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THE ROLE OF HALOGEN BONDING IN THE SYNTHESIS AND DESIGN OF TAP COMPLEXES

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Abstract. Halogenated 1,3,5-triazapentadiene (TAP) complexes are important coordination compounds with diverse structures and tunable electronic properties. This review examines the role of halogen bonding in their synthesis, structural organization, and functional design. Key concepts, including the σ-hole model and directional C–X···Lewis base interactions, are discussed. Synthetic routes such as ligand complexation, metal-templated condensation, and solvothermal methods are summarized. The cooperative effects of coordination, hydrogen, and halogen bonds in stabilizing molecular and supramolecular structures are highlighted. Studies of Mn, Fe, Co, Ni, Cu, Zn, and Pd complexes show that halogen bonding influences crystal packing and network formation. Computational analyses support the importance of these interactions. Applications in catalysis, crystal engineering, supramolecular chemistry, and functional materials are also reviewed. Overall, halogen bonding is a powerful tool for designing and controlling TAP-based metal complexes.

Keywords: halogen bonding; TAP complexes; 1,3,5-triazapentadiene; noncovalent interactions; σ-hole.

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List of abbreviations and notations:

TAP	Triazapentadiene
NMR	Nuclear magnetic resonance
IR	Infrared spectroscopy
UV-Vis	Ultraviolet–visible spectroscopy
X-ray	X-ray diffraction
THF	Tetrahydrofuran
DMSO	Dimethyl sulfoxide
ESI-MS	Electrospray ionization mass spectrometry
QTAIM	Quantum theory of atoms in molecules
NCI	Non-covalent interaction

Introduction

Halogenated triazapentadiene (TAP) complexes have attracted considerable attention as one of the promising directions in modern coordination and organic chemistry [1,2]. These compounds are of particular interest due to both their structural features and the physical-chemical parameters they exhibit [3]. The polydentate nature of the TAP ligand, the presence of electron-donor and electron-acceptor centres, as well as the electronic effects induced by the incorporation of halogen atoms (F, Cl, Br, I), significantly enhance the stability and reactivity of these complexes [4,5].

One of the most important characteristics of halogenated TAP complexes is their good solubility in a wide range of organic solvents (such as chlorinated solvents, aromatic hydrocarbons, alcohols, *etc.*) [6]. This property facilitates their use in both laboratory studies and practical applications. High solubility enables the application of these complexes in homogeneous catalytic systems, the development of functional materials, and various analytical methods [7]. In addition, these compounds exhibit considerable thermal and chemical stability, ensuring their long-term storage and usability under different conditions [8].

The incorporation of halogen atoms into the molecular structure affects the distribution of electron density in TAP complexes, thereby altering their spectral, redox, and coordination properties [9]. This, in turn, allows for the tuning of their optical, magnetic, and electrochemical parameters [10]. As a result, halogenated TAP complexes are being investigated as functional materials, sensor systems, catalysts, and potentially biologically active substances [11-13].

Recent studies in this field have demonstrated that various synthetic approaches are available for TAP complexes, including direct condensation reactions, stepwise ligand synthesis, and complexation reactions with metal salts [14,15]. By varying synthesis conditions (temperature, solvent, catalyst, molar ratios, *etc*.), it is possible to deliberately obtain complexes with different structures and tailored properties. The structure and properties of the resulting compounds are typically confirmed using modern physicochemical techniques such as NMR, IR, UV-Vis spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography [16-18].

Considering the above, the preparation of a review article that systematically covers the synthesis, structural features, physicochemical properties, and application areas of halogenated triazapentadiene complexes is both relevant and justified. Such a review can contribute to the generalization of existing scientific results, the identification of promising research directions, and the formation of a theoretical basis for future scientific and practical studies in this field.

Background

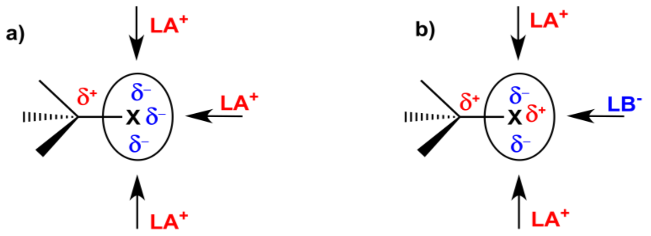
Theoretical basis of halogen bonding

The theoretical foundation of halogen bonding has been largely established through the systematic studies of Metrangolo, P and Resnati, G [19-26]. They demonstrated that, contrary to classical views, halogen atoms are not only electron-rich but can also exhibit a region of positive electrostatic potential in a specific direction. This concept led to the development of the σ-hole model (Scheme 1).

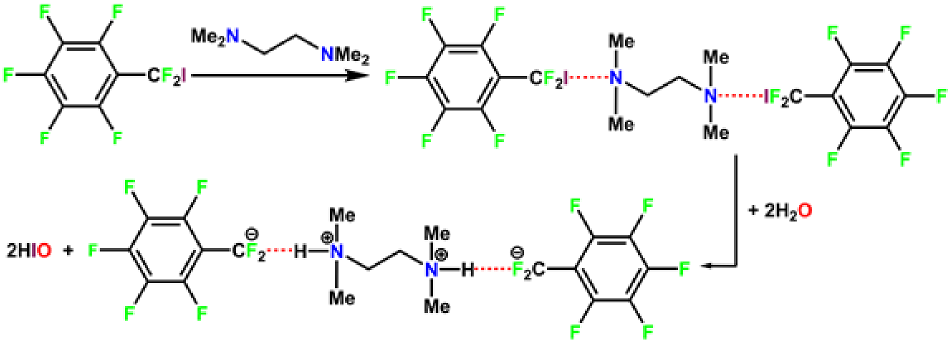
As shown in Scheme 1, the decrease in electron density along the C–X bond axis leads to the formation of a region of positive electrostatic potential, known as the *σ*-hole. This positive region enables directional electrostatic attraction with lone pairs of Lewis bases (such as N, O, S, halogens, *π*-systems, *etc*.).

Quantum-chemical and crystallographic studies carried out by Cavallo, G. *et al.* have demonstrated that a positive electrostatic region is formed on the extension of the C–X bond axis, located on the outer side of the halogen atom, which participates in directional interactions with Lewis bases [20,28-34]. Their work confirmed both the linear nature of halogen bonding and the strength trend following the order I > Br > Cl >> F.

Zhu, S. *et al.* investigated supramolecular systems formed *via* N···I halogen bonding and showed that the N···I distances are significantly shorter than the sum of the corresponding van der Waals radii (Scheme 2) [29].



Scheme 1. Schematic representation of the electron density distribution of covalently bound halogens *(a)* and the expected intermolecular interactions of halogen bonding *(b)* [27].



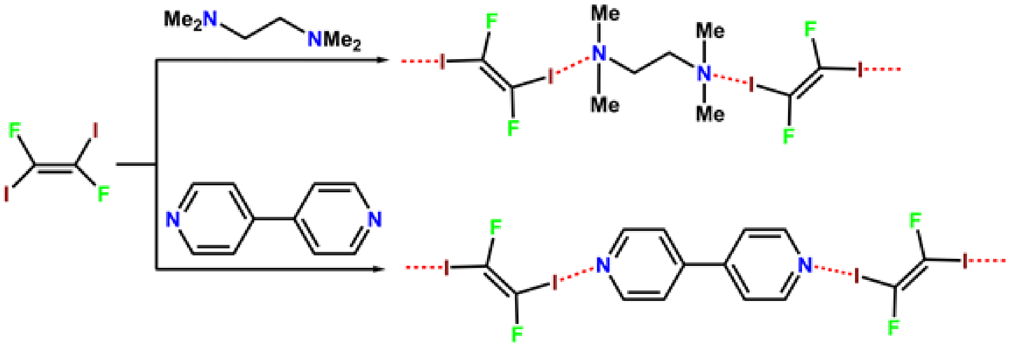
Scheme 2. Synthesis of a halogen-bonded adduct and its hydrolysis [29].

Burton, D.D. *et al.* demonstrated that halogen bonds in bidentate donor-acceptor systems can lead to the formation of one-dimensional infinite chains (Scheme 3) [35].

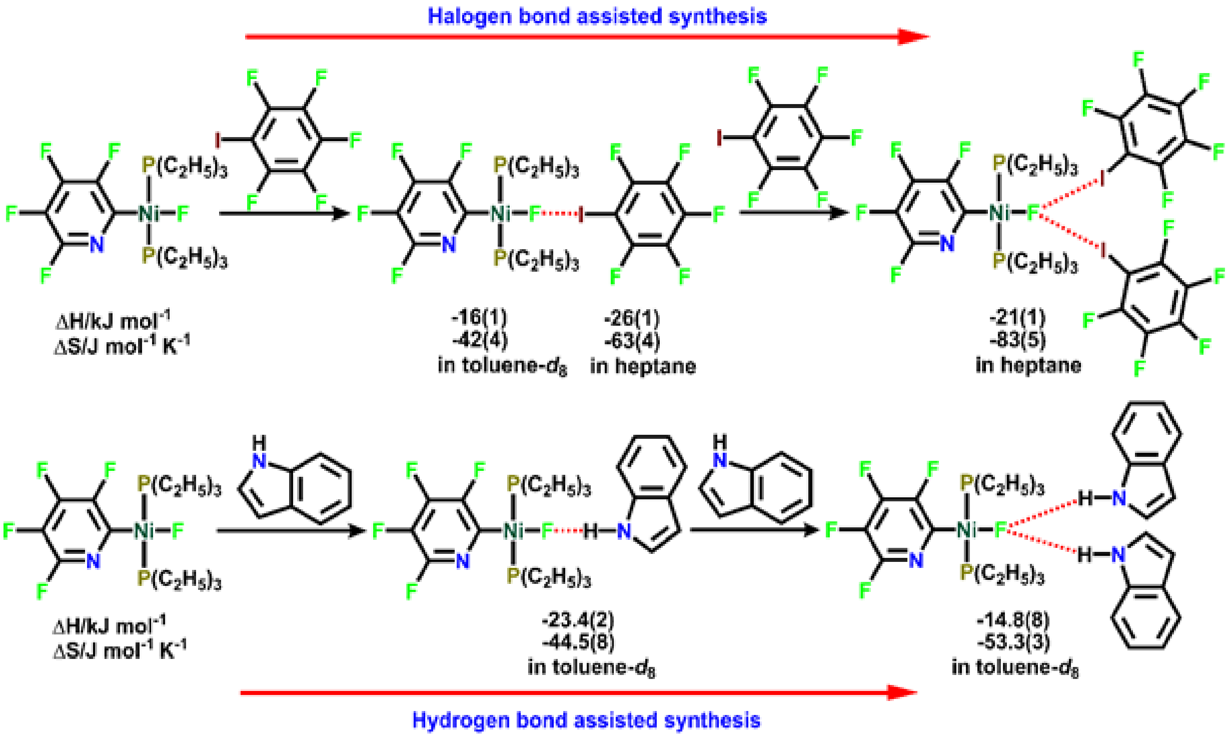
Libri, S. *et al.* compared the thermodynamic parameters of C–I···F–Ni and N–H···F–Ni interactions in metal–halogen systems and showed that halogen bonding can exhibit stability comparable to that of hydrogen bonding (Scheme 4) [36].

