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COMPLEX FORMATION BETWEEN PALLADIUM(II) AND AMINO ACIDS, PEPTIDES AND RELATED LIGANDS

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CONTENTS

A. INTRODUCTION

Interest in the study of reactions of the Pd(II) ion with amino acids, peptides and other ligands of biological importance began with the discovery of Rosenberg et al. that certain platinum complexes exhibit carcinostatic activity [1]. The difficulty in studying the platinum complexes directly is their kinetic inertness and due to the similarities in the general chemistry of Pt(II) and Pd(II), as well as the increased rates of reaction of Pd(II) ions (on average approximately 10^3 times faster than platinum), palladium analogues are studied instead of, or as well as, the platinum compounds. There is also a more general interest in the reactions of second and third row transition metals with ligands where there is a choice of 'soft' (b class) donor atoms and, in the case of palladium, possible deviations from the usual square planar geometry.

Difficulties are encountered in the study of aqueous solutions of $[Pd(H_2O)_4]^{2+}$ due to its slow hydrolysis in solutions of $pH > 1$ to give insoluble oxo-compounds of uncertain stoichiometry [2]. As a result, water-soluble complex ions of palladium are often used in stability constant experiments, e.g. $[PdCl_4]^{2-}$ or $[Pd(en)\ (H_2O)]^{2+}$. As a result, calculated constants are often conditional constants appropriate to ligand exchange reactions in which the exchanged ligand is not water.

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B. COMPLEX FORMATION WITH AMINO ACIDS

(i) Complex formation with S-containing amino acids

The largest volume of work on the preparation of complexes of palladium with amino acids has been performed using ligands containing sulphur atoms, in addition to the nitrogen and oxygen donor centres. These systems are of interest due to the preference of palladium for co-ordination by 'soft' donors.

The interaction of the Pd(II) ion with disulphides, thioethers and sulphur containing amino acids was used by Akerfeldt and Løvgren to determine the ligands quantitatively by spectroscopic methods [3]. McAuliffe [4] studied the IR spectra of $[PdCl_2Met]$, where $Met = CH_3S(CH_2)_2CH(NH_2)CO_2^-$, and suggested that coordination to the metal occurred through both the amino and thioether groups, the carboxylic acid being involved in intermolecular hydrogen bonding giving rise to a polymeric structure. The narrowness of the –OH out-of-plane deformation band and the insolubility of the material implied a non-planar structure. X-ray crystallographic studies have shown that the methionine does indeed co-ordinate in a bidentate fashion through S and N giving an approximately square planar configuration around the Pd atom, and that the molecules are associated as dimers, the unionised carboxyl group of one methionine being hydrogen bonded to the carboxyl group of an adjacent molecule [5,6].

More recently, Chernova et al. [7] prepared several complexes of palladium with methionine corresponding to the formulae: $[Pd(MetH)_2]Cl_2$, $[PdMet_2]$, $[Pd(MetH)Cl_2]$, $[PdMet(H_2O)]Br$, $[PdMet(H_2O)]Cl$ and $[Pd(NH_3)(MetH)_2]Cl_2$, and determined the co-ordination sites from the IR spectra. The complexes show a variety of structures: $[PdMetHCl_2]$ has an unionised carboxyl group with co-ordination through N and S as described previously [4–6], $[Pd(MetH)_2Cl_2]$ shows bands consistent with both ionised and unionised carboxyl groups, $[PdMet_2]$ shows the carboxyl to be ionised but not co-ordinated while $[PdMet(H_2O)]Cl$ gives no bands for the Pd–Cl stretch and the remainder of the spectrum indicates that the methionine is terdentate and that the structure is most probably polymeric. In $[Pd(NH_3)_2(MetH)_2]Cl_2$ co-ordination occurs only through the sulphur atom, the rest of the methionine molecule being in the zwitterionic form. The conductivities of the compounds were also measured. They show high values which were attributed to the acidic properties of inner sphere methionine. A more detailed investigation of conductivities was also undertaken and the dissociation constants determined [8]. The calculated values are consistent with the ionisation of bound methionine carboxyl groups and the hydrolysis of the inner sphere water molecules.

Vicol et al. [9] synthesised seven different complexes of Pd(II) with methionine and characterised them by analysis, thermogravimetry and UV and IR spectroscopy. Starting from the well known compound $[Pd(MetH)Cl_2]$, the platinum analogue of which was first prepared by Volstein [10], they prepared $[Pd(NH_3)MetCl]$, $[PdMetCl]_2$, $[Pd(Met)_2]Cl_2$, $[Pd(NH_3)_2Met]_2[PdCl_4]$, $[Pd(NH_3)_2(MetH)][PdCl_4]$, $[Pd(NH_3)_2(MetH)_2]Cl_2$, and $[Pd(NH_3)_2(MetH)_2][PdCl_4]$. All showed characteristics of square planar, d^8 ions in the spectra, but with variations in the metal–ligand bonding. For example, $[Pd(NH_3)MetCl]$ had sulphur–Pd bonds and an ionised COO^- group co-ordinated to the metal with the amino group free, $[Pd(NH_3)_2MetH][PdCl_4]$ had S and N co-ordination to Pd and an unionised COOH group, whereas $[Pd(NH_3)_2(MetH)_2]Cl_2$ had bonding to the metal through the sulphurs only with the methionine in the zwitterionic form as in ref. 7. Thermogravimetric analysis indicated the formation of intermediates containing sulphur and chloride bridges. The structure of [Pd(DL-ethionine)Cl_2] has been determined [11]. Values for the bond lengths and angles are not significantly different from those observed in the methionine complex [5,6].

S-Me-L-cysteine differs from methionine by having one less methylene group. Livingstone and Nolan prepared the complexes of this ligand and of ethionine with many transition metal ions including palladium and platinum [12]. The Pd complexes were of the type $[MLHX_2]$ where X = Cl or Br, and LH is S-Me-L-CysH. The complexes were isolated as the mono-hydrates, the presence of water being confirmed by the strong OH stretch in the infrared spectra. The IR spectra also showed a metal–sulphur stretching frequency (found only in the complexes of Pt and Pd) in the 385–378 nm region as well as the expected $\delta(NH_2)$ mode, indicating that the amino acid acts as a bidentate ligand, chelating via both S and N. The occurrence of $\nu_{as}(COO)$) at high frequency suggests that the carboxyl group is neither co-ordinated to the metal nor H-bonded. McAuliffe isolated both $[(PdL_2)(PdCl_4)]$ and $[Pd_3(HL)_2Cl_6]$ where L = S-Me-L-Cys [13,14]. This latter complex was shown to contain co-ordinated NH_2 groups, with bands at 3200 cm^{-1} for $\nu(NH_2)$ and 1573 cm^{-1} for $\delta(NH_2)$. A band at 1725 cm^{-1} ($\nu_{as}(COO)$) shows the presence of free, non-H-bonded carboxyl groups. Also, ν(Pd–S) appears at 385 cm^{-1} and ν(Pd–Cl) at 330 cm^{-1}. The most probable structure is shown

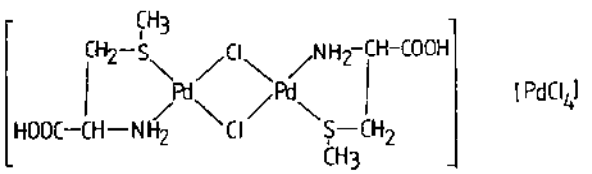

Fig. 1. The most probable structure of $[Pd_3(HL)_2Cl_6]$ where L = S-Me-L-Cys.

in Fig. 1. This is also supported by visible reflectance spectra and conductivity measurements.

