_3OH/OAc/ $OClO_3$)	Ref.
Bidentate ligands					
[Co(**3**)$_2$Cl$_2$]·4H$_2$O	2.106(7)	2.198(6)	2.413(4)		[21]
[Cu(**4**)$_2$(NO$_2$)][ClO$_4$]	2.109(4)	2.005(4)		2.091(5)	[22]
[Pd(**6**)Cl$_2$]	2.023(5)	2.023(5)	2.287(2)		[19]
[Ni(**11**)$_2$(ClO$_4$)][ClO$_4$]·C$_2$H$_5$OH^b	2.088(7)	2.018(6)		2.271(6)	[26]
	[2.075(7)]	[2.013(6)]		[2.266(6)]	
[Pd(**14**)Cl$_2$]	2.036(3)	2.004(3) (isoxazole)	2.277(1)		[18]
[Pd$_2$(**16**)$_2$Cl$_4$]	2.010(7)		2.265(3)		[18]
		2.332(3) (bridging)			
Tridentate ligands					
[Co(**18**)$_2$][NO$_3$]$_2$	2.088(4)	2.229(5)			[28]
[Cu(**18**)(pz)(BF$_4$)][BF$_4$]	1.950(4)	2.050(4)	2.517(3)		[29]
	[1.948(4)](pz)				
[Ni(**18**)$_2$][BF$_4$]$_2$	2.039(9)	2.176(9)			[30]
[Cu(**19**)Br$_2$]	1.949(2)	2.191(2)	2.5281(5)		[31]
[Cu(**19**)$_2$][CF$_3$SO$_3$]	2.036(4)				[32]
[Cu(**19**)Cl]$_2$	2.029(2)		2.3984(8) (bridging)		[32]
[Cu···Cu = 2.9511(7) Å]					
[Co(**20**)Cl$_2$]	2.008(3)	2.510(4)	2.285(2)		[33]
[Co(**20**)(NCS)$_2$]	2.022(6)	2.425(6)	1.990(6)		[33]
[Ni(**20**)(NCS)$_2$(CH$_3$OH)]	2.035(15)	2.276(14)	2.033(15)	2.130(13)	[33]
[Cu(**20**)Cl$_2$]	1.969(4)	2.182(4)	2.357(2)		[33]
[Cu(**20**)I]$_2$	2.052(6)		2.657(2)(bridging)		[33]
[Cu···Cu = 3.028(2) Å]					
[Zn(**20**)Br$_2$]	2.009(4)	[3.270(4)]	2.373(1)		[33]
[Ni(**21**)(NO$_3$)$_2$]	2.048(5)	2.128(5)		2.052(5) (mono-)	[34]
				2.151(5) (bi-)	
[Cu(**21**)I]	2.036(4)	2.445(4)	2.5231(7)		[35]
[Co(**23**)Cl$_2$]	2.041(2)		2.2350(8)		[37]
[Cu(**23**)Br$_2$]	1.985(5)	2.423(1)	2.434(1)		[37]
[Co(**23**)(NO$_3$)$_2$]	2.048(5)	2.401(5)		2.045(5) (mono-)	[38]

Table 1 (*Continued*)

	M–N(pz)	M–N(am)/py/bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/CH_3OH/OAc/$OClO_3$)	Ref.
				2.036(5) (bi-) 2.470(5) (bi-)	
$[Co(\mathbf{24})Cl][BF_4]$	1.981(4)	2.057(5)	2.207(2)		[40]
$[Cu(\mathbf{24})Cl][BF_4]$	1.970(8)	2.038(9)	2.247(3)		[40]
$[Co(\mathbf{24})Cl]_2[CoCl_4]$	1.993(3)	2.068(3)	2.216(1)		[40]
$[Cu(\mathbf{24})Cl]_2[CuCl_4]$	1.990(7)	2.022(7)	2.232(3)		[40]
$[Cd(\mathbf{24})(NO_3)_2]$	2.312(2)	2.300(2)		2.342(2) (bi-) 2.572(2) (bi-)	[41]
$[Cu(\mathbf{24})(NO_3)_2]$	1.962(6)	2.075(8)		2.102(8) (bi-) 2.540(8) (bi-) 2.487(7) (mono-)	[42]
$[Cu(\mathbf{24})(NO_3)(H_2O)][NO_3]$	1.977(7)	2.001(10)		2.072(8) (bi-) 2.683(10) (bi-) 2.395(10) (H_2O)	[42]
$[Cu(\mathbf{24})(OClO_3)(C_2H_5OH)][ClO_4]$	1.943(13)	2.006(9)		2.044(10) (C_2H_5OH) 2.607(12) ($OClO_3$)	[42]
$[Co(\mathbf{25})(NO_3)_2]$	2.071(9)	2.209(9)		2.060(8) (mono-) 2.172(8) (bi-) 2.216(8) (bi-)	[43]
$[Cu(\mathbf{25})Cl_2]\cdot C_2H_5OH$	1.992(4)	2.181(4)		2.361(2)	[43]
$[Cu(\mathbf{25})(NO_3)(H_2O)][NO_3]$	2.01(1)	2.34(1)		1.938(9) (H_2O) 2.00(1) (NO_3) 2.63(1) (NO_3) bi-?	[43]
$[Cu(\mathbf{26})(NO_3)_2]$	1.996(3)	2.330(3)		1.999(2) (mono-) 1.991(2) (mono-)	[42]
$[Cu(\mathbf{26})(C_2H_5OH)(OClO_3)][ClO_4]$	1.95(2)	2.09(2)		2.07(2) (C_2H_5OH) 2.34(2) ($OClO_3$)	[42]
$[Cu(\mathbf{26})(C_2H_5OH)(H_2O)][ClO_4]_2$	1.94(2)	2.12(2)		2.08(2) (C_2H_5OH) 2.09(2) (H_2O)	[42]
$[Ni(\mathbf{27})_2][ClO_4]_2$	2.076(4)	2.157(3)			[44]
$[Fe(\mathbf{28})_2][ClO_4]_2$	2.173(2)	2.274(2)			[52]
$[Cu(\mathbf{29})(OClO_3)]\cdot CH_2Cl_2$	1.942(2)	2.131(2)		2.426(3)	[53]

Table 1 (*Continued*)

	M–N(pz)	M–N(am)/py/ bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/ CH_3OH/OAc/ $OClO_3$)	Ref.
[Cu(**29**)(PPh_3)]	2.091(4)	2.097(4)	2.212(1) (PPh_3)		[53]
[Cu(**32**)$(NCS)_2$]	1.998(5)	2.246(6)	1.971(5)		[44]
[Fe$(\mathbf{35})_2$][NO_3]$_2$	1.962(4)	1.967(5)			[55]
[Co$(\mathbf{35})_2$][NO_3]$_2$	2.118(4)	2.118(4)			[55]
[Ni$(\mathbf{35})_2$][NO_3]$_2$	2.067(5)	2.076(5)			[55]
[Cu$(\mathbf{35})_2$][NO_3]$_2$	2.190(3)	2.020(3)			[55]
[Zn$(\mathbf{35})_2$][NO_3]$_2$ (monoclinic)	2.148(7)	2.121(7)			[55]
[Zn$(\mathbf{35})_2$]$(NO_3)_2 \cdot 0.32H_2O$ (Triclinic)	2.148(4)	2.131(4)			[55]
[Zn(**41**)Br_2]	2.06(1)		2.343(2)		[58]
Cu(**42**)BF_4	1.876(5)	2.197(4)			[39]
Cd(**42**)$(NO_3)_2$ ^{b}	2.277(2)	2.595(2)		2.430(2) (bi-) [2.458(2)]	[41]
	[2.248(2)]	[2.544(2)]		2.427(2) (bi-) [2.461(2)]	
[Co(**42**)$(NO_3)_2$]	2.133(2)	2.125(1)		2.186(3) (bi-) 2.308(3) (bi-)	[59]
[Zn(**43**)$(NO_3)_2$]	2.127(3)	2.217(2)		2.183(3) (bi-) 2.397(4) (bi-) 2.116(3) (bi-) 2.647(5) (bi-)	[59]
[Co(**44**)$(NO_3)_2$]	2.078(3)	2.584(1)		2.062(3) mono-) 2.180(3) (bi-) 2.249(3) (bi-)	[60]
[Ni(**48**)Cl_2]$\cdot CH_3CN$	2.078(11)	2.070(10) (*o*-phen)	2.315(3)		[63]
Tetradentate ligands					
[Zn(**49**)$(NCS)_2$]	2.014(6)	2.599(7)	1.927(7) 1.974(9)		[64]
[Cu(**50**)(NO_3)][NO_3]	2.074(3)	2.094(3)		1.940(3) mono-) 2.749(4)?	[67]
[Ni(**50**)(NO_3)][NO_3]	2.040(5)	2.115(5)		2.097(4) (bi-)	[67]

Table 1 (*Continued*)

	M–N(pz)	M–N(am)/py/ bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/ CH_3OH/OAc/ $OClO_3$)	Ref.
$[Cd(\mathbf{50})(NO_3)_2]$	2.363(3)	2.559(3)		2.377(3) mono-) 2.341(3) (bi-) 2.509(3) (bi-) 2.885(4)?	[67]
$[Co_2(\mathbf{50})_2F(H_2O)(C_2H_5OH)][BF_4]_3 \cdot (C_2H_5OH)_{0.5}$	2.037(7) [2.027(8)]	2.276(7) [2.322(7)]		2.031(6) (C_2H_5OH) 1.902(5) (F)	[68]
$[Co(\mathbf{50})(H_2O)(OAc)][ClO_4]$	2.139(9)	2.239(8)		2.112(8)(OAc) 2.076(6) (H_2O)	[69]
$[Cu(\mathbf{52})(H_2O)][BF_4]_2$	2.048(2)	2.114(2)		2.070(2)	[72]
$[Cu(\mathbf{53})][BF_4]$	2.002(4)	2.263(4)			[72]
$[Co(\mathbf{53})][BPh_4]_2$	1.947(8)	2.107(8)			[73]
$[Ni(\mathbf{53})Br][BPh_4] \cdot C_2H_5OH$	2.102(12)	2.141(11)	2.439(2)		[74]
$[Ni(\mathbf{53})Br][BPh_4] \cdot (CH_3)_2CO$	1.993(32)	2.072(27)	2.489(8)		[74]
$[Ni(\mathbf{55})(N_3)_2]$	2.138(2)	2.181(2)	2.053(2)		[75]
$[Cd(\mathbf{55})Cl_2]$	2.431(3)	2.478(3)	2.5012(9)		[76]
$[Cu(\mathbf{55})(NCS)_2]$					
at 298 K	2.193(4)	2.191(4)	2.034(4)		[77]
at 140 K	2.099(4)	2.242(4)	2.060(4)		
$[Ni(\mathbf{56})(NCS)_2]$	2.14(2)	2.15(2)	2.04(2)		[79]
$Ni(\mathbf{56})(BF_4)_2$	1.880(6)	1.949(6)			[79]
$[Cu(\mathbf{56})][BF_4]_2$ ^{b}	1.957(13) [1.947(13)]	1.992(14) [2.003(13)]			[79]
$[Ni(\mathbf{59})][BF_4]_2 \cdot H_2O$	1.90(1)	1.90(1)			[79]
$[Cu(\mathbf{59})][BF_4]_2 \cdot H_2O$	1.974(14)	2.064(16)			[79]
$Ni(\mathbf{61})(NCS)_2$	2.193(4)	2.021(5) 2.492(2) (S)			[81]
$[Cu(\mathbf{61})Cl_2]$	2.014(9)		2.238(3)		[82]
$[Cu(\mathbf{62})(H_2O)][BF_4]_2$	1.995(1)	2.365(5)		2.17(1) (H_2O)	[84]
$[Cu(\mathbf{63})(H_2O)][ClO_4]_2$	1.964(3)	1.992(3) (*o*-phen)		2.333(4) (H_2O)	[85]
Polydentate ligands					
$[Co(\mathbf{64})(H_2O)][ClO_4]_2 \cdot H_2O$	2.105(5)	2.255(5) (tert) 2.129(5) (sec)		2.129(4) (H_2O)	[86]

Table 1 (*Continued*)

	M–N(pz)	M–N(am)/py/ bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/ CH_3OH/OAc/ $OClO_3$)	Ref.
$[Mn(\mathbf{65})(ClO_4)][ClO_4]$	2.251(6)	2.502(6)		2.262(5)	[87]
$Co_2(\mathbf{66})(ClO_4)_4(H_2O)_2(CH_3OH)_{1.75}$					
$[Co_2(\mathbf{66})(CH_3OH)(H_2O)]^{4+}$	2.15(2) [2.08(2)]	2.27(2) [2.20(2)]		1.98(2)(H_2O) [2.05(2)](CH_3OH)	[88]
$[Co_2(\mathbf{66})(H_2O)_2]^{4+}$	2.03(2) [2.12(2)]	2.25(2) [2.33(2)]		2.15(2) [2.14(2)]	[88]
	Cu–N(im)	Cu–N(pz)	Cu–N(am)	Cu–Cl	
$Cu_2(\mathbf{67})Cl_3$ [Cu···Cu = 5.566 Å]	1.964(3) [1.919(4)]	2.082(4)	2.280(3)	2.2396(12) [2.2920(10)]	[89]
$Cu_2(\mathbf{67})Cl_4$ [Cu···Cu = 6.104 Å]	2.039(3) [1.938(5)]	2.056(5)	2.262(5)	2.2661(17) [2.2843(16)]	[89]
Bridging ligands					
	M–N(pz) (bridge)	M–N (articular)	M–N (terminal) py	M–Br/N_3 (bridge)	
$[Cu_2(\mathbf{68})_2Br_2]$ [Cu···Cu = 3.947(4) Å]	1.92(1)	2.05(1)		2.895(4)	[90]
$[Cu_2(\mathbf{69})_2][BPh_4]_2$ [Cu···Cu′ = 3.903(2) Å]	1.918(3)	2.068(3)	2.496(5)		[91]
$[Mn_2(\mathbf{71})_2][BPh_4]_2 \cdot 2C_6H_5CH_3$ [Mn···Mn = 4.181(2) Å]	2.145(4)	2.416(4)	2.258(4)		[92]
Bridging (macrocyclic) ligands					
	M–N(pz)	M–N/S (macro)	M–Cl/Br/ N_3/SO_4	M–O(H_2O)	
$[Cu_2(\mathbf{77})(N_3)][PF_6]_2.H_2O$ [Cu···Cu = 4.15 Å]	1.936(3)	2.077(4)	1.994(4)		[95]
$[Ni_2(\mathbf{78})(N_3)(H_2O)_2][ClO_4]_2 \cdot H_2O$ [Ni···Ni = 4.450(1) Å]	2.041(3)	2.098(3)	2.104(4)	2.164(3)	[96]

Table 1 (*Continued*))

	M–N(pz)	M–N(am)/py/ bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/ CH_3OH/OAc/ $OClO_3$)	Ref.
$[Cu_2(\mathbf{79})(SO_4)(H_2O)][PF_6]\cdot CH_3OH\cdot 2H_2O$	1.939(4)	2.043(4)–N 2.563(1)–S	1.967(4)	2.600(4)	[96]
[Cu···Cu = 4.156(1) Å]					
$[Cu_2(\mathbf{80})(Cl)][ClO_4]_2\cdot CH_3CN$	1.882(2)	2.132(2)–N 2.3970(8)–S	2.3660(8)		[96]
[Cu···Cu = 3.6971(1) Å]					
$[Cu_2(\mathbf{80})(Br)][ClO_4]_2\cdot H_2O$	1.880(6)	2.114(6)–N 2.393(2)–S	2.485(1)		[96]
[Cu···Cu = 3.760(1) Å]					
Bridging (salicylideneaminate) ligands					
$[Mn_4(\mathbf{81})_2(OCH_3)_4(CH_3OH)_4][ClO_4]_2\cdot 4CH_3OH$					[97]
	Mn–N(pz)	Mn–N	Mn–O	Mn–$OHCH_3$ Mn–OCH_3	
	2.014(6)	2.027(6)	1.883(5)	2.310(7) 2.027(5)	
[Mn(1)···Mn(2) = 3.485(3) Å; Mn(2)···Mn(2′) = 3.127(2) Å]					
Xylyl-based ligands	M–N(pz)		M–Cl		
$[Cu(\mathbf{83})Cl_2]\cdot 0.5CH_3OH$ [b]	1.984(4) [1.962(4)]		2.221(2) [2.239(2)]		[99]
$[Cu_2(\mathbf{83})_2Cl_4]$	1.996(6)		2.374(3) 2.357(2) (bridging)		[99]
[Cu···Cu = 3.480(3) Å]					
$[Co(\mathbf{83})Cl_2]$	2.004(2)		2.2397(9)		[99]
	Cu–N(pz)	Cu–N(amine)	Cu–O (H_2O/ClO_4)		
$[Cu_2(\mathbf{83})_2][BF_4]_2$	1.874(4)				[101]
[Cu···Cu = 6.350(3) Å]					
$[Cu_2(\mathbf{88})][BF_4]_2$	1.906(4)	2.195(3)			[102]
[Cu···Cu = 5.100(1) Å]					
$[Cu(\mathbf{95})_2(OClO_3)(H_2O)_2][ClO_4]$	2.004(4)	1.913(4)	2.411(3)		[104]
$[Ru(\mathbf{96})][ZnCl_4]\cdot 3H_2O$	2.097(8) [Ru–C: 2.129(9)]				[106]

Table 1 (*Continued*)

	M–N(pz)	M–N(am)/py/bzim O/S	M–X/NCS/N_3	M–O(OH_2/NO_3/CH_3OH/OAc/$OClO_3$)	Ref.
Phenolate-based ligands	M–N(pz)	M–N(amine)	M–O(phenolate)	M–OH/Cl//OAc/N_3	
[Cu(**104**)]	1.952(2)	2.195(3)	2.032(3)		[108]
[Zn_2(**105**)$_2Cl_2$]	2.1541(14)		2.0506(19)	2.2403(11)	[109]
[Zn···Zn′ = 3.2453(10) Å]					
[Cu_2(**109**)(OH)][BF_4]$_2$	2.049(10)	2.041(9)	1.965(8)	1.942(6)	[112]
[Cu···Cu = 3.053(4) Å]					
[Cu_2(**113**)][BF_4]	1.969(12)	2.195(10)	2.085(8)		[114]
[Cu···Cu = 3.825(3) Å]					
[Cu_2(**113**)(OAc)][ClO_4]$_2$·CH_3COCH_3	2.062(19)	2.083(15)	1.941(12)	1.943(14)	[115]
[Cu···Cu = 3.562(3) Å]					
[Cu_2(**113**)(N_3)][ClO_4]$_2$·THF	2.068(8)	2.067(8)	2.015(6)	2.007(8)	[115]
[Cu···Cu = 3.765(2) Å]					
Macrocyclic ligands	M–N(pz)	M–N(amine)	M–OH/Cl/CH_3CN		
[Ni(**117**)(CH_3CN)][BPh_4]$_2$	2.023(9)	2.091(8)	2.052(10)		[116]
[Fe(**118**)][ClO_4]$_2$ ^{c}	1.946(11) [1.905(11)] [1.996(13)]	1.97(2) [2.02(2)] [1.98(2)]			[119]
[Ni(**119**)][ClO_4]$_2$·0.5H_2O	2.056(6)	2.098(6)			[118]
[Zn(**119**)][ClO_4]$_2$·H_2O	2.104(5)	2.225(6)			[118]
[Fe(**119**)][$FeCl_4$]Cl	2.120(4)	2.274(4)			[119]
[Ni(**121**)]I_2	2.062(5)	2.160(5)			[121]
[Mn(**121**)][PF_6]$_2$·CH_3COCH_3	2.340(13)	2.501(1)			[122]
[Ni(**122**)][BPh_4]$_2$·2CH_3COCH_3	2.056(4)	2.175(4)			[121]
[Zn(**122**)][BPh_4]$_2$·CH_3COCH_3	2.244(13)	2.351(13)			[121]
[Cu_2(**125**)Cl_2(C_2H_5OH)$_2$][NO_3]$_2$	2.030(8) 2.484(7)-axial 2.832(7) (C_2H_5OH)	2.030(6)	2.252(4) (Cl)		[124]
[Cu···Cu = 7.137(10) Å]					

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[a] Depending upon the nitrate coordination mode mono-/bi- has been indicated: mono = monodentate; bi = bidentate.

[b] There are two molecules in the asymmetric unit.

[c] There are three molecules in the asymmetric unit.

2.2. One pyrazole and one pyridine

Pyrazolylmethylpyridines **3**–**5**, readily form 1:1 complexes with $PdCl_2$ [19]. Using **3** and **4**, new piano-stool ruthenium(II) complexes $[Ru(\eta^6\text{-}C_6H_6)(\mathbf{3})Cl][PF_6]$ and $[Ru(\eta^6\text{-}C_6H_6)(\mathbf{4})Cl][PF_6]$ were isolated and the structures of these complexes in CD_3CN solution were elucidated by ^1H NMR spectroscopy [20]. Using **3**, cobalt(II) ($S = 3/2$) and nickel(II) ($S = 1$) complexes of compositions $[Co(\mathbf{3})Cl_2]$, $[M(\mathbf{3})_2Cl_2].4H_2O$ (M = Co and Ni) and $[M(\mathbf{3})_3][ClO_4]_2\cdot H_2O$ (M = Co and Ni) have been prepared and their stereochemical properties investigated [21]. The X-ray structure of $[Co(\mathbf{3})_2Cl_2]\cdot 4H_2O$ reveals (Fig. 2) a *trans* octahedral coordination environment about cobalt [21]. From their theoretical value of 90°, the coordination angles range from 85.7(2) to 94.3(2)°, implying a distorted structure. The Co–N(pyridine) bond is appreciably longer (~ 0.1 Å) than the Co–N(pyrazole) bond. The pyrazole mean plane is inclined to the pyridine mean plane by an angle of ~ 120°. Thus, the six-membered chelate rings adopted by **3** exist in boat conformations. For tris-chelate complexes, analyses of their d–d transition energies reveal that **3** is a weak field ligand. Synthesis and characterization of a nitrite-bound copper(II) compound $[Cu(\mathbf{4})_2(NO_2)][ClO_4]$ have been achieved [22]. The structure of the cationic part reveals that the metal atom is coordinated by two pyridyl nitrogens, two pyrazole nitrogens and one oxygen atom of $NO_2{}^-$. Thus this is a nitrito-bound five-coordinate copper(II) complex. Based on the τ parameter (= 0.29) as defined by Addison et al. [23] ($\tau = 0$, square pyramidal geometry; $\tau = 1$, trigonal bipyramidal geometry), the coordination sphere of copper(II) is best described as distorted square pyramidal. The basal plane of the square pyramid is defined by a pyridine and a pyrazole N atoms of a ligand, a pyridine N atom of the other ligand, and an O atom of the nitrite ion. The pyrazole N atom of the second ligand forms the axial bond. The Cu atom is displaced from the equatorial plane towards the axial pyrazole nitrogen by 0.25 Å. A pyridyl ring of a given ligand is

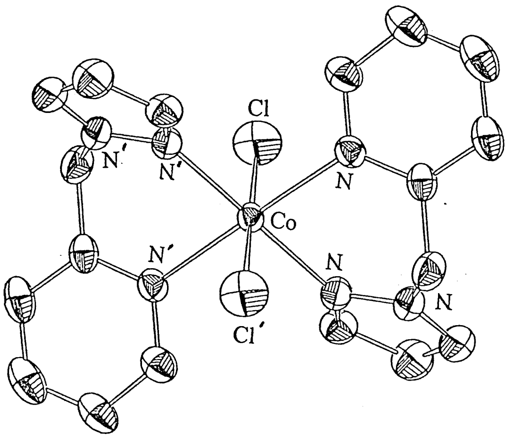


Fig. 2. X-ray crystal structure of $[Co(\mathbf{3})_2Cl_2]\cdot 4H_2O$ (adapted from Ref. [21]).

twisted to a pyrazole ring by an angle of ~52 or ~60°. Thus, the six-membered chelate rings exist in boat conformations. The spectral, magnetic, and redox properties of $[Cu(\mathbf{4})_2(NO_2)][ClO_4]$ have also been investigated.

