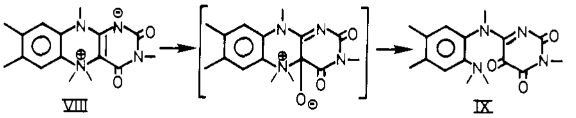
A suitable procedure for the synthesis of the desired trione (IX) was found in the reaction of 3,5,5-trimethyl-1,5-dihydrolumiflavin[24] (VIII) with a stoichiometric amount of *m*-chloroperbenzoic acid in $CHCl_3$ (followed by washing with aqueous $NaHCO_3$ solution and column chromatography on silica with $CHCl_3$ as eluant). By this means, IX was obtained in moderate yield (~20%). The structure of IX is proven by elemental analysis and IR, ^1H NMR, and finally ^{13}C NMR spectroscopy.[25] It represents the first isolated 6-aminopyrimidine-2,4,5(3*H*)-trione and thereby ends speculations[11] concerning its properties. Elemental analysis shows that C(5)=O is not hydrated, which is confirmed by four ^{13}C signals between 163 and 154 ppm. An sp^3-hybridized C(5) would absorb at much higher field (~70 ppm; cf. Ghisla et al.[4a] and Benkovic et al.[4b]). When compound IX is put into aqueous solution, spectral changes show fast hydration and, at higher pH values, probably hydrolysis. These reactions will be subject to further investigation.


VIII IX (7)

When 5-acetyl-3-methyl-1,5-dihydrolumiflavin[26] was treated with *m*-chloroperbenzoic acid, as in the case of VIII, again a new compound could be isolated.[27] In this case, the ^{13}C NMR spectrum shows a signal at 71 ppm, clearly indicating an sp^3-hybridized C(4a). We ascribe the 5-acetyl-4a-hydroxy-4a,5-dihydroflavin structure to the new product, although we cannot exclude a ring-opened hydrated form.

All attempts to convert the ketone IX with hydrazine to the hydrazone VIIc failed, which is not totally unexpected. Thus, alloxan (pyrimidine-2,4,5,6(1*H*,3*H*)-trione) oxidizes phenylhydrazine giving dialuric acid, nitrogen, and benzene.[28] We have not been successful in obtaining VII via condensation of IX with hydrazine salts, as described for alloxan.[29] The redox properties of IX, and its reactivity toward different carbonyl reagents and nucleophiles (amines and alcohols), are presently under investigation.

From our (preliminary) results, we can draw some conclusions of biological relevance. As our model (IX) is stable and does not "self-destruct" by intramolecular redox reactions, those arguments[11] against a 4a,5 ring opening during enzymatic catalysis are invalid. On the other hand, the UV spectrum of the model compound IX (λ_{max} 342 nm, ϵ 7120 M^{-1} cm^{-1}) clearly shows no resemblance to the spectrum of the enzyme-bound X (λ_{max} 390–420 nm, ϵ 15 000 M^{-1} cm^{-1})[30] (Figure 1). This finding does not support the proposal that the pyrimidine-2,4,5(3*H*)-trione structure I represents X, and reaction 3 appears to have no experimental basis. There remains the possibility of X being the *p*- or *o*-quinoid tautomer of I: a 4-hydroxypyrimidine-2,4-dione or a 2-hydroxypyrimidine-4,5-dione. These two tautomers are expected to be less stable than I and, therefore, less probable. Nonetheless, efforts are under way in this laboratory to synthesize these tautomers. Finally, the fluorescence properties[31] of IX, unless drastically altered by the apoprotein, do not support its role as the emitter for bacterial luciferase.

Acknowledgment. This work was supported by grants from the National Science Foundation and the National Institutes of Health. We are very grateful to Professors J. J. Villafranca and S. J. Benkovic for the natural abundance ^{13}C NMR spectra.

