TABLE 1 — DEPENDENCE OF THE RATE CONSTANT ON THE MOLARITY OF THE METAL COMPLEX AND ACID

[Temperature = $28 \cdot 0° \pm 0 \cdot 1°$; ionic strength = $3 \cdot 0$]

| $[Cr(Ox)_2(H_2O)_2^-]$ $(M)$ | $[H_3PO_4]$ $(M)$ | $10^3 \, k_{obs}$ $(min^{-1})$ |
|---|---|---|
| 0·002 | 3·0 | 6·41 |
| 0·003 | 3·0 | 6·42 |
| 0·004 | 3·0 | 6·28 |
| 0·005 | 3·0 | 6·18 |
| 0·006 | 3·0 | 6·36 |
| 0·008 | 3·0 | 6·39 |
| 0·006 | 1·0 | 1·33 |
| 0·006 | 1·5 | 2·07 |
| 0·006 | 2·0 | 2·93 |
| 0·006 | 2·5 | 4·68 |
| 0·006 | 3·5 | 7·82 |
| 0·006 | 4·0 | 10·62 |

medium a plot of log $k_{obs}$ versus $-H_0$ was made. The values of the rate constants obtained by varying the concentration of the metal complex and orthophosphoric acid are presented in Table 1. An increase in ionic strength from 0·5 to 3·0 increases $k_{obs}$ from $0·97 \times 10^{-3}$ min$^{-1}$ to $6·36 \times 10^{-3}$ min$^{-1}$ ([complex] = 0·006$M$ and [H$_3$PO$_4$] = 3·0$M$). This is in agreement with the change expected in a reaction between the ions of the same charge type. It was found that an increase in added [oxalate] from 0·002 to 0·008$M$ decreased the $k_{obs}$ from $2·26 \times 10^{-3}$ min$^{-1}$ to $1·21 \times 10^{-3}$ min$^{-1}$ ([complex] = 0·006$M$; [H$_3$PO$_4$] = 3·0$M$; $\mu = 3·0$).

The grass green product obtained in these studies appears to be identical with that formed in the substitution of Cr(OX)$_3^{3-}$ by H$_3$PO$_4$ with two broad absorption peaks around 430-450 nm ($\epsilon_M = 28·2$) and 580-610 nm ($\epsilon_M = 21·3$). Ion exchange studies failed to show the presence of either cationic or anionic phosphato complex in the product. Hence the product species may be possibly of the type Cr(H$_2$PO$_4$)(HPO$_4$) (ref. 2 and 7).

The following mechanism is suggested to explain all the experimental observations.

$$Cr(Ox)_2(H_2O)_2 + H^+ + H_2PO_4^- \overset{K_1}{\rightleftharpoons} Cr(Ox)(OxH)(H_2PO_4).$$
$$(H_2O)_2^-$$
$$\text{I}$$

$$\text{I} + H^+ + H_2PO_4^- \overset{K_2}{\rightleftharpoons} Cr(Ox)(H_2PO_4)_2(H_2O)^- + Ox^{2-} + 2H^+$$
$$\text{II}$$

$$\text{II} \overset{k_3}{\underset{slow}{\longrightarrow}} \text{products}$$
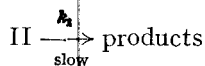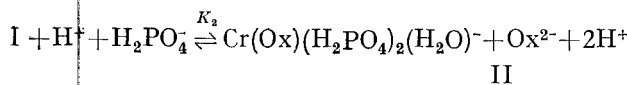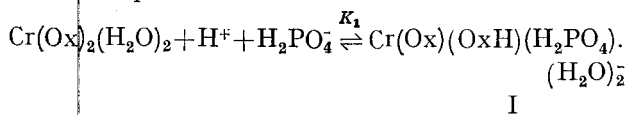
This leads to the rate law:

Rate = $k_1 K_1 K_2$[Complex][H$_2$PO$_4^-$]$^2$[ox$^{2-}$]$^{-1}$h$_0$

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## Methylpyrazine Complexes of Ag(I), Zn(II) & Cd(II) Nitrates

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1:1, 1:4 and 1:2 complexes of Ag(I), Zn(II) and Cd(II) nitrates, respectively, with methylpyrazine have been prepared and characterized on the basis of molar conductance, molecular weight and IR and far IR data. The Ag(I) complex is suggested to have a linear polymeric structure with a planar three-coordinate environment around the silver atoms with bridging methylpyrazine and terminal monodentate nitrate groups. The Zn(II) complex is suggested to have a tetrahedral environment of four nitrogen atoms of terminally bonded methylpyrazine molecules and ionic nitrates. The Cd(II) complex is suggested to have a monomeric octahedral environment around the cadmium atoms with monodentate methylpyrazine molecules and bidentate chelating nitrate groups at trans-positions to each other.

