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# Coordinating ability of phenylenediamines

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## Contents

## Abstract

The coordinating ability of aromatic diamines is conditioned both by the low basicity of the nitrogen atoms and their situation in *ortho*, *meta* or *para* positions on the aromatic ring.

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Important aspects of the aromatic diamines taking into account their possible applications are: processes based on electron transfer forming Würster type radical colored cations; trace analysis of metal ions and other species based on catalysis of the oxidative coloration system; the development of biosensors coated with poly(*o*-phenylenediamine) and their mutagenic and toxic character. *o*-Phenylenediamine ligands coordinate in a monodentate, chelating bidentate and bridging bidentate fashion in dinuclear complexes; *p*-phenylenediamine is mainly a bridging bidentate ligand as expected.

*Keywords:* Phenylenediamine; Basicity; Electron transfer; Mutagenicity; Toxicity Coordinating ability

## Nomenclature

| | |
|---|---|
| AN | aniline |
| 4-$CH_3O$-*o*-PDA | 4-methoxy-*o*-phenylenediamine |
| 4-Cl-*o*-PDA | 4-chloro-*o*-phenylenediamine |
| DBPA | di(2-butyl)-*N*,*N′*-*p*-phenylenediamine |
| DDA | durenediamine or 2,3,5,6-tetramethyl-*p*-phenylene-diamine |
| DMPD | dimethyl-*N*,*N*-*p*-phenylenediamine |
| dmso | dimethylsulphoxide |
| *m*-PDA | *m*-phenylenediamine |
| *o*-PDA | *o*-phenylenediamine |
| *p*-PDA | *p*-phenylenediamine |
| P-*m*-PDA | poly-*m*-phenylenediamine |
| P-*o*-PDA | poly-*o*-phenylenediamine |
| P-*p*-PDA | poly-*p*-phenylenediamine |
| PPDA | phenyl-*N*-*p*-phenylenediamine |
| 2,5-PyDA | 2,5-pyridinediamine |
| 2,6-PyDA | 2,6-pyridinediamine |
| 2-TA | 2-tolueneamine |
| 3-TA | 3-tolueneamine |
| 4-TA | 4-tolueneamine |
| TCNQ | 7,7,8,8-tetracyanoquinodimethane |
| 2,4-TDA | 2,4-toluenediamine |
| 2,5-TDA | 2,5-toluenediamine |
| 2,6-TDA | 2,6-toluenediamine |
| thf | tetrahydrofuran |
| TMPD | tetramethyl-*N*,*N*,*N′*,*N′*-*p*-phenylenediamine |

## 1. Introduction

The most simple aromatic amine is aniline which is a key organic compound for modern organic chemical industry. The first synthetic colouring materials were prepared from aniline [1]. At the time, chemical production on a large scale was unknown. Sir William Henry Perkin (1838–1907) designed a procedure to obtain aniline on a large scale by nitration of benzene followed by reduction of nitrobenzene [1]. In general, the primary aromatic amines including the diamines can be almost exclusively obtained by a combination of the nitration and reduction processes [2].

In this review, we focus on the properties and coordinating ability of aromatic diamines.

We emphasize the following aspects of the aromatic diamines taking into account their possible applications:

1. The less basic character of the aromatic diamines with respect to aliphatic diamines.
2. The electron donor character with processes based on electron transfer, especially with *p*-phenylenediamine derivatives.
3. Trace analysis of metal ions based on catalysis of the oxidative coloration system of phenylenediamines or its derivatives.
4. The development of amperometric biosensors based on redox enzyme carbon paste electrodes coated with poly(*o*-phenylenediamine).
5. Mutagenicity and toxicity.
6. Coordinating ability.

There have been no previous reviews on the coordinating ability of the phenylediamines per se.

## 2. Aromatic diamines: properties and applications

### 2.1. Basic character

The aromatic amines are less basic than aliphatic amines due to the delocalization of the electron-pair on the nitrogen atom toward the $\pi$ orbitals of the aromatic ring, the electron-density on the nitrogen atom available for bond formation thus being lower. The substituents on the aromatic ring influence the basicity of the diamines which increases for electron-donor substituents ($CH_3$, $OCH_3$, etc.) and decreases for electron-withdrawing substituents (Cl, $NO_2$, etc.). The *ortho*, *meta* or *para* positions of the substituent on the aromatic ring with respect to the nitrogen atom also have an influence on the basicity [3], as expected. Log *K* values for protonation of several aromatic diamines are shown in Table 1 [4–7], which also includes the log *K* for the aliphatic diamine ethylenediamine (en) [8] for comparison. The values (log *K*) for the first protonation are in good accord with those of aniline and tolueneamines (**9**–**12**) as expected [9] (Table 1). The basicity order *o*-PDA < 3,4-TDA < *m*-PDA < 2,6-TDA < 2,4-TDA < *p*-PDA < 2,5-TDA (**1**, **2**, **4**–**8**) for both protonation constants have been found. This order of basicity is *ortho* < *meta* < *para*. In substituting the methyl radical in the aromatic ring, the basicity of each group of the diamines increases slightly in the order *ortho* < *meta* <

Table 1
Protonation constants of phenylenediamines, pyridinediamines and phenyleneamines

(1) Protonation constants (log K) of phenylenediamines

*(a) In aqueous solution (25°C; $I = 0.1$ M in KCl)* [4]

| | en [8] | *o*-PDA | 3,4-TDA | *m*-PDA | 2,6-TDA | 2,4-TDA | *p*-PDA | 2,5-TDA | 4-Cl-*o*-PDA [8] | 4-$CH_3O$-*o*-PDA [8] |
|---|---|---|---|---|---|---|---|---|---|---|
| $H^+ + L \rightleftarrows HL^+$ | 9.89 | 4.61 | 4.97 | 5.01 | 5.07 | 5.26 | 6.22 | 6.28 | 3.94 | 5.10 |
| $H^+ + HL^+ \rightleftarrows H_2L^{2+}$ | 7.08 | 1.81 | 2.30 | 2.56 | 2.67 | 2.72 | 2.99 | 3.08 | 0.6 | |

*(b) In dioxane:water 70:30 v/v (25°C; $I = 0.1$ M in KCl), o-PDA* [5] *and dmso:water 80:20 wt/wt, 3,4-TDA (25°C; $I = 0.5$ M $NaClO_4$)* [6a] *and m-PDA (25°C; $I = 0.1$ M in $NaClO_4$)* [6b]

| | *o*-PDA | 3,4-TDA | *m*-PDA |
|---|---|---|---|
| $H^+ + L \rightleftarrows HL^+$ | 4.41 | 4.65 | 4.31 |

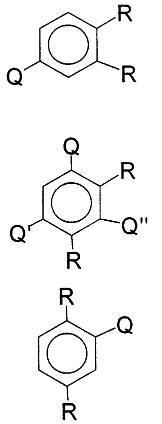
(2) Protonation constants (log $K$) of pyridinediamines in aqueous solution (25°C; $I = 0.1$ M in KCl) [7]

| | 2,6-PyDA | 2,5-PyDA |
|---|---|---|
| $H^+ + L \rightleftarrows HL^+$ | 6.62 | 6.58 |
| $H^+ + HL \rightleftarrows H_2L^{2+}$ | – | 2.20 |

(3) Protonation constants (log $K$) of phenyleneamines in aqueous solution (25°C; $I = 0.1$ M in KCl) [9]

| | AN | 2-TA | 3-TA | 4-TA |
|---|---|---|---|---|
| $H^+ + L \rightleftarrows HL^+$ | 4.65 | 4.57 | 4.96 | 5.09 |

*para* [4]. With the chloro atom as substituent in the aromatic ring the basicity is decreased by the electron-withdrawing effect [8].



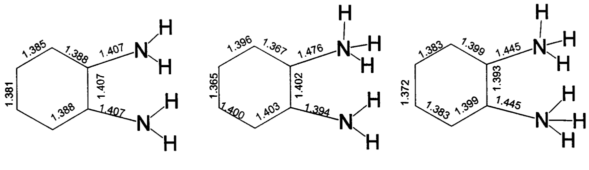
Diamines

$R = NH_2$

**1** Q= H (*o*-PDA)
**2** Q= $CH_3$ (3, 4-TDA)
**3** Q= Cl (4-Cl-*o*-PDA)
**4** Q=Q'=Q''=H (*m*-PDA)
**5** Q=$CH_3$, Q'=Q''=H (2,4-TDA)
**6** Q=Q'=H, Q''=$CH_3$ (2,6-TDA)
**7** Q= H (*p*-PDA)
**8** Q= $CH_3$ (2,5-TDA)
**9** R=$N(CH_3)_2$, Q=H (TMPD)

The ultraviolet electronic spectra of the aromatic diamines: *o*-PDA **(1)**, 3,4-TDA (**2**), 4-Cl-*o*-PDA (**3**), *m*-PDA (**4**), 2,4-TDA (**5**), 2,6-TDA (**6**), *p*-PDA (**7**) and 2,5-TDA (**8**) were studied in aqueous solution and as a function of the pH [10]. The results showed that in the diamines the same bands that exist in benzene and its derivatives are present [11]. The slight differences are explained by the position of the $-NH_2$ groups, electronic delocalization, inductive and symmetry effects [10,11]. Recently [12], ab initio calculations and vibrational spectroscopy on the phenylenediamine isomers have been carried out.

A number of crystal structures of phenylenediamines and protonated phenylenediamines have been determined. In the *o*-PDA derivatives, while the aromatic $C-NH_2$ bond distances range between 1.391(3) and 1.408(2) Å [13–16] (1.407(3) Å in *o*-PDA [17], Fig. 1(a)), the aromatic $C-NH_3^+$ bond length is longer and ranges between 1.445(11) and 1.476(13) Å [15,16,18–20] (1.476 in *o*-PDA·HCl [16], Fig. 1(b), and 1.445 Å in *o*-PDA·2HBr [19], Fig. 1(c)). Similar values for $p\text{-PDAH}_2^{2+}$: 1.49 Å in *p*-PDA·2HCl [21] and 1.47 Å in *p*-PDA·2HBr [22].



(a) $C_6H_4(NH_2)_2$ (b) $C_6H_4(NH_2)(NH_3^+)$ (c) $C_6H_4(NH_3^+)_2$

Fig. 1. Bond lenghs (Å) of the *o*-PDA and the protonated forms. Adapted from Refs. [17,16,19].