Synthetic strategies of TAP complexes

One of the most widely used methods for the synthesis of TAP complexes involves the reaction of a pre-synthesized 1,3,5-triazapentadiene (TAP) ligand with a metal ion. In this approach, the TAP ligand is first prepared independently and subsequently reacted with an appropriate metal salt to form the corresponding complex. One of the earliest studies on the synthesis of TAP complexes was reported by Brown, H.C. *et al.* in 1963 (Figure 1) [37]. They synthesized a TAP ligand bearing perfluoroalkyl substituents and then reacted it with metal acetates. During the reaction, a change in pH was observed, accompanied by deprotonation of the ligand, which subsequently coordinated to the metal centre in its anionic TAP form. Using this method, TAP complexes with Cu(II), Zn(II), Ni(II), and Hg(II) were obtained (Scheme 5).



Scheme 3. Formation of one-dimensional infinite networks *via* halogen bond-directed self-assembly [35].



Scheme 4. Comparison of enthalpy and entropy values for the formation of C–I···F–Ni halogen bonds and N–H···F–Ni hydrogen bonds, determined by NMR titration in solution [36].

Perfluoro-substituted TAP ligands exhibit broad coordination capabilities. Such ligands, for example compounds of the type C_3F_7–C(NR)–N=C(NHR)–C_3F_7, are typically synthesized *via* the reaction of primary amines with fluorinated imines of the type C_3F_7–CF=N–C_4F_9 [38-48]. The resulting TAP ligands generally coordinate to metal centres in their deprotonated anionic form *via* two donor atoms, acting as bidentate ligands and forming heteroligand complexes with various organometallic fragments (Scheme 6) [39,49]. Such complexes have been obtained with metal fragments including Pd(C_3H_5), Rh(cod), Ir(cod), and Rh$(CO)_2$. In addition, these ligands are capable of forming chelate complexes with metals such as Mg, Mn, Fe, Co, Ni, Cu, Zn, and Pd.

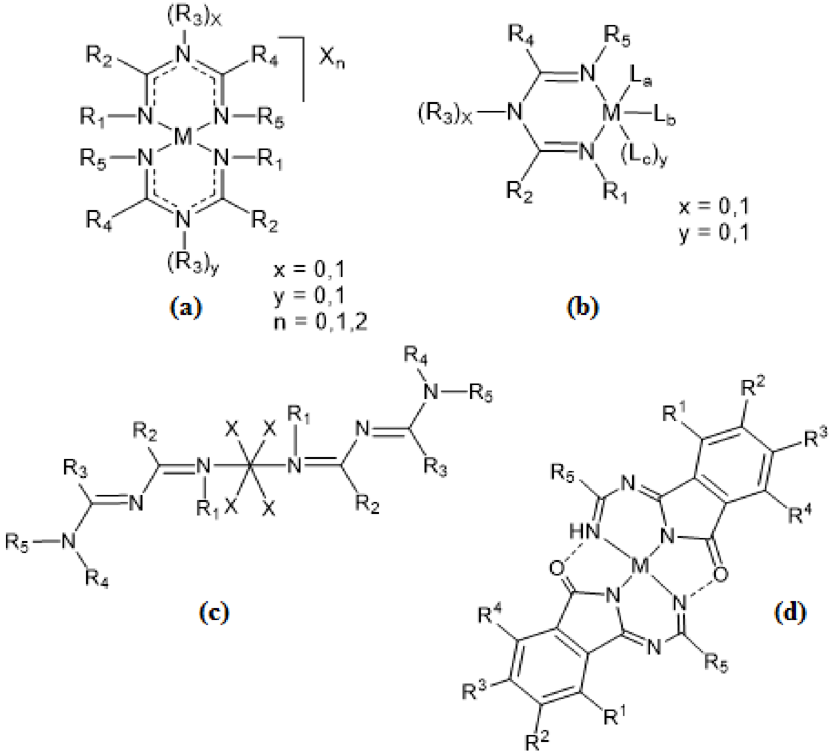
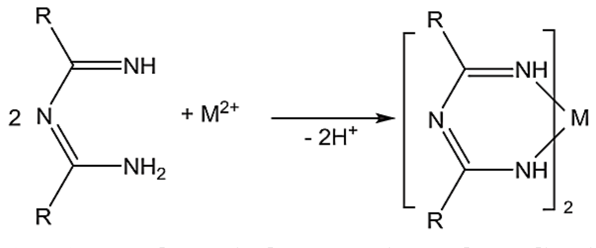
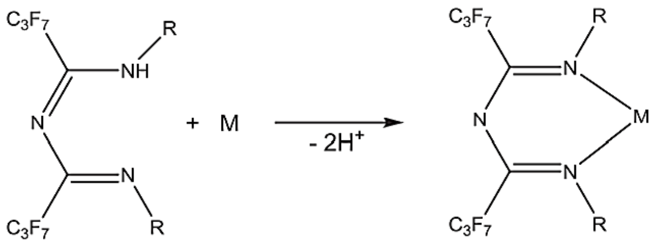


Figure 1. Schematic representation of different coordination and structural types of 1,3,5-triazapentadiene (TAP) ligands: chelate coordination of TAP ligands to a metal centre *(a)*; monodentate/heteroligand coordination mode *(b)*; open-chain TAP ligand framework *(c)*; metallacyclic TAP-based complex. M denotes a metal centre *(d)*; R_1–R_5 represent substituents; L_a, L_β, and Lc denote additional ligands; X denotes a counterion [37].



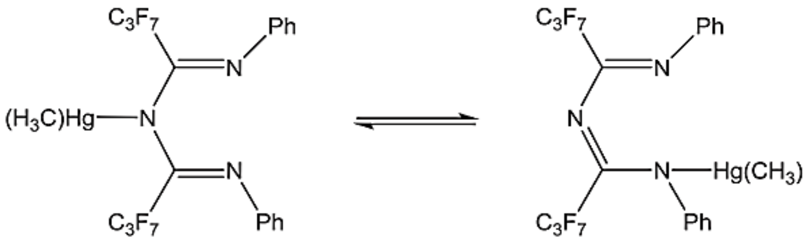
Scheme 5. Formation of M(TAP)$_2$ complexes *via* deprotonation and coordination of the TAP ligand [37].



Scheme 6. Coordination of a C_3F_7-substituted TAP ligand to a metal centre upon deprotonation and formation of a chelate complex [39,49].

One of the notable features of perfluoroalkyl triazapentadienes is their behaviour as weak monoprotic acids, with pKa values around 13–14. This property allows them to react with various bases to form metal salts. For instance, the reaction of C_3F_7–C(NPh)–N=C(NHPh)–C_3F_7 with *n*-butyllithium yields the corresponding lithium salt Li[C_3F_7–C(NPh)–N–C(NPh)–C_3F_7]. This intermediate can subsequently react with different reagents to produce a variety of metal derivatives. In some cases, unusual monodentate coordination modes of the TAP ligand are observed. For example, reactions with Me_3SiCl, $(Ph_3P)AuCl$, or MeHgCl may lead to coordination through only a single donor atom. X-ray crystallographic studies have shown that, in the solid state, the mercury complex coordinates *via* the central nitrogen atom of the TAP ligand, whereas in solution the coordination may shift to a terminal nitrogen atom. This indicates an equilibrium between two different coordination modes (Scheme 7) [39,40,48].

As illustrated in Figure 2, the $[N(CN)_2]^-$ (dicyanamide) ion present in $NaN(CN)_2$ undergoes *in situ* transformation into a TAP ligand under solvothermal conditions. This transformation follows the mechanism proposed by Kopylovich, M.N. *et al.* for the formation of $M(TAP)_2$ complexes [50]. According to the mechanism suggested by Kopylovich, M.N. *et al.* an intermediate compound of the type $[Cu(dca)_2]_n$ is formed in the initial stage of the reaction [51]. Subsequently, a methanol molecule performs a nucleophilic attack on this intermediate. As a result, one of the C≡N triple bonds is cleaved, and the nitrogen atom binds a proton from methanol, leading to the formation of an –NH group. Simultaneously, the methoxide group (–OMe) forms a bond with the carbon atom, resulting in a C–OMe linkage. The nucleophilic attack of methanol also affects the second C≡N group, ultimately leading to the formation of the TAP-type ligand framework. During this process, the NH groups of the resulting 1,3,5-triazapentadiene ligand coordinate to the Cu^{2+} ion, forming a metal complex with a bidentate ligand. Thus, under solvothermal conditions, the transformation of the dicyanamide ion leads to the formation of both the TAP ligand and the corresponding metal complex.



Scheme 7. Coordination isomerism arising from the binding of the $Hg(CH_3)$ fragment to different nitrogen donor atoms of the TAP ligand [39,40,48].

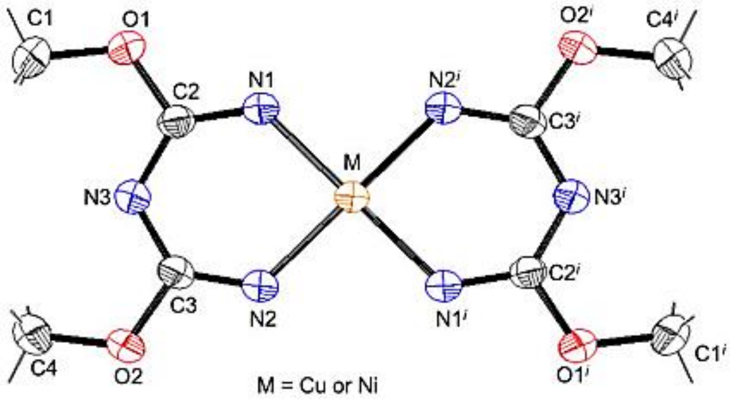


Figure 2. ORTEP representation with 45% probability ellipsoids showing atom labelling in $M(TAP)_2$ complexes (M = Cu(II) or Ni(II)) [50].

