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Anhydrooligomers of *o*-aminobenzaldehydes—the rich chemistry of the Busch macrocycles[1]

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Contents

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[1] Dedicated to Professor Daryle H. Busch on the occasion of his 70th birthday.

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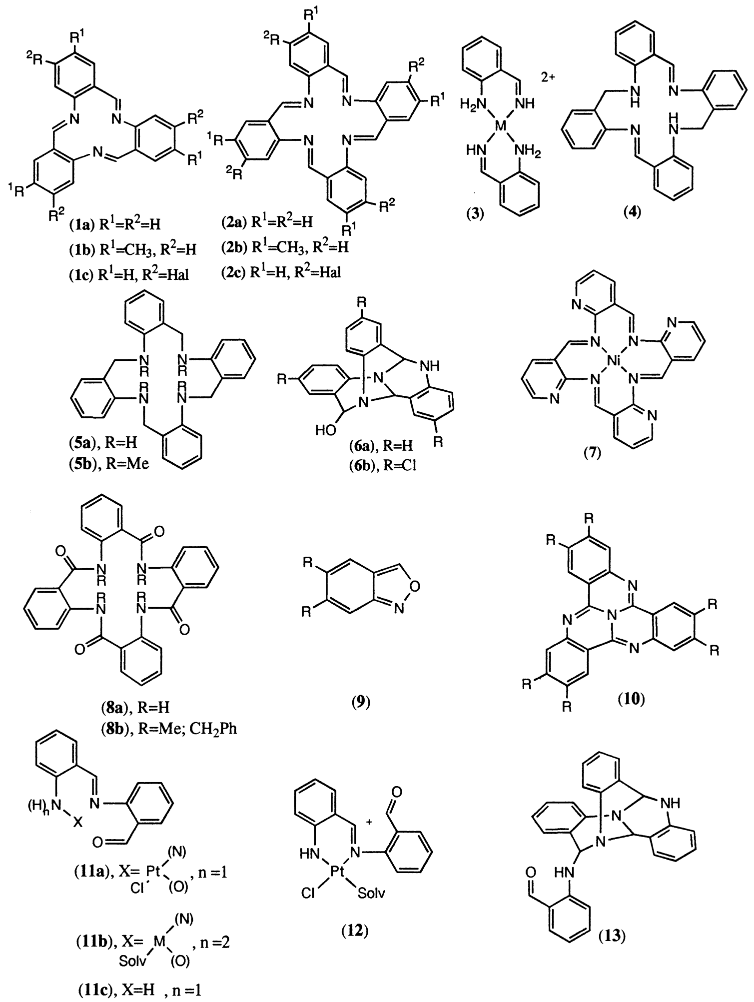
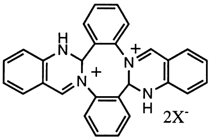


Fig. 1. *o*-Aminobenzaldehyde oligomers and related compounds.

Abstract

This review concerns macrocyclic coordination compounds formed in the metal-templated self-condensation reactions of *o*-aminobenzaldehyde and its derivatives. Both cyclic trimers (TRI) and cyclic tetramers (TAAB), as well as the products of nucleophilic addition, are described. Several synthetic approaches for the preparations of these materials, as well as factors influencing the TAAB/TRI ratio, are summarized. The role of the ligand in the redox chemistry of the coordinated metal ion is discussed, as are the products of ligand reduction. TAAB and TRI complexes as well as H_2TAAB salts exhibit several types of unusual isomerism; these are described. A variety of spectroscopic techniques have been applied in the study of these materials and the important results are summarized. Recent advances concerning the



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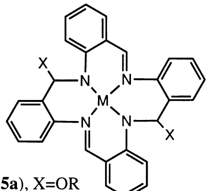
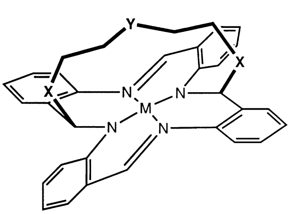
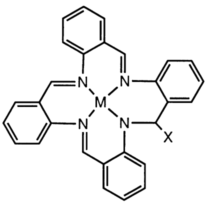


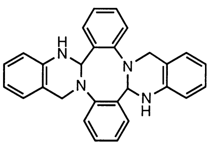
(**15a**), X=OR
(**15b**), X=NR^1R^2
(**15c**), X=$O(CH_2)_3NH_2$
(**15d**), X=R, CH_2Ph etc
(**15e**), X=$CH_2C(O)CH_3$



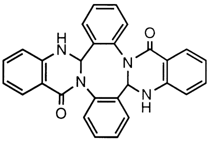
(**16a**), X=O, Y=NCH_3
(**16b**), X=O, Y=S
(**16c**), X=O, Y=O
(**16d**), X=NH, Y=$(CH_2)_2$



(**17a**), X=OCH_3
(**17b**), X=OC_2H_5



(**18**)



(**19**)

Fig. 1. (*continued*)

biochemical and anticancer activity of the titled compounds, as well as their analytical applications, are also mentioned. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: TAAB; TRI; Macrocyclic compounds; Template effect; Biological activity

1. Introduction: significance and historical notes

Metal complexes with ligands derived from *o*-aminobenzaldehydes (tris-anhydrotrimer (TRI) (**1**) and tetra-anhydrotetramer (TAAB) (**2**); see Fig. 1) constitute a specific class of coordination compounds in which the ligand and metal exert an unusually profound influence on one another's properties. Correct structures for these complexes were established in the early 1960s, in the wake of the recently formulated template hypothesis, and provided early support for this now universally accepted theory.

The metal complexes of TAAB and TRI, as well as the ligand salts, have provided interesting and unusual examples of isomerism, have attracted substantial attention from theoretical chemists, and, more recently, have shown promise in a variety of industrial and medicinal applications.

Despite the large number of papers now published on TAAB, TRI and related compounds, their chemistry has never been reviewed comprehensively as a separate topic. Certain aspects of their chemistry have been described in several reviews [1–3] and in books on the synthesis and physical chemistry of macrocycles [4–7].

This review covers the literature through the end of 1996 and includes some publications from 1997.

TAAB complexes played a pioneering role in both of the developmental stages of macrocyclic chemistry. During the first stage (late 1800s–early 1960s), when macrocyclic compounds such as the crown ethers [8] and phthalocyanines [9] were prepared serendipitously, without an appreciation for the chemical implications of their macrocyclic structures, TAAB derivatives were, to the best of our knowledge, the very first artificially synthesized macrocyclic compounds [10–12]. 65 years later, during the inception of modern macrocyclic chemistry, complexes of this ligand were among those compounds which fueled rapid development in the field.

The first synthesis of a macrocyclic TAAB complex in 1898, by Posner, was the adventitious result of an experiment directed towards other goals [11]. In an attempt to utilize anhydrous zinc(II) chloride as a catalyst for the Henry condensation between nitromethane and *o*-aminobenzaldehyde, Posner found that nitromethane did not participate in the reaction. Instead, he isolated an unexpected yellow crystalline product, which he described as an anhydroderivative of *o*-aminobenzaldehyde. The empirical formula for this condensation product, $C_7H_5N \cdot 0.5ZnCl_2$, was determined by Seidel in 1926 [12]. Ligand salts of TAAB were prepared by Friedländer and Henriques even earlier, in 1882, although the authors had no understanding of their structure [10]. In 1937 another group of German chemists investigated the condensation of *o*-aminobenzaldehyde with various metal ammino-complexes [13]. In doing so, they prepared a class of TAAB related complexes, which were described as benzaldimines (**3**) (Fig. 1).

The first deliberate investigation of the self-condensation of *o*-aminobenzaldehyde in the presence of metal ions was conducted by Eichhorn and Latif in 1954 [14]. In view of the limited separation and identification techniques available at that time and, more importantly, because the template concept had not yet been formulated, it is not surprising that they assigned incorrect open-chain trimeric structures to the resulting materials. Eichhorn and Latif did, however, make some important observations concerning the reactivity of their products; most notably, they found that the complexes were inert to both ligand- and metal-exchange reactions. They also observed color changes which occurred both upon addition of bases to the TAAB complexes and upon reaction of the copper complex with mercury. The transformations they recognized are now regarded as typical for many TAAB complexes.

Less than 10 years later, Busch and coworkers, obviously motivated by their recently developed template hypothesis [15], reinvestigated this self-condensation reaction [16–20]. They correctly proposed macrocyclic structures for both the TRI and TAAB complexes. Their structural formulations were soon confirmed by X-ray crystallography [21,22].

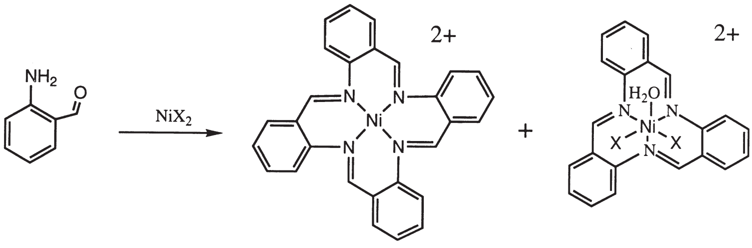
2. Methods of preparation

Neither the TAAB nor the TRI ligand seems to exist in the free state. Multiple attempts to demetallate the corresponding complexes by reaction with cyanides, sulfides or sodium amalgam failed to give free ligands. Attempts to deprotonate H_2TAAB salts or to dehydrogenate the partially saturated ligands (H_4TAAB (**4**) and H_8TAAB (**5a**); Fig. 1) were equally unsuccessful [5].

Although attempts to isolate the free ligands have been disappointing, the synthetic chemistry of the corresponding protonated derivatives, hydrogenated derivatives and transition metal complexes is well developed. Methods for their preparation are given below.

2.1. Template condensation of o*-aminobenzaldehyde and related compounds*

The self-condensation of *o*-aminobenzaldehyde in the presence of metal ions yields TRI and TAAB complexes [12,16–20,23–30]:



(1)

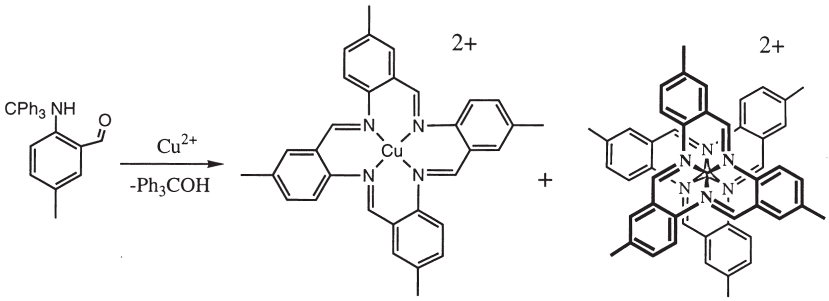
Factors which govern the TAAB/TRI ratio, and often lead to the exclusive preparation of one or the other complex, will be discussed in Section 2.3.