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(25) 6-[[2-(Dimethylamino)-4,5-dimethylphenyl]methylamino]-3-methylpyrimidine-2,4,5(3*H*)-trione (IX): $C_{16}H_{20}N_4O_3$ (M_r 316.35); mp 230–235 °C dec; IR (KBr) 1720 (C(5)=O), 1700 (C(4)=O), 1665 (C(2)=O) cm^{-1}; UV (acetonitrile) λ_{max} (ϵ, M^{-1} cm^{-1}) 229 (24 600), 245 (sh), 281 (12 900), 342 (7120) nm; ^1H NMR ($CDCl_3$) δ 7.10 (s, 1 H) and 6.87 (s, 1 H, C(3′,6′)H_2), 3.60 (s, 3 H, C(6)NCH_3), 3.39 (s, 3 H, N(3)CH_3), 2.51 (s, 6 H, C(2′)N$(CH_3)_2$), 2.24 (s, 6 H, C(4′,5′)$(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 162.7, 160.5, 159.7, 154.5 (C(2,4,5,6)), 139.2, 136.4, 136.4, 134.7, 124.9, 123.0 (C(1′,2′,3′,4′,5′,6′)), 43.0 (C(2′)N$(CH_3)_2$), 38.2 (C(6)NCH_3), 28.5 (N(3)CH_3), 19.6, 19.3 (C(4′,5′)$(CH_3)_2$). Anal. Calcd: C, 60.74; H, 6.37; N, 17.71. Found: C, 60.56; H, 6.43; N, 17.53.

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(27) 5-Acetyl-4a,5-dihydro-4a-hydroxy-3-methyllumiflavin or 6-[(2-(Acetylamino)-4,5-dimethylphenyl)methylamino]-3-methylpyrimidine-2,4,5-(3*H*)-trione hydrate: $C_{16}H_{18}N_4O_4\cdot{}^4/_3H_2O$ (M_r 354.36); mp 185–190 °C dec (to 3-methyllumiflavin); IR (KBr) 3400, 3250 (OH), 1735 (C(4)=O), 1690 and 1660 (C(2)=O and N(5)C=O), 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (s, 1 H) and 7.01 (s, 1 H, C(6,9)H_2), 3.63 (s, 3 H, N(10)CH_3), 3.36 (s, 3 H, N(3)CH_3), 2.36 (s, 6 H, C(7,8)$(CH_3)_2$), 2.10 (s, 3 H, C(5)$NCOCH_3$); ^{13}C NMR ($CDCl_3$) δ 173.0 (N(5)$COCH_3$), 165.9, 162.1, 155.7 (C(2,4,10a)), 136.5, 133.1, 132.5, 127.5, 124.9, 117.5 (C(5a,6,7,8,9,9a)), 71.0 (C(4a)), 31.9 (N(10)CH_3), 27.6 (N(3)CH_3), 22.5 (N(5)$COCH_3$), 19.6, 19.2 (C(7,8)$(CH_3)_2$). Anal. Calcd: C, 54.23; H, 5.88; N, 15.81. Found: C, 54.13; H, 5.58; N, 15.58.

(28) (a) Pellizzari, G. *G. Orosi* **1887**, *10* (7,8); *Gazz. Chim. Ital.* **1887**, *17*, 254. (b) Kuehling, O. *Ber. Deutsch. Chem. Ges.* **1891**, *24*, 4140.

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(30) In fact, the UV data of IX resemble more those of 4a-hydroxy-4a,5-dihydroflavins (cf. Ghisla, S.; Entsch, B.; Massey, V.; Husein, M. *Eur. J. Biochem.* **1977**, *76*, 139), which should lead to caution in ascribing 4a-FlOH structures (cf. reaction 2) to enzyme-bound intermediates solely on the basis of UV data.

(31) Compound IX is nonfluorescent in solution (solvent acetonitrile) and shows only very weak fluorescence (λ_{max} ~410–430 nm; λ_{max} (excitation) 330–340 nm) in DMF/ethylene glycol dimethyl ether glass at 77 K. Whether an excited state of IX can transfer its energy to another fluorescer (as proposed for a model reaction[2k]) will be subject to further investigation.

Intercalation of Potentially Reactive Transition-Metal Complexes in the Lamellar $MnPS_3$ Host Lattice

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The increasing interest in intercalated layer systems has remained largely centered, during the past years, on those systems exhibiting electrical conductivity.[1] Molecular reactions in the interlayer space are an attractive topic for research; recently, several novel organic reactions have been carried out in the interlayer space of layered silicates.[2-5] The catalytic[6,7] and photocatalytic[8,9] properties of organometallic intercalated silicates are also of great potential interest. This communication describes the synthesis of new intercalation compounds based on $MnPS_3$ host layers, containing large cationic species potentially suitable for further chemistry or photochemical experiments.