TAP ligands bearing sterically bulky substituents exhibit particularly interesting coordination properties. Such ligands can form half-sandwich-type complexes in which one side of the metal centre remains accessible. These complexes display high thermal and air stability and are considered promising for catalytic applications. For example, the reaction of Cu_2O with C_3F_7–C(NRdipp)–N=C(NHRdipp)–C_3F_7 yields a complex of the type [Cu{C_3F_7–C(NRdipp) NC(NRdipp)C_3F_7}(S)], where S= MeCN (Figure 3). This coordinated acetonitrile ligand can later be replaced by small molecules such as isocyanides, carbon monoxide, or ethylene [41,43,47].

Silver nitrile complexes of a similar type have also been synthesized. For example, in [Ag{C_3F_7–C(NRdipp)–N–C(NRdipp)–C_3F_7} (NCMe)], the TAP ligand coordinates *via* the central nitrogen atom. However, upon reaction with triphenylphosphine, the complex transforms into a chelate structure, binding to the metal through two donor atoms (Figure 4) [51].

Sterically hindered TAP ligands have also been prepared using methods developed by Ley and Müller. These ligands form complexes with metals such as Co(II), Ni(II), Pd(II), and Zn(II). In most cases, half-sandwich complexes of the type [MX(tap)] are observed. When copper(II) triflate is used, a symmetric octahedral complex of the type [CuX_2(tap)$_2$], containing two coordinated TAP ligands, can also be obtained. In these complexes, proton transfer from a terminal nitrogen atom to the central nitrogen atom is observed, while the TAP ligand remains in a neutral form [51].

TAP ligands are also capable of forming chelate complexes with lithium ions. In such systems, THF molecules act as additional ligands, leading to the formation of various coordination geometries, including tetrahedral and planar metallacyclic structures (Scheme 8) [52].

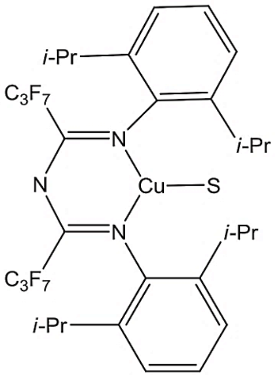


Figure 3. Structure of a copper complex with a perfluoro-substituted TAP ligand [41,43,47].

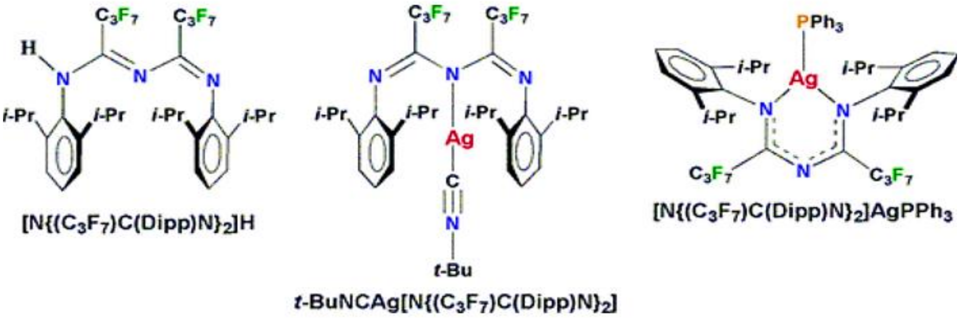
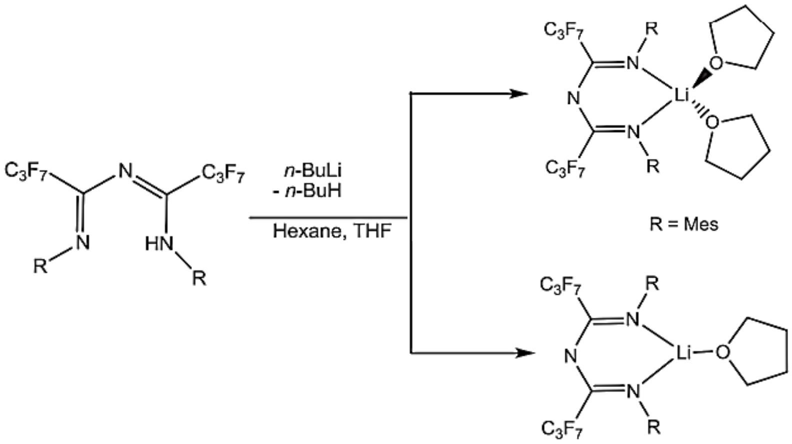


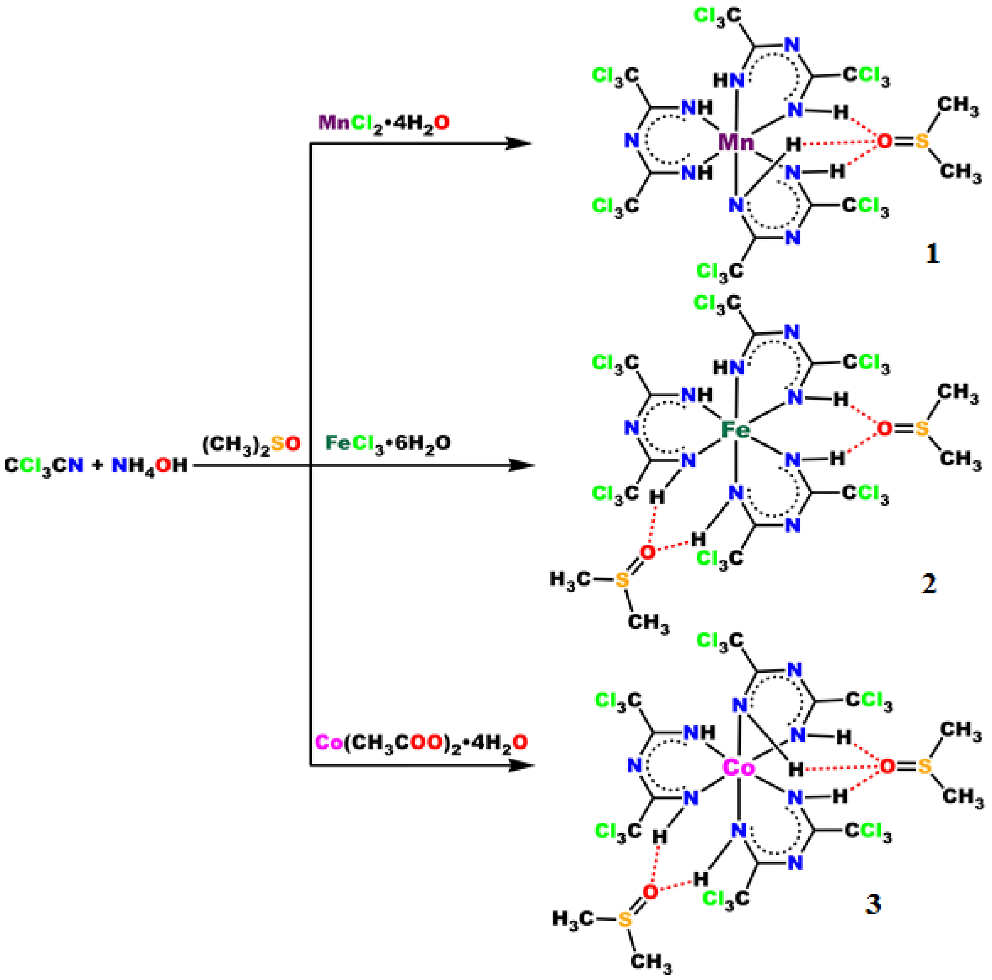
Figure 4. Synthesis and coordination behaviour of a perfluoro-substituted TAP ligand toward silver(I): formation of nitrile and triphenylphosphine complexe [51].



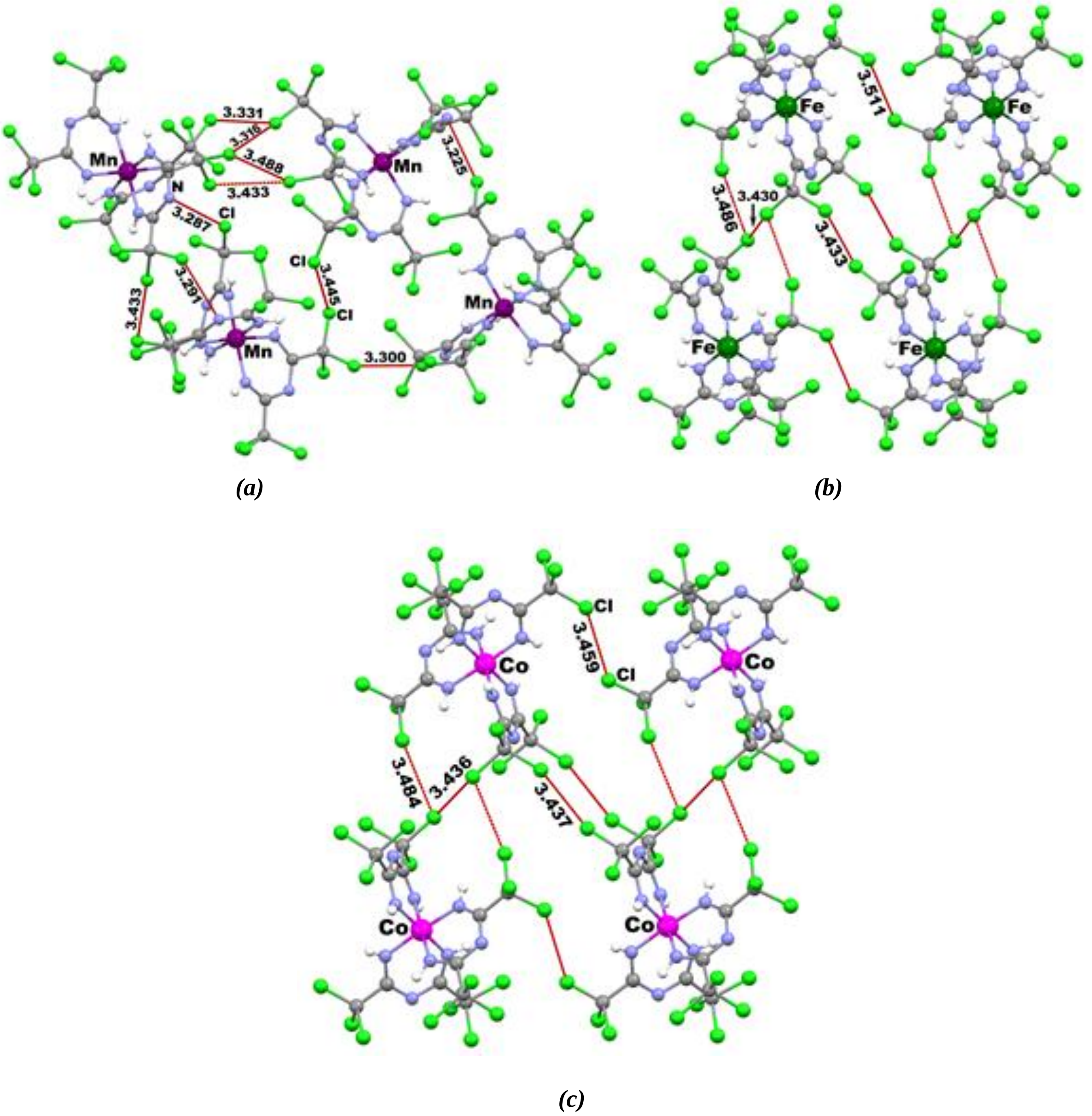
Scheme 8. Synthesis of lithium–TAP complexes *via* deprotonation with *n*-BuLi [52].