Using **6**, a dynamic phenomenon (Fig. 3) involving interconversion of two boat conformers of the complex $Pd(\mathbf{6})Cl_2$ was identified [19]. A single-crystal X-ray structure determination of $Pd(\mathbf{6})Cl_2$ at 133 K reveals that the bonding to the palladium atom is square planar with normal bond lengths [19]. Thus expected steric interactions resulting from the presence of the bornane moiety are not sufficient to induce the acute bonding deformations. The six-membered ring containing the palladium atom exists in a boat conformation (b in Fig. 3). The two planar pyrazole and pyridine rings are inclined to one other at an angle of ~71°. Compared to the situation [24] with directly linked heterocyclic rings, introduction of the methylene group between the two heterocyclic rings in **6** increases the 'bite' of the ligand by ~5°. Interestingly, there is an agostic interaction (2.77 Å) between the palladium atom and the methylene hydrogen. The ligand **7** also readily forms 1:1 complex with $PdCl_2$, and the resulting complex behaves as that with ligands **3**–**5** [19].

2.3. One pyrazole and one imidazole

The complexes $PtMe_2(\mathbf{8})$ and *fac*-$PtIMe_3(\mathbf{8})$ have been reported [25]. The latter complex undergoes fluxional behaviour involving inversion of the six-membered chelate rings.

2.4. One pyrazole and one benzimidazole

The coordination chemistry of the achiral ligand **9** [18] has not yet been explored. The ligand **10**, however, forms a variety of complexes: $Fe(\mathbf{10})_2(ClO_4)_2 \cdot C_2H_5OH$, $Ni(\mathbf{10})_2(NCS)_2 \cdot H_2O$, $Cu(\mathbf{10})_2(ClO_4)_2$, $Cu(\mathbf{10})(NCS)(ClO_4)$, and $Pd(\mathbf{10})Cl_2$ [18]. The ligand **11** also gives rise to a few complexes: $Pd(\mathbf{11})Cl_2$, which is insoluble; $Cu(\mathbf{11})_2(ClO_4)_2$ and $Ni(\mathbf{11})_2(ClO_4)_2 \cdot C_2H_5OH$ [18]. The nickel(II) complex has been structurally characterized [26]. The asymmetric unit contains two different stereoisomers of a cation of stoichiometry $Ni(\mathbf{11})_2(ClO_4)^+$ (Fig. 4); each of these possesses a chelating bidentate perchlorate. In both cations the bulky bornyl groups are *trans*. The two cations differ in that one has the ligands coordinated in a Λ

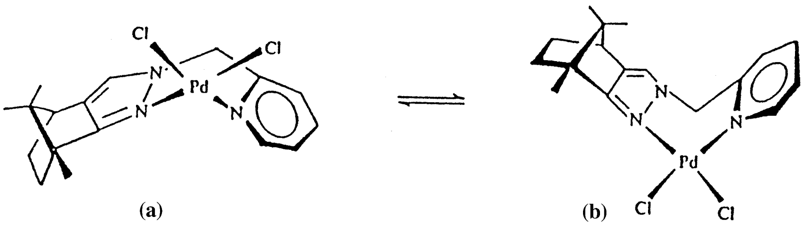


Fig. 3. Interconversion of boat conformers of $[Pd(\mathbf{6})Cl_2]$ (adapted from Ref. [19]).

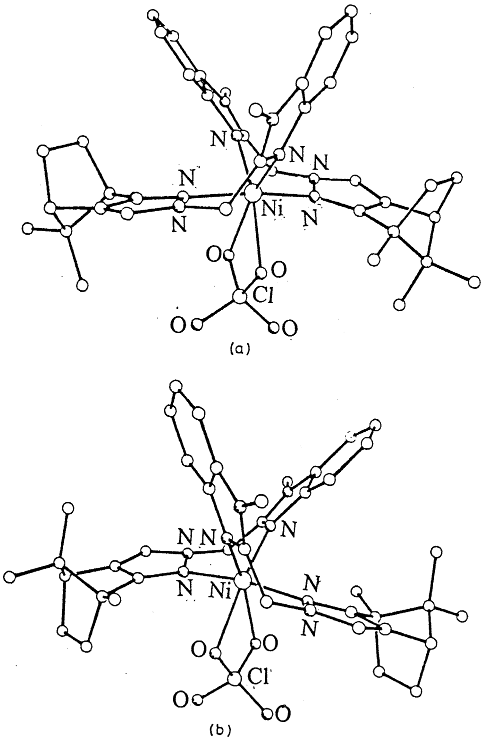


Fig. 4. X-ray crystal structure of two isomeric cations of [Ni(**11**)$_2$(ClO$_4$)][ClO$_4$]·C$_2$H$_5$OH (adapted from Ref. [26]).

configuration with the chelate rings in boat conformation α, whilst the other has a Δ configuration with the two chelate rings in conformation β (folding as shown in Fig. 3). Molecular models show that in all but the two observed isomers out of six possible isomers, there exist destabilizing steric interactions between the coordinated perchlorate and hydrogen atoms on the bornyl group. This conformational flexibility in the mode of coordination of the ligand has important consequences for the use of such ligands as chiral auxiliaries in asymmetric catalysis [18].

2.5. One pyrazole and one isoxazole

Reaction of **12** with [PdCl$_4$]$^{2-}$ gave [Pd(**12**)Cl$_2$], in which the ligand is presumably bound to the palladium through both the pyrazole and isoxazole nitrogens [18]. The chiral analogues **13** and **14** also form palladium(II) complexes. The ^{1}H NMR spectrum of [Pd(**13**)Cl$_2$] indicates the presence of two species: [Pd(**13**)Cl$_2$] and [Pd$_2$(**13**)$_2$Cl$_4$], in a ratio of $\sim$4:1. In the chloro-bridged binuclear species the ligand acts as a monodentate ligand. The crystal structure of [Pd(**14**)Cl$_2$] reveals it to be a *cis*-dichloro complex with bidentate coordination by the ligand. As expected the coordination about the palladium is square planar, the six-membered chelate ring is in a boat conformation. Interestingly, the Pd–Cl and Pd–N (isoxazole/pyridine) bonds are shorter in this complex than in Pd(**6**)Cl_2 (Table 1). This is probably a consequence of increased steric interactions in the pyridine complex where coordination occurs through the more sterically crowded nitrogen, but may also reflect the electronic difference between a π-excessive isoxazole ring and a π-deficient pyridine ring. Additionally, in the isoxazole complex there is a very significant flattening of the boat conformation of the six-membered chelate ring compared to that in Pd(**6**)Cl_2. This removes the agostic interaction in this complex.

2.6. One pyrazole and one thiophene

Reaction of **15** with $[PdCl_4]^{2-}$ gave Pd(**15**)$_2Cl_2$, which is indicative of only monodentate coordination to the palladium, presumably through the nitrogen of the pyrazole and with the thiophene ring non-coordinated [18]. Analogous reactions with **16** and **17** afforded [Pd_2(**16**)$_2Cl_4$] and [Pd(**17**)$_2Cl_2$], respectively. The latter complex has a *trans*-dichloro structure with monodentate coordination by the nitrogen atom of the ligand. The structure of a chloroform solvate of [Pd_2(**16**)$_2Cl_4$] has been determined, as a chloro-bridged dimer with monodentate nitrogen coordination of the ligand. The chiral ligands describe a *trans* geometrical relationship. The bonding geometry of the palladium atoms is square planar with an approximately square Pd_2Cl_2 central bridge. Although the thiophene sulfur atom is not coordinated to the palladium, there appears to be a weak axial interaction to the metal atom.

3. Tridentate ligands

In addition to the many bidentate ligands discussed above, there are a large variety of pyrazole-based ligands (**18**–**48**) which have tridentate chelation at each metal centre (Fig. 5). For several crystal structures, it is possible to demonstrate mutual relations between the bonding properties of pyridyl nitrogen and pyrazole nitrogen. The introduction of methyl substituents in the 3,5-positions of the pyrazole ring causes observation of the predominance of steric over electronic effect.

3.1. Two pyrazoles and one amine

Partial hydrolysis of the ligand tris(1-pyrazolylmethyl)amine [27,28] (its coordination chemistry has been described in the following section) in its solution with some of the metal salts results in the formation of bis(1-pyrazolylmethyl)amine (**18**). The crystal structure of Cu(**18**)(pz)$(BF_4)_2$ (pz = pyrazole) reveals that the copper(II) ion is in a square–pyramidal environment of four N atoms and one F atom [29]. The two pyrazole N atoms and the amine N atom of **18** and the pyrazole N atom form the base of the pyramid. An F atom of one of the BF_4^- anions is in the apical position. The rather long Cu–F distance of 2.517(3) Å indicates semi-coordination of the F atom, which is substantiated by the coplanarity of the Cu ion and the four N atoms of the base of the square pyramid. The bite of **18** is rather restricted as shown by the N(amine)–Cu–N(pyrazole) angles of ca. 82°. This restriction is compensated by the free pyrazole N–Cu–N(chelating pyrazole N) angles which are ca. 98°. The BF_4^- ion, which is semi-coordinated to the copper ion, is hydrogen bonded, through one of the other F atoms, to the N-hydrogen of a pyrazole

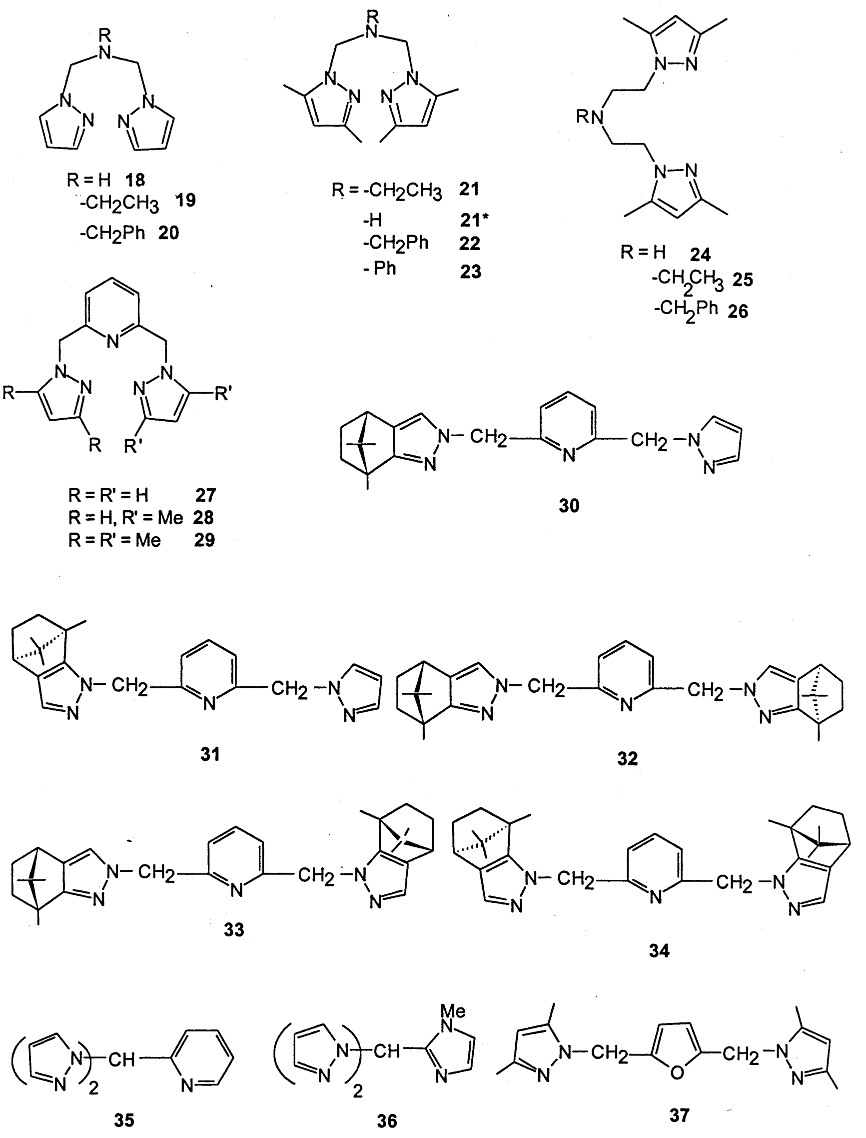


Fig. 5. Ligand structures (tridentate: **18**–**48**).

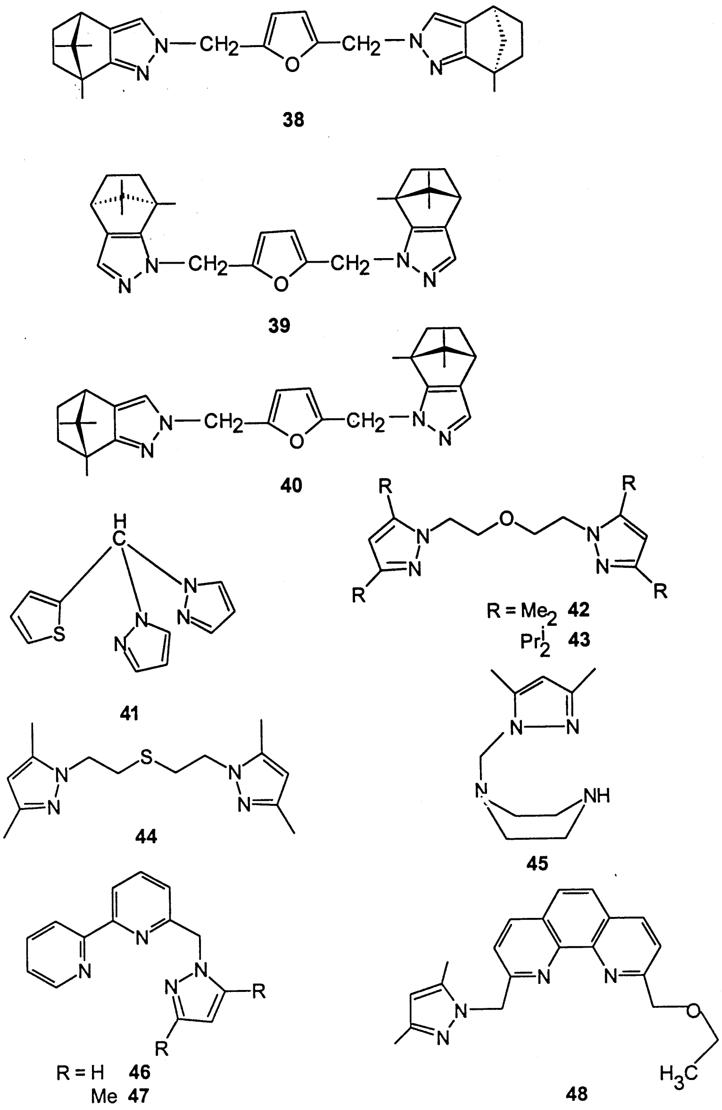


Fig. 5. (*Continued*)

molecule; this in turn is bound to another Cu ion, and so results in a chain-like structure with the chains along the *b* axis. The second BF_4^- anion is hydrogen bonded to the amine N-hydrogen of the ligand **18**. The X-ray structure of $[Ni(\mathbf{18})_2][BF_4]_2$ revealed that the geometry around the Ni(II) ion is almost octahedral [30], with the two ligand molecules in a *fac* configuration. The deviation from regular octahedral geometry is obviously imposed by the ligands in which the three ligand bonds from the pyrazole N to the amine N form too short a bridge to allow for a pyrazole–N to Ni to amine–N angle of 90°. This restricted angle is about 80°. Using **18**, with $M = Co^{2+}$ and Ni^{2+}, and $X = Cl^-$ and $NO_3{}^-$ octahedral complexes of formulation M(**18**)$_2$(X)$_2$ and with copper(II) the compounds Cu(**18**)(X)$_2$(H$_2$O)$_n$ with $X = Cl^-$ ($n = 1$) and $NO_3{}^-$ ($n = 0$) and Cu(**18**)(pz)X$_2$(H$_2$O) with $X = Cl^-$, NCS^- and $NO_3{}^-$ and pz = pyrazole were prepared [28]. The compound [Co(**18**)$_2$][NO$_3$]$_2$ was structurally characterized [28] to reveal that the cobalt(II) ion is coordinated in a slightly distorted octahedral array. The ligand chelates in the vicinal mode to the cobalt(II) ion and the coordination angles spanned by the pyrazole N to amine N bites of the ligands range from ~78.3 to 78.8°. Using ligand **19**, the compounds having the general formula [M(**19**)X$_2$] (M = Co, Cu, Zn or Cd X = Cl, Br, or NO$_3$; M = Ni, X = NO$_3$) and [M(**19**)$_2$]X$_2$ (M = Mn, Fe, Co, Ni, Cu, Zn or Cd; X = BF$_4$; M = Ni or Cu, X = NO$_3$) were prepared [31]. The crystal structure of [Cu(**19**)Br$_2$] reveals that the copper(II) ion is coordinated in a distorted square–pyramidal geometry ($\tau = 0.12$). The equatorial bromide, deforms the ideally square basal plane into a kite-like conformation, and the angles of Br–Cu–Br and N(aliphatic)–Cu–Br(equatorial) to respectively 112.75(2) and 151.14(6)°. These angles reflect the distortion towards a trigonal bipyramid. Using ligand **19**, copper(I) compounds with stoichiometries [Cu(**19**)X] (X = Cl, Br, I and SCN) and Cu(**19**)$_2$X (X = BF$_4$ and CF$_3$SO$_3$) were also prepared [32]. The crystal structure of [Cu(**19**)Cl]$_2$ reveals that each copper(I) ion is surrounded by two pyrazole nitrogens and by two chlorides. The compound is dimeric with the chlorides as the bridging atoms. Thus the ligand **19** chelates in a bidentate manner. The amine nitrogen–copper distance is too long to be considered as bonding [3.903(2) Å]. The geometry around copper is slightly distorted from tetrahedral, with angles ranging from 101.41(6) to 116.38(7)°. The X-ray structure of [Cu(**19**)$_2$][CF$_3$SO$_3$] reveals [32] that the copper(I) ion is surrounded by four nitrogen atoms of two ligand molecules. Only the pyrazole nitrogens contribute to the coordination, the tertiary amine nitrogens are too far away from the copper (3.91 Å) to be considered coordinating. The geometry around the copper is slightly distorted tetrahedral, with angles between 101.4(2) and 113.4(2)°.

Recently, an investigation of complexing properties of a newly prepared flexible ligand, **20** is reported [33]. This ligand reacted with metal ions to form [Fe(**20**)Cl$_3$], [Ni(**20**)(NCS)$_2$(CH$_3$OH)], [M(**20**)X$_2$] (M = Co^{II}, Cu^{II} or Zn^{II}, $X = Cl^-$, Br^- or NCS^-) and [(Cu(**20**)I)$_2$]. Most of the complexes have been structurally characterized. In [Co(**20**)Cl$_2$] the cobalt(II) ion is surrounded by two pyrazolyl nitrogen atoms, an amine nitrogen and two chloride ions in a geometry which can be described as intermediate between tetrahedral and trigonal bipyramidal. In fact, some angles between coordination bonds of cobalt(II), which range from 95.9(1) to 123.7(1)°, deviate substantially from ideal tetrahedral angles. The geometry around cobalt(II) in [Co(**20**)(NCS)$_2$] can also be described as intermediate between tetrahedral and trigonal bipyramidal. Here also some of the angles between coordination bonds deviate significantly from ideal tetrahedral angles [range 99.2(3)–122.6(3)°]. The coordination angles of the two N-bonded thiocyanates to the metal ion deviates from the linearity to a moderate degree [167.7(6) and 159.4(7)°]. The nickel(II) ion in [Ni(**20**)(NCS)$_2$(CH$_3$OH)] is six-coordinate with the ligand bound in a facial manner. Distortion from octahedral geometry is fairly substantial considering that the relevant angles lie between 76.0(3) and 96.6(7)°. Here also the coordination angles of the two N-bonded thiocyanates to the metal ion deviate from linearity [163.4(16) and 162.4(19)°]. Based on the τ parameter ($=0.10$), the coordination sphere of copper(II) in [Cu(**20**)Cl_2] is best described as distorted square pyramidal. The copper(II) ion lies 0.418(2) Å above the basal plane to an apical Cl atom. The copper(I) ion in [(Cu(**20**)I)$_2$] is surrounded by two pyrazole nitrogen atoms and by two bridging iodide ions. Two copper(I) ions and two bridging iodide ions form a planar Cu_2I_2 four-membered ring. The Cu–I–Cu bridging angle is 70.34(6)° and the I–Cu–I angle is 109.93(6)°. The benzylamine nitrogen–copper distances are 3.950(6) and 3.702(6) Å which are too long to be regarded as bonding. The coordination of copper(I) can be described as distorted tetrahedral with angles from 102.31(16) to 110.54(16)° for one copper and from 101.67(23) to 116.57(16)° for other copper. Interestingly, a Cu_2I_2 bridge was observed here because there is no ligand steric hindrance in contrast to the mononuclear complex [Cu(**21**)I] (see below) where methyl groups prevent association of the [Cu(**21**)I] moieties. In [Zn(**20**)Br_2], the zinc(II) ion is surrounded by two pyrazolyl nitrogen atoms and two bromide ions. The benzylamine nitrogen–zinc distance is 3.270(4) Å, which is too long to be considered as a bonding interaction. The coordination sphere of zinc(II) can be described as only distorted from tetrahedral with angles ranging from 105.58(11) to 115.66(16)°. In all the above complexes the pyrazole rings are not mutually coplanar.