The crystal structure of $[Pd(S\text{-}Me\text{-}L\text{-}Cys)Cl_2]H_2O$, determined by Battaglia et al. [15], shows that S-Me-L-Cys behaves as a bidentate ligand coordinating through both S and N forming a five-membered chelate ring. Co-ordination around Pd is distorted square planar, similar to $[Pd(Met)Cl_2]$ [6]. The structure has two crystallographically independent Pd atoms with similar inner co-ordination spheres but differences in the next nearest neighbours, giving rise to S–Pd–Pd chains. The interactions of Pd(II) with S-Me-L-cysteine have been studied using proton NMR methods by Jezowska-Trzebiatowska et al. at molar ratios of 1 : 1 and 1 : 2 [16]. From the chemical shift of the CH_2 protons it appears that sulphur is co-ordinated to the metal at all measured pH values and that the carboxylate group is a competitive co-ordination site to the N group over the pH range from 3 to 10. At higher pH the N group becomes more important. More recently the same group have concluded that the carboxylate remains unco-ordinated in any major species formed in solution using ^{13}C NMR and IR methods [17].

Chandrasekharan et al. described the preparation and characterisation of cysteine complexes of palladium and platinum [18]. From the IR spectra they deduced that cysteine co-ordinates through the sulphur and oxygen atoms, with the amino group protonated. Co-ordination around the metal is square planar and the possibility of isomerism exists in these complexes, although the isomers were not isolated. The same group also prepared ethyl cysteinate complexes of Pd and Pt of formula $[Pd(H_{-1}L)_2]$ where $L = HSCH_2CH(NH_2)COOC_2H_5$ [19]. These were diamagnetic and square planar with ν_{SH} and δ_{SH} absent in the IR, indicating that sulphur was co-ordinated. The value for the NH-stretch suggested that nitrogen was also co-ordinated.

Levason and McAuliffe prepared complexes of nickel, palladium and rhodium with L-cysteine [20]. Two palladium complexes were isolated corresponding to $[Pd_2(CysH)_3Cl]\cdot 2H_2O$ and [Pd(CysH)Cl]. The IR spectra of both these compounds showed unionised carboxyl groups, suggesting that sulphur and nitrogen act as donors. In $[Pd_2(CysH)_3Cl]\cdot 2H_2O$ a band at 279 cm^{-1} was assigned to a bridging cysteine ligand. The [Pd(CysH)Cl] complex is probably dimeric, as a Pd–Cl–Pd linkage was identified by ν(Pd–Cl) at 276 cm^{-1}. The structure was thought to be analogous to that assigned to $[Pd(penH)Cl]_2$, where penH is penicillamine, as shown in Fig. 2 [21].

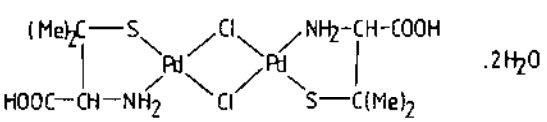

Fig. 2. Probable structure of $[Pd(penicillamine)Cl]_2$.

Pneumatikakis and Hajilidis prepared complexes of cysteine and cysteine methyl ester with Pd(II) and Pt(II), from $K_2[PdCl_4]$ and $PdCl_2$ at ratios of 1 : 1 and 1 : 2 (M : L) [22]. From the IR spectra the co-ordination sites were shown to depend on the molar ratio and the pH, similar to the previous work. Proton NMR measurements on compounds of palladium with L-cysteine indicate that co-ordination occurs through sulphur and nitrogen donors in both 1 : 1 and 1 : 2 complexes [16]. Zegzhda et al. prepared complexes of Pd with cysteine and measured the acid dissociation constants of –SH groups of co-ordinated cysteine [23]. For both *cis*- and *trans*-$[Pd(HCys)_2]$ they found values of $K_1 = 5.6 \times 10^{-7}$ and $K_2 = 5.1 \times 10^{-8}$, indicating that co-ordination to the metal was through nitrogen and oxygen.

Complexes formed by Pd(II) with L-cystine have been studied by NMR techniques to determine whether there was any interaction between the metal and the disulphide bridge, as occurs commonly in proteins [24]. In this case sulphur was the main site of co-ordination and there was no –S–S– bridge breaking on metal co-ordination. At high pH the disulphide group acts as a linkage between Pd(II) ions to give a polymeric structure. Similarly, CD measurements have shown no insertion of Pd(II) into the S–S bridge in complexes with insulin and cystine, only a conformational modification. Hydroxyl complexes were reported at high pH [25].

(ii) Complex formation with other amino acids

Complexes formed between Pd(II) and non-sulphur containing amino acids have not been studied in any systematic way. Wilson and Martin recorded the CD spectra of complexes of L-amino acids with Pd(II) and of mixed complexes with glycine, as well as some dipeptide complexes [26,27]. The absorption maxima of the spectra were consistent with 2 nitrogen and 2 oxygen donor atoms around the metal, when ligands were *N*-methyl-alanine, -valine and -glutamic acid, with a molar ratio (M : L) of 1 : 2, and for mixed complexes of metal, glycine and *N*-methyl amino acid at 1 : 1 : 1. From CD spectra it was shown that palladium forms similar complexes with amino acids as do copper and nickel, i.e. chelated 1 : 2 complexes [26]. With lysine, a potentially tridentate ligand, attempts to neutralise the ϵ-ammonium group gave precipitates in the presence of Pd(II). At low pH the ligand was bidentate.

Measurements were also made to determine the ring size at which transition occurs from N,O donors to N,N donors in tetragonal Pd(II) complexes, using 2,3-diaminopropionate and 2,3-diaminobutyrate, ornithine and lysine [26]. These ligands may co-ordinate through α-amino and COO^- groups giving five-membered chelate rings or through two nitrogen donors giving 5-, 6-, 7- or 8-membered rings respectively. With palladium and ornithine the

change-over occurs when there are equal concentrations of 5- and 7-membered rings, the larger ring being competitive with the 5-membered ring as a result of the preference of Pd(II) for nitrogen rather than oxygen donors.

