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Structure and Electronic Spectra of Purine-Methyl Viologen Charge Transfer Complexes

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Abstract

The structure and properties of the electron donor-acceptor complexes formed between methyl viologen (MV) and purine nucleosides and nucleotides in water and the solid state have been investigated using a combination of experimental and theoretical methods. Solution studies were performed using UV-vis and ¹H NMR spectroscopy. Theoretical calculations were performed within the framework of density functional theory (DFT). Energy decomposition analysis indicates that dispersion and induction (charge-transfer) interactions dominate the total binding energy, whereas electrostatic interactions are largely repulsive. The appearance of charge transfer bands in the absorption spectra of the complexes are well described by time-dependent (TD) DFT and are further explained in terms of the redox properties of purine monomers and solvation effects. Crystal structures are reported for complexes of methyl viologen with the purines 2'-deoxyguanosine 3'-monophosphate **GMP** (DAD'DAD' type) and 7-deazaguanosine **zG** (DAD'ADAD' type). Comparison of the structures determined in the solid state and by theoretical methods in solution provides valuable insights into the nature of charge-transfer interactions involving purine bases as electron donors.

Keywords

Donor-acceptor complex; energy-decomposition analysis; dispersion interaction; induction interaction; crystal structure; π -stacking

Introduction

Purines can serve as electron donors in the chemical, electrochemical, and photochemical oxidation of nucleosides or nucleotides, oligonucleotides, model duplexes, and native DNA or RNA.^{1,2} A number of studies have been devoted to understand the structure and properties of DNA model systems in relation to the oxidation potentials of their constituent purines.^{3–8} Whereas purine oxidation potentials have not been measured within oligonucleotides or duplex DNA or RNA, their relative ease of oxidation is thought to

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Author Contributions

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Notes

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Supporting Information Available: Optical spectra of the complexes. Details of the methods used for calculation of the equilibrium constants, extinction coefficients and oscillator strengths. Aliphatic regions of the ¹H NMR spectra. Details of the theoretical calculations. X-ray crystallographic data (Experimental part and CIF files) and complete Refs. 48, 57 and 65. This material is available free of charge via the internet at <http://pubs.acs.org>.

parallel that for the single nucleosides or nucleotides in water or polar aprotic solvents.⁹ The purines can also serve as electron donors in the formation of ground state complexes with acceptors including transition metal complexes, organometallics, and organic acceptors,^{10–14} including acceptors that function as intercalators with duplex DNA such as Pt(II)(L) (diamine) (L = 1,10-phenanthroline or 2,2'-dipyridine) and ethidium.¹⁵ Here, the appearance of weak long-wavelength charge transfer absorption bands has been taken as *prima facie* evidence for complex formation; however, the structure and electronic properties of these complexes have not been characterized at a high level of theory.

The interaction of the strong organic acceptor chloranil with purine bases was first reported over fifty years ago; however, the optical spectrum of the 1:1 Mulliken-type charge-transfer complex with guanine was not characterized for another decade. Methyl viologen **MV** (trade name para-quat) is another common acceptor that is known to disrupt photosynthesis by transfer of electrons from photosystem I to molecular oxygen and is among the most widely used herbicides world wide.¹⁶ For **MV**, the optical spectra of the charge-transfer complexes with **GMP** and **ATP** (adenosine triphosphate) were reported only a decade ago.¹⁷ In subsequent studies, complex formation between **MV** and **dG** was investigated in the gas phase by electrospray ionization-mass spectrometry;¹⁸ interaction of **MV** with DNA as a groove binder was studied;¹⁹ and externally bound **MV** was used as an electron acceptor in studies of electron transfer processes in DNA.^{20–22} However, **MV** has not been reported to intercalate into DNA and attempts to synthetically incorporate **MV** into DNA by means of covalent attachment have been unsuccessful.²³ In view of the importance of cationic π -acceptors as DNA intercalators and drugs²⁴ and of the purine bases as electron donors in DNA charge transport and oxidative strand cleavage, we sought further information about the simplest of charge transfer interactions such as between a single nucleoside/nucleotide and **MV**.

