Russian Chemical Reviews **71** (11) 969 – 980 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n11ABEH000758

Basic achievements in the coordination chemistry of modified monosaccharides

Yu A Zhdanov, Yu E Alekseev

Contents

I.	Introduction	969
II.	Metal complexes of monosaccharide *O*-derivatives	969
III.	Metal complexes of nitrogen-containing monosaccharide derivatives	972
IV.	Metal complexes of phosphorus-, sulfur- and selenium-containing monosaccharide derivatives	976
V.	Conclusion	978

Abstract. The published data on the complexation of chemically modified carbohydrates (acetalated and acetylated monosaccharides, carbohydrate podands and coronands as well as nitrogen-, phosphorus-, sulfur- and selenium-containing monosaccharide derivatives) are generalised and systematised. The structural diversity of the metal complexes formed is demonstrated and the effect of the ligand chirality on the chiralities of the corresponding coordination points is discussed. The bibliography includes 155 references.

I. Introduction

Various aspects of the coordination chemistry of natural carbohydrates have been detailed in a number of reviews.[1–8] The coordination chemistry of chemically modified carbohydrates has been studied in far less detail; the data available[8–11] discuss only some aspects of this field of research. The interest in this topic is connected with further improvement of methods of synthetic chemistry of carbohydrates.

Chemical modification of monosaccharides aimed at the preparation of ligands consists predominantly in the coupling of natural monosaccharides, which are continuously reproduced upon photosynthesis, to *a priori* complex-forming (in the extreme case, chelatogenic) fragments. This approach allows a considerable increase in the structural diversity of carbohydrate complexones, which are chiral by nature. Such complexones and their metal complexes are necessary for the preparation of chirally pure pharmaceuticals.

This review is an attempt to get a better insight into this branch of chemistry. The material presented herein is arranged according to the principle used in our previous review.[6] The ligands are classified into oxygen, nitrogen-, phosphorus-, sulfur- and selenium-containing monosaccharide derivatives according to the type of donor heteroatoms. Metal cations for each ligand class are cited in the order of complexity of their electronic configurations and in conformity with their positions in the Periodic Table, *i.e., s*-, *p*-, *d*- and *f*-metals.

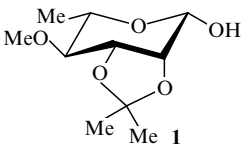
Yu A Zhdanov, Yu E Alekseev Institute of Physical and Organic Chemistry, Rostov State University, prosp. Stachki 194/2, 344090 Rostov-on-Don, Russian Federation. Fax (7-863) 243 46 67. Tel. (7-863) 265 04 77. E-mail: bell@ipoc.rsu.ru (Yu A Zhdanov)
Tel. (7-863) 243 46 00 (Yu E Alekseev)

Received 2 August 2002
Uspekhi Khimii **71** (11) 1090 – 1102 (2002); translated by R L Birnova

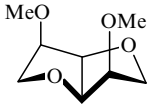
II. Metal complexes of monosaccharide *O*-derivatives

1. Complexes with *s*-metal cations

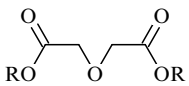
Free water-soluble monosaccharides represent[2,3,6] weak complexones of *s*-metal cations owing to strong competition of water molecules for the coordination of these cations. *O*-Alkylation (acylation) or acetalation of monosaccharides increases their hydrophobicities as a result of which the corresponding derivatives become soluble in organic solvents where they play the role of moderate *s*-metal complexones due to the lack of water. This can be exemplified by the acetalated monosaccharide **1** (see Ref. 12) and the di-*O*-methyl derivative **2**.[13] Thus substitution of the $O(CH_2)_2OH$ and $O(CH_2)_2O(CH_2)_2OEt$ fragments for the methoxy groups in compounds **1** and **2** yields[12,13] carbohydrate podands (acyclic analogues of crown esters);[2] their affinities for *s*-metal cations markedly exceed those of the starting monosaccharides. This is especially typical of podands **3** (R is a per-*O*-acetylated monosaccharide residue)[14] and **4**.[15]



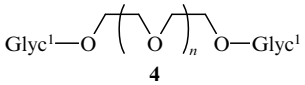
1



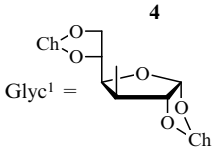
2



3

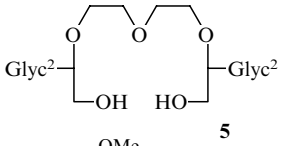


4

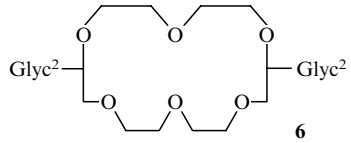


(Ch is cyclohexylidene); $n = 1-13$.

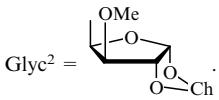
As can be judged from qualitative reactions, regioisomeric mixtures of podands and coronands (*e.g.*, compounds **5** and **6**)[15–19] readily bind alkali metal cations.



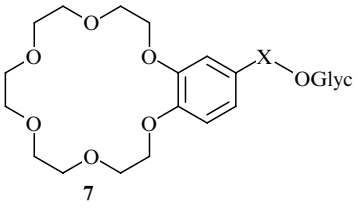
5



6

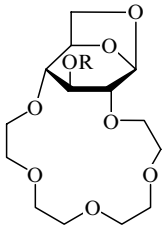


The coordination of coronands **7**,[20] **8**[21] and **9** (see Ref. 22) involves carbohydrate fragments. Ethers **10** (see Ref. 23) and a coronand **11** coordinate *s*-metals in a similar way, *i.e.*, with the involvement of carboxy groups.[24] This imparts additional stability to complexes of the above-mentioned ligands.



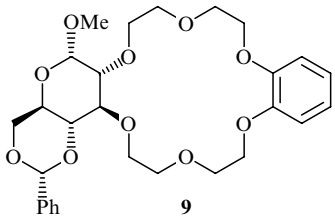
7

X = CH_2COCH_2, CH_2;
Glyc is an acetalated or acetylated monosaccharide residue.

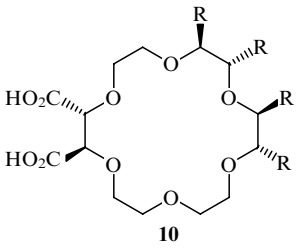


8

R = H, Ac.

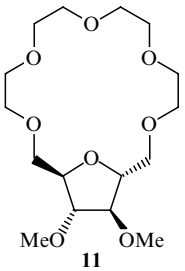


9



10

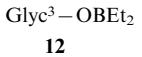
R = H, CO_2H.



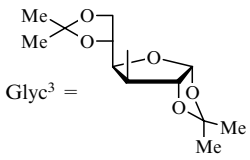
11

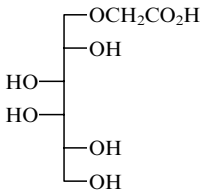
2. Complexes with *p*-metal cations

This type of complex, like complexes with *s*-metal cations, are relatively scarce. They include a series of borates of acetalated sugars (*e.g.*, compound **12** and its derivatives).[25] The *O*-carboxymethyl derivative **13** binds Al(III) and some *d*-metal cations.[26] In a homoleptic complex **14,** the aluminium atom and three carbohydrate ligands form a trigonal pyramid.[27]

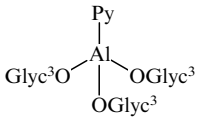


12





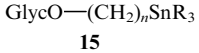
13



14

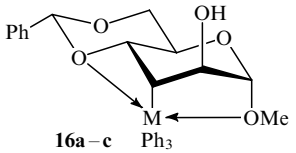
Py is pyridine.

The Sn(IV) complexes of the general formula **15** are the most extensively documented in the literature.[28–30] Organotin compounds with organometal fragments directly bound to the carbohydrate core[31,32] are characterised by intramolecular coordination of the type **16a**.[31]



15

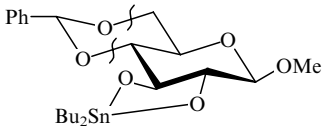
R = Me, Bu, Ph;
Glyc is an acetalated monosaccharide residue;
n = 0–2.



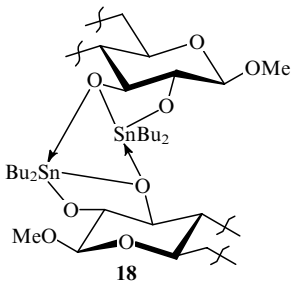
16a–c Ph_3

M = Sn (**a**), Si (**b**), Pd (**c**).

The stannylene carbohydrate acetals **17** form dimers **18**.[33,34] Some analogous derivatives form trimers and even pentamers.[34]

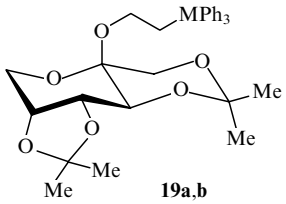


17



18

For other *p*-metals, only complexes of the type **16b**,**c** and **19a**,**b** have been described.[30]

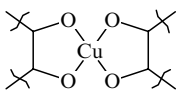


19a,**b**

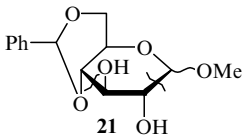
M = Si (**a**), Pb (**b**).

3. Complexes with *d*-metal cations

d-Metal complexes are especially fully and diversely represented in the coordination chemistry as a whole and in the coordination chemistry of modified monosaccharides, in particular, which to some extent is characteristic of complexes of monosaccharide *O*-derivatives. Thus the above-mentioned *O*-carboxymethyl derivative **13** is coordinated[26] not only with the *p*-cation of Al^{3+}, but also with *d*-cations Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+}. The formation of copper bischelates **20** in the selective *O*-alkylation (acylation) of the acetalated glycoside **21** in organic solvents in the presence of copper(II) has been described.[35]

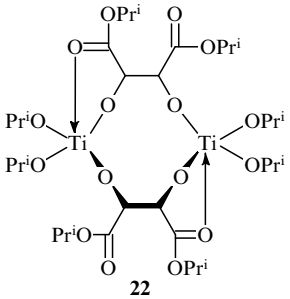


20

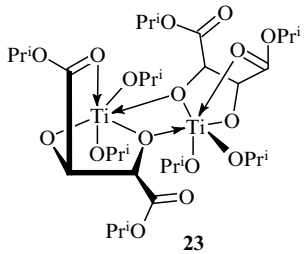


21

We failed to retrieve any literature data on complexes of monosaccharide *O*-derivatives with *d*-metal cations of subgroups IB and IIIB. *d*-Metal complexes of subgroup IVB were studied in some papers devoted to the use of monosaccharide Ti(IV) complexes in modern organic synthesis.[36–41] Ti(IV) complexes containing D- and L-tartaric acid derivatives, which are employed in the highly efficient enantioselective Sharpless epoxidation of allylic alcohols (optical yields 80% – 100%) have been studied in most detail.[36–38] (Sharpless was awarded a Nobel prize in 2001.[42]) The Sharpless catalysts form very diverse structures in solution[43,44] with cyclic (**22**)[36–38,45] and bridge-type (**23**) dimers predominating.[38,45,46]

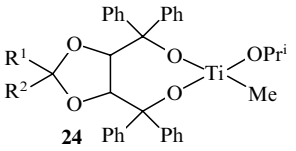


22

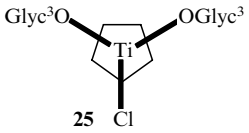


23

Titanium complexes **24** serve as nucleophilic reagents in some enantioselective transformations.[39–41] The chlorine atom in complex **25**,[47] which is a structural analogue of the complex **14**, is readily exchanged for alkyl and other groups, *e.g.*, the allyl group.[48] Like organometallic compounds, the substitution product adds enantioselectively to the carbonyl group.[48]



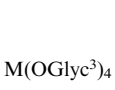
24



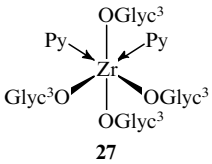
25

R^1 = H, Me; R^2 = H, Ph, Bu^t.