Histidine (His) is in itself an interesting ligand, having four potential donor centres: COO^-, NH_2 and two imidazole nitrogens. Chernova et al. have prepared several bis-histidine–Pd(II) complexes [28]. All were found to be square planar, co-ordination being through amino nitrogen in all cases, and through the imidazole nitrogen when the ligand was bidentate. No evidence for co-ordination via COO^- was found, neither was any evidence given for the ionisation of the pyrrole-type nitrogen.

The complex $[Pd(en)(His)]^+$ was also studied by CD spectroscopy together with several analogous compounds [29]. The co-ordination number around the metal ion was four and the ionisation which occurred with $pK_a = 10.83$ was shown to be due to the unbound pyrrole nitrogen of the imidazole ring. Addition of 0.5 equivalents of $[Pd(en)Cl_2]$ to 1 equivalent of $[Pd(en)(His)]^+$ and 1 equivalent of NaOH, resulted in the formation of a trinuclear complex with four nitrogen donors around each palladium. The spectrum of this solution was independent of pH suggesting that the hydrogens of the pyrrole nitrogens were readily displaced by Pd(II).

Crystal structures have been determined for several amino acid–Pd(II) complexes. The structure of $[Pd(II)(Pro)_2]$ (Pro = prolinate) consists of discrete molecules with square planar co-ordination around the palladium [30]. The two prolinate ions were *cis* to each other. Jarzab et al. determined the structures of $[Pd(II)\ (L\text{-}Tyr)_2] \cdot \frac{1}{2}H_2O$ and $[Pd(II)(L\text{-}Val)_2] \cdot H_2O$, and found

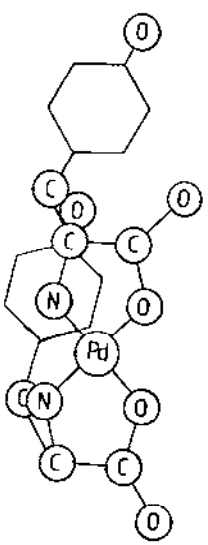

Fig. 3. Possible apical co-ordination of the tyrosine ring.

them both to be *cis*-isomers [31,32]. Sabat et al. [33] investigated apical co-ordination of the tyrosine ring to Pd by X-ray diffraction and found that the Pd–C interatomic distances between one tyrosine ring and the metal indicated direct interaction between the aromatic side chain and the metal ion and the possible interactions between the second aromatic ring and an adjacent Pd(II) ion, as shown in Fig. 3. The structure of [Pd(L-Ser)$_2$] (Ser = serinate) has also been studied [34].

Ornithine, $H_2N(CH_2)_2CH(NH_2)COOH$, has three potential donor sites but acts as a bidentate ligand towards Pd(II). Wilson and Martin concluded that equal amounts of 5- and 7-membered rings were formed in solution [26]. Nakayama et al. solved the structure of the [Pd(L-Orn)$_2$] complex and found two 7-membered rings as shown in Fig. 4 [35]. The Pd(II) was four co-ordinate towards nitrogen atoms in the usual square planar arrangements with both chelate rings in twisted-chair conformations.

Chernova et al. described the preparation and properties of complexes of Pd(II) with alanine and phenylalanine of formulae [PdL$_2$] and $K_2[PdL_2X_2]$ where X = halide [36] and of alanine and tyrosine where the acid dissociation constants of co-ordinated water in the complexes $[PdL(H_2O)_2]$ and $[PdL(H_2O)Cl]$ were measured [8].

An IR study of transition metal chelates of DL-isovaline was undertaken by Boudreau and Hooper [37] to show the variation in bond strengths of metal–N and metal–O bonds. Palladium showed stronger bonding to both N and O than did copper, nickel and cobalt, and bonds with a similar strength to those from platinum.

Crystal structures of several complexes of Pd(II) with glycine and chloride ligands have been determined [38–40]. [Pd(*cis*-Gly)$_2$]·$3H_2O$ is distorted square planar around Pd (2N and 2O) but nearest neighbouring oxygen atoms make an elongated octahedron around the metal ion [38].

Nakamoto recorded many IR spectra of aqueous solutions of metal chelates of amino acids and included one palladium-containing compound [41]. Measurements of the IR spectrum of anhydrous, solid *trans*-[Pd(Gly)$_2$] have carboxyl stretching frequencies of $\nu(COO)_{as} = 1642$ cm^{-1} and

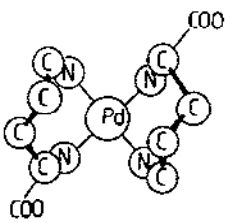

Fig. 4. Structure of the [Pd(L-Orn)$_2$] complex.

$\nu(COO)_{sym} = 1373\ cm^{-1}$, consistent with bonded COO^- groups. More unusual modes of co-ordination have been described [42]. $K[PdL_3] \cdot 2H_2O$ where L = glycinate was prepared, and its IR spectrum indicated a dimer. Addition of $AgNO_3$ at pH 6 gave $Ag_2[Pd_2L_6]$ whereas at pH 7 $Ag[PdL_3]$ was formed with two L^- ions monodentate and the third bidentate. $K_2[Pd_2L_6]$ was converted to *cis*-$[PdL_2]$ on addition of H^+ [43].

Sullivan recorded the CD spectra in both solution and the solid state of well characterised complexes of palladium and platinum with amino acids and peptides [44] as well as diammines [45]. The CD spectra of Pd(II) with amino acid amides were recorded by Komorita et al. [46–48] and of diammines by Ito et al. [49]. Several planar *cis*-(amino acid amide) complexes of Ni(II) and Pd(II) were prepared and characterised spectroscopically [46]. These all showed 4N co-ordination around the metal, palladium producing both *cis* and *trans* complexes with L-alanyl- and L-leucyl-amides while Ni gave only *trans* complexes. Similar square planar complexes were formed with L-valyl-, L-phenylalanyl- and L-prolyl-amides [48]. In the phenylalanylamide complex no apical co-ordination of the aromatic ring to the metal was found.

A polarographic technique for the quantitative determination of palladium using amino acid complexes has been reported [50]. Using an L : M ratio of 100 : 1 Kalapurna apparently produced the $[Pd(Gly)_3]^-$ species; unusually for palladium this would seem to be 6-co-ordinate as in the case of nickel. However further confirmation of the more common square planar configuration around Pd(II) came from the electronic spectra of mixed chelate compounds with α-amino acids [51].

Several ternary α-amino acid complexes of Pd(II) were prepared by Odani and Yamauchi, with histidine as one of the ligands [52]. Anomalies in the *d–d* region of the CD spectra were attributed to intramolecular ligand–ligand interactions between the unco-ordinated histidine carboxylate and the side chain of the second amino acid. While such hydrogen bonding would be expected to be weak in aqueous solutions, it was suggested that a similar mechanism could be invoked for transport of Cu(II) across bio-membranes via the ternary complex Cu(L-His)(L-amino acid) where the amino acids were asparagine, glutamine or threonine.