We report here a combined experimental and theoretical study of the electronic spectra, stability, and structure of the ground state complexes formed between **MV** and purine nucleosides/nucleotides in water (see Chart 1). Solution studies were performed with UV-vis and ¹H NMR spectroscopy. Theoretical calculations were performed with density functional theory (DFT): standard DFT calculations for equilibrium structures and interaction energies, density fitting-DFT-symmetry adapted perturbation theory (DF-DFT-SAPT)^{25–28} for interaction energy decomposition, and time-dependent DFT (TDDFT) for optical spectra. The formation of bound complexes having short stacking distances originates from the dominant dispersion and induction interactions. All complexes give rise to distinct charge-transfer bands in the visible region of the absorption spectra with absorption energies strongly influenced by the oxidation potentials of the nucleobases and solvation effects. Lastly, the crystal structures of **MV** with the nucleotide **GMP** and the nucleoside **zG** are reported, providing valuable insights into complex formation that complements the information gained from solution phase and theoretical studies.

Results and Discussion

Charge Transfer Complex Formation in Aqueous Solution

On mixing colorless aqueous solutions of the purine nucleosides and nucleotides (Chart 1) with a colorless solution of **MV**, we observed immediate coloration varying from yellow to dark red. These visual changes in the optical properties are reflected in the absorption spectra, where distinct long wavelength absorption bands appear upon complex formation (Table 1, Figure 1A). This can be attributed to the formation of 1:1 charge-transfer complexes between purines and **MV**, which gives distinct CT-bands in absorption spectra depending on the donor strengths of purines.²⁹ Formation of 1:1 complexes is supported by Job's plot analysis (see Supporting Information). A linear relation between the energy of the

absorption maxima vs. the purine oxidation potentials is indicative of Mulliken-type charge-transfer transitions (Table 1, Figure 1B).^{30,31} The absorption maxima of the charge transfer bands for **GMP** and **AMP** with **MV** are similar to the values previously reported by Kunkely and Vogler for **GMP** and **ATP**.¹⁷

The equilibrium constant for complex formation (K_{CT} , M^{-1}) and extinction coefficients (ϵ_{CT} , $M^{-1} cm^{-1}$) of CT-bands were obtained from the analysis of concentration dependent intensities of absorption maxima (Table 1, see Supporting Information).³² For the nucleosides, the value of K_{CT} for **dG** ($13 M^{-1}$) is significantly larger than for **dA**, **zG**, **zA** and **aA** (2.46 – $7.11 M^{-1}$), indicative of stronger binding for the former. However, for nucleotides, the values of K_{CT} for **AMP** and **GMP** are similar ($17 M^{-1}$ vs. $15 M^{-1}$) and comparable to **dG**. The larger K_{CT} for the nucleotides is plausibly due to weak Coulomb attraction between the negatively charged phosphate and positively charged **MV**.

In a previous study, the equilibrium constants for formation of some Pt(II) intercalator complexes with nucleotides were found to be substantially more negative than with nucleosides, a result attributed to ionic bonding between Pt^{2+} and phosphate.^{33–35} However, several synthetic receptors^{36–38} and metal organic complexes^{39,40} display similar equilibrium constants for complexation with nucleotides and nucleosides. Interestingly, the wavelength of the absorption maxima and oxidation potentials are insensitive to the presence (nucleotide) or absence (nucleoside) of the phosphate group (Table 1).