Other examples of sterically bulky TAP ligands have been synthesized by Masuda, J.D. and co-workers. They obtained a TAP-type ligand *via* the reaction of an imidoyl chloride with 2,6-diisopropylaniline and subsequently prepared the corresponding aluminium complexes by reacting this ligand with AlI_3 and $AlMe_3$. These reactions afforded complexes of the types $[AlI_2(tap)][AlI_4]$ and $[Al(Me)_2(tap)][Al(Me)_4]\cdot AlMe_3$. When aluminium hydride is used as a starting material, the corresponding Al-TAP hydride complexes can also be obtained [52].

In recent years, the use of halogen bonding as a rational design tool in the synthesis of TAP (1,3,5-triazapentadiene)-based complexes has attracted particular attention. Previous studies have shown that the cooperative effect of coordination, hydrogen, and halogen bonding directly influences both the formation mechanism of the complexes and their crystal architecture [53-60]. This approach is especially evident in metal-templated condensation reactions. The direct reaction of $CCl_3C{\equiv}N$ and ammonia with metal salts in a DMSO medium leads to the formation of tris{2,4-bis(trichloromethyl)-1,3,5-triazapentadienato}-M(III) complexes (Scheme 9), representing an important stage in TAP complex synthesis [61]. In this process, the ligand is formed in situ in the presence of the metal centre, while coordination bonds are formed simultaneously with hydrogen and halogen bonding interactions. Analysis of the crystal structures of the obtained complexes has shown that infinite chains are formed through Cl···Cl interactions (Figure 5). The correlation between Cl···Cl distances and the ionic radius of the metal demonstrates that the strength of halogen bonding depends on the nature of the metal centre. This cooperative effect results in a highly exothermic reaction and contributes to product stabilization.



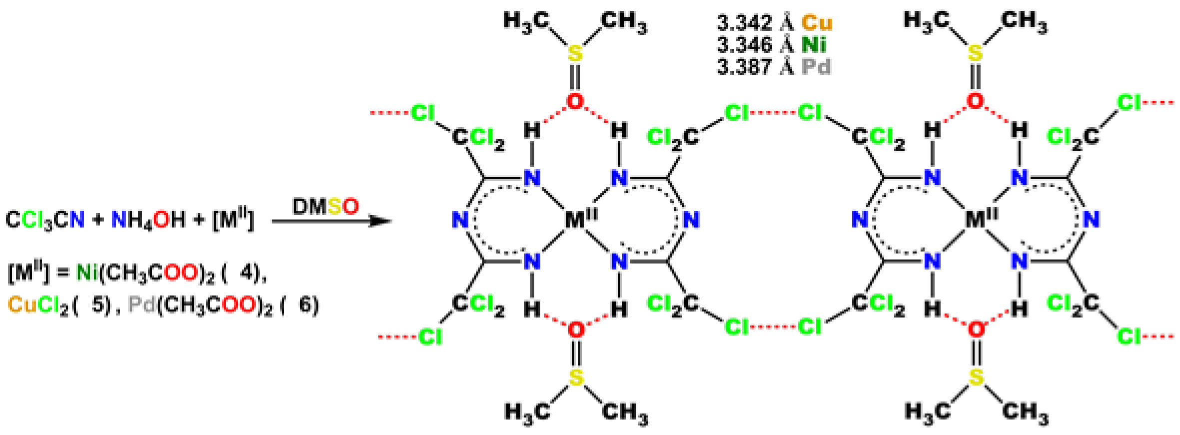
Scheme 9. Synthesis of TAP complexes (1–3) and the cooperative role of coordination, hydrogen, and halogen bonding in the process [61].



(a) *(b)*

(c)

Figure 5. Cl···Cl interactions in TAP complexes (1–3): Mn complex *(a)*, Fe complex *(b)*, Co complex *(c)*; DMSO molecules are omitted for clarity [61].

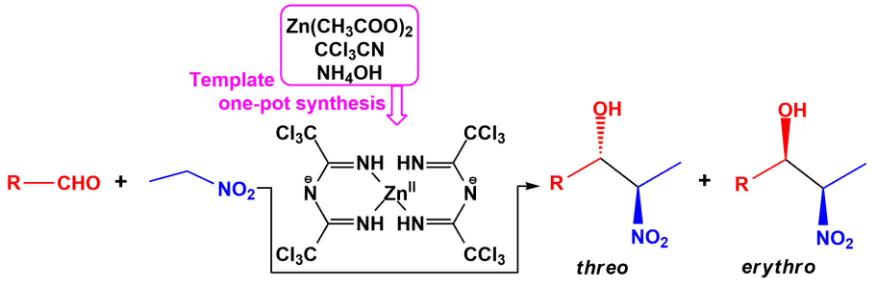


Scheme 10. Synthesis of TAP complexes (4–6) and the cooperative role of coordination, hydrogen, and halogen bonding in the process [70].

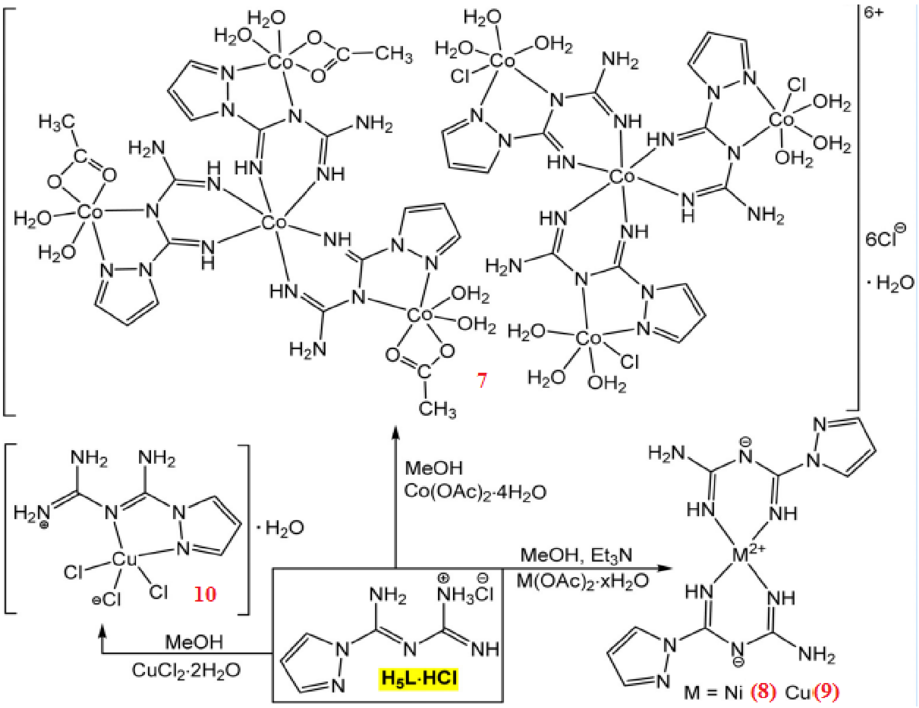
Through modification of the same methodology, bis{2,4-bis(trichloromethyl)-1,3,5-triazapentadienato}-M(II) complexes have been obtained (Scheme 10) [70]. In these systems, the (N)H groups of the ligand form hydrogen bonds with DMSO molecules, while the chlorine atoms of the CCl_3 fragments participate in Cl···Cl halogen bonding interactions. As a result, the combined action of coordination, hydrogen, and halogen bonding leads to the formation of a three-dimensional supramolecular architecture. The variation of Cl···Cl distances in the order Cu < Ni < Pd indicates that the electronic properties and ionic radius of the metal directly influence the supramolecular organization.

A zinc(II) complex containing chlorinated triazapentadiene ligands was synthesized in DMSO medium *via* a one-step templated condensation reaction of trichloroacetonitrile and ammonium hydroxide in the presence of zinc(II) acetate. (Scheme 11) As a result, bis(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)zinc(II) was obtained with a yield of 71%. The complex was fully characterized by elemental analysis, ESI-MS, IR spectroscopy, and single-crystal X-ray diffraction. IR spectral data confirmed the disappearance of the characteristic nitrile stretching band and the appearance of bands corresponding to NH and C=N groups, indicating successful ligand formation and coordination to the zinc centre. The catalytic activity of the complex was evaluated in the Henry (nitroaldol) reaction. Reactions carried out at room temperature afforded high yields of up to 99% and good diastereoselectivity (threo/erythro ratio up to 3:1). These results demonstrate that the synthesized Zn(II) complex acts as an efficient and readily accessible catalyst for diastereoselective carbon–carbon bond formation reactions [62].

As a result of similar synthetic approaches, Mahmudov, I. *et al.* obtained a series of new coordination compounds containing Co(II/III), Ni(II), and Cu(II) ions (Scheme 12) [63].



Scheme 11. Formation of diastereomeric *β*-nitroalcohols *via* the Henry (nitroaldol) reaction of aldehydes and nitroalkanes catalysed by a triazapentadienato Zn(II) complex [62].

