Table X. Substitution Energies (eV) for $M(CO)_5CS + CO \rightarrow M(CO)_6 + CS$

related ion	M = Cr	M = Mo[a]	M = W
$M(CO)_5^+$	0.84	1.05	1.27
$M(CO)_4^+$	0.78	0.89	1.01
$M(CO)_3^+$	0.82	0.87	0.91
$M(CO)_2^+$	1.12	1.07	1.03
$M(CO)^+$	1.02	1.13	1.23
M^+	0.91	0.99	1.07
av ± std dev	0.92 ± 0.13	1.00 ± 0.30	1.09 ± 0.14

[a] The number for $Mo(CO)_n^+$ is the average of $Cr(CO)_n^+$ and $W(CO)_n^+$ and results from the method used to estimate $A[Mo(CO)_n^+]$. The larger uncertainty reflects the uncertainty of the estimate.

The averages of these determinations, −6.4 ± 0.2, −6.4 ± 0.3, and −6.3 ± 0.2 eV, are preferred values for $\Delta H_f°[Cr(CO)_5CS(g)]$, $\Delta H_f°[Mo(CO)_5CS(g)]$, and $\Delta H_f°[W(CO)_5CS(g)]$, respectively.

Summary and Conclusions

The mass spectrometer has been used to determine and/or compare the values of several thermodynamic parameters of the group 6B hexacarbonyls and pentacarbonyl thiocarbonyls. From these results we conclude that for these compounds (1) fragmentation of the molecular ion in the mass spectrometer results in vibrational excitation of the free ligands produced, (2) substitution of CS for CO in $M(CO)_6$ lowers the ionization energy of the molecule by 0.1–0.4 eV, (3) the M–CS bond is significantly stronger than the M–CO bonds in all three pentacarbonyl thiocarbonyls, in both the molecule and the molecular ion, and (4) the calculations of the four strong–one weak bonding model are supportive of the hypothesis that substitution of the CS ligand for the one of the CO ligands results in weakening of the M–CO bond trans to the CS ligand.

These studies support the conclusions drawn from theoretical and experimental research performed elsewhere[8–12,22–24,31,32] and show that the electron-impact mass spectrometer can be a useful and reliable tool for probing the physical chemistry of inorganic molecules.

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The Association of Optically Active Ions. 2. The Pfeiffer-Active System Tris(1,10-phenanthroline)zinc(II) with Adenosine 5′-Monophosphate and Related Compounds

CLIFFORD CHING-YU LEE and PAUL HEMMES*

The system tris(1,10 phenanthroline)zinc(II) with adenosine 5′-monophosphate shows remarkable Pfeiffer activity. Noteworthy is the fact that the related compounds adenosine and α-ribose phosphate show little or no Pfeiffer activity in the pH range studied. The pH dependence indicates that a number of processes occur. At low pH the effect is most pronounced. It is concluded that short-range interaction between the purine base and the ligand rings is intimately involved in the ionic association process. The enhancement of the Pfeiffer effect in the protonated species may be due to a charge-transfer interaction from the ligands to the environmental compound. Protonation of the purine base would therefore make it a better electron acceptor. All Pfeiffer-active systems are shown by Job's method to involve 2 mol of environmental compound/mol of zinc complex.

Pfeiffer activity[1] is the nonadditivity of optical activity which sometimes results when a labile racemic component is added to a nonlabile optically active species. The two major mechanisms which have been proposed to account for this effect are the formation of diastereomeric ion pairs[2a,b] and the shifting of the racemization equilibrium due to an asymmetric electric field, leading to unequal activity coefficients and thus unequal concentrations.[3a,b] We have found a system which we feel clearly shows that the former mechanism provides a better description of the process. In addition this system provides some insight into the nature of the bonding between the components of the ion pairs.

Experimental Section

We have investigated the optical activity of the system 0.01 M tris(1,10-phenanthroline)zinc(II) with 0.02 M sodium adenosine 5′-monophosphate as a function of pH, as well as the system containing the same cation but 0.02 M sodium D-ribose phosphate. In addition we have studied solutions of 0.020 M adenosine with and without the zinc complex also as a function of pH.

The cation was prepared by mixing stoichiometric amounts of the ligand with a concentrated zinc chloride solution. (The 5′-AMP, 3′,5′-c-AMP, and sodium D-ribose phosphate were obtained from Sigma Chemical Co. and were used as received.) All other reagents were obtained from Fisher Scientific Co. and were used without further purification.