Further insight into the nature of complex formation was obtained from 1H NMR spectroscopy measurements in D_2O for **GMP:MV** and **AMP:MV**. We find that a change in color upon mixing is accompanied by changes in the 1H NMR chemical shifts (Figure 2). In both cases the aromatic protons exhibit upfield chemical shifts (**GMP:MV**: $\Delta\delta_{Ha} = 24.4$ Hz, $\Delta\delta_{Hb} = 57.1$ Hz, $\Delta\delta_{Hc} = 33.6$ Hz and **AMP:MV**: $\Delta\delta_{Ha} = 28.3$ Hz, $\Delta\delta_{Hb} = 61.5$ Hz, $\Delta\delta_{Hc} = 53.6$ Hz, $\Delta\delta_{Hd} = 24.2$ Hz) in agreement with π -stacked geometries for the charge-transfer complexes.^{41,42} Differences in the chemical shifts of the two complexes indicate different π -stacking geometries, whereas small changes observed in the chemical shifts in the aliphatic region of the spectra are consistent with weak H-bonding interactions between the ribose group and **MV** in the solution phase (see Supporting Information). Larger chemical shifts of the aromatic protons for CT-complex of **AMP** vs. **GMP** are consistent with its slightly higher equilibrium constant, albeit the decreased solubility of adenine vs. guanine in water may also be responsible for the difference in K_{CT} .^{43,44}

Deeper understanding of complex formation was obtained from theoretical calculations (see: Experimental/Theoretical Methodology for details). Calculations were performed, within the framework of density functional theory (M06-2X functional), on 1:1 complexes of the *N*-methylpurine bases **A(Me)**, **G(Me)**, **zA(Me)**, **zG(Me)** and **aA(Me)** with **MV**. Note that the ribose is replaced by methyl in these calculations as it would be quite challenging to sample the ribose configurations properly at this level. The optimized structures, which take into account effects of water solvation, are shown in Figure 3. All five structures display overlap of one pyridinium ring of **MV** with the 5- and 6-membered rings of purines. Interestingly, the overlap is primarily via the 6-membered ring in **A(Me)** and **zA(Me)**. The calculations yield short stacking distances (3.15 – 3.22 Å) and lower twist angles (25 – 44° see Table SI2) between the pyridine rings of **MV** compared to free **MV** (45°)⁴⁵ for all complexes, all pointing towards strong intermolecular interactions.

Interaction energies were calculated by the supramolecular approach, i.e. by subtracting the energies of the isolated base and **MV** from that of complex. Basis set superposition energy corrections were taken into account and the calculations were performed with ($E_{supra,water}$) and without (E_{supra}) inclusion the solvent polarization effects. Indeed, the interaction

energies for the complexes in water turn out to be rather large -14 to -10 kcal/mol (Table 2). Generally the ordering of $E_{\text{supra,water}}$ values is consistent with the trends shown by the equilibrium constants in Table 1, however entropic effects and the omitted ribose make such comparisons qualitative at best. Since the solvent (water) has a high dielectric constant and the **MV** is an ion (+2 charge), the strong influence of solvent polarization on the interaction energies is to be expected ($E_{\text{supra}} < 2E_{\text{supra,water}}$). Interestingly, this indicates that **MV** intercalation in DNA would yield stronger base-**MV** interactions compared to isolated bases in solution due to low polarity of the sugar-base environment of DNA.

Density fitting-density functional theory-symmetry adapted perturbation theory (DF-DFT-SAPT) calculations were employed to further explore the potential utility of **MV** as a DNA intercalator. This method not only provides more accurate interaction energies E_{SAPT} (Table 2) than does DFT, but also yields the decomposition of the interaction energy into physically meaningful components, namely electrostatic, dispersion and induction interactions (Table 3). Note that solvent polarization effects are not available in DF-DFT-SAPT, so these results are to be compared with E_{supra} in Table 2. This comparison is quite good, which therefore validates the results based on the M06-2X DFT calculations.

The interaction energies E_{SAPT} of the complexes are substantially more negative than the nucleobase stacking energies in DNA (the lowest of which is -17 kcal/mol for stacking of **G-C** bases),⁴⁶ in agreement with their shorter stacking distances. The strongest internucleobase interaction energies in DNA come from the Watson-Crick base pairs. For the above complexes, the interaction energies are even more negative than for an **A-T** base pair, -16 to -14 kcal/mol, whereas that for **G(Me):MV** is comparable to a **G-C** base pair, -31 to -28 kcal/mol.⁴⁶ The above analysis indicates the potential of **MV** as DNA intercalator.

