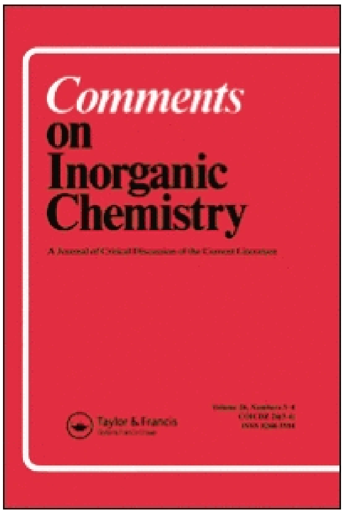

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STARBURST COMPLEXES OF DI-2-PYRIDYLAMINE DERIVATIVES WITH A BENZENE OR 1,3,5-TRIAZINE CORE

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STARBURST COMPLEXES OF DI-2-PYRIDYLAMINE DERIVATIVES WITH A BENZENE OR 1,3,5-TRIAZINE CORE

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Luminescent starburst organic molecules have attracted much recent attention primarily because of their potential applications in organic light emitting diodes. Starburst organic molecules that are functionalized by donor groups such as pyridyl are especially interesting because they can bind to metal ions to form unusual structures and supramolecular assemblies in addition to the introduction of redox properties and catalytic capability associated with the metal ions. This review focuses on starburst molecules that contain 2,2′-dipyridylamino groups with a C_3 symmetry. The smallest members of this group of starburst molecules involve a central benzene core or a 1,3,5-triazine core which are covered in this review. Larger starburst molecules that involve 1,3,5-triphenylbenzene, 1,3,5-tris(biphenyl)benzene, 2,4,6-triphenyltriazine or 2,4,6-tris(biphenyl)triazine as the central core are not discussed in the present review. The structural variation and luminescent properties of various metal complexes involving the small starburst ligands are described.

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INTRODUCTION

Interest in starburst derivatives of di-2-pyridylamine, dpa, has stemmed from the intersection of two fundamental ideas: a) both deprotonated dpa and aromatic derivatives of dpa have been demonstrated as potential emitting compounds for electroluminescent (EL) devices,[1] and b) starburst molecules have been shown to form good amorphous films, a prerequisite for efficient EL devices.[2] The starburst dpa derivatives 1,3,5-tris(di-2-pyridylamino)benzene, tdab, and 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine, tdat, were first reported[3] by our group in 2002, and used as the emitting compounds in EL devices. A modified synthesis of tdat and a series of tdat metal complexes have since been reported.[4]

Each of the ligands tdab and tdat have three dpa subunits or "arms," arranged at 120° angles around a central aromatic ring system, which can act as chelating donors to three different metal centers, or, theoretically, as monodentate donors to six different metal ions. The tdat ligand also has three nitrogen atoms on the central triazine ring that could theoretically participate in coordination, but this bonding mode has not yet been observed. In contrast, the protons on the central benzene ring in tdab can be activated in the presence of the appropriate metal ions, thus enabling the tdab ligand to form cyclometallated complexes.[5] The possible bonding modes by the tdab ligand and the tdat ligand to metal centers that utilize all the three dpa units are shown in Chart 1.

In the absence of coordination, both ligands adopt a propeller-like configuration, in which the pyridyl groups are twisted out of the plane of the central aromatic ring, as shown by the crystal structures[6] of tdab and tdat in Figure 1. Although the pyridyl groups are not coplanar with the central ring, the amino nitrogen atoms of the dpa subunits remain conjugated with the central ring system. This can be seen by the fact that the planes formed by the amine nitrogen atom and the pyridyl carbon atoms to which it is bound (hereafter referred to as the NC_2 plane) are coplanar with the plane of the central ring. Clearly the conjugation of the amino lone pair with the central ring is favored since it will increase the overall stability of the molecule (hereafter referred as the electronic effect). However, this stabilization via the electronic effect could be overcome by unfavorable steric hindrance, as revealed by the structures of several of the metal complexes of tdab and tdat (*vide infra*). The pyridyl groups can rotate about the C(py)-N(amine) bond, which builds a certain degree of flexibility into the ligand system, and is responsible for

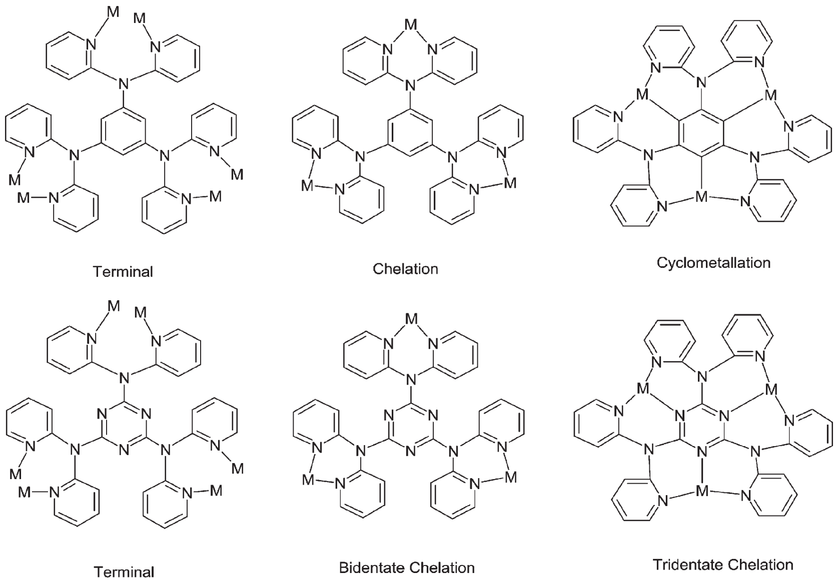


Chart 1. Typical bonding modes of tdab and tdat.

some of the fluxional behaviors of the metal complexes. Furthermore, if the ligand is not coordinatively saturated, there exists the possibility of dynamic exchange between coordinated sites and non-coordinated sites in solution.