The template self-condensation of *o*-aminobenzaldehyde is one of the most dramatic and well-defined examples of a template reaction. The structures of the products derived from both the template and non-template condensations are well established and differ substantially from one another. TAAB and/or TRI complexes are obtained through the template condensation of *o*-aminobenzaldehyde in the presence of Fe^{2+} [24,26,27], Co^{2+} [28], Ni^{2+} [16–18,23,29], Cu^{2+} [16,17,23,29], Zn^{2+} [12,23], Pt(II) and Pd(II) [31]. The cobalt(III) complexes are prepared *in situ* via the oxidation of reaction mixtures containing Co^{2+} and *o*-aminobenzaldehyde [19,20]. The initial hypothesis that dimeric, metal–metal-bonded Co(II) complexes form under these conditions [32] was later proven to be incorrect [19]. The iron(III) complexes can be readily prepared from the Fe(II) complexes by chemical oxidation [26]. The template condensation of *o*-aminobenzaldehyde in the presence of oxovanadium(IV) is also accompanied by spontaneous oxidation of the metal ion. The reaction product is a binuclear oxovanadium(V) complex, containing two TRI moieties and two bridging OH-groups [25]. Eichhorn and Latif [14], and later Melson and Busch [17], pointed out that Mn^{2+} does not induce template condensation of *o*-aminobenzaldehyde to form TAAB or TRI complexes. These findings were reinvestigated and confirmed by Potter and Taylor [33]. The condensation products of this reaction were found to be identical to the previously investigated metal-free bisanhydro trimer (**6a**) (Fig. 1; see Section 2.2) and its ethoxy derivative. Similar reactivity was also reported for dioxouranium(VI) (see p. 87 of Ref. [6]).

Certain binuclear molybdenum(II) complexes act as templates in *o*-aminobenzaldehyde self-condensation reactions giving products closely related to TAAB [34,35]. These reactions will be discussed in Section 3.1. The Shukla group investigated oxotitanium(IV) and oxozirconium(IV) and reinvestigated oxovanadium(IV) and dioxouranium(VI) in the template condensation of *o*-aminobenzaldehyde [36]. Principally on the basis of elemental analysis and IR, the products were described as 1:1 oxocation/TAAB complexes. Inconsistencies between the authors' verbal and pictorial descriptions of the compounds, in combination with their apparent unawareness of Refs. [6,28], bring their structural conclusions into question.

Several aromatic and heterocyclic aminocarbonyl compounds were also found to participate in related oligocyclizations. Jircitano *et al.* reported the preparation of a TAAB related Ni(II) complex (**7**) (Fig. 1) from 2-amino-3-pyridinecarboxaldehyde [37]. Despite an initial report to the contrary [38], *o*-aminophenylketones were found to undergo cyclotrimerization processes leading to the formation of TRI-related ligands and copper(II) complexes [39,40]. Anthranilic acid tetramerizes, in the presence of several transition metal ions, forming a square planar complex with (**8a**) (Fig. 1) in the case of Cu^{2+}, or octahedral complexes, with (**8a**) and two additional axial ligands, in the cases of Co^{2+}, Ni^{2+} and Zn^{2+} [41]. Alkylated derivatives of the anhydrotrimers prepared from 2-aminobenzoic acid and 3-aminobenzoic acid, as well as the alkylated anhydrotetramers (**8b**), were studied by Ollis and coworkers [42–44]. Anthranils (**9**) (Fig. 1) condense to form tricycloquinazolines (**10**) (Fig. 1) when heated in the presence of ammonium acetate. The products are related to TRI and its substituted derivatives [45,46].

The first step in the template condensation of *o*-aminobenzaldehyde most likely includes initial template dimerization of *o*-aminobenzaldehyde activated by coordination to the metal ion. In the case where kinetically inert Pt(II) was used as a template, a reaction intermediate (**11a**) (Fig. 1) containing deprotonated *o*-aminobenzaldehyde anhydrodimer was isolated and thoroughly characterized [47–51]. A similar intermediate, derived from the addition of Pt(II) to 2-amino-5-chlorobenzaldehyde (**6b**) was also detected and isolated [52]. This is in contrast to 2-amino-5-methylbenzaldehyde [53]. The latter material (bearing an *N*-triphenylmethyl protecting group) is transformed directly to complexes of the macrocyclic ligand (**2b**):

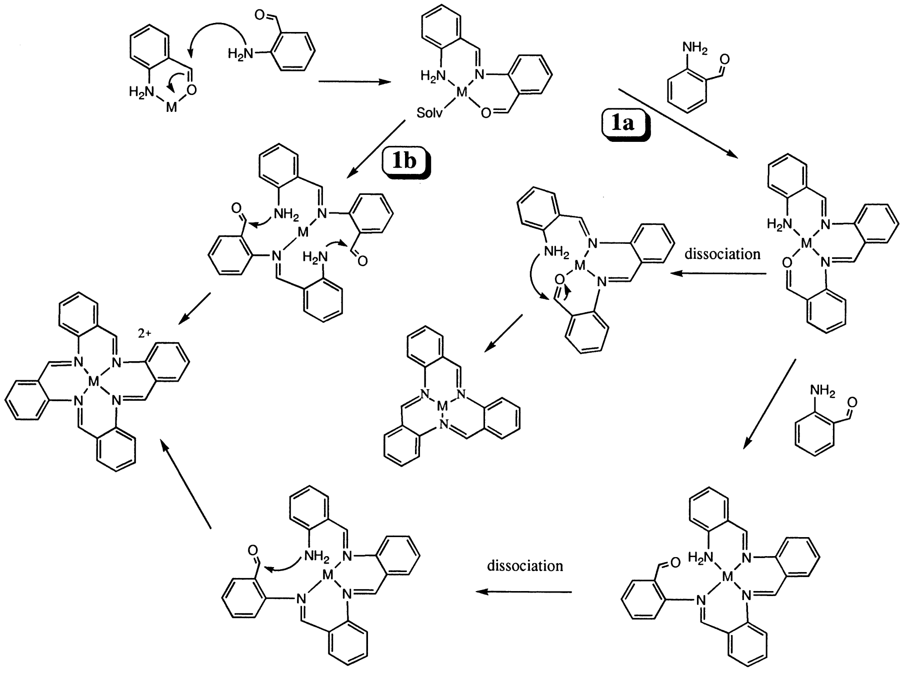


(2)

This observation illustrates the influence of *o*-aminobenzaldehyde substituents on the rate of condensation. Electron-donating substituents activate the amine function and facilitate the cyclization reaction, thus making the isolation of the intermediates impossible. Electron-withdrawing substituents retard the condensation substantially. Even in the presence of the highly effective template ion Ni^{2+}, 2-amino-5-chlorobenzaldehyde fails to undergo template condensation and the desired macrocyclic complex must be prepared via an alternative method [38].

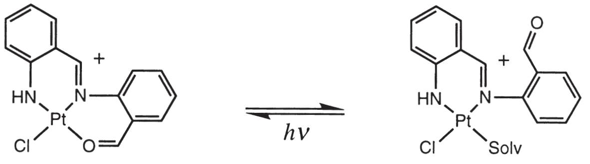
Two possible pathways have been suggested for the transformation of the intermediate (**11b**) into the macrocyclic complex [17,18,54] (Scheme 1). The first one (Scheme 1(a)) involves the stepwise addition of one or two molecules of *o*-aminobenzaldehyde followed by cyclization of the terminal groups. The thermodynamic template effect would be an operating factor in all steps of such a mechanism. Only the final cyclization step could be accelerated by the kinetic template effect. The alternative mechanism, obviously applicable only for TAAB complexes (Scheme 1(b)), requires initial dissociation of complex (**11b**) giving the free ligand (**11c**). One equivalent of (**11c**) then condenses with an equivalent of (**11b**) to give the macrocyclic complex. The rigidity of the both (**11b**) and (**11c**) may play an important role in the condensation. The analog of (**11c**), in which the azomethine bond has been hydrogenated, does not condense in the presence of metal ions to form H_4TAAB (**4**) [55].

Certain observations support the possibility of reaction intermediate (**11a**/**b**) dissociating. A deep purple solution of (**11a**) in DMSO or acetonitrile becomes light orange after storage in a dark place. This color change has been attributed to



Scheme 1. Two alternative pathways for the preparation of TAAB complexes by template condensation.

displacement of the aldehyde donor by solvent to give (**12**) (Fig. 1) [48,49]:



(**11a**) (**12**) (3)

This reaction is reversible and (**11a**) is regenerated when the solution is exposed to visible irradiation. This reversible dissociation was labeled a "photochromic swinging gate". Triphenylphosphine, and some other donor molecules, have been shown to displace the aldehyde irreversibly, forming complexes with non-coordinated pendant aminobenzaldehyde [48–50].

It has been demonstrated that coordination of the aldehyde group to the metal ion is critical in the template preparations of TAAB and TRI complexes, and elegant evidence for these was based on the photodissociation process described above. Complex (**12**) does not react to an appreciable extent with amines such as 1,2-diaminobenzene, 1,2-diaminoethane, *o*-aminobenzylamine, methylamine, etc. This is in contrast to complex (**11a**) which readily forms the corresponding Schiff bases [51]. These findings seem contrary to some of the early mechanisms [54] (Scheme 1(b)) and it may be that coordination of the aldehyde is significantly more important for the formation of TRI complexes than it is for TAAB complexes.

The significance of coordinated amino-group activation in these cyclo-oligomerization processes is not clear. The reaction of *o*-(diphenylphosphino)benzaldehyde with complex (**11a**), in which the terminal amino-group was expected to be activated by coordination and subsequent deprotonation, gives a mixture of products [50]. Formation of the expected trimeric Schiff base, comprised of two *o*-aminobenzaldehyde and one *o*-(diphenylphosphino)benzaldehyde fragments, was not detected.

2.2. Preparation from o-*aminobenzaldehyde oligomers*

It has been known for a long time that *o*-aminobenzaldehyde undergoes miscellaneous self-condensation reactions during storage and especially upon acidification (see Ref. [12] and references cited therein). It is now generally accepted that, in the absence of metal ions, *o*-aminobenzaldehyde forms at least three anhydrooligomers (**6a**, **13** and **14**; Fig. 1) [56,57]. All of them are useful starting materials for the preparation of TRI and TAAB complexes.