The interaction energy components provide valuable information on the nature of the interaction between **MV** and the purine bases. The largest contribution to the interaction energy is the dispersion interaction, -19 to -15 kcal/mol, which is lower (stronger interaction) than for stacked nucleobases, -12 to -9 kcal/mol. The induction energy is substantially more attractive in the complexes compared to the stacked nucleobases in DNA, and primarily responsible for their larger attractive E_{SAPT} . The higher order contributions δHF are attractive and only amount to 10–15% of the total interaction energy.

The large induction energy can be attributed to the presence of a substantial amount of charge transfer in the ground state of the complex, which can account for the large value of K_{CT} for **dG:MV** as well as the negative value of $E^{(1)}$ for **G(Me):MV** (Tables 1 and 3).²⁵ To confirm this, the DF-DFT-SAPT calculations were performed on neutral bipyridines (BiPy obtained by removing the methyl groups on **MV**) and purine bases using the optimized coordinates of the complexes (see Supporting Information). Since the LUMO energy of the BiPy is substantially higher than **MV**, negligible charge transfer character is expected from the ground state of the former. Indeed, the induction energy is smaller in magnitude, with values that are comparable to stacked nucleobases. The electrostatic energy is repulsive for all complexes, except **G(Me):MV**. Similar results were also obtained for the stacked nucleobases in DNA.

In above analysis, an accurate description of the electronic ground state properties of the complexes provided information about the DNA intercalation properties of **MV**. Similarly, an accurate description of the excited CT-states of the complexes would be required to understanding the excited state and optical properties of DNA-MV intercalated complexes.⁴⁷ Therefore, the intricate relations between optical spectra, redox properties, solvent polarization and supramolecular structure were investigated. For a qualitative

picture, charge transfer excitations can be described by the excitation of an electron from the HOMO orbital of the purine base to the LUMO orbital of **MV** (Figure 4). The corresponding ionization potential (*IP*) of purine bases and electron affinities (*EA*) of the **MV** were calculated using the monomer geometries extracted from the respective optimized geometries of the complexes. The calculated energy difference (ΔE_{IP-EA}) correlates well with the excitation energies (Table 4). The coulomb interaction of the atomic charges on oxidized purine and reduced **MV** will account for a large part of the energy correction to ΔE_{IP-EA} needed to calculate the excitation energies. The exact correction factor will depend on the relative orientation of the two molecules in the complex.

More precise calculations of excitation energies were performed by time-dependent density functional theory (Table 4). The close agreement between experimental and calculated values not only indicates the correct description of excited states by TDDFT, but also verifies that the optimized geometries are reasonable. Purine bases are neutral polar molecules, whereas methyl viologen is a highly polar dicationic species. Therefore, solvent polarization effects in water are expected to play an important role in determining their optical properties. In order to account for the effect of solvation on the optical properties, the TDDFT calculations were performed by including and excluding the polarization continuum model (CPCM) (see Supporting Information). The calculated excited energies without solvent polarization effects results in a large red shift of the excitation maxima, whereas the corresponding oscillator strengths are nearly the same. This difference is due to larger stabilization of the HOMO energy relative to the LUMO after the energy of solvation that increases the energy gap substantially. Thus, solvation effects are crucial to describe the optical properties.

X-ray Crystallographic Analysis of Nucleobase:Methyl Viologen Complexes

Crystal structures have been obtained for 2:1 complex **GMP:MV** (Figure 5) and the 1:1 complex of **zG:MV** (Figure 6), permitting for the first time the direct comparison of experimental structures for purines with an organic acceptor in the solid state with calculated structures in solution. The most significant structural feature of the **GMP:MV** complex is the intercalation of **MV** between pairs of **GMP** bases in a DAD'DAD' type complex. The **GMP**'s are assembled along the crystal *b*-axis of the unit cell as antiparallel double strands with hydrogen bonding between the Watson-Crick edge of the guanine molecules and the phosphate group from the opposite strand (Figure 5b).

