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Interactions of metal-based and ligand-based electronic spins in neutral tripyrrindione π dimers

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Abstract

The ability of tetrapyrrolic macrocycles to stabilize unpaired electrons and engage in π – π interactions is essential for many electron-transfer processes in biology and materials engineering. Herein, we demonstrate that the formation of π dimers is recapitulated in complexes of a linear tripyrrolic analog of naturally occurring pigments derived from heme decomposition. Hexaethyltripyrindione (H₃TD1) coordinates divalent transition metals (i.e., Pd, Cu, Ni) as a stable dianionic radical and was recently described as a robust redox-active ligand. The resulting planar complexes, which feature a delocalized ligand-based electronic spin, are stable at room temperature in air and support ligand-based one-electron processes. We detail the dimerization of neutral tripyrrindione complexes in solution through electron paramagnetic resonance (EPR) and visible absorption spectroscopic methods. Variable-temperature measurements using both EPR and absorption techniques allowed determination of the thermodynamic parameters of π dimerization, which resemble those previously reported for porphyrin radical cations. The inferred electronic structure, featuring coupling of ligand-based electronic spins in the π dimers, is supported by density functional theory (DFT) calculations.

TOC image

The planar Cu(II) and Pd(II) complexes of hexaethyltripyrindione (H₃TD1) feature delocalized ligand-based electronic spins and can engage in π – π interactions leading to the formation of π dimers. Variable-temperature EPR and visible absorption spectroscopic methods, as well as DFT calculations, capture the electronic structure of a new class of cofacial oligopyrrolic dimers and the corresponding thermodynamic parameters of the dimerization reactions.

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Supporting Information.

The following files are available free of charge:

Additional structural and electrochemical characterization data, analysis details of variable-temperature EPR and absorption data, details of DFT calculations (PDF) Detailed crystallographic information and data for [Cu(TD1)(H₂O)(BF₄)] (CIF)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

INTRODUCTION

The interaction of delocalized π -radicals^{1–3} to form cofacial dimers and stacked architectures is an important aspect of the chemistry of stable organic radicals^{4–9} and of several metal complexes of redox-active ligands hosting unpaired electrons.^{10–13} In recent years, π – π interactions have been incorporated in the design of functional molecular materials featuring tunable optical and conductive properties.^{14–19} In biology, π – π interactions between tetrapyrrolic macrocycles are key to numerous electron transfer processes,²⁰ such as those originating at the bacteriochlorophyll dimer (*special pair*) in bacterial photosynthetic reaction centers.^{21, 22} Inspired by the combination of π – π electronic interactions²³ and one-electron redox chemistry in biological tetrapyrroles, the chemistry of π dimers of porphyrin radical cations^{24–26} continues to attract considerable attention.^{27–32} Herein, we document the first characterizations in solution of neutral π dimers featuring ligand-based radicals on tripyrrolic complexes.

Linear oligopyrrolic analogs of urinary pigments were recently identified as redox-active ligands capable of hosting unpaired electrons in transition metal complexes.^{33–35} We discovered that the tripyrrindione ligand $\text{H}_3\text{TD1}$ (Chart 1) coordinates $\text{Pd}(\text{II})$ as a planar radical dianion.³³ The ligand-based radical in the resulting complex $[\text{Pd}(\text{TD1}^*)(\text{H}_2\text{O})]$ (in which the fourth coordination position is occupied by a water molecule) is delocalized on the tridentate pyrrole-based scaffold and is stable at room temperature. Notably, this system undergoes reversible ligand-based one-electron processes and can be isolated in three different redox states. Analogous $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ complexes of square planar geometry were recently isolated (Chart 1), and the presence of ligand-based unpaired spins was confirmed by magnetometry and, for the $\text{Ni}(\text{II})$ complex, EPR spectroscopy.³⁵ In all cases, the crystal structures of these neutral planar complexes featuring ligand-based radicals revealed the formation of tightly bonded π dimers with stacking distances ranging from 3.19 to 3.27 Å (Figure S1, SI).³⁵ These observations in the solid state prompted us to investigate potential intermolecular communication between electronic spins in solution.