(iii) Stability constants of amino acid complexes with Pd(II)

As mentioned earlier, the determination of formation constants of Pd(II) systems is made more difficult than in the case of other metals as a result of the unstable nature of the Pd^{2+} aquo ion in aqueous solutions. This has led to the use of complex ions, especially $[PdCl_4]^{2-}$, as the metal ion source. The inclusion of extra species involving Cl^- ions as ligands as well as the

amino acid in the calculation of formation constants then becomes necessary. Values reported in the literature are given in Tables 1 and 2.

Maley and Mellor [53] attempted to calculate log K_1 and log K_2 values for palladium complexes with glycine from potentiometric titrations but did not take $[PdCl_x]^{(2-x)}$, [PdCl(Gly)] or similar species into the calculations. Similarly, Farooq et al. [54] calculated the overall formation constant, K_S, where

$$K_S = [MA_2]/[M][A^-]^2 \text{ using } [M] = [MCl_4]^{2-}$$

TABLE 1

Literature values for stability constants of complexes with palladium(II)

(i) Amino acids

Ref.	Ligand	Pd(II) Source	Background	T (°C)	log K_1	log K_2	log β_2
53	Glycine	$K_2[PdCl_4]$			9.12	8.43	17.55
54	Glycine	$Na_2[PdCl_4]$		27			17.50
55	Glycine	$Na_2[PdCl_4]$	1 M($NaClO_4$)	20	15.25	12.25	27.50
60	Aspartic acid	$PdCl_2$	0.1 M($NaClO_4$)	25	10.44	7.70	18.14
59	Aspartic acid		0.1 M(KNO_3)	30	10.55	7.7	18.25
61	Aspartic acid	$K_2[PdCl_4]$	0.1 M(KCl)	25		11.3	
54	Asparagine	$Na_2[PdCl_4]$		27			15.12
63	Asparagine	$Pd(ClO_4)_2$	3 M($NaClO_4$)	25			[a]
62	Asparagine	$PdCl_2$	0.1 M($NaClO_4$)	25	9.15	8.50	17.65
60	Glutamic acid	$PdCl_2$	0.1 M($NaClO_4$)	25	10.38	7.46	17.84
61	Glutamic acid	$Na_2[PdCl_4]$	0.1 M?	25		10.00	
62	Glutamine	$PdCl_2$	0.1 M($NaClO_4$)	25	9.10	8.35	17.45
61	HAADP [b]	$[PdCl_4]^{2-}$	0.1 M(KCl)	25		10.5	
61	HAPIM [b]	$[PdCl_4]^{2-}$	0.1 M(KCl)	25		11.5	
54	D/L-alanine	$Na_2[PdCl_4]$	?	27			18.12
54	D/L-serine	$Na_2[PdCl_4]$		27			16.84
54	D/L-valine	$Na_2[PdCl_4]$		27			17.52
54	L-leucine	$Na_2[PdCl_4]$		27			18.20
54	L-proline	$Na_2[PdCl_4]$		27			15.70
54	D/L-methionine	$Na_2[PdCl_4]$		27			17.00
54	Taurine	$Na_2[PdCl_4]$		27			13.40

(ii) Dicarboxylic acids (at 30 °C and I = 0.1 M (KNO_3) [59])

Ligand	pK_1	pK_2	pK_3	pK_4	log K_1
EDDS [c]	3.25	4.0	8.5	9.4	13.6
EDG [c]	3.75	4.85	8.93	9.75	13.4

[a] $\log \beta_{1101} = 12.11$, $\log \beta_{110\text{-}1} = 9.1$, $\log \beta_{1111} = 18.29$, $\log \beta_{111\text{-}1} = 17.0$.

[b] HAADP = 2-aminohexanedioic acid, HAPIM = 2-aminoheptanedioic acid.

[c] EDDS = *N*,*N*′-ethylenediaminedisuccinic acid; EDG = *N*,*N*′-ethylenediamine(bis-α-glutamic acid).

for many different amino acids (A^-). The value for glycine was in good agreement with that of Maley. Anderegg and Malik have calculated values for log K_1 for the Pd(II)–glycine system by ligand exchange and by spectroscopic methods [55]. These values (Table 1) are much greater than in the two preceding cases since they refer to equilibria involving only aquo ions. The difference between log β_2 for the two sets of complexes is around 10 log units which is in reasonable agreement with log β_4 for $[PdCl_4]^{2-}$ determined by Elding [56] and Hancock and Evers [57,58] although there are differences in temperature and ionic medium. Farooq et al. have also calculated values of log K_S for several different amino acids, using Albert's method [54]. Results are given in Table 1. Due to the random selection of amino acids studied, little can he deduced from the values.

Sunar and Trevedi [59] calculated both formation constants and proton dissociation constants for complexes of palladium with aspartic acid, as well as with *N*, *N'*-ethylenediaminedisuccinic acid and *N*, *N'*-ethylenediamine (bis-α-glutamic acid). Values for log K_1 and log K_2 are in good agreement with those calculated by Singh and Srivastava where the palladium is initially present as $PdCl_2$ [60]. More recently Frye and Williams [61] have

TABLE 2

Complex formation between $[Pd(en)(H_2O)_2]^{2+}$ and amino acids at 25 °C

Ligand	log K_1	pK_a	Background	Ref.
Glycyl-glycine	9.60(3) [a]	3.76(1) [a]	0.1 M(KNO_3)	70
Glycineamide	8.64(2)	2.47(1)		70
L-Asparagine	10.46(1)	6.46(1)	0.5 M(KNO_3)	71
L-Glutamine	10.76(1)	9.03(2)		71
Glycine	11.21(1)			72
L-Alanine	11.22(1)			72
Sarcosine	11.28(1)			72
N,*N*-dimethylglycine	11.02(1)			72
L-Leucine	11.41(1)			72
L-Phenylalanine	10.86(1)			72
L-Proline	12.16(3)			72
L-Tryptophan	10.83(3)			72
S-Me-L-Cysteine	9.38(1), log $K_1^H = 1.18(1)$			72
L-Methionine	9.14(3), log $K_1^H = 0.74(2)$			72
Ethanolamine	7.88(2)	5.16(2)	0.1 M(KNO_3)	73
L-Serine	11.01(1)	8.51(1)		73
L-Threonine	10.96(1)	8.05(1)		73
L-Homoserine	11.09(2)	9.60(2)		73
L-Hydroxyproline	11.47(2)	10.82(2)		73

[a] Values in parentheses are quoted errors on last decimal place.

measured the ionisation and stability constants of Pd(II) and Pt(II) complexes of α-aminodicarboxylic acids, including aspartic and glutamic acids. These values are not consistent with those found by Singh and Srivastava [60] or by Sunar and Trevedi [59] (see Table 1); however the background, temperatures and method of calculation differed.