The ligand **21**, gives rise to the following copper(I) compounds: [Cu(**21**)X] (X = Cl, Br, I and SCN) and Cu(**21**)$_2$$BF_4$ [32]. The compounds having the compositions [M(**21**)X_2] (M = Co, Ni, Cu or Zn; X = Cl, Br or NO_3) and [M(**21**)$_2$][ClO_4]$_2$ (M = Co or Ni) were also prepared [34]. The X-ray structure of [Ni(**21**)(NO_3)$_2$] shows that the nickel(II) ion is surrounded by two pyrazole nitrogens, one tertiary amine nitrogen and three oxygen atoms of two nitrate anions [34]. In fact, one nitrate behaves as a bidentate and the other as a monodentate ligand. The N(aliphatic)–Ni–N(pyrazole) angles are ca. 80°, and deviate significantly from the ideal coordination angles of 90°. It appears that the geometry of the ligand **21** is not very well suited for regular octahedral coordination of the nickel ion. It is remarkable that the adaptation to the demands of coordination is effected through an adjustment of the coordination angles and not through an adjustment of the coordination bond lengths. On the other hand, the bond angles around the aliphatic N atom do not diverge greatly from the ideal tetrahedral angles, probably as a consequence of the symmetrical position of the amine nitrogen in the ligand. Interestingly, the two pyrazole rings themselves are not coplanar, the angle between their planes being 17.6(2)°. The structure of [Cu(**21**)I] reveals that the copper(I) ion is coordinated to two pyrazole nitrogens, one tertiary amine nitrogen and to the unusual non-bridging I^- ion [35]. The geometry of the Cu environment can be described as intermediate between a tetrahedron and (but closer to) a trigonal pyramid, with the N(pyrazole)–Cu–N(pyrazole) and the N(pyrazole)–Cu–I bond angles of ca. 120° and the two N(pyrazole)–Cu–N(aliphatic) angles of ~ 76 and ~ 134°. Using ligand **22**, copper(II) complexes [Cu(**22**)(Cl)$_2$]Cl_2 and

$[Cu_2(\mathbf{22})_2(OCH_3)_2][BF_4]_2$ were prepared and the ability of the complexes to catalyze the oxidation of catechol to quinone was studied [36]. Using ligand **23**, the compounds having the general formulae $[M(\mathbf{23})X_2]$ (M = Co, Cu or Zn; X = Cl or Br and M = Co; X = SCN or NO_3), and $[Cu_2(\mathbf{23})(SCN)_3]$ were prepared. In some compounds (M = Co or Zn; X = Cl, Br and M = Co; X = SCN or NO_3) the ligand acts as a bidentate ligand and in others (M = Cu; X = Cl, Br or SCN) as a tridentate ligand [37]. In all compounds the anions are also bonded. The X-ray structure of $[Co(\mathbf{23})Cl_2]$ reveals that the cobalt(II) ion is surrounded by the two pyrazole nitrogens and the two chloride ions in a slightly distorted tetrahedral configuration. Thus, the ligand **23** utilizes only two of the three potential donor sites for coordination thereby acting as a bidentate ligand. The distance between the cobalt ion and the aniline nitrogen is 3.854(2) Å. Instead of coordinating, the lone pair on the nitrogen atom conjugates to the aromatic system of the phenyl ring as can be seen from the angles around the aniline nitrogen which lie close to 120°. In $[Cu(\mathbf{23})Br_2]$ the copper(II) ion is surrounded by two pyrazole nitrogens and one anilino nitrogen atom and two Br^- ions in a configuration which can be described as distorted trigonal bipyramidal. The ligand **23** now utilizes all its donor sites for coordination and acts as a tridentate ligand. The pyrazole nitrogens occur as axial ligands. The aniline nitrogen and the Br^- ions occupy equatorial positions. As the anilino nitrogen atom is involved in coordination, the lone pair is no longer available for conjugation to the aromatic system of the phenyl ring. The N(aliphatic)–Cu–N(pyrazole) and N(aliphatic)–Cu–N(pyrazole) angles are at ~ 80° and deviate significantly from the ideal coordination angle of ca. 120°. Apparently the geometry of the ligand is not very well suited for regular trigonal bipyramidal coordination of the copper ion, leading to an adjustment of the coordination angles, as before with ligand **21**. The X-ray structure reveals that in $[Co(\mathbf{23})(NO_3)_2]$ the Co(II) ion is coordinated to three ligand N atoms and to three nitrate O atoms [38]. One nitrate ion coordinates monodentately, and one coordinates bidentately. The geometry of the Co(II) ion can be described as being intermediate between a distorted trigonal bipyramid and a square pyramid ($\tau =$ 0.58). As the O atoms of the bidentately coordinated nitrate group form a bite angle of only 55.7(2)° with the Co ion, such a bidentate coordination could be considered as occupying one coordination site of the metal complex [38].

Using ligand **24**, the copper(I) complex $[Cu(\mathbf{24})][BF_4]$ was reported and it's reaction with carbon monoxide was investigated [39]. Cobalt(II), copper(II) and zinc(II) complexes with the ligand **24** and chloride and/or tetrafluoroborate as the anion have been isolated and characterized by spectroscopic techniques. Some of the complexes were structurally characterized [40]. The coordination sphere of the metal(II) atom in $[M(\mathbf{24})Cl][BF_4]$ (M = Co, Cu) is satisfied by two pyrazole nitrogens and one amine nitrogen. The coordination geometry around the cobalt(II) atom can be described as distorted tetrahedral. The geometry around the copper(II) atom can be described as square planar distorted towards tetrahedral, with the largest angle N(pyrazole)–Cu–N(pyrazole) now being 155°. The metal(II) atom in the $[M(\mathbf{24})Cl]^+$ cation of $[M(\mathbf{24})Cl]_2[MCl_4]$ (M = Co, Cu) is surrounded by three nitrogens from the ligand and one chloride anion. The coordination geometry around the cobalt(II) atom can be described as distorted tetrahedral. The coordination geometry around the copper(II) atom can be described as distorted tetrahedral, where the distortion is towards square planar although the largest angle of 141° is still far from the 180° for a square. Interestingly, experiments designed to obtain M:L = 1:2 compounds using excess of ligand resulted solely in the formation of 1:1 compounds. The crystal structure of [Cd(**24**)(NO_3)$_2$] may be described as made up of two uncharged discrete molecules separated by ordinary van der Waals distances, in which the two molecules differ in the coordination of the nitrate ligands [41]. The structure reveals that the geometry about the central metal atom may be described as pentagonal bipyramidal with three nitrogen donor atoms from **24** bound to the metal in a T-shaped fashion. Two pyrazole nitrogens make up the axial locations and amine nitrogen one of the equatorial positions of the pentagonal bipyramid. The remaining four equatorial positions are made up from oxygen atoms of two bidentate nitrate groups. It is interesting to note that, although the coordinating oxygen atoms of the nitrate groups lie in a well-defined plane, the binding of the metal to a nitrate group is asymmetric with average Cd–O distances of 2.34 and 2.57 Å. Although the second metal–oxygen interaction is clearly much weaker than the first, it is still part of the coordination sphere (^{113}Cd NMR spectra).

The copper(II) complexes of **24** and **26** have been studied as powders and solutions by a variety of techniques [42]. The crystal structure of Cu(**24**)·2NO_3/Cu(**24**)·2NO_3·H_2O contains two symmetrically independent complexes [Cu(**24**)(NO_3)$_2$] and [Cu(**24**)(NO_3)(H_2O)][NO_3] which are very similar. The most important difference between the two molecules is the coordination of a nitrite group in the former complex; a water molecule occupies this position in the latter complex. The metal coordination geometry is intermediate between that of a distorted trigonal bipyramid and an octahedron. The basal plane is formed by the nitrogen atoms of the two pyrazole rings and the amine nitrogen. These atoms make a T-shaped arrangement around the metal ion. The N(pyrazole)–Cu–N(pyrazole) angles slightly deviate from linearity, in the former complex it is 165.6(3)° and in the latter complex it is 165.9(3)°. The copper centres are displaced out of this plane in the direction of coordinating nitrate groups. Interestingly, these nitrate groups coordinate an isobidentately with one short and one long distance (Table 1). In the former complex, there is another nitrate which coordinates monodentately. In the latter complex, this position is taken up by a water molecule. In the structure of complex [Cu(**24**)($OClO_3$)(C_2H_5OH)][ClO_4] the copper(II) ion is four coordinated by two pyrazolyl nitrogen atoms and an aliphatic nitrogen atom from ligand and an ethanol oxygen atom. In addition to these short contacts, an additional long-range interaction between one of the perchlorate oxygens and copper is observed [distance 2.607(12) Å]. Some new coordination compounds of **25** were reported and for three complexes X-ray structural characterization has been achieved [43]. The geometry of the Co(II) ion in [Co(**25**)(NO_3)$_2$] is distorted octahedral, with the ligand is in the *mer* conformation. One of the nitrate ions is monodentate, the other nitrate is quite symmetrically bidentate coordinated to the cobalt ion. The environment of the Cu(II) ion in [Cu(**25**)Cl_2]·C_2H_5OH is distorted square pyramidal with the two pyrazole nitrogens and the two chloride ions in the square plane and the amine nitrogen at the apex. As the ligand occupies the apex of the square pyramid and two *trans* positions in the square, it is coordinated in a *mer* conformation. The distortion index parameter assumes a value of $\tau = 0.35$. The Cu(II) ion in [Cu(**25**)(NO_3)(H_2O)][NO_3] is in a distorted ($\tau = 0.18$) square pyramidal environment of the two pyrazole nitrogens, a water oxygen atom, and an oxygen atom of one of the nitrate ions in a square and the amine nitrogen at the apex. Now the ligand is not straight as in [Cu(**25**)Cl_2]·C_2H_5OH; however, it is folded and occupies one face of the square pyramid in a *fac* conformation. The nickel compound [Ni(**25**)(NO_3)$_2$] is isomorphous with the cobalt nitrate compound, as shown by X-ray powder diffraction. Interestingly, attempts to synthesize coordination compounds with a metal to ligand ratio of 1:2 were not successful. Model studies on octahedral [M(**25**)$_2$]$^{2+}$ indicated that methyl substituents on the 3- and 5-positions of pyrazole rings of a facially or of a meridionally coordinated **25** ligand protrude to such an extent that a second ligand cannot approach the M^{2+} ion. This steric hindrance is also due to the four-bond chelate bites of **25**, which cause the N–M–N coordination angles to be somewhat larger than 90°, thereby pushing the methyl substituents inward. Similar ligands with unsubstituted pyrazole groups are, of course, able to form M:L = 1:2 compounds, as for example, [Ni(**21**)(NO_3)$_2$] [34].

The structure of complex [Cu(**26**)(NO_3)$_2$] reveals (Fig. 6) that the copper(II) ion is five coordinated by three nitrogen donors from the ligand and two oxygen atoms from the nitrate counter ions. The geometry is best described as a square pyramid with a trigonal bipyramidal distortion ($\tau = 0.17$). The basal plane is formed by the pyrazole nitrogen atoms and the nitrate oxygen atoms. The copper ion is displaced 0.194(10) Å out of the basal plane in the direction of aliphatic nitrogen atom. One nitrate oxygen atom shows a long-range interaction with the copper atom, the distance being 2.6213(18) Å. The X-ray analysis of [Cu(**26**)(C_2H_5OH)Y][ClO_4]$_n$ (Y = H_2O, $n = 2$, or ClO_4^-, $n = 1$) revealed two different structures [Cu(**26**)(C_2H_5OH)($OClO_3$)][ClO_4] and [Cu(**26**)(C_2H_5OH)(H_2O)][ClO_4]$_2$, which are

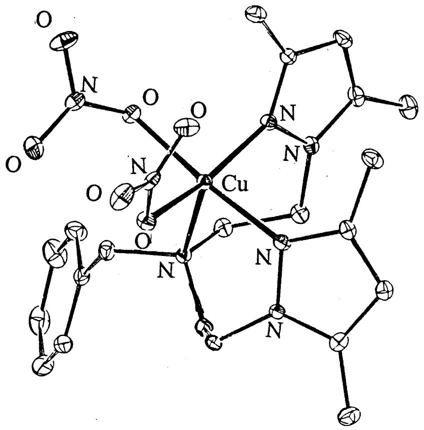


Fig. 6. X-ray crystal structure of [Cu(**26**)(NO_3)$_2$] (adapted from Ref. [42]).

present in the unit cell in a 1:1 ratio. The two structures are very similar and are best described as five coordinated copper(II) complexes with a trigonal bipyramidal distortion around copper(II). The most important difference between the two compounds is the coordination of a perchlorate molecule in the former complex, whereas a water molecule occupies this position in the latter complex. In the former complex, the distortion from an idealized trigonal bipyramid towards a square pyramid was calculated to be, $\tau = 0.62$. The interaction of the perchlorate molecule with the copper(II) centre is rather weak (Table 1). The angles found for the former complex are slightly different from those found for the latter complex. However, in both the complexes the ligand **26** coordinates to the copper centre in a T-shaped structure. The angles made by the axial oxygen atoms O(ethanol) and O(perchlorate) with the aliphatic amine (with Cu as the vertex) are 118.9(7) and 110.6(7)°, respectively. For the latter complex, the O(ethanol)–Cu–N(aliphatic) angle is 108.6(7)°, and the O(water)–Cu–N(aliphatic) angle is 104.5(8)°. For the latter complex, the distortion from an idealized trigonal bipyramid towards a square pyramid was calculated to be, $\tau = 0.37$. The most striking difference between the nitrate complexes to be noted is the change in arrangement of the ligands around the metal centre that has occurred upon benzylation of the central amine nitrogen. With **24**, the basal plane is comprised of three N donors, whereas when using **26** this plane is formed by two N donors and two O donors and the amino nitrogen has moved out of the basal plane to occupy an apical position. The relative positions of the pyrazole units with respect to the metal centre have also changed. In the complex with **24** they are almost in a trans configuration, whereas in the complex with **26** they are *cis* positioned. Apart from the different spatial arrangement of the ligands and the anions around the copper centre; changes have also taken place in the coordination distances (Table 1). The change that occurs with the perchlorate series upon benzylation of the central amino nitrogen are less dramatic than that within the nitrate series. When the overall geometries are compared an increase in coordination number from four in $[\mathrm{Cu}(\mathbf{26})(\mathrm{OClO_3})(\mathrm{C_2H_5OH})][\mathrm{ClO_4}]$ and five in both $[\mathrm{Cu}(\mathbf{26})(\mathrm{C_2H_5OH})(\mathrm{OClO_3})][\mathrm{ClO_4}]$ and $[\mathrm{Cu}(\mathbf{26})(\mathrm{C_2H_5OH})(\mathrm{H_2O})][\mathrm{ClO_4}]_2$ are observed. An interesting observation is also the ca. 0.1 Å lengthening of the Cu–N(amine) bond when the benzyl group is present. The redox behaviour of these complexes have been investigated to reveal their comparatively high $E_{1/2}$ values. It is explained by the fact that the Cu(II) complexes have the correct ligand geometry for the stabilization of Cu(I).

3.2. Two pyrazoles and one pyridine

The preparations of bis-ligand complexes, $[\mathrm{M^{II}}(\mathbf{27})_2]^{2+}$ (M = Fe, Ni and Ru) were reported [44]. The X-ray structure of $[\mathrm{Ni}(\mathbf{27})_2][\mathrm{ClO_4}]_2$ revealed that the bonding geometry about the nickel atom is close to symmetrical octahedral. Interestingly, the Ni–N(pyridine) bond length is longer than the Ni–N(pyrazole) bond lengths. The pyrazole mean planes are inclined to the pyridine mean plane at angles of 42.7 and 63.2°. Hence the six-membered chelate rings exist in boat conformations. The syntheses of the complexes $[\mathrm{M^{II}}(\mathbf{27})(\mathrm{NCS})_2]$ (M = Ni and Cu) and $[\mathrm{Pd_3}(\mathbf{27})_2\mathrm{Cl_6}]$ were also reported.

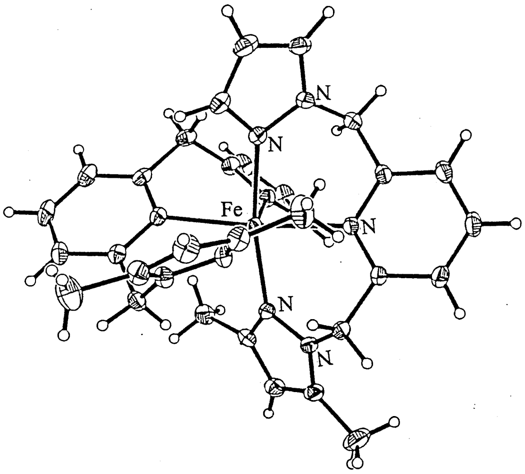


Fig. 7. X-ray crystal structure of the cationic part of [Fe(**28**)$_2$][ClO$_4$]$_2$, for clarity only one ligand has been labelled (adapted from Ref. [52]).

Systematic studies have been done with the ligands **27**–**29** and the influence of methyl substitution near the donor site of their high-spin bis-ligand iron(II) complexes has been explored [45]. The distorted octahedral Fe^{II}N$_6$ complexes display easily identifiable paramagnetically shifted ^{1}H NMR resonances. Steric crowding near the donor site for complexes with ligand **28** and **29** reduces the ligand-field strength (10 Dq) relative to **27**. By observation of the Fe^{III}/Fe^{II} redox couples it has been nicely demonstrated that steric effects due to 3-Me substituents predominate over the electronic effect of 5-Me substituents. This observation has been extended with high-spin manganese(II) [46] and cobalt(II) [47] complexes of these ligands. The bis-ligand distorted octahedral Ni^{II}N$_6$ complexes display easily identifiable paramagnetically shifted ^{1}H NMR resonances [48]. A proper manipulation of the size of the central metal ion can also give rise to an opposite effect in which electronic effects predominate over steric factors. Studies with a group of bis-ligand complexes of ruthenium(II) this notion has been justified [49]. A mixed-ligand ruthenium(II) complex [Ru(**27**)(MeL)][ClO$_4$]$_2$·H$_2$O [MeL = 2-pyridylethyl-(2-pyridylmethyl)methylamine] has been prepared and characterized [50]. The complex [Fe(**27**)$_2$][ClO$_4$]$_2$·H$_2$O displays in the solid-state anomalous magnetic properties which are associated with a temperature-induced singlet $(^1A_1) \rightleftharpoons (^5T_2)$ transition [51]. Mössbauer spectral data confirmed this and revealed separate contributions from the singlet and quintet species with a strong temperature dependence of their relative intensities. Variable-temperature magnetic and Mössbauer studies established that [Fe(**28**)$_2$][ClO$_4$]$_2$·2H$_2$O and [Fe(**29**)$_2$][ClO$_4$]$_2$·2H$_2$O are purely high-spin species. For [Fe(**27**)$_2$][ClO$_4$]$_2$·H$_2$O three d–d transitions originating from the quintet and singlet state were identified. To underpin the chemical significance of the above-mentioned properties of these systems, an X-ray structural analysis of [Fe(**28**)$_2$][ClO$_4$]$_2$ was done [52]. A fairly distorted octahedral coordination was observed (Fig. 7). This arises from the steric crowding between the methyl groups near the donor site. The average Fe–N(pyridine) bond length is the longest among known bis- or tris-(ligand) iron(II) complexes with $Fe^{II}N_6$ coordination. Interestingly, the two pyrazole mean planes of each ligand make an angle of 60.3 and 68.4° to each other. The pyridine mean plane is tilted to adjacent pyrazole rings within a ligand at angles of 48.2 and 59.1° and 59.6 and 59.7°. Thus the six-membered chelate rings exist in boat conformations. The paramagnetically shifted ^1H NMR resonances demonstrate that the solid-state structure is retained in solution. Two mononuclear copper(I) complexes of **29** have been prepared [53]. In [Cu(**29**)($OClO_3$)]·CH_2Cl_2 the copper(I) is coordinated to two pyrazole nitrogens, one pyridyl nitrogen and one perchlorate oxygen. The Cu–O bond [2.426(3) Å] is characteristic of a weak bond and this type of weakly coordinated copper(I) perchlorate is uncommon. The geometry around the Cu is a highly distorted tetrahedron and can be described as distorted trigonal-planar coordination if perchlorate coordination is excluded. The coordination angles are: N(pyrazole)–Cu–N(pyrazole) 148.74(8)°; N(pyridine)–Cu–N(pyrazole) 98.33(7)° and 97.26(8)°. The displacement of Cu with respect to the mean plane of the ligand is 0.395 Å, reveals the three-coordinate behaviour. Interestingly, the six-membered chelation rings assume distorted-chair conformations. In [Cu(**29**)(PPh_3)] the copper(I) is coordinated to two pyrazole nitrogens, a pyridyl nitrogen and a PPh_3. The coordination angles are: N(pyrazole)–Cu–N(pyrazole) 118.1(2)°; N(pyridine)–Cu–N(pyrazole) 93.9(2) and 88.6(2)°. Here the chelation rings assume a boat-like structure. A variable-temperature ^1H NMR study of both complexes revealed that the methylene carbon of the latter complex is chiral at low temperatures. Carbon monoxide formed a terminal adduct with the former complex. Two chiral ligands **30** and **31** and the copper(II) complex with the former ligand [Cu(**30**)$(NCS)_2$] were also prepared [44]. Three more chiral ligands **32**–**34** were prepared and two copper(II) complexes with **32** and **33**, as that obtained with ligand **30**, were prepared. The copper(II) complex [Cu(**32**)$(NCS)_2$] was structurally characterized, revealing that the coordination about the copper atom is intermediate between trigonal bipyramidal, with axial pyrazole nitrogen, and square pyramidal, with axial

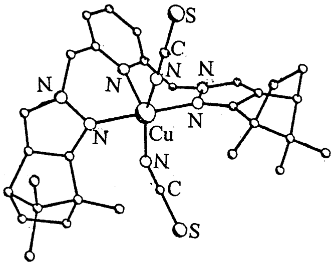


Fig. 8. X-ray crystal structure of the cationic part of [Cu(**32**)$(NCS)_2$] (adapted from Ref. [44]).

pyridine nitrogen (Fig. 8). In this case also, the Cu–N(pyridine) bond is substantially longer than the Cu–N(pyrazole) bond lengths. Here the pyrazole mean planes are inclined to the pyridine ring at angles of 41.2 and 49.0°. Again the six-membered chelate rings exist in boat conformations [44].

Using the unsymmetrical tripodal ligand **35** [54], the metal(II) complexes $[\mathrm{M^{II}}(\mathbf{35})_2][\mathrm{NO_3}]_2$ (M = Fe, Co, Ni, Cu or Zn) were prepared and examined by X-ray crystallography and single-crystal electronic spectroscopy [55]. The zinc complex crystallizes in both the monoclinic and triclinic systems, the monoclinic complex being isomorphous with those of cobalt and copper. Apart from the copper(II) complex, the tridentate ligands subtend 'bite' angles of 83.8(2)–86.9(2)° with the interligand N–M–N angle ca. 7° larger, resulting in a slight trigonal distortion from octahedral geometry. For all of the complexes the 'bite' of the tripod ligand and geometry of the ligand results in an orientation of each ring with the M–N direction. This effect is more pronounced for the pyrazole rings. The ligand **35** produces a relatively strong ligand field, consistent with the rather short metal–nitrogen bond lengths in the complexes (Table 1). The structural studies, and the application of the angular overlap model to the spectroscopic results, provide new information on the bonding characteristics of tripod ligands and a comparison of pyrazole and pyridine groups. The spectroscopic analysis reveals that the pyridine group is a slightly stronger σ-donor than the pyrazole groups, with both amines acting as weak π-donors.

3.3. Two pyrazoles and one imidazole

Using ligand **36** two organometallic complexes $[\mathrm{Ph_2MePt}(\mathbf{36})]\mathrm{I}$ and $[\mathrm{Me_2Pt}(\mathbf{36})\mathrm{I}]\mathrm{I}$ were synthesized and characterized by electrospray ionization mass spectrometry [56].