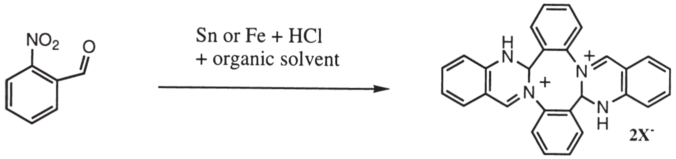
The bis-anhydrotrimer (**6a**) crystallizes from slightly acidified aqueous solutions of *o*-aminobenzaldehyde; 2-amino-5-chloro-benzaldehyde behaves similarly to form (**6b**) [38,56]. These materials are rearranged in their reaction with nickel(II) salts forming either octahedral mono-TRI or bis-TRI complexes, depending on the stoichiometry of the reagents used [56,58]. In the case of the mono-TRI complexes the other octahedral face is occupied by solvent molecules and anions. These monodentate ligands can be replaced by the addition of another equivalent of bis-anhydrotrimer (**6a**), but not by its chlorinated analog ClTRI (**6b**). In contrast to this, $Ni(ClTRI)(NO_3)_2(C_2H_5OH)$ reacts with unsubstituted bis-anhydrotrimer (**6a**) forming the mixed TRI–ClTRI complex. This difference was explained by the more reactive properties of (**6a**).

Whereas Ni^{2+}- and VO^{2+}-promoted bis-anhydrotrimer (**6a**) rearrangement leads to the exclusive formation of TRI complexes [25,38], this is not always the case. In contrast, Fe^{2+} and Cu^{2+} react with the bis-anhydrotrimer (**6a**) to form TAAB complexes exclusively [26,56].

Self-condensation of *o*-aminobenzaldehyde under strongly acidic conditions gives dicationic products (**14**) often abbreviated as H_2TAAB salts [57]. The same material can be obtained from *o*-aminobenzaldehyde and BF_3 in acetic acid [59]. The structure of these bright-red crystalline materials was disputed for many years [12,60], until Busch and coworkers, on the basis of spectroscopic and preliminary X-ray data, suggested the correct structure (**14**) [57]. The existence of two alternative conformers for H_2TAAB salts has recently been demonstrated [61] (see Section 4.3).

Bis-anhydrotrimer (**6a**), tris-anhydrotetramer (**13**), and $Zn(TAAB)^{2+}$ can also be converted to (**14**) by acidification [57]. The formation of (**14**) tetrabromocobaltate also accompanies the template condensation of *o*-aminobenzaldehyde in the presence of $CoBr_2$ [23]. Our attempts to prepare monomethyl-substituted H_2TAAB salts by the co-condensation of bis-anhydrotrimer (**6a**) and 4-methyl-2-aminobenzaldehyde in acidic media gave a statistical mixture of unsubstituted, mono-, bis-, tris- and tetra-substituted H_2TAAB salts, indicating that structural rearrangement of (**6a**), and possibly (**13**), into (**14**) probably involves the dissociation of oligomers into individual monomeric units [62].

An alternative method for the preparation of (**14**), based on the direct reduction of *o*-nitrobenzaldehyde by tin or iron in a mixture of hydrochloric acid and a neutral organic solvent, has recently been suggested [61]:



(4)

This method is convenient because it obviates the need for preparation of unstable *o*-aminobenzaldehyde.

Busch and coworkers demonstrated that H_2TAAB salts can be used as versatile starting materials for the preparation of miscellaneous macrocyclic compounds [57]. In reactions with metal acetates, H_2TAAB salts give, with few exceptions, the corresponding TAAB complexes. Chromium(III), manganese(II) [63], iron(II) [57,64], cobalt(II), nickel(II), copper(II) [53,57], copper(I) [65], zinc(II) [53,66], palladium(II) [53], and rhodium(III) [57] complexes have been prepared by this route. In the case of reaction of tetramethyl-substituted H_2TAAB salts with copper(II) acetate, the formation of both TAAB and TRI complexes was detected [53,67]. Reaction with $VOCl_2$ gives TRI complex exclusively [25]. $H_2TAAB(BF_4)_2$

reacts with potassium tetrachloroplatinate(II) analogously to free *o*-aminobenzaldehyde to give (**11a**), which is the same product formed from the reaction of free *o*-aminobenzaldehyde and potassium tetrachloroplatinate(II) [47]. Some other synthetic applications of H_2TAAB salts will be described in Section 3.1 and Section 3.2.

Hydrolysis of H_2TAAB salts, preferably in biphasic aqueous–organic systems, provides a convenient method of preparation for the trisanhydrotetramer (**13**) [12,56]. This material reacts with Ni^{2+} and Cu^{2+} in a manner analogous to that of the bisanhydrotrimer (**6a**). In the case of Ni^{2+}, the formation of both TAAB and TRI complexes was observed [38], whereas Cu^{2+} produces complexes of the tetrameric ligand, TAAB, exclusively [56].

The isomerization processes described above and some other well established synthetic transformations, such as spontaneous cleavage of the protecting group in Eq. (2), clearly indicate that metal complexes of the cyclic oligomers of *o*-aminoaldehyde are a thermodynamic sink and, consequently, can be prepared in a variety of ways with remarkably high yields.

2.3. TAAB vs TRI: the influencing factors

The template oligomerizations and rearrangements described above produce metal complexes of two azamacrocyclic ligands, TAAB and TRI. The ratio in which these two types of complex are formed depends on the precise balance of several influencing factors.

Firstly, the geometry of the template ion plays the most important role [18]. For octahedral ions the final cyclization step may occur on either trigonal face or around the tetragonal perimeter. Consequently, a mixture of TRI and TAAB complexes is expected, and such behavior is typical for cobalt and nickel ions [16–18,23,28]. Platinum(II) and palladium(II), which are typically tetragonal, give TAAB complexes exclusively [31].

Secondly, the size of the template ion was suggested as an influencing factor by Hawley and Blinn [25]. In reactions promoted by the very small vanadyl ion, several starting materials, including *o*-aminobenzaldehyde, the bisanhydrotrimer (**6a**) and, most importantly, H_2TAAB salts (**14**), gave TRI complexes exclusively. A small central ion simply cannot coordinate TAAB which has a relatively large cavity. An alternative explanation was also suggested in the same paper; the reaction product contains the VO_2^+ cation, which typically has its oxo ligands arranged cis to one another. This geometry may prevent equatorial TAAB coordination and facilitate, instead, the coordination (and stabilization) of TRI.

Thirdly, the relative solubilities of the trimeric and tetrameric products may be an influencing factor as well. This can be illustrated by the simultaneous formation of sparingly soluble CuMeTRI nitrate and highly soluble $CuMeTAAB^{2+}$ in the template condensation of protected 2-amino-5-methylbenzaldehyde [67]. This is in contrast to the exclusive formation of poorly soluble $CuTAAB^{2+}$ from unsubstituted *o*-aminobenzaldehyde [16,17,23]. Only limited data are available concerning the influence of other substituents on the TAAB/TRI ratio. In template condensations with Ni^{2+}, 4-fluoro-, 4-chloro-, and 4-bromo-2-aminobenzaldehydes give substituted trimeric complexes of (**1c**). With copper, only fluoro-substituted *o*-aminobenzaldehyde gives substituted TRI complex; the chloro- and bromo-derivatives give substituted CuTAABs [30].

Finally, the preferential transformation of the trimer (**6a**) into TRI complexes and the tetramers (**13** and **14**) into TAAB complexes suggests that there is a tendency toward conservation of degree of oligomerization. The Ni^{2+} template rearrangement of trimer (**6a**) gives TRI complex exclusively, whereas, in the same reaction, tetramer (**14**) gives only TAAB. Template condensation of the *o*-aminobenzaldehyde monomer, in contrast, gives a TAAB/TRI mixture [16–18,38,57]. There are several transformations, however, where this tendency is completely overridden by other factors: copper-driven rearrangement of anhydrotrimer (**6a**), for example, gives TAAB complex exclusively and the previously mentioned preparation of VO_2^+ TRI complexes from H_2TAAB salts is another exception of the same sort [25,56]. These paradoxical transformations cannot be explained without acknowledging oligomer dissociation. Such dissociation may even involve TAAB complexes which are generally very inert in this respect (see Section 3.1 for more details).

2.4. Metal exchange reactions

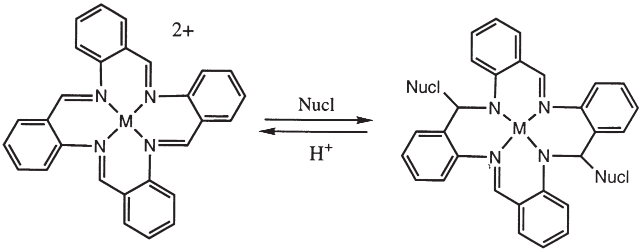
Iron(II), cobalt(II) and copper(II) TAAB complexes have been prepared using metal ion exchange reactions [26,66,68]. Zinc complexes of H_4TAAB and H_8TAAB served as starting materials in a kinetic study where the substitution of zinc by copper was investigated [66]. The reverse process, replacement of copper by zinc, can be carried out by treating CuTAAB with zinc amalgam [69].

A metal ion exchange reaction is the cleanest known method for TAAB complex preparation. No rearrangement processes are known to occur. This may relate to the postulated associative mechanism and to the related formation of bimetallic TAAB intermediates [66]. Such a mechanism precludes the generation of presumably unstable, free TAAB and assumes that the TAAB structure is secured, throughout the course of reaction, by the coordination of one or two metal ions.

3. Reactions

3.1. Nucleophilic addition

The reaction of nucleophilic reagents with TAAB complexes results in nucleophilic addition at the azomethine carbons:



(5)

These reactions are reversible. Upon acidification the TAAB complexes are regenerated along with the conjugate acids of nucleophiles. Nucleophilic addition is regio- and stereo-specific, producing predominantly the racemic trans isomers. Electrostatic factors favor addition of the second negatively charged nucleophile at the most distant position.

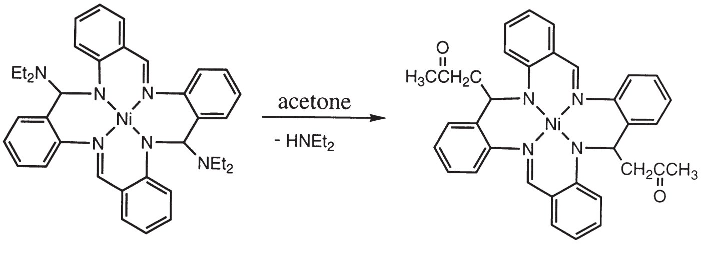
These reactions have been studied most thoroughly for the Cu(II) and Ni(II) complexes. They react with alkoxides and amines, forming neutral complexes of types (**15a**) and (**15b**) respectively (Fig. 1) [70–74]. The nucleophilic addition of bifunctional molecules produces either monocyclic complexes (**15**), or basket-like complexes (**16**) (Fig. 1), depending on the length of the spacer [75–78]. Diamines and dialkoxides, in which the nucleophilic centers are separated by less than five atoms always give monocyclic products (**15**).