Whereas π dimers of metalloporphyrin π -cation radicals in solution are well documented,^{36–38} the tripyrrindione complexes offer the first opportunity to observe the dimerization of ligand-based radicals in neutral complexes of linear oligopyrroles. Unlike porphyrins and other tetrapyrrolic macrocycles, tridentate oligopyrroles allow access to the

metal center in the plane of the ligand and are therefore more amenable to major modifications, a significant advantage for functional tailoring of properties.³⁹

RESULTS AND DISCUSSION

EPR and DFT study of neutral tripyrrindione π dimers

Because hexaethyltripyrindione complexes feature delocalized ligand-based radicals, we sought to employ electron paramagnetic resonance (EPR) methods to examine the intermolecular communication between electronic spins in solution.

Whereas the d^8 complex $[\text{Pd}(\text{TD1}^*)(\text{H}_2\text{O})]$ presents the characteristic EPR spectrum of an organic (ligand-based) radical ($g \approx 2.003$) in liquid solution at room temperature, the reversible loss of this signal at lower temperatures provided an initial indication of putative π stacking and formation of an EPR-silent dimeric species through antiferromagnetic coupling of ligand-based spins.³³

For the analogous d^9 complex $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$, we found that the room-temperature magnetic moment (Evans methods) is $\mu_{\text{eff}} = (2.81 \pm 0.02) \mu_{\text{B}}$. This finding is consistent with the SQUID magnetometry data reported by Bröring and coworkers,³⁵ as well as with the expected value for a Cu(II) complex featuring a ferromagnetically coupled ligand-based radical ($S = 1$, without significant population of the singlet state).^{36, 40} In this complex, a metal-based unpaired electron formally resides in the $d_{x^2-y^2}$ orbital of the Cu(II) center, which is orthogonal to the π orbitals of the tripyrrindione scaffold hosting the ligand-based electronic spin. This results in a ferromagnetic interaction between the unpaired electrons and in stabilization of the triplet state, as previously observed in Cu(II) complexes featuring planar radical ligands,^{40–44} including porphyrin cation radicals,^{36, 45} in which the magnetic orbitals are orthogonal.

As previously reported,³⁵ $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ is EPR-silent at room temperature in spite of the triplet ground state ($S = 1$). This observation is likely explained by very short relaxation times.^{41, 42} Similarly, the Cu(II) complex of a tetrapyrrolic bilindione ligand featuring a ligand-based radical is EPR-silent at room temperature.⁴⁶ In a frozen solution, on the other hand, the EPR spectrum of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ is readily observable (Figure 1, top panel) and is characteristic of a Cu(II) dimeric species. A notable feature of this signal is the pair of intense lines at magnetic fields $B_0 \sim 303$ and 345 mT, which represent the $g_{\perp}$ components of the Cu(II) signal split by the magnetic dipole interaction. Additionally, the half-field signal observed at $B_0 \sim 130$ – 180 mT corresponds to the $m_S = 2$ transition, which becomes partly allowed as a result of significant dipole interaction between the Cu(II) centers.⁴⁷

The observation of a Cu(II) dimer in frozen solutions of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ is consistent with the formation of a stacked π dimer (represented schematically in Chart 2a). In this system, the strong antiferromagnetic exchange coupling between the ligand-based spins renders the ligand-based radicals EPR-silent, and the interaction between the metal-based unpaired electrons results in the EPR spectrum of the dimeric Cu(II) species shown in Figure 1 (top panel). From the ~ 42 mT splitting between the perpendicular components of the spectrum (the two major lines in the spectrum of Figure 1), the distance between the Cu(II) centers

can be estimated as $R_{Cu-Cu} \sim 4.1 \text{ \AA}$ (see SI for details) in good agreement with the $Cu \cdots Cu$ distances (4.4534(6) and 4.6083(7) $\text{\AA}$) observed in the crystal structures.³⁵ Similar spectra were reported for π dimers of radical cations of Cu(II) octaethylporphyrin³⁷ and β -oxooctaethylchlorin.³⁸