$MnPS_3$ belongs to a class of lamellar semiconducting materials[10] known, as the structurally analogous transition-metal dichalcogenides, to intercalate electron-donor species, such as amines[11] or cobaltocene.[12] It has been recently shown that $MnPS_3$

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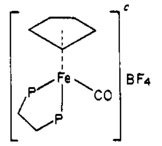
Table I. New Organometallic Intercalates Obtained by Cation Exchange with Hydrated Potassium or Sodium Preintercalated in $MnPS_3$

reacting species	intercalate formula[a]	basal spacing, Å	compd
	$Mn_{0.8}PS_3[K]_{0.4}[H_2O]_{\sim 1}$	9.43	I
	$Mn_{0.5}PS_3[Na]_{1.0}[H_2O]_{\sim 4}$	12.10	II
$Cr(en)_3Cl_3$[c]	$Mn_{0.8}PS_3[Cr(en)_3]_{0.14}[H_2O]_{\sim 1.5}$	11.20	III
	$Mn_{0.5}PS_3[Cr(en)_3]_{0.3}[Na]_{0.1}[H_2O]_{\sim 1.7}$	11.03	IV
$Ru(bpy)_3Cl_2$	$Mn_{0.8}PS_3[Ru(bpy)_3]_{0.15}[K]_{0.1}[H_2O]_{\sim 1.5}$	15.2	V
	$Mn_{0.5}PS_3[Ru(bpy)_3]_{0.22}[Na]_{0.5}[H_2O]_{\sim 2}$	15.2	VI
	$Mn_{0.8}PS_3[Cp(diphos)COFe]_{0.18}[K]_x[H_2O]_{x'}$[c] $Mn_{0.5}PS_3[Cp(diphos)COFe]_{0.23}[Na]_y[H_2O]_{y'}$[c]	17.8 17.8	VII[b] VIII[b]
	nonintercalated $MnPs_3$	6.50	

[a] All the formulas were obtained from a full elemental analysis (except for oxygen), unless otherwise stated. [b] Analysis data for potassium or sodium have not been obtained. [c] P P = diphos = 1,2-bis(diphenylphosphino)ethane; en = 1,2-diaminoethane.

was also capable of taking up certain cations from an aqueous solution, giving intercalation compounds in which the electric charge was balanced by the loss of manganese cations by the layers.[13] However, this reaction appears to be limited to monocations of relatively small size. We have found that this limitation can be overcome by synthesizing in a first step hydrated alkali metal intercalates of $MnPS_3$ and then performing cation exchange with more sophisticated species.

As already described,[13] the potassium intercalate $Mn_{0.8}PS_3[K]_{0.4}[H_2O]_{1.0}$ (I) is obtained by treating $MnPS_3$ with an aqueous KCl solution. A sodium intercalate $Mn_{0.5}PS_3[Na]_{1.0}[H_2O]_{4.0}$ (II) can also be obtained by treating $MnPS_3$ with an aqueous concentrated NaCl solution in the presence of EDTA and 0.1 M NaOH;[14] the synthesis is carried out under a nitrogen atmosphere to avoid oxidation of the manganese ions in basic medium. Both intercalates show a series of very sharp 00*l* X-ray reflections (up to 006), characteristic of the interlamellar distance (basal spacing); this parameter increases by 5.60 and 2.93 Å after intercalation of Na^+ and K^+, respectively; from these values, it can be inferred that the strongly polarizing Na^+ ions are accompanied by a double layer of solvating water molecules, while K^+ is only solvated by a single layer.[15] As a result of the presence of interlamellar water, the intercalated alkali ions (particularly Na^+) are highly mobile and may be exchanged with a number of cationic species; a few selected cases are described below to demonstrate the wide applicability of the method.

All the following experiments have been conducted under a nitrogen atmosphere in Schlenk tubes protected from light. Treatment of I and II for 12 h at room temperature with a 10^{-1} M aqueous solution of $Cr(en)_3Cl_3$ yields III and IV, respectively (Table I). The significantly larger basal spacing of III with respect to IV reflects weaker ionic packing forces due to a lower guest content.

The tris(2,2′-bipyridyl)ruthenium dication is a particularly interesting species because of its role in the photochemical reduction of water.[16] Intercalation of this large species was achieved by treating I or II with an aqueous solution of $Ru(bpy)_3Cl_2$ for 3 days at 50 °C. The UV/visible spectra of the new intercalates V and VI (Table I) are shown in Figure 1 to illustrate the high transparency of these materials.