It was initially suggested that formation of the basket-like complexes, (**16a**) and (**16b**), is substantially facilitated by coordination of a sulfur or nitrogen donor atom which has been built into the middle of the bridge. ESR data for the complex (**16a**), however, shows that axial coordination of the nitrogen atom is very weak (see Section 5.3) [76,77]. The terminal amino-groups in complex (**15c**) were also found to be non-coordinated [73]. Later, the basket-like complexes (**16c**) and (**16d**) were prepared using bridges which have only non-coordinating groups in the middle [72,76,78]. The most important requirement for formation of the bridged complexes is that both nucleophilic additions occur on the same face of the macrocycle.

The reaction of TAAB complexes with some of the simplest monofunctional nucleophiles, alkali metal hydroxides, is unexpectedly complex [70,79]. Surprisingly, the hydroxide ion cannot compete with amines or ammonia in nucleophilic addition to the TAAB azomethine bonds. When hydroxide ion is the only nucleophile available, partial hydrolysis of TAAB takes place [70]; acidification of the reaction products affords mixtures of the TAAB and TRI complexes. Similarly, treatment of $Ni(TRI)^{2+}$, first with sodium hydroxide and then with acid, produces the same $Ni(TAAB)^{2+}/Ni(TRI)^{2+}$ mixture.

The addition of carbon nucleophiles, originating from organolithium or organomagnesium reagents, to $Ni(TAAB)^{2+}$ and H_2TAAB^{2+} produces neutral $Ni(R_2TAAB)$ complexes (**15d**) or H_2R_2TAAB ligand respectively [80]. The latter react with metal ions to give two families of metal complexes, $M(H_2R_2TAAB)^{2+}$ and $M(R_2TAAB)$. Deprotonation can be achieved by addition of an appropriate proton sponge.

In certain cases one nucleophile can replace another. Nucleophilic substitution has been detected for (**15b**). Complex (**15e**) for example was produced through the displacement of diethylamine groups with the enolate of acetone [81]. The equilibrium of this reaction (Eq. (6)) is most likely shifted to the right on account of diethylamine's volatility.



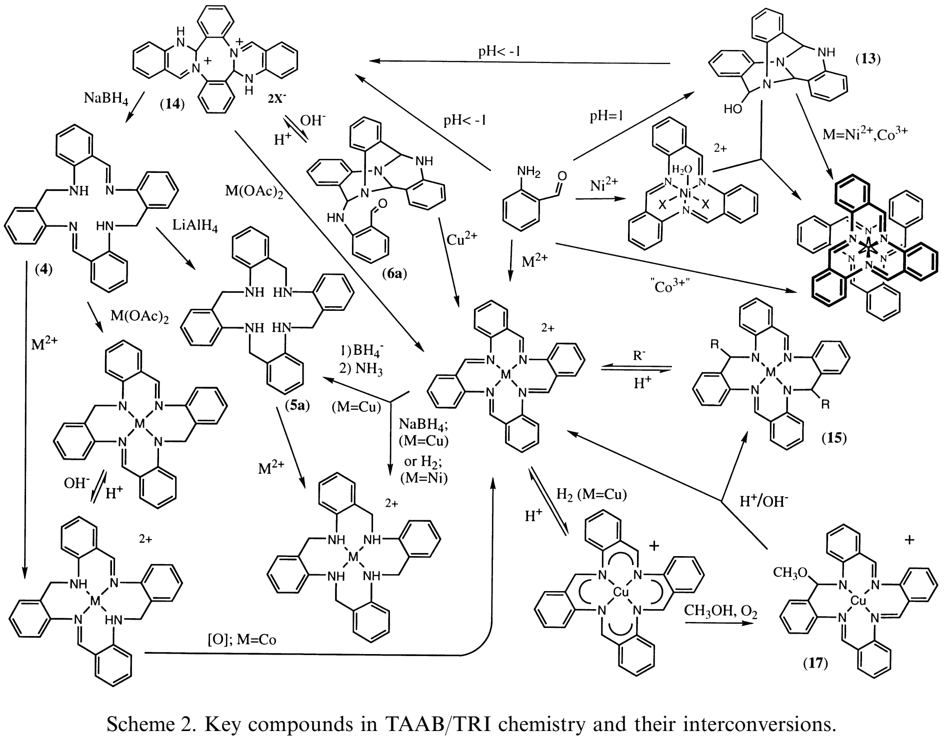
(6)

Nucleophilic addition was also observed for iron, cobalt, palladium and platinum TAAB complexes [82–86]. In many cases difficulties have been encountered in isolating the corresponding reaction products. Several products resulting from the nucleophilic addition of amino acids to $Pd(TAAB)^{2+}$ and $Pt(TAAB)^{2+}$ were, however, isolated in a pure form and studied by NMR and MS [85]. Kinetic studies show that for $Pd(TAAB)^{2+}$ and $Pt(TAAB)^{2+}$, addition of the first nucleophile is the rate-determining step [86].

Nucleophilic addition reactions are also common for dimeric TAAB complexes. Template condensation of *o*-aminobenzaldehyde, on the binuclear templates $[Mo_2Cl_8]^{4-}$ and $[Mo_2(O_2CCF_3)_4(PR_3)_2]^{4-}$, in ethanol gives binuclear complexes with ligands (**15a**, R = Et) and (**17b**) (Fig. 1) directly [34,35]. The oxide-bridged iron(III) complex, (TAAB)Fe–*o*-Fe$(TAAB)^{4+}$, reacts with alkoxides to give the neutral compound $(CH_3O)_2(TAAB)Fe–O–Fe(TAAB)(OCH_3)_2$ [26].

The product of a single nucleophile addition (**17a**) can be prepared by oxidation of $Cu(TAAB)^+$ in methanol (Scheme 2) [87]. The resulting complex is only moderately stable and undergoes disproportionation in both acidic and basic media.

The chemisorption of copper(II) and nickel(II) TAAB complexes on the surface of γ-aminopropylsilica leads to the formation of covalently bound products which arise from the nucleophilic addition of the γ-aminopropyl groups to the cationic TAAB complexes [88].



Scheme 2. Key compounds in TAAB/TRI chemistry and their interconversions.

3.2. Redox reactions

The redox reactions of TAAB complexes are classified below as either predominantly metal-related or predominantly ligand-related transformations. One must realize, however, that a clear distinction between these two types of redox reaction is not always possible. This is due both to the strong influence which the metal ion and ligand have on one another's properties and to the fact that the HOMO and/or LUMO are composed of both metal and ligand atomic orbitals.

3.2.1. Redox reactions involving the macrocyclic ligand

Two partially hydrogenated derivatives (**4** and **5a**) of the ligand (**2a**) can be readily obtained from H_2TAAB salts (**14**) [57]. Reaction of (**14**) with borohydride gives a yellow isomer of H_4TAAB (**4**) (Scheme 2). Repeated recrystallization of this yellow isomer from acetonitrile gives the white isomer (**18**) (Fig. 1).

Yellow H_4TAAB (**4**) can be further reduced by lithium aluminum hydride or by hydrogen in the presence of PtO_2. This reaction (Scheme 2) results in formation of the fully saturated ligand H_8TAAB (**5a**). The same ligand can also be prepared through the borane reduction of quinazolinone (**19**) (Fig. 1) [89]. Schindler and Szalda have recently suggested a third way to synthesize free H_8TAAB: preparation by borohydride reduction of $CuTAAB^{2+}$ in acetonitrile [90] (Scheme 2). Attempts to prepare other reduced TAAB derivatives, such as H_6TAAB, were unsuccessful [91].

Both H_4TAAB and H_8TAAB form stable complexes with transition metals. The former ligand can react with metal ions to form either neutral or cationic complexes [91,92]. Reaction of H_4TAAB with metal acetates causes ligand deprotonation and the formation of neutral MH_2TAAB complexes (Scheme 2). A single complex with the monodeprotonated ligand H_3TAAB^- has also been synthesized by a rather unexpected route. Oxidation of the $H_4TAAB \cdot [Rh_2(CO)_4Cl_2]$ adduct results in formation of $RhH_3TAABCl_2$. The interaction of H_4TAAB with metal salts derived from strong acids, yields cationic complexes $M(H_4TAAB)^{n+}$. The neutral complexes, MH_2TAAB, and cationic complexes, MH_4TAAB^{n+}, can be interconverted by changing the pH [91] (Scheme 2).

Infrared and electronic spectroscopy data indicate that oxidation of $Co(H_4TAAB)^{2+}$ results in ligand dehydrogenation and formation of $Co(TAAB)^{2+}$ rather than simple oxidation to form the Co(III) complex [91].

The first H_8TAAB complex was synthesized by Busch and coworkers via catalytic hydrogenation of $NiTAAB^{2+}$ [87]. The identity of the resulting NiH_8TAAB^{2+} was later verified by independent preparation of the same complex from the free ligand [57]. Copper(II) and zinc(II) complexes of H_8TAAB were synthesized soon after, either by direct interaction of the metal ion with free ligand or by substitution of zinc with copper [5,66]. X-ray structures of the copper(II) and nickel(II) complexes, as well as the ethyl acetate adduct of the free ligand, have recently become available [90]. The same paper describes the preparation and X-ray structural characterization of tetra-*N*-methylated H_8TAAB (**5b**). No metal complexes of (**5b**) have been isolated.

Neither hydrogenated TRI derivatives nor their metal complexes have been described in the literature. Related *N*-substituted macrocycles have been described by Ollis and coworkers [42–44].

3.2.2. Redox reactions involving the metal center

The TAAB ligand is a heteroanalog of the alternating hydrocarbon tetrabenzo[16]annulene and, therefore, not aromatic in the Hückel sense. Its 32 electron π system is just two electrons short of having highly stable, 34 π-electron aromaticity. Consequently, TAAB complexes are very prone to undergo chemical [87] and electrochemical [68,93] reduction. A number of electrochemical, ESR, IR and magnetic studies on the cobalt, nickel and copper complexes indicate that, in the case of one-electron reduction, the ligand can be reduced to the aromatic $TAAB^{2-}$ anion by gaining a second electron from the metal ion [68,93]. An alternative point of view in which metal ion reduction is considered to predominate is based on ESCA, indirect NMR comparisons and extended Hückel calculations [94–96]. The apparent contradiction between these two approaches can be reconciled by realizing that the HOMO of the reduced complex is comprised, almost equally, of ligand and metal atomic orbitals.

$Cu(TAAB)^+$ is a widely studied reduced TAAB complex. $Cu(TAAB)^{2+}$ can be readily reduced either electrochemically [68,79,93,97] or chemically using mercury [14,87], hydrogen at low pressure [87], ascorbic acid [95,98–104], hydroxylamine [105], glutathione [106] or one of several substituted dihydroxybenzenes [107–109]. The royal-blue $Cu(TAAB)^+$ which forms can be formulated as either $[Cu^{III}(TAAB^{2-})]^+$ or as $[Cu^{I}(TAAB)]^+$. In accordance with the first formulation, the favorable combination of ligand aromaticity and a d^8 metal ion in an effective D_{4h} environment results in a complex which is remarkably stable.