3.4. Two pyrazoles and one furan

The achiral ligand **37**, structurally related to the tridentate 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**29**), has been reported [18]. The chiral derivatives **38**–**40** were also prepared. However, all attempts at isolating $\mathrm{Fe^{2+}}$, $\mathrm{Cu^{2+}}$, and $\mathrm{Ni^{2+}}$ complexes by reacting these ligands with the perchlorate salt of the metal, followed by the addition of sodium thiocyanate, have not been successful [18].

3.5. Two pyrazoles and one thiophene

Using **41** [57], the complexes $[\mathrm{Zn}(\mathbf{41})\mathrm{X_2}]$ (X = Cl, Br, I) were prepared and the bromide complex was structurally characterized [58]. The geometry around zinc is highly distorted tetrahedral with the Br–Zn–Br angle (116°) having the largest and the N–Zn–N angle (90°) having the smallest value. The thiophene sulfur was found to be non-coordinating.

3.6. Two pyrazoles and one ether

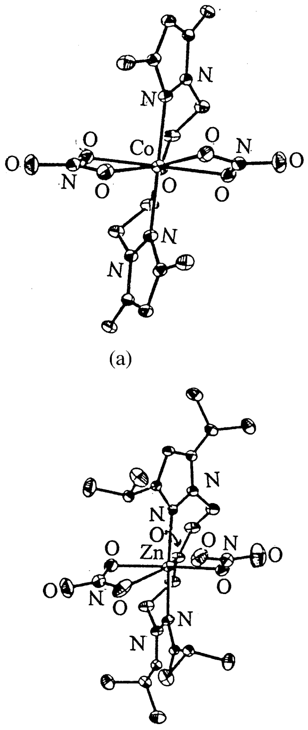
The copper(I) chemistry with **42** was investigated [39]. The X-ray structure of [Cu(**42**)][BF_4] reveals that it has a T-shaped structure in which the Cu atom sits 0.067(1) Å out of the plane described by the ligand donor atoms. The Cu–N distances are appreciably shorter. In fact, the shortness of the copper–pyrazole bonds suggests that the interaction of the ether oxygen with copper may be very weak [2.197(4) Å], barely perturbing what is essentially a two-coordinate copper(I) species. Reaction of the copper(I) complexes with CO in nitromethane solution neatly demonstrated the formation of carbonyl adducts.

As in [Cd(**24**)(NO_3)$_2$], the crystal structure of [Cd(**42**)(NO_3)$_2$] may be described as made up of two uncharged discrete molecules separated by ordinary van der Waals distances, in which the two molecules differ in the coordination of the nitrate ligands [41]. The geometry about the cadmium atom may be described as a very distorted pentagonal bipyramidal with five oxygen donor atoms (four from two nitrate groups and one from the ligand **42**) making up the equatorial plane. Interestingly, the dihedral angles between nitrate groups in two molecules are 6.86(9) and 36.8(7)°. Additionally, the least-squares plane of the five oxygen equatorial donor ligands in both molecules show displacements of the nitrate oxygen atoms from this plane. Clearly, these molecules are conformationally different molecules. The axial ligands are nitrogen atoms from the ligand **42** and are distorted from linearity with a N(pyrazole)–Cd–N(pyrazole) angle of 152.5(1)°. This distortion is due mostly to the constraints placed on the system by a much longer Cd–O(ether) distance of 2.595(2) Å compared to the analogous Cd–N(pyrazole) distance of 2.277(2) Å as well as the different geometry of the ligand imposed by the oxygen in the framework.

A new ligand bis[3,5-diisopropylpyrazolyl)ethyl]ether (**43**) has recently been specifically designed [59] to model the binding aspects of zinc to protein backbones in enzymes. The X-ray structures of Co(**42**)(NO_3)$_2$ and Zn(**43**)(NO_3)$_2$ reveal that the ligand adopts a T-shaped or meridional arrangement in which the nitrogen donors are *trans* to each other (Fig. 9). Another feature of interest in comparison of the above two structures is the difference in coordination modes adopted by the nitrate ligands. While both nitrate ligands of the Co(II) complex exhibit bidentate coordination modes, the two nitrate ligands in the Zn(II) complex behave differently. One is bidentate and the other one is anisobidentate.

3.7. Two pyrazoles and one thioether

Using the ligand 1,5-bis(3,5-dimethylpyrazol-1yl)-3-thiapentane (**44**) the compounds [M(**44**)(NCS)$_2$] (M = Co or Zn), [Ni(**44**)(NCS)$_2$(H_2O)], Cu(**44**)(F)(BF_4), M(**44**)Cl_2 (M = Co or Cu), Zn(**44**)Cl_2·0.5EtOH, M(**44**)(NO_3)$_2$ (M = Co or Cu), Cu(**44**)X (X = Br or Cl), [Cu(**44**)]BF_4·H_2O and Ag(**44**)(NO_3) have been isolated [60]. The cobalt(II) ion in [Co(**44**)(NO_3)$_2$] is coordinated (Fig. 10) by the three ligand donors, viz., two pyrazole nitrogens and one thioether and two nitrate anions. One nitrate ion is monodentate and the other is bidentate. The coordination



(a)

(b)

Fig. 9. X-ray crystal structures of (a) [Co(**42**)(NO_3)$_2$] and (b) [Zn(**43**)$_2$(NO_3)$_2$] (adapted from Ref. [59]).

geometry is distorted octahedral. The angles at cobalt(II) formed by the ligand bites are 86.54(9) and 88.9(1)°, which is close to the ideal octahedral geometry. This is most likely due to the large bite of the ligand, i.e. capable of forming six-membered chelate rings.

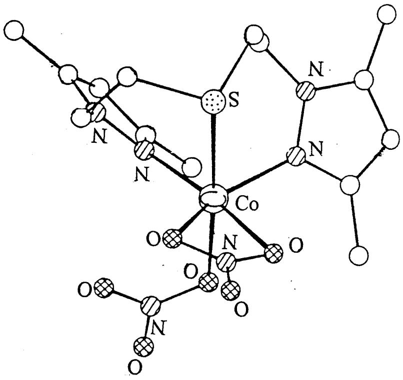


Fig. 10. X-ray crystal structure of [Co(**44**)(NO_3)$_2$] (adapted from Ref. [60]).

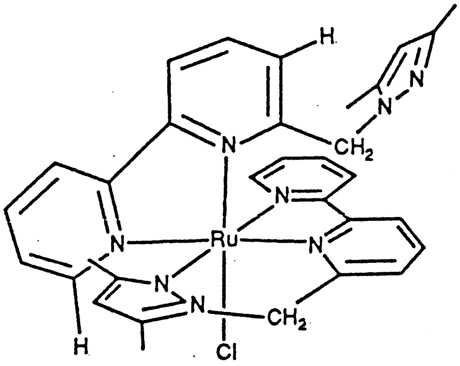


Fig. 11. The structure of $[Ru(\mathbf{47})_2Cl]^+$ (adapted from Ref. [62]).

3.8. One pyrazole and one piperazine

The mixed-ligand compound Cd(**45**)(dmpz)$(NO_3)_2$ (dmpz = 3,5-dimethylpyrazole) was formed [61] from the partially hydrolyzed ligand *N*,*N*′-bis(3,5-dimethylpyrazol-1-ylmethyl)-piperazine (**58**) (see below).

3.9. One pyrazole and one bipyridine

Homoleptic bis-tridentate complexes of the ligands **46** and **47** were prepared by the reaction of the ligands with ruthenium trichloride in refluxing ethanol/water [62]. The complexes were isolated as their PF_6^- salts and characterized by ^1H NMR spectroscopy. The ^1H NMR spectrum of the crude product obtained from **47** indicated a mixture of products. Chromatographic separation and subsequent ^1H NMR measurements on two separated complexes allowed isolation of a small amount of a pure complex (Fig. 11), in which one of the ligands **47** acts in a tridentate mode and the other is bidentate with coordination by the bipyridine component of **47**. The lower yield for the formation of $Ru(\mathbf{47})_2^{2+}$ and the accompanying formation of an unexpected product can be attributed to destabilization of $Ru(\mathbf{47})_2^{2+}$ due to a strong steric interaction between the C5″-methyl group of the ligand and the central pyridine ring of the other ligand. In the complexes $Ru(\mathbf{46})_2^{2+}$ and $Ru(\mathbf{47})_2^{2+}$ the pyrazole ring is *trans* to a π-deficient pyridine ring, thereby offering the possibility of synergic electron donation from the pyrazole through the metal to the pyridine. The introduction of electron-donating methyl groups also decreases the Ru^{III}/Ru^{II} potentials by approximately 0.025 V per methyl group.

3.10. One pyrazole, one phenanthroline, and one ether

A new pyrazole-based chelating ligand 2-(((3,5-dimethyl-*N*-pyrazolyl)methyl)-1,10-phen-anthroline-9-ylmethyl)ethyl ether (**48**) has been synthesized [63]. The dichloronickel(II) complex of **48** was prepared and the complex [Ni(**48**)Cl_2]·CH_3CN was structurally characterized. It adopts a five-coordinate trigonal bipyramidal geometry (Fig. 12), with one phenanthroline and one pyrazolyl nitrogen atom axial while the other phenanthroline nitrogen atom and the chloride ligands are equatorial. Due to the presence of basic phenanthroline backbone the ligand stabilizes the nickel(I) state, at least on the cyclic voltammetric time scale, as revealed by a reversible Ni^{II}/Ni^{I} wave at $E_{1/2} = -0.68$ V versus Ag/AgCl.

4. Tetradentate ligands

In all the complexes described above the metal is bound to the ligand through two pyrazole nitrogens only. The stability of resulting complexes can be increased by incorporating one more pyrazole ring and making them to provide tetradentate coordination to each metal, with the increased chelate effect. Many such ligands (**49**–**63**) exist (Fig. 13) and are the subject of this section.

4.1. Three pyrazoles and one tertiary amine

The Zn(II) ion in [Zn(**49**)$(NCS)_2$] is surrounded by two pyrazole N atoms of **49** and two N atoms of the isothiocyanate anions [64]. The geometry around Zn is distorted tetrahedral with angles ranging from 97.8 (3) to 119.8 (3)°. It cannot be excluded that some bonding also occurs from Zn to the amine N as the Zn–N(amine) distance is 2.599 (7) Å. The resulting approximately trigonal pyramidal coordination geometry is rather unusual for Zn. In this respect it is of interest that the equatorial NCS ligand coordinates to Zn almost linearly with an angle of 174.6 (7)° and the axial one with an angle of 149.8 (7)°. Another remarkable feature of this compound is the third pyrazole group of the ligand **49** which does not coordinate to the Zn. Using **49** two different types of compounds were synthesized with Co(II) and Cu(II) [28]. In the compounds $M^{II}(\mathbf{49})X_2(H_2O)_n$, with M = Co, Ni, and Cu, X = Cl^-, NCS^- and/or $NO_3{}^-$ and $n = 0$ or 1, the anions take part in the coordination of the metal ion resulting in penta- or hexa coordination. In the

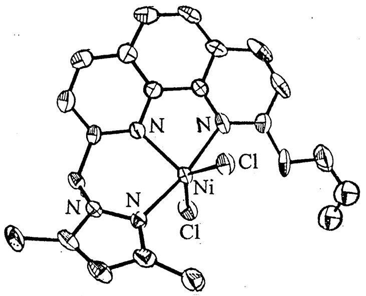


Fig. 12. X-ray crystal structure of [Ni(**48**)Cl_2]·CH_3CN (adapted from Ref. [63]).

compounds $M_3^{II}(\mathbf{49})_2X_6$ with M = Co, Cu, Zn and X = Cl^- and NCS^-, autoanion formation occurs, resulting in $[M(\mathbf{49})X]_2[MX_4]$ with both five-coordinated and four-coordinated metal ions. The complexes were characterized by spectral measurements.

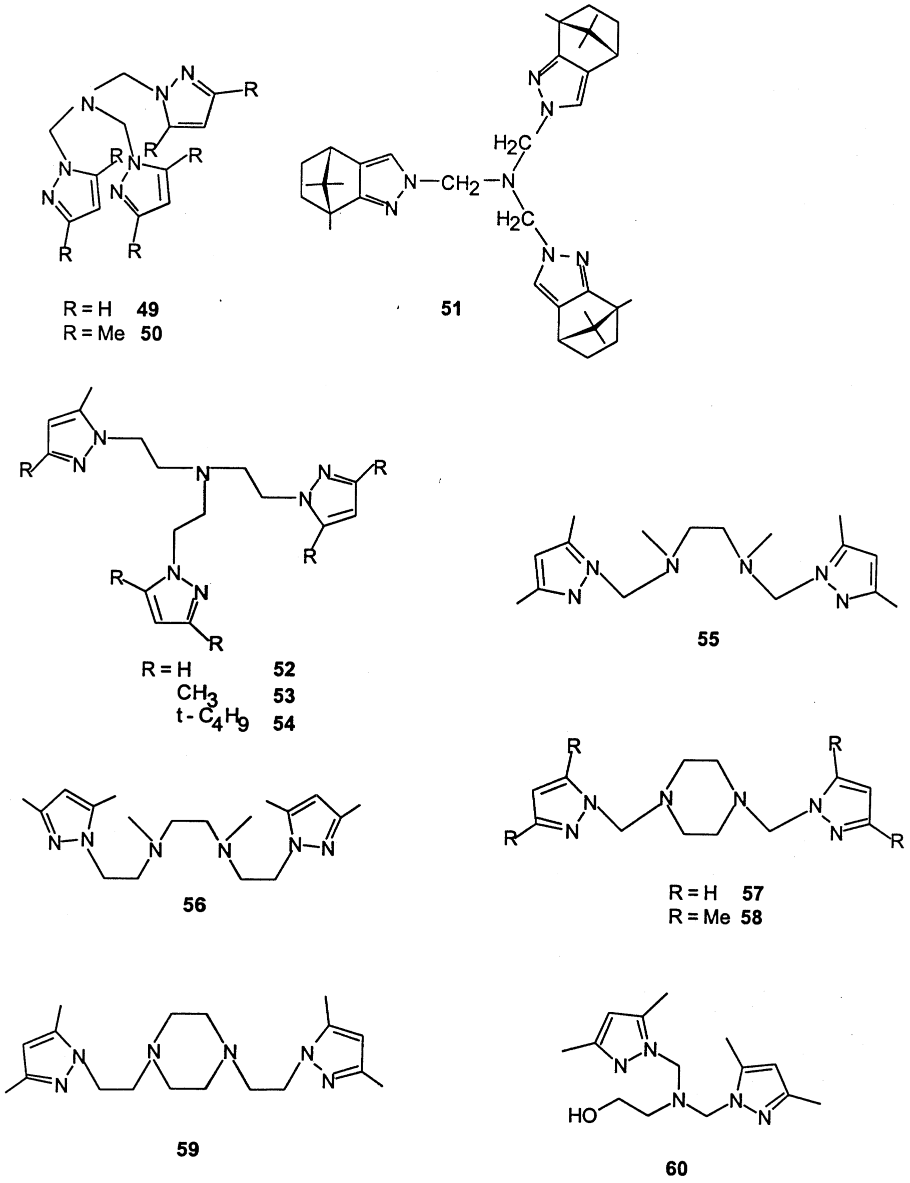
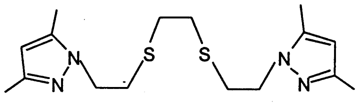


Fig. 13. Ligand structures (tetradentate: **49**–**63**).



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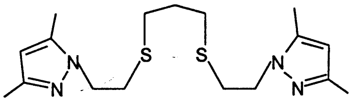

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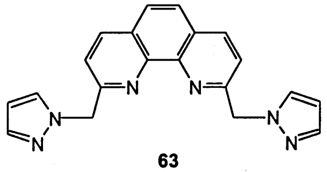

63

Fig. 13. (*Continued*)

The coordinating capacity of **50** was investigated towards iron(II), cobalt(II), and nickel(II) [65]. The complexes have the formula M(**50**)X(BPh_4) (M = Fe, X = Cl, Br; M = Co, X = Cl, Br, I, NCS; M = Ni, X = Cl, Br), Ni(**50**)F(BPh_4).acetone, Fe(**50**)$(NCS)_2$, and Co(**50**)$(NO_3)_2$. The coordination geometries of the complexes were proposed on the basis of physicochemical data. The iron complexes are penta- and hexa-coordinated; the cobalt complexes seem to have coordination geometry between trigonal-bipyramidal and tetrahedral. The nickel derivatives have a dimeric hexa-coordinated structure with a ferromagnetic exchange coupling between adjacent metal atoms. It was considered that the apical nitrogen is 'semi-coordinated', with the geometry of the complex intermediate between trigonal bipyramidal and tetrahedral. The complexes [Co(**50**)(H_2O)][ClO_4]$_2$ and [Co(**50**)(N_3)][ClO_4] were prepared and characterized [66]. These complexes act as a spectroscopic model of cobalt(II)-substituted carbonic anhydrase. The aqua complex was found to have two acidic groups in the pH range 5.5–9.5, which are attributed to the bound water ($pK_a \approx 9$) and to the apical nitrogen ($pK_a \approx 7.4$). It was shown that the deprotonation of the coordinated water can by itself cause a dramatic change in the electronic spectra of the cobalt(II) chromophore and a strong reduction of the anion affinity for the solvent coordination site. The crystal structures of three compounds of composition M^{II}(**50**)$(NO_3)_2$ (M = Cu, Ni or Cd) were determined [67]. In each compound the ligand utilizes each of its four potential donor sites. The structures of Cu and Ni compounds comprise [M(**50**)(NO_3)]$^+$ cations, and NO_3^- anions. For the Cu compound, the structure is trigonal bipyramidal (considering coordination angles) and for the Ni compound it is distorted octahedral. Here the nitrate ion is coordinated in a symmetric bidentate mode, yielding a *cis*-NiN_4O_2 chromophore. The structure of the Cd compound can either be described as distorted bicapped octahedral or less preferably as distorted octahedral if both O atoms are considered to occupy one coordination site. The equatorial plane is formed by the three pyrazole N atoms and one O atom from nitrate, with the Cd atom about 0.7 Å out of the plane. This distortion is due to the limited ability of the ligand **50** to fold around the relatively large Cd atom, because of the presence of methylene bridges between the central nitrogen atom and the respective pyrazole rings. An oxygen atom of one of the nitrate ions completes this plane. One of the Cd–O(nitrate) bond lengths is of the same order of magnitude, while the other Cd–O(nitrate) bond length and Cd–N(amine) have lengths greater than 2.5 Å. One O atom of the other nitrate ion is considered to be semi-coordinating. Using the ligand **50**, the synthesis and characterization of the BF_4^- compounds, which are all dimers, have the general formula $M_2(\mathbf{50})_2F(BF_4)_3(C_2H_5OH)_x(H_2O)_y$ (M = Co, Cu, Zn; $x = 0$–1.5; $y = 1$–2), $Ni_2(50)_3(BF_4)_4(H_2O)_2$ and $Ni_2(50)_2F_2(BF_4)_2(C_2H_5OH)_{0.5}$ were described [68]. The fluorides are formed upon BF_4^- decomposition. The nitrate compounds have the general formula $M(\mathbf{50})(NO_3)_2$ (M = Co, Ni, Cu, Zn). The Cl^- and SCN^- compounds have the general formula $[M(\mathbf{50})X]_2(MX_4)(C_2H_5OH)_x$-$(H_2O)_y$ (M = Co, Cu, Zn; X = Cl, NCS; $x = 0.5$–1; $y = 0$–1.5) and $Ni(\mathbf{50})X_2(H_2O)_x$ (X = Cl, NCS; $x = 0$–1.5). In all compounds **50** acts as a chelating tripodal tetradentate ligand. In the cases of Co, Cu and Zn also one counterion (F, monodentate NO_3, Cl or NCS) is coordinated to the metal ion, resulting in five coordination. Octahedrally based six-coordination is found in all Ni(II) cases, with two counterions (F, Cl or NCS) or one bidentate NO_3^- bound to the nickel ion. Six nitrogen atoms donated by two **50** in the case of $Ni_2(\mathbf{50})_3(BF_4)_4(H_2O)_2$ yield a distorted-octahedral geometry. In the case of five-coordination (M = Co, Cu, Zn; anion = BF_4, NO_3, Cl, NCS) the coordination geometry is distorted trigonal bipyramidal. The X-ray structure of $[Co_2(\mathbf{50})_2F(H_2O)(solv)][BF_4]_3 \cdot (solv)_{0.5}$ [solv = C_2H_5OH] revealed [68] that the two Co(II) ions have different surroundings. One Co atom is surrounded by four nitrogens and one oxygen and the other Co is surrounded by four nitrogens and one fluoride. In both cases the coordination geometry is distorted trigonal bipyramidal. The angles between the amine nitrogen, the Co atom and the respective pyrazole nitrogens vary from 75 to 80°, thus deviating significantly from the ideal coordination angle of 90°. This too small angle is due to the limited dimensions of the ligand. Opening up the bite of the ligand thereby enlarging the three five-membered rings formed by **50** and the central Co(II) ion would impose a severe strain on the ligand.

With **50** compounds of general formula $[M(\mathbf{50})(H_2O)(OAc)][ClO_4]$ [M = Co(II) or Ni(II); octahedral] and $[M(\mathbf{50})(OAc)][ClO_4]$ [M = Co(II) or Cu(II)] were synthesized [69]. The ligand **50** got hydrolyzed partly in forming the compound $[Cu(\mathbf{21^*})(dmpz)(OAc)(H_2O)][ClO_4]$, where **21*** is bis(3,5-dimethyl-1-pyrazolylmethyl)amine and dmpz is 3,5-dimethylpyrazole. The X-ray structure of $[Co(\mathbf{50})(H_2O)(OAc)][ClO_4]$ reveals that the cobalt ion is approximately octahedral formed by the tetradentate ligand coordination, by one O atom of the acetate ion and by the O atom of the water molecule, with the amine N and the water O in the axial positions. The coordinated acetate anion is both intra- and inter-molecular hydrogen bonded to the hydrogen atom of the coordinated water molecule, thus forming infinite chains of cation.

The kinetics of the oxidation of catechol and/or 3,5-di-*tert*-butylcatechol to quinones (tyrosinase modelling) using trigonal bipyramidal Cu(II) complexes $[Cu_2(\mathbf{50})_2F(H_2O)_2][BF_4]_3$, $[Cu(\mathbf{50})NO_3][NO_3]$, $[Cu(\mathbf{50})Cl]X$ ($X = BPh_4$, Cl), and $[Cu(\mathbf{50})(H_2O)][BF_4]_2$ has been studied [70,71]. These complexes were found to act as catalysts towards the oxidation of catechols.

A new ligand **51** gave $[Co(\mathbf{51})Br][BPh_4]\cdot H_2O$ [18]. The Cu(I) and Cu(II) complexes of **52**–**54** were described [72]. The geometry of $[Cu^{II}(\mathbf{52})(H_2O)][BF_4]_2$ is square pyramidal, with the Cu atom sitting 0.178 Å above the plane defined by N(amine), O(water), and two pyrazole nitrogens. The geometry of $[Cu^{I}(\mathbf{53})][BF_4]$ is distorted trigonal pyramid since the Cu atom is only 0.298 Å above the plane formed by the three pyrazole nitrogens. Interestingly, the Me···Me interaction is > 4.0 Å, implying that the observed geometry is not due to a expected pocket created at the bottom of the molecule. Thus, the observed geometry is simply the most stable configuration that the ligand can adopt. Most interestingly, these complexes exhibit unusual electrochemistry as a result of pronounced environmental effects. The $E_{1/2}$ values for the three Cu(I) complexes are 0.49 (ligand **52**), 0.67 (ligand **53**), and 0.94 V (ligand **54**) versus SCE (saturated calomel electrode). The very high Cu^{II}/Cu^{I} redox potential for the last complex results because of the alkyl groups on the pyrazole rings form a nonpolar pocket, protecting the Cu atom from approach of the solvent or a counterion that would stabilize the $2+$ state.