To further corroborate the formation of π dimers at low temperatures, we took advantage of the coupling between the ligand-based spins to observe the spectrum of magnetically isolated TD1-bound Cu(II) centers in a sample containing a mixture of $[Cu(TD1^*)(H_2O)]$ and $[Pd(TD1^*)(H_2O)]$ in 1:10 molar ratio. Assuming the dimerization to be nonselective with respect to the coordinated ion, about 95% of the copper-containing π dimers should have a Cu/Pd composition rather than a Cu/Cu one. Since the Pd(II) center is diamagnetic in the square planar tripyrrindione complex, the only paramagnetic species in the Cu/Pd π dimer would be the Cu(II) center (Chart 2b). Indeed, the obtained EPR spectrum (Figure 1, bottom panel) shows the typical signal of a monomeric Cu(II) species. The parallel components of the g -tensor ($g_{\parallel}$) and hyperfine interaction of the Cu nucleus ($A_{\parallel}$), 2.224 and 19 mT, respectively, are typical for a Cu(II) center bound to one oxygen and three nitrogen donors.⁴⁸ The narrow signal at $g \approx 2.004$ corresponds to residual monomeric $[Pd(TD1^*)(H_2O)]$. Taken together, these EPR experiments demonstrate the formation of π dimers of neutral tripyrrindione complexes.

Electronic structure calculations at the PBE0/def2-tzvp level with the broken symmetry approximation and COSMO solvation model for toluene support the formation of the π dimers of $[Cu(TD1^*)(H_2O)]$ in solution at low temperatures. We used this level of theory as it provides a good balance between cost and accuracy for many systems displaying weak spin coupling, often negating the use of higher-level CAS-SCF MRCI levels of theory for describing such systems. Despite the well-known inadequacies of DFT for capturing weak and through-space interactions, we find that the computational results are consistent with the experimental data.

Our computational results show that the isolated monomers yield an $S = 1$ ground state with the α spin density localized on the Cu^{2+} ion (0.62 spins), ligating atoms (0.31 spins), and the $TD1^* \pi$ system (0.92 spins) (Figure 2). Owing to the orthogonality of the Cu^{2+} and $TD1^* \pi$ unpaired spins, there is weak ferromagnetic coupling of the two spin orbitals ($J = 2.7 \text{ cm}^{-1}$; with spin Hamiltonian $H_{12} = -2JS_1S_2$), resulting in a paramagnetic complex. Further, we find that the formation of the π dimer with antiferromagnetic coupling of the ligand-based spins is favorable in solution by 2.07 kcal mol⁻¹.⁴⁹ In agreement with the experimentally determined representation of the spins shown in Chart 2a, the unpaired α spin density is localized on the two Cu^{2+} ions (0.62 spins per Cu^{2+}) and ligating atoms (0.29 spins over the ligands), while the antiferromagnetically coupled α and β spins are localized on the tripyrrindione π systems.

Effects of one-electron oxidation to the cationic complex

In order to obtain the EPR spectroscopic signature of the TD1-bound Cu(II) center in the absence of the ligand-based electronic spin, we sought to perform a one-electron oxidation of the ligand system. The cyclic voltammogram of $[Cu(TD1^*)(H_2O)]$ (Figure S2, SI) presents a one-electron oxidation event that is quasi-reversible and occurs at the same

potential as that observed for the ligand-based oxidation of $[\text{Pd}(\text{TD1}^*)(\text{H}_2\text{O})]$ (-0.052 V vs Fc/Fc^+ in CH_3CN with $(n\text{-Bu}_4\text{N})(\text{PF}_6)$ as a supporting electrolyte).³³ Correspondingly, the reaction of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ with AgBF_4 (Scheme 1) led to a ligand-based oxidation and formation of a new species, in line with our previous observations for the palladium complex.³³