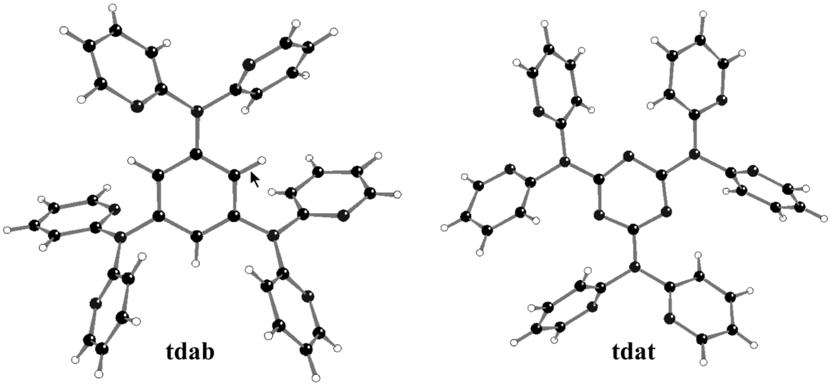


Figure 1. Structures of tdab and tdat.

For a ligand system with such an abundance of pyridyl groups, it is not surprising that there is rich coordination chemistry. At present, complexes of tdab or tdat have been prepared with a number of the late transition metals, including Co(II),[6] Ni(II),[7] Cu(II),[8] Zn(II),[6,9] Pd(II),[5,9] Ag(I),[10] and Pt(II).[8b,10] Due to the relative ease of synthesis for tdat, complexes of tdat are more abundant than those of tdab. The complexes of tdat and tdab range from discrete molecules to coordination polymers, and have varied properties, from luminescence to catalytic activity, depending upon the metal centre and counterion present. This review article is organized according to metal ions with emphasis on structural variation and luminescence.

Ag^I COMPLEXES

Silver(I) nitrate complexes have been obtained for both tdab and tdat ligands.[10] The reaction of three equivalents of $AgNO_3$ with tdab produced a colorless powder with the composition of $[(AgNO_3)_3(tdab)]$, **1**. While no single-crystals were isolated from this reaction, a related complex with a larger starburst ligand,[11] $[(AgNO_3)_3(tdapb)]$ (tdapb = 1,3,5-tris(4-(di-2-pyridylamino)phenyl)benzene), has been found to exhibit a 2D-polymeric structure. We therefore believe that **1** is also very likely to display a 2D structure. Compound **1** is blue-luminescent in solution with an emission maximum at 408 nm, but has no observable luminescence in the solid state, like $[(AgNO_3)_3(tdapb)]$.

In contrast to the reaction of $AgNO_3$ with tdab, the reaction of three equivalents of $AgNO_3$ with tdat under the same reaction conditions produced a tetranuclear complex with the composition of $[Ag_4(NO_3)_4(tdat)]_n$, **2**. The pyridyl groups in **2** are bound to the Ag(I) centers in two different modes: a terminal mode and a chelate mode as shown in Figure 2. However, unlike the typical chelate mode shown in Chart 1 where two pyridyl groups from the same dpa unit are bound to the metal center, the chelation in **2** involves two pyridyl groups from two adjacent dpa units. This unusual bonding mode is likely caused by the preference of the Ag(I) ion for a linear bonding mode. Three of the four nitrate anions are bound to the Ag(I) centers and further function as bridging ligands to link the tetranuclear units together into a 2D extended coordination polymeric structure. Another important feature is that in **2**, the pyridyl groups of the dpa subunits are tilted such that the NC_2 planes are perpendicular to the central triazine ring, indicating that the steric

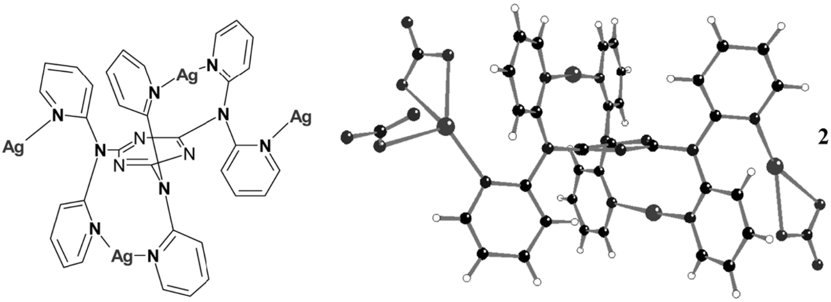
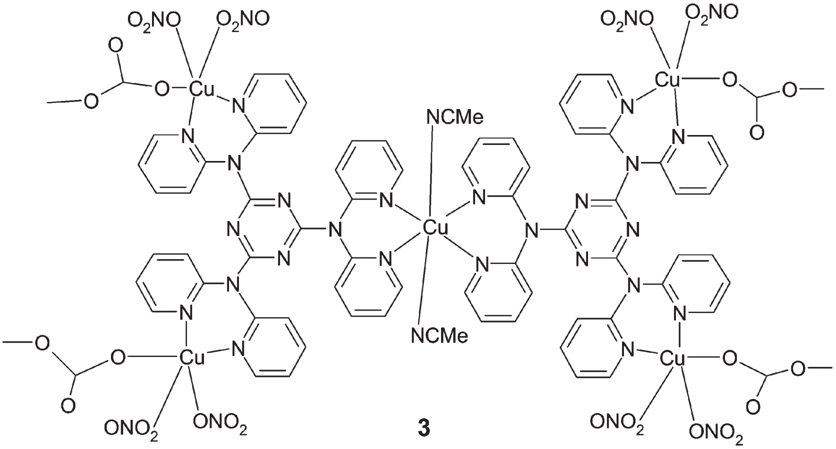


Figure 2. Diagram showing the connectivity in **2**, right: the crystal structure of **2**.

effects of coordination to the metal centres overcome the electronic benefits of conjugation to the central ring. Like compound **1**, compound **2** is blue-luminescent in solution, with a maximum emission at 387 nm, but no luminescence is observed in the solid state. The proximity of the heavy silver ions to the tdat ligand may be responsible for the fluorescent quenching through the heavy atom effect.