The $Cu(TAAB)^{2+}/Cu(TAAB)^+$ redox couple is readily reversible, which, in a combination with a sharp redox-triggered color change from yellow to blue, makes it a convenient redox indicator. $Cu(TAAB)^{2+}$ has been used as a probe for the investigation of redox reactions on the surface of silica [107–109] and in an assay for ascorbic acid determination [110]. The oxidants, which provided the best reversibility, were dioxygen and H^+ [108]. Some other oxidants, such as iodine in DMSO or nitric acid, caused irreversible ligand degradation [62].

Solvents have a profound influence on the $Cu(TAAB)^{2+}/Cu(TAAB)^+$ redox couple. Since polar solvent axial coordination is more characteristic for the copper(II) complex than the $Cu(TAAB)^+$ complex, higher redox potentials were observed in polar solvents and an inverse correlation between donor number and redox potential was found [79]. The self-exchange rate constant for the $Cu(TAAB)^{2+}/Cu(TAAB)^+$ redox couple was found to be $5 \times 10^5\ M^{-1}\ s^{-1}$, which falls in the upper decile of known values for copper complexes [95]. This suggests that the electron transfer related reorganization energy is relatively small. Marcus theory has been applied to the electron transfer reaction between ascorbate anion and $Cu(TAAB)^{2+}$ [111]. Results consistent with those from previous studies were obtained when the Cu^{2+} radius, rather than an average macrocyclic cation radius, was used for the calculation of collision frequency. This reflects the ability of the ascorbic acid anion to approach the copper atom directly in the activated complex.

Nickel, copper and cobalt complexes of neutral TAAB or the $(TAAB)(OCH_3)_2^{2-}$ anion can undergo two substantially different electrochemical reduction processes, depending on whether protic and aprotic solvents are used [68,93]. In methanol the total number of electrons added is sufficient to reduce M(II) to M(0) and to hydrogenate all of the azomethine linkages, thus forming H_8TAAB complexes. In aprotic acetonitrile, however, the ligand is not hydrogenated and $M(TAAB)^0$ and $M(TAAB)^+$ complexes are obtained. The neutral nickel complex reacts readily with methanol giving Ni $(TAAB)(OCH_3)_2$ and hydrogen. The nickel(II) TAAB complex can also be oxidized in acetonitrile to form an Ni(III) complex [68]. Some other oxidation processes involving cobalt and iron TAAB complexes have been mentioned in Section 2.1.

3.3. Reactions involving anions and axial ligands

Most of the transition metal ions encapsulated by TAAB, or coordinated in a perched fashion to a single TRI ligand, also interact, to some extent, with anions or solvent molecules. The extent of these interactions is determined by the electronic configuration of the metal ion and by the nature of the ligand. With the exception of their strong ability to stabilize polyiodide chains, the behavior of TAAB and TRI metal complexes is similar to the behavior of other complexes with tetradentate and tridentate macrocyclic ligands.

Nickel(II), which is able to form square planar and octahedral complexes, realizes these tendencies in different ways with TRI and TAAB. Since there is no possibility of building a square plane from the small, rigid, tridentate TRI, this ligand always forms octahedral complexes. One-to-one metal–ligand stoichiometry requires the coordination of additional ligands. The second octahedral face can be occupied by anions and/or by solvent molecules [21,38,58,112].

Depending on the degree of ligand unsaturation and on the coordinating ability of the anions present, axial interactions may or may not be observed for Ni(II) complexes with 16-membered ligands. For TAAB complexes, both square planar and pseudo-octahedral complexes have been prepared [17,22,113], whereas only octahedral and five-coordinate complexes have been obtained for H_4TAAB and H_8TAAB [87,92]. Their ability to retain coordinated water molecules, even *in vacuo* over P_4O_{10} reflects the tendency of hydrogenated TAAB derivatives to retain their axial ligands. Miscellaneous adducts of $Ni(TAAB)^{2+}$ with neutral nitrogen donors have also been described [112,114–116].

The interaction of Fe(TAAB) complexes with axial ligands has also been described in great detail [26,27,117–120]. The ligands studied include carbon monoxide, nitric oxide, thiocyanate, nitrite, cyanide, isocyanides, nitriles, phosphines, sulfur-containing heterocycles and nitrogen-containing heterocycles. Anionic ligands and imidazole form the most stable complexes. In contrast to heme, $Fe(TAAB)^{2+}$ binds carbon monoxide and isocyanides rather weakly [27]. A linear correlation has been found between the pK_a values of a series of nitrogenous heterocycles and log K for their coordination to $Fe(TAAB)^{2+}$ as a second axial ligand. Heterocycles bearing bulky substituents next to the coordinating nitrogen are exceptions to this trend [117].

The addition of the first axial ligand facilitates $Fe(TAAB)^{2+}$ to $Fe(TAAB)^{3+}$ oxidation, whereas the addition of a second axial ligand understandably retards this process [118]. Most of the iron(III) TAAB complexes are represented as oxide-bridging species. These iron–oxygen–iron bridges were found to be unusually difficult to cleave; only fluoride in acidic media destroys $Fe_2(TAAB)_2O^{4+}$ to form $Fe(TAAB)FX_2$ complexes [26].

Pseudo-octahedral M(TAAB) complexes were also studied for cobalt(II,III) [20,28], copper(I,II), palladium(II) [121,122], chromium(III) [63] and ruthenium(II) [123]. Cobalt(II) forms at least three types of complex with solvents, depending on the number of coordinated molecules and the field strength. These three types of complex each have distinctive ESR behavior, which will be discussed in Section 5.3. The copper(II) complex binds axial ligands rather weakly [77], but better than $Cu(TAAB)^{+}$. This follows from the increases in $Cu(TAAB)^{2+}/Cu(TAAB)^{+}$ redox potential which are observed in solvents with greater donor numbers [79].

Palladium(II), platinum(II) and, to some extent, nickel(II) TAAB complexes are able to stabilize octaiodide $(I_8)^{2-}$ chains, providing a typical example of a large anion being stabilized by a large cation. The palladium and platinum complexes were initially described as partially oxidized materials $M(TAAB)(I_3)_{2.7}$, similar to some extensively studied semiconducting “pseudo-one-dimensional” compounds [124,125]. The same group later revised their formulation, on the basis of X-ray crystallographic data, having found that their materials contain an $(I_8)^{2-}$ anion composed of two I_3^- units weakly coupled via an elongated I_2 [126]. Nickel forms an analogous complex, but only in the absence of coordinating solvents [127].

Interest in investigating the magnetic and electroconducting properties of “pseudo-one-dimensional” TAAB systems (see Section 5.3) has led to the preparation of tetracyanoquinodimethane (TCNQ) [128], copper-maleonitriledithiolate [129] and tetracyanoethylene (TCNE) [65] derivatives. Solvent can exert a substantial influence on the stoichiometry of the TCNQ derivatives: $Cu(TAAB)(TCNQ^{\cdot -})_2$ precipitates from aqueous solutions, whereas mixed-valent $[Cu(TAAB)]_2(TCNQ^{\cdot -})_3$ forms in methanol.

4. Isomerism and structural aspects

4.1. TAAB complexes and related materials

Extensive X-ray crystallographic studies have been performed on the TAAB complexes of nickel [21,22,81,90,114,127,129,130], copper [53,90], palladium [125,126], platinum [47,49] and ruthenium [123]. Regardless of the metal ion, anions, and axial ligands present, coordinated TAAB retains a saddle shape with approximate S_4 symmetry (Fig. 2). The metal ions are generally located in the middle of the N_4 plane. Average metal–nitrogen distances were found to be 2.004–2.039 Å for palladium, 2.034 Å for platinum, 2.022 Å for ruthenium, 1.902 Å

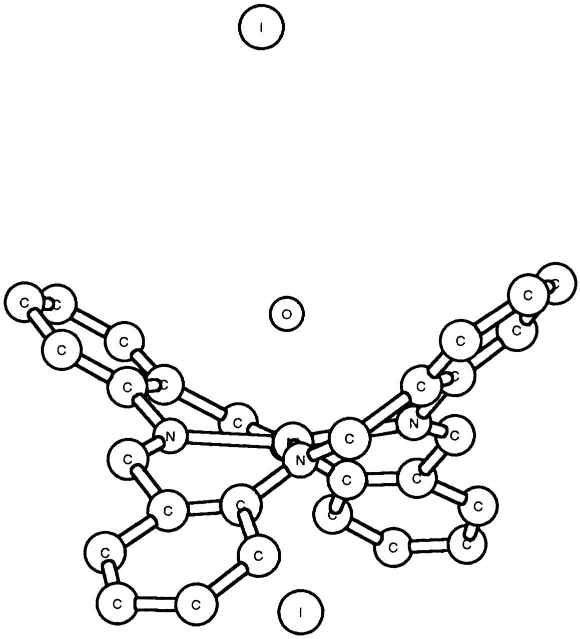


Fig. 2. X-ray crystal structure of Ni(TAAB)$I_2 \cdot xH_2O$. Redrawn from fractional coordinates given in Ref. [22].

for low-spin square planar nickel(II) complexes and 2.007–2.047 Å for a variety of tetragonal, hexacoordinated high-spin nickel(II) complexes. The relative insensitivity of the metal–nitrogen distances to the nature of the metal ion reflects the rigidity of the highly unsaturated ligand. The longer nickel–nitrogen bond length observed for high-spin nickel(II), relative to low-spin nickel(II), was explained on the basis of d orbital occupancy. The d orbitals, which are antibonding with respect to Ni–N interaction, are occupied in the high-spin case, but are unoccupied in the low-spin case [22].

S_4 symmetrical TAAB complexes understandably have no stereoisomers, and the formation of other types of geometric isomer is also unknown. The addition of a single axial ligand, or two different axial ligands, to a TAAB complex lowers the symmetry to C_2 and generates a pair of enantiomers. Asymmetric complexes of this type, derived from $FeTAAB^{2+}$, were detected by ^1H NMR [27].