## 2.2. Processes based on electron transfer in p-phenylenediamine and derivatives

Aromatic amines are known to undergo a series of photophysical and photochemical processes based on electron transfer [23–25]. It is well known that the parent TMPD (**9**) is a powerful electron donor, and it has been extensively studied [26]. The radical cation $TMPD^+$ has been important in the development of radical cation chemistry [27a]. It was the first organic radical cation prepared [27b]. It was first formulated as a radical cation by Weitz in 1928 [27c], and it was one of the first organic radicals to be studied by EPR [27d]. Its rate of intermolecular 'self' electron exchange (between TMPD and $TMPD^+$) was one of the first measured [28] and the solvent and temperature effects have been thoroughly studied [29]; it has played a central role in the application of electron transfer theory (ET Theory) [30] to organic compounds. In contrast, the radical Würster's blue cation $TMPD^+$ clearly has its charge delocalized over the eight atom π system and it has equivalent planar nitrogen atoms, as has been confirmed by the X-ray structural study: perchlorate [31], iodide [32], chloride [33], $[Ni(C_3S_5)_2]^{3-}$ [34] and β-$[Mo_8O_{26}]^{4-}$ salt [35]. The perchlorate salt exhibits a temperature-dependent phase transition with the consequence of altered magnetic properties: paramagnetism at high temperatures and diamagnetism at low [36]. It also presents a room temperature conductivity of about $10^{-3}$ S $cm^{-1}$[37]. Charge-transfer complexes of the type $TMPD^+$ $A^-$ have also been prepared with TMPD as donor ($D^+$) and ($TCNQ^-$) [38], pentacyanocyclopentadienyl ($PCCP^-$) [39], tetracyanoplatinate $[Pt(CN)_4]^{2-}$ [40], bis(maleonitriledithiolato)nickelate(III) $[Ni(MNT)_2]^-$ [34,41] and β-$[Mo_6O_{28}]^{4-}$ [35] as the acceptor ($A^-$). Laser photolysis studies revealed that the acetylperoxyradicals in aerated benzene solutions react with TMPD, to yield the ion–pair complex [42]. Photoinduced electron transfer in donor–acceptor aryl dyads based on TMPD as the donor, has been also studied [43]. Analogously, charge localization in a dihydrazine analogue of $TMPD^+$ has been found [44]. The photooxidation (ET) reaction of TMPD by maleic anhydride has been studied in alcoholic media by a time-resolved EPR technique [45]. Peroxyl radicals, $RO_2^{\bullet}$ (R = H, alkyl, aryl) are important reactive intermediates formed in many oxidation reactions of inorganic and biological materials. They serve as chain propagators and may cause detrimental effects in biological systems. Typical of the electron-transfer reactions appear to be the oxidations of ascorbate ions [46] and of TMPD [47]. Carbon tetrabromide and some other polyhaloalkanes are also reduced by TMPD [48]. TMPD is a facile electron donor and chromophoric substrate for dopamine β-monoxygenase [49].

Thus TMPD and similar donors have the potential for redox properties which, in conjunction with bound redox-active transition-metal ions, may lead to complexes with both metal ion and ligand-based redox chemistry.

Functionalized *p*-phenylenediamine derivatives using arene-iron chemistry has been prepared [50]. The chemistry of many $17e^-$ organometallic radicals has been developed in the past two decades. The results have been intrinsically interesting, particularly so in that most of these radicals are very reactive [51]. In the absence of other reagents, the 17e$^-$ molybdenum radical ($\eta^5$-$C_5H_5$)Mo(CO)$_3$ combines to form the stable dimer [CpMo(CO)$_3$]$_2$. In the presence of TMPD, however, an electron transfer process ensues in which the normally persistent radical TMPD$^{\bullet +}$ is produced [52].

Recently, Wimalacena et al. [53] demonstrated that the well-characterized reducing agent, DMPD [53,54], supports the activity of dopamine β-monoxygenase, leading to a spectrophotometric assay for that enzyme. DMPD is also capable of functioning as the requisite electron donor for enzyme PAM (peptidilglycine α-amidating mono-oxygenase) turnover, thus providing a spectrophotometric assay for PAM catalysis based on monitoring DMPD oxidation [55]. The mechanism of the heterogeneously catalysed reaction between DMPD and $[Co^{III}(NH_3)_5Cl]^{2+}$ at silver, gold and silver-on-gold (Ag/Au) discs has been studied by means of electrochemical methods [56]. The effects of the antioxidants *N*,*N*′-diphenyl-1,4-phenylenediamine (DPPD) on arteriosclerosis in ApoE-deficient mice [57] and the effect of monoclonal antibody against peroxidase-catalysed oxidation of *o*-PDA [58] have been studied.

The electrochemical oxidation of 2,6-dichloro-1,4-phenylenediamine was studied at a glassy carbon electrode in a 50% vol. methanol-water mixture containing 0.1 M $HClO_4$. Single sweep voltammograms are compared with curves obtained by digital simulation [59].

### 2.3. Trace analysis of metal ions based on catalysis of the oxidative coloration system of phenylenediamines or its derivatives

The kinetic catalytic method has proven to be an attractive means for trace analysis of metal ions. Ultratrace levels (nanogram and/or subnanogram amounts) of metal ions which act as catalysts for an appropriate indicator reaction can be determined under optimal conditions with simple instrumentation [60]. The addition of a ligand as an activator to the metal-catalyzed reaction improves the sensitivity and/or selectivity of these methods [60,61]. The catalytic effects of the metal on the colour-forming system of *m*-PDA with DMPD or PPDA in the presence of hydrogen peroxide has been used as indicator reaction. A spectrophotometric flow-injection method has been developed for the determination of subnanogram amounts of manganese(II) based its catalytic effect on the oxidative coupling of DMPD with *m*-PDA in the presence of hydrogen peroxide [62]. Similarly, nanogram levels of iron(II-III) [63] and Cu(II) [64] have been determined based on the catalytic effect of the metal on the oxidative coupling of PPDA with *m*-PDA in the presence of hydrogen peroxide. Previously [65], a spectrophotometric catalytic determination of an ultratrace amount of iron(III) based on the oxidation of DMPD by hydrogen peroxide in water was used. Other derivatives of *p*-phenylenediamine (*p*-PDA) have been used for the determination of trace iron(III) [66]. A highly sensitive method for the determination of vanadium has been developed by spectrofluorimetric monitoring of the vanadium catalyzed oxidation

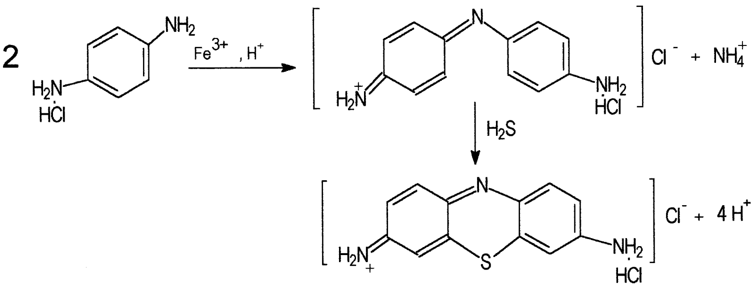


Fig. 2. Fluorogenic reaction of sulfide with *p*-PDA and $Fe^{3+}$ to form thionine. Adapted from Ref. [71].

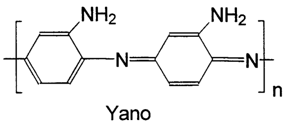
of *o*-phenylenediamine (*o*-PDA) with bromate in the presence of gallic acid as an activator [67]. Trace copper impurity has been determined spectrophotometrically in DBPA [68].

Hydrogen sulfide, a by-product of many industrial processes, is toxic. Measuring trace amounts of sulfide in biological materials has not been successful because of sensitivity and selectivity limitations. A specific colorimetric method based on the formation of methylene blue by the reaction of sulfide with DMPD in the presence of an oxidizing agent has been widely used for the determination of sulfide at the micromole level [69]. The fluorescent properties of the thionine and methylene blue were studied, and the formation of thionine was applied to the spectrofluorimetric determination of sulfide [70]. *p*-PDA or its substituted analogues react specifically with sulfide in the presence of iron(III) under acidic conditions to form thiazinate derivatives, and thionine is the corresponding derivative obtained by the reaction of sulfide with *p*-PDA (Fig. 2) [71]. The fluorescence quantum yield of thionine is larger than that of methylene blue. This permits the determination of trace amounts of sulfide in human blood by high performance liquid chromatography (HPLC) with fluorimetric detection using pre-column derivation with *p*-PDA and iron(III) to form thionine [71]. A study has also been carried out of the photometric determination of organic compounds containing sulfidril, disulfide and alkilthio groups, in solution and in air, based on the reactions with mercury salts and DPD [72]. Recently, the fluorimetric determination of epinefrine with *o*-PDA has been developed [73]. Colorimetric determination of urinary xanthurenic using oxidative coupling reaction with *N*,*N′*-diethyl-*p*-phenylenediamine has been studied [74]. DMPD is used as an alternative reductant for peptidilglycine α-amidating monooxygenase catalysis [75]. *o*-PDA has also been used as fluorescence system in the enzymatic assay of serum uric acid [76].

## *2.4. The development of amperometric biosensors based on redox enzymes carbon paste electrodes coated with poly (o-phenylenediamine)*

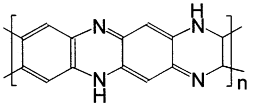
Polyaniline and its derivatives have attracted much attention due to their interesting electrical, electrochemical and optical (linear and nonlinear) properties

[77]. These polymers exhibit multiple insulating-conducting and electrochromic transitions which are based on redox and/or protonation-deprotonation processes. With these properties, polyanilines are certainly one of the most promising classes of conducting polymers for industrial applications. It is interesting to develop ladder analogs of polyaniline in order to force a coplanar conformation of the backbone (which should increase the conjugation) and to increase the thermal stability of these materials and to improve other properties and applications. Poly-*o*-phenylenediamine (P-*o*-PDA) has attracted much attention due to its novel properties and wide applications.



Yano

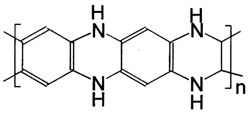
**10**



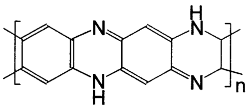
Oyama

**11**

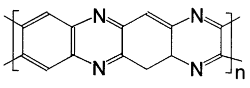
P-*o*-PDA, one of the conducting polymers, can be prepared either by chemical polymerization [78] or by the electropolymerization [79] of *o*-PDA in an acid solution as stable films on electrode surfaces. This polymer has useful functions that differ from those of other polymers. It is widely studied as an electrochromic display material [80], as electrocatalyst for the reduction of oxygen [81], in humidity sensors [82], as electrode modified materials [83], for its electrochromic properties [80,84], pH response [85], protection against metal corrosion [86] etc. The kinetics of the electrode reaction of P-*o*-PDA films have also been studied [87]. In order to elucidate these functions and to develop new devices (based on polymer film-coated electrodes) the structure of P-*o*-PDA has been studied by different techniques [88–94]. Yano [89] found that virgin P-*o*-PDA is a conductive polymer with a molar mass of 11 000 g $mol^{-1}$ and has a 1–4-substituted benzenoid-quinoid molecular structure similar to polyaniline (**10**, **11**) (cyclic voltammetry studies in dmso solutions). However, Wu [90] by mean of studies of the redox process of P-*o*-PDA film in strong acid solution by in situ resonance Raman spectroscopy, in situ UV-vis subtractive reflectance spectroscopy and cyclic voltammetry, suggests that the structure of P-*o*-PDA is dominated by a ladder polymer with phenazine rings (Oyama structure [88]); at least three states of P-*o*-PDA, reduced state **(12)**, semi-oxidized state **(13)** and total-oxidized state **(14)**, are formed in the redox process.



**12** Red(I)



**13** Semi-ox(II)



**14** Total-ox(III)

Biosensor-membrane-based amperometric redox enzyme electrodes form a major class of biosensors that have continued to enjoy considerable attention in recent years [95]. The need for chemical sensing in clinical and industrial environments is diverse, and biosensor technology generally offers several benefits over many established wet chemical and instrument-based techniques. To date, only a relatively small number of biosensors, however, enjoy any commercial success, and this may in part be due to a number of common problems that still need to be addressed, particularly those relating to robustness and reliability [96]. The advantages that biosensors afford can only be achieved if the sensor meets the required specificity, sensitivity and robustness for a particular application [97]. Within clinical analyses, for example, the sensor must resist both the detrimental effects of outer surface biofouling and working electrode passivation [98]. A common approach to overcome these problems is to employ tailored membranes. The development of ultra-thin polymer-film composite membranes stemmed from established techniques used in the chemical separations field [99]. Ultra-thin polymer-film composite membranes have been identified as being potentially extremely useful for the development of widely differing technologies, ranging from bioreactors to waste management [100]. Ultra-thin P-*o*-PDA composite membranes [97,99–101] provide outer surface biocompatibility, permselective screening of interferent solutes and linearization of sensor response and have permitted the development of a glucose oxidase enzyme electrode for the determination of glucose concentration in whole blood [101].