IN continuation of our work[1,2] on the complexes of pyrazine and its derivatives, we report the preparation and characterization of Ag(I), Zn(II) and Cd(II) nitrate complexes of methylpyrazine.

The complexes were prepared by adding an excess of the ligand to hot solutions of the respective metal nitrates in ethanol, Ag(I) complex crystallized out immediately while Zn(II) and Cd(II) complexes crystallized on concentration of the solutions by slow evaporation. The complexes were filtered, washed with ethanol and dried in vacuo [the Ag(I) complex was dried at ~90°]. Metal and nitrate were estimated gravimetrically[3]. The complexes are fairly soluble in dimethylformamide and methanol. IR spectra were recorded in nujol and hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer.

Ag(methylpyrazine)NO$_3$; m.p. 176° [Found: Ag, 41·1; NO$_3$, 23·7. Calc.: Ag, 40·9; NO$_3$, 23·5%].

Zn(methylpyrazine)$_4$(NO$_3$)$_2$; m.p. 66° [Found: Zn, 22·0; NO$_3$, 11·6. Calc.: Zn, 21·9; NO$_3$, 11·5%].

Cd(methylpyrazine)$_2$(NO$_3$)$_2$; m.p. 130° [Found: Cd, 26·5; NO$_3$, 29·0. Calc.: Cd, 26·4; NO$_3$, 29·2%].

Analytical data show that Ag(I), Zn(II) and Cd(II) nitrates form 1:1, 1:4 and 1:2 complexes respectively with methylpyrazine. Molar conductivities of ~10$^{-3}M$ solutions in dimethylformamide and methanol demonstrate that the Ag(I) complex behaves as 1:1 electrolyte ($\Lambda_M = 110$ ohm$^{-1}$ cm$^2$ mole$^{-1}$) while the Zn(II) (160-170 ohm$^{-1}$ cm$^2$ mole$^{-1}$) and Cd(II) (~180 ohm$^{-1}$ cm$^2$ mole$^{-1}$) complexes behave as 1:2 electrolytes. Strong bands in the IR spectra (IR band positions in cm$^{-1}$) in the region 1500-1300 assigned to nitrate groups mask some

of the bands due to the organic moiety in this region.

Methylpyrazine may act as a unidentate or a bidentate ligand. Geometry of this molecule precludes chelation but favours coordination of the two donor sites to different metal ions thus leading to the formation of polymeric structures. IR spectral studies have shown that in metal complexes where methylpyrazine is bonded through only one of its nitrogen atoms medium intensity bands appear in the regions 950-1000 and ~1250 (refs 1, 2). Such bands are absent in methylpyrazine-bridged polymers of long chain but weak bands appear when the chain length is short. The intensity of these bands has been considered as a measure of chain length in metal complexes[1,2].

Ag(I), Zn(II) and Cd(II) being $d^{10}$ ions, do not show $d{\rightarrow}d$ transitions and, therefore, electronic spectral and magnetic susceptibility measurements are not helpful in assigning the stereochemistry of these complexes. Information on the tentative stereochemistry of the present compounds has been derived mainly from a comparison of the IR bands due to nitrate groups with similar modes in compounds of established structures.

The free nitrate ion ($D_{3h}$ symmetry) shows three IR active fundamentals — $v_2$, $v_3$ and $v_4$. $v_1$ is normally IR-inactive but is usually observed as a weak band in the IR spectra of solid compounds containing ionic nitrates probably because of the crystal interactions. On coordination[4-9] the local symmetry of the nitrate group is lowered to $C_{2v}$ with the result that all the modes become IR-active, shifts in the band positions occur and the degeneracy of $v_3$ and $v_4$ is lifted. Since the local symmetry of the mono- and bi-dentate nitrate groups is the same, both the bonding types exhibit similar splittings of the fundamental modes[4-9]. However, the magnitude of separation of $v_1$ and $v_4$ frequencies of coordinated nitrate groups affords a useful criterion for distinguishing between the mono- and bi-dentate nitrates[6]. The magnitude of separation of these bands is smaller for the mono- than for the bi-dentate nitrates. Recently it has been established that the number and the relative energies of the nitrate combination modes in the region 1800-1700 may be used in distinguishing the various coordination modes of the nitrate groups[6,10]. Compounds with ionic nitrates exhibit only one weak band in this region while those with mono- or bidentate nitrates show two bands the separation of which is generally smaller (6-26) for the mono- than for the bi-dentate (20-66) nitrates.