A Cu^{II} COMPLEX

In 2002, Reedijk, et al., reported a coordination polymer[8] of copper(II) nitrate with tdat with the formula of $[Cu_{2.5}(NO_3)_5(CH_3CN)(tdat)]_n$, **3**,



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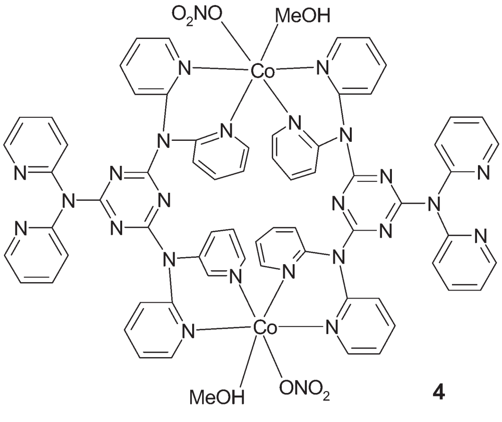
the first such complex reported. While a 3:1 metal:ligand ratio was employed in the reaction, the resulting complex only incorporated 2.5 equivalents of $Cu(NO_3)_2$. Two of the Cu(II) ions are chelated by one dpa unit and are further bound by nitrate anions. The third Cu(II) ion is chelated by two dpa units, one from the same tdat ligand that are bound to the other two Cu(II) ions, the other from a neighboring tdat ligand. As a result, complex **3** is a pentanuclear Cu(II) complex. This pentanuclear unit is further linked together via bridging nitrate ligands to form a 1D ladder-like structure. The NC_2 planes in each of the three dpa arms are all coplanar with the central triazine ring, indicating the presence of conjugation with the amine nitrogen atoms. Complex **3** was used as a catalyst in the oxidation of di-*t*-butylcatechol to the corresponding quinone,[7] achieving a 47% conversion after three hours, at a concentration of 1.7 mol%.

A DINUCLEAR Co^{II} COMPOUND

The reaction of tdat with two equivalents of $Co(NO_3)_2$ produced the dinuclear complex[6] $[Co(NO_3)(CH_3OH)(tdat)]_2(NO_3)_2$, **4**. Compound **4** contains two tdat ligands that are linked together by two Co(II) ions. Each cobalt(II) center is chelated by two dpa subunits from the two tdat ligands, and is further coordinated by a nitrate anion and a methanol solvent molecule to complete the octahedral coordination sphere. The third dpa subunit does not participate in any coordination bonding, but



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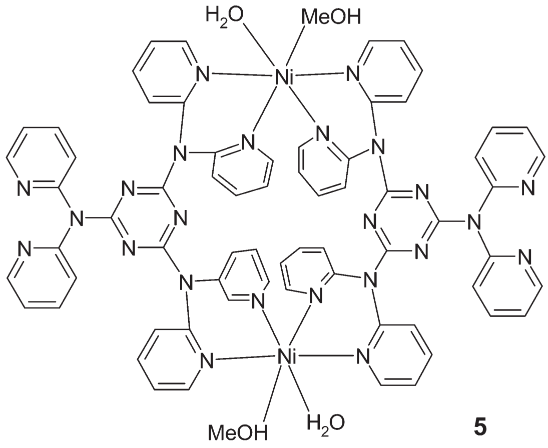
behaves in a similar manner as in the free ligand. The remaining nitrate anions are not coordinated to any metal center, but are involved in relatively strong hydrogen-bonding interactions with methanol solvent molecules trapped in the lattice, and a weak C–H · O interaction with a hydrogen atom of one of the non-coordinating pyridyl groups. The NC_2 planes are again coplanar with the central triazine ring, as seen in the Cu(II) complex, **3**.

A DINUCLEAR Ni^{II} COMPLEX

The reaction of three equivalents of $Ni(ClO_4)_2$ with tdat produce a dinuclear Ni(II) complex[7] with the formula of supramolecular dimer, $[Ni(H_2O)(CH_3OH)(tdat)]_2(ClO_4)_2$, **5**. The structure of this dinuclear complex is similar to that of **4**, which is not entirely surprising given the well demonstrated similarity of cobalt(II) and nickel(II) coordination compounds.[12] The perchlorate anions are not involved in coordination, as expected, and the octahedral coordination sphere of the Nickel(II) ion is filled by two chelating dpa subunits, along with one water molecule and one methanol solvent molecule. In contrast to complex **4**, the non-coordinated dpa subunit forms a pair of hydrogen-bonds to one methanol solvent molecule. The same methanol solvent molecule also acts as a hydrogen-bond acceptor to the coordinated water molecule of an adjacent dimer. The coordinated water molecule also hydrogen-bonds



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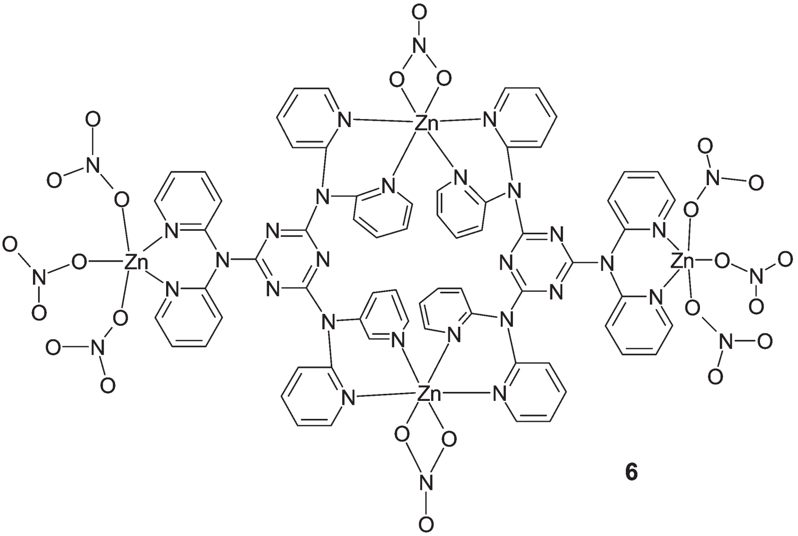
to a second non-coordinating methanol solvent molecule in the lattice, which hydrogen-bonds to one of the perchlorate anions. The coordinated methanol solvent molecule is involved in a similar hydrogen-bonding situation to a third methanol solvent molecule, which hydrogen-bonds to the second perchlorate anion. The NC_2 planes are all coplanar with the central triazine ring system, as in **3** and **4**.