Optical rotations were measured at the sodium D line on a Rudolph polarimeter fitted with a photoelectric detector using a filtered sodium

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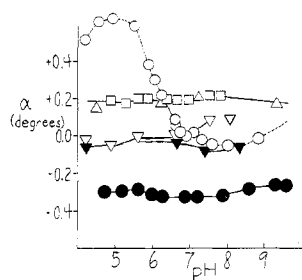
Figure 1. The pH dependence of the optical rotations of nucleosides, nucleotides, and related compounds: O, 5'-AMP + $Zn(phen)_3^{2+}$; ●, 5'-AMP alone; □, ribose phosphate + AMP; △, ribose phosphate alone; ▼, adenosine + $Zn(phen)_3^{2+}$; ▽, adenosine alone.
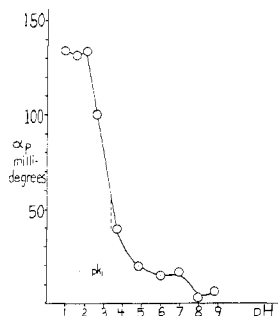

Figure 2. pH dependence of $Ni(phen)_3^{2+}$ (*l*-malic acid data from ref 4).

lamp. A thermostated 1.0-dm cell was used. The solution pH was measured on a Radiometer pH meter and was adjusted by adding HCl or NaOH.

Results

The results of the investigation for the systems are shown in Figure 1. From this figure it is evident that ribose phosphate does not produce a Pfeiffer activity in the $Zn(phen)_3^{2+}$ cation over the pH range studied. It should be mentioned that in more basic solutions (pH >9) hydroxide ions bind to the cation with replacement of phenanthroline. We have been able to show the presence of new Pfeiffer-active species in this basic region. These results will be the subject of a future communication.

The electrically neutral adenosine molecule also shows little, if any, Pfeiffer activity. The reproducibility of these optical rotations was not as good as that for the other systems so it is difficult to say if there is or is not a small Pfeiffer activity. However, it is clear that AMP has a far greater Pfeiffer activity than either ribose phosphate or adenosine. For AMP the observed Pfeiffer activity changes most rapidly in the region of pH $\simeq pK_2$ for 5'-AMP. Similar behavior has been found but not recognized earlier[4] (Figure 2).

In order to assess the role of electrostatic charge, as a means of stabilizing the associated species, we have measured the Pfeiffer activity of 3',5'-c-AMP with the zinc complex. These results are shown in Figure 3. Furthermore, in order to assess the stoichiometry of the Pfeiffer-active species, we made a Job's method plot for 5'-AMP plus zinc complex at two pH values, one on each side of pK_2 (Figure 4). Raman spectra of $Zn(phen)_3^{2+}$ + AMP mixtures are the sum of the spectra of the components, showing that the coordination sphere of Zn remains intact.

Discussion

Since ribose phosphate contains the same ionizable group and the same optically active centers as 5'-AMP, we can immediately conclude that long-range electrostatic interactions
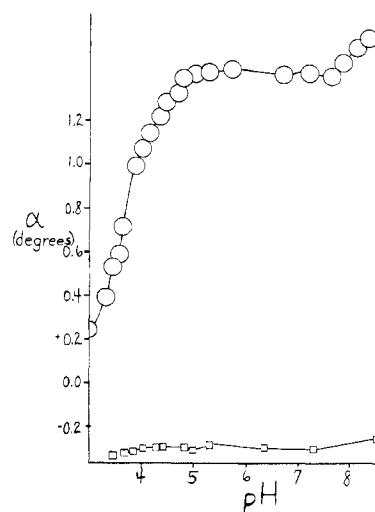

Figure 3. pH dependence of 3',5'-c-AMP (squares) and of $Zn(phen)_3^{2+}$ (circles).