The search for the ideal glucose sensor continues to be one of the main focuses of biosensor research despite more than three decades of intense investigation since the development of the first electrochemical glucose sensor by Clark and Lyons in 1962 [102]. This is mainly due to the important role of such a glucose monitoring sensor in industrial [103,104] and clinical [105–107] applications, ranging from the analysis of fermentation media [103] to the development of the artificial β-cell or pancreas for the treatment of the metabolic disease diabetes mellitus [108]. *o*–PDA forms a self-sealing, highly insulating thin (ca. 10 nm) membrane containing trapped enzyme molecules when electropolymerized onto a Pt anode in enzyme–electrolyte solution [109]. In the recent years, $H_2O_2$-detecting biosensor glucose oxidase-modified-P-*o*-PDA-coated Pt (Pt/P-*o*-PDA/$GO_x$) have been reported as interference 'free', having a high enzyme activity and a low response time, making them suitable for detecting glucose directly in biological systems [101,109–111].

Analogously, a bioenzyme-P-*o*-PDA-modified carbon paste electrode for the amperometric detection of L-lactate [112] has been constructed. L-lactate is an important metabolite for the determination of which a reliable, sensitive and fast analytical method is required in clinical, food and bioprocess analysis [113]. Biosensors for electrocatalytic detection of nicotinamide coenzymes and amperometric detection of ethanol have also been prepared [114]. Polymer film P-*m*-PDA and P-*p*-PDA has also been studied to prepare biosensors [115–117].

### 2.5. Mutagenicity and toxicity

Arylamines are classic promutagens and procarcinogens, and have been used to resolve questions involving mutagenic activation, cancer induction, and human polymorphic sensivity to environmental agents [118]. Some of these agents are direct-acting mutagens, while others are substrates for mammalian activation by the cytochrome P-450-mediated pathway as well as prostaglandin H synthase [119] and plant peroxidases [120]. The ultimate mutagenic agents form DNA adducts which induce genetic damage. Arylamines have been used to study the mechanism of plant activation [121]. Plant activation is the process by which a promutagen is activated into a mutagen by a plant system [122].

Tobacco cells in suspension cultures activated *m*-PDA into a product that was mutagenic in Salmonella typhymurium (the genetic indicator organism) [123]. 4-nitro-*o*-PDA is metabolically activated by chlorophyll-containing plant extracts [124]. *p*-PDA has a mutagenic modulating effect on the oxidation of *o*-PDA and *m*-PDA with $H_2O_2$ in the salmonella test [125]. Watanabe [126] found Phenazine derivatives as the mutagenic reaction product *o*-PDA or *m*-PDA derivatives with $H_2O_2$. *Emblica officinalis Gaertn.* (Indian Gooseberry) fruit extract on sodium azide and 4-nitro-*o*-PDA induced mutagenesis in *Salmonella typhymurium* [127].

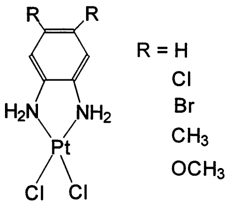
Arylamines are important environmental mutagens and carcinogens; however, this class of compounds has not been extensively investigated using the alkaline Comet assay [128]. This rapid and sensitive assay has been used to analyze the genotoxic properties of physical and chemical agents under in vitro and in vivo conditions, as well as in human monitoring. Since plant systems activate arylamines into stable mutagens [121], the possibility exists that plant-activated arylamine products may induce genotoxic damage in animals that consume contaminated plant material. Plewa et al. [129], using the Comet assay, found that *m*-PDA directly induced DNA damage in human lymphocytes.

*p*-PDA is the main aromatic amine used in hair dye formulations [130]. Many azo dyes used by the industry also contain the *p*-PDA moiety [131]. Upon azo reduction of these compounds by environmental or intestinal microorganisms, *p*-PDA is released [131,132]. Studies of mutagenicity and toxicity of *p*-PDA and its derivatives comparing with AN, *o*-PDA and *m*-PDA have been carried out [133]: AN is not very toxic, but an addition of another amino group at the *ortho*- or *para*-position increases its toxicity. Such a phenomenon does not occur when another amino group is added at the *meta*- position. The *p*-PDA is more toxic than *o*-PDA, which in turn is more toxic than the *m*-PDA. The position of the amino group also affects the mutagenic activity: *o*-PDA and *m*-PDA were more mutagenic than *p*-PDA to tester strain TA98 [133]. The approximate sequence of potency in inducing chromosomal aberrations was: *p*-PDA > *o*-PDA > *m*-PDA. This sequence is in parallel with their cytotoxicities, but does not correlate with their mutagenicities [133].

*p*-PDA produces contact anaphylaxis [134], occupational allergy [135], contact secondary leukoderma [136], breathing difficulties [137], myotoxic activity [138], tumor necrosis [139], etc. Dissociation of allergenic and immunogenic functions in contact sensitivity to *p*-PDA has been studied [140] as well as PDA-induced hepatoxyte cytotoxite redox [141].

*o*-PDA also presents dangerous properties [142]. *o*-PDA is used as a fluorogenic substrate in the peroxidase-mediated enzyme-linked immunosorbent assay [143]. However, low density lipoprotein is protected from oxidation and the progression of atherosclerosis is slowed in cholesterol-fed rabbits by the antioxidant *N*,*N*′-diphenyl-*p*-PDA [144]. Also, TMPD is a facile electron donor and chromophoric substrate for dopamine beta-monooxygenase [49] and the formation and reactions of Würster's blue radical cation during the reaction of TMPD with oxyhemoglobin have been studied [145].

Dichloro (*o*-phenylenediamine) platinum(II) complexes, $Cl_2$(*o*-PDA)Pt(II), were among the first *cis*-platin analogs found to possess antitumor activity [146–148]. These complexes showed reduced systemic toxicity, and thus had therapeutic indices more favorable than that of *cis*-platin [146]. However, $Cl_2$(*o*-PDA)Pt(II) complexes were not developed further because they showed cross-resistance in L1210 cells made resistant to *cis*-platin [149]. Interest in platinum complexes with coordinated *o*-phenylenediamines waned even more when it was found that these compounds are potent mutagens in the Ames test with Salmonella typhimurium [150]. For example, the simplest analog, $Cl_2$(*o*-PDA)Pt(II) (**15**) is over ten times more mutagenic than *cis*-platin. However, more recently, Köckerbauer and Bednarski [151] considered that the unique biological activities of $Cl_2$(*o*-PDA)Pt(II) complexes suggested that the chemistry of these compounds was deserving of more detailed study, in particular, their aqueous chemistry, which has received only scant attention in the past [147]. They found [151] that the weak growth inhibitory activities of **15** complexes on human cancer cells in vitro were likely a result of their poor chemical stability in the culture medium. Based on a knowledge of the decomposition pathways, analogues were designed to be resistant to these types of reactions. Both **16** and **17** complexes were considerably more stable than **15** under aqueous conditions, as well as being more effective in inhibiting the growth of human cancer cells in vitro. This work demonstrates the value of aqueous stability studies in the development of more effective antitumor Pt complexes.



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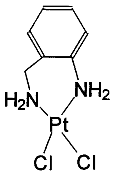
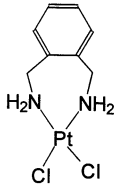


**16**



**17**

## 2.6. Coordinating ability

### 2.6.1. Thermodynamic studies

Work on the thermodynamic stability in solution of aromatic diamine complexes is scarce.

The coordinating ability in aqueous solution of *o*-PDA (**1**), 3,4-TDA (**2**), *m*-PDA (**4**), 2,4-TDA (**5**) and *p*-PDA (**7**) with Co(II), Ni(II) and Cu(II) was studied potentiometrically [152]. The results indicate that phenylenediamines do not form very stable complexes with the metallic bivalent ions because of their weak basicities and because of the large steric requirements of the ligands. For Cu(II) the formation was confirmed for the complexes CuL and $CuL_2$ [8] for *o*-phenylenediamines in aqueous solution (25°C, $I = 0.1$); for the CuL complex the $\log K$ values were determined: *o*-PDA, 4.55; 3,4-TDA, 4.74; $4\text{-}CH_3O$-*o*-PDA, 4.78; and 4-Cl-*o*-PDA, 3.32, in accord with the electron-donor character of the radicals $CH_3$ and $OCH_3$ and the electron-withdrawing character of the Cl atom. In the mixed-solvent dioxane-water 70:30 (v/v) (25°C; $I = 0.1$ M (KCl)), for 1:1 complex Co(II)-*o*-PDA, $\log K = 1.95$ was found [5]. The complex is very weak.

### 2.6.2. *o*-Phenylenediamine complexes

The dichloro(*o*-phenylenediamine)platinum(II) complexes prepared by O'Connors et al. [146] were considered in the paragraph Mutagenicity and toxicity, taking into account that they possess antitumor activity [146–148] and are also potent mutagens [150]. The relationship between their stability in aqueous solution and their antitumor activity was also investigated [151].

Earlier reports on the coordinating ability of the *o*-PDA involved weak unidentate linkages in Co(II), Ni(II) and Zn(II) complexes with four or six *o*-PDA molecules and of Cu(II) and Cd(II) with one to three diamine molecules [153–155]. The exceptions were $Cu[NO_3]_2$(*o*-PDA)$_2$, $Cu(SO_4)$(*o*-PDA)$_2$ and $CdCl_2$(*o*-PDA) which appeared to contain a bidentate diamine [153–156]. However, from magnetic and visible spectral studies several workers suggested that $Ni(NO_2)_2$(*o*-PDA)$_2$, $NiCl_2$(*o*-PDA)$_2$ and $Ni(SO_4)$(*o*-PDA)$_2$ contained a bidentate diamine [157]. Complexes of Co(II) and Cu(II) halides containing a ligand: metal ratio > 1 are known to be unstable [158].

New complexes were reported [159–162]: Ni(II) complexes containing two, three, four or six molecules of *o*-PDA and some new complexes of 3,4-TDA with three, four or six molecules present were characterized by magnetic, infrared and electronic spectra, thermal analysis and X-ray powder photograph measurements [159]. Complexes of Co(II) and Zn(II) were also characterized [159]. Similarly, other complexes of *o*-PDA of types M(*o*-PDA)$X_2$, M(*o*-PDA)$_2X_2$ and M(*o*-PDA)$_3X_2$ ($X = Cl^-$, $Br^-$, $NO_3^-$, etc.) with Co(II), Ni(II) and Cu(II) were prepared and characterized [160]. *o*-PDA can act as a chelating or as a bridging ligand (IR and electronic spectra and magnetic measurements) [159]. A crystal-structure determination [163] of the Ni(II) complex, [Ni(*o*-PDA)$_6$]$Cl_2$ showed that the correct formulation is [Ni(*o*-PDA)$_4$]$Cl_2$·2*o*-PDA (Fig. 3), with two bidentate equatorial ligands, two monodentate axial ligands and two lattice *o*-PDA molecules rather than with

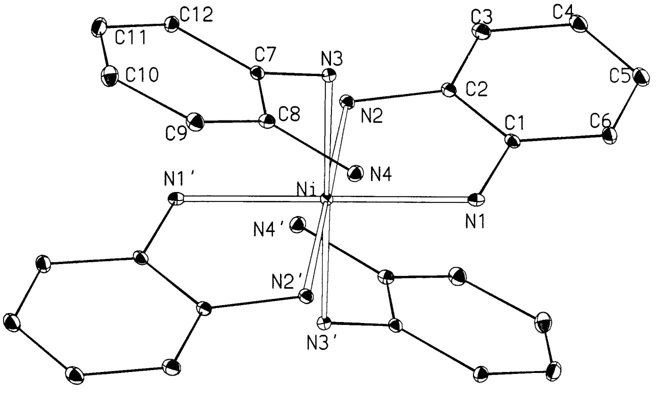
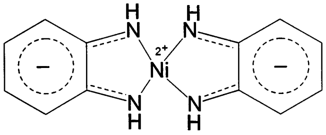


Fig. 3. ORTEP view of the $[Ni(o\text{-}PDA)_4]^{4+}$ cation in the compound $[Ni(o\text{-}PDA)_4]Cl_2\cdot 2\cdot o\text{-}PDA$. Drawn using data from Ref. [163].

six monodentate ligands as first proposed [159]. Peng et al. have prepared and structurally characterized the complexes $[Co^{II}(s\text{-}bqdi)_2]$ (s-bqdi = semi-*o*-benzoquinonediimine monoanion, Fig. 4(f)), $[Co^{III}Cl(s\text{-}bqdi)_2]\cdot DMF$ [164], $[Co^{III}(s\text{-}bqdi)_2(py)]Cl$ (Co atom is in a square pyramidal geometry) and $[Cu^{II}L(py)_2]$ ($L^{2-}$ = *N*,*N*′-bis(toluene-*p*-sulfonyl)-*o*-phenylenediiminato, similar Fig. 4(c); Cu atom is in a distorted tetrahedral geometry) [165].