The chiral ligands in the homoleptic complexes **26** based on diacetone glucose [27] and the oxygen-rich periphery form cavities which favour further coordination. X-Ray diffraction analysis data suggest that two pyridine and two carbohydrate ligands in the complex **27** are localised in the equatorial plane of the pseudo-octahedral structure.[27]



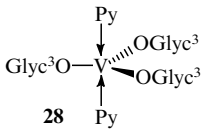
26



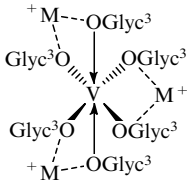
27

M = Ti, Zr, Hf.

In the case of *d*-metals of subgroup VB, the vanadiumdi-*O*-isopropylidene-D-glucose complex **28** is the only complex described so far.[49] According to X-ray diffraction analysis data, the ligands in this complex form a propeller-shaped structure having a Λ-configuration. Reaction of the complex **28** with lithium and sodium alcoholates of di-*O*-isopropylidene-D-glucose yields complexes $[V(OGlyc^3)_6M_3]$ (M = Li, Na) where the carbohydrate ligands form an environment for M^+ which resembles that of the solvate complex (structure **29**).[50] Thus, metal complexes of modified sugars can in principle be used as ligands for group IA metal ions:

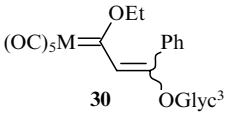


28



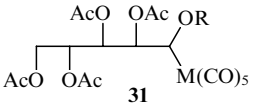
29 M = Li, Na.

Carbohydrate-containing *d*-metal complexes of subgroup VIB are represented in the literature by carbene complexes of two types. The first of them includes complexes **30**[51] where the acetalated carbohydrate moiety is in the β-position relative to the carbene carbon atom. In the second type of complex (**31**),[52] the acetylated carbohydrate fragment is linked directly to the carbene carbon atom.



30

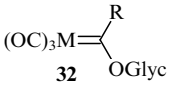
M = Cr, W.



31

R = Me, Et; M = Cr, Mo, W.

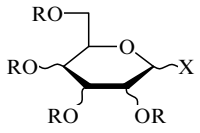
Carbene complexes of the second type (*e.g.*, **32**) have been known for *d*-metals of subgroup VIIB.[53]

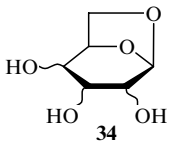


32

R = Ph, tolyl; M = Mn, Re; Glyc is a protected monosaccharide residue.

Complexes **33** were prepared [54] from acetylated glycosyl bromides by exchange reaction with $NaMn(CO)_5$. Interactions of 1,6-anhydrohexopyranoses **34** with Mn^{2+}, Mn^{3+} and Mn^{4+} follow the Angyal rule;[3,6] the ligand complexes with the axial-equatorial-axial orientation of the three vicinal hydroxy groups are the most stable.[55]

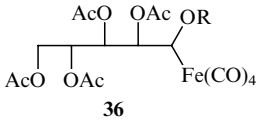




34

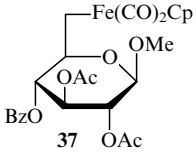
33: R = Ac; X = $Mn(CO)_5$;
35: R = Me; X = $Fe(CO)_2Cp$
(Cp is cyclopentadienyl).

The structurally unique iron carbonyl complexes **35**,[56] **36**[52] and **37**[57] and the π-complex **38**[58] are of interest among carbohydrate compounds of group VIII metals. μ^3-Carbine clusters, *e.g.,* compound **39**, have been prepared.[59]

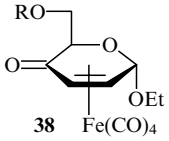


36

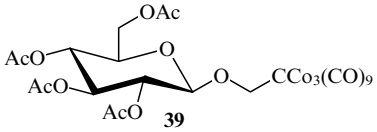
R = Me, Et.



37



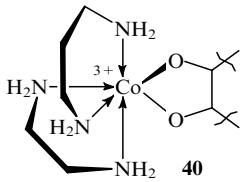
38



39

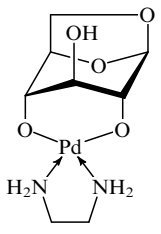
R = H, Ts.

In strongly alkaline aqueous media, vicinal diol groups of partially protected monosaccharides undergo deprotonation; the deprotonated forms of these compounds coordinate the metal complex *trans*-$[(en)_2CoCl_2]Cl$ (en is ethylenediamine) to yield complexes **40** with a predominant Λ- or Δ-configuration depending on the stereochemistry of the monosaccharide.[60]

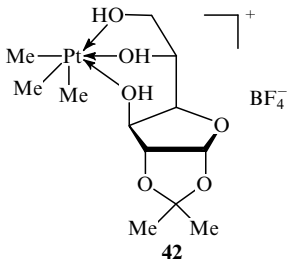


40

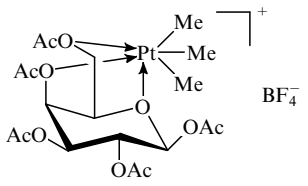
Complex $[Pd(OH)_2(en)]$ reacts with 1,6-anhydro-β-D-glucose (levoglucosan) in strongly alkaline aqueous solutions[7] to afford complex **41** (by analogy with the complex **40**). The complex $[PtMe_3(Me_2CO)_3]^+BF_4^-$ is coordinated with acetalated aldoses (*e.g.*, di-*O*-isopropylidene-D-glucose $Glyc^3OH$) to give the complex **42** with elimination of the terminal isopropylidene protective group. Per-*O*-acetylated aldoses form complexes similar to **43**.[7,61]



41



42



43

III. Metal complexes of nitrogen-containing monosaccharide derivatives

The predominance of nitrogen-containing ligands in coordination chemistry on the whole [62] is also characteristic of the coordination chemistry of carbohydrates. Nitrogen-containing monosaccharide derivatives coordinate virtually all known metals.

1. Complexes with *s*-metal cations

The majority of *s*-metal complexones in the series of nitrogen-containing monosaccharides, *e.g.*, the amino derivatives **44**, **45**,[63] **46**–**48**,[64] **49** and [65,66] **50** [67,68] and the amido derivatives **51**–**59**, have simple structures.[69] Typical *s*-metal complexones, such as the azapodands **60** (see Ref. 70) and **61** have also been prepared.[69] The ability of these compounds to form complexes with *s*-metals was estimated by qualitative reactions.[64]

$Glyc^4—NH(CH_2)_2OH$ **44**

$Glyc^5—CH_2NH(CH_2)_2OH$ **45**



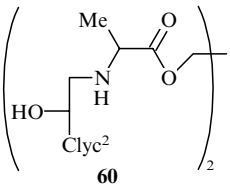
$Glyc^2—CH(OH)CH_2X$ **46**–**50**

$Glyc^5—COX$ **51**–**54**

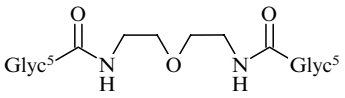
$Glyc^1—OCH_2COX$ **55**, **56**

$Glyc^4—OCH_2COX$ **57**–**59**

Compound	X
46	NH_2
47, **51**, **55**, **57**	$NH(CH_2)_2OH$
48, **52**, **56**, **58**	$N(CH_2CH_2OH)_2$
49	$NHC(CH_2OH)_3$
50	$NHCHRCO_2^-\ Na^+$ (R = H, Me, CH_2Me, CH_2OH, $CH_2C_6H_4OH$-4)
53, **59**	$NHCH_2CO_2^-\ Na^+$
54	$NHCHMeCO_2^-\ Na^+$

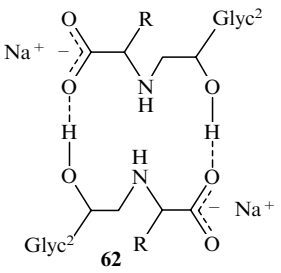


60



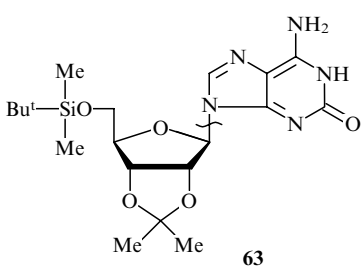
61

The podand activity of *N*-glycosylaminocarboxylates is probably due to their ability [70,71] to form the dimers **62** in non-polar media. The formation of the tetramer **64** from the acetalated *N*-glycoside, *viz*., guanosine **63**, which also occurs in non-polar media, is yet another example of aggregation of cavity-free compounds into those with cavities.[72–74] The tetramer **64** forms stable L_2M complexes (L = **64**) with K^+ and Cs^+ where the coordination apparently involves the carbonyl oxygen atoms. An important role is played by the structure of the carbohydrate fragment; thus substitution of *O*-acetyl groups for the isopropylidene protective group in compound **63** prevents aggregation.[74]

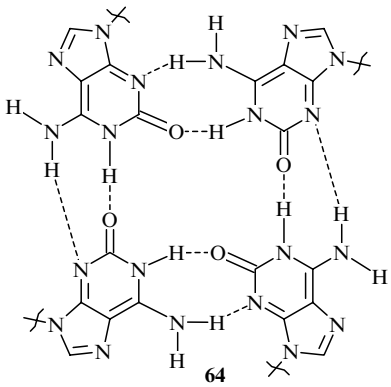


62

R = H, Et.