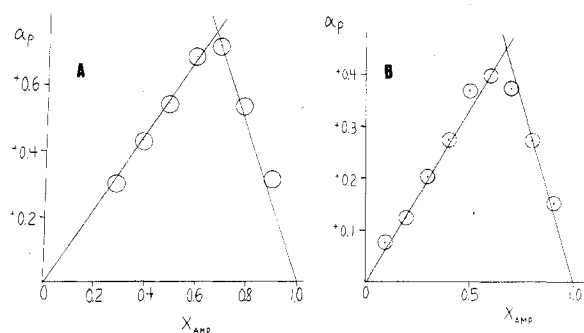**Figure 4.** Job's method plot of 5'-AMP and $Zn(phen)_3^{2+}$ (23 °C): (A) pH 5.9; (B) pH 7.3.

are not the cause of Pfeiffer activity. Ribose phosphate should set up the same electrical field at long distance as AMP. Hence if a long-range asymmetric electric field is the cause of Pfeiffer activity, we expect ribose phosphate and 5'-AMP to be very similar in Pfeiffer activity. Thus we conclude short-range interactions must be of prime importance in Pfeiffer systems. Theoretical calculations by Schipper[5] have shown that, in order for an electric field to show the asymmetry of the ligands, terms involving quadrupole and octupole moments must be significant. Clearly these terms will only be of significance for very close distances of approach of the species. This argues for the diastereomeric pair model, despite the fact that Schipper considers "unassociated" species in his calculations. As a second short-range interaction which can, in principle, lead to differences in diastereomeric ion pair stability, one must consider hydrogen bonding. Kirschner[6] has shown that hydrogen bonding can account for the properties of some Pfeiffer-active systems. The tris(phenanthroline) complex can only be a hydrogen-bond acceptor, and then only by bonding to the π clouds above and below the plane of the ligand. The hydrogen-bond donor is either the sugar or the base. Since neither adenosine nor ribose phosphate is effective in Pfeiffer activation, there seems to be no strong influence of hydrogen bonding. If there were cooperative H-bonding effects only in the nucleotide, then the conformation of the nucleotide must be syn (according to molecular models) which is unfavorable for nucleotides such as AMP. Furthermore if the pH dependence of Pfeiffer activity is due, in part, to hydrogen bonding involving the protonated phosphate group as

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Table I. Influence of Absolute Ethanol on the System $Zn(phen)_3^{2+}$ + AMP[a]

% ethanol v/v	$\alpha_{obsd}(A)$	$\alpha_{obsd}(B)$	α_p
0	+0.561	−0.302	+0.863
1	+0.393	−0.307	+0.200
3	+0.179	−0.328	+0.507
6	−0.109	−0.342	+0.233
10	−0.300	−0.351	+0.051
14	−0.398	−0.325	−0.073
20	−0.466	−0.383	−0.083
24	−0.490	−0.353	−0.137

[a] A = $Zn(phen)_3Cl_2$ (0.01 M) + AMP (0.02 M); B = AMP (0.02 M).

donor, then we would expect that 3′,5′-c-AMP would show less Pfeiffer activity than AMP since it has but one proton with a pK_a comparable to the first proton on AMP. To test this we measured the Pfeiffer activity of 3′,5′-c-AMP with zinc phenanthroline complex. The very large Pfeiffer effect we found in the basic region (Figure 3) is due to the fully deprotonated c-AMP anion. Therefore hydrogen bonding cannot be a significant source of stability in this type of Pfeiffer-active system.

Another factor which had been suggested by Nordquist[7] as a source of Pfeiffer activity is water structure enhanced ionic association (hydrophobic bonding). In view of the great number of hydrogen-bonding acceptor and donor sites on the nucleotide, we considered it unlikely that hydrophobic bonding was significant. As further confirmation of this, we measured the Pfeiffer activity in water–alcohol mixtures of 5′-AMP and zinc complex. These results are shown in Table I. Quantitative analysis of these data is not possible due to the influence of solvent composition on pH, but one fact is clear, namely, the Pfeiffer activity has not been reduced to zero by 24% v/v ethanol. Clearly the structure of water must be badly disrupted in this mixture. The decrease in Pfeiffer activity when solvent composition is changed is well documented[8] but is probably due to causes other than changes in water structure.