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The neutral complex $Ni[C_6H_4(NH)_2]_2$ was reported in 1927 [166] as a dark purple complex prepared by air oxidation of a solution of Ni(II) and *o*-PDA in aqueous

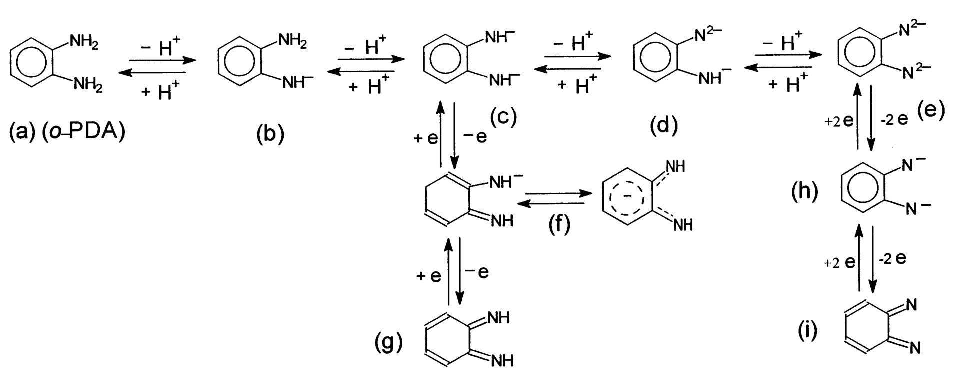


Fig. 4. Deprotonated and oxidized forms of the *o*-PDA.

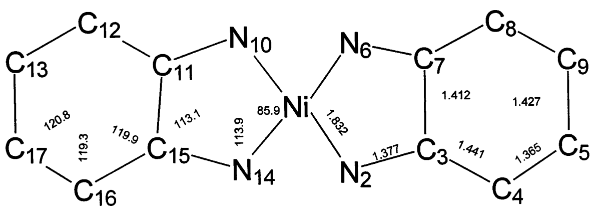
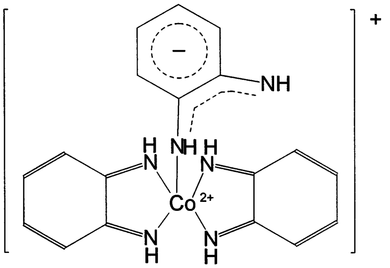


Fig. 5. The planar $Ni[C_6H_4(NH)_2]_2$ molecule showing the average lenghs and angles for bonds assumed to be chemically equivalent. Adapted from Ref. [167].

ammonia. The complex was formulated as the Ni(IV) complex of the dianion of *o*-PDA (Fig. 4(c)). The crystal structure has been determined by Hall and Sodelberg [167]. The observed planar structure (Fig. 5) seems inconsistent with a formulation based on Ni(IV) ($d^6$), but it supports the assignment of this compound as the central member (**18**) of a family of complexes which are interrelated by electron-transfer reactions [168,169] (Figs. 4(c, f and g)). This complex (**18**) can perhaps best be described as two spin coupled $C_6H_4(NH)_2$ radical ions (Fig. 4(f)) coordinated to Ni(II) ($d^8$), giving a diamagnetic complex. Similar complexes, $M^{II}[o\text{-}(NH)_2C_6H_4]_2$ M = Co, Pd, Pt, with the monoanionic benzosemiquinonediimine form **(18)** (Fig. 4(f)) were also prepared [169]. Co(II)-salts catalyze the autoxidation of *o*-PDA in a slightly alkaline solution. By air oxidation of the $[Co^{II}(o\text{-PDA})_3]^{2+}$ ion is obtained a low spin Co(II) complex, which was structurally characterized [170]: the complex has a square pyramidal arrangement, the Co-$N_4$-plane distance being only 0.5 Å; two of the aromatic ligands have the oxidation state of a benzoquinonediimine (two rings (g), Fig. 4) while the third, coordinated by one amino group only, is pseudosemiquinoid (one ring (f), Fig. 4) (Fig. 6, **19**).



**19**

Hieber [171] has reported that reaction of *o*-PDA with $Fe(CO)_5$ yields a complex $[Fe(o\text{-PDA})_3][Fe_3(CO)_{11}]$. Complexes of *o*-PDA with Fe(II) halides have been prepared and characterized by infrared, electronic and Mössbauer spectroscopy and magnetic susceptibility measurements [172]. Compounds having two, three, four and six *o*-PDA ligands per iron have been isolated. The complexes are of high spin and IR data indicate that some complexes involve bidentate ligands and others unidentate ligands. The oxidation of the yellow $[Fe^{II}(CN)_4(o\text{-PDA})]^{2-}$ with molec-

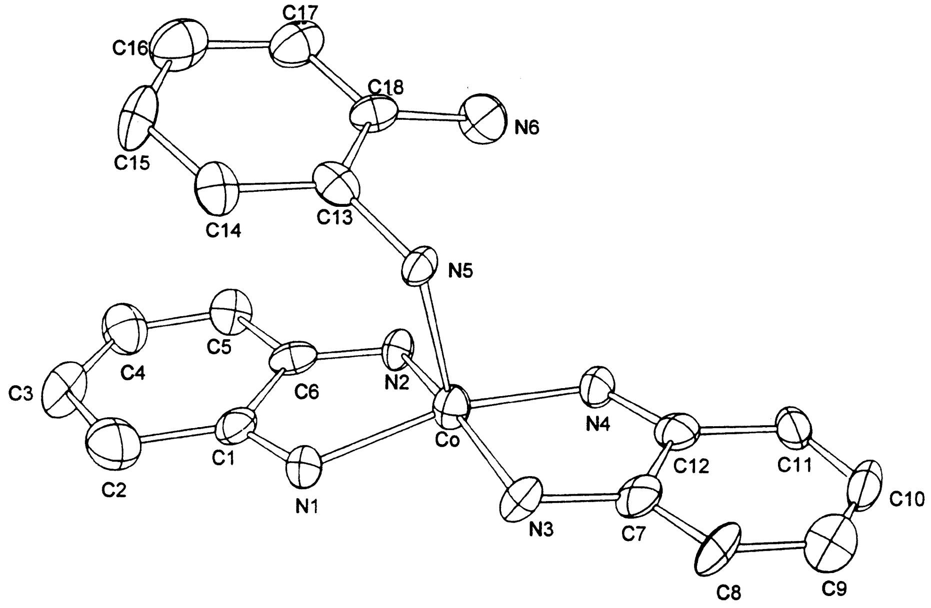


Fig. 6. ORTEP view of the $[Co^{II}(o\text{-PDA})_3]^+$ ion. Adapted from Ref. [170].

ular oxygen yields a very intensely purple colored product thought [173] to contain the stabilized *o*-benzoquinonediimine ligand (Fig. 4(g)) [168,169]. The X-ray diffraction structure determination (Fig. 7) [174] indicates that the two electron oxidation products of *o*-PDA have been stabilized by coordination to low spin iron(II) in the complex anion $[Fe(CN)_4(C_6H_4(NH)_2)]^{2-}$. The chemical and structural evidence conclusively demonstrates that the oxidation product contains stabilized *o*-benzoquinonediimine (Fig. 4(g)). The complexes $[Fe^{II}(bqdi)_3][PF_6]_2$

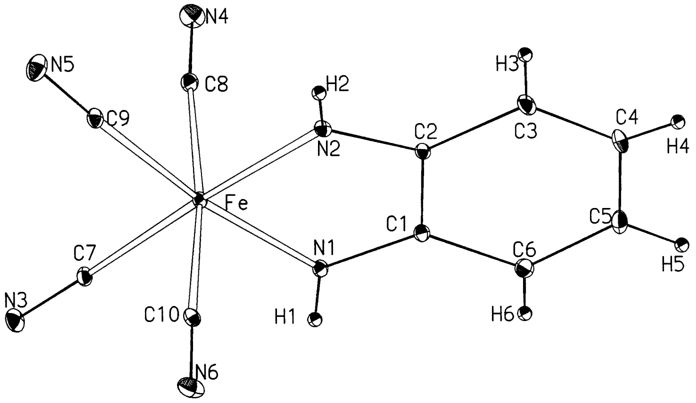


Fig. 7. ORTEP view of the $[Fe(CN)_4(C_6H_4(NH)_2)]^{2-}$ ion. Drawn using data from Ref. [174].

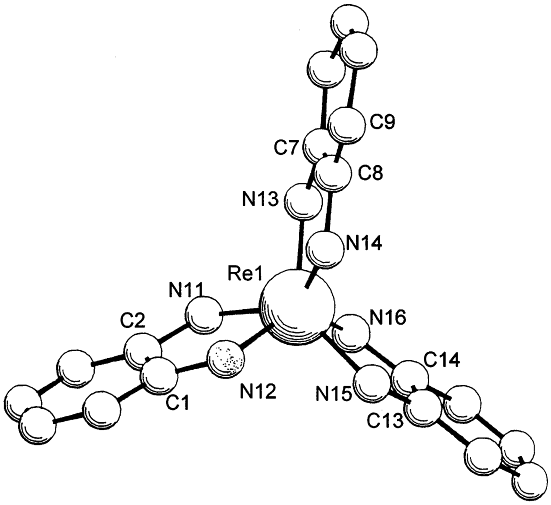


Fig. 8. View of the cation $[Re(o\text{-}PDA)_3]^+$. Adapted from Ref. [178].

(bqdi = *o*-benzoquinonediimine, Fig. 4(g))[164], $[Rh^{II}(PPh_3)_2(s\text{-}bqdi)Cl]$ (s-bqdi = semi-*o*-benzoquinonediimine, bidentate, Fig. 4(f); the Rh atom has a coordination geometry between square pyramidal and trigonal bipyramidal) [175], $[Ru^{II}(o\text{-}PDA)(bqdi)_2](PF_6)_2$ (*o*-PDA, Fig. 4(a); bqdi = *o*-benzoquinonediimine, Fig. 4(g); the Ru atom is bound to the three bidentate ligands in a trigonally distorted octahedron) [176] and $[Ru^{II}(bipy)_2(bqdi)][PF_6]_2$ (bipy = 2,2′-bipyridyl; bqdi, Fig. 4(g)) [177] have also been prepared and characterized.