Tewari and Srivastava have reported the stability constants of Pd(II) complexes with glutamine and asparagine [62]. These are in reasonable agreement with other calculated values for glycine [53,54], glutamic acid [60] and aspartic acid [59,60], and can be assumed to represent the formation of a bis-chelate via the α-amino and carboxyl groups since, at the pH of the measurements (pH 2–5), it is unlikely that the amide nitrogen would be deprotonated and co-ordinated. Similarly, no account was taken of any chloride ion complexation to the metal in these calculations. More recently, and with the help of computers, Graham and Williams have studied potentiometrically the complexes formed between palladium (and nickel), asparagine (asn) and chloride ions [63]. Glass electrodes were used to follow pH and silver/silver chloride electrodes to monitor free chloride ion concentration. The complexes reported were: $[Pd(asn)H]^{2+}$, $[Pd(asn)OH]$, $[Pd(asn)ClOH]^{-}$, and $[Pd(asn)ClH]^{+}$ with $\log \beta$ values of 12.11, 9.1, 17.0 and 18.29 respectively. It seems likely that the co-ordination around the metal is square planar in all cases although no direct assignment of donor atoms could be made. The complexes formed by nickel(II)/asn/Cl have different stoichiometries and this was explained by the preference of palladium for planar bonding while nickel readily accepts octahedral geometry and therefore form a $[Ni(asn)_2ClOH]$ chelate.

Anderegg and Malik [55] have also studied the equilibria in solutions of palladium(II) with iminodiacetic acid (IDA) and diaminoethanetetraacetic acid (EDTA) and its higher homologues, as well as exchange equilibria occurring in the presence of a second ligand such as halide or thiocyanate ion. The calculated values for the IDA–Pd complex were $\log K_1 = 17.5$, $\log K_2 = 9.3$ ($T = 20\,^{\circ}C$ and $\mu = 1$ M ($NaBr/NaClO_4$)). The authors suggested that comparison of these values with those calculated by Castillo-Mastos and Gonzalez-Vilchez [64,65] are "not meaningful as the latter were obtained by inadequate means" [55]. Castillo-Mastos calculated values of $\log K_1 = 9.62$ and $\log K_2 = 5.25$ using $PdCl_2$ in HCl solution and did not take into account additional parasitic complexes with Cl^{-} ions, although they agree that the constants reported are only "conditional".

Anderegg and Malik also measured the stability of the palladium complex with EDTA and obtained the value $\log K_1 = 24.5$ (20 °C, 1 M NaBr [55]). They commented that the value calculated by MacNevin and Kriege [66] ($\log K_1 = 18.5$) was obtained from EMF measurements using a non-reversible palladium electrode, and also discounted the value of Briscoe and

Humphries [67]. These values show that palladium forms one of the most stable EDTA complexes among divalent transition metals (e.g. for Cu(II) $\log K_1 = 18.8$ and for Ni(II), $\log K_1 = 18.6$). More recently Kragten has calculated $\log K_1$ as 26.4 from replacement experiments with thorium [68].

Complexes of palladium with diaminoethane are well known. Rasmussen and Jorgensen have calculated $\log K_2$ for $[Pd(en)_2]^{2+}$ as 18.4 and estimated $\log K_1$ as being greater than 20 [2]. This is one of the largest formation constants for a diaminoethane complex with a divalent metal. Khurtova et al. [69] have prepared Pd(II) complexes of diaminoethane and a ternary complex with EDTA, and measured stability constants ($\log K_1 = 15.36$, $\log K_2 = 14.64$, various ionic strengths, $T = 22\,^{\circ}C$). They mention that calculated constants show some disagreement.

Lim has used the complex $[Pd(en)(H_2O)_2]^{2+}$ to determine formation constants with amino acids and similar ligands [70–73]. His results are summarised in Table 2. The calculated constants show good mutual agreement and variations found can be explained by differences in co-ordination centre, overall charge, and ring size, consistent with similar changes found with other divalent metal complexes. They are also compatible with the results of Anderegg and Malik for glycine [55] (e.g. $\log K_2$ (i.e. $[Pd(Gly)]^+ + Gly \rightarrow [Pd(Gly)_2]$) = 12.25). For $[Pd(en)]^{2+} + Gly \rightarrow [Pd(en)Gly]^+$ Lim quotes $\log K = 11.2$ (different conditions). The pK_a values for the deprotonation of the amide nitrogen in the case of glycyl-glycine and glycinamide [70] (3.76 and 2.47 respectively) were in good agreement with that found by Wilson and Martin [26,27] (3.5 log units).

Co-ordination of L-asparagine and L-glutamine is assumed to be initially via amine and carboxyl donors, the amide becoming deprotonated and co-ordinated at high pH [68]. The difference in pK_a for these complexes reflects the difference between a 6- and 7-membered chelate ring, the seven membered ring being less stable, although Wilson and Martin showed that a 7-membered ring with 2 N donors was competitive with a 5-membered N and O ring in the ornithine complex [26].

The $\log K_1$ values for $[Pd(en)(Met)]^+$ and $[Pd(en)(Me\text{-}Cys)^+]$ are consistent with the bonding envisaged for sulphur-containing amino acids by Warren et al. [6] and Livingstone and Nolan [12], i.e. through the amine N and sulphur with the carboxyl group still protonated.

The possibility of co-ordination of substituted alcohol groups to palladium has also been investigated. All the ligands used show a deprotonation consistent with displacement of carboxylate groups and co-ordination by alkoxide, a situation also found with Cu^{2+} complexes except in the case of hydroxyproline where co-ordination of the alkoxide to the same metal ion as the amine group is sterically unfavourable (ref. 73 and references therein).

C. COMPLEX FORMATION WITH DI- AND TRIPEPTIDES

Palladium has been shown to be an effective ion for inducing peptide hydrogen ionisations to form chelated complexes with di- and tripeptides [26,27]. With neutral tripeptides Pd(II) promotes ionisations of one $-NH_3^+$ and two peptide nitrogens to give a planar complex at neutral pH with 3 N and one carbonyl oxygen donor. With dipeptides the fourth co-ordination site around the metal is assumed to be Cl^- or H_2O. Titrations show that OH^- is not a ligand until above pH 8. The pK_a value for Pd(II) induced deprotonations of peptide nitrogens is about 3.5. This value is 2, 5 and 7 pK_a units less than for Cu(II), Ni(II) and Co(II) respectively. CD spectra indicate that in dipeptides containing amino acids with acidic side chains, e.g. glutamic acid, there is no co-ordination from the side chain COO^- to the palladium ion.