We attribute the Pfeiffer activity in these systems to a donor–acceptor interaction between the phenanthroline rings as donors and the purine ring as an acceptor. This interaction is presumed basically weak, being on the order of (2 or 3)kT. The electrostatic interaction between the ionized phosphate group and the divalent zinc complex adds to the overall stability. This would account for why adenosine itself is a poor Pfeiffer-activating group. The ring and the phosphate are acting in a synergistic manner. When the pH is lowered, it is the base which is protonated,[9] making it a better electron acceptor and thus enhancing Pfeiffer activity. It is important to recognize that if one assumes diastereomeric ion pairs as the source of Pfeiffer activity, what is truly important is not so much the number of ion pairs but the *difference* in stabilities of the complex containing the D form of the labile cation and the complex containing the L form. We assume therefore that when the proton is removed from the AMP species, what remains is a doubly ionized phosphate chain whose interaction with the cation is stronger than the charge-transfer interaction between the cation and the base. Thus more ion pairs are formed, but the stability of these is not dependent on the cation configuration. This process is shown schematically in Figure 5.

In this scheme we assume that charge-transfer bonding to the protonated ring is more important than the electrostatic interactions.[9,10] This is not too surprising since the bulk of
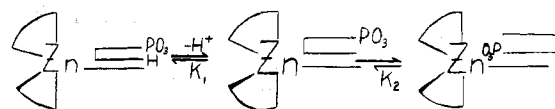

Figure 5. Schematic diagram of the bonding of AMP, protonated and unprotonated, to $Zn(phen)_3^{2+}$. K_1 and K_2 are the equilibrium constants for the steps. Only one of two AMP molecules is shown. Only the oxygen atom of the PO_3 group can come close to the Zn center in the complex.

Table II

dye	$[Zn(phen)_3^{2+}]$, M	$10^5 \times$ [dye], M	λ_{max}, nm
acridine orange·HCl	0	1.33	492[a]
acridine orange·HCl	4.4×10^{-2}	1.33	505
alizarin	0	1.0	520
alizarin	5×10^{-2}	1.0	540

[a] For acridine orange it is known that aggregation occurs (M. F. Lamm and D.M. Neville, Jr., *J. Phys. Chem.*, **69**, (1965)). In the presence of $Zn(phen)_3^{2+}$ changes in bond shape occur consistent with formation of monomers at the expense of dimers. For solution of acridine orange (3.6×10^{-6} M) containing large quantities of $Zn(phen)_3^{2+}$ (3.9×10^{-2} M), Beer's law is obeyed for the visible spectrum of the dye with $\epsilon = 6.10 \times 10^4$.

these reactants precludes very close approach of the ions under any circumstances. In fact, the high Pfeiffer activity of c-AMP may well represent a better compromise between charge transfer to ring bonding and closer approach of charged centers available to the more compact c-AMP compared to the 5′-AMP. Upon deprotonation an equilibrium exists between two types of ion pairs, the first in which charge-transfer interactions are important and the second where closest approach of ions is important. If we assume the second is most important for the deprotonated base ($K_2 > 1$), it would seem likely that Pfeiffer activity should decrease since the ionized group (the phosphate) is in a nonchiral immediate environment. In the charge-transfer complexes the planar arrangements of the rings induce a greater steric constraint with the possibility of greater stereospecific interactions. Thus more discrimination between D and L isomers of the cation will be observed in the charge-transfer system even though the actual number of ion pairs may be smaller. It should be noted that hydrogen bonding of the sugar hydroxyl groups may well be significant in the discrimination of D and L forms of the complex. This is not contradictory to our previous argument since before we were testing to see if hydrogen bonding was the dominant factor in stability of the overall complex. Furthermore our model explains some of the solvent effects previously noted. In a solvent with less polarity than of water but with a higher polarizability, the solvation of the phenanthroline rings may eliminate the charge-transfer interaction (the solubility of phenanthroline in nonpolar but polarizable solvents implies a strong solute–solvent interaction). The discrimination between enantiomers would therefore decrease, and less Pfeiffer activity would result. This was in spite of the fact that the dielectric constant would be lower, and therefore more ion pairs would result.

As further confirmation of the charge-transfer nature of the interaction between the phenanthroline rings and the environmental compounds, we used a model system, $Zn(phen)_3^{2+}$ + acridine dyes. The visible spectra of these dyes show a shift of λ_{max} to a higher frequency in the presence of the zinc complex than in pure water (Table II). Furthermore, from Pfeiffer-activity studies of the pairs of environmental com-

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Table III. Influence of Electron-Donating Substituents[a] on Pfeiffer Activity[a]

compd	α_p	compd	α_p
d-cinchonine	−0.384	*l*-strychnine	−0.210
d-quinidine[b]	−0.177	*l*-brucine[b]	−0.179
l-cinchonidine	+0.337		
l-quinine[b]	+0.140		