IR spectrum of the 1:1 Ag(I) complex shows additional bands at 1260 and 980 indicating that the methylpyrazine is bonded through both the ring nitrogens and the complex has a short chain-length polymeric structure[1,2]. In addition to ligand bands, Ag(I) complex shows bands at 1442, 1312, 1015, 820, 730 and 718 which are assigned to $v_4$, $v_1$, $v_2$, $v_6$, $v_5$ and $v_3$ modes, respectively, due to coordinated nitrate group. Moreover, two weak bands (1760, 1745) with a separation of 15 appear in the region 1800-1700. The observed separation (130) (ref. 6) of $v_4$ at 1442 and of $v_1$ at 1312 and of the combination modes (15) (ref. 10) indicate the presence

of terminally bonded monodentate nitrate group. From a consideration of bidentate bridged nature of methylpyrazine (*vide supra*) and terminally bonded monodentate nitrate group it is suggested that this complex has a short chain length polymeric structure with a three-coordinated environment of ligand atoms (two nitrogens from bridging methylpyrazine molecules and an oxygen atom of the terminal monodentate nitrate group) around the silver atoms.

The 1:4 Zn(II) complex exhibits medium intensity bands at 1255 and 980 characteristic of terminally bonded methylpyrazine molecules[1,2]. It behaves as a 1:2 electrolyte indicating that both the nitrate groups are ionic in solution. IR spectrum of this complex shows a strong broad band at 1370 due to $v_3$ and medium intensity bands at 833 and 720 due to $v_2$ and $v_4$ modes, respectively. Moreover, a weak band at 1045 due to $v_1$ (normally IR-forbidden in ionic nitrates) is observed probably due to site-symmetry effects. Further, IR spectrum exhibits only one band of very weak intensity in the combination mode region, 1800-1700. These features clearly indicate the presence of ionic nitrates in the solid state in this compound[4-10]. From a consideration of terminally bonded methylpyrazine molecules and ionic nitrates the complex is tentatively assigned a four-coordinated monomeric tetrahedral structure in the solid state.

Besides the medium intensity bands at 1260 and 940 due to terminally bonded methylpyrazine molecules[1,2], the 1:2 Cd(II) complex shows bands at 1470, 1290, 1050, 816, 735 and 710 assigned to $v_1$, $v_4$, $v_2$, $v_6$, $v_3$ and $v_5$ modes, respectively, due to coordinated nitrate groups. These bands are absent in the uncoordinated methylpyrazine and Cd(II) chloride, bromide, iodide or thiocyanate complexes reported earlier[1]. Two weak bands at 1765 and 1725 with a separation of 40, and the observed separation of 180 of $v_1$ and $v_4$ modes due to coordinated nitrate groups, suggest the presence of only bidentate nitrate groups in this complex[6,10]. With bidentate chelating nitrate groups and terminally bonded methylpyrazine molecules (*vide supra*) the 1:2 Cd(II) complex is tentatively assigned a monomeric octahedral structure in the solid state. The absence of a band in the region 1800-1790 in the IR spectrum of Cd(II) complex eliminates the possibility of polymeric structures involving monodentate, $M-O(NO_2)-M$, or bidentate, $M-O(NO)$ $-O-M$, bridging nitrate groups[11]. Finally molecular weight determination of this compound by Rast's method (observed 475, calc. 424) is also consistent with the monomeric structure for the complex in the solid state. Since the fundamental modes due to coordinated nitrate groups in this compound do not exhibit greater splitting than expected for $C_{2v}$ symmetry, the two nitrate groups must be *trans* to each other[5]. The metal atoms in this complex are thus likely to have a six-coordinated monomeric octahedral environment of four oxygen atoms (from two terminally bonded bidentate chelating nitrate groups) and two nitrogen atoms of the terminally bonded methylpyrazine molecules. Because of the weak $Ag-ONO_2^{12}$ and Cd⟨O⟩NO⟨O⟩ bonds[7,12], the

Ag—O (nitrate) and Cd—O (nitrate) stretching modes could not be observed above 200.