X-ray diffraction analysis of the oxidized complex (Figure 3) indicated that the primary coordination sphere of the copper center maintains the three pyrrolic nitrogen donors of the tripyrrindione and the aquo ligand. The Cu–N bond distances are similar to those found in other tripyrrolic complexes^{50–53} and in the parent compound $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$.³⁵ As expected for a ligand-based oxidation and also observed in the case of $[\text{Pd}(\text{TD1}^*)(\text{H}_2\text{O})]$,³³ the redox state of the ligand system affects (up to ± 0.05 Å) the C–N and C–C bond lengths in the conjugated system. In addition, the structure revealed a bound tetrafluoroborate anion (Cu–F, 2.498(1) Å). Although BF_4^- is typically considered a non-coordinating anion, several bonding contacts to Cu(II) centers in nitrogen-rich coordination spheres have been observed.^{54–56} The resulting pentacoordinate geometry of $[\text{Cu}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ is distorted square pyramidal ($\tau = 0.23$),⁵⁷ with one of the fluorine atoms (F3) of the BF_4^- ion occupying the apical position. Whereas the tripyrrindione ligand framework is essentially planar in the neutral complex $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$, it adopts a helical conformation in the oxidized cationic complex. The hydrogen bonds between the aquo ligand and the terminal carbonyl group are maintained, but they are elongated (to 2.6097(14) and 2.6479(14) Å) relative to the parent neutral complex.³⁵

At room temperature, the effective magnetic moment (Evans method) of $[\text{Cu}^{\text{II}}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ is $\mu_{\text{eff}} = (1.70 \pm 0.02) \mu_{\text{B}}$ as expected for a Cu(II) complex with a single unpaired spin ($S = 1/2$). The EPR spectra of this species were observable both in liquid solution at room temperature and in frozen solution at 77 K (Figure 4). In both cases, the signal is consistent with a monomeric Cu(II) complex, indicating that the oxidized species (lacking an unpaired electron on the tripyrrindione ligand) does not undergo a detectable dimerization at low temperatures. The isotropic g -factor determined from the liquid solution spectrum is $g_{\text{iso}} \approx 2.118$, and the isotropic hfi constant is $a_{\text{iso}}(\text{Cu}) \approx 8.3$ mT. Remarkably, the frozen solution spectrum of $[\text{Cu}^{\text{II}}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ is practically identical to that of the $[\text{Cu}^{\text{II}}(\text{TD1}^*)(\text{H}_2\text{O})]/[\text{Pd}^{\text{II}}(\text{TD1}^*)(\text{H}_2\text{O})]$ heterodimer (Figure 1, bottom panel), denoting that neither the redox state of the ligand nor the dimer formation noticeably affect the electronic structure of the TD1-bound Cu(II) center. This spectrum also suggests that the tetrafluoroborate counter ion is not retained as a coordinated ligand in toluene solution.

Electronic structure calculations (PBE0/def2-tzvp/COSMO) support these observations and indicate that the oxidation of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ to $[\text{Cu}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ is a ligand-centered process. In the oxidized complex (Figures S8–S9, SI), the α spin density is found localized on the Cu^{2+} ion (0.66 spins) and ligating atoms (0.27 spins). Furthermore, we were unable to locate a stable π dimer structure for either the BF_4 -ligated or unligated complex, suggesting that $[\text{Cu}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ or $[\text{Cu}(\text{TD1})(\text{H}_2\text{O})]^+$ will not dimerize in solution.

Thermodynamic parameters of dimerization

The EPR spectra of the Cu(II) and Pd(II) tripyrrindione complexes obtained at room temperature and at 77 K correspond to two limiting situations of (nearly) all complexes being either monomeric or dimeric, respectively. To investigate the dimerization equilibrium and determine the corresponding thermodynamic parameters, we performed variable-temperature EPR measurements.