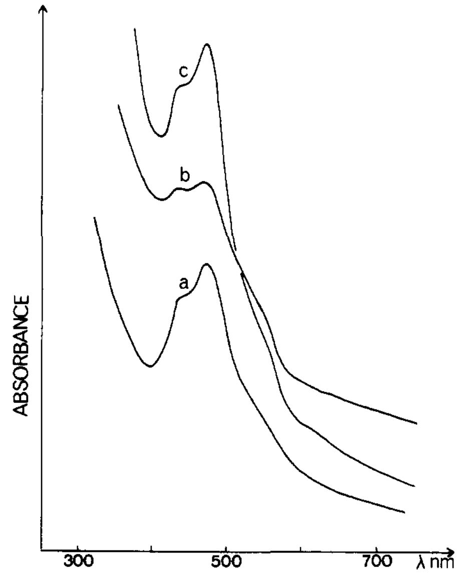


Figure 1. UV-visible spectra of KBr pellets of (a) $Ru(bpy)_3Cl_2$, (b) intercalate V, and (c) intercalate VI.

The intercalation of the cyclopentadienylcarbonyl(diphos)iron monocation (Table I) was attempted, as this large species is typical of many compounds encountered in organometallic chemistry. Its tetrafluoroborate salt dissolved in a mixture of acetone and water at 60 °C and kept over I or II for 1 week at the same temperature yielded VII and VIII, respectively (Table I).

The X-ray diffractograms of the obtained intercalates (III to VIII) all show a series of well-defined, sharp 00*l* lines, up to 006. The values of the basal spacing deduced from these sets of reflections (Table I) are consistent with the estimated van der Waals size of the guest molecules.

The IR transmittance spectra of the intercalates show, in addition to the host lattice bands[17] (605, 555, 450 cm^{-1}), a number of bands readily assignable to the guest complexes; these bands are not significantly shifted (within ±3 cm^{-1}) with respect to the bands of the corresponding starting complexes, except for the carbonyl group of the iron complex, the frequency of which is found at lower wavenumber in the intercalates than in the tetrafluoroborate salt (1967 and 1982 cm^{-1}, respectively).

The few examples described in this communication show that a new field of research appears in the intercalation chemistry of the layered chalcogenide systems in which the balance of electric charges results from a cation deficit in the layers instead of an electron transfer. The transparency of such materials and the potential chemical or photochemical reactivity of the guest species provide the basis for further developments in the chemistry of low dimensional host structures.

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Copper(II) Hemocyanin Models

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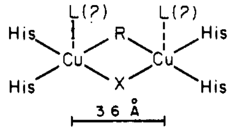
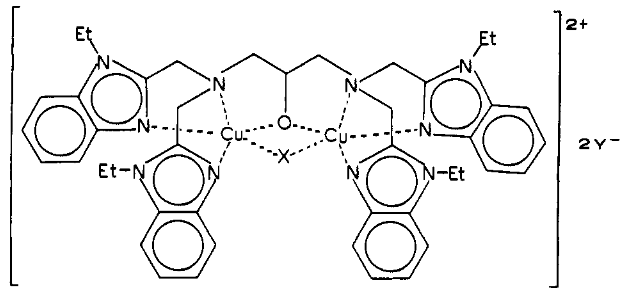
The structural picture of the active site of hemocyanin emerging from recent chemical and spectroscopic studies has set the stage for a detailed model compound approach. For oxy- and methemocyanin the collective evidence from vibrational,[1,2] magnetic,[3] chemical,[4] and electronic[1,4,5] data requires a dinuclear copper(II) site having endogeneous and exogenous bridging ligands which mediate strong antiferromagnetism resulting in diamagnetism ($-J > 550$ cm^{-1}). The exogenous bridge X is O_2^{2-} in oxyhemocyanin and is N_3^-, OAc^-, etc., in methemocyanin derivatives. The endogeneous light atom bridge R is unknown although there are frequent suggestions of an O-atom donor because of the 425-nm absorption in the UV-VIS spectrum.[4] Moreover, bridging ligands such as hydroxide, phenoxide, or carboxylate are well-known to mediate strong antiferromagnetic coupling. The popularity of phenoxide may be at odds with the absence of enhanced tyrosine vibrational modes in resonance Raman studies of oxyhemocyanin.[1,2] For the remaining ligands, EXAFS data point to two[6] or three[7] N- or O-atom donors, two of which must be imidazole from histidine.[6] The Cu···Cu separation of oxyhemocyanin is close to 3.6 Å.[6,7] Approximate tetragonal stereochemistry about copper is inferred from electronic spectroscopy.[4] We report herein the synthesis and structural characterization of a dinuclear copper(II) complex which mimics these structural features.