New complexes of Re(VII) and Re(VI) with *o*-PDA have been prepared and characterized [178]. The interaction of trimethylsilyl perrhenate, $ReO_3(OSiMe_3)$ or $Re_2O_7$ with *o*-PDA gives the homoleptic amido complex cation of Re(VII), $[Re\{o\text{-}(HN)_2C_6H_4\}_3]^+$(rings (c), Fig. 4) (**a**), as its perrenate salt. The cation can be reduced by sodium to the neutral Re(VI) species $Re[o\text{-}(HN)_2C_6H_4]_3$ (**b**), which can be reoxidised by $AgPF_6$ to the cation as its hexafluorophosphate salt. Interaction of (**a**) with KOH leads to the singly (rings (c), Fig. 4) and doubly deprotonated species (rings (d), Fig. 4), $Re[o\text{-}(HN)_2C_6H_4]_2\ [o\text{-}(HN)NC_6H_4]$ (**c**) and $K[Re\{o\text{-}(HN)_2C_6H_4\}\{o\text{-}(HN)NC_6H_4\}_2]$ (**d**). The X-ray crystal structure of the cation (**a**) as the acetone solvate of the perrhenate shows a trigonal prismatic geometry (Fig. 8), which is also confirmed for (**b**), (**c**) and (**d**). Interaction of $OsO_4$ with *o*-PDA gives the Os(VIII) complex *trans*-$OsO_2[(HN)_2C_6H_4]_2$. Infrared, $^1H$-NMR, EPR and electronic absorption and cyclic voltammetric studies were also made.

New complexes of the Cr(II) with *o*-PDA have been prepared and characterized [179]: $[Cr(o\text{-}PDA)_2(NCS)_2]$, $[Cr(o\text{-}PDA)_4]Br_2$, $[Cr(o\text{-}PDA)_2I_2]\cdot 1.5EtOH$, $[Cr(o\text{-}PDA)Cl_2]$, $[Cr(o\text{-}PDA)_6]Cl_2$ and $[Cr(o\text{-}PDA)_4][CF_3\text{–}SO_3]_2$. According to IR spectra, the first two complexes contain a monodentate diamine, the next two a bidentate diamine and the last two both a mono- and a bidentate diamine; thus $[Cr(o\text{-}PDA)_6]Cl_2$ is more correctly formulated as $[Cr(o\text{-}PDA)_4]Cl_2\cdot 2o\text{-}PDA$. Crystal struc-

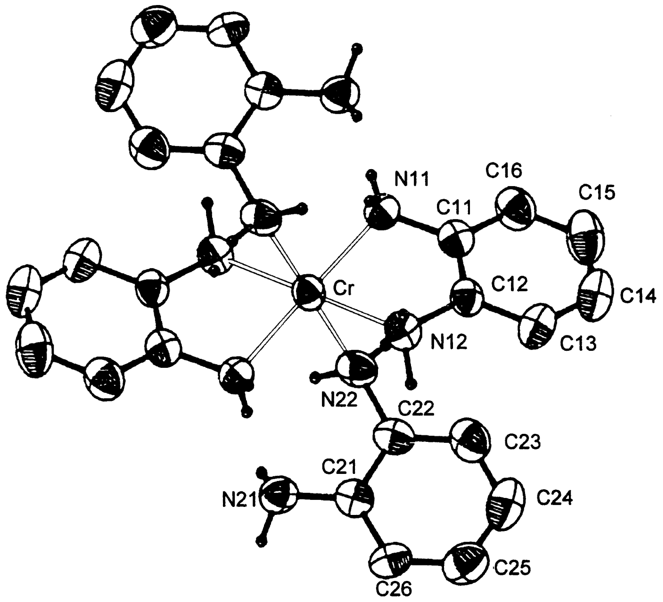


Fig. 9. View of the cation $[Cr(o\text{-PDA})_4]^{2+}$ in the complex $[Cr(o\text{-PDA})_4][CF_3SO_3]_2$ with two bidentate diamine molecules and two monodentate diamine molecules. Adapted from Ref. [179].

ture determinations confirm the assignments for $[Cr(o\text{-PDA})_2(NCS)_2]$ and $[Cr(o\text{-PDA})_4][CF_3SO_3]_2$. In this last structure (Fig. 9) the coordination sphere consists of two bidentate diamine molecules, with two more distant, axially positioned molecules, similar to $[Ni^{II}(o\text{-PDA})_4]^{2+}$ cation [163].

The red *o*-phenylenediamido complex of Cr(IV) $Cr[o\text{-}(NH)_2\text{-}C_6H_4]Cl_2(PMe_2Ph)_2$ has been obtained [180] and its X-ray crystal structure determined (Fig. 10). The molecule has an octahedral geometry with a chelating diamido function (ring (c), Fig. 4), *cis*-chlorines and *trans*-phosphines, having $C_2$ symmetry. Although a vast number of Cr(III) amine complexes are known [181], none appears to have *o*-PDA

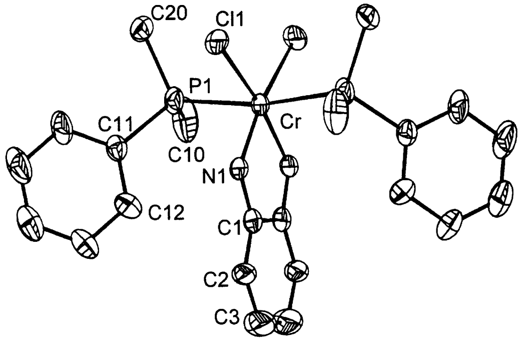


Fig. 10. Molecular structure of $Cr[o\text{-}(NH)_2\text{-}C_6H_4]Cl_2(PMe_2Ph)_2$. Adapted from Ref. [180].

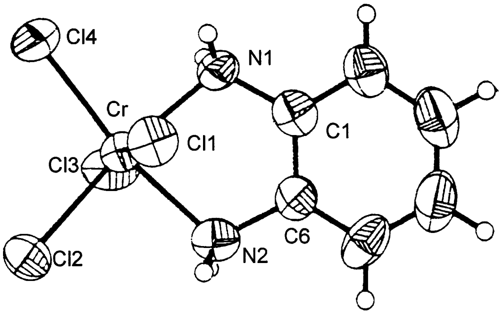


Fig. 11. The structure of the anion in the salt $[PPh_3(CH_2Ph)][CrCl_4((H_2N)_2C_6H_4)]$. Adapted from Ref. [182].

as ligand. Using the ligands *o*-PDA and 4,5-dimethyl-*o*-PDA, anionic Cr(III) complexes of the type $[CrCl_4(o\text{-PDA})]^-$ have been isolated as quaternary phosphonium salts from interaction of $CrCl_3(thf)$ and the ligand in the presence of $[PPh_4]Cl$ or $[PPh_3(CH_2Ph)]Cl$ [182]. Interaction in the absence of quaternary phosphonium salts gives $[CrCl_2(o\text{-PDA})]Cl$. The interaction of $[P(CH_2Ph)Ph_3][CrCl_4\{o\text{-}(NH_2)_2C_6H_2Me_2\}]$ with $AgO_3SCF_3$ and the $[CrCl_2(o\text{-PDA})_2]Cl$ with trifluoromethanesulfonic acid and diethyl ether leads to the unusual Cr(IV) octahedral triflate compounds $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$ (**a**) and $Cr(O_3SCF_3)_4\text{-}[(H_2N)_2C_6H_4]$ (**b**), respectively. The crystal structures of the compounds $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4\}]$ (the structure of the anion is shown in (Fig. 11)), (**a**) and (**b**) have been determined. All have octahedral structures with chelating diamines. Similarly, from $VCl_3(thf)_3$ were obtained V(III) complexes $[VCl_4(o\text{-PDA})]^-$ or $[VCl_2(o\text{-PDA})_2]Cl$ e.g. with $4,5\text{-}(CH_3)_2\text{-}o$-PDA. The crystal structure of $[PPh_4(VCl_4([(NH_2)_2C_6H_2Me_2)]$ has been determined. Mn(II) complexes *trans*-$MnI_2(o\text{-PDA})_2$ and similarly with $4,5\text{-}(CH_3)_2\text{-}o$-PDA have also been prepared [182].

The interaction of $WCl_6$ and *o*-PDA in PrOH affords the binuclear compound $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]$ (two rings (b) and one chelate ring (e), Fig. 4) [183]. The structure (Fig. 12) indicates that the metal centres, which are related by symmetry, have octahedral coordination with a *mer* arrangement of the three chlorides. The link to the bridging $(\mu\text{-}C_6H_4(N)_2)$ ligand involves a W=N double bond (1.75(2) Å). The chelating 1-(HN), $2\text{-}(H_2N)C_6H_4$ gives W–N bond lengths of 1.92(2) (amido) and 2.29(2) Å (amino); the latter bond is *trans* to the multiply bonded imine function. This molecule contains the first example of a bridging $1,2\text{-}(N)_2C_6H_4$ group formally derived from *o*-benzoquinonediimine. Examples of bridging $1,2\text{-}(HN)_2C_6H_4$ are, however, known [184,185] for ruthenium. The synthesis of $[Ru_2\text{-}\{\text{-}\mu\text{-}(NH)_2C_6H_4\}\text{–}(CO)_4(PPh_3)_2]$ in good yield [184] (Fig. 13), the first binuclear ruthenium(I) complex stabilized by benzeno-1,2-diamide and having the shortest Ru–Ru distance (2.560(1) Å) reported for ruthenium(I) species, allowed studies of its reactivity towards Lewis acids and ligand-substitution reactions, as for example reaction with diphosphines to give the dinuclear complex

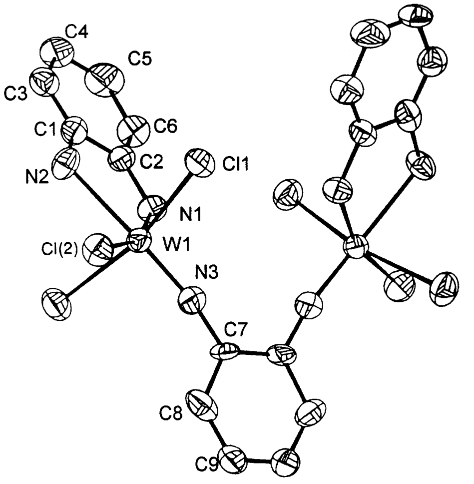


Fig. 12. The structure of $\{WCl_3[1\text{-}(HN),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]$. Adapted from Ref. [183].

$[Ru_2\{\mu\text{-}1,2\text{-}(HN)_2C_6H_4\}\{\mu\text{-}(Ph_2P)_2\text{–}CH_2\}(CO)_2(PPh_3)_2]$, which structure has been determined [185]. Carugo et al. [186] have analysed the known crystal structures of metal complexes containing *o*-PDA derivatives in the form of the benzenediamine dianion (Fig. 4(c)), benzosemiquinonediimine monoanion (Fig. 4(f)) or neutral benzoquinonediimine (Fig. 4(g)) [163–165,167,170,174–178,187,188]. The results are compared with literature oxidation-state assignments, and discussed in terms of the back-bonding ability of the ligands.

Ab initio Hartree–Fock calculations have been carried out on the complex $L_2Pt(\eta^2\text{-}O_2)$ and its derivatives $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XY)$ obtained by reaction with HX ($HX = H_2O$, HCl, HOO–CH, $NH_3$) and HXYH (HXYH = *o*-PDA, etc.) [189]. In theoretically optimized molecular structures of the $(PH_3)_2Pt(OOH)(XYH)$ obtained by internal protonation reaction with *o*-PDA, the ligand is monodentate, while in $(PH_3)_2Pt(OOH)(XY)$ complexes obtained by an internal protonation reaction, the ligand *o*-PDA is bidentate.

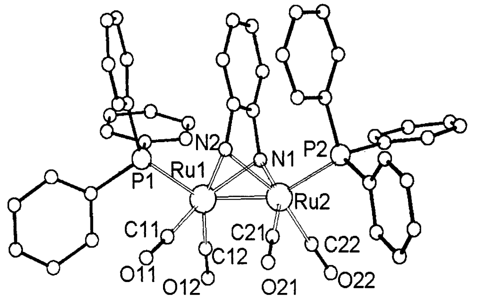


Fig. 13. PLUTO view of the binuclear complex $[Ru_2\text{-}\{\text{-}\mu\text{-}(NH)_2C_6H_4\}\text{-}(CO)_4(PPh_3)_2]$. Adapted from Ref. [184].