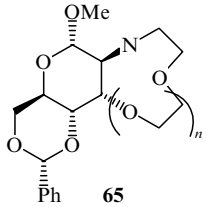


63

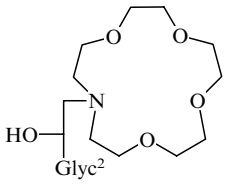


64

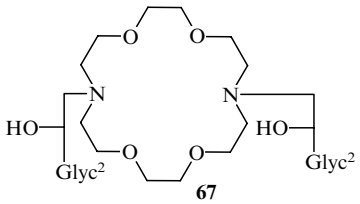
A series of carbohydrate azacrown ethers **65** form stable complexes with Na^+ and K^+ ions [$\log K_{st} = 4-6$ (in $CDCl_3$)].[75] The azacoronands **66** and **67** (see Ref. 64) catalyse the enantioselective reduction of a prochiral ketone acetophenone under phase-transfer conditions with optical yields of 48% and 20%, respectively.[76]



65 $n = 3, 4$.



66



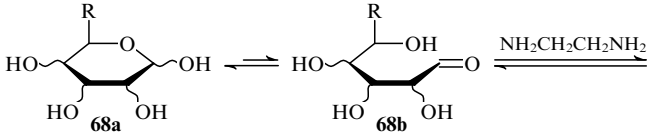
67

2. Complexes with *d*-metal cations

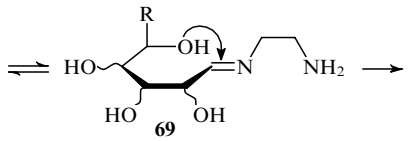
In contrast to the poorly investigated coordination of nitrogen-containing monosaccharide derivatives with *p*-metal cations, there is a considerable body of data on analogous complexes with *d*-metal cations.

a. Complexes of *N*-glycosides and related compounds

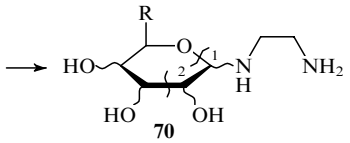
N-Glycosides containing chelate-forming fragments as aglycons are unstable; therefore, their complexes with metals are prepared using different approaches, *e.g.*, reactions of aldoses with ethylenediamine with subsequent addition of copper(II) halides to the reaction mixtures.[77] At first, aldose **68a** as the aldehyde (form **68b**) reacts with ethylenediamine to produce the Schiff base **69**, which is immediately cyclised into *N*-glycoside **70**. In turn, the free amino group in compound **70** reacts with the aldose resulting in bis-*N*-glycoside, which yields complex **71** upon addition of copper(II) salts. [77] In the case of *N*,*N*′- and *N*,*N*-dimethylethylenediamine, only one amino group is involved in the formation of *N*-glycosides; the resulting complexes have the structures **72a** and **72b,** respectively.



68a **68b**

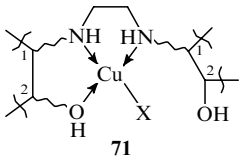


69



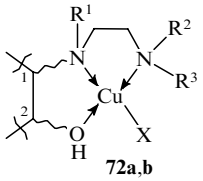
70

R = H, CH_2OH.



71

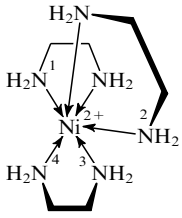
X = Cl, Br.



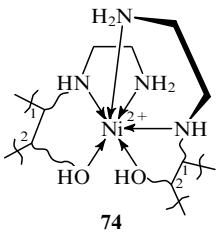
72a,**b**

72a: $R^1 = R^2 = Me$, $R^3 = H$;
72b: $R^1 = H$, $R^2 = R^3 = Me$.

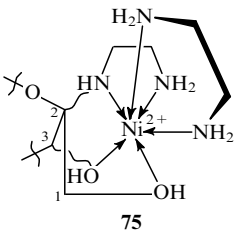
The reactions of aldoses with $[Ni(en)_3]^{2+}$ (**73**) afford the biscarbohydrate complexes **74**.[9,78] Apparently, the aldehyde form **68b** first reacts with the amino groups N(1) and N(2) of the complex **73** as is shown in the previous scheme, **68b** → **69** → **70**, the reacting ligands being localised in the coordination sphere of the complex. Further, the hydroxy groups at C(2) of the carbohydrate residues incorporated into the metal complex displace the ligand with the amino groups at N(3) and N(4) from the coordination sphere (as in the case of formation of the complex **40**) and are coordinated with the central metal atom (the formation of metal complexes by ligand exchange [62]). The reactions with ketoses yield monocarbohydrate complexes **75**;[9,78,79] noteworthy, the coordination involves the primary hydroxy group at C(1) in addition to the secondary hydroxy group at C(1).



73

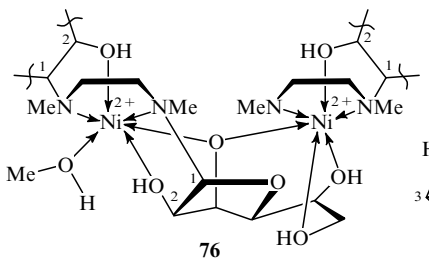


74

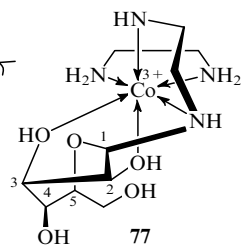


75

Reaction of D-mannose with the Ni(II) – *N*,*N*′-dimethylethylenediamine complex yields compound **76** having unusual bridging structure;[9,80] one of the carbohydrate ligands in this complex assumes a furanose form seldom occurring in carbohydrate metal complexes. The $[Ni(tn)_3]^{2+}$ complex (tn is trimethylenediamine) reacts with aldoses like $[Ni(en)_3]^{2+}$ to yield products analogous to the complex **74**.[9,81] A similar result was obtained in the case of the Ni(II) β-alanine complex.[9,82]



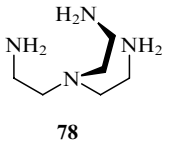
76



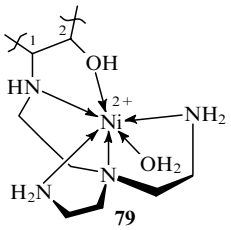
77

Substitution of Co^{3+} for Ni^{2+} significantly changes the mode of coordination of the carbohydrate ligand: the conformation of the six-membered ring of the single carbohydrate ligand in complex **77** is considerably distorted, which facilitates involvement of the hydroxy group at C(3) in the coordination.[9,83,84]

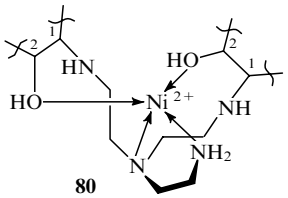
The main principles of the geometry of the metal complexes under discussion are retained in the case of a structurally more complex amino component, *viz*., *N*,*N*-bis(2-aminoethyl)-ethylenediamine (tren) **78**. Thus the reaction with nickel(II) yielded mono- (**79**) (in the case of D-glucose) and biscarbohydrate (**80**) complexes (in the case of D-mannose).[85]



78

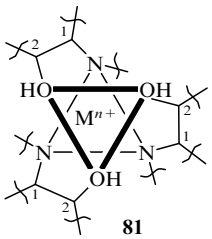


79

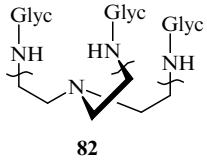


80

Triscarbohydrate complexes **81** with Ni^{2+} (see Refs 9, 85 and 86) and Co^{3+} (see Refs 9, 85 and 87) using *N*-glycosides **82** as ligands could also be synthesised.



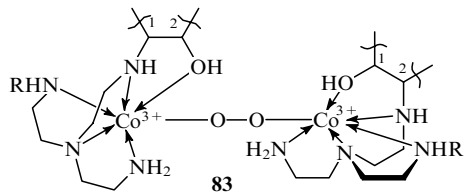
81



82

M = Ni^{2+}, Co^{3+}.

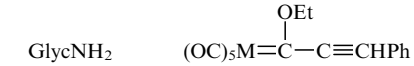
All the metal complexes synthesised are characterised by a specific anomeric configuration (α or β) of the glycosidic imino group, λ- or δ-conformation of the five-membered metallocycles and helical Λ- or Δ-configuration [88] of the chelate point owing to the transfer of chirality from the carbohydrate ligands to the metal centre. Reversible chiral inversion of the Λ-diastereomer into the Δ-diastereomer in complex **81** (M = Co^{3+}) after substitution of the sulfate ion as the counterion for the halide ion has been described for the first time.[87] The synthesis of a bridging double-charged complex **83** based on D-glucose is another step forward.[89]



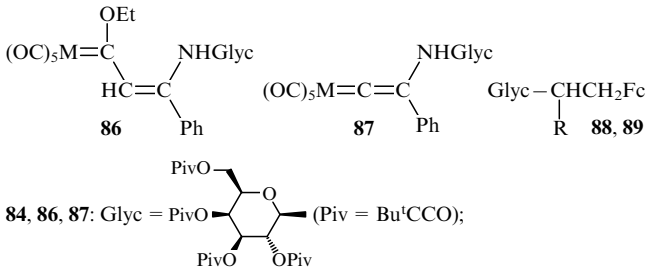
83

R is D-glucose residue.

In a similar scheme (*viz*., by the reaction of a carbohydrate ligand with a metal-containing derivative), starting from *N*-glycoside **84** and alkynylcarbene complexes **85**, a mixture of complexes **86** and **87** (3 : 2) was obtained.[90] Ferrocenyl derivatives **88** and **89** were synthesised analogously.[91]



84 **85**

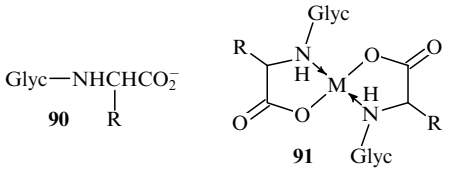


86 **87** **88, 89**

84, 86, 87: Glyc = PivO (Piv = Bu^{t}CCO);

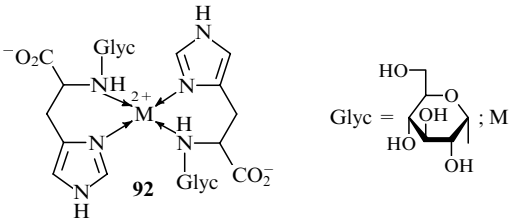
85–87: M = Cr, W; **88, 89**: Glyc is a protected or free monosaccharide; Fc is ferrocenyl; R = H (**88**), CH_2Fc (**89**).

The N,O-coordination of amino acid *N*-glycosides **90** (as salts) is a characteristic of complexes **91** with salts $M^1_2[M^2Cl_4]$ (M^1 = Na, K; M^2 = Pt, Pd).[7,92] *N,N*-Coordination (structure **92**) is observed only in the case of histidine.[7,92]



90 **91**

R = H, Me, CH_2OH, CH(OH)Me, CH_2CONH_2, $(CH_2)_2CO_2Na$.