An interesting cobalt(II) complex $[Co(\mathbf{53})][BPh_4]_2$ was synthesized and structurally characterized [73]. An examination of the structural parameters shows that the coordination polyhedron about the cobalt can be described as a trigonal pyramid distorted toward a tetrahedron. In fact the three angles at the cobalt atom and including the aliphatic nitrogen atom, with values of about 100°, diverge from the ideal tetrahedron value of 109.5° toward the ideal 90° value of the apical angles in a trigonal pyramid. The remaining three angles, with an average value of 117.5° approach the 120° value of the equatorial angles in the same ideal geometry. The displacement of the cobalt atom above the equatorial plane (0.31 Å) evidences the tetrahedral distortion of the complex. Surprisingly, this complex exhibits absorption spectrum characteristic of five-coordinated trigonal bipyramidal complexes of Co(II). Nickel(II) complexes with **53** were also prepared and characterized [74]. A case of distortional isomerism for the five-coordinate complex cation $[NiBr(\mathbf{53})]^+$ has been ascertained through X-ray analyses of the compounds $[NiBr(\mathbf{53})][BPh_4]\cdot C_2H_5OH$ (yellow) and $[NiBr(\mathbf{53})][BPh_4]\cdot CH_3COCH_3$ (emerald). In the former compound two pyrazole nitrogen donor atoms of the ligand occupies the two axial positions of trigonal bipyramid, whereas the central amine and the third pyrazole nitrogen donor atom are lying in the equatorial plane together with the Ni and Br atoms. The square pyramid of the emerald compound is formed at the equatorial positions by the three pyrazole nitrogen donor atoms of the ligand and by a Br atom. The apical position is occupied by the central amine nitrogen atom. The two isomers have geometries approaching the ideal trigonal bipyramidal and square pyramid, respectively.

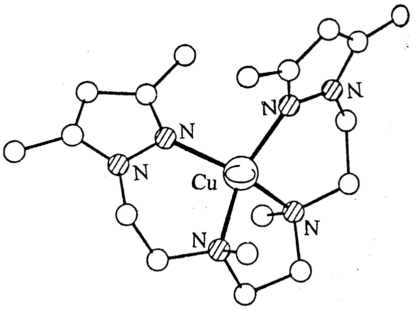

Fig. 14. X-ray crystal structure of one of the cations of $[Cu(\mathbf{56})_2][BF_4]_2$ (adapted from Ref. [79]).

Using the tripodal ligand **53**, copper(II) complexes $[Cu(\mathbf{53})Cl]Cl$ and $[Cu(\mathbf{53})(H_2O)][BF_4]_2$ were prepared and the ability of these complexes to oxidize 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-*o*-benzoquinone has been studied (catecholase activity) [71].

4.2. Two pyrazoles and two tertiary amines

The ligand **55** reacts with divalent transition metal ions in combination with small, coordinating anions to form $M(\mathbf{55})X_2$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, X = NCS; M = Mn, Co, Ni, Zn, Cd, $X = N_3$; M = Mn, Cd, X = Cl, Br) [75]. The crystal structure of $[Ni(\mathbf{55})(N_3)_2]$ reveals [75] that the Ni(II) ion is in octahedral coordination with the *cis*-positioned mono-coordinated azido groups. The molecule $[Cd(\mathbf{55})Cl_2]$ has a symmetrical *cis* coordination [76] analogous to that of $Ni(\mathbf{55})(N_3)_2$. The Cd octahedron is more distorted than the Ni octahedron. This can be seen from comparison of the N(pyrazole)–M–N(pyrazole) angle, which is 151° in the Cd compound and 171° in the Ni compound. The steric constraints of the ligand obviously make it more suitable to accommodate the smaller Ni(II) ion than the larger Cd(II) ion. On the other hand, the more distorted octahedron is able to accommodate the larger Cl^- anions, which do not bind to the smaller ion in combination with the **55** ligand. The X-ray structure determinations of $[Cu(\mathbf{55})(NCS)_2]$ were done at 140 and at 298 K [77]. It has the expected (cf Ni and Cd structures) *cis* octahedral coordination environment around copper(II). The ligand geometry does not change significantly with change in the temperature; however, the Cu–N bonds vary with temperature (Table 1). The tetradentate ligand **55** also forms coordination compounds of stoichiometry $[M^{II}(\mathbf{55})X(H_2O)_n][ClO_4]$ [M = Co, Ni, Cu and Zn; X = Cl, Br; $n = 0$ or 1). With cobalt and nickel six-coordinate compounds and with copper and zinc five-coordinate compounds were formed [78]. With the ligand 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (**56**) several coordination compounds were obtained: (Cu, Ni)$(\mathbf{56})(BF_4)_2$, (Co, Ni, Cu, Zn)$(\mathbf{56})Cl_4$, $Co_3(\mathbf{56})_2(NCS)_6$ and $Cu_2(\mathbf{56})(NCS)_3$ [79]. The complexes $[Cu(\mathbf{56})][BF_4]_2$ (Fig. 14), $[Ni(\mathbf{56})][BF_4]_2$ and $Ni(\mathbf{56})(NCS)_2$ were characterized by single-crystal X-ray diffraction studies. Generally, the coordination by the ligands is square planar. The complex Ni(**56**)$(NCS)_2$ contains two additional *trans* coordinating thiocyanate anions. The coordination of the copper atoms in both molecules [the asymmetric unit contains two almost identical Cu(**56**)$^{2+}$ species] is intermediate between tetrahedral and square planar. A significant difference is found in the conformation at the chiral nitrogen atoms as expected from the chirality of the complex cation: one molecule is the (*R*,*R*) diastereoisomer of the ligand and the other is the (*S*,*S*) diastereoisomer. The chloride compounds are, except for Ni(II), all dinuclear with MN_2Cl_2 chromophores. The nickel(II) compound contains square planar Ni(**56**)$^{2+}$ cations and tetrahedral $NiCl_4{}^{2-}$ anions. The thiocyanate compound of Ni(II), which is isomorphous with the corresponding Zn(II) compound, has octahedral $MN_2N'_2N''_2$ chromophores. The cobalt compound crystallizes as [Co(**56**)(NCS)]$_2$Co(NCS)$_4$ with five-coordinate cobalt in the cation. With copper thiocyanate **56** forms the mixed-valence compound Cu_2(**56**)$(NCS)_3$, with [Cu(**56**)]$^{2+}$ and $[Cu(NCS)_3]^{2-}$.

4.3. Two pyrazoles and one piperazine

Complexes of **57** having the formulas M(**57**)X (M = Cu; X = Cl), M(**57**)X_2 (M = Zn; X = Cl, Br) and M_2(**57**)X_3 (M = Cu, Zn; X = Cl, Br) were prepared [61]. In all compounds the ligand acts as tetradentate and in all cases the anions are coordinated to the metal ions. Most compounds with **58** have the general formula M_2(**58**)X_4 (M = Cu, Zn, Mn, Cd with X = Cl; M = Cu, Zn with X = Br^-; and M = Cu with X = NO_3, SCN) [61]. In all compounds the ligand acts as tetradentate. In all cases the anions are coordinated to the metal ions. It is interesting to note that with **58** only dinuclear compounds are formed. Apparently the formation of mononuclear compounds, in which the ligand **58** acts as a mononucleating tetradentate ligand, is not favourable, probably due to the sterical hindrance caused by the pyrazole methyl groups. With the ligand **59** the compounds [(Ni,Cu)(**59**)](H_2O)-$(BF_4)_2$, (Ni,Co)(**59**)$(NCS)_2$, Zn_2(**59**)$(NCS)_4$, (Ni,Co,Cu, Zn)$_2$(**59**)Cl_4 and Cu_2(**59**)$(NCS)_3$ were obtained [79]. The chloride compounds form dinuclear compounds with MN_2Cl_2 chromophores. However, in addition to the green form of [Ni(**59**)][$NiCl_4$] a purple isomer Ni_2(**59**)Cl_4, with a tetrahedral NiN_2Cl_2 chromophore, was obtained. The ligand field spectra of Ni(**59**)$(NCS)_2$ and the isomorphous cobalt compound show typical octahedral chromophores. With copper thiocyanate a mixed-valence compound [Cu(II)(**59**)][Cu(I)$(SCN)_3$] was formed. The compounds [(Ni,Cu)(**59**)]BF_4]$_2$·H_2O have been structurally characterized.

4.4. Two pyrazoles, one tertiary amine, and an alcohol

Using a new tripodal ligand **60** mononuclear five-coordinate Cu(II) complexes of the type [Cu(**60**)X]Y where X = H_2O, NO_3, Br, Cl, or N_3 and Y = BF_4, NO_3, Br, or Cl have been prepared. The complexes were tested for their reactivity towards the oxidation of catechol to quinone [80].

4.5. Two pyrazoles and two thioethers

The nickel ion in [Ni(**61**)$(NCS)_2$] is in a distorted octahedral geometry [81]. The ligand coordinates through two pyrazole N atoms in a *trans* position and the two S atoms in a *cis* position. The thiocyanate anions coordinate through their N atoms in a *cis* position. The distortion from octahedral symmetry is not very large considering that the relevant angles lie between 85.1 and 96.7°. Coordination compounds of **61** with MCl_2 (M = Fe, Mn, Ni, Co, Zn, Cu or Cd), MBr_2 (M = Mn, Co, Ni or Zn), $Cu(BF_4)_2$ and CuX (X = BF_4, NCS, Cl, Br or I) have also been described. The general formula for the divalent metal salt is [M(**61**)X_2] and for Cu(I), [Cu_2(**61**)X_2] [82]. With $CuCl_2$ two modifications were obtained. The copper atom in the green form of [Cu(**61**)Cl_2] is coordinated by two pyrazole nitrogens and two chloride atoms in a distorted square–planar geometry (Fig. 15) [82]. The pyrazole groups are in *trans* position to each other. The tetrahedral distortion of the square–planar geometry is clearly demonstrated by the angles N(pyrazole)–Cu–N(pyrazole) and Cl–Cu–Cl; which are respectively 161.0(2) and 160.4(1)°. The dihedral angle between the two CuNCl planes is 27°. The copper atom is not coordinated to the sulphur atoms. The X-ray structure of the red form of [Cu(**61**)Cl_2] reveals its polymeric structure [82]. The two copper(II) compounds Cu(**61**)$(H_2O)X_2$ (X = BF_4 and ClO_4) exhibit high redox potential for the Cu^{II}/Cu^{I} couple [83]. The copper atom in [Cu(**62**)(H_2O)]$[BF_4]_2$ [84] is coordinated by two pyrazole nitrogen atoms, two thioether S atoms, and a water O atom. The coordination geometry around copper can be best described as a distorted trigonal bipyramid ($\tau = 0.65$). The equatorial plane is made up of one pyrazole nitrogen, one sulfur, and one oxygen.

4.6. Two pyrazoles and one phenanthroline

The BF_4^- and ClO_4^- salts of the copper complexes of **63** were synthesized both in the Cu(I) and Cu(II) states [85]. The X-ray structure of the copper(II) complex

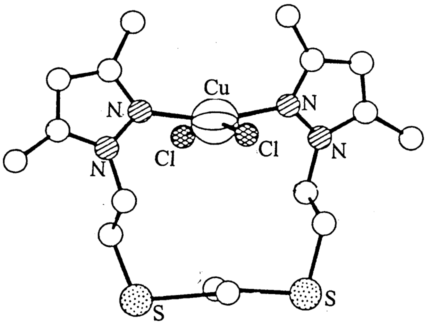

Fig. 15. X-ray crystal structure of [Cu(**61**)Cl_2] (adapted from Ref. [82]).

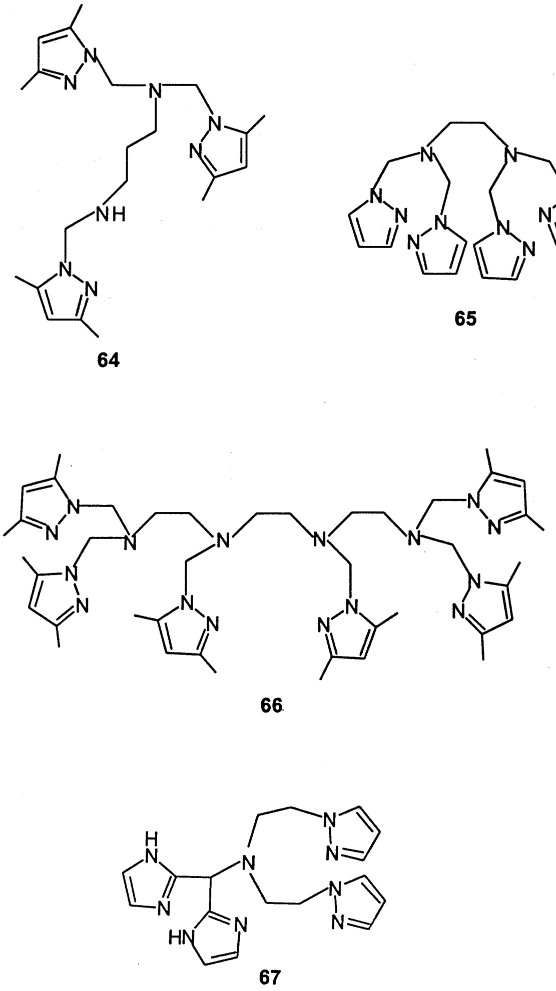

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Fig. 16. Ligand structures (polydentate: **64**–**67**).

and also of the free ligand were determined. The copper(II) complex [Cu(**63**)(H_2O)][ClO_4]$_2$ adopts a five coordinate geometry. The geometry at copper is best described as trigonal bipyramidal with two nitrogen atoms, one from the phenanthroline moiety and one from the pyrazole as axial ligation. Two nitrogen atoms one from phenanthroline and the other from pyrazole ligation and the water comprise equatorial coordination. This complex exhibits a reversible Cu^{II}/Cu^{I} response at 0.037 V versus Ag/AgCl. Electronic absorption spectroscopic characteristics reveal that the geometry around the copper ion to be trigonal bipyramidal.

5. Polydentate ligands

The ligands of pertinence to this section (**64**–**67**) are compiled in Fig. 16.

5.1. Three pyrazoles, one secondary, and one tertiary amine

Coordination compounds of the type M(**64**)(anion)$_2$·(H$_2$O)$_x$ were prepared in which M is one of the divalent metals Co, Ni, Cu, and Zn, the anion is ClO_4^- and BF_4^-, and $x = 1$–3 [86]. In all compounds the ligand is pentadentate. The six-coordination is completed by one water molecule. The X-ray structure of [Co(**64**)(H$_2$O)][ClO$_4$]$_2$·H$_2$O reveals that the cobalt(II) ion is surrounded by five nitrogens and one oxygen from one of the two water molecules. The three pyrazole nitrogens and the tertiary amine lie in the equatorial plane; the secondary amine lies above this plane. The coordination geometry is thus distorted octahedral. The angle between the bonds of the cobalt ion to the two amines is about 93°. The N(amine)–Co–N(pyrazole) angles are about 78° and is must be due to the restricted ligand bite.

5.2. Four pyrazoles and two tertiary amines

Coordination compounds of the type M(**65**)(anion)$_2$(H$_2$O)$_x$ were prepared in which M is one of the divalent metals Mn, Fe, Co, Ni, Cu, Zn, and Cd, the anion is ClO_4^- or BF_4^-, and $x = 0$–1 [87]. The ligand is hexadentate in all compounds. For Mn, Fe, Cd, and Zn (in this case only for the perchlorate compound) also one counterion is coordinated to the metal ion, resulting in seven coordination. In the case of six-coordination (M = Co, Ni, and Cu and the zinc fluoroborate compound) the coordination geometry is close to octahedral. The X-ray structure of Mn(**65**)(ClO$_4$)$_2$ (Fig. 17) reveals that the manganese(II) ion is surrounded by six nitrogens and one oxygen from one of the two perchlorate anions. The four pyrazole nitrogens lie in a more or less rectangular arrangement around the Mn ion. Together with the oxygen atom of perchlorate, they form five of the six vertices of an octahedron. When it is viewed in this way at the direct environment of the

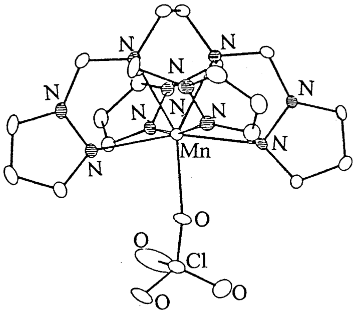


Fig. 17. X-ray crystal structure of the cationic part of [Mn(**65**)(ClO$_4$)][ClO$_4$] (adapted from Ref. [87]).

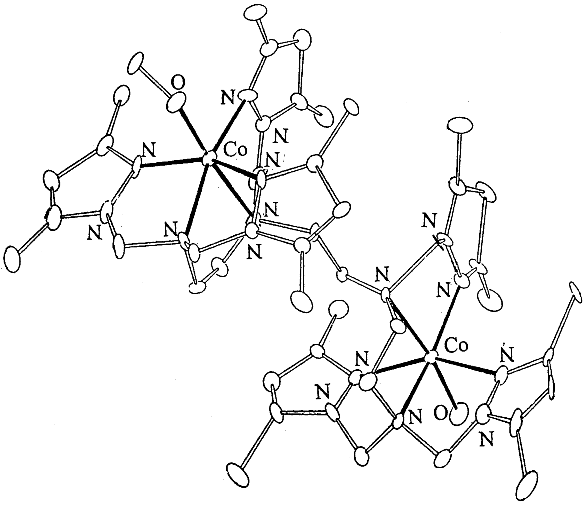


Fig. 18. X-ray crystal structure of $[Co_2(\mathbf{66})(H_2O)(CH_3OH)]^{4+}$ in the crystal of $Co_2(\mathbf{66})(H_2O)_2(ClO_4)_4(CH_3OH)_{1.75}$ (adapted from Ref. [88]).

manganese ion, it is only logical to consider the apex of the octahedron to be formed by the two tertiary nitrogen atoms together. Therefore, the coordination geometry around the central metal ion can best be described as bicapped octahedral. This rather unusual configuration can be attributed to the size of the metal ion and the limited flexibility of the ligand. The coordination angles formed between the bonds from manganese to the tertiary amine nitrogen on the one hand and the bonds from manganese to the pyrazole nitrogens on the other hand are significantly smaller than 90°, as is the coordination angles between the N(amine) to Mn bonds. Accommodation of these angles to 90°, octahedral coordination angles, would impose severe strain on the five 5-membered rings formed by the ligand and the central metal ion and, consequently, on the ligand itself.

5.3. Six pyrazoles and four tertiary amines

The ligand 1,1,4,7,10,10-hexakis(3,5-dimethylpyrazol-1-ylmethyl)-1,4,7,10-tetraaza-decane (**66**) was prepared and it's coordination compounds of the type $M_2(\mathbf{66})(ClO_4)_4(H_2O)_x$, [M = Co, Ni, Cu, Zn and $x = 4$–8] and $M_2(\mathbf{66})(A)_2(ClO_4)_2(H_2O)_x$ [M = Co and Ni; A = NCS or Cl; $x = 4$–8] [88]. The unit cell of $Co_2(\mathbf{66})(H_2O)_2(ClO_4)_4{\cdot}(CH_3OH)_{1.75}$ contains $[Co_2(\mathbf{66})(H_2O)_2]^{4+}$ and $[Co_2(\mathbf{66})(H_2O)(CH_3OH)]^{4+}$ in a nearly centrosymmetric configuration with eight perchlorates and several solvent molecules packed around the cations (Fig. 18). The ligand **66** acts as a decadentate, dinucleating ligand to the two cobalt atoms, occupying five coordination positions of an octahedron for each cobalt atom. The sixth position is occupied by a water or methanol oxygen atom, completing the octahedral coordination for the cobalt atoms. The coordination octahedron is quite distorted, with angles varying from 73 to 109°.

5.4. Two pyrazoles, two imidazoles, and one tertiary amine

Recently, the synthesis and characterization of the copper(II) complexes with a new dinucleating ligand, 1,5-bis(1-pyrazolyl)-3-[bis(2-imidazolyl) methyl]azapentane (**67**) and its deprotonated form have been achieved to model the active site of copper–zinc superoxide dismutase [89]. Two complexes, an imidazolato-bridged complex [Cu_2(**67**)Cl_3] and a non-imidazolato-bridged complex [Cu_2(**67**)Cl_4] were obtained. In [Cu_2(**67**)Cl_3], one of the copper(II) centres is coordinated by an imidazolate nitrogen, an imidazole nitrogen, and two chloride ions. The coordination polyhedron is strongly distorted toward a tetrahedron, the dihedral angles between best planes through Cl–Cu–Cl and N(imidazolate)–Cu–N(imidazole) being equal to 43.98(13)°. The other copper(II) centre is coordinated by an imidazolate nitrogen, two pyrazole nitrogens, a tertiary amine, and a chloride ion. This copper(II) centre is out of the plane towards the axially ligated pyrazole nitrogen by 0.176 Å. The coordination environment formed by the donor atom set is best described by a distorted square-based pyramid, as the bond distances of the mutually opposite donor atoms are practically equal ($\tau = 0.116$). In [Cu_2(**67**)Cl_4] (Fig. 19), one of the copper(II) ions is coordinated by an imidazole nitrogen and three chloride ions. The coordination polyhedron is almost a tetrahedron. The other copper(II) centre is coordinated by an imidazole nitrogen, two pyrazole nitrogens, a tertiary amine, and a chloride ion. The environment formed by this donor atom set is again described by a distorted square-based pyramid ($\tau = 0.13$). This copper(II) centre is out of the plane towards the axially ligated pyrazole nitrogen by 0.292 Å. Temperature-dependent magnetic susceptibility study of [Cu_2(**67**)Cl_3] shows antiferromagnetic behaviour with $2J = -96$ cm^{-1}. A low concentration of this complex catalyzes the dismutation of superoxide at biological pH, demonstrating that it is a good model for superoxide dismutase.

6. Bridging ligands

Many ligands exist (Fig. 20) in which a pyrazole group is present as a spacer between the two terminal coordination units (**68**–**81**). Understandably, such ligands

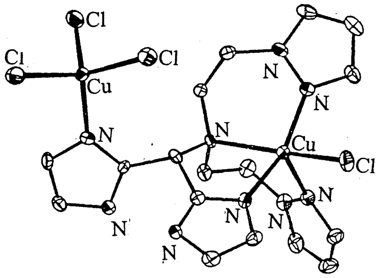


Fig. 19. X-ray crystal structure of [Cu_2(**67**)Cl_4] (adapted from Ref. [89]).