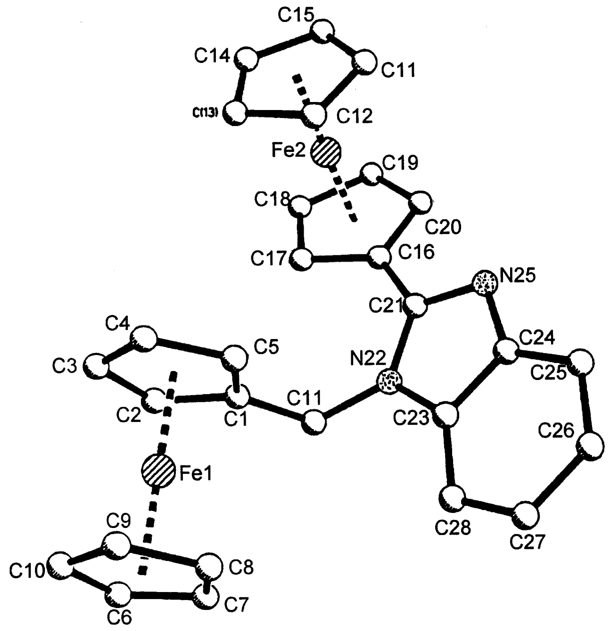
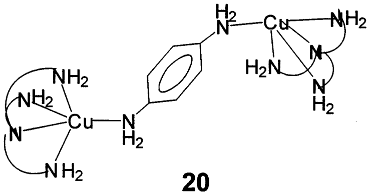


Fig. 14. Crystal structure of *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole. Adapted from Ref. [190].

The reaction of ferrocenecarbaldehyde with *o*-PDA in the presence of *p*-toluenesulphonic acid results in the synthesis of *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole (Fig. 14) [190].

### 2.6.3. *m*- And *p*-phenylenediamine complexes

Studies of coordination compounds of *m*-PDA and *p*-PDA in solid state are rare, possibly because these ligands can only coordinate one nitrogen atom to metal atom by means of a weak linkage. However, Falthouse and Hendrickson [191] have reported a series of binuclear copper(II) complexes of the form $[Cu_2(tren)_2(DA)](Y)_4$, where tren is 2,2′,2″-triamino-triethylamine, DA represents an aromatic diamine such as *p*-PDA or durenediamine (DDA) and $Y^-$ is variously $NO_3^-$, $ClO_4^-$ or $PF_6^-$. Additionally vanadyl complexes of the form $[VO(hfac)_2]_2$ (DA) have also been prepared, where $hfac^-$ is 1,1,1,5,5,5,-hexafluoroacetylacetonate and DA is *p*-PDA or DDA. The Cu(II) binuclear complexes (**20**) are the first discrete compounds to be isolated containing redox-active aromatic diamines.



**20**

Antiferromagnetic exchange interactions are found for all Cu(II) complexes. The molecule of *p*-PDA is a bridge between both Cu(II) ions (**20**). The *g* value of 2.011 is closest to the free-electron value of 2.0023 for any of the compounds in this study. This pattern is clearly indicative of a trigonal-bypiramidal copper(II) coordination geometry with a $d_z^2$ ground state. The *p*-PDA compound shows the greatest antiferromagnetic interaction indicating the effectiveness of a predominantly $d_z^2$ orbital in transmitting antiferromagnetic interaction. No interactions could be detected in the vanadyl complexes. These complexes provide an opportunity to observe the effect of altering the metal ion ($Cu^{2+}$ to $VO^{2+}$) and its ground state ($d_z^2$ to $d_{xy}$) on the magnetic exchange interaction.

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## References

[1] J. McMurry, Organic Chemistry, Chap 26, 3rd Edition, Brooks/Cole, New York, 1992.
[2] L.F. Fieser, M. Fieser, Organic Chemistry, Chap. 25, 3rd Edition, Reinhold, New York, 1958.
[3] W.J. Hehre, L. Random, P.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986, p. 386.
[4] A. Mederos, F.G. Manrique, J.V. Herrera, M. Alvarez-Romero, An. Quim. 77B (1981) 294.
[5] R.J. Motekaitis, A.E. Martell, Inorg. Chem. 27 (1988) 2718.
[6] (a) R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, P. Núñez, G. Germain, T. Debaerdemaeker, Inorg. Chim. Acta 256 (1997) 319. (b) R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, F. Lloret, J. Cano, M. Julve, C. Ruiz-Pérez, X. Solans, J. Chem. Soc. Dalton Trans. (1997) 4327.
[7] A. Mederos, J.V. Herrera, A. Benítez, A. Rancel, An. Quím. 84B (1988) 5.
[8] (a) R.M. Smith, A.E. Martell, Critical Stability Constants, Vol. 2, Plenum Press, New York, 1975, pp, 49–50; Vol. 6, 1989, p. 472. (b) K Kina, K. Toci, Bull. Chem. Soc. Jpn. 44 (1971) 1289.
[9] R.M. Smith, A.E. Martell, R.J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes Database. Version 2.0, US Department of Commerce, Gaithersburg, MD20899, 1995.
[10] (a) A. Mederos, F.G. Manrique, J.V. Herrera, M. Alvarez-Romero, J.M. Felipe, An. Quim. 82B (1986) 133. (b) F.G. Manrique, A. Mederos, A. Rodríguez-González. A. Hardisson, Y.G. Smeyers, An. Quim. 69 (1973) 305.
[11] D.C. Harris, M.D. Bertolucci, Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy, Oxford Molecular Symmetry, Van Nostrand, London, 1965, pp. 203–211 and 242–246.
[12] R. Noto, M. Leone, S.L. Fornili, J. Mol. Struct. 422 (1998) 35.
[13] A. Domenicano, E.F. Serantoní, L.R. di Sanseverino, Acta Crystallogr. Sect. B 33 (1977) 1664.
[14] C. Stålandske, Cryst. Struct. Commun. 10 (1981) 1081.
[15] C. Stålandske, Acta Crystallogr. Sect. B 32 (1976) 2806.
[16] C. Stålandske, Acta Chem. Scand. 26 (1972) 2962.
[17] R. Taylor, D. Kennard, Acta Crystallogr. Sect. B 39 (1983) 517.
[18] C. Stålandske, Acta Crystallogr. Sect. B, 30 (1974) 1586.

[19] C. Stålandske, Acta Chem. Scand. 26 (1972) 3029.

[20] K. Kozawa, T. Uchida, Bull. Chem. Soc. Jpn. 55 (1982) 943.

[21] R. Chandrasekaren, Acta Crystallogr. Sect. B 25 (1969) 369.

[22] Q. Won Choi, Ch. Hoe Koo, J. Suk Oh, Ch. Soo Yoo, Daehan Hwahak Hwoejee 9 (1965) 174.

[23] S.G. Cohen, A. Parola, G.H. Parsons, Chem. Rev. 73 (1973) 141.

[24] H. Masuhara, N. Mataga, Acc. Chem. Res. 14 (1981) 312.

[25] G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401.

[26] R. Foster, Organic Charge Transfer Complexes, Academic Press, New York, 1969.

[27] (a) H.D. Roth, Tetrahedron 42 (1986) 6097. (b) C. Würster, Chem. Ber. 12 (1879) 522 and 2071; C. Würster, R. Sendtner, Chem. Ber. 12 (1879) 1803; C. Würster, E. Schobig, Chem. Ber. 12 (1879) 1807. (c) E. Weitz, Z. Electrochem. 34 (1928) 538. (d) S.I. Weissman, J. Townsend, D.E. Paul, G.E. Pakt, J. Chem. Phys. 21 (1953) 2227.

[28] C.R. Bruce, R.E. Norberg, S.I. Weissman, J. Chem. Phys. 24 (1956) 473.

[29] G. Gramp, W. Jaenicke, Ber. BunsenGes. Phys. Chem. 88 (1984) 325; 88 (1984) 335; 95 (1991) 904.

[30] (a) N. Sutin, Prog. Inorg. Chem. 30 (1983) 441. (b) R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.

[31] J.L. De Boer, A. Voss, Acta Crystallogr. Sect. B 835 28 (1972) 839.

[32] (a) J.L. De Boer, A. Vos, K. Huml, Acta Crystallogr. Sect. B 24 (1968) 542. (b) J. Yamauchi, H. Fujita, Bull. Chem. Soc. Jpn. 63 (1990) 2928.

[33] A. Mani, B.M. Vedavathi, K. Vijayan, Curr. Sci. 51 (1982) 192.

[34] D. Reefman, J.P. Cornelissen, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, Inorg. Chem. 30 (1991) 4928.

[35] D. Attanasio, M. Bonamico, V. Fares, L. Suber, J. Chem. Soc. Dalton Trans. (1992) 2523.

[36] (a) Z.G. Soos, R.C. Hughes, J. Chem. Phys. 48 (1968) 1066. (b) Z.G. Soos, H.J. Keller, K. Ludolf, J. Queckbörner, D. Wehe, S. Flandrois, J. Chem. Phys. 74 (1981) 5287.

[37] J.S. Miller, Extended Linear Chain Compounds, Vols. 1–3, Plenum Press, New York, 1982, 1983.

[38] A.W. Hanson, Acta Crystallogr. Sect. B 24 (1968) 768.

[39] T.P. Radhakrishnan, Z.G. Soos, H. Endres, J.J. Azevedo, J. Chem. Phys. 85 (1986) 1126.

[40] (a) H. Endres, W. Jentsch, H.J. Keller, R. Martin, W. Moroni, D. Nöthe, Z. Naturforsch. Teil B 34 (1979) 140. (b) H. Endres, H.J. Keller, W. Moroni, D. Nöthe, Inorg. Nucl. Chem. Lett. 12 (1976) 825.

[41] (a) M.J. Hove, B.M. Hoffman, J.A. Ibers, J. Chem. Phys. 56 (1972) 3490. (b) B.L. Ramkrishna, P.T. Manoharan, Inorg. Chem. 22 (1983) 2113.

[42] M. Hoshino, M. Kagata, H. Seki, H. Seto, J. Am. Chem. Soc. 118 (1996) 2160.

[43] (a) G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401. (b) Y. Hirata, N. Mataga, J. Phys. Chem. 88 (1984) 3091. (c) R.D. Fossum, M.A. Fox, J. Phys. Chem. B 101 (1997) 2526.

[44] S.F. Nelsen, R.F. Ismagilov, D.R. Powell, J. Am. Chem. Soc. 118 (1996) 6313.

[45] H. Honma, H. Murai, K. Kuwata, J. Phys. Chem. 98 (1994) 2571.

[46] (a) J.E. Packer, R.L. Willson, D. Bahnemann, K.D. Asmus, J. Chem. Soc. Perkin Trans. II (1980 )296; (1983) 1133. (b) R.E. Huie, P. Nefa, P. Int. J. Chem. Kinet. 18 (1986) 1185. (c) R.E. Huie, D. Brault, P. Nefa, Chem. Biol. Interact. 62 (1987) 227.

[47] (a) S. Fujita, S. Steenken, J. Am. Chem. Soc. 103 (1981) 2540. (b) D.K. Hazra, D.K. Steenken, J. Am. Chem. Soc. 105 (1983) 4380. (c) P. Nefa, R.E. Huie, S. Mosseri, L.V. Shastri, J.P. Mittal, P. Maruthamuthu, J. Phys. Chem. 93 (1989) 4099.

[48] L. Eberson, M. Ekström, Acta Chem. Scand. 43 (1989) 86.

[49] K. Wimalasena, D.Sh. Wimalasena, Biochem. Biophys. Res. Commun. 175 (1991) 920.