The addition of nucleophiles to TAAB complexes generates a stereocenter at each of the effected carbon atoms. For the most common type of these derivatives, where two nucleophiles are attached, the existence of four stereoisomeric forms, shown in Fig. 3, has been postulated [70]. The cis–trans designation refers to the relative placement of the nucleophiles, whereas the d,l or meso designates the relative configurations of the two asymmetric carbon atoms. At least two different stereoisomers were detected by ^1H NMR for Ni(TAAB)$(OEt)_2$, although neither of them was isolated in the pure form. Electrostatic repulsion favors the trans addition of

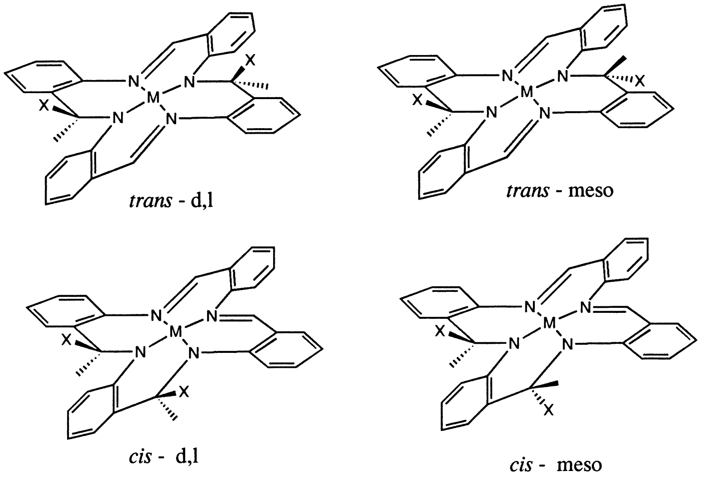


Fig. 3. Four stereoisomers possible for the products of nucleophilic addition to M(TAAB) complexes.

nucleophiles, and the only X-ray structure available for a product of nucleophilic addition is in agreement with this assumption [81]. Cis-addition of nucleophiles (along with predominant trans-addition) has been postulated for molybdenum TAAB complexes [34].

4.2. TRI complexes

Unlike TAAB complexes, mono-TRI complexes are chiral and can be separated into individual enantiomers [131]. The addition of a second TRI ligand results in the formation of two types of complex (Fig. 4) with different relative positioning of the second TRI ligand. If from the point of reference of the metal center, the repeating units on the two TRI ligands progress in opposite directions with respect to one another (one clockwise, the other counter-clockwise) the resulting complex

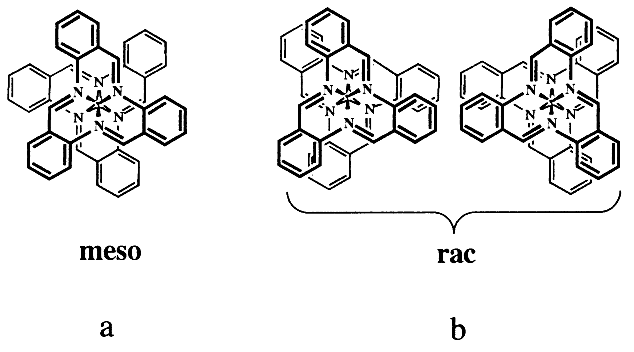


Fig. 4. The (a) meso and (b) racemic forms of bis(TRI) complexes.

is a meso form (Fig. 4(a)). If they progress in the same direction (both clockwise, or both counter- clockwise) the resulting complex is racemic (Fig. 4(b)).

Different metal ions seem to favor different relative positioning of the ligands. $Co(TRI)_2^{3+}$ was separated into meso and rac components, with the racemate being about three times more abundant than the meso form. The racemate was later successfully resolved into the individual diastereomers [19]. A subsequent X-ray structure determination, for one of the diastereomers, revealed extremely short distances between the benzene rings of the two TRI ligands, with the closest C–C contacts averaging 2.9 Å. Furthermore, the torsional distortion about the molecular threefold axis (about 8°) increases overlap of the benzene pairs, suggesting that interaction between two TRI ligands is attractive, rather than repulsive [132]. In contrast to this, $Ni(TRI)_2^{2+}$ and $Cu(MeTRI)_2^{2+}$ seem to exist exclusively in the meso form. The meso structure was assigned to the nickel complex on the basis of the disappearance of optical activity which occurred upon addition of the second TRI ligand to the partially resolved $Ni(TRI)(NO_3)_2H_2O$. If the resulting $Ni(TRI)_2^{2+}$ had had the d,d and/or l,l geometrical arrangements (rac) the optical activity would have been preserved [38]. The structure of the $Cu(MeTRI)_2$ has been determined crystallographically (Fig. 5) [67]. The large thermal anisotropies, observed for the coordinated nitrogen atoms, in a combination with D_3 symmetry,

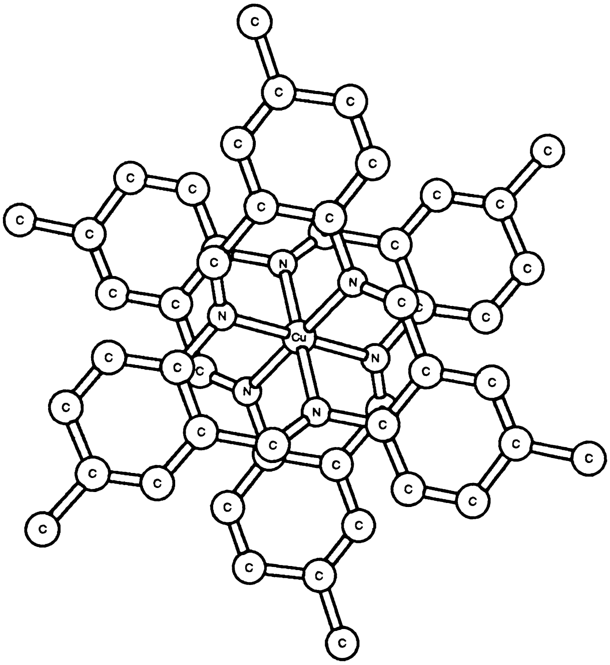


Fig. 5. View of the $Cu(MeTRI)_2^{2+}$ cation along the C_3 axis. Redrawn from fractional coordinates given in Ref. [67].

which seemingly contradicts the Jahn–Teller theorem (orbitally degenerate E_1 ground state), indicates that a dynamic Jahn–Teller effect is operable for $Cu(MeTRI)_2^{2+}$.

4.3. H_2TAAB salts

The NMR spectra of H_2TAAB salts are extremely complex, suggesting the presence of different isomeric and/or conformeric forms in solution. A number of structural formulae have been suggested for the H_2TAAB isomers [59,60,133], although only two different conformers have been characterized crystallographically. Most H_2TAAB salts are red in the solid form, their molecules are saddle shaped (Fig. 6(a)). In many cases this conformation is stabilized by multiple hydrogen bonds with anions [133,134]. $H_2TAAB(SnCl_3)_2$ exists in two different forms: red and yellow. The red isomer has the usual saddle conformation, whereas the yellow one is twisted (Fig. 6(b)) [61].

5. Spectroscopic studies of TAAB and TRI complexes

5.1. Infrared spectroscopy

This, the most easily accessible spectroscopic technique, provides extremely convenient diagnostic information on the formation of TAAB and TRI complexes and on their most common transformations. Both TAAB and TRI complexes have a very characteristic pattern in the region 1650–1550 cm^{-1}, which consists of three very strong bands. The band at ca 1570 cm^{-1} is attributed, on the basis of hydrogenation experiments [87], to the C=N stretching mode, whereas the bands at ca 1590 and 1610 cm^{-1} were assigned to the two ring modes of the benzene moiety. The intensity of the C=N stretch is often lower for TRI complexes than it is for TAAB complexes. This rule is not universal, however, and can only be applied reliably to Ni complexes [19]. Reduction of the metal ion lowers the energies and intensities of these bands [68]. Intensities are also lower for TAAB derivatives with electron-donating substituents [53].

The nucleophilic addition products have essentially the same IR pattern, with the C=N stretch significantly shifted (ca 40 cm^{-1}) to lower energies [70]. The C=N

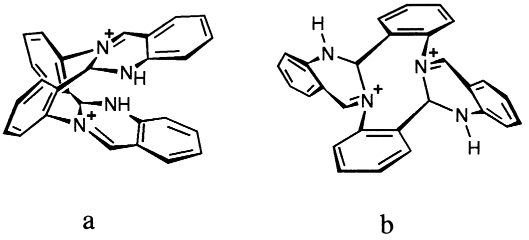


Fig. 6. (a) Saddle-shaped and (b) twisted conformers of H_2TAAB salts.

stretch for H_2TAAB salts is intermediate (ca 1555 cm^{-1}) between those for metal TAAB complexes (1570 cm^{-1}) and those for the products of nucleophilic addition (ca 1530 cm^{-1}) [57].

5.2. Electronic spectra

TAAB is a strong field equatorial ligand. Axial ligands with poor coordinating ability do not influence the ground state of the complexes in most cases. Axial ligands with greater coordinating ability, such as I^- or NCS^-, may cause significant changes in the electronic spectra. Complexes of both the TAAB and TRI ligands have a number of interligand and charge transfer bands overlapped with d–d bands.

Nickel complexes of TRI and TAAB give the most readily interpretable electronic spectra and, consequently, have been studied most often. General discussion concerning the electronic spectra of macrocyclic complexes with axial ligands has been provided by Busch and coworkers [135]. Some improvements based on an angular overlap model were later suggested by Andruh *et al.* [115,116]. The spectra of the nickel TAAB complexes have been interpreted assuming effective D_{4h} symmetry with two major transitions for high spin tetragonal complexes at about 8000–10 500 cm^{-1} and 18 000–20 000 cm^{-1} assigned to $^3B_{2g}+{}^3E_g \leftarrow {}^3B_{1g}$ and $^3A_{1g}+{}^3E_g \leftarrow {}^3B_{1g}$ respectively [17]. The electronic spectra of $Ni(H_4TAAB)^{2+}$ and $Ni(H_8TAAB)^{2+}$ were treated similarly [87,92]. The planar $Ni(TAAB)^{2+}$ complexes with non-coordinating counter-ions show one absorption band at about 19 000 cm^{-1} assigned to the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition [17]. Mono-TRI nickel complexes have pseudo-octahedral symmetry and show four bands in their electronic spectra: $^3T_{2g} \leftarrow {}^3A_{2g}$ at about 10 500 cm^{-1}; $^1E_g \leftarrow {}^3A_{2g}$ at about 12 500 cm^{-1}; $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ at about 18 500 cm^{-1}, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ at about 25 000 cm^{-1}.

The spectra of bis-TRI nickel(II) complexes have been interpreted assuming effective D_{3d} symmetry, because strong trigonal distortion is evident from the crystallographic data described above. Three bands at approximately 11 300, 14 500 and 20 200 cm^{-1} were assigned to $^3A_{1g} \leftarrow {}^3A_{2g}$, $^3E_g \leftarrow {}^3A_{2g}$ and charge transfer $+ {}^3A_{2g} \leftarrow {}^3A_{2g}$ respectively [58].

The high extinction coefficients observed for the products of nucleophilic additions to $Ni(TAAB)^{2+}$ indicate that their spectral bands are not pure d–d transitions. The number of bands and their positions correspond well to the electronic spectra of the metalloporphyrins and were interpreted in a similar manner [71].