The **GMP:GMP** π -stacking distance (3.289 Å) and the **GMP:MV** π - π stacking distances (3.286 and 3.315 Å) are all somewhat shorter than the average 3.4 Å stacking distance in B-DNA.^{48,49} To our knowledge, this is the first example of a 2:1 charge transfer complex with nonequivalent D-A distances. The π -overlaps for the non-equivalent **GMP:MV** complexes are slightly different, the complex with the shorter stacking distance having overlap between the purine six-membered ring and one of the two pyridinium rings of **MV** and the complex with the longer stacking distance having overlap with both purine rings (Figure 7). The one-dimensional DAD'DAD' strands are cross-linked by coordination of the deoxyribose 3'-hydroxyl and guanine carbonyl oxygen with sodium cations (Figure 5A).

The most significant structural feature of the 1:1 complex **zG:MV** is the formation of infinite alternating stacks of **zG** and **MV** in a DAD'ADAD' type structure (Figure 6). Hydrogen bonding between the deoxyribose 3-hydroxyl of one stack and the amino group of the deazaguanine in the adjacent strand results in pair-wise assembly of the one-dimensional stacks. The **zG:MV** π - π stacking distances for the two **zG:MV** pairs in the unit cell are 3.351, 3.304 Å and 3.287, 3.448 Å. There is partial overlap of both **MV** rings with both the five- and six-membered rings of **zG** (Figure 7B).

In addition to gross differences in their crystal packing, **GMP:MV** and **zG:MV** differ in more subtle features of their molecular geometries, as summarized in Table 5. The **MV** torsion angles for both structures are significantly smaller than the torsion angle for free **MV** in solution (45°).⁴⁵ This difference may reflect crystal packing forces as well as π -stacking interactions of **MV** with guanine. The slightly smaller dihedral angle for the crystal structure of **MV** with **zG** than with **GMP** (9.5° vs. 16.5°) may reflect more extensive π -overlap in the **MV:zG** complex. **MV** is reported to adopt a planar geometry when its charge transfer complex with mesitylene is included in a polycyano-polycadmte clathrate.⁵⁰ Crystal packing forces together with weak non-covalent interactions including hydrogen bonding can account for the differences between the sugar puckers and torsion angles in the two complexes and those in the parent **GMP** and **zG**.^{51–53} The highly flexible sugar rings are able to adapt to the demands of the complex crystal structures of **GMP:MV** and **zG:MV**.

Several key features of the analysis of crystal structures, including the short stacking distances and flatter **MV** conformations, are consistent with theoretical calculations. It should be noted that the relative orientation of the molecules in the crystal structure doesn't precisely match the calculations. Differences between the calculated and observed structures may arise from a combination of crystal packing forces, differences in solvation and the absence of sugar and phosphate groups in the calculated structures, as well as the shallow potential energy surfaces and weaker intermolecular interactions in π -stacked molecules.⁵⁴ The existence of 2:1 CT-complex for **GMP:MV** in the crystalline phase indicates the possibility of 2:1 complex formation in solution studies where the two phenyl rings of **MV** would form a complex with two nucleobases in a similar fashion. Even though plausible, the low concentrations and small equilibrium constants would prevent 2:1 complex formation. Moreover, no distinct optical signature appeared in concentration dependent UV-vis spectra that would indicate 2:1 complex formation (Figure S11–12).