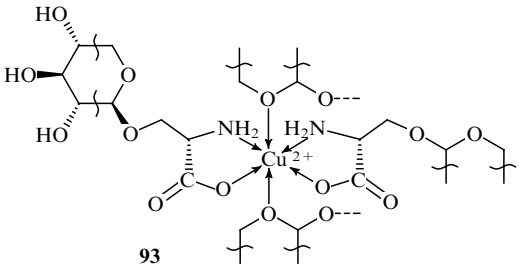


92

Glyc = ; M = Pt, Pd.

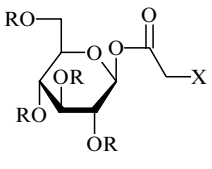
b. Complexes of *O*- and *C*-substituted monosaccharides with nitrogen-containing fragments

The central metal atom in the copper complex **93** of *O*-(β-D-xylopyranosyl)-L-serine is surrounded[93] by four carbohydrate ligands with a distorted octahedral configuration.



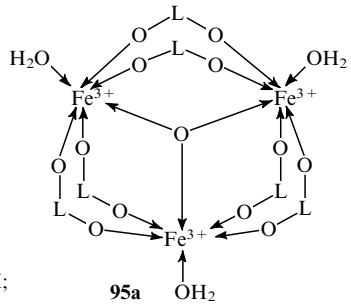
93

The D-glucopyranosyl ester of glycine **94a** and its partially (**94b**) and fully substituted (**94c**) derivatives coordinate Fe(III) exclusively through the oxygen atoms of the carboxy groups to yield complexes **95a–c**,[94] their structures are simpler the larger the number of protective groups.

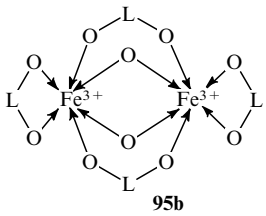


94a–c (O–L–O)

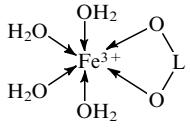
a: R = H, X = $NH_3 \cdot CF_3CO_2H$;
b: R = Ac, X = $NH_3 \cdot CF_3CO_2H$;
c: R = Ac, X = $NHCO_2Bu^t$.



95a

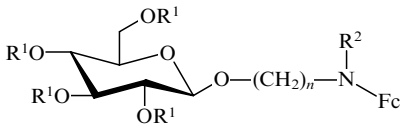


95b



95c

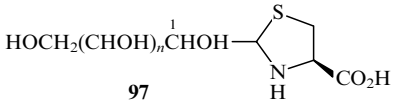
O-Glycoside analogues **96** of the ferrocenyl derivatives **88** and **89** have been prepared.[95]



96

R^1 = H, CH_2Ph; R^2 = Me, CH_2Fc; *n* = 2, 3, 5.

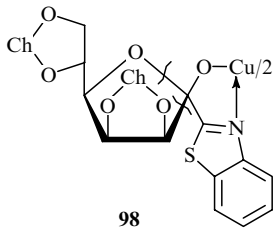
The type of coordination in 2-[poly(hydroxyalkyl)]thiazolidine-4-carboxylic acids **97** depends on the nature of the metal ion.[96–98] The Cr^{2+} cation in complexes ML_2 (L = **97**), as in α-amino acid metal complexes, is coordinated through the imino group and the carboxy group of the heterocyclic fragment.[96] Similar structures are formed with Zn^{2+}, the latter being coordinated at the hydroxy group through the C(2) atom of the carbohydrate residue.[97] The Pd^{2+} cation is coordinated through the nitrogen and sulfur atoms of the heterocyclic fragment [98] (the so-called competitive coordination [62]). It is interesting to note that the stability constants of zinc complexes depend on the chirality of the C(1) atom of the carbohydrate fragment.[97]



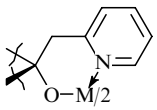
97

n = 2, 3

Metal complexes **98–102** were prepared in high yields using the electrochemical method.[99,100] The copper chelates **98**, **99a** and **101** possess a distorted planar configuration of the chelate point, and other complexes have octahedral structures.[99,100]

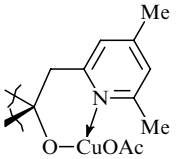


98

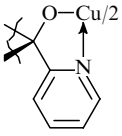


99a–c

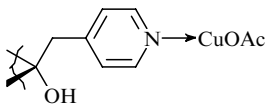
M = Cu (**a**), Ni (**b**), Co (**c**).



100



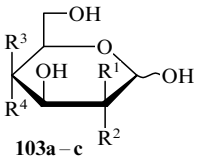
101



102

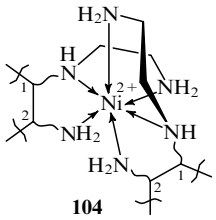
c. Complexes of amino sugars and their derivatives

D-Glucosamine (**103a**), D-mannosamine (**103b**) and D-galactosamine (**103c**) react with $[Ni(en)_3]^{2+}$ to yield complexes **104**[9,101] similar to complexes **74** containing an amino group at C(2) instead of a hydroxy group. Reactions of D-glucosamine **103a** with $[Co(NH_3)_3]^{3+}$, $[Co(en)_3]^{3+}$ and $[Co(phen)_2]^{3+}$ (phen is phenanthroline) yield complexes **105** by a ligand exchange mechanism.[9,102] The use of an alternative workup of the D-glucosamine (**103a**)–$[Co(en)_3]^{3+}$ mixture (see Ref. 103) gave eight monocarbohydrate metal complexes.

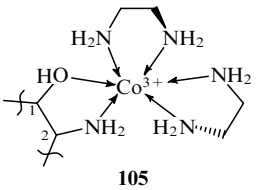


103a–c

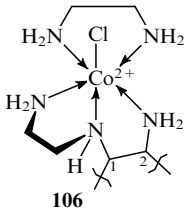
a: $R^1 = R^3 = H$, $R^2 = NH_2$, $R^4 = OH$;
b: $R^1 = NH_2$, $R^2 = R^3 = H$, $R^4 = OH$;
c: $R^1 = R^4 = H$, $R^2 = NH_2$, $R^3 = OH$.



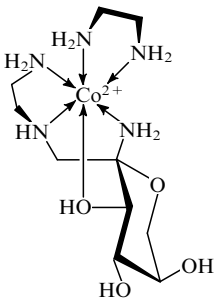
104



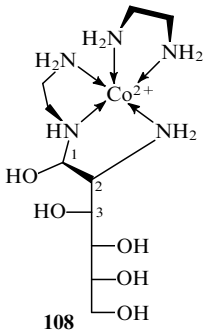
105



106



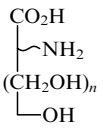
107



108

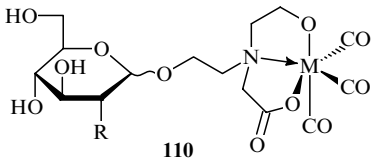
Among the complexes isolated,[103] only compound **106** with a pyranose form of the carbohydrate ligand is a normal product. In the other complexes, D-glucosamine **103a** is transformed into both D-mannosamine **103b** by the Lobry de Bruyn–van Ekenstein rearrangement,[104,105] and D-fructosylamine by the Amadori rearrangement [105] (complex **107**). Complex **108** where D-glucosamine exists in an unusual open aminal form is of most interest. The complexes formed are diastereomerically pure and have a Δ- or Λ-configuration at the chelate point. The study [103] is undoubtedly one of the key studies in the coordination chemistry of carbohydrates, since it demonstrates extreme flexibility of unprotected monosaccharides in complexation with metals.

The oxidation products of the glycosidic hydroxy group of 2-amino sugars, *i.e.*, the carbohydrate α-amino acids **109**, coordinate *d*-metal ions only through the carboxy and amino groups.[106–108] Complexes **110** provide yet another illustrative example of the non-involvement of the carbohydrate fragment in the coordination.[109]



109

$n = 3, 4$.



110

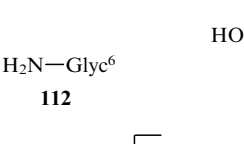
R = H, OH; M = Re, Tc.

Monoamino sugars of the type **103a–c** form complexes **111** with platinum metals.[9,110] The protected amino sugar **112** yields complexes of analogous structures.[9,110] In the case of synthetic vicinal diamino sugars, coordination (*e.g.*, with the formation of the complex **113**) follows the same scheme.[9]

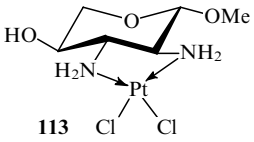
cis-$[MCl_2(H_2NGlyc)_2]$

111

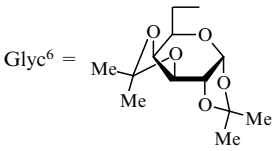
M = Pd, Pt; Glyc is a protected or free monosaccharide.



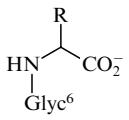
112



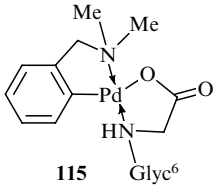
113



The reaction of protected *N*-glycosylaminocarboxylates **114** with platinum metal complexes gives complexes **115–117**.[9,111]

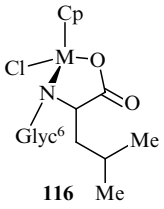


114

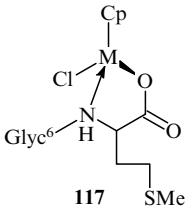


115

R = H, CH_2CHMe_2, CH_2Ph, $(CH_2)_2SMe$.



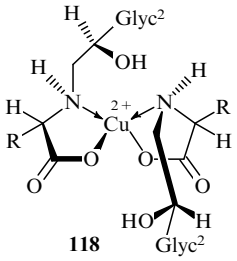
116



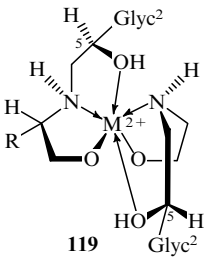
117

M = Rh, Ir.

Complexes of *N*-glycosylaminocarboxylate **50** with Cu^{2+} (**118**) have a square-planar structure, whereas with Co^{2+} and Ni^{2+} ions, octahedron **119** is formed involving the hydroxy groups at the C(5) atom of the carbohydrate fragment.[19,112–115]



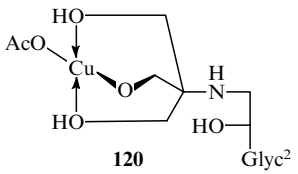
118



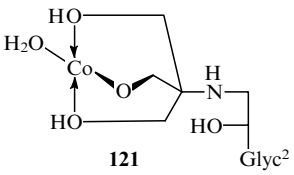
119

M = Ni(II), Co(II).