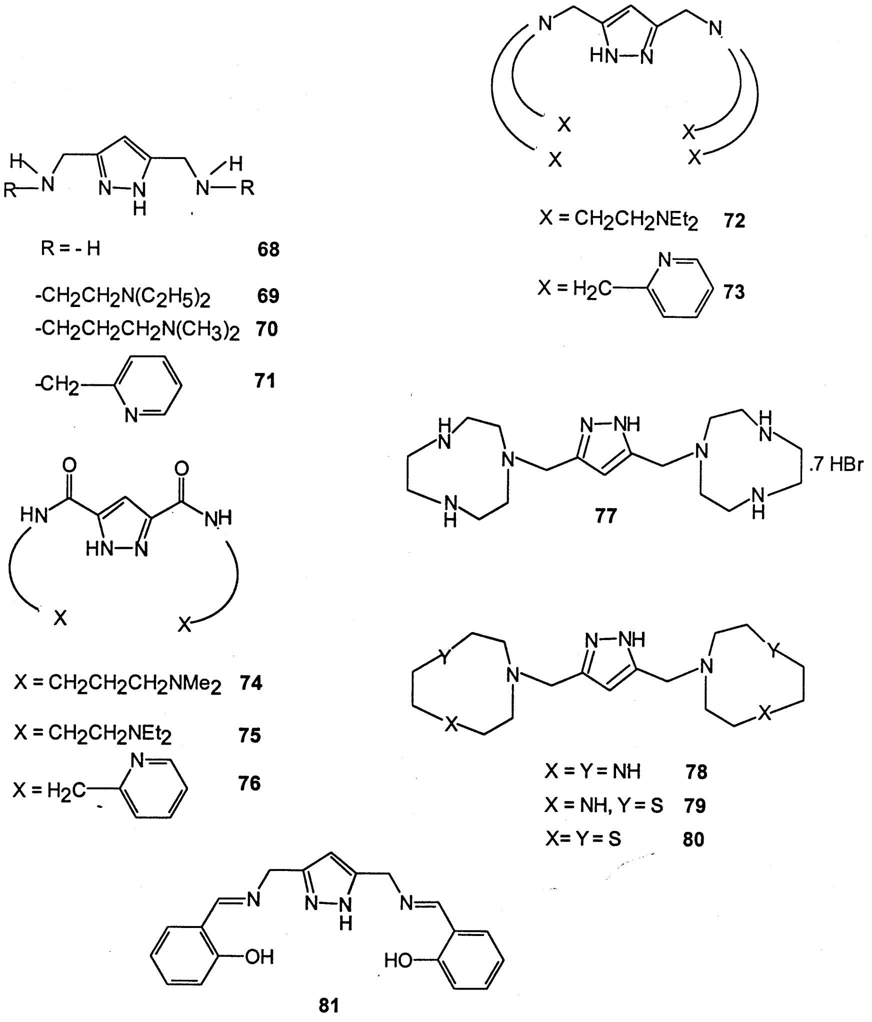


Fig. 20. Ligand structures (bridging: **68**–**81**).

are potentially capable of acting as bridging ligands and offer great potential, particularly for the preparation of heteronuclear/polynuclear complexes.

6.1. One pyrazole and two primary amines

The ligand **68** forms binuclear copper(II) complexes of the formula [Cu_2(**68**)$_2X_2$] (X = Cl, Br) [90]. The crystal structure of [Cu_2(**68**)$_2Br_2$] reveals a nearly planar binuclear copper(II) skeleton doubly bridged by the pyrazolate anions. The bromide ion is located at the axial site of the copper ion but the Cu–Br bond distance is significantly elongated. Thus, the configuration around each copper can be regarded as a distorted square pyramid. The copper ion is shifted by 0.156 Å out of the least-squares plane towards the axial bromide ion. Cryomagnetic investigations (80–300 K) revealed a significant antiferromagnetic interaction through the pyrazolate bridges: $J = -200.8$ cm^{-1} for the chloro complex and -192.0 cm^{-1} for the bromo complex.

6.2. One pyrazole, two secondary amines, and two tertiary amines

The new dinucleating ligands, 3,5-bis[(2-diethylamino)ethylaminomethyl]pyrazole (**69**) and 3,5-bis[(3-dimethylamino)propylaminomethyl]pyrazole (**70**) afford binuclear copper(II) complexes of the formula $[Cu_2(ligand)_2][BPh_4]_2$ [91]. The structure of $[Cu_2(\mathbf{69})_2][BPh_4]_2$ reveals that the cation has a binuclear structure, comprising two copper(II) ions and two ligands in the anionic form. The articular nitrogens and the pyrazolate nitrogens coordinate to the copper(II) ions to form an essentially planar Cu_2N_8 skeleton, doubly bridged by the pyrazolate groups. Each copper is coordinated in a square pyramidal geometry, where basal plane is formed by the two pyrazolate nitrogens and the 'articular' nitrogens and the apical site by one of the 'terminal' nitrogens but the other terminal nitrogen is not coordinated. Variable-temperature (10–300 K) magnetic susceptibility studies revealed a strong antiferromagnetic spin exchange in both complexes: $J = -214$ cm^{-1} for $[Cu_2(\mathbf{69})_2]^{2+}$ and -181 cm^{-1} for $[Cu_2(\mathbf{70})_2]^{2+}$.

6.3. One pyrazole, two secondary amines, and two pyridines

A newly designed dinucleating ligand 3,5-bis[*N*-(2-pyridylmethyl)aminomethyl]pyrazole (**71**) gave a di(μ-pyrazolato)-dimanganese(II) complex $[Mn_2(\mathbf{71})_2]$-$[BPh_4]_2$ [92]. The ditoluene adduct of which has been structurally characterized (Fig. 21). It reveals a di(μ-pyrazolato)dimanganese(II) core. The geometry about each

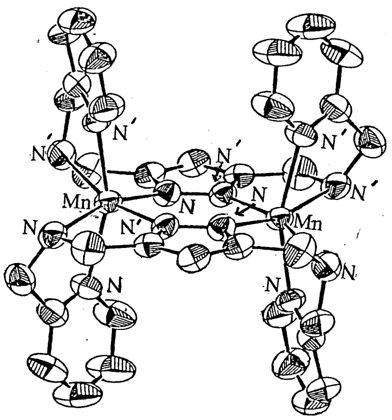


Fig. 21. X-ray crystal structure of the cationic part of $[Mn_2(\mathbf{71})_2][BPh_4]_2{\cdot}C_6H_5CH_3$ (adapted from Ref. [92]).

Mn is regarded as a distorted octahedron with two pyrazolate nitrogens on the basal plane and two pyridyl nitrogens at the axial sites. All the Mn–N bond distances are longer than 2.1 Å in accord with the high-spin manganese(II). The Mn(1)–N(articular) bond lengths are significantly elongated (Table 1), probably due to a strain in the dinuclear core. The most noticeable feature in this structure is the coordination behaviour of the pendant pyridyl groups. That is, two pyridyl nitrogens of one ligand, coordinated to two different Mn centres, are situated on the same side with respect to the plane of the di(μ-pyrazolato)dimanganese(II) core. The complex showed catalytic activity towards disproportionation of H_2O_2 in DMF at 0°C.

6.4. One pyrazole and six tertiary amines

The new binucleating pyrazole ligand 3,5-bis{*N*,*N*-bis[2-(diethylamino)ethyl]-amino-methyl}pyrazole (**72**) forms cobalt(II) and copper(II) complexes of the general formula $[M_2(\mathbf{72})(X)][BPh_4]_2 \cdot n(\text{acetone})$ ($M = Co$, Cu; $X = CH_3COO^-$, N_3^-; $n = 0$–3), where two metal ions are bridged by the endogenous pyrazolate group and the exogenous X group [93]. Electronic spectra of the cobalt(II) and copper(II) complexes suggest a trigonal–bipyramidal configuration around each metal ion. Magnetic properties (75–300 K) reveal that the cobalt(II) complexes $[Co_2(\mathbf{72})(CH_3COO)][BPh_4]_2 \cdot$acetone and $[Co_2(\mathbf{72})(N_3)][BPh_4]_2 \cdot$2acetone both show a slight increase of magnetic moment with lowering of temperature. $[Cu_2(\mathbf{72})(CH_3COO)][BPh_4]_2$ shows a weak antiferromagnetic spin-coupling, $2J = -14.04$ cm^{-1} and $[Cu_2(\mathbf{72})(N_3)][BPh_4]_2 \cdot$acetone exhibits a much lowered magnetic moment owing to a strong antiferromagnetic spin coupling.

The ligand **72** formed μ-pyrazolato-μ-carboxylato-dimanganese(II) complex $[Mn_2(\mathbf{72})(O_2CCH_3)][BPh_4]_2$, which showed catalytic activity towards disproportionation of H_2O_2 in DMF at 0°C. Together with the observation of a ligand-to-metal charge-transfer band characteristic of $Mn^{IV} = O$, a mechanistic scheme has been inferred [92].

6.5. One pyrazole, two tertiary amines, and four pyridines

The ligand 3,5-bis[*N*,*N*-di(2-pyridylmethyl)aminomethyl]pyrazole (**73**) formed a μ-pyrazolato-μ-carboxylato-dimanganese(II) complex, $[Mn_2(\mathbf{73})(O_2CC_6H_5)][BPh_4]_2$. The complex showed catalytic activity towards disproportionation of H_2O_2 in DMF at 0°C [92].

6.6. One pyrazole, two amides, and two tertiary amines

New dinucleating ligands 3,5-bis-{*N*-[3-(dimethylamino)propyl] carbamoyl}-pyrazole (**74**) and 3,5-bis{*N*-[2-(diethylamino)ethyl]ethyl]carbamoyl}pyrazole (**75**) have been prepared [94]. The binuclear copper(II) complexes with azide or acetate ion as an exogenous bridge, $[Cu_2L(N_3)(H_2O)_2] \cdot H_2O$ ($L = \mathbf{74}$ or **75**) and $[Cu_2(\mathbf{74})$-

$(O_2CCH_3)]\cdot 2CH_3OH$ have been obtained. Cryomagnetic investigations (5–300 K) reveal a significant antiferromagnetic spin exchange for the azide-bridged complexes ($2J = -594$ cm^{-1} for **74** and $2J = -670$ cm^{-1} for **75**), but a ferromagnetic spin exchange ($2J > +17.8$ cm^{-1}) for the acetate-bridged complex. The azido-bridged complexes are EPR silent. A quickly prepared DMF frozen solution of the acetate-bridged complex (which is otherwise unstable) displays X-band signals characteristic of a spin-triplet ($S = 1$) state, together with signals due to a spin doublet ($S = 1/2$) attributable to monomeric copper(II).

6.7. *One pyrazole, two amides, and two pyridines*

A new dinucleating ligand 3,5-bis[*N*-(2-pyridylmethyl)carbamoyl]pyrazole (**76**) has also been accomplished [94]. The binuclear copper(II) complex with azide ion as an exogenous bridge, $[Cu_2(\mathbf{76})(N_3)(H_2O)_2]\cdot H_2O$ has been obtained. Temperature-dependent (5–300 K) magnetic studies reveal that the Cu(II) centres are antiferromagnetically coupled ($2J = -742$ cm^{-1}). The complex is EPR silent.

6.8. *One pyrazole and two tridentate macrocycles*

The new bis-macrocycle 1,1′-[(1*H*-pyrazol-3,5-diyl)bis(methylene)]bis[1,4,7-triaza-cyclo-nonane] (**77**) was synthesized and its complexation with Cu^{2+} studied [95]. Potentiometric and spectrophotometric titrations indicate that a series of both mononuclear and binuclear complexes are formed in solution. A binuclear complex $[Cu_2(\mathbf{77})(N_3)][PF_6]_2\cdot H_2O$ has been structurally characterized. The two Cu(II) ions are in a square–pyramidal coordination geometry. The axial ligand is one of the N-atoms of the 1,4,7-triazacyclononane ring, whereas at the base of the square pyramid, the other two N-atoms of the macrocycle, one N-atom of the pyrazolide and one of the azide, both of which are bridging the two metal centres. The temperature dependence (1.7–400 K) of the magnetic susceptibility of this complex reveals the presence of a strong antiferromagnetic coupling.

Bis-macrocyclic ligands consisting of two N_3- (**78**), N_2S- (**79**), or NS_2-(**80**)-cyclononane rings were also prepared [96]. They form dinuclear Cu(II) and Ni(II) complexes which are able to bind one additional exogenous bridging ligand such as Cl^-, Br^-, N_3^-, $SO_4{}^{2-}$, and 1*H*-pyrazol-1-ide. Three copper(II) complexes $[Cu_2(\mathbf{79})(SO_4)(H_2O)][PF_6]\cdot CH_3OH\cdot 2H_2O$ (Fig. 22), $[Cu_2(\mathbf{80})Cl][ClO_4]_2\cdot CH_3CN$ and $[Cu_2(\mathbf{80})Br][ClO_4]_2\cdot H_2O$ have been structurally characterized. Each Cu(II) centre is coordinated by the three donor atoms of the macrocyclic ring, by a pyrazolediyl N-atom, by an atom of the exogenous bridging ligand, and sometimes by a solvent molecule. In the majority of the Cu(II) complexes, the metal ion exhibits square–pyramidal or trigonal–bipyramidal coordination geometry, except in the complex $[Cu_2(\mathbf{79})(SO_4)(H_2O)]^+$, in which one Cu(II) is hexacoordinated with the participation of a water molecule. The X-ray structure of the azido-bridged dinuclear Ni(II) complex $[Ni_2(\mathbf{78})(N_3)(H_2O)_2][ClO_4]_2\cdot H_2O$ reveals that both Ni(II) centres have octahedral coordination geometries. In all complexes, the 1*H*-pyrazolediyl group connecting the macrocycles is deprotonated and bridges the two metal centres,

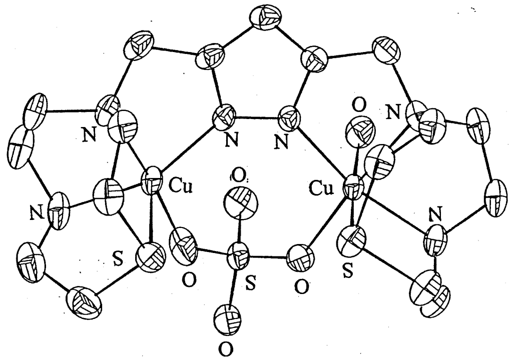


Fig. 22. X-ray crystal structure of the cationic part of $[Cu_2(\mathbf{79})(SO_4)(H_2O)][PF_6]\cdot CH_3OH\cdot 2H_2O$ (adapted from Ref. [96]).

which, depending on the exogenous ligand, have distances between 3.6 and 4.5 Å. The dinuclear Cu(II) complexes are strongly antiferromagnetic. The 2J values are: $[Cu_2(\mathbf{79})(N_3)][PF_6]_2$ (≥ -1040 cm^{-1}); $[Cu_2(\mathbf{79})(\text{pyrazolate})][ClO_4]_2$ (-300 cm^{-1}) and $[Cu_2(\mathbf{80})Cl][ClO_4]_2$ (-272 cm^{-1}). Cyclic voltammetry of the Cu(II) complexes in MeCN reveals a strong dependence of the potentials $Cu_2^{II} \rightarrow Cu^{II}Cu^{I} \rightarrow Cu_2^{I}$ on the nature of the donor atoms of the macrocycle as well as on the type of bridging molecule.

6.9. One pyrazole and two salicylaldimines

A new pyrazole-based dinucleating ligand 3,5-bis(salicylideneamino)methyl)-pyrazole (**81**) affords a complex $[Mn_4(\mathbf{81})_2(OCH_3)_4(CH_3OH)_4][ClO_4]_2\cdot 4CH_3OH$ [97].

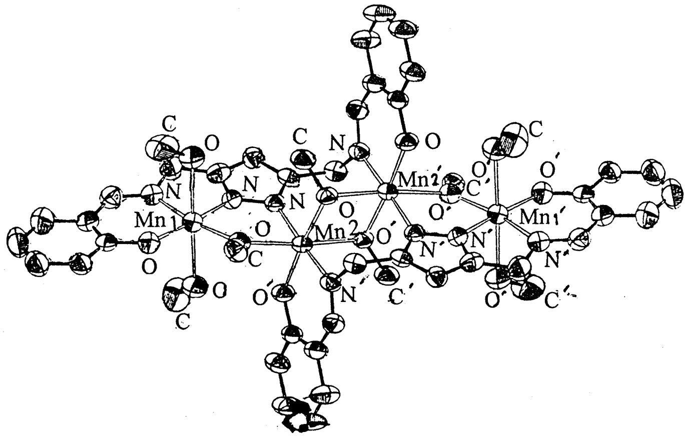
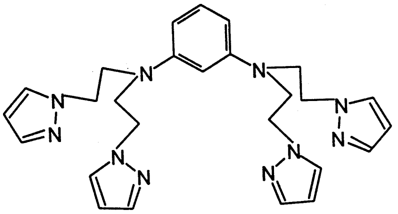


Fig. 23. X-ray crystal structure of the cationic part of $[Mn_4(\mathbf{81})_2(OCH_3)_4(CH_3OH)_4]$–$[ClO_4]_2\cdot 4CH_3OH$ (adapted from Ref. [97]).



82

Fig. 24. Ligand structure (*m*-phenylenediamine-based: **82**).

Its X-ray structure (Fig. 23) revealed the dimerized tetranuclear structure with a linear array of four manganese ions for the complex cation. Each terminal Mn(III) ion is bound to one NNO-coordination site of dideprotonated **81**, through the pyrazole nitrogen and salicylideneaminate nitrogen and oxygen and has a six-coordinate environment together with two methanol oxygens and one methoxide oxygen acting as the bridge to the adjacent internal Mn(III) ion, Mn(2). The Mn–O(CH_3OH) bond distances are elongated relative to the other four bond distances, may be due to the Jahn–Teller distortion for high spin Mn(III) ion. The pyrazolate nitrogen of the other NNO site of the ligand coordinates to the adjacent internal Mn ion, Mn(2), but the salicylideneaminate N and O are associated with coordination to another internal Mn(III) ion, Mn(2′). In the same way N(pyrazolate) coordinates to Mn(2′) while salicylaldiminate N and O coordinates to Mn(2), affording the linear array of Mn(1) Mn(2)---Mn(2′)---Mn(1′). Two internal Mn(III) ions Mn(2) and Mn(2′), are bridged to each other by two methoxide oxygens. The geometry about Mn(2) is also six-coordinate with pyrazolate N, salicylideneaminate N and O and bridging methoxide oxygens. The Jahn–Teller distortion is seen along the O(methoxide)–Mn(2)–O(methoxide) axis.

7. *m*-phenylenediamine-based ligand

A binucleating ligand **82** providing tridentate N coordination with an *m*-phenylenediamine spacer (Fig. 24), was synthesized [98]. The copper(I) complex of **82** reacts [98] rapidly at room temperature (r.t.) with dioxygen in methanol to an intensely violet-coloured species. From which a violet coloured organic compound was isolated, after removal of the copper ions. This compound was not thoroughly characterized; however, ^1H and ^{13}C spectra suggested that the phenyl ring of the ligand has undergone some type of oxidation. Using this ligand an air-stable green dicopper(II) complex with pyrazolate bridge was isolated in the solid state. In methanol the complex dissolved to give a violet solution with an electronic spectrum nearly identical to that observed for the reaction of the dicopper(I) complex with dioxygen.

8. Xylyl-/mesityl/-based ligands

Fig. 25, compiles a new class of pyrazole-containing ligands, the poly(pyrazol-1-ylmethyl)benzene (**83**–**102**), discussed in this section. These ligands are expected to exhibit a variety of modes of coordination, including participation by the benzene ring as a donor group. It should be mentioned here that a sizeable number of

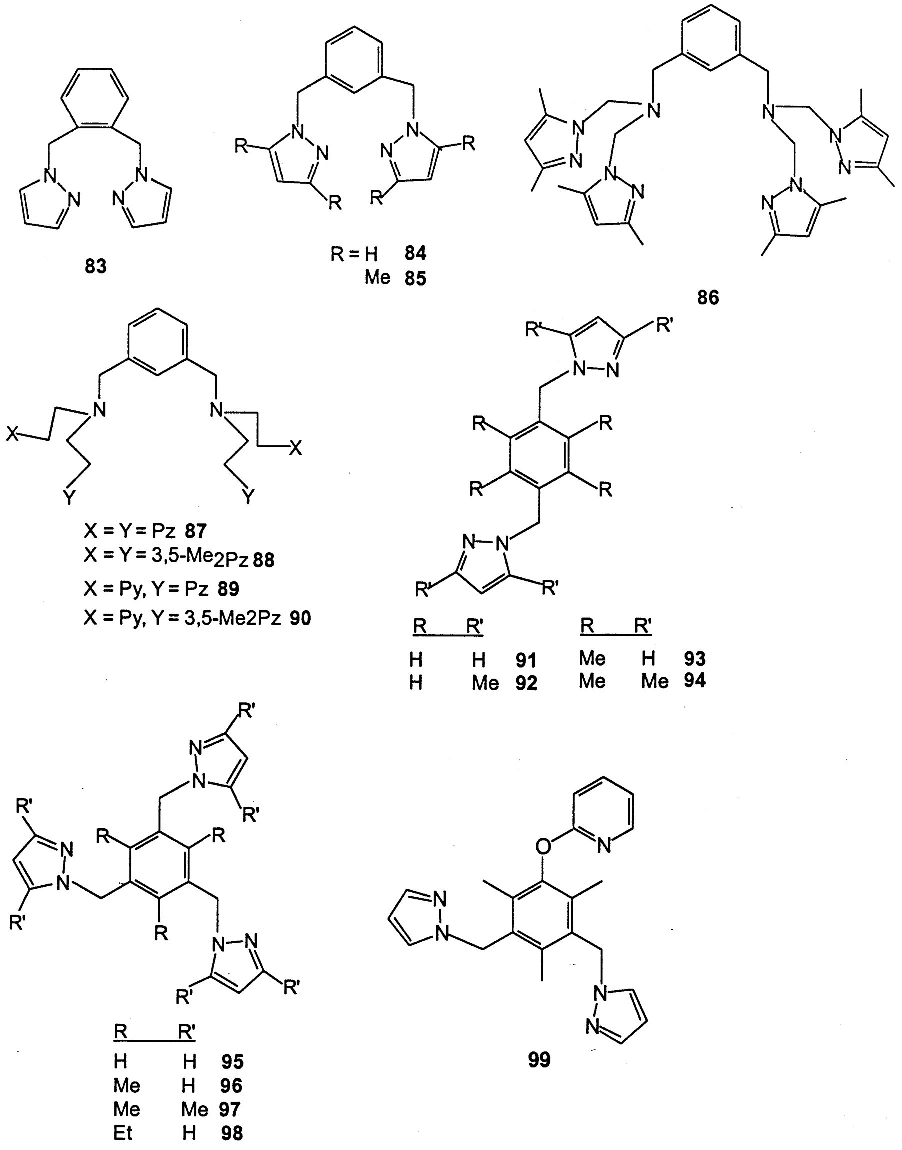
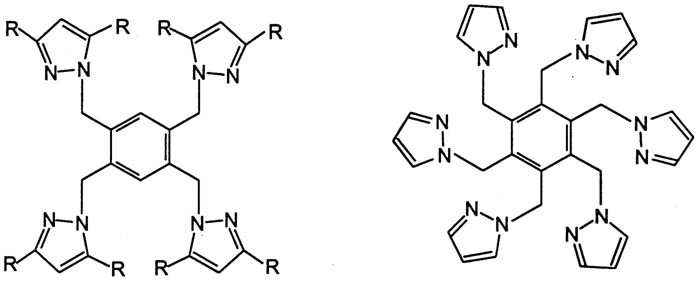


Fig. 25. Ligand structures (xylyl-based: **83**–**102**).