The apparent failure of **MV** to intercalate in DNA most likely is related to its size and shape. **MV** is smaller than a purine-pyrimidine base pair and our efforts to obtain either experimental or computational evidence for formation of a stable **MV**-base pair complex have been unsuccessful. Whereas it forms DAD' type stacked complexes with **GMP** and **zG**, these have axial geometries which allow for equal overlap with both guanosines. In contrast, the helical DNA structure would permit only partial overlap between **MV** and adjacent bases. A large torsional angle would also reduce overlap between **MV** and the adjacent bases. Its concentrated positive charge may also account for its preferred function as a groove binder.¹⁹

Conclusions

We have conducted an in-depth investigation into ground state complexes of purine nucleosides and nucleotides with methyl viologen in water. A series of purine bases was considered for this study. From careful analysis of experimental results and theoretical calculations, we demonstrate the existence of weakly bound complexes with low equilibrium constants, and dependence of the CT-state energies on the oxidation potentials of the bases and water solvation effects. An accurate energy decomposition analysis, within density functional theory-symmetry adapted perturbation theory (DF-DFT-SAPT), afforded detailed analysis of the role of various intermolecular interactions to total binding energy, and comparison of various interaction energies with stacking and base-pairing interactions in DNA. This systematic analysis is highly valuable since π -conjugated acceptors are intercalating drugs for DNA.⁵⁵ Lastly, we have reported crystal structures of two of the above studied purine-methyl viologen complexes yielding valuable insights into the intermolecular interactions responsible for complex formation (direct proof of short stacking distance and flatter **MV** molecules, but also information on the role of sugar and phosphate

groups in complex formation). We expect this work to impact future studies on DNA intercalating drugs as well as photophysical studies on DNA model systems utilizing a variety of π -acceptors including methyl viologen.

Experimental/Theoretical Methodology

Materials

Guanosine 5'-monophosphate disodium salt (**Na₂GMP**), adenosine 5'-monophosphate disodium salt (**Na₂AMP**), 2-deoxyguanosine (**dG**), 2-deoxyadenosine (**dA**) and methyl viologen dichloride (**[MV]Cl₂**) were purchased from Sigma-Aldrich. 7-Deaza-2-deoxyguanosine (**zG**), 7-deaza-2-deoxyadenosine (**zA**), and 2-amino-2-deoxyadenosine (**aA**) were purchased from Barry and Associates. All materials were used without further purification. Single crystals of the **GMP:MV** salt, and **zG:MV** complex were prepared by dissolving equimolar amounts of salts in water followed by vapor diffusion of ethanol over a period of several weeks. Obtained by this method were orange and dark red colored single crystals, respectively.

Electronic Spectroscopy

Optical spectra were carried out with either an Agilent 8453 UV-vis spectrophotometer or a Perkin-Elmer Lambda 2 UV spectrophotometer equipped with a Peltier sample holder. Formation constants and extinction coefficients were evaluated by fitting the thermodynamic equations, as described in Supporting Information.³²

Electrochemistry

Electrochemical measurements were performed with CHI1202 ElectroChemical Analyzer (CHI instruments), in a low volume electrochemical cell from BASi Analytical Instruments equipped with a three electrode system consisted of a 2 mm carbon paste working electrode, platinum wire counter electrode and Ag/AgCl reference electrode. The carbon paste oil base purchased from BASi Analytical Instruments was packed into a Teflon tube of 2 mm internal diameter with a copper wire used as the electrical connection. The working electrode was polished after each run. Solutions of 1 mM to 10 mM nucleosides or nucleotides in phosphate buffer solution, pH 7.2, and 100 mM NaCl were prepared immediately prior to electrochemical measurements. Square wave voltammograms (SWV) were obtained with 50 mV pulse amplitude, 50 ms pulse width and a 5 mV step potential. All potentials are referred to the Ag/Ag⁺ couple. All measurements were done at room temperature.