Zn^{II} COMPLEXES

Complex of $Zn(NO_3)_2$

When three equivalents of $Zn(NO_3)_2$ are added to tdat, the resulting complex is a tetranuclear Zn(II) complex[6] with the formula of $[Zn_2(NO_3)_4(tdat)]_2$, **6**. Two tdat ligands are linked together by two Zn(II) ions in a similar manner as observed in **4** and **5**. However, unlike compounds **4** and **5**, where the third dpa unit is not coordinated, the third dpa unit in **6** is chelated to a Zn(II) center. The Zn(II) centers that link two tdat ligands have an approximate octahedral geometry while the remaining zinc(II) centers have a trigonal bipyramidal geometry. The NC_2 planes are coplanar with the central triazine ring. The complex should be blue-luminescent, based on our own knowledge on tdat



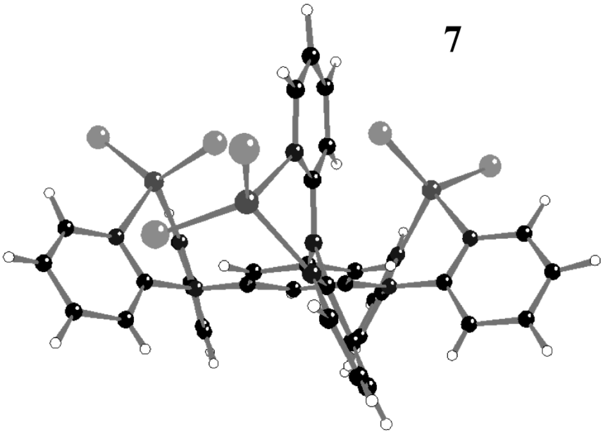
6

complexes, although no luminescence data were given in the original report.[6]

Complexes of $ZnCl_2$

Several complexes of Zn(II) chloride with tdab and tdat have been reported by our group.[9]

Tdab: The reaction of $ZnCl_2$ with tdab yielded a blue luminescent complex 7 with the formula of $(ZnCl_2)_3$(tdab), regardless of the stoichiometry used in the reaction. The three $ZnCl_2$ units are chelated to three dpa units, respectively. In the crystal structure, two of the three $ZnCl_2$(dpa) units are found on the same side of the central benzene ring and the amino atoms of these two dpa units are coplanar with the central benzene ring. The third $ZnCl_2$(dpa) unit is twisted sideways such that the dpa unit is nearly perpendicular to the central benzene ring, which can be attributed to steric interactions between the chloride ligands.



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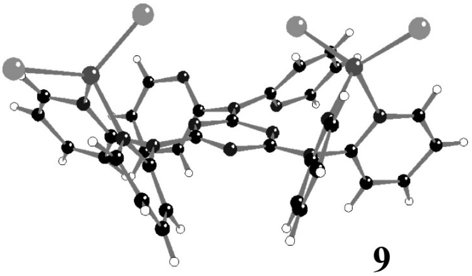
Tdat: The reactivity pattern of tdat with $ZnCl_2$ appears to be quite different from that of tdab. The product from the reaction of tdat with $ZnCl_2$ appears to follow the stoichiometry of the reactants. Zn(II) complexes with metal:ligand ratios of 1:1, $[ZnCl_2(tdat)]$, **8**, 2:1, $[(ZnCl_2)_2(tdat)]$, **9**, and 3:1, $[(ZnCl_2)_3(tdat)]$, **10**, have all been isolated from reaction mixtures with the correct reactant stoichiometry. While



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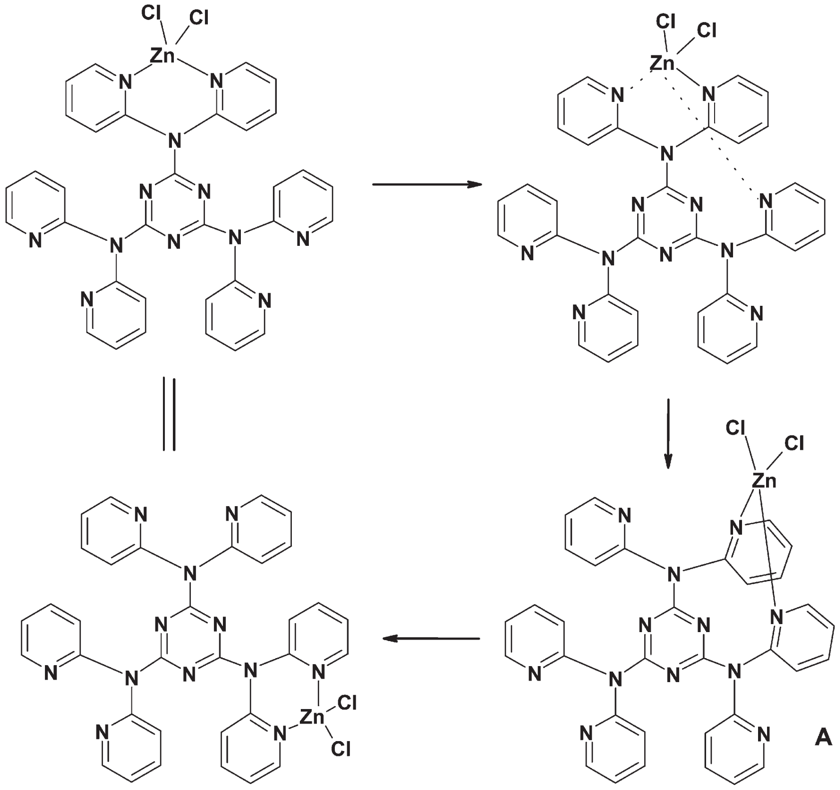
no X-ray crystal structure was determined for the 3:1 complex **10** and the 1:1 complex **8**, the NMR spectral data indicated that **10** is very likely to have the same structure as that of **7**. The crystal structure of **9** was determined by X-ray diffraction analysis which revealed that the two $ZnCl_2$(dpa) units are on the same side of the central triazine ring and all three NC_2 planes are approximately coplanar with the central triazaine ring. Complexes **8** and **9** are fluxional in solution as revealed by ^1H NMR experiments. For compound **8**, at room temperature, only a set of broad chemical shifts, corresponding to the $ZnCl_2$(dpa) unit, are observed in the ^1H NMR spectrum. As the temperature is decreased, the one set of chemical shifts are gradually resolved into two sets with a 2:1 ratio, which correspond to the ratio of uncoordinated and coordinated dpa units. We believe that the exchange process likely involves an intermediate such as **A** as shown in Scheme 1, in which two pyridyl groups from two separate dpa nits coordinate to the $ZnCl_2$ centre. Complexes **7–10** are all luminescent, with emission maxima between 378 nm and 426 nm in CH_2Cl_2 solution.