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## Polarographic Study of Zn(II)-Tryptophan System

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Polarographic behaviour of Zn(II) in the presence of DL-tryptophan and NaClO as supporting electrolyte has been studied. The system yields two waves, however, the second is masked by a maximum at low tryptophan/Zn(II) ratios. The maximum disappears on increasing the [tryptophan] but at this stage the second wave is considerably suppressed and is finally eliminated on further increase of tryptophan/Zn(II) ratio. The first wave which represents an irreversible electrode process is due to Zn(II)-tryptophan complex. The rate constant and the product '$\alpha n_a$' for the electrode reaction have been evaluated.

CHELATES of Pb(II), Cu(II) and Cd(II) with L-tryptophan were first reported by Quintin and Roglizzo[1]. Pleticha[2] has reported polarographic studies of complexes of Co(II), Ni(II), Fe(II) and Mn(II) with several amino acids including L-tryptophan. Chandra and Srivastava[3] and Lal and Christian[4] have also dealt with different aspects of Ni(II)-L-tryptophan system.

The present note deals with polarographic study of Zn(II)-tryptophan system in NaClO₄ as supporting electrolyte. Sodium perchlorate has been specially used to avoid any possibility of complex formation of Zn(II) with the anion of the supporting electrolyte. The use of buffer has also been avoided for the same reason. Since the kinetic studies were envisaged, use of any surface-active agent has also been avoided.

The d.m.e. (Sargent, USA) had the following characteristics $m^{2/3}t^{1/6} = 2.140$ mg$^{2/3}$ sec$^{-1/2}$ in $0.1M$ NaClO₄ at $-0.11$ V versus SCE. All the chemicals used were of BDH or E. Merck (AR grade). ZnCl₂ was used as the depolarizer. The experimental set up and the procedure were similar to those reported earlier[5].

The diffusion coefficients have been experimentally determined using Dawson cell[6] and '$n$' calculated thereafter by Ilkovic equation, corresponding to the first wave has been found to be between 1·7 and 2·2. Such discrepancies in calculated values of '$n$' are not unusual[7].

The potential dependent heterogeneous rate constant $k_{f,h}$ is related to $E$ by the following two relations[8,9] (1) and (2).

$$k_{f,h} = k_{f,h}^0 \exp[-\alpha n_a F(E + 0.2412)/RT] \quad \dots(1)$$

$$k_{f,h} = KT/h\delta \exp\left[\frac{-\Delta G^{\ddagger} + \alpha n_a F(E + 0.2412)}{RT}\right] \quad \dots(2)$$

Equating the value of log $k_{f,h}$ at $E = 0$ from the two relations we get $\Delta G^{\ddagger}$ (kcal) at 25° and is obtained by the relation (3).

$$\Delta G^{\ddagger} = \frac{-5.706}{4.18}[\log k_{f,h}^0 - 8.16\alpha n_a - 6.79] \quad \dots(3)$$

Zn(II) yields a single well defined wave with $E_{1/2} = -1.0365$ V (versus SCE) and slope 0·040 V in $0.1M$ NaClO₄. On the addition of tryptophan to the system [1 mM Zn(II), 1 mM tryptophan and $0.1M$ NaClO₄] the following significant changes are observed in the current-potential curves:

(a) $E_{1/2}$ is shifted to more negative potential and becomes 0·1066 V.

(b) The wave becomes more drawn out with slope = 0·095 V.

(c) The wave is closely followed by a maximum. However, it is not on the rising portion and thus does not interfere with the quantitative study of the wave.

As the tryptophan/Zn(II) ratio is increased keeping Zn(II) constant at 1 mM, the wave records a gradual shift towards more negative potentials till [tryptophan] reaches 5 mM. There is no change at [tryptophan] = 6 mM. This is followed by a positive shift at 7 mM and between [tryptophan] 7 mM to 20 mM, the $E_{1/2}$ remains practically constant.

The height of the maximium gradually decreases with an increase in [tryptophan] till 4 mM and from 4 mM to 6 mM it is reduced to a rounded hump. At 7 mM the rounded hump also disappears and in its place a small second wave appears which changes neither in shape nor in position till 15 mM tryptophan ($i_d = 1.088$ and $-E_{\frac{1}{2}} = 1.225$ V). However, this second wave disappears completely at 20 mM tryptophan.

The fact that on the addition of tryptophan the $E_{\frac{1}{2}}$ is shifted to more negative potentials and