$Co(TAAB)^{3+}$ complexes have three absorption regions at 14 000–16 000 cm^{-1}, 19 000–21 000 cm^{-1} and 25 000–29 000 cm^{-1}. The second and the third bands are asymmetrical and contain more than one component. These spectra can be interpreted assuming the C_{4v} or D_{4h} symmetry [20].

D_3, rather than O_h symmetry was assumed for $Co(TRI)_2^{3+}$ complexes, since a circular dichroism study clearly identified at least two components in the bands observed at ca 21 800 cm^{-1} and 28 500 cm^{-1} [19,132].

Interpretation of spectral data obtained for other metal ions is substantially more difficult owing to substantial overlap of d–d, intraligand, and charge transfer bands. Spectroscopic data for the iron, copper, and palladium complexes are listed in Refs. [27,34,84,87].

5.3. Magnetic susceptibility and magnetic resonance

Magnetic susceptibility and magnetic resonance studies provided significant insight concerning the electronic structures of transition metal TAAB complexes. The first example of singlet–triplet ground state crossover observed for macrocyclic complexes was described by Melson and Busch for Ni(TAAB)X_2 [113]. Non-coordinating anions give diamagnetic complexes exclusively, whereas complexes with strong field axial ligands exhibit behavior consistent with a triplet ground state. Over a small range of ligand field strengths, specifically those observed for Cl^-, Br^- and I^-, the energy separations between the singlet and triplet states were comparable with thermal energies and, consequently, thermal distribution was observed. Somewhat surprisingly, iodide exhibits a field strength stronger than that of chloride and bromide; this is in contrast to the usual spectrochemical series observed for first row transition metals. This difference is probably related to the presence of stoichiometric amounts of water in the crystal lattices of the chloride and bromide salts, whereas the iodide salt is anhydrous. Water molecules are quite likely hydrogen bonded to the chloride and bromide ions, thus inhibiting their coordinating abilities.

Nickel(II) complexes of the H_4TAAB and H_8TAAB hydrogenated ligands always have coordinated axial ligands (water in most cases) and, consequently, are paramagnetic [87,90,92].

Crossover phenomena similar to those observed for nickel were later detected for iron(II) complexes. The magnetic moment value for Fe(TAAB) $(CH_3CN)_2](BF_4)_2$ (2.62 μ_B) suggests either an intermediate spin state ($S=1$) or equilibrium between high spin ($S=2$) and low spin ($S=0$) forms. The magnetic susceptibility of the complex does not obey the Curie–Weiss law, indicating the existence of a spin equilibrium [119]. The same paper describes a second example of spin equilibria for $[Fe(TAAB)(CH_3CN)(NO)](BF_4)_2$. In this case, the low-spin ($S=1/2$) form coexists with the intermediate-spin ($S=3/2$) form.

The magnetic properties of dimeric (TAAB)Fe–O-Fe(TAAB) complexes have also been studied [26]. Their behavior is in agreement with a simple binuclear model involving exchange between two Fe(III) ions having $S=5/2$.

ESR studies of $Co(TAAB)^{2+}$ complexes also reveal the existence of several forms with different ground states. The nature of the predominant form depends on the coordinating strength of the solvent [28]. ESR parameters substantially different from those given in [28] were published by Nishida *et al.* [136].

ESR has also been used extensively in the investigation of copper TAAB complexes. Several ESR techniques (X-band, Q-band, spin–echo) were applied to determine whether or not the donor atom in the middle of the bridge (for compounds **16a**–**c**) coordinates to the central metal atom. This, in turn, could have clarified the role of this donor atom, if any, in the formation of bridged complexes. Spin–echo experiments indicate weak, but real, interactions between Cu and N_{ax}, whereas optical spectra and X-band ESR did not reveal any interaction [76,77].

Triaxial anisotropy was found for products of nucleophilic addition to $Cu(TAAB)^{2+}$, suggesting significant deviation from tetragonal symmetry, despite obvious delocalization. As anticipated, Cu–N bonds in the nucleophilic addition products have substantially more covalent character than those in the parent $Cu(TAAB)^{2+}$ [74].

In the case of Cu(TAAB)(TCNQ) complexes, the unpaired electron is distributed between two different (Cu and TCNQ) magnetic sites giving an average *g* value. No magnetic interactions were observed, however, between Ni(TAAB) and a Cu(II)-containing counter-ion [129]. ESR has also been applied for the detection of $Ni(TAAB)^{3+}$ [68].

NMR spectroscopy was used for the evaluation of exchange processes and for structural studies. Line broadening studies for $Ni(TAAB)^{2+}$ and $Ni(TRI)^{2+}$ in DMF show that the exchange of solvent molecules is substantially faster for the former complex, reflecting the lability of tetragonally distorted Ni(II) complexes [112]. The self-exchange rates for Cu(II)/Cu(I) TAAB complexes fall in the upper end of the range of values observed for other Cu(II)/Cu(I) couples, suggesting that the ligand reorganization energy is relatively low [95].

NMR structural investigations include determination of the arginine reactive site in its nucleophilic addition to $Pd(TAAB)^{2+}$ [85], as well as some isomerism studies for ligand-substituted Ni and Mo complexes [70,35].

5.4. Mössbauer spectra

A number of iron TAAB complexes were studied by this method [24,119]. $[Fe(TAAB)(CH_3CN)_2](ClO_4)_2$ exhibits spectral parameters somewhat similar to those of the porphyrins. This is in contrast to the oxo-bridged Fe(III) complexes which give a surprisingly different ΔE_q value. For $[Fe(TAAB)(OMe)_2]_2O$, which is supposedly quite similar to the porphyrins owing to negative charge on the ligand, the difference in ΔE_q values was explained on the basis of stereochemical complications originating from the presence of two sp^3 carbon atoms in each anionic ligand [24].

Mössbauer spectra of $[Fe(TAAB)(CH_3CN)_2](BF_4)_2$ and $[Fe(TAAB)(CH_3CN)(NO)](BF_4)_2$, studied at 298 and 77 K, are consistent with the magnetic susceptibility data described above and reveal the equilibrium between high- and low-spin forms [119].

5.5. X-ray photoelectron spectra

Data obtained by this method provide significant information concerning atom oxidation states and relative charges. The relatively low Cu_{2p} binding energies found for $[Cu(TAAB)](NO_3)$ support formulation of this compound as the Cu(I)–neutral ligand complex, rather than the $Cu(III)–TAAB^{2-}$ complex [94] (see also Section 3.2.2). Study of mixed-valent Cu(I)–Cu(II)–TAAB–TCNQ complexes allows for the detection of copper in both oxidation states [128].

The N_{1s}, $Pd_{3d5/2}$ and $Pt_{4f7/2}$ binding energies obtained for $M(TAAB)(OH)ClO_4$ complexes on the one hand, and $M(TAAB)(ClO_4)_2$ complexes, on the other hand, suggest that nucleophilic addition of OH^- did not occur for these compounds. Otherwise a substantial decrease in binding energy would be expected [85].

$Ni(H_4TAAB)$ complexes with different axial ligands show no splitting between the N_{1s} secondary amine peak and the N_{1s} azomethine peak. A correlation between N_{1s} binding energy for the macrocyclic nitrogen atoms and the position of the axial ligand in the spectrochemical series was observed for these compounds [137].

6. Kinetic and mechanistic studies

The kinetics of $Cu(TAAB)^{2+}$ reduction by ascorbic acid, hydroxylamine, and glutathione were studied in a number of papers [100,101,104–106]. Reduction by ascorbic acid was studied in the greatest detail and reveals many features common for all of these reactions. The proposed radical-chain mechanism explains the induction period observed for the formation of $Cu(TAAB)^+$ in the presence of dioxygen, as well as other reaction features. $Cu(TAAB)^{2+}$ was postulated to form a complex with ascorbate:

$$Cu(TAAB)^{2+} + HAsc^- \leftrightarrow Cu(TAAB)(HAsc)^+ \tag{7}$$

The resulting complex decomposes, giving an ascorbate radical and $Cu(TAAB)^+$:

$$Cu(TAAB)(HAsc)^+ \rightarrow Cu(TAAB)^+ + Asc^{\cdot -} + H^+ \tag{8}$$

The ascorbate-radical is oxidized by dioxygen, producing the superoxide radical and dehydroascorbic acid:

$$Asc^{\cdot -} + O_2 + H^+ \rightarrow DAsc + HO_2^{\cdot} \tag{9}$$

Superoxide, in turn, oxidizes $Cu(TAAB)^+$ back to $Cu(TAAB)^{2+}$. Some other processes, such as reaction of the superoxide radical with ascorbate or the ascorbate radical and reduction of Cu^{2+} by ascorbate radical, were also postulated [104]. The net result of these processes is catalytic oxidation of ascorbic acid by dioxygen.

No induction period was observed for the reduction of $Cu(TAAB)^{2+}$ by hydroxylamine. This was explained by the inability of the $NHOH^{\cdot}$ radical (unlike the ascorbate radical) to react with molecular oxygen, at reasonable rate, to form the $O_2^{-\cdot}$ radical responsible for $Cu(TAAB)^+$ reoxidation [105].

Two parallel pathways (acid dependent and acid independent) have been suggested for the reduction of $Cu(TAAB)^{2+}$ by glutathione, suggesting that molecular glutathione, as well as the glutathione anion, can serve as a reducing agent. No Cu(TAAB)–glutathione complexes have been detected in this system [106].

As a part of a more general study on the oscillating catalytic oxidation of organic substrates by dioxygen [138], the Cu(TAAB)–ascorbic acid–O_2 system was investigated by Labuda and coworkers: oscillations which had a chaotic random character were observed after a 35–40 min induction period; the wave-like oscillations of redox potential, absorbance, and polarographic current lasted for about 1.5 h, until the H_2O_2 was completely consumed [102,103].

Two groups have investigated the kinetics and mechanism of axial ligand substitution on $Fe(TAAB)X_2$ complexes [27,120]. The kinetics are consistent with a dissociative mechanism. A small concentration of the high-spin, labile complex was suggested to be responsible for the unexpectedly fast ligand exchange rate [120]. Several generalizations have been made based on the comparison of several classes of iron(II) macrocyclic complexes: (1) axial π-acceptors are less reactive trans to methylimidazole than trans to pyridine; (2) N-donors trans to benzyl isocyanide are more inert than N-donors trans to a second molecule of the same N-donor; (3) N-donors bind according to their pK_b [120].

The last statement was refined in a detailed study involving $Fe(TAAB)^{2+}$ with some 20 different axial ligands [117]. A linear correlation between the stability constants and the pK_a values was observed for ligands able to coordinate to $Fe(TAAB)^{2+}$ without significant steric interactions. Steric factors became significant for 2- and 2,6-substituted pyridines. Deviations from linearity were observed for these nitrogenous bases.