The spectra of monomeric [Pd(TD1[•])(H₂O)] and dimeric [Cu(TD1[•])(H₂O)] in toluene (0.54 mM and 0.88 mM, respectively) were recorded using non-saturating microwave (mw) power levels at different temperatures (higher than the glass transition temperature T_g , 117 K). The double integrals of these spectra over the magnetic field were multiplied by the absolute temperature to make the obtained values directly proportional to the spin concentrations (Figures S3 and S4, SI). The temperature-dependent concentrations were then used to estimate the equilibrium constants and hence the changes in Gibbs free energy of dimerization (red squares in Figure 5, see SI for details).

The dark blue solutions of the tripyrrindione complexes at room temperature were found to turn deep purple upon cooling and then resume the original color when allowed to warm up. Indeed, the dimerization equilibria of both complexes could also be monitored via UV-visible absorption measurements in toluene (Figure 6). Upon dimerization, the main band at ~600 nm (610 nm for the Pd complex, 599 nm for the Cu complex) undergoes a blue shift by about 70 nm (with new maxima at 543 nm and 526 nm, respectively). Concurrently, the low-energy band at ~900 nm (947 nm for Pd, 922 nm for Cu) gives place to a broad peak with maximum absorption at about 1000 nm. Similar spectral changes upon dimerization were also described for porphyrin cation-radicals.^{24, 25, 38}

The intensity of the narrow near-infrared peak at ~900 nm in the UV-vis spectra is a convenient measure of the monomer concentration and was used to estimate dimerization equilibrium constants and G values at various temperatures (Figure 5). Notably, the energies of dimerization obtained from UV-vis absorption data are in excellent agreement with those found by EPR measurements (red squares and circles, Figure 5) and were combined to estimate the dimerization enthalpy and entropy changes (Table 1). This agreement between parameters of dimerization from different experimental methods indicates that no additional equilibria are detected within the examined concentration range (from 50 μ M for visible absorption experiments to ~500–900 μ M for EPR). The obtained thermodynamic parameters are comparable to those reported for dimers of several metal complexes of cationic porphyrin π -radicals.^{25, 58, 59} The dimers of tripyrrindione complexes therefore reproduce the stability of porphyrin radical dimers achieved through the cofacial overlap of macrocyclic π systems and formation of a π – π bonding interaction.

The dimerization of Cu(II) and Pd(II) tripyrrindiones was also studied in MeOH solutions in order to probe the effects of a polar, protic solvent. Because of its high and variable dielectric constant ($\epsilon \approx 33$ at 298 K and ≈ 71 at 180 K), which dramatically reduces the EPR sensitivity, MeOH is not a practical solvent for EPR studies of dimerization; however, the equilibrium could be monitored by UV-visible absorption spectroscopy. The spectra obtained for methanolic solutions of [Pd(TD1[•])(H₂O)] and [Cu(TD1[•])(H₂O)] are generally

similar to those obtained for toluene solutions (Figure S5, SI). Comparison of the corresponding thermodynamic parameters (Table 1 and blue circles, Figure 5) indicated that the dimerization reaction is more favored in MeOH solutions. This observation is therefore in line with previously reported trends indicating that solvents of higher dielectric constants tend to stabilize the dimer.²⁵ In the present case, the relative stabilization of the dimeric species $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]_2$ observed in methanol is accompanied by a noticeable structural adjustment. Indeed, the EPR spectrum of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]_2$ in a frozen glassy methanol solution (Figure S6, SI) exhibits a dipolar splitting between the $g_{\perp}$ components that is about 30% greater than that found in toluene (55 mT vs. 42 mT), a spectroscopic change that translates into a $\sim 10\%$ decrease of the distance between the Cu(II) centers in the p dimer (3.7 Å vs 4.1 Å).