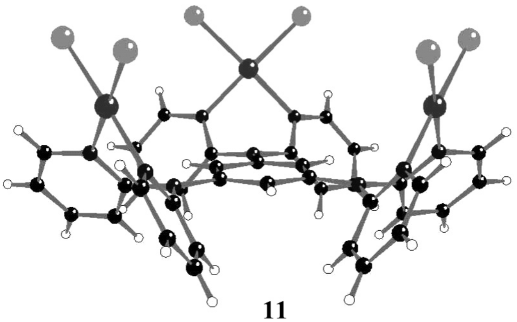
Pt^{II} COMPLEXES

Complexes of $PtCl_2$

Tdab and tdat complexes that contain the $PtCl_2$ unit were synthesized from the reaction of K_2PtCl_4 with tdab or tdat by using solvent-layering techniques.[9] Yellow needles of trinuclear complexes with the formula of $[(PtCl_2)_3(tdab)]$, **11**, and $[(PtCl_2)_3(tdat)]$, **12**, were obtained. The molecular structure of these two compounds are quite similar. Each dpa unit is chelated to a $PtCl_2$ unit. The Pt(II) center has a typical square planar geometry. All NC_2 planes are coplanar with the central benzene or



Scheme 1.



11

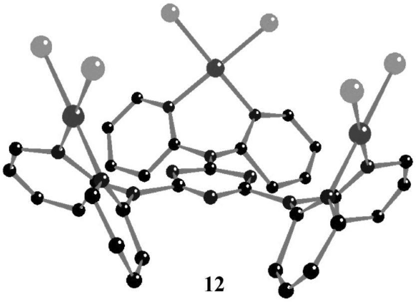

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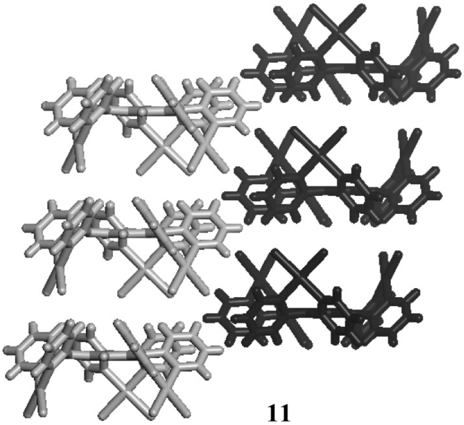
Figure 10.

triazine rings. An important feature of **11** and **12**, as revealed by X-ray diffraction analysis is that all three $PtCl_2$(dpa) units in the molecule are oriented on the same side with respect to the central ring such that the molecule has a bowl shape. This feature is in sharp contrast to the structure of the Zn(II) complex **7** where the three $ZnCl_2$(dpa) units do not have the same orientation. The bowl-shaped structure of **11** and **12** is made possible by the fact that each Pt(II) center has a square planar geometry, which allows all the chloride ligands to be on the same side of the molecule without significant inter-ligand interaction, which is not possible to achieve for the Zn(II) complex.

The difference between **11** and **12** lies in their extended crystal packing. In the crystal lattices, the bowl-shaped molecules of **11** and **12** stack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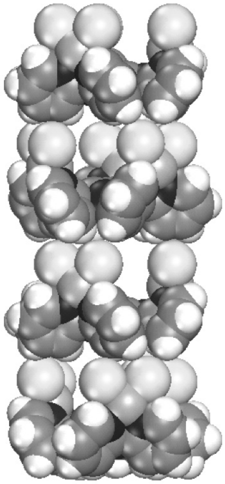
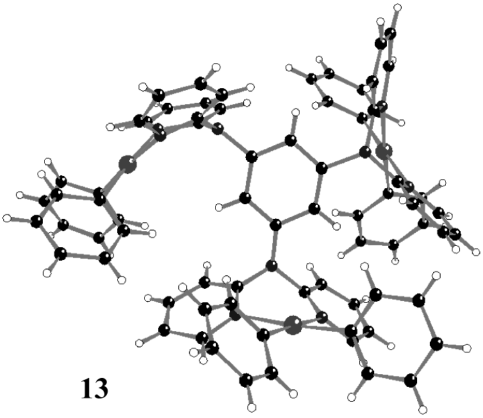


12

to form a polar column, which is favored by intermolecular electrostatic interactions between the electronegative chloride and the electropositive protons of the tdab or tdat ligand. Complex **12** predominantly crystallizes in an asymmetric arrangement, in which the columns of bowls are stacked directly upon each other, held in place by weak C–H···Cl interactions. The crystal lattice is polar, as all of the columns are oriented in the same direction. The columns in the crystal lattice of complex **11** were found to run in opposite directions as shown here. Complexes **11** and **12** are insoluble in organic solvents, precluding their study by NMR spectroscopy, but are blue-luminescent in the solid state, with emission maxima at 411 nm and 414 nm respectively.