Kinetic studies of $Fe(TAAB)^{2+}$ oxidation in the presence of different nitrogen-containing heterocyclic bases reveal a decrease in oxidation rate under conditions when hexacoordinated complexes are formed [118]. In contrast, at lower nitrogen base concentrations, when pentacoordinate complexes dominate in solution, the oxidation rate is higher than that observed for the parent $Fe(TAAB)(CH_3CN)_2^{2+}$. Peroxidase-like activity was also found for $Fe(TAAB)^{2+}$–nitrogen base complexes.

An associative mechanism was proposed for the metal–metal substitution reactions:

$$ZnL^{2+} + Cu^{2+} \rightarrow CuL^{2+} + Zn^{2+} \qquad (10)$$

where L = TAAB, H_4TAAB, and H_8TAAB. A $ZnLCu^{4+}$ intermediate was detected spectrophotometrically in the case of H_4TAAB [66]. The degree of saturation exerts a significant influence on the rates and activation energies of the processes studied. Rigid square planar TAAB does not provide a favorable environment for tetrahedral Zn^{2+} and substitution by Cu^{2+} proceeds rapidly. Saturated, flexible H_8TAAB is better able to assume a tetrahedral geometry and substitution is relatively slow. H_4TAAB has rate and activation energy intermediate between those observed for TAAB and those observed for H_8TAAB.

Stepwise nucleophilic addition of lysine and arginine was detected for $Pd(TAAB)^{2+}$ and $Pt(TAAB)^{2+}$ [86]. Addition of the first nucleophile was found to be the rate-determining step. The hydroxide ion can compete effectively with amino acids, especially in the case of palladium. Consequently, the mixed complexes M(TAAB)(OH)(Arg) and M(TAAB)(OH)(Lys) were detected.

7. Theoretical calculations

In order to understand the electronic structure of TAAB complexes, and to explain some features of their reactivity, quantum chemistry calculations were performed [96,139–141]. The compounds studied include Fe^{II}(TAAB), Co^{II}(TAAB) [139], $Cu^{0–III}$(TAAB) [96,139,140], $Ni^{0–III}$(TAAB) [96,139,140], and the hypothetical

H_2TAAB ligand [139]. Extended Hückel [139] and CNDO [139,140] methods, using the restricted Hartree–Fock (RHF) approximation, were used to calculate the molecular orbital structures of the complexes, as well as atomic charges and bond populations (using Mulliken population analysis). Although it was later shown that the RHF method is inadequate to describe highly symmetric compounds with extensive conjugation, such as TAAB or porphyrin complexes [141], detailed results of unrestricted Hartree–Fock calculations have never been reported.

Upon complexation with M(II) (M = Fe, Co, Ni, Cu), the atomic charges on both the nitrogen donor atoms and the adjacent carbon atoms of TAAB become less negative than those in the hypothetical free ligand. This suggests that the metal–ligand interaction is dominated by ligand-to-metal electron donation. The positive charges on the metal ions decrease in the series Fe(II) > Co(II) > Ni(II) > Cu(II) and exceed the corresponding charges in the porphyrin complexes by ca $0.2\bar{e}$. In contrast to porphyrin complexes, a substantial charge alternating effect is observed for the TAAB ring in M(II)(TAAB) complexes. Remarkably, the azomethine carbon atoms become electrophilic centers, with positive charges comparable with those of the central metal ions. This explains the nucleophilic addition reactions to the macrocyclic ring discussed in Section 3.1 [139]. Reduction of the complexes leads to a significant increase in electron density on the azomethine carbon atoms and, consequently, a decrease in their electrophilic character [140].

Significant attention has been paid to the electronic structures of the reduced TAAB complexes, especially that of Cu(TAAB)$^+$. Comparison of the free ligand orbital structure with the Cu(I) d(x^2–y^2) energy level shows that the cluster of occupied ligand π-orbitals straddles the energy level of the metal d-orbital. This leads to the conclusion that, in Cu(I) species, no electron transfer from the ligand to the metal should occur [96]. Direct calculations for Cu(TAAB)$^{2+}$ and Cu(TAAB)$^+$ gave similar results: with increasing total charge of the complex the electron density on the copper center decreases, mainly because of a loss of electron density in the 3d orbitals. For example, the population of the 3d(xy) orbital decreases from $1.404\bar{e}$ in Cu(TAAB)$^{2+}$ to $0.911\bar{e}$ in Cu(TAAB)$^+$ [140]. The reduction of Cu(TAAB)$^{2+}$ is accompanied by changes in the orbital composition of the HOMO and LUMO. Whereas the contribution of the metal 3d(xy) orbital in the LUMO of the Cu(II) complex is equal to 11.7%, it increases to 46.7% in the HOMO of the reduced complex [140]. Consequently, the reduction of Cu(TAAB)$^{2+}$ involves the metal ion to a considerable extent. The changes of effective charge on the copper center also confirm this interpretation: Cu(TAAB), −0.047; Cu(TAAB)$^+$, 0.071; Cu(TAAB)$^{2+}$, 0.291; Cu(TAAB)$^{3+}$, 0.498. Interestingly, the changes in atomic charges on the metal center are much smaller for the series of Ni complexes: Ni(TAAB), 0.154; Ni(TAAB)$^+$, 0.246; Ni(TAAB)$^{2+}$, 0.322; Ni(TAAB)$^{3+}$, 0.347. The compositions of the frontier molecular orbitals for the nickel complexes differ from those of the copper complexes: both the LUMO in Ni(TAAB)$^{2+}$ and the HOMO in Ni(TAAB)$^+$ are essentially ligand orbitals. The one-electron reduction of Ni(TAAB)$^{2+}$ results in an increase of electron density on the ligands, especially the azomethine carbon atoms. This result is relevant to the observation that C=N bonds are easily reduced in Ni(TAAB)$^{2+}$, whereas a one-electron reduction of the metal center occurs for Cu(TAAB)$^{2+}$. Further reduction to the M(TAAB)^{0} species leads to an increase in electron density on the ligand benzene rings [140].

The McLachlan approximation has been applied to π-electron, open-shell, crystal orbital calculations on columnar stacks of TAAB radical ions [142]. The valence and conduction bands were found to be sufficiently broad for the band model to be applied to extrinsic bulk semiconduction at a 0.373 nm interplanar spacing.

8. Biochemical, medicinal, and other applied aspects of TAAB chemistry

Nuclease-like activity was found for Cu(TAAB)$^{2+}$ in the presence of ascorbic acid and dioxygen [143–146]. The hydrophobicity and saddle-shape of the TAAB ligand facilitates the binding of its complexes to certain unpolar base pairs of DNA, or other polynucleotides. The ability of Cu(TAAB)$^{+}$ to react with dioxygen and generate oxygen radicals under these conditions (Eqs. (7)–(9)) leads to the oxidative cleavage of single- and double-stranded DNA fragments. Unlike the copper bis-1,10-phenanthroline complex, which reversibly changes its coordination geometry from square-planar to tetrahedral upon reduction and does not exhibit sequence specificity, the Cu(TAAB) complex is AT specific, presumably owing to its constant molecular shape dictated by the rigid ligand.

In a number of studies, the ability of Cu(TAAB)$^{+}$ to catalyze the dismutation of superoxide anion-radicals (SOD activity) was examined using pulse-radiolytically or chemically generated $O_2^{-\cdot}$ [147–150]. Cu(TAAB) exhibited record high activity for Cu-containing SOD models, with the majority of the superoxide decaying within 10 ms. Cu(TAAB) exhibits about 3% of the activity of natural Cu_2Zn_2 SOD. Cu(TAAB) is a rare example of a SOD model which is stable in the presence of strong biological chelators (i.e. serum albumine). This, along with its external hydrophobicity, which assures solubility in lipid layers and/or between the stacked base pair of DNA, suggests Cu(TAAB) as a possible tool for controlling superoxide levels in lipophilic tissues.

With possible connections to its nuclease and SOD activities, CuTAAB and several of its halogenated analogs were found to have substantial antitumor [30,151] and antileukemic [147] activity. Cu(TAAB)Cl_2 is the only highly active anticancer complex among 1109 copper, 134 silver and 106 gold complexes studied by the National Cancer Institute (USA) [151]. It was later shown that certain substituted TAAB complexes are even more active and comparable in activity with *cis*-platin against human lung adenoma [30].

The existence of an induction period in the reduction of Cu(TAAB)$^{2+}$ to Cu(TAAB)$^{+}$ by ascorbic acid in the presence of dissolved dioxygen provides the basis for kinetic methods of oxygen determination. The formation of intensely colored royal-blue Cu(TAAB)$^{+}$ is not observed until dioxygen is almost completely consumed (see Eqs. (7)–(9)). The duration of the induction period is a measure of the dioxygen concentration. This method is applicable over a 0.5 to 32 mg l^{-1} concentration range [152].

The same reagent adsorbed on the surface of silica, is used in the reusable assay for ascorbic acid determination [110]. The depth of blue color reflects the ascorbate concentration. The silica indicator can be regenerated by oxidation of $Cu(TAAB)^+$ under acidic conditions.

The extraction of metals using a variety of macrocyclic ligands, including H_4TAAB and H_8TAAB, was studied by Zolotov and coworkers [153–155]. Copper is selectively extracted, from a large number of other metal ions, by H_4TAAB. Quantitative extraction of copper is not affected by comparable amounts of iron(III), or 1000-fold amounts of Co, Mn, Ni, and Zn ions. This separation scheme based on selective extraction may be applied for the determination of copper by atomic absorption in Ni samples [153].

H_8TAAB can also selectively extract copper in the presence of Bi, Cd, Co, Cr, Mn, Mg, Ni, and Pb, while Ag, Hg, and Pd are partially extracted. The addition of ascorbic acid accelerates the extraction of copper by H_8TAAB [154].

In an agreement with extraction data described above for H_4TAAB, this ligand was found to be the least active of several nitrogen-containing macrocyclic ligands for the transport of Fe(III) through a dichloroethane liquid membrane. This was explained by ligand rigidity and by the high solubility of the iron complex in water [156].

Bearing in mind (1) structural similarities between phthalocyanines and TAAB complexes (including the possibility of layered structure formation) and (2) the significant improvement of charge/discharge and life cycle characteristics obtained for Li batteries upon addition of phthalocyanines to the cathode materials [157], the influence of $Cu(TAAB)^{2+}$, $Cu(H_4TAAB)^{2+}$, and $Cu(H_8TAAB)^{2+}$ on the performance of lithium cells has been investigated [158]. The best capacity (up to 1295 A h kg^{-1}) was found for $Cu(TAAB)^{2+}$; this value is only slightly lower than those observed for phthalocyanine complexes.

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