R = H **100**
Me **101**

102

Fig. 25. (*Continued*)

m-xylyl-based pyrazolyl ligands and their coordination chemistry, has been developed primarily from the standpoint of modelling dinuclear copper proteins, hemocyanin and tyrosinase [15–17]. The complexes with ligands having recent origin are included here.

8.1. *o*-Xylyl-based

The ligand 1,2-bis(pyrazol-1-ylmethyl)benzene (**83**), where the two pyrazolyl coordinating sites are separated by a *o*-xylyl spacer, has been prepared [99,100] and it's coordination chemistry investigated [99]. It reacts with copper(II) chloride affording two types of complexes, the green monomer [Cu(**83**)Cl_2]·0.5CH_3OH and the yellow–green dimer [Cu_2(**83**)$_2Cl_4$], which have been structurally characterized. In the monomeric complex the copper(II) ion is coordinated by two pyrazole nitrogen atoms and two chloride ions, and the copper ion in this complex has a distorted tetrahedral geometry. In the dimeric complex the two copper(II) ions and two bridging chloride ions form a cetrosymmetric planar four-membered ring. In this case each copper(II) ion is coordinated by five donors: two pyrazolyl nitrogen atoms, two bridging chloride ions and a non-bridging chloride ion that occupies the fifth (axial) coordination site. The copper(II) ion is 0.403 Å above the basal plane. Thus here the geometry at each copper(II) centre is distorted square pyramidal ($\tau = 0.11$). The effective magnetic moments of 1.85 μ_B (monomer) and 1.82 μ_B per copper (dimer) suggest that the dicopper(II) centre in the latter complex has no strong magnetic interaction. For both the complexes the X-band powder EPR spectra at r.t. show an axial signal. Both the complexes exhibit in MeCN identical cyclic voltammograms. The cyclic voltammogram for the monomer shows a quasi reversible Cu^{II}/Cu^{I} response at 0.49 V versus Ag/AgCl. The cobalt(II) analogue of the monomeric copper(II) complex, [Co(**83**)Cl_2] was also synthesized and structurally characterized. The angles at the cobalt(II) ion clearly indicate a slight distortion away from the ideal tetrahedral geometry. The effective magnetic moment of this complex is 4.60 μ_B in conformation with the $S = 3/2$ state. It exhibits a broad isotropic signal at 77 K with the g value of 3.813.

8.2. *m*-Xylyl-based

Although the synthesis of the ligand **84** has been reported in the literature [100], it's coordination chemistry has not been explored. However, reaction between it's methyl-substituted derivative **85** and $[Cu(CH_3CN)_4][BF_4]$ yielded $[Cu_2($**85**$)_2][BF_4]_2$ [101]. The structure reveals (Fig. 26) the extremely short Cu–N(pyrazole) distances, resulting from the low coordination number, although backbonding into the π^* orbital of the aromatic pyrazole ring cannot be ruled out. The N(pyrazole)–Cu–N(pyrazole) angle of 160° is smaller than the expected linear arrangement of donors in two-coordinate Cu(I). The Cu···Cu distance [6.350(3) Å] is large enough to presume that each copper atom acts as it would in a monomeric complex. Cyclic voltammetric experiment reveals an irreversible wave with an anodic peak potential of 1.27 V versus SCE in CH_3CN at a glassy carbon electrode. Reaction between this complex and carbon monoxide results in the formation of carbonyl derivatives.

Using the ligand *N*,*N*,*N*,*N*′-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)-α,α′-diamino-*m*-xylene (**86**), copper(II) complexes of the type $[Cu_2($**86**$)X_2]Y_2$ where $X = OCH_3$ or Cl and $Y = Cl$ or BF_4 were prepared [36]. The ability of the complexes to catalyze the oxidation of catechol to quinone was studied by spectrophotometry. The binuclear complex $[Cu_2($**86**$)(OCH_3)_2][BF_4]_2$ reacts fastest where the other three complexes have slower rates of oxidation.

A group of four *m*-xylyl-based binucleating ligands **87**–**90** were synthesized [102,103]. The cationic part of the structure of the dicopper(I) complex of **88**, $[Cu_2($**88**$)][BF_4]_2$ reveals [102] that the copper atom sits 0.206(1) Å from the plane formed by the three N atoms in a T-shaped coordination sphere. Using the ligands **87**–**90**, the reaction chemistry of their copper(I) derivatives has been thoroughly studied. All of the complexes react via four-electron reduction of the dioxygen molecule to give bis(μ-hydroxy)copper(II) dimers [103]. In CH_3CN solution the dimeric copper(I) complexes exhibit Cu^{II}/Cu^{I} redox process in the range 0.309–0.565 V versus SSCE.

8.3. *p*-Xylyl-based

The ligands **91**–**94** were synthesized [100] and reaction of a methanol solution of **94** with $PdCl_2$ in 2 M HCl resulted in the isolation of a diprotonated ligand coordinated to a $PdCl_4^{2-}$ unit. The X-ray structure reveals that the ligand dication is hydrogen bonded to the $PdCl_4^{2-}$ anion.

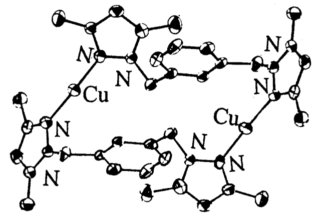


Fig. 26. X-ray crystal structure of the cationic part of $[Cu_2($**85**$)_2][BF_4]_2$ (adapted from Ref. [101]).

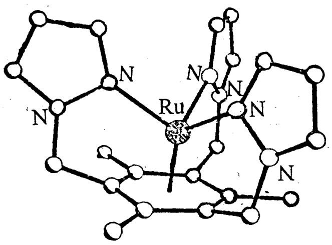


Fig. 27. X-ray crystal structure of the cationic part of [Ru(**96**)][$ZnCl_4$]·$3H_2O$ (adapted from Ref. [106]).

8.4. Mesityl-based

The new trifunctional pyrazolyl ligand, 1,3,5-tris(pyrazol-1-ylmethyl)benzene ligand (**95**) and its substituted derivatives **96**–**98** have also been synthesized [100,104,105]. Copper(II) and cobalt(II) complexes of **95** have been reported [104]. X-ray analysis reveals that the complex [Cu(**95**)$_2$(ClO_4)(H_2O)$_2$][ClO_4] is a mononuclear copper(II) compound. The copper atom is coordinated by two pyrazolyl nitrogen atoms from two ligands, two water molecules in the square plane and an oxygen atom of a perchlorate ion at the apical position. This gives rise to a distorted square pyramidal coordination sphere of copper(II). Thus each ligand has two dangling pyrazole arms.

Reaction of **96** with [Ru(DMSO)$_4$$Cl_2$] affords a complex in which a coordinated metal is simultaneously involved in η^6-bonding to the benzene ring [average Ru–C bond: 2.129(9) Å] and tripodal pyrazole coordination to suitably placed ligand [average Ru–N: 2.097(8) Å] [106]. Fig. 27 shows a perspective view of the structure of cation. The coordination about the ruthenium atom is distorted octahedral. The distance of the ruthenium atom from the centroid of the benzene ring is 1.579 Å. This indicates a stronger metal–arene interaction in this compound, given the corresponding distances (1.67–1.70 Å) in the previously reported structures [20]. This is undoubtedly reinforced by multiple chelate effects. The benzene ring is measurably distorted towards a chair conformation.

The ligand **98** was designed to pre-organize the three pyrazole rings on the same side of the benzene ring. In fact, reaction of **98** with $PdCl_2$ results in the self-assembly of a three-dimensional cage [105]. X-ray structure of this compound ($PdCl_2$)$_6$(**98**)$_4$.8(CH_3)$_2$SO·$8H_2O$ (Fig. 28) reveals that it consists of a ten-component, three-dimensional metallosupra-molecular adamantanoid cage compound of six *trans*-dichloro palladium units bridged by four molecules of **98**. The six palladium atoms are arranged in a pseudo-octahedral array, while the four molecules of **98** form a tetrahedrally disposed internal core of benzene rings of approximately 4.7 Å internal radius. Within this core resides a single (disordered) (CH_3)$_2$SO molecule (used in the recrystallization step). One of the ligands has all three terminal methyl groups directed towards the internal core, while the other three ligands have one methyl group directed outside the core. The diagonally opposite palladium atoms have separations ranging from 13.26 to 15.54 Å. This cage structure is maintained in solution (^{1}H NMR).

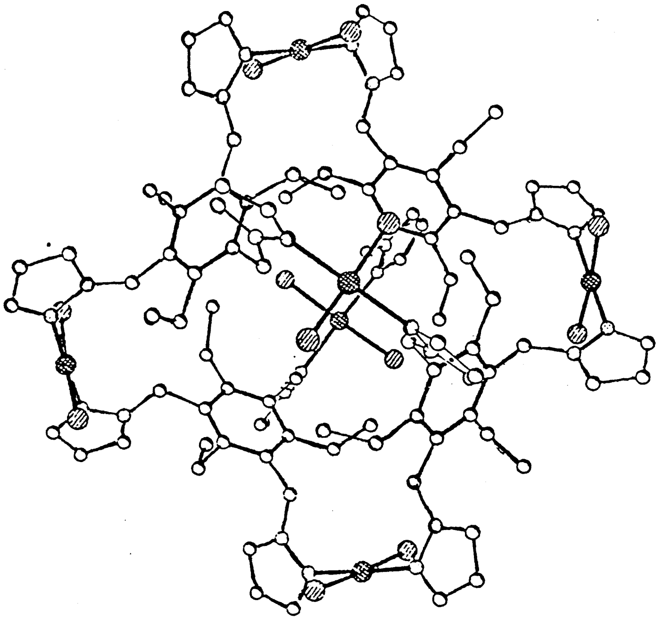


Fig. 28. Perspective view of the X-ray crystal structure of $(PdCl_2)_6(\mathbf{98})_4 \cdot 8(CH_3)_2SO \cdot 8H_2O$; solvent molecules are not shown for clarity (adapted from Ref. [105]).

A new ligand **99** reacts with $[Ru(DMSO)_4Cl_2]$ to form a complex analogous to that obtained with **96** [106].

8.5. *Bis(o-xylyl)-based*

The ligands **100** and **101** have been synthesized [100]. No report exists in the literature on their coordinating properties.

8.6. *Hexasubstituted benzene*

The relative orientations of the pyrazolylmethyl substituents of **102** was determined from its X-ray structural analysis [100].

9. Phenol-based mononucleating and dinucleating ligands

A compilation of all the phenol-based ligands considered in this section (**103**–**116**) is available in Fig. 29. Due to availability of an anionic phenolate group these class of ligands add extra stability to the resulting complexes.

9.1. One phenol and one pyrazole

The ligand **103** was synthesized [107]; however, attempts to isolate Mo(VI) complex using **103** failed.

9.2. One phenol, two pyrazoles, and one aromatic amine

The potassium salt of the ligand **104** reacts with $Cu(CH_3CN)_4(BF_4)$ in methanol to give Cu(**104**) [108]. The other ligands with $X = OCH_3$, SCH_3, CH_3 react to form the corresponding cationic copper(I) complexes, Cu(ligand)(BF_4). That these tripod ligands should be useful chelating agents for other metals has been demonstrated as well: Co(**104**)(BF_4)·H_2O, Mn(**104**)(ClO_4)·1/2THF. The crystal structure of Cu(**104**) [108] reveals that the copper(I) centre adopts a geometry that is distorted slightly from trigonal pyramidal, and the copper ion sits 0.178 Å above the plane formed from phenolate oxygen atom and two pyrazole nitrogens.

9.3. One bridging phenol and two terminal pyrazoles

A new bifunctional ligand 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (**105**) was prepared [109]. The structure of a discrete zinc(II) complex [Zn_2(**105**)$_2$$Cl_2$] with the ligand in it's deprotonated form was determined. The coordination sphere of Zn [109] is roughly square pyramidal (Fig. 30) with two phenolate oxygen bridges and two nitrogen atoms of pyrazole as the base and a chloride ion at the apex. The two chloride ions are in a *trans* arrangement. The Zn atom is displaced from the coordinated N_2O_2 plane by 0.5943(13) Å toward the chloride ion. The phenolate oxygen bridge angle, Zn–O–Zn′, is 104.62(8)° and the phenolate oxygen atom is three-coordinated in a planar fashion.

9.4. One bridging phenol, two terminal pyrazoles, and two tertiary amines

The ligand **106** reacts with $Cu(ClO_4)_2$ and azide ion in aqueous methanol to give the binuclear Cu(II) dimer Cu_2(**106**)(N_3)(ClO_4)$_2$·CH_3OH, in which N_3^- likely bridges the copper atoms in a 1,3-fashion [110]. It is diamagnetic at r.t., and the singlet-triplet transition energy is greater than 2000 cm^{-1}. Two Cu(I) carbonyl adducts were formed, Cu_2(**106**/**107**)$(CO)_2$(BF_4). In CH_3CN the Cu(I) dimers react with dioxygen irreversibly to produce oligomeric μ-oxo species [110].

9.5. One bridging phenol, four terminal pyrazoles, and two tertiary amines

Using the binucleating ligand **108** the copper(II) complexes of the form [Cu_2(**108**)X][BF_4]$_2$ where $X = Cl^-$ or N_3^- were synthesized [111]. A μ-hydroxo bridged complex [Cu_2(**109**)(OH)][BF_4]$_2$ has been structurally characterized [102,112]. The cationic part of this complex reveals that for one of the copper(II) centres the geometry is best described as square pyramidal; but for the other, it is more distorted, bordering on trigonal bipyramidal. The square pyramidal Cu atom sits out of the plane comprising O(phenoxide), O(hydroxo), N(pyrazole), and N(amine) by 0.269(2) Å, toward axial pyrazole N. Quite interestingly, the Cu_2O_2 ring is not planar (the dihedral angle between the two CuO_2 planes is 4.1°). Variable-temperature magnetic susceptibility measurements (6–300 K) demonstrate

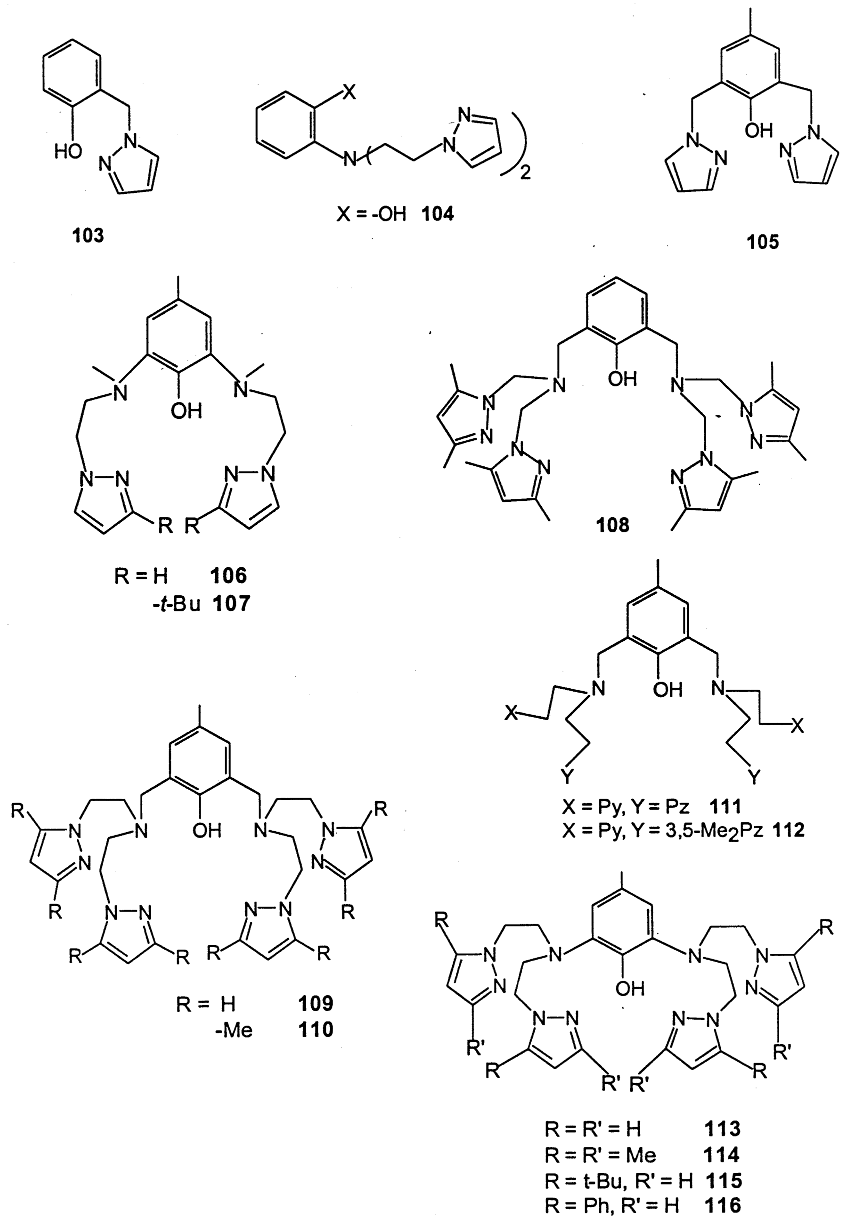


Fig. 29. Ligand structures (phenol-based: **103**–**116**).

strong antiferromagnetic coupling ($2J = -420$ cm^{-1}) between the copper(II) centres.

When a methanolic solution of Cu(CH_3CN)(PF_6) was added to a methanolic solution of ligands **109** and **110** and KOH, disproportionation reaction occurred. However, using **109** and **110** the dicopper(I) phenol complexes [Cu_2(**109**/**110**)][PF_6]$_2$ and [Cu_2(**109**/**110**)(CO)$_2$(PF_6)$_2$·H_2O were prepared [113]. New hybrid dinucleating ligands containing pyrazole and pyridine rings for terminal coordination (**111** and **112**) were also synthesized [113]. The dicopper(I) phenol as well as phenolate complexes [Cu_2(**111**/**112**)][PF_6]$_2$·$x$$H_2O$ (for **111** $x = 0$ and for **112** $x = 3$), Cu_2(**111**)(CO)$_2$(PF_6)$_2$·4CH_3CN·THF, Cu_2(**112**)(CO)$_2$(PF_6)$_2$, and [Cu_2(**111**/**112**)][PF_6] were prepared. The reaction chemistry of their copper(I) derivatives have been investigated. At r.t., all the complexes (both phenolate and phenol) react with dioxygen and are oxidized to the μ-phenoxo-μ-hydroxo Cu(II) complexes. These complexes were also prepared independently from the ligand and copper(II) perchlorate. In dry CH_2Cl_2 at −78°C, an orange solution of the Cu(I) phenolate complex [Cu_2(**111**/**112**)][PF_6] reacts very rapidly with dioxygen to form a purple Cu(II)-peroxo adduct, which was characterized by an intense band at ~500 nm with a shoulder at ~630 nm (a peroxide to Cu(II) CT band). The species was stable only below −50°C. The dinuclear copper(I) phenol complexes without coordinated CO also react with dioxygen at low temperature, this time to form μ-OOH Cu(II) species. The same species was also obtained by protonation with HPF_6 of the peroxo species formed from [Cu_2(**111**/**112**)][PF_6] or by treatment of the corresponding μ-phenoxo-μ-hydroxo copper(II) dimers with H_2O_2.

Using the ligand **113**, the first copper(I) dimer having only a single phenolate bridge was prepared and structurally characterized [114]. The structure of cation portion of [Cu_2(**113**)][BF_4] with deprotonated ligand reveals that each copper ion resides in a distorted tetrahedral environment. Each copper has two pyrazole N coordination, one tertiary amine N coordination and a bridging phenolate O and Cu(1)–O–Cu(2) angle of 133.0(4)°. On reaction with dioxygen it undergoes irreversible oxidation to a dimeric or oligomeric μ-oxo species. The synthesis and characterization of **113** and two copper(II) derivatives with deprotonated ligand have been described [115]. Both the μ-acetato and the μ-1,3-azido copper(II) complexes have been structurally characterized. The structure of the cationic part of [Cu_2(**113**)(OAc)][ClO_4]$_2$·CH_3COCH_3 reveals that one of the copper(II) centres can be described as having a square–pyramidal geometry with axial position occupied by a pyrazole N atom. The geometry about other copper(II) can be described as a distorted trigonal-bipyramid. The cationic part of [Cu_2(**113**)(N_3)][ClO_4]$_2$·THF reveals that the two copper atoms have very similar coordination geometries. The geometry about each copper atom is described as tetragonal. Variable temperature magnetic susceptibility measurements demonstrate strong antiferromagnetic coupling ($2J = -1800$ cm^{-1}) for the azido derivative but negligible magnetic interaction between the copper ions in the acetato complex. Hoping that a sterically hindered analogue of the ligand **113** might prevent the bimolecular reduction of dioxygen by increasing the stability of the copper(II)-peroxo species, Sorrell et al. [98] synthesized a number of binucleating ligands **114**–**116**. The designed ligands

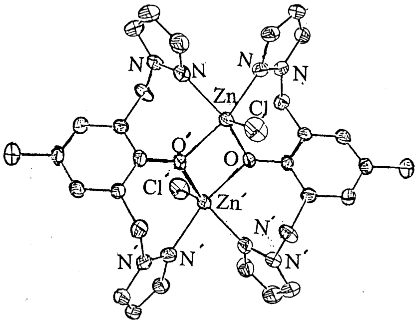


Fig. 30. X-ray crystal structure of [Zn_2(**105**)$_2$$Cl_2$] (adapted from Ref. [109]).

were such that they could probe the effect on dioxygen reactivity by varying the steric bulk at the reactive face of the resulting copper(I) complexes. They prepared several copper(II) complexes. Surprisingly, introduction of substituents to provide steric shielding of the presumed dioxygen binding site prevented reactions of these copper(I) complexes with dioxygen in a variety of solvents even at r.t. That this behaviour was not a direct consequence of steric effects was demonstrated by the synthesis of a Cu(II) derivative having a bridging acetate group, [Cu_2(**114**)(OAc)]$^{2+}$. Interestingly, the complex is not magnetically coupled. Treatment of this complex with a 10-fold excess of azide ion gave the corresponding azido complex in the solution-state. It was reasoned that steric effects cannot account for the lack of reactivity of the copper(I) complexes with dioxygen. Instead, introduction of substituents on the pyrazole rings raises the Cu^{II}/Cu^{I} potential, thereby stabilizing the Cu(I) state.

10. Macrocyclic ligands

A recent development in the coordination chemistry of pyrazole-based ligands has been the attachment of pyrazole group(s) to a macrocyclic framework. The ligands considered in this section (**117**–**126**) are compiled in Fig. 31. The coordination chemistry of these ligands is largely the chemistry of the macrocyclic ligands.