Tetramer formation has been shown to occur in Pd(II) complexes of glycyl-L-histidine, L-alanyl-L-histidine and L-alanyl-D-histidine with Cu(II), Ni(II) and Pd(II) [74]. Complex formation occurs through ionisation of the peptide nitrogens to give 3 N donor atoms around each metal ion. At pH around 9.6 a further proton is ionised and the vis–UV spectra show pronounced blue shifts due to co-ordination of the pyrrole nitrogen and resulting tetramer formation. Pitner et al. measured CD spectra for several tripeptide complexes of Pd(II) [29]. They show replacement of the carboxylate group on the Pd by OH^- at $pK = 11.7$. The complex with glycyl-L-alaninamide was shown to have 4 Pd–N bonds. Complex formation by glycyl-L-histidine was also studied by Kozłowski and Matczak-Jon, using NMR techniques [75]. Since the pH was kept between 4 and 9.5 no pyrrole N ionisation and co-ordination was observed.

Nance prepared several dipeptide complexes of Pd(II) and Pt(II), and characterised them by IR, NMR and CD studies [76]. Nance et al. [77] used CD, ^1H NMR and electronic absorption spectroscopy to determine Pd(II) co-ordination in dipeptide complexes and the changes that might occur as the pH was raised from 1 to 13. They showed that at pH < 1 dipeptides were not co-ordinated to Pd(II), and at pH 13 carboxylate was replaced by OH^- in the co-ordination sphere, in agreement with Pitner et al. [29].

Several ^1H NMR conformational studies have been performed on dipeptide and tripeptide complexes of Pd(II), usually to determine the position of aromatic side chains. Kozlowski used PMR to determine the co-ordination in 1 : 1 and 1 : 2 complexes of Pd(II) with glycyl-L-aspartic acid and showed that in the 1 : 1 complex the amino N and α-carboxyl O were co-ordinated, and the α-carboxyl group held a pseudo-axial position, while in the 1 : 2 complex only nitrogen atoms were co-ordinated [75,78]. Similarly, in complexes of glycyl-L-tyrosine the aromatic ring in the most stable

conformation is over the complex plane, suggesting again weak interaction with the metal ion when the ligand is tridentate [79]. When the ligand become bidentate at high pH the conformation changes and the metal–aromatic ring interaction is broken. This was also shown to be the case for glycyl-L-phenylalanine, L-phenylalanyl-glycine [80], L-alanyl-L-tyrosine, D-leucyl-tyrosine [81] and L-tyrosyl-glycyl-glycine and glycyl-L-leucyl-L-tyrosine [82], where the ligands are terdentate at low pH and tridentate at pH > 10. Both 1 : 1 and 1 : 2 complexes with dipeptides were described.

Vestues and Martin used *vicinal* proton coupling constants to determine rotamer populations in complexes of Pd(II) and Ni(II) with amino acids and peptides, containing both aromatic and aliphatic side chains [83]. They found that for aromatic side chains (e.g. phenylalanine and tyrosine) and aliphatic (e.g. isoleucine and valine) conformations which disposed the side chains to a position over the metal were favoured. They discounted stacking of aromatic rings as a factor in this, as well as hydrophobic interactions, and mentioned that attractive interactions between metal ion and aliphatic side chains are not popular. The final possibility is that side chains prefer space over a metal to interaction with solvent.

Kozlowski and Siatecki used NMR methods to determine the co-ordination of L-alanyl-L-serine to palladium and copper ions [84]. They showed that, in 1 : 1 complexes, as the carboxylate group becomes non-co-ordinating at pH 13, serine hydroxyl becomes deprotonated and forms the third co-ordination site in both metal complexes. In 1 : 2 complexes the co-ordination is through four nitrogens as expected. Spectroscopic methods (EPR, NMR, visible) were employed to ascertain whether Cu(II) or Pd(II) could co-ordinate to a substituted peptide nitrogen atom in di- and tripeptides with proline as the carboxylate terminal residue [85]. No co-ordination to the prolyl nitrogen was found but other complexes formed were as in previous examples.

Several different complexes were found when Pd(II) interacts with methionine-containing dipeptides due to the extra co-ordination site afforded by the thioether sulphur [86]. For Pd(II)–glycyl-L-methionine at a ratio of 1 : 2 and pH 13, two complexes exist in equilibrium, both having amino $-NH_2$ and amide N^- co-ordinated, the difference being due to S co-ordination. In 1 : 1 ratio solutions the complex with a co-ordinated SCH_3 group is very stable and exists over the wide pH range of 3–13. In dipeptides with N-terminal methionine at low pH and a 1 : 1 M : L ratio, complexes have co-ordinated thioether and methionyl-NH_2 groups. At pH 7 the peptide nitrogen is deprotonated and co-ordinates to the Pd(II) ion the sulphur becoming co-ordinated to the next palladium ion, forming a dimer. This explains why the deprotonation of the peptide nitrogen occurs at a higher pH than in the previous cases. In [Pd–Met–X] complexes (X = another

residue) at a ratio of 1:2 and at low pH, sulphur and amino N are co-ordinated while at higher pH four nitrogens become co-ordinated to the metal. In contrast to Cu(II), Pd(II) does not seem to co-ordinate the deprotonated –OH group in threonine residues in 1:2 complexes.

More recently a study of the complexation of Pd(II) with S-containing dipeptides has been reported [87]. NMR and CD spectroscopic measurements of Pd(II) complexes of glycyl-S-Me-L-cysteine, S-Me-L-cysteinyl-glycine and S-Me-L-Cys-S-Me-L-Cys, show that the S-Me-L-cysteinyl residue binds through both N and S, as in the case of the amino acid. However, co-ordination of the thioether sulphur to the metal centre creates a chiral centre on the sulphur leading to the formation of two diastereoisomers, which are observed in solution. There are larger conformational changes between complexed and uncomplexed S-Me-L-Cys residues. There is also a strong S–Pd(II) charge transfer band observed in the UV region of the CD spectra.

Glutathione, L-glutamyl-L-cysteinyl-glycine, has a large variety of possible donor atoms. Chow et al. prepared a solid complex of formula: $[Pd(GluH_2)Cl] \cdot 3H_2O$ where $GluH_3^+ = {}^+NH_3(COO^-)CHCH_2CH_2CONHCH(CH_2SH)CONHCH_2COOH$ [88]. The IR spectrum of this compound showed free COOH and ν(Pd–Cl) in a region suitable for a Pd–Cl–Pd bridge, with ν(S–H) missing, implying S co-ordination. The suggested structure is a dimer with two bridging chlorides and a five-membered ring from S to the peptide nitrogen (between glutamyl and cysteinyl residues as shown in Fig. 5) in preference to a similar six-membered ring between S and the cysteinyl-glycine peptide N. Zegzhda et al. prepared two complexes of glutathione with palladium of formulae $[PdCl_2(GluH)]^{2+}$ and $[PdCl_2(GluH)_2]^+$ and measured their stability and acid dissociation constants [23]. More recently, Zegzhda and Zegzhda have followed the complex formation of palladium with glutathione by potentiometry [89]. The initial