The low-temperature dimerization of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$ in solution is also supported by time-dependent DFT calculations (TD-DFT; PBE0/def2-tzvp/COSMO), which accurately reproduce the electronic absorption spectra shown in Figure 6 (Figure S7, SI). Upon dimerization, we calculate a red shift of a low-energy band from 932.0 to 1020.4 nm, which are best described as intraligand π – π charge transfer bands. Furthermore, the experimentally observed blue shift of an intense (predominantly ligand-based) charge transfer band from 596.7 to 518.9 nm upon dimerization is also reproduced. The TD-DFT calculations also reproduce the experimentally observed changes in the energy of the weaker features found between 950 and 650 nm. Finally, we note that the TD-DFT calculations predict an interligand charge transfer band at low energy (2053 nm). Collectively, the results of our computational work are in full agreement with the description of tripyrrindione π dimer formation afforded experimentally by EPR and UV-visible absorption methods.

CONCLUSIONS

The ability to engage in π – π interactions is critical to the paramount importance of tetrapyrrolic macrocycles in biological electron transfer. For instance, a π dimer of bacteriochlorophylls (*special pair*) in the reaction centers of bacterial photosynthetic systems is at the origin of a multi-electron transfer sequence. Whereas porphyrins have been by far the most studied synthetic compounds in this context, tripyrrindiones form a new class of platforms for π dimerization.

Although a number of metal complexes of linear tripyrrolic ligands are known,^{39, 60} the tripyrrindione system is the first to present reversible dimerization through π – π interaction of ligand-based electronic spins in solution. We have shown that EPR and UV-visible absorption spectroscopic methods capture the electronic structure of the dimers and the thermodynamic parameters of the dimerization reactions for both $[\text{Pd}(\text{TD1}^*)(\text{H}_2\text{O})]$ and $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$. Computational work, including time-dependent DFT calculations, fully supports the experimental conclusions and completes our description of the interactions between electronic spins in tripyrrindione π dimers. Coupled with the availability of reversible one-electron redox processes on the tripyrrindione scaffold, these findings could lead to a variety of applications involving the engineering of conduction, magnetism and electron transfer properties.

EXPERIMENTAL SECTION

Materials and Methods

(4*Z*,10*Z*)-2,3,7,8,12,13-hexaethyl-(15*H*,17*H*)-tripyrin-1,14-dione (H₃TD1)⁶¹ and [Cu(TD1*)(H₂O)]³⁵ were prepared as previously described. Tetrahydrofuran (THF), acetonitrile (CH₃CN), diethyl ether (Et₂O), and dichloromethane (CH₂Cl₂) were dried by passage through a solvent purifier. All other reagents were obtained commercially and used as received.

UV/visible spectra were recorded on an Agilent 8453 UV/vis spectrophotometer. For variable-temperature absorption measurements, the cryogenic nitrogen gas flow system ER 4111VT (Bruker) was used. The flow system was equipped with a custom-made probehead placed between the spectrophotometer light source and detector modules. Because of the cylindrical geometry of the dewar tubing, the samples were also cylindrical: we have used thin-wall quartz tubes with 4 mm ID (Wilmad part number 707-SQ-250M). To avoid gas bubble formation at low temperatures (due to decreased solubility) and loss of transparency, the samples were degassed by purging with helium gas for 15 minutes and then immediately sealed by capping and wrapping in parafilm.

Solution magnetic moments were measured by the Evans method^{62, 63} using reported diamagnetic corrections.⁶⁴ A solution of the paramagnetic complex in CD₃CN was transferred into a 5-mm NMR tube, and a Wilmad[®] coaxial insert filled with the deuterated solvent was employed as an internal reference. Solution magnetic susceptibilities were calculated based on the difference in chemical shift for the ¹H NMR resonance of the residual solvent protons in neat CD₃CN and in the solution containing the paramagnetic species. ¹H NMR data were recorded at the University of Arizona NMR Facility on a Bruker DRX-500 instrument.