10.1. A tridentate macrocycle and two pendant pyrazole arms

The pyrazole-functionalized ligand 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (**118**, vide infra) forms a nickel(II) complex [Ni(**118**)][BPh_4]$_2$. This complex affords by slow recrystallization from an CH_3CN–C_2H_5OH solution the new compound [Ni(**117**)(CH_3CN)][BPh_4]$_2$ where **117** is the new ligand 1,4-bis(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane [116,117] formed from **118** by a N-dealkylation reaction and loss of a pendant arm. Its crystal structure has been determined to reveal that the nickel atom is in a six-coordinate environment formed by the five N atoms provided by the ligand **117** and by the CH_3CN nitrogen atom.

10.2. A tridentate macrocycle and three pendant pyrazole arms

The ligand **118** forms stable complexes with 3d metal cations of formula [M(**118**)]Y_2 (M = Fe, Y = BPh_4; M = Cu, Y = ClO_4; M = Zn, Y = BPh_4]. The complexes were isolated in the solid state and characterized by standard physicochemical methods [116]. A new potentially hexadentate ligand 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane (**119**) has been synthesized [118]. In protonated form, **119**·6HCl, it reacted with metal perchlorates to give the complexes [M(**119**)][ClO_4]$_2$·$n$$H_2O$ (M = Ni, $n = 0.5$; M = Zn, $n = 1$) and [Fe(**119**)]ClO_4]$_3$·H_2O. The magnetic moments at r.t. of the nickel(II) (3.28 μ_B) and the iron(III) complex (2.34 μ_B) are in the normal ranges for the high-spin and low-spin configurations of these ions, respectively. The structures of the nickel(II) and the zinc(II) complexes have been determined by X-ray crystallography [118]. In both complex cations the metal ion is six-coordinate, bound by the three nitrogen atoms of the macrocycle and by three pyrazole nitrogen atoms with a coordination geometry intermediate between trigonal prismatic and octahedral in the nickel complex but closer to trigonal prismatic in the zinc complex. The pyrazole-functionalized macrocycles **118** and **119** gave mixed-valence iron complexes of formula [Fe(**118**/**119**)[$FeCl_4$]Cl, which are considered to contain the high-spin iron(II) [Fe(**118**/**119**)]$^{2+}$, besides [$FeCl_4$]$^-$ and Cl^- anions [119]. The diamagnetic compound [Fe(**118**)][ClO_4]$_2$ has also been obtained. There is evidence for the iron(II) compound in [Fe(**119**)][$FeCl_4$]Cl being formed in the reduction of iron(III), accomplished by primary alcohols in the presence of **119**·6HCl. The structure of the compound [Fe(**119**)][$FeCl_4$]Cl, as revealed by the X-ray analysis [119], consists of isolated [Fe(**119**)]$^{2+}$, [$FeCl_4$]$^-$ and Cl^- ions. The iron(II) in the complex cation is coordinated by the six nitrogen-donor atoms of **119**, with a geometry similar to that of the [M(**117**)][ClO_4]$_2$·$n$$H_2O$ (M = Ni, $n = 0.5$; M = Zn, $n = 1$) [118]. The cyclic voltammogram of [Fe(**119**)][$FeCl_4$]Cl in CH_3CN displays two well-resolved one-electron redox processes at 0.03 and at 0.59 V versus NHE. The relevant redox couples are [$FeCl_4$]$^{-/2-}$ and [Fe(**119**)]$^{3+/2+}$, respectively. The Fe^{III}/Fe^{II} potential of the [Fe(**119**)]$^{3+/2+}$ couple indicates that the remarkable stability of the [Fe(**119**)]$^{2+}$ species with respect to its oxidation by O_2 must be due to kinetic factors. The formation of purple diamagnetic compound [Fe(**118**)][ClO_4]$_2$ is at variance with the presence of the high-spin [Fe(**118**)]$^{2+}$ cation in the solid compound [Fe(**118**)][$FeCl_4$]Cl. The attainment of two different spin states by the [Fe(**118**)]$^{2+}$ cation suggests that it is at the verge of the high-spin-low-spin transition for six-coordinated iron(II). Solid state effects due to the different anions employed may then be decisive in determining the spin state of iron(II). The cationic part of [Fe(**118**)][ClO_4]$_2$ reveals that it has closely similar coordination environment as that in [Fe(**119**)]$^{2+}$. Now, the Fe–N(pyrazole) bond distances are in the range 1.90–1.96 Å. The large differences in bond distances to the metal between the two compounds support the assumption that the high-spin metal ion in the complex cation for the ligand **119** is iron(II), ruling out definitely the alternative formulation [Fe^{III}(**119**)][$Fe^{II}Cl_4$]Cl for that compound.

10.3. A tetradentate macrocycle and three/four pendant pyrazole arms

A potentially hexadentate pyrazole-containing tetradentate macrocyclic ligand 1,7-dimethyl-4,10-bis(pyrazol-3-ylmethyl)-1,4,7,10-tetraazacyclododecane (**120**) was prepared and its nickel(II) and zinc(II) complexes were prepared and characterized [120]. A new pyrazole-containing tetraazamacrocyclic ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (**121**) has also been prepared [121]. This potentially octadentate ligand gives iron(II), nickel(II), and copper(II) complexes of general formula [M(**121**)]Y_2 (M = Ni, Y = Br, I, ClO_4; M = Fe, Y = BPh_4; M = Cu, Y = Cl), which have been isolated in the solid state and characterized. The structure of [Ni(**121**)]I_2 reveals that the nickel atom is six-coordinated, with approximate octahedral geometry, by the four nitrogen atoms of the macrocycle and two pyrazole nitrogens belonging to nonadjacent pendant arms of **121**, the other two arms being uncoordinated. The four amine nitrogens span two contiguous faces of the distorted octahedron about the nickel atom, and the pyrazole nitrogens occupy the remaining pair of *cis* positions in the coordination polyhedron. The main deviations of the idealized geometry, possibly imposed by geometric requirements of the ligand, are due to (i) incomplete folding of the 12-membered ring and (ii) inability of the nitrogen atoms of the macrocycle bearing dangling groups to reach *trans* positions in the coordination sphere. The ligand **121** reacts with hydrated $NiCl_2$ and $ZnCl_2$ containing $NaBPh_4$, giving two complexes [M(**122**)][BPh_4]$_2$·$n(CH_3)_2CO$ [M = Ni, $n = 2$; M = Zn, $n = 1$], where **122** is the new ligand 1,4,7-tris(1-pyrazolylmethyl)-10-(ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane originating from **121** by substitution of an ethoxo group for the pyrazole group in one of the pendant arms. The X-ray structures of these two complexes have been determined to reveal that the nickel complex is six-coordinated, with one pyrazole group and the ethoxo group uncoordinated, whereas the zinc complex is seven-coordinated (Fig. 32), with the ethoxy group uncoordinated [121]. The ligand **121** gives with manganese(II) the complex [Mn(**121**)][PF_6]$_2$·$(CH_3)_2CO$ and with iron(II) species of formula [Fe(**121**)$_x$(**122**)$_{1-x}$][PF_6]$_2$·$0.5CH_3COCH_3$·$0.5C_2H_5OH$ ($x = 0.31$). The crystal structure of the manganese(II) compound reveals (Fig. 33) that the manganese(II) atom is coordinated by the eight nitrogen atoms of the ligand **121**. X-ray analyses on the isomorphous crystals of the iron(II) species have shown that these contain both eight- and seven-coordinate iron(II) in complex cations, respectively formed by the **121** and **122** ligands. Both the Fe–N(macrocyclic) and Fe–N(pyrazole) distances are shorter by 0.13 and 0.04 Å, respectively, than the corresponding distances in the manganese(II) compound.

Two pyrazole-based dinucleating ligands derived from 1,4,8,11-tetraazacyclotetradecane (cyclam), **123** and **124** were synthesized. These ligands form stable Cu(II) complexes of the form [Cu_2(**123**/**124**)(H_2O)][BF_4]$_4$ and these complexes catalyze the oxidation of catechol to quinone, but at substantially different rates [123].

10.4. Four pyrazoles and four secondary amines

Very recently a novel 30-membered macrocycle **125** containing four endocyclic neutral pyrazole groups has been reported [124]. The addition of two equivalents of

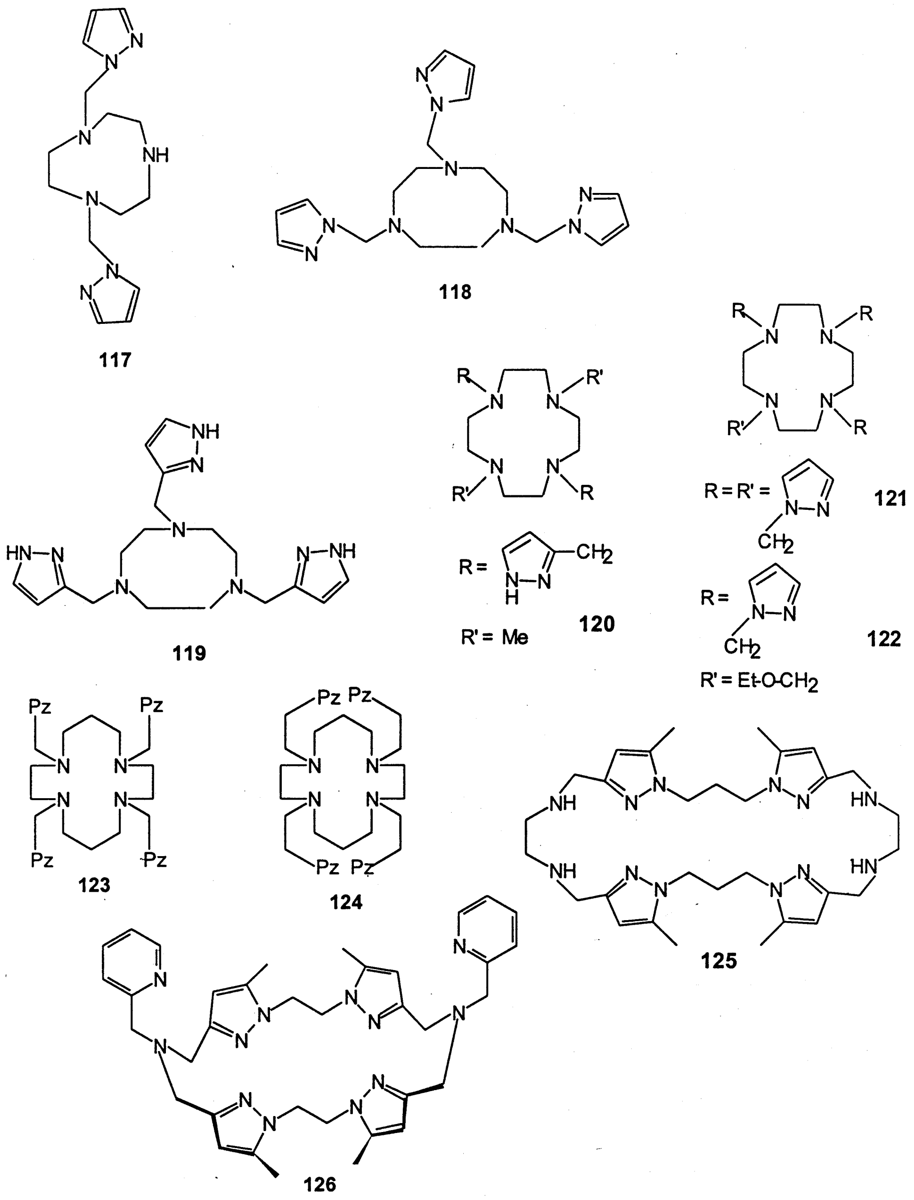


Fig. 31. Ligand structures (macrocyclic-based: **117**–**126**).

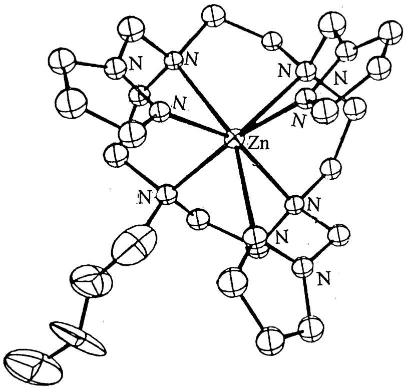


Fig. 32. X-ray crystal structure of the cationic part of $[Zn(\mathbf{122})][BPh_4]_2{\cdot}CH_3COCH_3$ (adapted from Ref. [121]).

$Cu(NO_3)_2$ to a solution of **125** yields the dinuclear mixed-anion copper(II) complex with formula $[Cu_2(\mathbf{125})Cl_2(C_2H_5OH)_2][NO_3]_2$. The X-ray structure (Fig. 34) shows **125** with two copper(II) ions each bound in a distorted square pyramidal fashion. Each copper ion is equatorially coordinated by two secondary amine donors of the ethylenediamine spacer and one pyrazole. The last equatorial position is occupied by a chloride ion. Each copper ion is axially coordinated by a second pyrazole. An

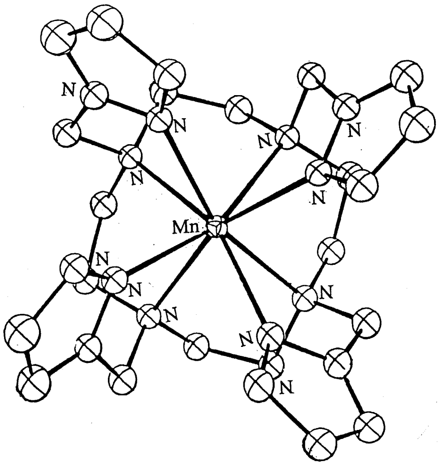


Fig. 33. X-ray crystal structure of the cationic part of $[Mn(\mathbf{121})][PF_6]_2{\cdot}(CH_3)_2CO$ (adapted from Ref. [122]).

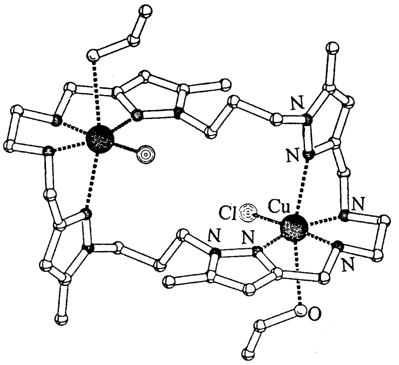


Fig. 34. X-ray crystal structure of the cationic part of $[Cu_2(\mathbf{125})Cl_2(C_2H_5OH)_2][NO_3]_2$ (adapted from Ref. [124]).

ethanol molecule is weakly bound to each copper ion in an axial position. The crystal structure shows that each copper(II) ion is bound in a square pyramidal N_4X chromophore.

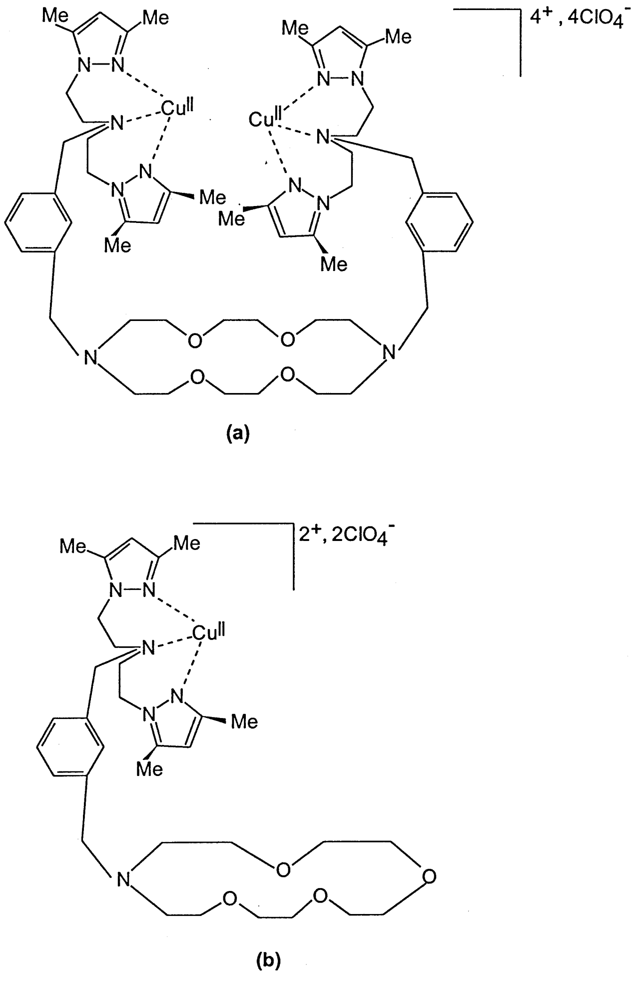
10.5. Four pyrazoles and two tertiary amines with two pendant pyridyl arms

A new macrocyclic ligand with two methylpyridyl groups as pendant arms (**126**) [125] reacts with two equivalents of $[Cu(CH_3CN)_4]X$ salts in CH_3CN solution to yield dinuclear Cu(I) complexes of general composition $[Cu_2(\mathbf{126})]X_2$ ($X = ClO_4{}^-$ or $PF_6{}^-$) [126]. Reaction of this dicopper(I) complexes with O_2 in CH_3CN at 21°C generates a *trans*-μ-1,2-peroxodicopper(II) species, $[Cu_2(\mathbf{126})(O_2)]^{2+}$. For the $PF_6{}^-$ salt the dicopper(II) complex has been isolated as a purple powder, stable at r.t. The species can be generated in CH_3OH, (21°C) as well. It is the first example of a dinuclear copper complex capable of binding molecular O_2 at r.t. in a protic solvent.

10.6. Pyrazole-based crown ether systems

The ligands from which two novel copper(II) crown ether–pyrazole complexes (**a** and **b**) (Fig. 35) are derived were synthesized by treating α-bromo-α′-{bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amino}-*m*-xylene with the corresponding diaza- and aza-crown ethers in DMF [127]. The ligands were mixed with two equivalents (for **a**) and one equivalent (for **b**) of $Cu(ClO_4)_2{\cdot}6H_2O$ in methanol to give the di- and mono-nuclear complexes **a** and **b**, respectively. The homogeneous solution of **a**, however, decolorized rapidly, indicating the formation of a copper(I) complex. Proof that **a** indeed had reduced to the copper(I) state came from electrochemical experiments on samples of **a** and **b**. The chemical reduction reaction follows a pathway different from the electrochemical oxidation/reduction of **a**. It has been assumed that in the former case a cooperative action (metal–metal distance ~ 18 Å, from CPK space-filling model) between the two copper(II)-centres is necessary to achieve the observed reduction of complex **a**. This is based on the observation that formaldehyde was produced during the reaction: a two electron oxidation of methanol requires two copper(II) ions as electron acceptors. Whether a K^+ ion could induce the aggregation of **b** (two molecules of **b** with a K^+ ion) and influence the reduction of the copper(II) centre, titration of the $ZnCl_2$ derivative of **b** with potassium picrate was done. This experiment confirmed the predominant existence of sandwich complexes at low K^+ concentration.

A novel metallohost containing a substrate-binding site and two copper ions held by two bis-pyrazole ligand sets (Fig. 36) has recently been described [128]. The cavity of this molecule binds dihydroxybenzene guests. In the presence of benzylic alcohols the Cu(II) centres of the metallohost are reduced to Cu(I) and the alcohols



(a)

(b)

Fig. 35. Dinuclear (a) and mononuclear (b) copper(II) diazacrown ether complexes (adapted from Ref. [127]).

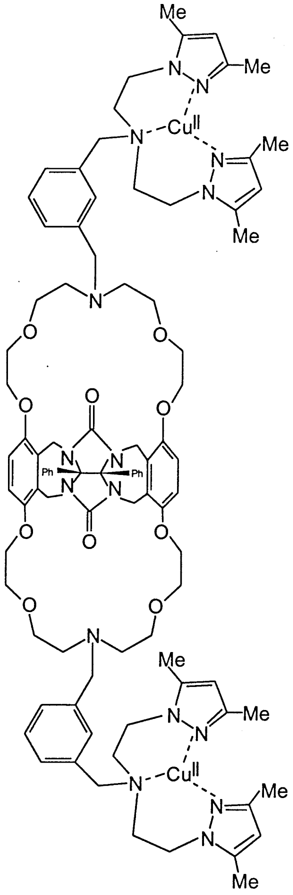


Fig. 36. The receptor with two copper(II) ions bound to it (adapted from Ref. [128]).

are oxidized to aldehydes. Benzylic alcohols possessing phenolic hydroxyl functions are extremely effective in the reduction reaction. It is believed that they are bound in the cavity of the metallohost and are properly oriented with respect to the copper centres.

11. Conclusions

In this review the use of a novel class of pyrazole-based chelating ligands in the development of coordination chemistry has been surveyed. The bonding properties of nearly hundred crystal structures in connection with the metal coordination geometry have been discussed. The structures described in this review give a clear demonstration of the flexibility of the geometries around the metal ion, provided by a novel class of pyrazole-based chelating ligands.

It has been demonstrated that the geometries, nuclearities, and reactivity properties of a particular compound can be controlled by the change in the coordination mode of chelating ligands in the coordination sphere of metal ions; by the placement of substituent groups near donor site of a ligand. In particular, the use of highly hindered ligands has enabled the isolation/generation of compounds with novel structures. Many bridging ligands have been designed and magnetic properties of the resulting compounds have significantly contributed to our understanding of metal–metal interactions such as magnetic coupling and reactivity properties from the viewpoint of bioinorganic chemistry.

It is evident from the extant literature that synthesis and characterization of coordination complexes of this class of ligands has been a primary emphasis of research, and that somewhat less attention has been directed toward detailed examination of their reactivity. Future exploitation of the unique bonding characteristics of a particular compound for discovering and understanding reactivity properties is anticipated. In view of the breadth of the coordination chemistry already uncovered by pyrazole-based chelating ligands, it is anticipated that the extent of future designing of new ligands will depend on the imagination of the researcher, based on the nature of the research problem.

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Appendix: ligand syntheses

The following list gives references to the method for preparation of the ligands discussed above: **1**, **2** [18], **3**–**7** [19], **8** [25], **9**–**17** [18], **18** [28–30], **19** [27,31,32], **20** [33], **21** [32], **22** [36], **23** [27,37], **24** [39,42], **25** [43], **26** [42], **27** [44], **28** [45], **29** [45,53], **30**–**34** [44], **35** [54], **36** [56], **37**–**40** [18], **41** [57], **42** [39], **43** [59], **44** [60], **45** [61], **46**, **47** [62], **48** [63], **49** [27,28], **50** [27,65,68], **51** [18], **52** [72], **53** [72,73], **54** [72], **55** [27,75,78], **56** [79], **57**, **58** [27,61], **59** [27,79], **60** [80], **61** [81], **62** [84], **63** [85], **64** [86], **65** [87], **66** [88], **67** [89], **68** [90], **69**, **70** [91], **71** [92], **72** [93], **73** [92], **74**–**76** [94], **77** [95], **78**–**80** [96], **81** [97], **82** [98], **83** [99,100], **84** [100], **85** [101], **86** [36], **87**–**90** [103], **91**–**94** [100], **95** [100,104], **96**, **97** [100], **98** [106], **99** [105], **100**–**102** [100], **103** [107], **104** [108], **105** [109], **106**, **107** [110], **108** [111], **109** [112], **110**–**112** [113], **113** [115], **114**–**116** [98], **117** [116], **118** [117], **119** [118], **120** [120], **121**, **122** [121], **123**, **124** [123], **124** [121], **125** [124], **126** [125].

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