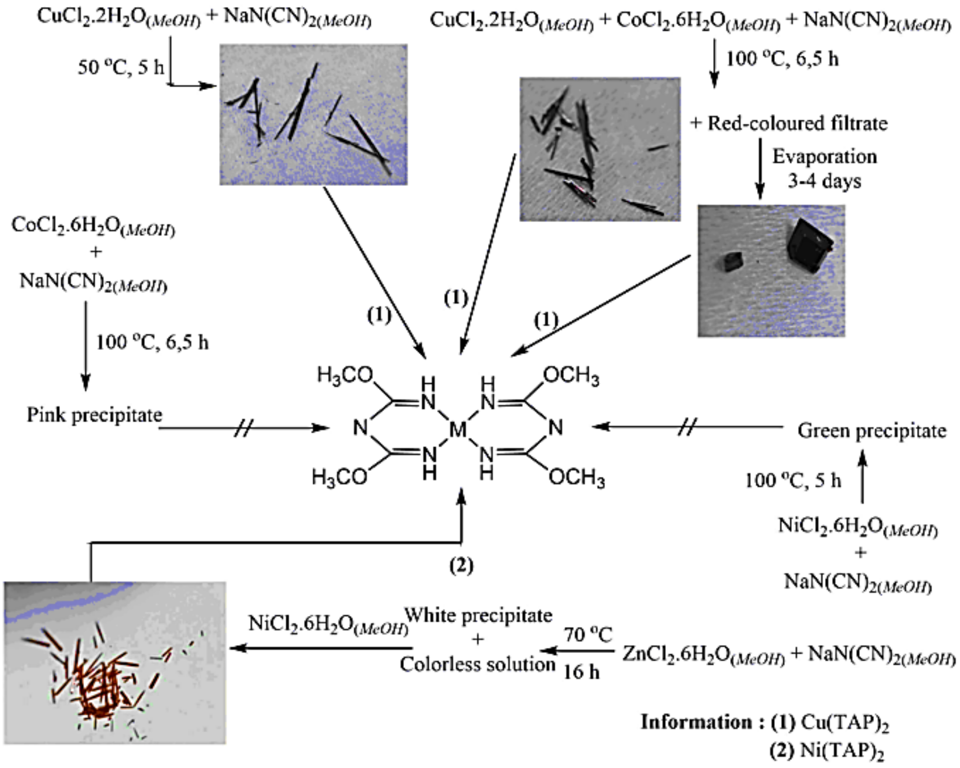


Scheme 12. Synthesis of compounds 7–10 [63].

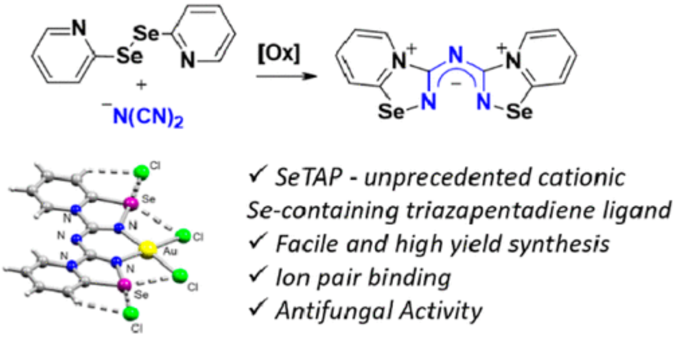
Dasna, I.W. *et al.* reported that the synthesis of the $Cu(TAP)_2$ complex can be achieved *via* a solvothermal method by reacting $CuCl_2·2H_2O$ with $NaN(CN)_2$ in methanol [64]. This method is considered one of the simplest and most efficient routes for obtaining $Cu(TAP)_2$. The formation of the resulting crystals is illustrated in Scheme 13. An alternative approach involves the use of mixed metal salts. In this method, $CuCl_2·2H_2O$ and $CoCl_2·6H_2O$ are dissolved in methanol, followed by the addition of a methanolic solution of $NaN(CN)_2$. This reaction also yields $Cu(TAP)_2$ crystals. The crystals may form directly in the autoclave or precipitate upon evaporation of the filtrate. Although the crystal morphology differs, their colour and melting point remain the same.

Attempts to synthesize $Co(TAP)_2$ using the same solvothermal method were unsuccessful. Similarly, the solvothermal reaction of $NiCl_2·6H_2O$ with $NaN(CN)_2$ in methanol produced only a green precipitate rather than the desired $Ni(TAP)_2$ complex. Therefore, a modified method was employed for $Ni(TAP)_2$ synthesis. Initially, $ZnCl_2·6H_2O$ and $NaN(CN)_2$ were reacted under solvothermal conditions in methanol, yielding a colourless solution and a white precipitate. Subsequently, a solution of $NiCl_2·6H_2O$ was added to this mixture, and the system was reheated under solvothermal conditions. This stepwise approach successfully afforded $Ni(TAP)_2$ crystals [64].

Sapronov, A.A. *et al.* described the preparation of a new selenium-based cationic triazapentadiene ligand system. The ligand is formed by the reaction of 2-pyridylselenyl derivatives with sodium dicyanamide in a 2:1 molar ratio, leading to sodium complexes containing a selenium-based triazapentadiene (SeTAP) framework (Scheme 14) [65].



Scheme 13. Synthetic strategy for $M(TAP)_2$ (M = Cu, Ni) compounds using the solvothermal method [64].



✓ SeTAP - unprecedented cationic Se-containing triazapentadiene ligand
✓ Facile and high yield synthesis
✓ Ion pair binding
✓ Antifungal Activity

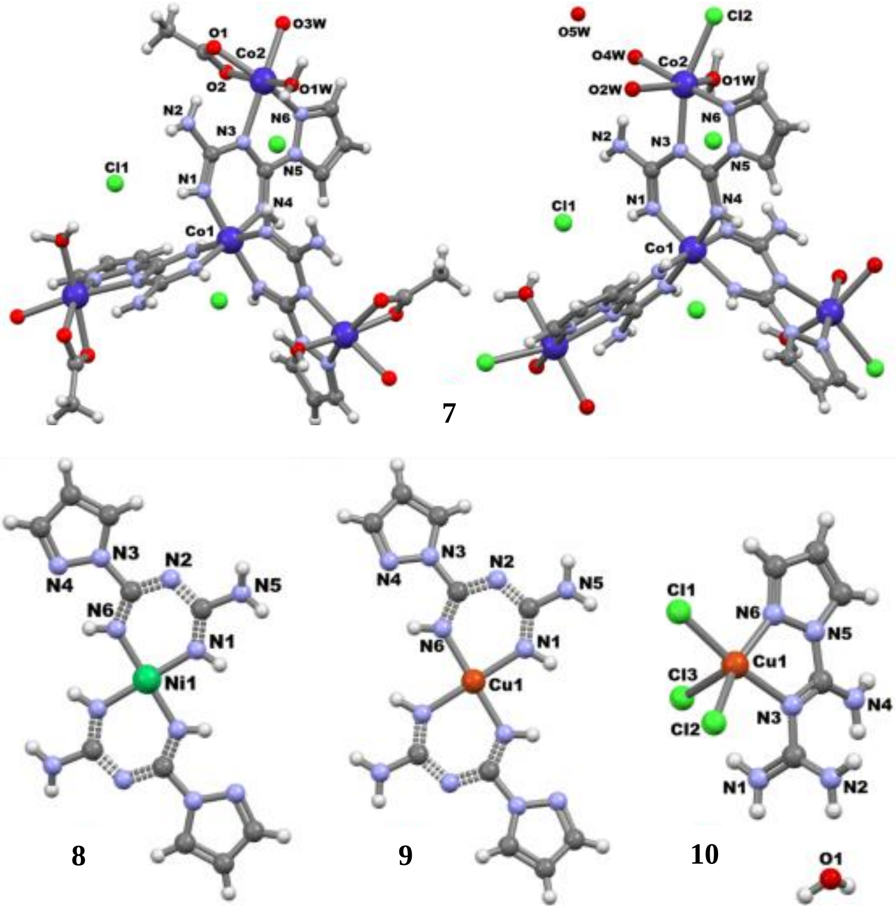
Scheme 14. Oxidation reaction, structure, and properties of a selenium-containing triazapentadiene ligand (SeTAP) [65].

In the subsequent step, transmetalation reactions from sodium to other metals provide an efficient route to various SeTAP metal complexes. This approach has been successfully applied using metal precursors such as $CuCl_2$, $AgNO_3$, $NaAuCl_4$, and $FeCl_3$. Density functional theory (DFT) calculations were performed to investigate and rationalize the chalcogen bonding interactions observed in the crystal structures. In addition to structural studies, the SeTAP ligand and its corresponding metal complexes were evaluated for antifungal activity. Among the tested phytopathogenic fungi, *Phoma eupyrena* exhibited particularly high sensitivity to most of the investigated compounds [65].

Physicochemical properties of halogenated TAP complexes

Halogenated 1,3,5-triazapentadiene (TAP) complexes form coordination compounds with various transition metals and exhibit diverse structural and physicochemical properties. The crystal structures of halogen-containing complexes clearly reflect the characteristics of the coordination environment around the metal centre. For example, in certain Co(III)/Co(II) complexes (**7**–**10**), the metal atom adopts a distorted octahedral coordination environment surrounded by nitrogen donor atoms (Figure 6). In contrast, Ni(II) and Cu(II) complexes typically exhibit square-planar coordination geometry, where the metal centre is coordinated by two bidentate TAP ligands. In these systems, metal–nitrogen bonds indicate the presence of a delocalized N–C–N framework, which contributes to the overall stability of the complexes.

Studies on copper(II) systems conducted by Virovets, A.V. *et al.* have demonstrated the role of halogen bonding in both kinetic and thermodynamic control mechanisms (Figure 7) [66]. In compounds **11** and **12**, C–I···Cl interactions form rapidly, leading to the generation of kinetic products. However, in the more stable compound **13**, a Cu_3 cluster structure forms initially, followed by the construction of a two-dimensional network through I···Cl halogen bonding interactions. This finding indicates that halogen bonding not only governs crystal packing but can also direct reaction pathways and product selectivity.