[a] All solutions contain 0.01 M Zn(phen)$_3$Cl$_2$ and 0.02 M activating agent.   [b] The methoxy derivative of the pair.

pounds Zn(phen)$_3$ plus (cinchonine or quinidine), (strychnine or brucine), or (cinchonidine and quinine) there is further evidence of charge-transfer interaction. The second compound in each pair enclosed in parentheses is a ring-substituted derivative of the first with a methoxy group substituting a hydrogen. The results of Pfeiffer-activity studies are shown in Table III. When the aromatic ring on the various alkaloids is substituted with an electron-donor group, the Pfeiffer activity is markedly reduced. All of these observations are consistent with the assumption that the environmental compound is an electron acceptor. In a further attempt to support this contention we studied the UV spectrum of these systems at 0.01 M concentration and with the use of a 0.10-mm cell (since we have a presumed association, high dilutions would dissociate the complex so no results could be expected at 10^{-4} M). Unfortunately no significant change in the spectrum of the phenanthroline ligands could be obtained. This is not too surprising since the molar absorptivity of a charge-transfer band of this type is likely to be on the order of 10^2. This band will be buried in the transition within the rings with an absorptivity of more than 10^4. Thus even if binding is quanti-

tative, the expected change in absorbance is on the order of 1% or less. The short path length also makes differential measurements rather unreliable. NMR results however support this model. Ogino and Kumagi[2b] had found that the chemical shifts of the phenanthroline protons as well as the chemical shifts of the protons on the heterocyclic base in the alkaloid were altered when the complex and the alkaloid were mixed. The protons on the aliphatic groups of the alkaloid showed a much smaller change. The observed shifts were those expected for ring currents and strongly suggested $\pi-\pi$ interactions.

The 2 to 1 stoichiometry of the super complexes found in this study is quite striking. We have found that this stoichiometry is quite general. It is not related to the electrostatic interaction since both mono- and divalent AMP anions are bound as are positively charged alkaloid cations.[2a]

In summary we feel that Pfeiffer activity in these systems is due to the formation of a complex containing predominantly 2 mol of environmental compound/mol of tris(phenanthroline)zinc. This aggregate is held together largely by charge-transfer interactions between the phenanthroline ligand and an acceptor group on the environmental compound, this interaction being augmented by electrostatic factors. The two stabilizing forces have different steric requirements, and thus a complex Pfeiffer activity results as one enhances one of these forces.

Registry No. Zn(phen)$_3$$^{2+}$, 28293-61-0; NaAMP, 132-00-3.

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Triboluminescence, Single-Crystal Polarized Absorption and Photoluminescence, and High-Pressure Studies of Linear-Chain Manganese(II) Compounds

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((CH$_3$)$_3$NH)$_3$Mn$_2$Cl$_7$, a linear-chain manganese(II) compound which contains both six-coordinate and four-coordinate manganese sites, is brightly triboluminescent. Both the triboluminescence and the photoluminescence spectra exhibit simultaneous emissions from both sites. The emission and d–d absorption spectra are assigned by using single-crystal polarization techniques. The triboluminescence is assigned to the ^{4}E → ^{6}A transition from the six-coordinate manganese ion and the ^{4}T$_1$ → ^{6}A transition from the four-coordinate manganese ion. A comparison of the emission intensities shows that the triboluminescence is equivalent to the high-pressure photoluminescence with $P < 2 \pm 1$ kbar. The relationship between the pressure and the mechanism of the triboluminescence excitation is discussed.

Triboluminescence (TL), the emission of light caused by the application of mechanical stress on crystals, occurs from a large number of compounds.[2,3] The best studied of these are aromatic compounds.[2,4] Triboluminescence from metal complexes is less common.[5] The TL of uranyl salts,[6] europium complexes,[4,7] and tetrahedral manganese salts[8] has been

spectroscopically studied. In addition, TL from tetracyanoplatinate crystals has been observed.[5,9]

Crystals of ((CH$_3$)$_3$NH)$_3$Mn$_2$Cl$_7$,[10] which contain chains of face-sharing MnCl$_6$ octahedra and discrete MnCl$_4$$^{2-}$ ions in the crystal lattice, triboluminesce brightly in the red region of the visible spectrum.[11] A similar salt, (CH$_3$)$_4$NMnCl$_3$,[12]

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