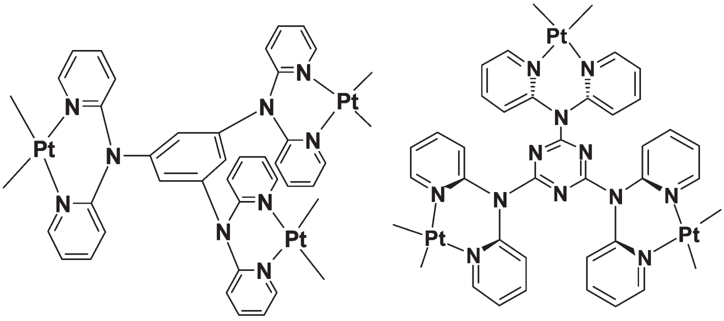
Organoplatinum(II) Complexes

Organoplatinum(II) complexes[13] of tdat and tdab that contain the $PtPh_2$ unit were synthesized from the reaction of tdat or tdab with $[PtPh_2(SMe_2)]_n$ ($n = 2, 3$). Two complexes with the formula of $[(PtPh_2)_3(tdab)]$, **13**, and $[(PtPh_2)_3(tdat)]$, **14** have fully characterized. In contrast to the $PtCl_2$ complexes, these two complexes cannot form the bowl-shaped structures as in **11** and **12** due to steric interactions



13

among the phenyl groups. As a result, either a pinwheel-type structure or the up-and-down structure as shown in Chart 2 are adopted. The pinwheel structure is favored by the tdab complex **13** because it minimizes the non-bonding interactions between the protons of the central benzene ring and the protons of the phenyl groups. As a consequence of the pinwheel structure, all NC_2 planes are no longer conjugate with the central benzene ring. This loss of conjugation is clearly compensated by the minimization of the steric interactions in the pinwheel structure. The structure of **13** is therefore a case where steric effect dictates



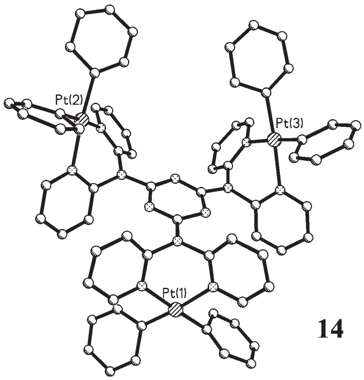
Pin-wheel **Up and down**

Chart 2.

the structure of the molecule. In the crystal structure of **13**, two of the Pt(dpa)Ph_2 units are perpendicular to the central benzene ring while the NC_2 unit of the third Pt(dpa)Ph_2 unit retains partial conjugation with the central benzene ring. In solution, complex **13** adopts the pinwheel structure as indicated by variable temperature ^1H NMR study that showed all three Pt(dpa)Ph_2 units are equivalent and do not undergo any dynamic exchange over the temperature range of 223 K–298 K.

The up-and-down structure is favored by the tdat complex **14**. This is not totally surprising since the tdat ligand has no protons on the central ring, hence the steric interaction between the central ring and the phenyl rings is not as serious as that in **13**. In addition, because the nitrogen atoms are more electronegative than the carbon atoms, the conjugation of the amino lone pair electrons of the dpa unit with the central triazine ring becomes more favorable for **14**, compared to that for **13**. The structure of **14** is therefore a case where electronic effect dictates the structure of the molecule. Variable temperature ^1H NMR experiments established that **14** retains the up-and-down structure in solution at temperatures below 283 K. At elevated temperature, dynamic exchange between the up and down Pt(dpa)Ph_2 units occurs with a very large activation energy ($\sim$154(10) kJ/mol). Both complexes are luminescent as frozen CH_2Cl_2 solutions at 77 K, with phosphorescent emission maxima at 460 nm and 495 nm for **13** and **14**, respectively, which were attributed to ligand centered π - π^* transitions.

The syntheses of $Pt(CH_3)_2$ analogues of compounds **13** and **14** were attempted. However, the complexes of $Pt(CH_3)_2$ were found to be very



14

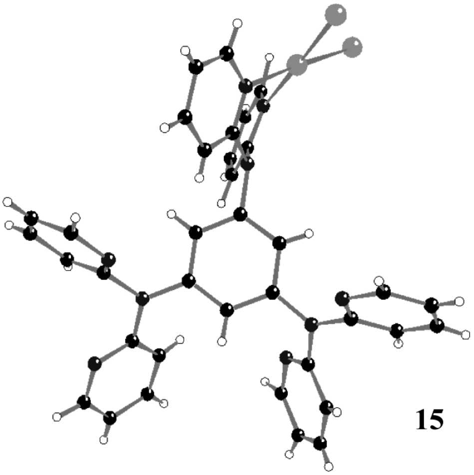
reactive and unstable at ambient temperature and as result the full characterization on $Pt(CH_3)_2$ complexes of tdat and tdab has not been achieved.

Pd^{II} COMPLEXES

The coordination chemistry of tdab and tdat with Palladium(II) is highly dependent on both the counter-ion, the stoichiometry of the reaction, and the reaction condition.

Reactions with $PdCl_2(PhCN)_2$

The reaction of tdab with one equivalent of $PdCl_2(PhCN)_2$ yielded the mononuclear complex,[5b] $[(PdCl_2)(tdab)]$, **15**. The chelated dpa subunit of **15** is twisted such that the NC_2 plane is almost perpendicular to the plane of the central benzene ring. This effect is likely due to steric packing effects. At ambient temperature, only one set of chemical shifts corresponding to the dpa unit is observed in the ^1H NMR spectrum, indicating that dynamic exchange is present in solution, likely in a similar fashion as that proposed for compound **8**.



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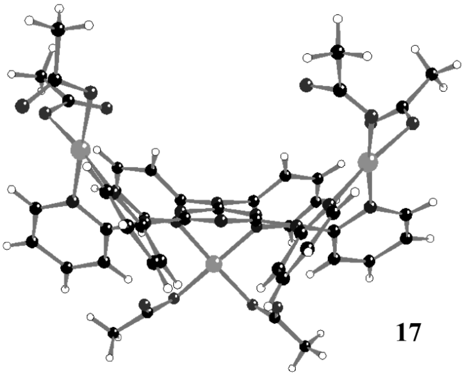
The reaction of tdab with three equivalents of $PdCl_2(PhCN)_2$ and tdab produced the 3:1 chelate complex,[5b] $[(PdCl_2)_3(tdab)]$, **16**. This complex is isostructural with its Pt(II) analogue **11**. No luminescence was observed for the Pd(II) complexes.