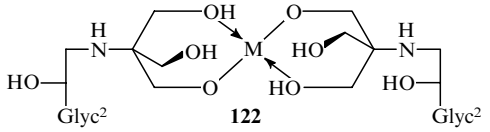
The structures of complexes of a carbohydrate amino derivative **49** with *d*-metal cations depend on the basicity of the medium. In alkaline media, reactions with the corresponding metal acetates yield monocarbohydrate complexes **120** and **121**, while in neutral media, biscarbohydrate complexes **122** are formed.[66]



120



121

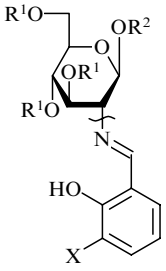


122

M = Cu(II), Ni(II).

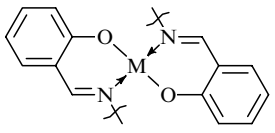
Some papers describe metal complexes of the Schiff bases prepared from natural and synthetic amino sugars. Thus the

Schiff bases **123a**,**b** of both unprotected and protected D-glucosamine form ordinary bischelates **124**,[116–118] while the carboxylic derivative **123c** reacts with Cu(II) to give the binuclear bridging complex **125**.[117] In the case of Pt(II), the coordination involves the nitrogen atoms to yield complex **126**[7] due to the absence of a donor substituent in the *ortho*-position of the aromatic ring (all the hydroxy groups in the carbohydrate fragment are acetylated).



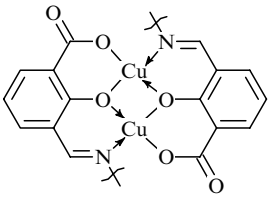
123a–c

a: R^1 = Ac, R^2 = Me, X = H;
b: R^1 = R^2 = X = H;
c: R^1 = Ac, R^2 = Me, X = CO_2H.

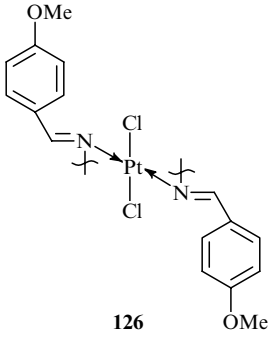


124

M = Cu(II), Zn(II), Co(II) VO^{2+}.

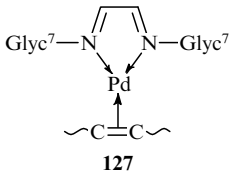


125

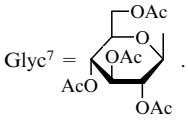


126

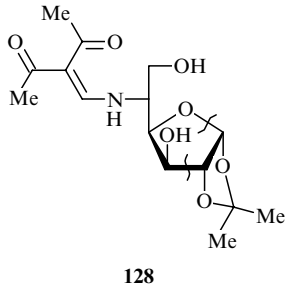
Mixed zero-valent palladium complexes **127** in which the double Schiff base is used as a carbohydrate ligand and dimethyl fumarate, fumarodinitrile and maleic anhydride are used as alkene components, have been synthesised.[119].



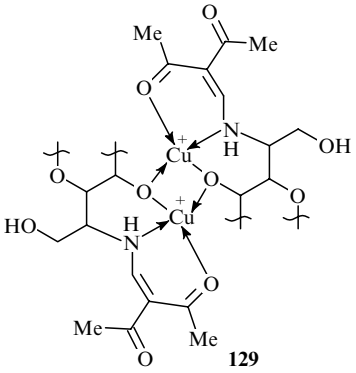
127



The coordination capabilities of amino sugars can be significantly enlarged owing to the introduction of coordinating fragments into the amino group as can be exemplified by the β-oxoenamino derivatives **128**, which form binuclear complexes **129** with copper.[120]

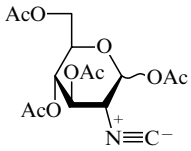


128

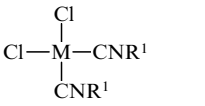


129

The ability of isocyanides, *e.g.*, compound **130** obtained from D-glucosamine, to enter into ligand exchange reactions was successfully employed[121] in the preparation of complexes **131–136** with different structures. Complexes **132** and **134** can add other isocyanides as well as amines and alcohols, *e.g.*, with the formation of complexes **137**.[122]

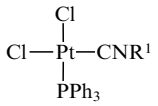


130 (CNR^1)

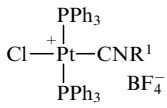


131

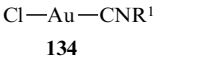
M = Pd, Pt.



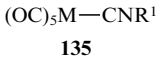
132



133

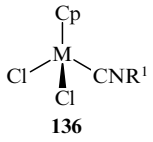


134



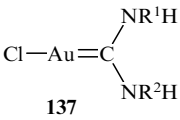
135

M = Cr, W.



136

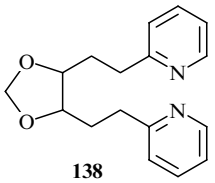
M = Rh, Ir.



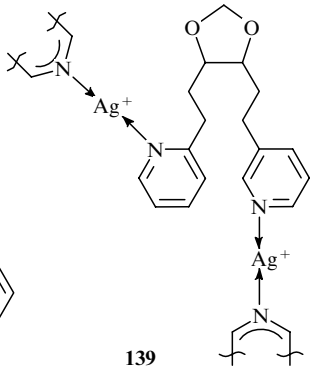
137

R^2 = Bu^t, Ph.

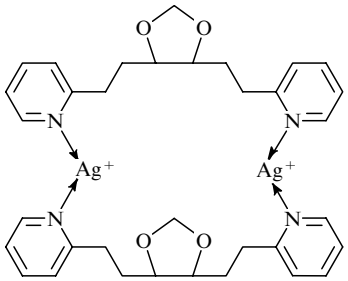
Special mention should be made of a yet another interesting peculiarity of the complexation of the compounds under discussion. The feasibility of a transfer of chirality from a carbohydrate ligand to a metal centre in metal complexes of chemically modified carbohydrates was demonstrated above. A most illustrative example of this phenomenon is the reaction of the diol derivatives **138** (obtained from tartaric acid) with silver triflate,[122] which yields either the polymeric complex **139** in the form of a right- or left-handed helix (supramolecular polymeric complexes, helicates[123]), or, in the case of the *meso*-diol, the cyclic dimer **140**, depending on the chirality of the starting diol.



138



139

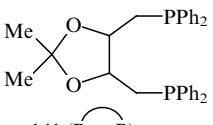


140

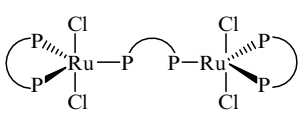
IV. Metal complexes of phosphorus-, sulfur- and selenium-containing monosaccharide derivatives

The discovery by Wilkinson of the ability of chlorotris(triphenylphosphine)rhodium(I) to efficiently catalyse homogeneous hydrogenation of alkenes at room temperature[124] gave a strong impetus to the appearance of a vast number of publications devoted to the molecular design and applications of this type of catalyst including enantioselective ones. This, in turn, generated the need for the synthesis of some organophosphorus carbohydrate derivatives, such as phosphines, phosphinites, phosphites and hydrogen phosphonates and phosphates.

Chiral phosphines DIOP (**141**) are the most popular phosphine ligands used in catalysis; the ruthenium complex DIOP–Ru_2Cl_4[(−)-DIOP]$_3$ has a hypothetical structure **142**.[125,126]

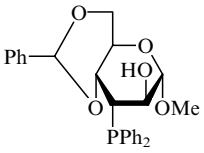


141 (P P)

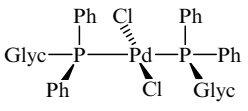


142

The monophosphine ligand **143** reacts with Pd(II) to give complex **144**.[127]

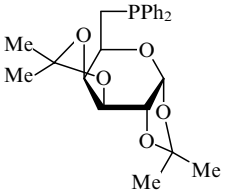


143 ($GlycPPh_2$)

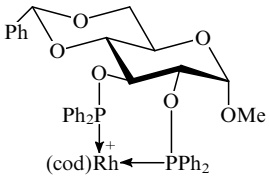


144

A series of $[Rh(cod)(PPh_2Glyc)_2]ClO_4^-$ complexes (cod is cyclooctadiene) have been synthesised from acetalated monosaccharide monophosphine derivatives, *e.g.*, compound **145**.[7]



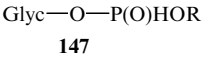
145 ($GlycPPh_2$)



146

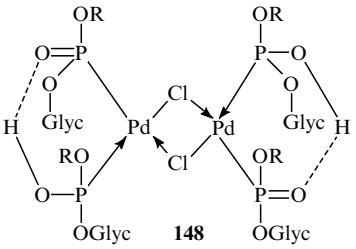
Synthetically more accessible phosphinites react with Rh(III) to yield complexes **146**[3, 128–132] similar to monophosphine complexes of the acetalated ligands **145**.

Many studies by Russian investigators have been devoted to the complexation of carbohydrate phosphites (see, *e.g.*, a review [133]). Thus hydrogen phosphonates derived from acetalated monosaccharides **147** yield palladium complexes **148**.[134–137]



147

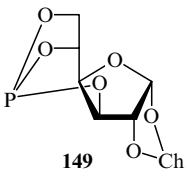
R = Et, Pr, Pr^i;
Glyc is an acetalated monosaccharide residue.



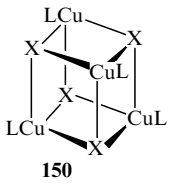
148

Treatment of the readily available phosphite $(Glyc^3O)_3P$ with Cu(CO)Cl gives the tetramer $\{CuCl[P(OGlyc^3)_3]\}_4$ having a cubic structure.[138]

The bicyclophosphite complexes LCuX (L = **149**; X = Br, I),[139–142] with a cubic structure (**150**) in the solid state, have been prepared.[143]

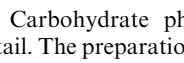


149



150

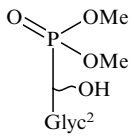
Phosphorodiamidites **151** form complexes $(\eta^3\text{-}C_3H_5)Pd(L)Cl$ and $L_2Rh(CO)Cl$ [144] as well as *trans*-$[PtCl_2L_2]$ (L = **151**).[145] Their structures and the coordination sites of metal ions have not been established.[144, 145]



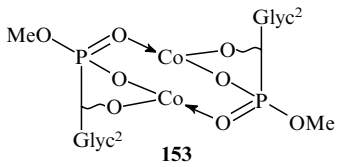
151

Glyc is an acetalated monosaccharide residue.

Carbohydrate phosphates have been investigated in less detail. The preparation of a cobalt complex with the phosphonate **152**[146] having a hypothetical dimeric structure **153** has been reported.