A wide variety of new chelating benzimidazole ligands is accessible by condensation of 1,2-diaminobenzene with carboxylic acid functionalities.[8,9] For the present study, condensation of 2-hydroxy-1,3-diaminopropanetetraacetic acid with 4 equiv of 1,2-diaminobenzene followed by N-alkylation with bromoethane provided a good yield (>70%) of L-Et, an excellent binucleating ligand for copper(II). Treatment with CuY_2 ($Y = BF_4^-$, ClO_4^-) followed by an anionic ligand X (N_3^-, OAc^-, pyrazolate, $HCOO^-$, NO_2^-, etc.) gives isolable green or blue crystalline materials[10] of the following structure.



The deprotonation of the ligand to give the alkoxide bridge is spontaneous.

While the acetate complex ($X = OAc^-$, $Y = ClO_4^-$) is essentially spin free ($\mu^{25} = 1.83\ \mu_B$ per Cu), most derivatives ($X = NO_2^-$, pyrazolate, etc.) have reduced magnetic moments indicative of antiferromagnetic coupling.[11] The azide complex, however ($X = N_3^-$, $Y = BF_4^-$), is diamagnetic at room temperature. Since fully diamagnetic copper(II) dimers are rare,[12,13] and since azidomethemocyanin is diamagnetic,[14] we decided to structurally characterize this azide complex by X-ray crystallography.[15] $[Cu_2(L\text{-}Et)(N_3)][BF_4]_2$ crystallizes from acetonitrile–ether as green prisms, and the structure of the discrete dispositive cation is shown in Figure 1. Each copper atom is coordinated to a tertiary amine and two *N*-ethylbenzimidazoles. The bridging alkoxide and the 1,3-azide bridge complete five-coordination. There is a C_2 axis passing through the alkoxide C3–O2 bond and the central N7 atom of the azide. However, the azide is not coplanar with the Cu–O–Cu plane (dihedral angle = 7.0°) (see Figure 2). The Cu···Cu separation is 3.615 (3) Å. Such a close approach of the metal atoms in a 1,3-μ-azido complex is quite unexpected. All previously reported 1,3-μ-azido complexes have Cu···Cu separations ≥5 Å.[12,16,17] Figure 2 shows the inner coordination sphere, illustrating that the copper stereochemistry is quite removed from an ideal geometry. It can be viewed as a distorted tetragonal pyramid with the longer (dashed) copper–benzimidazole bond as the apical bond [Cu–N4 = 2.11 (1) Å]. A similar distance has been observed for apical copper–imidazole in tetragonal copper(II)[18] and, as expected, is significantly longer than the basal benzimidazole bond [Cu–N2 = 1.99 (1) Å].[19] Such tetragonality is probably very important in dictating a $(d_{x^2-y^2})^1$ ground state and optimizing superexchange via the bridging ligands to give diamagnetism. By contrast, the paramagnetic acetate complex $[Cu_2(L\text{-}Et)(OAc)][ClO_4]_2$ has a more nearly trigonal-bipyramidal stereochemistry about copper and a likely $(d_{z^2})^1$ ground state.[9,20] Although bridging azide is known

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(15) $[Cu_2(L\text{-}Et)(N_3)][BF_4]_2$: monoclinic; $a = 19.08$, $b = 23.89$, $c = 13.23$ Å; $\beta = 116.21°$; $Z = 4$; space group $C2/m$; Mo Kα radiation; 1631 independent nonzero [$I > 2\sigma(I)$] reflections with 2θ between 3.5 and 45°; $R = 9.5\%$. Disorder in the BF_4^- and ethyl groups mars the precision of the structure, but the essential features described here are undoubtedly correct. A redetermination at low temperature is planned.

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(19) If the present structure is viewed as a distorted trigonal bipyramid with N1–Cu–N6 as the axis, unreasonably large distortions of the "equatorial" ligand angles from 120° must be tolerated [N2–Cu–O2 = 143.8 (4); N2–Cu–N4 = 98.6 (5); N4–Cu Also, the Cu–N2 and Cu–N4 bonds to benzimidazole are quite unequal [1.99 (1) and 2.11 (1) Å, respectively). By contrast, the acetate derivative has equatorial ligand angles of 119.4, 113.5 and 121.6° and the copper–benzimidazole bond lengths are equal within 1 SD.[9]

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