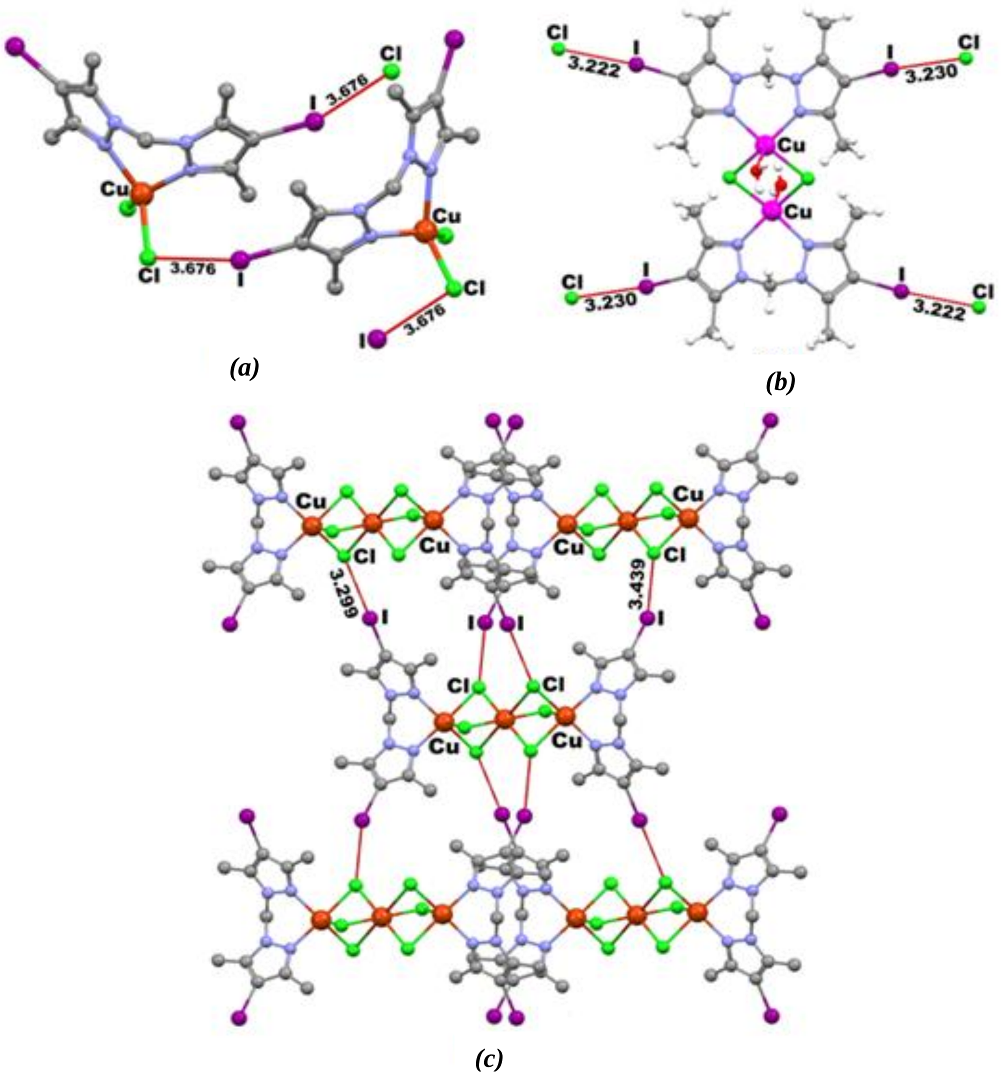


7

8 **9** **10**

Figure 6. Crystal structures of compounds 7–10 with partial atom labelling. In the structure of compound 7, hydrogen atoms attached to O2W, O3W, O4W, and O5W could not be located.

Halogen–nitrogen interactions of the type C–X···NC(M), investigated by Ormond-Prout, J.E. *et al*. provide additional stabilization within coordination environments (Scheme 15) [67]. In halopyridinium-hexacyanometallate systems, the variation in halogen bond ц lengths depending on the nature of the metal centre demonstrates that the metal ion can indirectly modulate the strength of halogen bonding. This concept is particularly relevant for TAP ligands, as their NCNCN backbone contains three nitrogen donor centres that can act as effective acceptors for halogen bonding interactions.

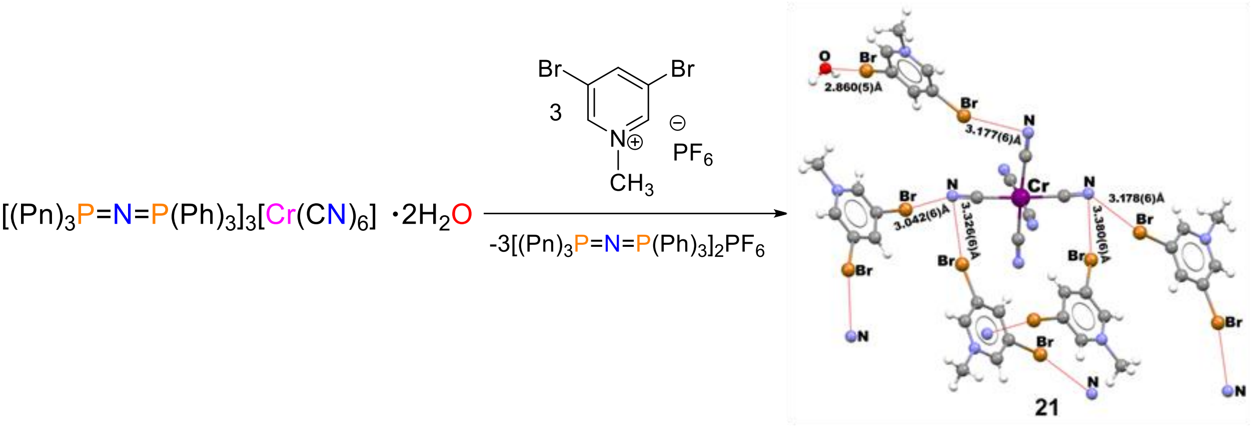


(a)

(b)

(c)

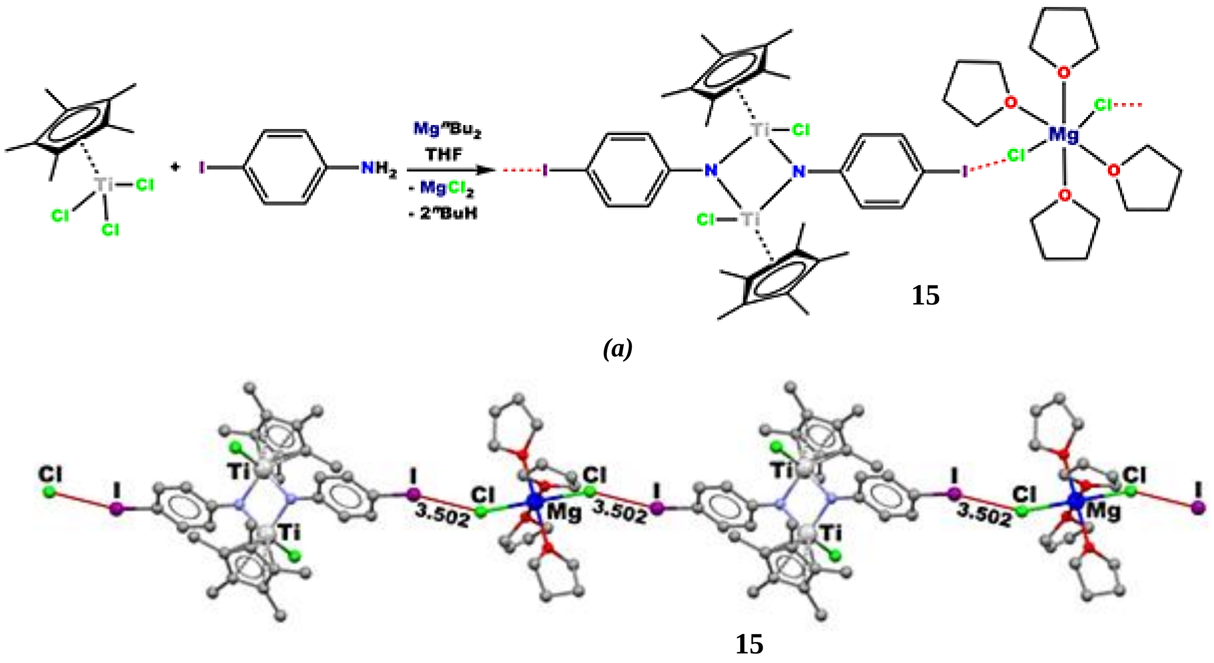
Figure 7. Halogen bonding in compounds 11–13: compound 11 *(a)*, compound 12 *(b)*, compound 13 *(c)* [66].



Scheme 15. Synthesis and structure of compound 21 showing C–Br···N and C–Br···O halogen bonds [67].

In a titanium-based system synthesized by Vidal, F. *et al.* the formation of a one-dimensional chain structure via Mg–Cl···I–C type halogen bonding has been demonstrated (Scheme 16) [68]. This example shows that metal–halogen fragments can act as acceptors in halogen bonding and that metallacyclic structures enhance the σ-hole potential of the halogen atom, thereby strengthening the directionality of the interaction. It was particularly noted that substitution of iodine with chlorine prevents the formation of halogen bonding, indicating the decisive role of the halogen nature.

Tris(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato) complexes of Mn(III), Fe(III), and Co(III) were reported to be synthesized *via* a one-step templated reaction of trichloroacetonitrile with ammonia in DMSO in the presence of the corresponding metal salts. The obtained compounds were characterized by elemental analysis, IR spectroscopy, ESI-MS, and single-crystal X-ray diffraction. Structural studies revealed that both intra- and intermolecular halogen and hydrogen bonding interactions play a crucial role in stabilizing the complexes. A correlation between the ionic radii of the metal centres and intermolecular Cl···Cl distances was observed in the crystal structures. Furthermore, these complexes, along with their Cu(II) analogues, act as efficient catalyst precursors in the oxidation of 1-phenylethanol with tert-butyl hydroperoxide under microwave irradiation. Under low-power microwave conditions, a turnover number (TON) of up to 5.0 × 10^3 was achieved within one hour, affording acetophenone in yields up to 99% (Figure 8) [69].



15

(a)

15

(b)

Scheme 16. Synthesis of compound 15 *(a)*; 1D arrangement in 15 via Mg–Cl···I–C halogen bonding interactions *(b)* [68].

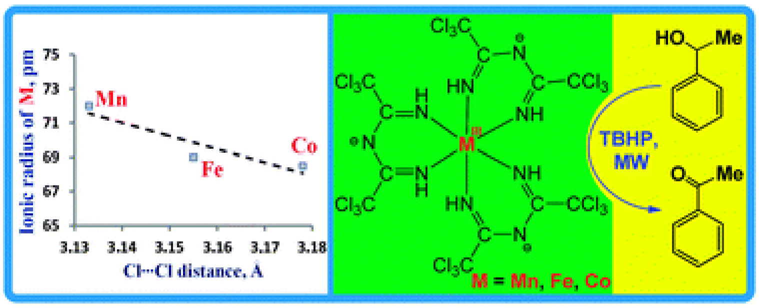


Figure 8. Correlation between metal ion radius (Mn, Fe, Co) and Cl···Cl halogen contacts in tris(trichloromethyl)-substituted TAP complexes, and their catalytic application in the oxidation of 1-phenylethanol in the presence of TBHP [69].