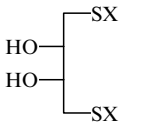


152



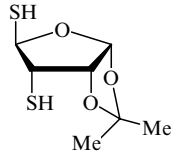
153

Some papers are devoted to sulfur- and selenium-containing monosaccharides, particularly thiolates and selenolates. These compounds are, in principle, soft bases, therefore the complexes of the corresponding carbohydrate derivatives with soft cations, such as Au^+, and platinum metal cations (the principle of hard and soft acids and bases [147]), have been studied first. Thus dithiol **154a** forms a mixed complex **154b** with gold(I).[148] The HS–SH group in the dithiol–rhodium complex **155a** forms a part of the chelate centre (structure **156**).[7] The iridium cation in complex **157** prepared from the thioethers **155b** (R = Me, Pr^i, Ph) is coordinated in a similar way.[7]

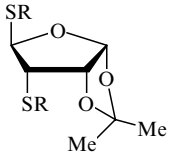


154a,**b**

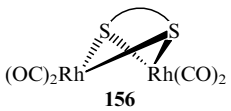
a: X = H
b: X = $AuPEt_3$.



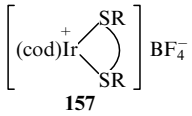
155a (HS SH)



155b (RS SR)

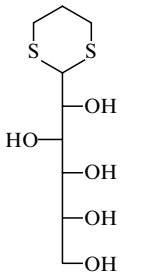


156

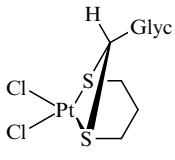


157

The readily available carbohydrate dithianes react smoothly with $K_2[PtCl]_4$; thus compound **158** yields the complex **159**.[7]



158

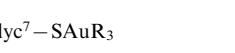


159

A fairly large number of papers are devoted to complexes of acetylated β-D-thioglucose **160**. Gold complexes **161** are used in medicine [149, 150] along with analogous gold complexes containing a deacetylated carbohydrate fragment. Iron, ruthenium, tungsten and platinum complexes **162**–**165** with acetylated thioglucose have been described.[7]

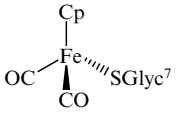


160

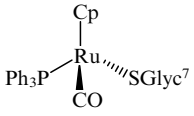


161

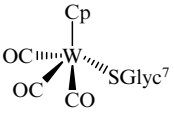
R = Me, Et, Pr^i, Bu.



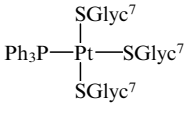
162



163



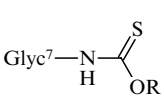
164



165

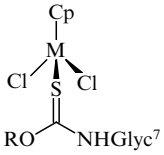
Some complexes of sulfur- and nitrogen-containing carbohydrate ligands have been investigated. Thiocarbamates **166** react

with bridge binuclear platinum complexes to yield complexes **167** – **172**.[7]

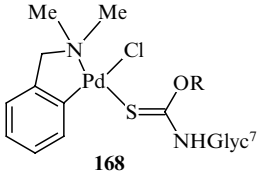


166

R = Me, Et.

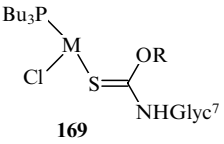


167

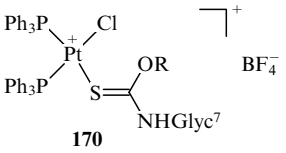


168

M = Rh, Ir.

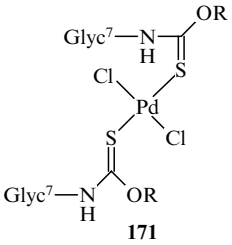


169

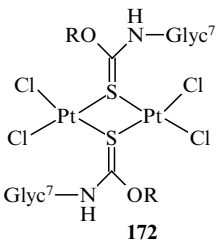


170

M = Pd, Pt.

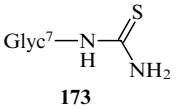


171

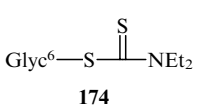


172

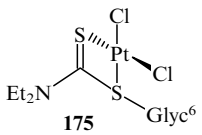
The metal atom in complexes with the thiourea ligand **173** (L) $[M(\eta^5\text{-Cp})Cl_2L]$ (M = Rh, Ir), $[Pd(o\text{-}C_6H_4CH_2NMe_2)ClL]$ and $[MCl_2L_2]$ (M = Pd, Pt) is coordinated through the nitrogen atoms.[7] The ligand **174** containing an *N*,*N*-dithiocarbamoyl fragment forms the complex **175** with bidentate *S*,*S*-coordination.[7]



173

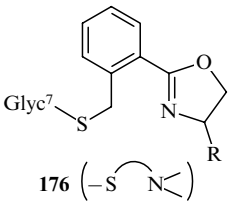


174

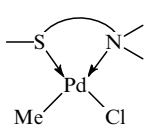


175

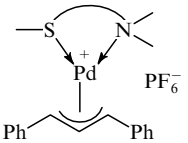
The dihydrooxazole thioglucose derivatives **176** form complexes **177** and **178** with palladium.[7] By virtue of its allylic structure, the latter complex is represented by two diastereomers differing in the position of the central allylic proton relative to the dihydrooxazole substituent R.



176



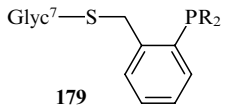
177



178

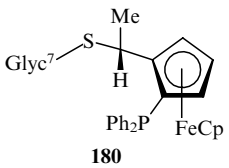
R = Pr^i, Ph.

π-Allylic complexes are also typical of ligands **179** and **180** containing both sulfur and phosphorus. Thus the aryl ligand **179** forms complexes **181**,[7, 151] whereas the ferrocenyl ligand **180** yields the complex **182**.[7, 152] Zero-valent palladium complexes **183** have also been prepared. An analogous derivative of the unsaturated thio sugar **184** coordinates the Rh(II) cation to yield the structure **185**.[7]

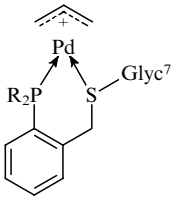


179

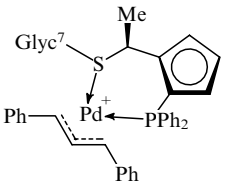
R = Ph, Ch.



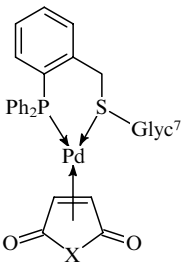
180



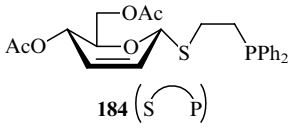
181



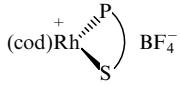
182



183

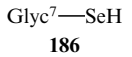


184

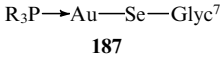


185

Selenium-containing monosaccharides described in the literature are represented only by the selenoglucose derivative **186**, which was used as a source of complexes **187** – **191** having different structures.[7, 153] The latter complex represents a mixture of three diastereomers **191a** – **c**.[153]

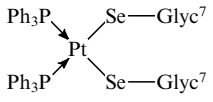


186

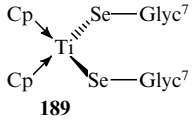


187

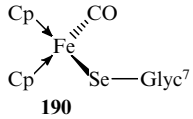
R = Me, Et, Ph.



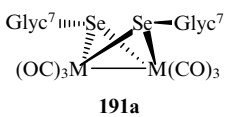
188



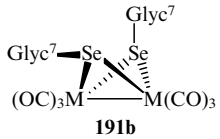
189



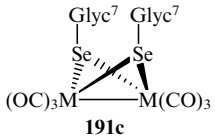
190



191a



191b



191c

M = Fe, Ru.

V. Conclusion

The progress in the coordination chemistry of carbohydrates is favoured by three main factors, *viz*., inexhaustibility of this class of compound due to continuous photosynthetic reproduction, the diastereomeric purity of carbohydrates and the chirality of metal complexes formed from them, which is associated with chirality transfer from the ligands to the metal centres.

Chemical modification of monosaccharides enables one to enhance considerably their coordination capabilities, particularly owing to the diversity of their oxygen donor centres. Moreover, hydrophobisation of starting monosaccharides makes possible the preparation and further utilisation of their metal complexes in non-aqueous media.

Localisation of coordination points of monosaccharide metal complexes localised in close proximity to the ligands often changes their conformation, anomeric configuration and even the nature as a result of molecular rearrangements (see, *e.g*., Ref. 6 and this review). Mention should be made in this connection of the conversion of oximes of the aldehydo-forms of monosaccharides into the corresponding amides in the presence of Cu^{2+} (Beckman rearrangement).[154] Although such rearrangements are still very rare, their number will inevitably increase and, as a consequence, novel methods for the modification of carbohydrates by complexation with metals will be developed. At present, the chemistry of carbohydrates is still imperfect due to the use of accessory reagents, formation of side products, *etc*.[155] In our opinion, progress in this area will be achieved through further development of the coordination chemistry of modified carbohydrates.