[50] A.J. Pearson, A.M. Gelormini, J. Org. Chem. 61 (1996) 1297.

[51] (a) T.J. Meyer, J.V. Caspar, Chem. Rev. 85 (1985) 187. (b) M.C. Baird, Chem. Res. 88 (1988) 1217. (c) D. Astruc, Chem. Rev. 88 (1988) 1189.

[52] J. Balla, J.H. Espenson, A. Bakac, J. Chem. Phys. 99 (1995) 3598.

[53] K. Wimalasena, D.S. Wimalasena, Anal. Biochem. 197 (1991) 353.

[54] (a) P.S. Rao, E. Hayon, J. Phys. Chem. 79 (1975) 1063. (b) L. Michaelis, M.P. Schubert, S. Granick, J. Am. Chem. Soc. 61 (1939) 1981.

[55] C. Li, Ch.D. Oldham, Sh.W. May, Biochem. J. 300 (1994) 31.

[56] Y.-H. Chen, U. Nickel, M. Spiro, J. Chem. Soc. Faraday Trans. 90 (1994) 617.
[57] R.K. Tangirala, F. Casanada, W. Pelinski, Arteriosc. Thromb. Vasc. Biol. 15 (1995) 1625.
[58] D.I. Metelitza, N.V. Girina, T.V. Cherendnikova, Biochemistry 60 (1995) 1269.
[59] Th. Wandlowski, D. Gosser Jr., E. Arkinele, R. de Levie, V. Horak, Talanta 40 (1993) 1789.
[60] (a) H.A. Mottola, Kinetics Aspects of Analytical Chemistry, Wiley, New York. 1988. (b) D. Pérez-Bendito, M. Silva, Kinetics Methods in Analytical Chemistry, Horwood, Chichester, 1988.
[61] T. Kawashima, S. Nakano, Anal. Chim. Acta 261 (1992) 167.
[62] S. Nakano, M. Nosawa, M. Yanagawa, Anal. Chim. Acta 261 (1992) 183.
[63] S. Nakano, K. Tsujii, T. Kawashima, Talanta 42 (1995) 1051.
[64] S. Nakano, K. Nakaso, K. Noguchi, T. Kawashima, Talanta 44 (1997) 765.
[65] K. Hirayama, N. Unohara, Anal. Chem. 60 (1988) 2573.
[66] (a) S. Kreingold, L. I. Sosenkova, Zh. Anal. Khim. 26 (1971) 332. (b) T. Kawashima, Y. Kozuma, S. Nakano, Anal. Chim. Acta 106 (1979) 355. (c) S. Nakano, M. Odzu, M. Tanaka, T. Kawashima, Mikrochim. Acta 1 (1983) 403.
[67] S. Kawakubo, K. Ogihara, M. Iwatsuki, Analyst 120 (1995) 2719.
[68] J.K. Gupta, Talanta 38 (1991) 1167.
[69] Standard Methods for the Analysis of Water and Wastewater, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, 16th edition, 1985, pp. 470–478.
[70] Y. Yamamoto, M. Umeda, K. Morishige, Y. Nishikawa, Bunseki Kagaku 37 (1988) 421.
[71] Y. Ogasawara, K. Ishii, T. Togawa, Sh. Tanabe, Analyst 116 (1991) 1359.
[72] V.P. Yakimova, J. Anal. Chem. (URSS) 46 (1991) 993.
[73] J. Yang, G. Zhang, Y. Ding, Anal. Chim. Acta 363 (1998) 105.
[74] E. Ohtsuki, M. Suzuki, M. Takayanagi, Biol. Pharmacol. Bull. 17 (1994) 139.
[75] C. Li, C.D. Oldham, S.W. May, Biochem. J. 300 (1994) 31.
[76] M. Suzuki, M. Takayanagi, T. Yashiro, Chem. Pharm. Bull. 39 (1991) 2745.
[77] (a) R. de Surville, M. Jozefowicz, L.T. Yu, J. Perichon, R. Buvet, Electrochim. Acta 13 (1968) 1451. (b) A.F. Díaz, J.A. Logan, J. Electroaanal. Chem. 111 (1980) 111. (c) R. Noufi, A.J. Nozik, J. Wite, L. Warren, J. Electrochem. Soc. 129 (1982) 2261. (d) W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. I 82 (1986) 2385. (e) E.M. Genies, C. Tsintavis, J. Electroanal. Chem. 195 (1985) 109, (f) M. Leclere, J. Guay, L.H. Dao, Macromolecules 22 (1989) 649. (g) Y. Wei, W.W. Focke, G.E. Wnek, A. Ray, A.G. MacDiarmid, J. Phys. Chem. 93 (1989) 495. (h) D. MacInnis Jr., B.L. Funt, Synth. Met. 25 (1988) 235. (i) J.A. Osaheni, S.A. Jenekhe, H. Vanherzeele, J.S. Meth, Chem. Mat. 3 (1991) 218. (j) G.D'Aprano, M. Leclerc, G. Zotti, J. Electroanal. Chem. 351 (1993) 145.
[78] (a) H.C. Bach, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 7 (1966) 576. (b) E. Tsuchida, M. Kaneko, Y. Kurimura, Kogyo Kagaku Zasshi 72 (1969) 772.
[79] (a) B.M. Prasad, D. Sing, R.A. Misra, J. Polym. Mat. 13 (1996) 157. (b) H.B. Mark Jr., F.C. Anson, Anal. Chem. 35 (1963) 722.
[80] (a) J. Yano, K. Terayama, S. Yamasaki, J. Mater. Sci. 31 (1996) 4785. (b) J. Yano, S. Kai, K. Ogura, J. Mater. Sci. Lett. 12 (1993) 1791.
[81] (a) T. Ohsaka, T. Watanabe, F. Kitamura, N. Oyama, K. Tokuda, J. Chem. Soc. Chem. Commun. (1991) 1072. (b) J. Premkumar, R. Ramaraj, J. Appl. Electrochem. 26 (1996) 763.
[82] (a) K. Ogura, H. Shiigi, M. Nakayama, J. Electrochem. Soc. 143 (1996) 2925. (b) K. Ogura, M. Kokura, M. Nakayama, J. Electrochem. Soc. 142 (1995) L152.
[83] M.D. Levi, E. Yu. Pisarevskaya, Electrochem. Acta 37 (1992) 635.
[84] (a) J. Yano, Y. Higuchi, Kobunshi Ronbunshu 47 (1990) 817. (b) N. Oyama, T. Ohsaka, K. Chiba, K. Takahashi, Bull. Chem. Soc. Jpn. 61 (1988) 1095.
[85] (a) W.R. Heineman, H.J. Wieck, A.M. Yacynych, Anal. Chem. 52 (1080) 345. (b) G. Cheek, C.P. Wales, R.J. Nowak, Anal. Chem. 55 (1983) 380. (c) I. Rubinstein, Anal. Chem. 56 (1984) 1135.
[86] A. Volkov, G. Tourillon, P.C. Lacaze, J.E. Dubois, J. Electroanal. Chem. 116 (1980) 279.
[87] K. Chiba, T. Ohsaka, N. Oyama, J. Electroanal. Chem. 217 (1987) 239.
[88] K. Chiba, T. Ohsaka, Y. Ohnuki, N. Oyama, J. Electroanal. Chem. 219 (1987) 117.
[89] J. Yano, Ts. Nagaoka, J. Electroanal. Chem. 410 (1996) 213.

[90] L.-L. Wu, J. Liu, Zh.-H. Lin, J. Electroanal. Chem. 417 (1996) 53; 440 (1997) 173.

[91] M.-A. Goyectte, M. Leclerc, J. Electroanal. Chem. 382 (1985) 17.

[92] (a) K. Martinusz, G. Lang, G. Inzelt, J. Electroanal. Chem. 433 (1997) 1. (b) K. Martinusz, G. Inzelt, G. Horanyi, J. Electroanal. Chem. 395 (1995) 293.

[93] A. Malinauskas, R. Holze, Ver. Bunsenges, Phys. Chem. 101 (1997) 1851.

[94] T. Komura, Y. Funahasi, T. Yamaguti, K. Takahasi, J. Electroanal. Chem. 446 (1998) 113.

[95] J. Wang, Anal. Chem. 67 (1995) 487.

[96] E. Kress-Rogers (Ed.) Handbook of Biosensors and Electronic Noses, CRC Press, London, 1997.

[97] (a) S.P.J. Higson, P.M. Vadgama, Med. Eng. Comput. 32 (1994) 601. (b) J. Wang, L. Chen, F. Lu, Electroanalysis 8 (1996) 1127.

[98] S.P.J. Higson, M.A. Desai, I. Christie, P.M. Vagdama, J. Chem. Soc. Faraday Trans. 89 (1993) 2847.

[99] C. Liu, W.J. Chen, C.R. Martin, J. Membr. Sci. 65 (1992) 113.

[100] C.R. Martin, B. Ballarin, C. Brumlick, D.R. Lawson, ACS Symp. Ser. 556 (1994) 158.

[101] S. Myler, S. Eaton, S.P.J. Higson, Anal. Chim. Acta 357 (1997) 55.

[102] L.C. Clark Jr., Lyons, Ann. NY Acad. Sci. 102 (1962) 29.

[103] B. Grundig, C. Krabisch, Anal. Chim. Acta 222 (1989) 75.

[104] M. Senda, Ann. NY Acad. Sci. 613 (1990) 79.

[105] M.E. Meyerhoff, Clin. Chem. 36 (1990) 1567.

[106] M.A. Arnold, M.E. Meyerhoff, CTR Crit. Rev. Anal. Chem. 20 (1988) 149.

[107] D.J. Claremont, J.C. Pickup, in: A.P.F. Turner, I. Karube, G.S. Wilson (Eds.), Biosensors: Fundamentals and Applications, Oxford University Press, New York, 1987, pp. 356–376.

[108] (a) J.S. Soeldner, K.W. Change, S. Aisenberg, J.M. Hiebert, in: J. Urquhart, F.E. Yates (Eds.), Temporal Aspects of Therapeutics, Plenum Press, New York, 1973, pp. 181–207. (b) D.G. Velho, G. Reach, D.R. Thevenot, in: A.P.F. Turner, I. Karube, G.S. Wilson (Eds.), Biosensors: Fundamentals and Applications, Oxford University Press, New York, 1987, pp. 390–408.

[109] (a) C. Malitesta, F. Palmisano, L. Torsi, P.G. Zambonin, Anal. Chem. 62 (1990) 2735. (b) W. Sohn, P.W. Stoecker, W. Carp, A.M. Yacynych, Electroanalysis 3 (1991) 763.

[110] R.D. O'Neill, Analyst 119 (1994) 767.

[111] (a) J.P. Lowry, K. McAteer, S.S. El Atrash, A. Duff, R.D. O'Neill, Anal. Chem. 66 (1994) 1754. (b) J.P. Lowry, K. McAteer, S.S. El Atrash, R.D. O'Neill, J. Chem. Soc. Chem. Commun. (1994) 2483. (c) E. Dempsey, J. Wang, M.R. Smyth, Talanta 40 (1993) 445. (d) F. Moussy, D.J. Harrison, D.W. O'Brien, R.V. Rajotte, Anal. Chem. 65 (1993) 2072. (e) J. Wang, H. Wu, Anal. Chim. Acta 283 (1993) 683. (f) P.N. Bartlett, P.R. Birkin, Anal. Chem. 66 (1994) 1552. (g) F. Palmisano, A. Guerrieri, M. Quinto, P.G. Zambonin, Anal. Chem. 67 (1995) 1005. (h) T. Yao, M. Satomura, T. Nakahara, Electroanalysis (NY) 7 (1995) 395. (i) K. McAteer, R.D. O'Neill, Analyst 121 (1966) 773.