Reactions with $Pd(OAc)_2$

Tdat: The reaction of $Pd(OAc)_2$ with tdat produced the 3:1 chelate complex,[5b] $[(Pd(OAc)_2)_3(tdat)]$, **17**, regardless of the stoichiometry of the reaction. The dpa units in **17** are chelated to the Pd(II) centers in an up-and-down fashion, similar to that of **14**, with two of the $Pd(OAc)_2$(dpa) units above the triazine ring, and one below. This up-and-down structure is again favored by the conjugation of the amino nitrogen atoms with the central triazine ring. The fact that not all Pt(dpa)$(OAc)_2$ units are on the same side of the triazine ring can be attributed to the steric interactions between the acetate ligands. In the same manner as observed for **14**, complex **17** was found to retain its up-and-down structure in solution. At temperature above 270 K, **17** undergoes a dynamic exchange involving the inter-conversion of the up- and down- $Pd(OAc)_2$(dpa) units. Again no luminescence was observed for **17**.

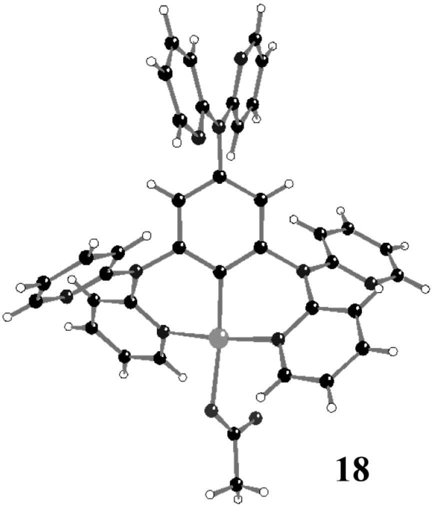
Tdab: The reaction of $Pd(OAc)_2$ with tdab displays a very complex pattern. The reaction of one equivalent of $Pd(OAc)_2$ with tdab at room temperature produced an interesting *NCN*-pincer complex,[5b] $[Pd(OAc)(tdab^-)]$, **18**. In this complex, two pyridyl groups from two different dpa units are chelated to the Pd(II) center. In addition, a carbon atom of the central benzene ring is also bound to the Pd(II) center. The



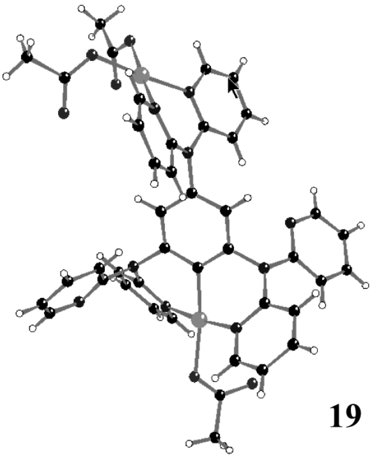
17

fourth coordination site is occupied by the remaining acetate ligand. Cyclometallation via *ortho* C–H activation has been frequently observed in Pd(II) and Pt(II) compounds.[14] However, we have not seen any evidence to support the occurrence of cyclometallation involving tdab and Pt(II) centers. The addition of one equivalent of $Pd(OAc)_2$ to compound **18** resulted in the isolation of the unusual dinuclear complex[15] $[Pd_2(OAc)_3(tdab^-)]$, **19**. Complex **19** can also be obtained directly from the reaction of tdab with two equivalents of $Pd(OAc)_2$. The two Pd(II) centers in **19** display two different bonding modes – chelation and cyclometallation. The chelated dpa subunit is twisted out of the plane of the central benzene ring, in a similar fashion to that of **15**. The fact that we did not isolate a dinuclear complex where both Pd(II) centers have the cyclometallation bonding mode is most likely due to steric effects that prevent the 2nd cyclometallation from occurring.

The reaction of tdab with three equivalents of $Pd(OAc)_2$ at room temperature did not yield a cyclometallated species, but the trinuclear chelate complex,[5b] $[Pd(OAc)_2]_3(tdab)$, **20**. Complex **20** adopts the pinwheel structure in the solid state as revealed by X-ray diffraction analysis. The pinwheel shape appears to be the result of weak C–H···O hydrogen bonding interactions between the central benzene ring protons



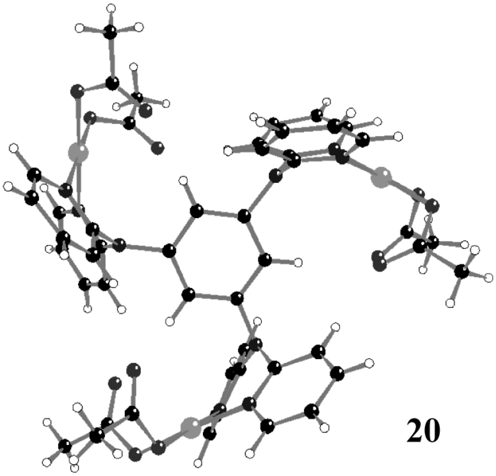
18



19

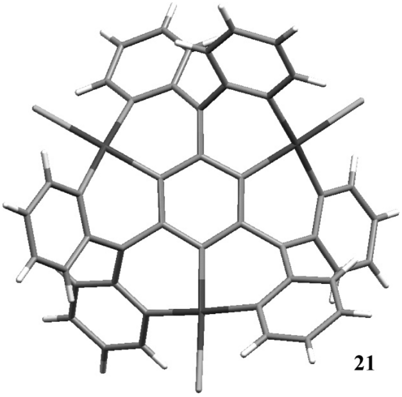
and the non-coordinated acetate oxygen atoms. Again, there is no conjugation between the amino nitrogen atoms of the dpa units and the central benzene ring. We believe that this pin-wheel structure is favored by both steric effects and the electrostatic interactions between the benzene protons and the acetate oxygen atoms. Heating compound **20** to high temperature did not result the formation of any clcolmetallated compounds. This is likely due to the fact that the Pd(II) ions in **20** are locked in place by both the dpa chelates and the hydrogen bonding interactions between the oxygen atoms of the acetates and the hydrogen atoms of the benzene ring, which make it impossible for further transformation such as cyclometallation that involves a substantial rearrangement of the molecule. The pinwheel structure of **20** is retained in solution, as indicated by the chemical shift of the central ring protons (shifted from 6.78 ppm in the free ligand to 9.20 ppm in the complex) in the ^{1}H NMR spectrum and the observation of only one set of chemical shifts due to the $Pd(dpa)(OAc)_2$ units. None of the Pd(II) acetate complexes of tdat or tdab are luminescent.