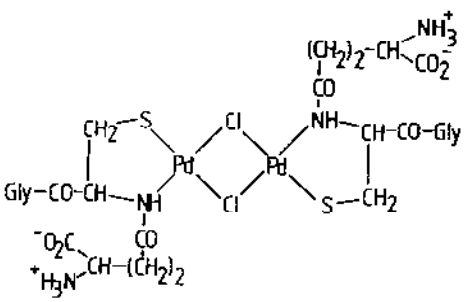

Fig. 5. Suggested structure of $[Pd(GluH_2)Cl]_2$ where $GluH_3^+ = {}^+NH_3(COO^-)CHCH_2CH_2CONHCH(CH_2SH)CONHCH_2COOH$ [88].

palladium source was $[PdCl_4]^{2-}$ and they calculated formation constants for the reactions

$$[PdCl_4]^{2-} + HGlu^{2-} \rightarrow [Pd(GluH)Cl_{4-n}]^{n-4} + nCl^-$$

where $K = 1.2 \pm 0.2 \times 10^9$ and

$$[PdCl_4]^{2-} + H_2Glu^- \rightarrow [Pd(GluH_2)Cl_{4-n}]^{3-n} + nCl^-$$

where $K - 3.3 \pm 0.1 \times 10^2$. Co-ordination sites were not reported.

$[Pd(NH_3)_2(GluH_2)_2][PdCl_4]$ was also isolated and studied by IR spectroscopy. The spectrum showed no S–H bond indicating Pd–S bond formation but the other co-ordination sites could not be identified clearly. NMR and absorption spectroscopy were used to study the Pd(II) glutathione system [90]. Palladium was shown to interact differently to copper, nickel or cobalt. In the glutathione: Pd 1 : 1 system a seven-membered ring is formed between the amino N and the deprotonated nitrogen of the first peptide bond. This is not found in complexes of other metals. Only after the co-ordination of the peptide nitrogen does the sulphur become associated with the metal. Co-ordination sites were determined by the "average environment" rule since the NMR spectra were unresolved. A possible structure for the 2 : 1 complex was also suggested, with strong Pd–S bonds.

REFERENCES

1 B. Rosenberg, L. Van Camp, J.E. Trosko and V.H. Mansour, Nature (London), 222 (1969) 385.
2 L. Rasmussen and C.K. Jorgensen, Acta Chem. Scand., 22 (1968) 2313.
3 S. Äkerfeldt and G. Løvgren, Anal. Biochem., 8 (1964) 223.
4 C.A. McAuliffe, J. Chem. Soc. A, (1967) 641.
5 N.C. Stephenson, J.F. McConnell and R.C. Warren, Inorg. Nucl. Chem. Lett., 3 (1967) 553.
6 R.C. Warren, J.F. McConnell and N.C. Stephenson, Acta Crystallogr., Sect. B, 26 (1970) 1402.
7 N.N. Chernova, I.G. Kurskii and V.V. Strukov, Russ. J. Inorg. Chem., 23 (1978) 239.
8 N.N. Chernova and I.G. Kurskii, Russ. J. Inorg. Chem., 23 (1978) 561.
9 O. Vicol, N. Hurduc and I.A. Scheider, J. Inorg. Nucl. Chem., 41 (1979) 309.
10 L.M. Volstein and M.F. Mogilevkina, Russ. J. Inorg. Chem., 8 (1963) 304.
11 F. Bigoli, E. Leporati and M.A. Pellinghelli, Acta Crystallogr., Sect. B, 35 (1979) 1465.
12 S.E. Livingstone and J.D. Nolan, Inorg. Chem., 7 (1968) 1447.
13 C.A. McAuliffe and S.G. Murray, Inorg. Chim. Acta Rev., (1972) 103.
14 C.A. McAuliffe, Inorg. Chem., 12 (1973) 1699.
15 L.D. Battaglia, A.B. Corradi, C.G. Palmieri, M. Nardelli and M.E.V. Tani, Acta Crystallogr., Sect. B, 29 (1973) 762.
16 B. Jezowska-Trzebiatowska, A. Allain and H. Kozlowski, Bull. Acad. Pol. Sci., 25 (1977) 971.
17 B. Jezowska-Trzebiatowska, A. Allain and H. Kozlowski, Inorg. Nucl. Chem. Lett., 15 (1979) 279.