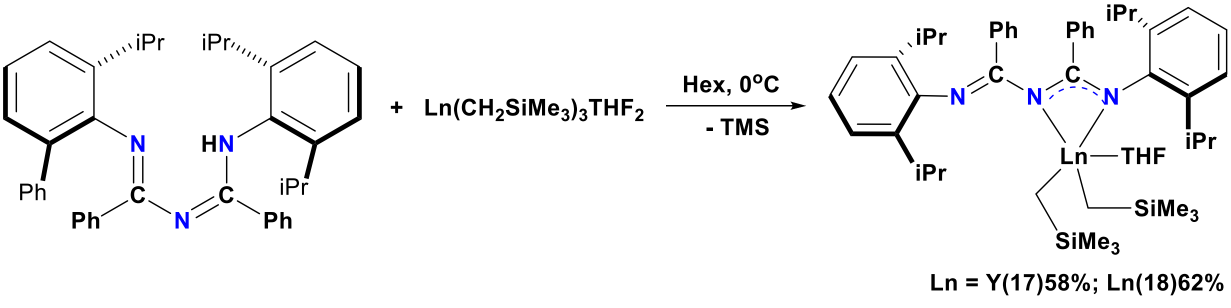
Mononuclear Ni(II), Cu(II), and Pd(II) complexes containing chlorinated 1,3,5-triazapentadienato ligands have also been reported to be synthesized *via* templated condensation of trichloroacetonitrile with ammonia in DMSO in the presence of the respective metal salts (Figure 9). The obtained compounds, with the general formula $\{M[NH{=}C(CCl_3)NC(CCl_3){=}NH]_2\}[(CH_3)_2SO]_2$, were isolated in moderate to good yields. These complexes were fully characterized by ESI-MS, IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. Structural analysis showed that the metal centre adopts a square-planar coordination environment, with two monoanionic triazapentadienato ligands chelating the metal ion and positioned around an inversion centre. In the solid state, resonance-assisted hydrogen bonding occurs between the N–H groups of the ligand and the oxygen atoms of DMSO molecules. Additionally, Cl···Cl interactions between trichloromethyl substituents contribute to the formation of two-dimensional supramolecular networks. These findings indicate that chlorinated triazapentadiene complexes can serve as versatile building blocks for supramolecular architectures directed by hydrogen and halogen bonding interactions [70].

Functional applications

1,3,5-Triazapentadiene ligands belong to a class of multifunctional ligands that play an important role in coordination chemistry. These ligands form stable complexes with metal centres and are widely used in the synthesis of various organic, coordination, and supramolecular compounds. In particular, triazapentadiene complexes are known to play a significant role in metal-mediated activation of nitrile groups. Such reactions enable the formation of new heterocyclic and coordination compounds.

The 1,3,5-triazapentadiene-type ligand 2,6-iPr$_2$C$_6$H$_3$NC(Ph)NC(Ph)NHC$_6$H$_3$$iPr_2$-2,6 (**16**) was synthesized following a previously described procedure [71]. Using this ligand, bis(alkyl) complexes of rare-earth metals were synthesized *via* alkane elimination reactions. In preparative-scale reactions, equimolar amounts of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) and ligand (**16**) were reacted in hexane at 0°C. As a result, the following bis(alkyl) complexes were obtained: [2,6-iPr$_2$C$_6$H$_3$NC(Ph)NC(Ph)NC$_6$H$_3$$iPr_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF), where Ln = Y (**17**) and Lu (**18**). These complexes were isolated as bright yellow microcrystalline solids in yields of 58% and 62%, respectively (Scheme 17).

Figure 9. Supramolecular structure in TAP complexes (M= Ni, Cu, Pd) formed *via* hydrogen bonding and Cl···Cl halogen interactions [70].



Scheme 17. Synthesis of complexes 17 and 18 [71].

In these complexes, the metal centre is coordinated by four nitrogen atoms, forming a square-planar geometry. Analysis of the crystal structure indicates electron delocalization between the metal centre and the ligand, which enhances the stability of the metallacyclic framework. These structural features contribute to the wide applicability of triazapentadiene ligands in coordination chemistry.

The reaction of ligand **16** with $Sc(CH_2SiMe_3)_3(THF)_2$ results in cleavage of a C–N bond in the 1,3,5-triazapentadiene framework, yielding a μ₂-bridged dianionic amidinate ligand and forming a dimeric mono(alkyl) complex $[\{\mu_2\text{-}i\mathrm{Pr}_2C_6H_3NC(Ph)N\}Sc(CH_2SiMe_3)(THF)]_2$ (Scheme 18). This complex was isolated as pale yellow crystals in 43% yield and is highly sensitive to air and moisture. However, it exhibits notable thermal stability, showing no decomposition in benzene-d_6 at 20°C over two weeks and remaining stable upon heating at 60°C for 6 hours [72].

The catalytic and supramolecular significance of TAP complexes

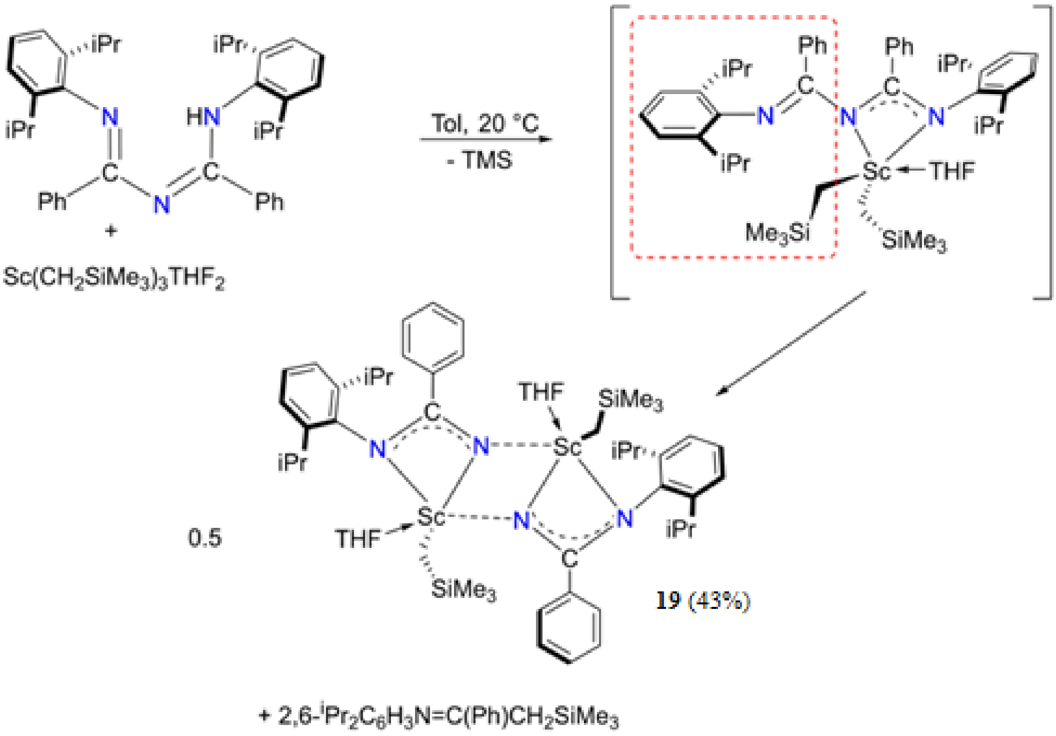
TAP complexes formed with transition metals exhibit significant potential in catalytic processes. Palladium-based complexes are of particular interest in this regard. During catalytic cycles, palladium can readily interconvert between Pd(II) and Pd(0) oxidation states, which underlies its catalytic activity in a wide range of organic transformations. Consequently, palladium complexes are widely employed in the formation of C–C and C–heteroatom bonds.

The activation of nitrile groups in the presence of palladium plays a crucial role in the synthesis of TAP-type complexes. Studies have shown that Pd(II)-mediated reactions of nitrile compounds can lead to products with diverse coordination and supramolecular architectures. Variation of reaction conditions, particularly the solvent, results in the formation of products with different structural features.

For example, when 2,2,2-trichloro acetonitrile reacts with an ammonia source in the absence of a palladium catalyst, simple amide products are predominantly formed. However, in the presence of a Pd(II) catalyst, the reaction yields various coordination complexes and heterocyclic structures (Scheme 19) [73].

The complexes obtained from these reactions exhibit distinct coordination environments in their crystal structures. Notably, in some cases, the coexistence of both Pd(II) and Pd(0) centres within the same structure has been observed, which is of particular importance for catalytic systems [74].

X-ray crystallographic studies have shown that TAP ligands form square-planar coordination environments with palladium ions. In such systems, the metal ion coordinates with nitrogen atoms of the ligand, resulting in stable chelate structures.

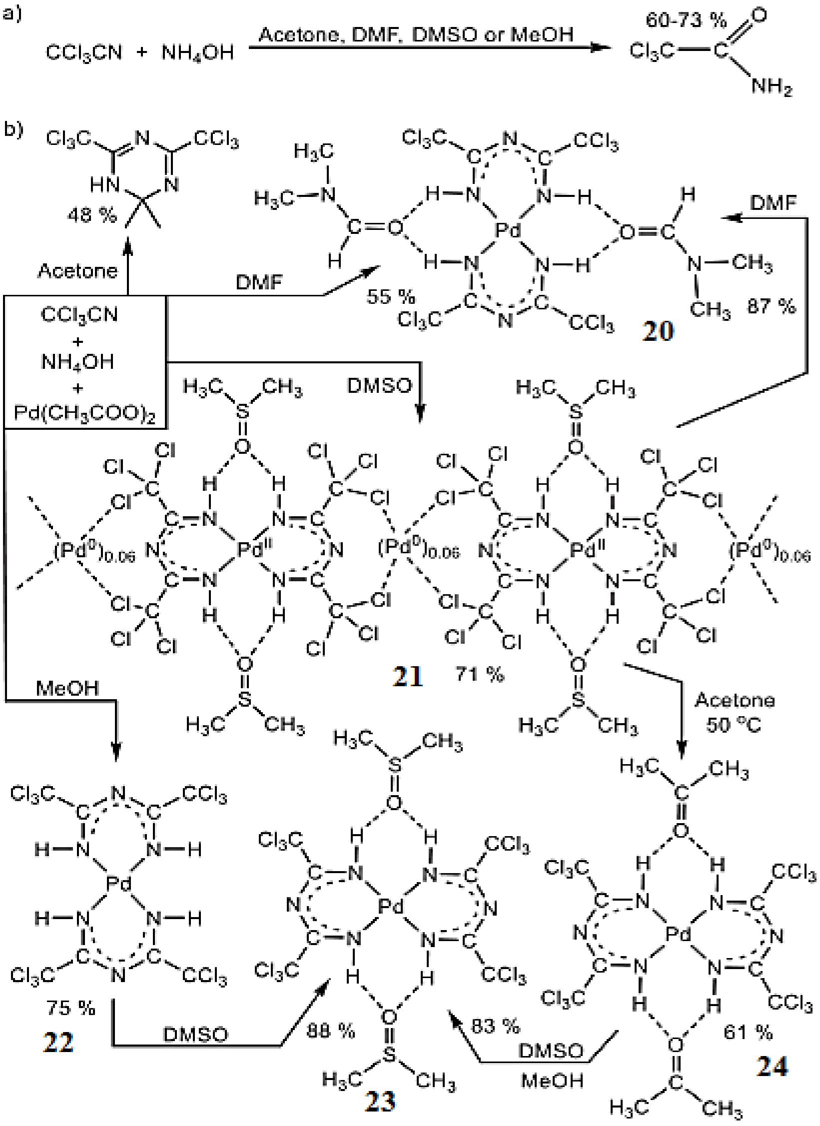


Scheme 18. Synthesis of complex 19 [72].