An unusual triply cyclometallated species,[5a] $[(PdCl)_3(tdab^{3-})]$, **21**, has been reported by Steel group, from the reaction of $Pd(OAc)_2$ and tdab in refluxing benzene for seven days, followed by the addition of KCl. The mechanism for the formation of **21** has not been well understood. However, for complexes **18** and **19**, we believe that the most likely

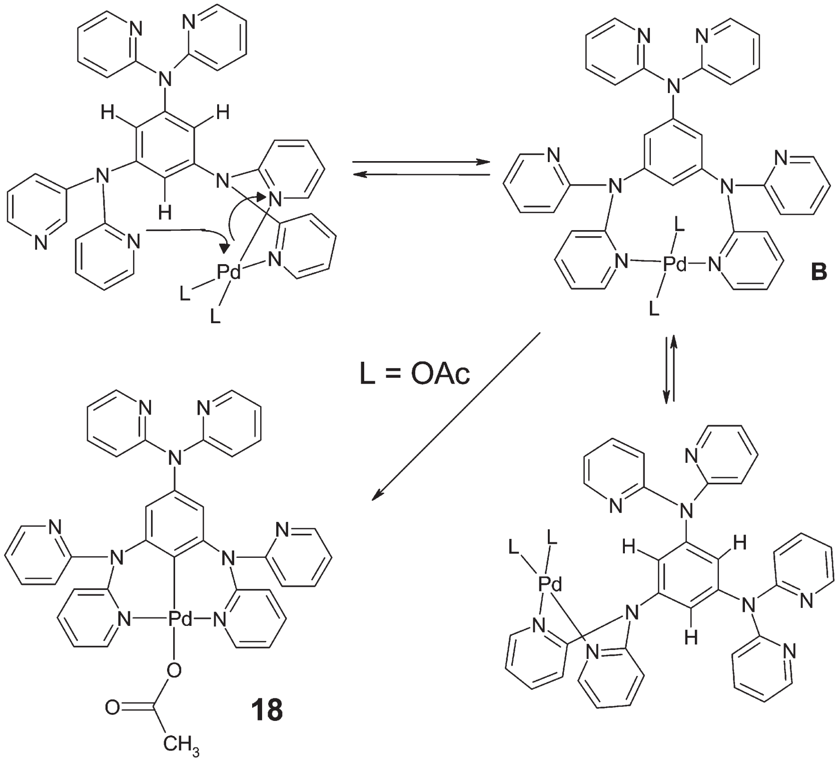


20

mechanism involves an intermediate such as **B** as shown in Scheme 2. The formation of species **B** is supported by the dynamic behavior of complex **15**, where **B** is likely the key intermediate for intramolecular site exchange of the $PdCl_2$ unit in **15**. When the chloride is replaced by the acetate ligand, the acetate ligand is likely to interact with the proton on the central benzene ring via electrostatic interaction, and



21



Scheme 2.

subsequently extract the proton and eliminate as HOAc and result in the formation of the cyclometallated complex.

CONCLUSIONS

The starburst tdat and tdab ligands have been demonstrated to be able to bind to various metal ions to form complexes that display versatile structural features. The most common binding mode for the tdat ligand is chelation through the two pyridyl groups on the same dpa unit. For tdab, in addition to the chelation mode, *N,C,N*-cyclometallation mode has been observed in Pd(II) complexes. The terminal binding mode is only observed for Ag(I) complexes. The metal ion can be chelated by either one dpa unit or two dpa units from two tdat or tdab ligands to form either discrete molecules or polymers. In the presence of weakly coordinating counter-ions such as nitrate or perchlorate, the metal center is often chelated by two dpa units from two ligands. For relatively strongly coordinating counter-ions such as acetate, chloride or phenyl, the metal ion is usually chelated by one dpa unit. For trinuclear complexes with the general formula of $(ML_2)_3$(tdat) or $(ML_2)_3$(tdab), three types of molecular structures have been observed, namely bowl-shaped structures, pinwheel, and up-and-down structures. The bowl-shaped structure is favored by metal ions that have a square-planar geometry with relatively small ligands such as chloride. The up-and-down structure is favored by the tdat ligand with metal ions that have a square-planar geometry with relatively large ligands such as acetate and phenyl. Both bowl-shaped structure and the up-and-down structure are stabilized by the conjugation of the amino lone pair of the dpa unit with the central ring. The pinwheel structure is favored by the tdab ligand with metal ions that have a square planar geometry with relatively large ligands such as acetate and phenyl. In the pinwheel structure, the loss of amino lone-pair conjugation of the dpa unit with the central ring is compensated by either intramolecular hydrogen bonding interactions and the minimization of steric interactions among ligands. Complexes that display the up-and-down structures in the solid state are usually fluxional in solution due to the presence of a dynamic exchange between the up and the down dpa-chelating units. Complexes of tdat or tdab that contain paramagnetic metal ions such as Co(II), Cu(II) and Ni(II) are in general not luminescent. Zn(II) and Ag(I) complexes of tdat and tdab usually display ligand-centered blue fluorescence. Pt(II) complexes usually display ligand centered phosphorescence while Pd(II) complexes of tdat or tdab are in general not luminescent. The high reactivity/instability displayed by the $Pt(CH_3)_2$ complexes of tdat or tdab in common organic solvents at ambient temperature indicates the potential use of these complexes in activation of small molecules, especially C$-$H bonds, which are being examined by our group.

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