18 M. Chandrasekharan, M.R. Udapa and G. Aravamudan, Inorg. Chim. Acta, 7 (1973) 88.
19 M. Chandrasekharan, M.R. Udapa and G. Aravamudan, J. Inorg. Nucl. Chem., 36 (1974) 1417.
20 W. Levason and C.A. McAuliffe, Inorg. Nucl. Chem. Lett., 13 (1977) 123.
21 S.T. Chow, C.A. McAuliffe and B.J. Sayle, J. Inorg. Nucl. Chem., 35 (1973) 4349.
22 G. Pneumatikakis and N. Hajilidis, J. Inorg. Nucl. Chem., 41 (1979) 429.
23 G.D. Zegzhda, S.I. Neikovskii, T.V. Zegzhda, F.M. Tulyupa and N.A. Dorifeeva, Tezisy. Dokl. Vses. Sovesheh. Khim. Anal. Teknol. Blagorodn. MeH 10th, 1 (1976) 101.
24 H. Kozlowski, G. Formicka-Kozlowska and B. Jezowska-Trzebiatowska, Bull. Acad. Pol. Sci., 26 (1978) 153.
25 H. Lam-Thanh and S. Fermandjian, J. Chem. Phys., 74 (1977) 361.
26 E.W. Wilson Jr. and R.B. Martin, Inorg. Chem., 9 (1970) 528.
27 E.W. Wilson Jr. and R.B. Martin, Inorg. Chem., 10 (1971) 1197.
28 N.N. Chernova, V.V. Strukov, G.B. Avetikyan and V.N. Chernonozhkin, Russ. J. Inorg. Chem., 25 (1980) 872.
29 T.P. Pitner, E.W. Wilson Jr. and R.B. Martin, Inorg. Chem., 11 (1972) 738.
30 T. Ito, F. Marumo and Y. Saito, Acta Crystallogr., Sect. B, 27 (1971) 1062.
31 T.C. Jarzab, C.R. Hare and D.A. Langs, Cryst. Struct. Commun., 3 (1973) 395.
32 T.C. Jarzab, C.R. Hare and D.A. Langs, Cryst. Struct. Commun., 3 (1973) 399.
33 M. Sabat, M. Jezowska and H. Kozlowski, Inorg. Chim. Acta, 37 (1979) L511.
34 R.S. Vagg, Acta Crystallogr., Sect. B, 35 (1979) 341.
35 Y. Nakayama, K. Matsumoto, S. Ooi and H. Kurova, J. Chem. Soc., Chem. Commun., (1973) 170.
36 N.N. Chernova, L.P. Shakhova and Yu.N. Kukuskin, Russ. J. Inorg. Chem., 21 (1976) 1671.
37 P.A. Boudreau and R.J. Hooper, J. Inorg. Nucl. Chem., 39 (1977) 1247.
38 I.A. Baidina, N.V. Podberezskaya, V.V. Bakakin et al., Zh. Strukt. Khim., 20 (1979) 544.
39 I.A. Baidina, N.V. Podberezskaya, S.V. Borisov and E.V. Golubovskaya, Zh. Strukt. Khim., 21 (1980) 188.
40 I.A. Baidina, N.V. Podberezskaya and S.V. Borisov, Zh. Strukt. Khim., 21 (1980) 198.
41 K. Nakamoto, Y. Morimoto and A.E. Martell, J. Am. Chem. Soc., 83 (1961) 4528.
42 N.A. Shestakova, U.F. Kuklinia and G.D. Mal'chikov, Izv. Sib. Otd. Akad. Nauk. SSSR Ser. Khim. Nauk., 2 (1977) 102.
43 N.A. Shestakova, E.V. Golubovskaya, G.D. Mal'chikov and Z.A. Grankina, Koord. Khim., 4 (1978) 587.
44 E.A. Sullivan, Can. J. Chem., 57 (1979) 62.
45 E.A. Sullivan, Can. J. Chem., 57 (1979) 67.
46 T. Komorita, J. Hidaka and Y. Shimura, Bull. Chem. Soc. Jpn., 41 (1968) 854.
47 T. Komorita, J. Hidaka and Y. Shimura, Bull. Chem. Soc. Jpn., 42 (1969) 168.
48 T. Komorita, J. Hidaka and Y. Shimura, Bull. Chem. Soc. Jpn., 44 (1971) 3353.
49 H. Ito, J. Fujita and K. Saito, Bull. Chem. Soc. Jpn., 40 (1967) 2584.
50 P.B. Kalapurna, Curr. Sci., 47 (1978) 674.
51 O. Vicol and St. Repede, Buletinul. Institutuli Politechnic du Iasi, XXVI, (1980) 37.
52 A. Odani and O. Yamauchi, Bull. Chem. Soc. Jpn., 54 (1981) 3773.
53 L.E. Maley and D.P. Mellor, J. Austr. Sci. Res., A2 (1949) 579.
54 O. Farooq, N. Ahmad and A.V. Malik, J. Electroanal. Chem., 48 (1973) 475.
55 G. Anderegg and S.C. Malik, Helv. Chim. Acta, 59 (1976) 1498.
56 L.I. Elding, Inorg. Chim. Acta, 6 (1972) 647.
57 R.D. Hancock and A. Evers, Inorg. Chem., 15 (1976) 995.

58 R.D. Hancock and A. Evers, (a) Nat. Inst. Metall. S.A. Rep. No. 1822 (1976); (b) J. Inorg. Nucl. Chem., 39 (1977) 1031.
59 O.P. Sunar and C.P. Trevedi, J. Inorg. Nucl. Chem., 33 (1971) 3990.
60 M.K. Singh and M.N. Srivastava, J. Inorg. Nucl. Chem., 34 (1972) 2067.
61 H. Frye and G.H. Williams, J. Inorg. Nucl. Chem., 41 (1979) 591.
62 R.C. Tewari and M.N. Srivastava, Acta Chim. Acad. Sci. Hung., 83 (1974) 259.
63 R.D. Graham and D.R. Williams, J. Chem. Soc. Dalton Trans., (1974) 1123.
64 M. Castillo-Mastos and F.A. Gonzalez-Vilchez, Anal. Quim., 71 (1975) 594.
65 F.A. Gonzalez-Vilchez and L.M. Castillo, J. Inorg. Nucl. Chem., 37 (1975) 316.
66 W.M. MacNevin and O.H. Kriege, J. Am. Chem. Soc., 77 (1955) 6149.
67 G.B. Briscoe and S. Humphries, Talanta, 16 (1969) 1403.
68 J. Kragten, Talanta, 25 (1978) 239.
69 L.N. Khurtova, S.N. Vinogradov and L.M. Firyulina, Russ. J. Inorg. Chem., 22 (1977) 1330.
70 M.C. Lim, J. Chem. Soc. Dalton Trans., (1977) 15.
71 M.C. Lim, J. Chem. Soc. Dalton Trans., (1977) 1398.
72 M.C. Lim, J. Chem. Soc. Dalton Trans., (1978) 726.
73 M.C. Lim, Inorg. Chem., (1981) 1377.
74 P.J. Morris and R.B. Martin, J. Inorg. Nucl. Chem., 33 (1971) 2913.
75 H. Kozlowski and E. Matczak-Jon, Inorg. Chim. Acta, 32 (1979) 143.
76 L.E. Nance, Ph.D. Thesis, Pacific, 1972.
77 L.E. Nance, A.F. Schreiner and H.G. Frye, Bioinorg. Chem., 3 (1974) 135.
78 H. Kozlowski and M. Jezowska, Chem. Phys. Lett., 47 (1977) 452.
79 H. Kozlowski and B. Jezowska-Trzebiatowska, Chem. Phys. Lett., 42 (1976) 246. Erratum: Chem. Phys. Lett., 46 (1977) 519.
80 H. Kozlowski, G. Formicka-Kozlowska and B. Jezowska-Trzebiatowska, Org. Magn. Reson., 10 (1977) 146.
81 H. Kozlowski, M. Jezowska and H. Szyszuk, J. Mol. Struct., 50 (1978) 73.
82 H. Kozlowski, Inorg. Chim. Acta, 31 (1978) 135.
83 P.I. Vestues and R.B. Martin, J. Am. Chem. Soc., 102 (1980) 7906.
84 H. Kozlowski and Z. Siatecki, Chem. Phys. Lett., 54 (1978) 498.
85 B. Jezowska-Trzebiatowska, E. Matczak-Jon and H. Kozlowski, Bull. Acad. Pol. Sci., 26 (1978) 145.
86 B. Jezowska-Trzebiatowska, T. Kowalik and H. Kozlowski, Bull. Acad. Pol. Sci., 26 (1978) 223.
87 B. Decock-Le Reverend, C. Loucheux, T. Kowalik and H. Kozlowski, Proc. XXII Int. Conf. Coord. Chem., Budapest, 1982, p. 539.
88 S.T. Chow, C.A. McAuliffe and B.J. Sayle, J. Inorg. Nucl. Chem., 37 (1975) 451.
89 G.D. Zegzhda and T.V. Zegzhda, Russ. J. Inorg. Chem., 23 (1978) 1826.
90 B. Jezowska-Trzebiatowska, G. Formicka-Kozlowska and H. Kozlowski, Bull. Acad. Pol. Sci., 26 (1978) 561.