References

1. R J Ferrier *Adv. Carbohydr. Chem. Biochem.* **35** 31 (1978)
2. N S Poonia, A V Bajaj *Chem. Rev.* **79** 389 (1979)
3. S J Angyal *Adv. Carbohydr. Chem. Biochem.* **47** 1 (1989)
4. K Burger, L Nagy, in *Biocoordination Chemistry* (Ed. K Burger) (London: Ellis Horwood, 1990) p. 236
5. D M Whitfield, S Stojkovski, B Sarkar *Coord. Chem. Rev.* **122** 171 (1993)
6. Yu E Alekseev, A D Garnovskii, Yu A Zhdanov *Usp. Khim.* **67** 723 (1998) [*Russ. Chem. Rev.* **67** 649 (1998)]
7. D Steinborn, H Junicke *Chem. Rev.* **100** 4283 (2000)
8. Yu E Alexeev, A D Garnovskii, I S Vasilchenko, Yu A Zhdanov *Russ. J. Inorg. Chem.* **46** (Suppl. 3) 235 (2001)
9. S Yano *Coord. Chem. Rev.* **92** 113 (1988)
10. Yu E Alekseev, A D Garnovskii, A S Burlov, Yu A Zhdanov *Ros. Khim. Zh.* **40** (4–5) 155 (1996) [a]
11. Yu E Alekseev, Yu A Zhdanov *Nauchnaya Mysl' Kavkaza. Prilozhenie* (Spetsvypusk) 7 (2001)
12. A H Haines, K C Symes, A G Wells *Carbohydr. Res.* **41** 85 (1975)
13. E P Serebryakov, R I Abylgaziev, E A El'perina, L M Suslova, in *II Vsesoyuznaya Konferentsiya po Khimii Makrotsiklov (Tez. Dokl.), Odessa, 1984* [The IIth All-Union Conference on the Chemistry of Macrocycles (Abstracts of Reports), Odessa, 1984] p. 16
14. W Rasshofer, W M Müller, F Vögtle *Chem. Ber.* **112** 2095 (1979)
15. T P Sudareva, Yu E Alekseev, V A Tyumenev, Yu A Zhdanov, in *VII Vsesoyuznaya Konferentsiya po Khimii i Biokhimii Uglevodov (Tez. Dokl.), Pushchino, 1982* [The VIIth All-Union Conference on the Chemistry and Biochemistry of Carbohydrates (Abstracts of Reports), Pushchino, 1982] p. 133
16. Yu A Zhdanov, Yu E Alexeev, T P Sudareva, V M Kharkovski, in *The 5th European Symposium on Carbohydrates. (Abstracts of Reports), Prague, 1989* A-151
17. Yu A Zhdanov, Yu E Alekseev *Zh. Vses. Khim. O-va im. D I Mendeleeva* **31** 188 (1986) [a]
18. Yu A Zhdanov, Yu E Alekseev, T P Sudareva, V A Tyumenev *Dokl. Akad. Nauk SSSR* **256** 1393 (1982) [b]
19. Yu E Alekseev, Doctoral Thesis in Chemical Science, Rostov State University, Rostov-on-Don, 1995
20. A H Haines, I Hodgkinson, C Smith *J. Chem. Soc., Perkin Trans. 1* 311 (1983)
21. J Jindřich, M Černy, T Truka, M Miloš *Collect. Czech. Chem. Commun.* **56** 2950 (1991)
22. K Suwinska, G D Andeetti *J. Inclus. Phenom.* **1** 71 (1983)
23. P J Dutton, T M Fyles, S R Hausen *J. Inclus. Phenom.* **7** 173 (1989)
24. J A Haslegrave, J F Stoddart, D J Thompson *Tetrahedron Lett.* 2279 (1979)
25. K M Taba, R Köster, W V Dahlhoff *Synthesis* 399 (1984)
26. M I Goguadze, N S Melua, M E Shishniashvili *Izv. Akad. Nauk Gr.SSR, Ser. Khim.* 124 (1983)
27. D N Williams, U Piarulli, C Floriani, A Chiesi-Villa, C Rizzoli *J. Chem. Soc., Dalton Trans.* 1243 (1994)
28. O J Taylor, J L Wardell *J. Chem. Res. S* 98 (1989)
29. R J Cox, S J Garden, R A Howie, O A Melvin, J L Wardell *J. Organomet. Chem.* **516** 213 (1996)
30. K J Hale, L Hough, A C Richardson *Carbohydr. Res.* **177** 259 (1988)
31. S M S V Doidge-Harrison, I W Nowell, P J Cox, R A Howie, O J Taylor, J L Wardell *J. Organomet. Chem.* **401** 273 (1991)
32. L A Burnett, S M S V Doidge-Harrison, S J Garden, R A Howie, O J Taylor, J L Wardell *J. Chem. Soc., Perkin Trans. 1* 1621 (1993)
33. S David, S Hanessian *Tetrahedron* **41** 643 (1985)
34. T B Grindley, R Thangarasa *Can. J. Chem.* **68** 1007 (1990)
35. E Avela *Sucr. Belg.* **92** 337 (1973)
36. K B Sharpless, S F Woodard, M G Finn, in *Selectivity a Goal for Synthetic Efficiency* (Weinheim: Verlag Chemie, 1984) p. 377
37. M G Finn, K B Sharpless, in *Asymmetric Synthesis. Chiral Catalysis* Vol. 5 (Ed. J D Morrison) (Orlando: Academic Press, 1985) p. 247
38. Yu E Raifel'd, A M Vaisman *Usp. Khim.* **60** 241 (1991) [*Russ. Chem. Rev.* **60** 123 (1991)]
39. H Brunner *Synthesis* 645 (1988)
40. B Weidmann, D Seebach *Angew. Chem.* **95** 12 (1983)
41. D Seebach, A K Beck, M Shiess, L Widler, A Wonnacott *Pure Appl. Chem.* **55** 1807 (1983)
42. R Stevenson *Chem. Br.* **37** 24 (2001)
43. P G Potvin, P C C Kwong, M A Brook *J. Chem. Soc., Chem. Commun.* 773 (1988)
44. P G Potvin, R Gau, P C C Kwong, S Bianchet *Can. J. Chem.* **67** 1523 (1989)
45. M G Finn, K B Sharpless *J. Am. Chem. Soc.* **113** 113 (1991)
46. I D Williams, S F Pedersen, K B Sharpless, S J Lippard *J. Am. Chem. Soc.* **106** 6430 (1984)
47. M Riediker, A Hafner, U Piantini, G Rihs, A Togni *Angew. Chem., Int. Ed. Engl.* **28** 499 (1989)
48. M Riediker, R O Duthaler *Angew. Chem., Int. Ed. Engl.* **28** 494 (1989)
49. J Ruiz, C Floriani, A Chiesi-Villa, C Guastini *J. Chem. Soc., Dalton Trans.* 2467 (1991)
50. U Piarulli, D N Williams, C Floriani, G Gervasio, D Viterbo *J. Chem. Soc., Chem. Commun.* 1409 (1994)
51. R Aumann *Chem. Ber.* **125** 2773 (1992)
52. K H Dötz, W Straub, R Ehlenz, K Reseke, R Meisel *Angew. Chem.* **107** 2023 (1995)
53. H Fisher, J Schleu, G Roth *Chem. Ber.* **128** 373 (1995)
54. P DeShong, G A Slough, V Elango *J. Am. Chem. Soc.* **107** 7788 (1985)
55. J Doležal, E Julùková, M Cerný, M Copanica *J. Electroanal. Chem. Interfacial Electrochem.* **52** 261 (1974)
56. G L Trainor, B E Smart *J. Org. Chem.* **48** 2447 (1983)
57. H H Baer, H R Hanna *Carbohydr. Res.* **102** 169 (1982)
58. M B Yunker, B Fraser-Reid *J. Org. Chem.* **44** 2742 (1979)
59. J Kerr, B Robinson, J Simpson, in *Metal-Containing Molecules. The 1st Chianti Electrochemistry Meeting (Abstracts of Reports), Siena, 2000* p. 61
60. J Burger, P Klüferg *Chem. Ber.* **128** 75 (1995)
61. H Junicke, R Kluge, D Steinborn *J. Inorg. Biochem.* **81** 43 (2000)
62. A D Garnovskii, I S Vasil'chenko, D A Garnovskii *Sovremennye Aspekty Sinteza Metallokompleksov* (Modern Aspects of the Synthesis of Metal Complexes) (Rostov-on-Don: LaPO, 2000)
63. Yu A Zhdanov, Yu E Alekseev, T P Sudareva *Dokl. Akad. Nauk SSSR* **284** 354 (1985) [b]
64. Yu A Zhdanov, Yu E Alekseev, T P Sudareva, V G Alekseeva *Zh. Obshch. Khim.* **63** 416 (1993) [c]
65. Yu A Zhdanov, Yu E Alekseev, E L Korol', T P Sudareva *Dokl. Akad. Nauk SSSR* **322** 1097 (1992) [b]
66. Yu A Zhdanov, Yu E Alekseev, E L Korol', T P Sudareva, V G Zaletov *Zh. Obshch. Khim.* **65** 1564 (1995) [c]
67. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii *Dokl. Akad. Nauk SSSR* **291** 872 (1986) [b]
68. Yu A Zhdanov, Yu E Alekseev, V A Kogan, V M Khar'kovskii *Zh. Obshch. Khim.* **59** 1881 (1989) [c]
69. Yu A Zhdanov, Yu E Alekseev, T P Sudareva, V M Khar'kovskii *Zh. Obshch. Khim.* **62** 2587 (1992) [c]
70. V M Khar'kovskii, Yu E Alekseev, V A Kogan, Yu A Zhdanov *Zh. Obshch. Khim.* **60** 1653 (1990) [c]
71. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii, T P Sudareva *Dokl. Akad. Nauk SSSR* **306** 112 (1989) [c]
72. D S Lawrence, T Jiang, M Levett *Chem. Rev.* **95** 2229 (1995)
73. S K Tirumala, J T Davis *J. Am. Chem. Soc.* **119** 2769 (1997)
74. J T Davis, S K Tirumala, A L Marlow *J. Am. Chem. Soc.* **119** 5271 (1997)
75. P Bako, L Fenichel, L Toke, B E Davison *J. Chem. Soc., Perkin Trans. 1* 2514 (1989)
76. Yu A Zhdanov, Yu E Alekseev, E L Korol', T P Sudareva, V G Alekseeva *Zh. Obshch. Khim.* **63** 1495 (1993) [c]
77. T Tanase, K Mano, Y Yamamoto *Inorg. Chem.* **32** 3995 (1993)
78. S Takizawa, H Sugita, S Yano, S Yoshikawa *J. Am. Chem. Soc.* **102** 7969 (1980)
79. T Tsubomura, S Yano, S Yoshikawa, K Toriumi, T Ido *Polyhedron* **2** 123 (1983)
80. T Tanase, K Kurihara, S Yano, K Kobayashi, T Sakurai, S Yoshikawa, M Hidai *Inorg. Chem.* **26** 3134 (1987)
81. H Shioi, S Yano, K Toriumi, T Ito, S Yoshikawa *J. Chem. Soc., Chem. Commun.* 201 (1983)
82. T Tsubomura, S Yano, S Yoshikawa *Inorg. Chem.* **25** 392 (1986)
83. K Ishida, S Yano, S Yoshikawa *Inorg. Chem.* **25** 3552 (1986)
84. K Ishida, S Nonoyama, T Hirano, S Yano, M Hidai, S Yoshikawa *J. Am. Chem. Soc.* **111** 1599 (1989)
85. B Gyurcsik, L Nagy *Coord. Chem. Rev.* **203** 81 (2000)
86. T Tanase, M Doi, R Nouchi, M Kato, Y Sato, K Ishida, K Kobayashi, T Sakurai, Y Yamamoto, S Yano *Inorg. Chem.* **35** 4848 (1996)