[112] (a) M.J. Lobo-Castañon, A.J. Miranda-Ordieves, D. Tuñon-Blanes, 346 (1997) 165. (b) E. Dempsey, J. Wang, Talanta 40 (1993) 445.

[113] F. Scheller, F. Schubert, Biosensors, Elsevier, Amsterdam, 1992.

[114] (a) M.J. Lobo, A.J. Miranda, J.M. López-Fonseca, P. Tuñón, Anal. Chim. Acta, 325 (1996) 33. (b) M.J. Lobo, A.J. Miranda, P. Tuñón, Biosens. Bioelectron. 12 (1997) 511.

[115] (a) S. Shi-Hui, X. Yuan-Jin, N. Li-Hua, Y. Shou-Zhuo, Talanta 42 (1995) 469. (b) J. Wang, L. Chen, L. Deng-Bai, Analyst. Commun. 34 (1997) 217.

[116] Ch.-H. Yang, T.-Ch. Wen, J. Electrochem. Soc. 144 (1997) 2078.

[117] F. Cataldo, Eur. Polymer J. 32 (1996) 43.

[118] J.W. Weisburger, in: C.M. King, L.J. Romano, D. Sahuetzle (Eds.), Carcinogenic and Mutagenic Responses to Aromatic Amines and Nitroarenes, Elsevier, New York, 1988, pp. 3–19.

[119] (a) F.P. Guengerich, M.A. Butler, T.L. McDonald, F.F. Kadlubar, in: C.M. King, L.J. Romano, D. Schuetzle (Eds.), Carcinogenic and Mutagenic Responses to Aromatic Amines and Nitroarenes, Elsevier, New York, 1988, pp. 89–95. (b) T.H. Eling, T.W. Petry, M.F. Hughes, R.S. Krauss, in: ibid, pp. 161–172.

[120] (a) M.J. Plewa, S.R. Smith, E.D. Wagner, Mutat. Res. 247 (1991) 57. (b) T. Gichner, G.C. López, E.D. Wagner, M.J. Plewa, Mutat. Res. 306 (1994) 165.

[121] (a) K.Y. Seo, J. Riley, D. Cortez, E.D. Wagner, A.J. Plewa, Mutat. Res. 299 (1993) 111. (b) M.J. Plewa, E.D. Wagner, Annu. Rev. Genet. 27 (1993) 93. (c) E.D. Wagner, S.R. Smith, H. Sin, M.J. Plewa, Environ. Mol. Mutagen 23 (1994) 64.
[122] M.J. Plewa, Environ. Health Perspect. 27 (1978) 45.
[123] T. Gitcher, D.A. Stavreva, N. Cerovská, E.D. Wagner, M.J. Plewa, Mutat. Res. 331 (1995) 127.
[124] J.M. Gentile, G.J. Gentile, Mutat. Res. 250 (1991) 79.
[125] T. Watanabe, T. Hirayama, S. Fukui, Mutat. Res. 245 (1990) 15.
[126] T. Watanabe, Mutat. Res. 227 (1989) 135.
[127] (a) I.S. Grover, S. Kaur, Ind. J. Exper. Biol. 27 (1989) 207. (b) L. Wilson, T. Williamson, J. Gronowski, Mutat. Res. 307 (1994) 185. (c) P. Isern, J. Riera, J. Sitjes, Mutat. Res. 312 (1994) 25.
[128] R.R. Tice, in: D.H. Phillips, S. Venitt (Eds.), Environmental Mutagenesis, BIDS Scientific, Oxford, 1995.
[129] M.J. Plewa, E.D. Wagner, T.-W. Yu, D. Anderson, Environ. Mol. Mutagen 26 (1995) 175.
[130] B.N. Ames, H.O. Kammen, E. Yamasaki, Proc. Natl. Acad. Sci. USA 72 (1975) 2427.
[131] K.-T. Chung, S.E. Stevens Jr., Environ. Toxicol. Chem. 12 (1993) 2121.
[132] K.-T. Chung, S.E. Stevens Jr., C.E. Cerniglia, Crit. Rev. Microbiol. 18 (1992) 175.
[133] (a) K.-T. Chung, C.A. Murdock, S.E. Stevens Jr., Y.-S. Li, C.-I. Wei, T.-S. Huang, M.W. Chu, Toxicol. Lett. 81 (1995) 23. (b) M.M. Shahin, Mutat. Res. 307 (1994) 83
[134] T. Fukunaga, R. Kawagoe, T. Kanzaki, Contact Dermatitis 35 (1996) 185.
[135] P. Rebandel, E. Rudzki, Contact Dermatitis 33 (1995) 138.
[136] R. Braucaccio, D.E. Cohen, Contact Dermatitis 32 (1995) 313.
[137] H. Yagi, Hum. Exper. Toxic. 15 (1996) 617; Food Chem. Toxicol. 34 (1996) 1195.
[138] R. Munday, Chem. Biol. Interact. 82 (1992) 169.
[139] T.W. Salcedo, H.B. Fleit, J. Immunol. Methods 148 (1992) 209.
[140] M. Krastera, F.J. Nicolás, G. Chabeau, Int. Arch. Allerg. Immunol. 102 (1993) 200.
[141] C. Sood, S. Khan, P.J. O'Brien, Biochim. Biophis. Acta 1335 (1997) 343.
[142] Dangerous properties of industrial materials rep. 15 (1995) 92.
[143] V.S. Mekler, S.M. Bystryak, Anal. Chim. Acta 264 (1992) 359.
[144] C.P. Sparrow, T.W. Doebber, J. Olszewski, J. Clin. Invest. 89 (1992) 1885.
[145] C. Storle, Chemico Biol. Interact. 78 (1991) 321.
[146] T.A. Connors, M. Jones, W.C.J. Ross, P.D. Braddock, A.R. Khokhar, M.L. Tobe, Chem. Biol. Interact. 5 (1972) 415.
[147] G.R. Gale, L.M. Loretta, M. Atkins, E.M. Walker, A.B. Smith, S.J. Meischen, Proc. Soc. Exp. Biol. Med. 142 (1973) 1349.
[148] S.J. Meischen, G.R. Gale, L.M. Lake, C.J. Frangakis, M.G. Rosemblum, F.M. Walker, L.M. Atkins, A.B. Smith, J. Natl. Cancer Inst. 57 (1976) 841.
[149] H.J. Burchenal, K. Kalaher, K. Dew, L. Lokys, Cancer Treat. Rep. 63 (1979) 1493.
[150] C. Hansch, B.H. Venger, A. Panthananickal, J. Med. Chem. 23 (1980) 459.
[151] R. Köckerbauer, P.J. Bednarski, J. Inorg. Bioch. 62 (1996) 281.
[152] F.J. Andres-Ordax, J.M. Merino, Bull. Soc. Chim. France (1980) I–61.
[153] (a) W. Hieber, C. Schliessmann, K. Ries, Z. Anorg. Chem. 180 (1929) 89. (b) W. Hieber, H. Appel, Z. Anorg. Chem. 196 (1931) 193. (c) W. Hieber, R. Wiesboeck, Chem. Ber. 91 (1958) 1146.
[154] M. Papafil, Ann. Sci. Univ. Jassy 20 (1934) 139.
[155] M.S. Barbinok, I.S. Bukhareva, Zhur. Neorg. Khim. 10 (1965) 861; Russ. J. Inorg. Chem. 10 (1965) 464.
[156] R. Lematescu, Ann. Sci. Univ. Jassy 18 (1933) 404.
[157] (a) D. Bandyopadhayay, J. Indian Chem. Soc. 34 (1957) 798. (b) S. Prasad, V. Krishnan, J. Indian Chem. Soc. 35 (1958) 352. (c) S. Prasad, Y.M. Reddy, M.S. Seethapathy, J. Indian Chem. Soc. 42 (1965) 46. (d) G. Maki, J. Chem. Phys. 29 (1958) 162.
[158] K. Wuethrich, S. Fallab, Helv. Chim. Acta 3 (1964) 841.
[159] D.R. Marks, D.J. Phillips, J.P. Redfern, J. Chem. Soc. A (1967) 1464; (1968) 2013.
[160] E.J. Duff, J. Chem. Soc. A (1968) 434.
[161] G.A. Renovich, W.A. Baker, J. Chem. Soc. A (1969) 75.
[162] J.A. Kakazai, G.A. Melson, Inorg. Chim. Acta 2 (1968) 186.

[163] R.C. Elder, D. Koran, H.B. Mark Jr., Inorg. Chem. 13 (1974) 1644.

[164] S.-M. Peng, C.-T. Chen, D.-S. Liaw, C.-I. Chen, Y. Wang, Inorg. Chim. Acta 101 (1985) L31.

[165] P.-H. Cheng, H.-Y. Cheng, C.-C. Lin, S.-M. Peng, Inorg. Chim. Acta 169 (1990) 19.

[166] F. Feigl, M. Fürth, Monatsch. 48 (1927) 45.

[167] G.S. Hall, R.H. Sodelberg, Inorg. Chem. 7 (1968) 2300.

[168] E.I. Stiefeld, J.H. Waters, E. Billig, H.B. Gray, J. Am. Chem. Soc. 87 (1965) 3016.

[169] A.L. Balch, R.H. Holm, J. Am. Chem. Soc. 88 (1966) 5201.

[170] M. Zehnder, H. Löliger, Helv. Chim. Acta 63 (1980) 754.

[171] W. Hieber, A. Lipp, Chem. Ber. 92 (1959) 2075.

[172] G.A. Renovitch, W.A. Baker, J. Chem. Soc. A (1969) 75.

[173] V.L. Goedken, J. Chem. Soc. Chem. Commun. (1972) 207

[174] G.G. Christoph, V.L. Goedken, J. Am. Chem. Soc. 95 (1973) 3869.

[175] S.-M. Peng, K. Peters, E.M. Peters, A. Simon, Inorg. Chim. Acta 101 (1985) L35.

[176] H.-Y. Cheng, S.-M. Peng, Inorg. Chim. Acta 169 (1990) 23.

[177] P. Belser, A. von Zelewsky, M. Zehnder, Inorg. Chem. 20 (1981) 3098.

[178] A.A. Danopoulos, A.C.C. Wong, G. Wilkinson, M.B. Hursthouse, B. Hussain, J. Chem. Soc. Dalton Trans. (1990) 315.

[179] J. Jubb, L.F. Larkworthy, L.F. Olivier, D.C. Povey, G.W. Smith, J. Chem. Soc. Dalton Trans. (1991) 2045.

[180] W.-H. Leung, A.A. Danopoulos, G. Wilkinson, B.H. Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1991) 2051.

[181] L.F. Larkworthy, K.B. Nolan, P. O'Brien, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 3, sect. 35.4.2, Pergamon Press, Oxford, 1987.

[182] C. Redshaw, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1992) 1803.

[183] C. Redshaw, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1992) 555.

[184] S. García-Granda, R. Obeso-Rosete, J.M. Rubio, A. Anillo, Acta Crystallogr. Sect. C 46 (1990) 2043.

[185] A. Anillo, R. Obeso-Rosete, M.A. Pellinghelli, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1991) 2019.

[186] O. Carugo, K. Djinovic, M. Ricci, C.B. Castellani, J. Chem. Soc. Dalton Trans. (1991) 1551

[187] M.-L. Hsieh, M.-C. Cheng, S.-M. Peng, Inorg. Chim. Acta 145 (1988) 1.

[188] S.-M. Peng, D.-S. Liaw, Inorg. Chim. Acta 113 (1986) L11.

[189] P. Fantucci, S. Lolli, M. Pizotti, Inorg. Chem. 33 (1994) 2779.

[190] A. Benito, R. Martínez-Mañez, J. Payá, J. Soto, M.J.L. Tendero, E. Sinn, J. Organomet. Chem. 503 (1995) 259.

[191] T.R. Felthouse, D.N. Hendrickon, Inorg. Chem. 17 (1978) 2636.