In one of the characterized structures, an unusual interaction between a Pd(0) atom and chlorine atoms has been observed. These interactions can be interpreted as a combination of halogen bonding and semi-coordination. A fragment of the crystal structure is presented in Figure 10 [75,76].

In these structures, noncovalent interactions play a crucial role in supramolecular organization. In particular, halogen and hydrogen bonding interactions contribute significantly to the stability of the crystal lattice.

The electronic properties and metal–ligand interactions in TAP complexes have also been investigated using theoretical computational methods. Molecular electrostatic potential (MEP) analysis has shown that positive potential regions (σ-holes) are formed along the extension of C–Cl bonds. These regions facilitate the formation of halogen bonds.



Scheme 19. General scheme for the formation of TAP-type complexes *via* Pd(II)-mediated activation of nitrile groups (reactions carried out in different solvents) [73].

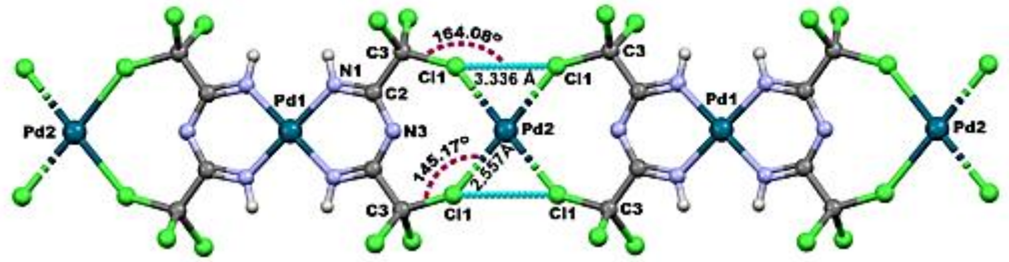


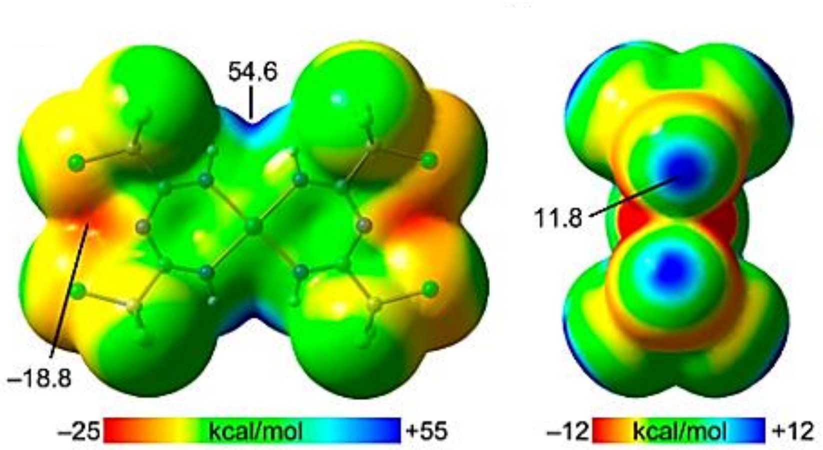
Figure 10. Fragment of the crystal structure of a TAP complex containing Pd(II) and Pd(0) centres, illustrating Pd–Cl interactions [75,76].

MEP maps are shown in Figure 11 and help to rationalize the nature of noncovalent interactions in TAP complexes.

Furthermore, QTAIM and NCI analyses have revealed strong interactions between Pd and Cl atoms. The calculated interaction energy is approximately −29 kcal/mol, which corresponds to strong noncovalent interactions (Figure 12).

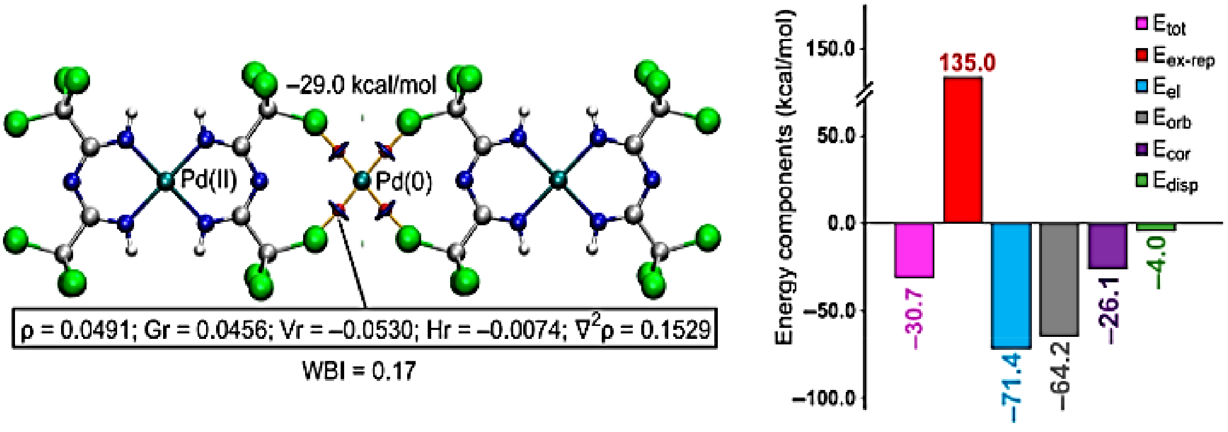
To further elucidate orbital interactions, Natural Bond Orbital (NBO) analysis was performed. The results indicate that the lone pair of the palladium atom can donate electron density into the antibonding orbital of the C–Cl bond. At the same time, back-donation from chlorine atoms to the palladium centre is also observed (Figure 13).

Thus, palladium complexes based on TAP ligands exhibit considerable potential in catalysis, supramolecular chemistry, and the development of new functional materials. The combined influence of noncovalent interactions and coordination bonding enables fine control over the structure and reactivity of these systems. These features provide a strong scientific basis for further exploration and broader applications of TAP complexes in future studies.



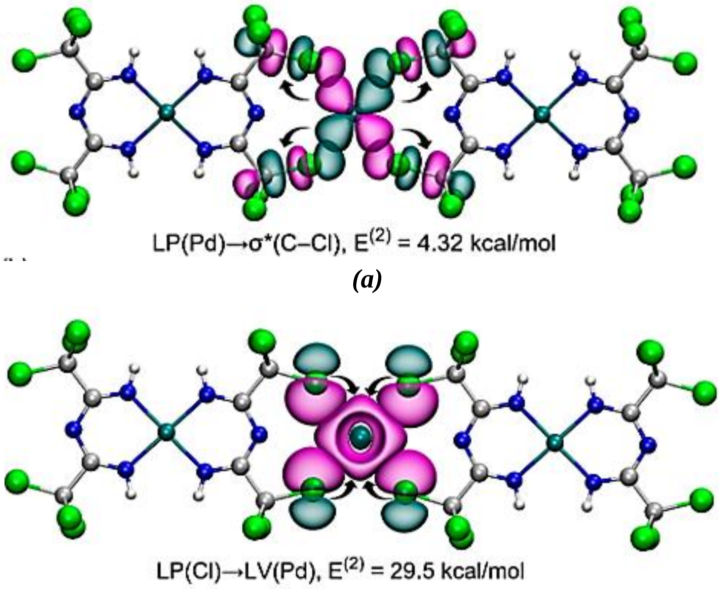
(a) *(b)*

Figure 11. MEP surfaces of the Pd(II) {NH–C(CCl$_3$)–NC(CCl$_3$)–NH}$_2$ fragment of compound 18: top view *(a)* and lateral view *(b)*. Selected values are given in kcal/mol.



(a) *(b)*

Figure 12. Combined QTAIM (red = bond critical point, orange line = bond path) and NCIPlot (RDG = 0.4, color scale: −0.04 a.u. ≤ (signλ_2)ρ ≤ 0.04 a.u.) analysis of the Pd^0 [Pd^{2+}{NH–C(CCl$_3$)–NC(CCl$_3$)–NH}$_2$]$_2$ assembly in compound 4 *(a)*. EDA Kitaura–Morokuma analysis of the trimeric assembly, showing total energy (*E*_tot), exchange–repulsion (*E*_ex-rep), electrostatic (*E*_el), orbital (*E*_orb), correlation (E_cor), and dispersion (*E*_disp) components in kcal/mol *(b)*.



(a)

(b)

Figure 13. NBOs and second-order perturbation energies in compound 18.

Conclusions

Halogenated 1,3,5-triazapentadiene (TAP) complexes represent a promising class of compounds of significant interest in coordination chemistry. Studies have shown that the polydentate nature of the TAP ligand and the electronic effects introduced by halogen atoms enhance the stability, coordination behaviour, and reactivity of these complexes. In particular, halogen bonding plays a key role in the formation of supramolecular architectures and in regulating crystal packing.

As discussed in this review, halogenated TAP complexes can be synthesized using various strategies, including complexation of preformed ligands with metal ions, metal-templated condensation reactions, and solvothermal methods. These approaches have enabled the preparation of structurally diverse complexes with metals such as Cu, Ni, Co, Zn, Pd, Fe, and others. Modern physicochemical techniques have been essential for confirming their structures and properties.

One of the main advantages of halogenated TAP complexes lies not only in their intriguing structural features but also in their functional potential. These compounds are promising candidates for applications in catalysis, supramolecular chemistry, the design of functional materials, and potentially in biological systems. Therefore, future research focusing on the synthesis of new derivatives, deeper investigation of halogen bonding, and expansion of practical applications is of great importance.

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