doi> 87. S Yano, M Nakagoshi, A Teratani, M Kato, T Onako, M Sida, T Tanase, Y Yamamoto, H Ueburo, Y Ohashi *Inorg. Chem.* **36** 4187 (1997)
88. C J Hawkins *Absolute Configuration of Metal Complexes* (New York: Wiley-Interscience, 1971)
doi> 89. T Tanase, T Onaka, M Nakagoshi, I Kinoshita, K Shibata, M Doe, J Fujii, S Yano *Inorg. Chem.* **38** 3150 (1999)
90. R Aumann *Chem. Ber.* **127** 725 (1994)
doi> 91. J L Kerr, J S Landells, D S Larsen, B H Robinson, J Simpson *J. Chem. Soc., Dalton Trans.* 1411 (2000)
92. J Chen, Th Pill, W Beck *Z. Naturforsch., B: Chem. Sci.* **44** 459 (1989)
93. L J T Deblaere, M Highan, B Kamenar, P W Kent, S K Prout *Biochem. Biophys. Acta* **286** 441 (1972)
doi> 94. M Tonković, Š Horvat, J Horvat, S Musić, O Hadžija *Polyhedron* **9** 2895 (1990)
doi> 95. J S Landells, J L Kerr, D S Larsen, B H Robinson, J Simpson *J. Chem. Soc., Dalton Trans.* 1403 (2000)
96. J Chen, Th Pill, W Beck *Z. Naturforsch., B: Chem. Sci.* **45** 404 (1990)
97. T Gajda, L Nagy, K Burger *J. Chem. Soc., Dalton Trans.* 3155 (1990)
98. T Gajda, L Nagy, N Rozlosnik, L Korecz *J. Chem. Soc., Dalton Trans.* 475 (1992)
99. Yu A Zhdanov, O A Osipov, N M Gontmakher, V P Grigor'ev, A D Garnovskii, O N Nechaeva, N N Bogdashev, Yu E Alekseev, V G Alekseeva, T A Yusman *Dokl. Akad. Nauk SSSR* **227** 882 (1976) [b]
100. Yu A Zhdanov, O A Osipov, V P Grigor'ev, A D Garnovskii, Yu E Alekseev, N M Gontmakher, V G Alekseeva, T A Yusman, V G Zaletov, N N Bogdashev, O N Nechaeva *Koord. Khim.* **3** 3 (1977) [d]
101. S Yano, Y Sakai, K Toriumi, T Ito, H Ito, S Yoshikawa *Inorg. Chem.* **24** 498 (1985)
doi> 102. S Bunel, C Ibarra, E Morada, V Calvo, A Blasko, C A Bunton *Carbohydr. Res.* **239** 185 (1993)
103. J M Harrowfield, M Mocerino, B W Skelton, W Y Wei, A H White *J. Chem. Soc., Dalton Trans.* 783 (1995)
104. J C Speck Jr *Carbohydr. Chem.* **13** 63 (1958)
105. N K Kochetkov, A F Bochkov, B A Dmitriev, A I Usov, O S Chizhov, V N Shibaev *Khimiya Uglevodov* (The Chemistry of Carbohydrates) (Moscow: Khimiya, 1967)
106. A Gergely, P Szarvas, I Korondun *Acta Chim. Hung.* **26** 313 (1961)
107. M Miyazaki, T Senshu, Z Tamura *Chem. Pharm. Bull.* **14** 114 (1966)
doi> 108. M A Diaz-Diez, F J Garcia-Barros, F J Higes-Rolando, A Bernalte-Garcia, C Valenzuela-Calahorro *Polyhedron* **12** 2519 (1993)
doi> 109. J Petrig, R Schibli, C Dumas, R Alberto, P A Schubiger *Chem. Eur. J.* **7** 1968 (2001)
110. G Thiel, W Z Beck *Z. Naturforsh., B: Chem. Sci.* **38** 1081 (1983)
111. Y Zhou, B Wagner, K Polborn, K Sunkel, W Beck *Z. Naturforsh., B: Chem. Sci.* **49** 1193 (1994)
112. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii, in *V Vsesoyuznoe Soveshchanie po Khimii Nevodnykh Rastvorov Neorganicheskikh i Kompleksnykh Soedinenii (Tez. Dokl.), Rostov-na-Donu, 1987* [The Vth All-Union Meeting on the Chemistry of Nonaqueous Solutions of Inorganic and Complex Compounds (Abstracts of Reports), Rostov-on-Don, 1987] p. 39
113. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii, V G Zaletov, A G Starikov *Dokl. Akad. Nauk SSSR* **312** 115 (1990) [b]
114. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii, V G Zaletov, A G Starikov *Zh. Neorg. Khim.* **36** 914 (1991) [e]
115. Yu A Zhdanov, V A Kogan, Yu E Alekseev, V M Khar'kovskii, in *V Vsesoyuznoe Soveshchanie po Khimii Nevodnykh Rastvorov Neorganicheskikh i Kompleksnykh Soedinenii (Tez. Dokl.), Rostov-na-Donu, 1987* [The Vth All-Union Meeting on the Chemistry of Nonaqueous Solutions of Inorganic and Complex Compounds (Abstracts of Reports), Rostov-on-Don, 1987] p. 196
116. M J Adam, L D Hall *J. Chem. Soc., Chem. Commun.* 234 (1979)
117. M J Adam, L D Hall *Can. J. Chem.* **60** 2229 (1982)
118. A P Toropova, M M Ishankhodzhaeva, N A Parpiev *Issledovanie Kompleksoobrazovaniya Cu(II), Ni(II) i VO(II) s Shiffovym Osnovaniem na Osnove Glyukozamina* [Investigation of Complexation of Cu(II), Ni(II) and VO(II) with Schiff's Base Derived from Glucosamine]; article deposited in the GF NTI GKNT RUz No. 2227-Uz94 (Tashkent, 1994); *Ref. Zh. Khim.* 6 V 57 DEP (1995)
doi> 119. C Borriello, M L Ferrara, I Orabona, A Panunzi, F Ruffo *J. Chem. Soc., Dalton Trans.* 2545 (2000)
doi> 120. R Wegner, M Gottschaldt, H Görls, E-G Jager, D Klemm *Angew. Chem., Int. Ed.* **39** 595 (2000)
121. Th Pill, K Polborn, W Beck *Chem. Ber.* **123** 11 (1990)
122. T Suzuki, H Kotsuki, K Isobe, N Moriya, Y Nakaguwa, M Ochi *Inorg. Chem.* **34** 530 (1995)
123. J-M Lehn *Supramolecular Chemistry. Concepts and Perspectives* (Weinheim: VCH, 1995)
124. J A Osborn, F H Jardine, J F Young, G Wilkinson *J. Chem. Soc. A* 1711 (1966)
125. B R James, D K W Wang, R F Voigt *J. Chem. Soc., Chem. Commun.* 574 (1975)
doi> 126. K Ohkubo, I Terada, K Sugahara, K Yoshinaga *J. Mol. Catal.* **7** 421 (1980)
127. J-C Shi, D-X Wu, T-B Weng, M-C Hong, Q-T Liu, B-S Kang, S-J Lu, H-Q Wang *J. Chem. Soc., Dalton Trans.* 2911 (1996)
128. D Sinou, G Descotes *React. Kinet. Catal. Lett.* **14** 463 (1980)
doi> 129. R Selke, C Fackiam, H Foken, H Heller *Tetrahedron: Asymmetry* **4** 369 (1993)
doi> 130. R Selke *J. Organomet. Chem.* **370** 241 (1989)
doi> 131. R Selke *J. Organomet. Chem.* **370** 249 (1989)
132. A Kumar, G Oehme, J P Roque, M Schwarze *Angew. Chem.* **106** 2272 (1994)
133. K N Gavrilov, I S Mikhel' *Koord. Khim.* **25** 83 (1999) [d]
doi> 134. E E Nifant'ev, T S Kukhareva, M Yu Antipin, Yu T Struchkov, E I Klabunovsky *Tetrahedron* **39** 797 (1983)
135. E E Nifant'ev, T S Kukhareva, M P Koroteev, E I Klabunovskii, V A Pavlov *Dokl. Akad. Nauk SSSR* **253** 1389 (1980) [b]
136. E E Nifant'ev, T S Kukhareva, L S Gorshkova, V A Pavlov, E I Klabunovskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 1915 (1979) [f]
137. E E Nifant'ev, T S Kukhareva *Zh. Obshch. Khim.* **49** 757 (1979) [c]
doi> 138. M Stolmar, C Florian, G Gervasio, D Viterba *J. Chem. Soc., Dalton Trans.* 1119 (1997)
139. E E Nifant'ev, M P Koroteev, A A Zharkov *Zh. Obshch. Khim.* **54** 1663 (1984) [c]
140. E E Nifant'ev, M P Koroteev, S A Rumyantseva, A M Il'inets, N K Kochetkov *Zh. Obshch. Khim.* **60** 345 (1990) [c]
141. E E Nifant'ev, A T Teleshev, M P Koroteev *Zh. Obshch. Khim.* **53** 1640 (1983)
142. M P Koroteev, E E Nifant'ev *Zh. Obshch. Khim.* **63** 481 (1993) [c]
143. E E Nifant'ev, M P Koroteev, A M Koroteev, M Yu Antipin, K A Lysenko, V K Bel'skii, L Tsao *Dokl. Akad. Nauk* **353** 508 (1997) [b]
144. E E Nifant'ev, A T Teleshev, M P Koroteev, S A Ermishkina, E M Abbasov *Koord. Khim.* **7** 311 (1981) [d]
145. E E Nifant'ev, E V Chechegoeva, V M Zhelyaev *Dokl. Akad. Nauk SSSR* **287** 874 (1986) [b]
146. Yu A Zhdanov, G K Kist'yan, A A Shvets *Zh. Obshch. Khim.* **63** 945 (1993) [c]
147. A D Garnovskii, A P Sadimenko, O A Osipov, G V Tsintsadze *Zhestko-Myagkie Vzaimodeistviya v Koordinatsionnoi Khimii* (Hard–Soft Interactions in Coordination Chemistry) (Rostov-on-Don: Rostov State University, 1986)
doi> 148. G Stocco, F Gattuso, A A Isab, C F Shaw III *Inorg. Chim. Acta* **209** 129 (1993)
149. B M Sutton, in *Platinum, Gold, and Other Metal Chemotheurapetic Agents (ACS Symposium Series)* Vol. 209 (Washington, DC: American Chemical Society, 1987) p. 355
150. *Koordinatsionnye Soedineniya Metallov v Meditsine* (Metal Coordination Compounds in Medicine) (Kiev: Naukova Dumka, 1986) p. 110
doi> 151. P Barbaro, A Currao, J Herrmann, R Nesper, P S Pregosin, R Salzmann *Organometallics* **15** 1879 (1996)
doi> 152. A Albinati, P S Pregosin, K Wick *Organometallics* **15** 2419 (1996)
153. T Pill, W Breu, H Wagner, W Beck *Chem. Ber.* **124** 713 (1991)
154. Yu A Zhdanov, Yu E Alekseev, T P Sudareva *Dokl. Akad. Nauk SSSR* **283** 580 (1978) [b]
doi> 155. P K Klüfers, T Kunte *Angew. Chem., Int. Ed.* **40** 4210 (2001)

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[d] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[e] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[f] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*