Theoretical

The electronic structure calculations have been performed within the framework of density functional theory (DFT). The equilibrium structures of the complexes are obtained from DFT calculations with Mo6-2X hybrid meta xc-functional⁵⁶ and a 6-311G(d,p) basis set using GAMESS(US) version 11 (08/2011).⁵⁷ In these calculations, the effect of water solvation is implicitly taken into account by utilizing the polarizable continuum model (CPCM).^{58,59} The redox properties (electron affinity *EA* of methyl viologen acceptor and ionization potentials *IP* of the purine donors) were also obtained using the above xc-functional, basis set and solvation model (CPCM). The interaction energies were obtained using supramolecular approach, by subtracting the energies of isolated base and MV from that of the complex, taking basis set superposition error (BSSE) into account. These calculations were performed with ADF 2012 program^{60,61} using M06-2X xc-functional,⁵⁶ TZP basis set, and COSMO solvent polarization model.^{62,63} Note that CPCM is an implementation of COSMO in PCM framework and therefore both methods are expected to

yield comparable results.^{63,64} The contribution of the various intermolecular interactions, namely electrostatic, induction and dispersion interactions, and the total interaction energies have been evaluated using the density fitting- density functional theory- symmetry adapted perturbation treatment (DF-DFT-SAPT) analysis implemented into MolPro version 2010.1.⁶⁵ The excited state properties of the complexes, namely the electronic excitation energies and oscillator strengths of the charge transfer states, have been calculated by time-dependent density functional theory (TDDFT) with M06-2X hybrid meta xc-functional, a 6-311G(d,p) basis set, and using implicit solvation model (CPCM) implemented in GAMESS(US).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Absorption spectra of the [zA:MV] molecular complex as a function of the concentration of zA, at [MV] = 7.1 mM. (b) Mulliken plot for MV complexes with various nucleobase donors, as indicated.

Figure 2. ^1H NMR spectra of (A) $\text{GMP}_2^{-2}\text{Na}^+$ and 1.0 equiv ($\text{MV}^{2+} + 2\text{Cl}^-$) and (B) $\text{AMP}_2^{-2}\text{Na}^+$ and 1.0 equiv ($\text{MV}^{2+} + 2\text{Cl}^-$) in D_2O , recorded at room temperature (at 500 MHz).

Figure 3. Calculated structures for the complexes of MV with the 9-*N*-methylpurine bases (a) adenine, (b) guanine, (c) 7-dezaadenine, (d) 7-deazaguanine, and (e) 2-aminoadenine.

Figure 4.

The energy diagram of occupied and unoccupied fragment MOs of G(Me):MV. The vertical arrow indicates the (lowest energy singlet) charge transfer excitation of complex, with HOMO consisting primarily of fragment G(Me)-HOMO and LUMO consisting of fragment MV-LUMO.

Figure 5.

A) Fragment of crystal structure of $[(\text{GMP}_2)_2(\text{Na}^+)_2(\text{MV}^{2+})]$ showing the asymmetric unit cell. Sodium cations shown as blue colored tetragonal pyramidal polyhedra and phosphates groups as a purple colored trigonal pyramidal polyhedra. Hydrogens and free water molecules omitted for clarity. B) Infinite 2:1 stacks of GMP:MV from the crystal structure along the b axis formed with the aid of hydrogen bonding interactions between pairs of GMP anions.

Figure 6.

A) Unit cell along *a*-axis of the 1:1 complex **zG** with MV. Chloride anions are shown as green ellipsoids. B) Infinite 1:1 stacks of **zG**:MV from the crystal structure

Figure 7.
Relative orientation of the nucleobase donors with respect to the plane of pyridine moiety of MV acceptor in single crystalline state for **GMP:MV** and **zG:MV** complexes

Chart 1.

Chemical structures of purine nucleosides/nucleotides and methyl viologen studied in this work. Numbering of atoms included for GMP

Table 1Optical and redox properties, and formation constants of NuBase:MV complexes^a

Complex	E°_{OX} (V) ^b	λ_{CT} (nm)	K_{CT} (M ⁻¹)	ϵ_{CT} (M ⁻¹ cm ⁻¹)
zG:MV	0.81	450	3.91	369
aA:MV	1.03	416	2.46	553
dG:MV	1.11	385	13.54	61
zA:MV	1.13	402	7.11	238
GMP:MV	1.13	403	15.10	248
dA:MV	1.36	352	5.29	103
AMP:MV	1.44	353	17.07	199

^a In aqueous media, at room temperature (see Supporting Information for details).^b Vs Ag/AgCl, see Experimental Section.