The continuous-wave (CW) EPR experiments were carried out at the University of Arizona EPR Facility on an X-band EPR spectrometer Elexsys E500 (Bruker) using a rectangular resonator operating in TE₁₀₂ mode (Bruker, ER 4102ST). The variable-temperature measurements for *T* > 120 K were performed using the cryogenic nitrogen gas flow system ER 4111VT (Bruker). For the measurements at *T* < 77 K, a helium flow system based on the ESR900 flow cryostat (Oxford instruments) was used. The measurements at liquid nitrogen temperature were conducted using a finger dewar.

Low- and high-resolution mass spectra were acquired at the University of Arizona Mass Spectrometry Facility. Elemental analyses were performed by Numega Resonance Labs, San Diego, CA.

Cyclic voltammograms (CV) were obtained on a Gamry Reference 600 potentiostat employing a single-compartment cell and a three-electrode setup comprising a glassy carbon working electrode, a coiled platinum wire auxiliary electrode and Ag/AgCl quasi-reference electrode. Measurements were conducted at ambient temperature under an argon atmosphere in CH₃CN containing 0.1 M (*n*-Bu₄N)(PF₆) (triply recrystallized) as an auxiliary electrolyte.

Sample concentrations were 1–2 mM. All electrochemical data were referenced to the ferrocene/ferrocenium couple at 0.00 V.

Synthesis of [Cu(TD1)(H₂O)(BF₄)]

Silver(I) tetrafluoroborate (3.6 mg, 0.018 mmol) was added as a solid to a stirred solution of [Cu(TD1[•])(H₂O)] (10 mg, 0.02 mmol) in dry dichloromethane (10 mL). The mixture was stirred for 20 minutes, filtered through a Celite plug and then the solvent was removed under reduced pressure. The residue was washed several times with diethyl ether, re-dissolved in dry dichloromethane, and layered with diethyl ether. Blue crystals of the desired complex were collected by filtration (9.2 mg, 78%). UV/Vis (CH₃CN): λ_{max} (ϵ) 328 (27,000), 452 (7,100), 666 nm (18,900 M⁻¹ cm⁻¹). HRMS-ESI (m/z): [M–H₂O]⁺ calcd for [C₂₆H₃₂N₃O₂Cu], 481.1791; found, 481.1789. Anal. Calcd. for [C₂₆H₃₄N₃O₃Cu][BF₄] (CH₂Cl₂): C, 48.3; H, 5.4; N, 6.2%; found: C, 48.8; H, 5.8; N, 6.5%.

Structure refinement of [Cu(TD1)(H₂O)(BF₄)]

Purple plates were obtained by slow diffusion of diethyl ether in a dichloromethane solution at room temperature. Data were collected, solved and refined in the triclinic space group P-1. All non-H atoms in this structure, as well as the hydrogen atoms H3A and H3B of the coordinated water molecule centred at O3, were located in the difference Fourier map. The asymmetric unit contained one coordination compound and one dichloromethane molecule. All wholly occupied non-H atoms were refined anisotropically. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom ($1.5 \times U_{eq}$ for methyl hydrogen atoms). Their positions were then refined using a riding model. No restraints or constraints were used in the final model. The highest residual Fourier peak was $+0.77 \text{ e.}\text{\AA}^{-3}$ approx. 0.78 Å from Cl(2). The deepest Fourier hole was found to be $-0.74 \text{ e.}\text{\AA}^{-3}$ approx. 0.70 Å from Cl(2). The crystal data collection parameters are summarized in Table S1 (SI).

Electronic Structure Calculations

All electronic structure calculations were performed using *ORCA* v. 3.0.3⁶⁵ with *ORCA*'s VeryTightSCF convergence criteria and VerySlowConv convergence strategies. All calculations employed the PBE0 hybrid functional and the def2-tzvp basis set. Reduced systems employed the broken symmetry approximation. Models to more accurately capture dispersion interactions were not employed because they yielded non-sensible results. Only the single-point calculations on geometry-optimized structures employed the COSMO solvation model with parameters set for toluene ($\epsilon = 2.4$; $r = 1.497$), as geometry optimizations displayed an unreasonably large deviation from experimental values owing to the additional numerical noise introduced by the COSMO model. J values are reported using the $J = -(E_{HS} - E_{BS})/(\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS})$ formalism. TD-DFT calculations were performed probing the first 20 spin-allowed transitions. A 1180 cm⁻¹ red shift was applied to all transitions to account for the inherent blue-shift of TD-DFT calculated excitations relative to the experimental data. Isosurface plots were generated using *Chimera* v. 1.11.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

EPR spectra of π dimers of tripyrrindione complexes in frozen glassy toluene solutions. Top panel: [Cu(TD1•)(H₂O)]; experimental conditions: mw frequency, 9.340 GHz; mw power, 2 mW; magnetic field modulation amplitude, 0.8 mT; temperature, 20 K. Bottom panel: mixture of [Cu(TD1•)(H₂O)] and [Pd(TD1•)(H₂O)] (1:10 molar ratio); experimental conditions: 9.438 GHz, 2 mW, 0.5 mT, 77 K.

Figure 2. Spin density plots of dimeric (left) and monomeric (right) $[\text{Cu}(\text{TD1}\cdot)(\text{H}_2\text{O})]$. The α spin density is given as the blue isosurfaces and the β spin density is given as the red isosurfaces.

Figure 3.

Crystal structure of $[\text{Cu}(\text{TD1}\bullet)(\text{H}_2\text{O})(\text{BF}_4)]$. Carbon-bound hydrogen atoms in calculated positions and a CH_2Cl_2 molecule are omitted for clarity. In the side view (bottom panel), the peripheral ethyl groups are not shown. Thermal displacement ellipsoids are set at the 50% probability level (CCDC 1452414).

Figure 4.

EPR spectrum of the oxidized complex $[\text{Cu}(\text{TD1})(\text{H}_2\text{O})(\text{BF}_4)]$ in liquid toluene solution at room temperature (top) and frozen glassy toluene solution at 77 K (bottom panel).

Experimental conditions: mw frequency, 9.650 GHz (a) and 9.447 GHz (b); mw power, 2 mW; magnetic field modulation amplitude, 0.5 mT.

Figure 5.

Temperature dependences of the Gibbs free energy of dimerization of the Pd(II) (a) and Cu(II) (b) tripyrindione complexes. Values were obtained from EPR measurements (squares) and visible absorption measurements (circles) in toluene (red) or methanol (blue) solutions.

Figure 6. Temperature-dependent UV-visible absorption spectra of 50 μ M solutions of [Pd(TD1•)(H₂O)] (a) and [Cu(TD1•)(H₂O)] (b) in toluene.

Scheme 1. Ligand-based oxidation of $[\text{Cu}(\text{TD1}^*)(\text{H}_2\text{O})]$.

Chart 1.

Hexaethyltripyrin-1,14-dione and its complexes with divalent transition metals.

Chart 2.
Schematic representation of electronic spins in π dimers of tripyrrindione complexes.

Table 1Thermodynamic parameters of π dimerization

complex/solvent	H (kcal mol ⁻¹)	S (cal mol ⁻¹ K ⁻¹)
[Pd(TD1•)(H ₂ O)]/toluene ^a	-9.9	-29
[Pd(TD1•)(H ₂ O)]/MeOH ^b	-10.3	-22
[Cu(TD1•)(H ₂ O)]/toluene ^a	-8.6	-30
[Cu(TD1•)(H ₂ O)]/MeOH ^b	-9.6	-26

^aValues from EPR and UV-vis absorption data;^bValues from UV-vis data. The estimated error is ± 0.3 kcal mol⁻¹ on H and ± 1.5 cal mol⁻¹ K⁻¹ on S for all data sets.