Table 2

Interaction energies of the complexes calculated by supramolecular approach (MO6-2X/TZP) and by perturbative DF-DFT-SAPT (PBE0/AVTZ). The unit of energy is kcal/mol

Complex	$E_{\text{supra,water}}$	E_{supra}	E_{SAPT}
A(Me):MV	-10.50	-22.87	-20.49
G(Me):MV	-13.36	-31.95	-28.89
zA(Me):MV	-11.55	-24.05	-21.11
zG(Me):MV	-12.22	-24.72	-21.47
aA(Me):MV	-13.44	-28.18	-24.82

Table 3

First- and second-order perturbative DFDFT- SAPT energies, namely electrostatic $E^{(1)}$, induction $E_i^{(2)}$ and dispersion $E_D^{(2)}$ energies (respective exchange contributions have been added), and higherorder contribution δHF for the complexes. The unit of energy is kcal/mol

Complex	$E^{(1)}$	$E_i^{(2)}$	$E_D^{(2)}$	δHF
A(Me):MV	3.11	-5.61	-15.62	-2.37
G(Me):MV	-1.26	-7.06	-17.59	-2.98
zA(Me):MV	3.59	-5.74	-16.18	-2.79
zG(Me):MV	6.57	-6.44	-18.29	-3.31
aA(Me):MV	3.19	-6.18	-18.99	-2.84

Table 4

The excitation energies (λ_{max}) and oscillator strengths (f) of the CT-states of complexes obtained by TDDFT calculations and from experimental absorption spectra. The calculated difference between the IP of purine and EA of MV is also provided

Complex	$\lambda_{\text{max-calcd}}$ (nm)	$\lambda_{\text{max-exp}}$ (nm)	f_{cal}	f_{obs}	ΔE_{IP-EA} (eV)
A(Me):MV	380	352	0.006	0.003	4.43
G(Me):MV	415	385	0.003	0.003	4.04
zA(Me):MV	429	402	0.012	0.008	3.97
zG(Me):MV	493	450	0.016	0.013	3.63
aA(Me):MV	465	416	0.010	0.019	3.79

Table 5

Selected geometric parameters for the crystal structures of the two non-equivalent molecules of **GMP** and **zG** in their complexes with **MV**. (Atom numbering shown in Chart 1)

Complex	GMP(A):MV	GMP(B):MV	zG:MV (A)	zG:MV (B)
MV ²⁺ , torsion, deg(°)	16.5(3)		12.88, 13.02	9.32, 9.64
<i>d</i> (π , π), [Å]	3.286	3.315, 3.289 ^a	3.314	3.282
Sugar pucker,	C(4)- <i>endo</i> , C(5)- <i>exo</i>	C(4)- <i>endo</i> , C(5)- <i>exo</i>	C(4)- <i>endo</i> , C(5)- <i>endo</i>	C(4)- <i>exo</i> , C(5)- <i>endo</i>
Conformational torsion angles				
N-glycosidic torsion (χ)	−87.06°	−74.37°	−124.27°	−97.52°
N-glycosidic conform.	<i>syn</i>	<i>syn</i>	<i>anti</i>	<i>anti</i>
O(7)C(3)C(2)O(1) conform.	<i>gauche</i>	<i>gauche</i>	<i>gauche</i>	<i>gauche</i>
O(7)C(3)C(2)O(1) torsion (γ)	61.74°	66.05°	72.21°	60.31°
C(4)C(3)C(2)O(1) conform.	<i>trans</i>	<i>trans</i>	<i>trans</i>	<i>trans</i>
C(4)C(3)C(2)O(1) torsion (δ)	178.96°	−178.69°	−169.84°	176.91°

^aDistance between two nonequivalent guanine units.