

Complexes of Chromium(III) with Pyrazole & Its Methyl Derivatives: A pH-Metric Study

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The stabilities of complexes of chromium(III) with pyrazole and methyl substituted pyrazoles have been studied pH-metrically in 1:1 (v/v) aqueous ethanol at 25°C, using KNO_3 as a supporting electrolyte. The formation of the 1:1 to 1:6 metal-ligand complex species in solution has been substantiated. The effect of substituents of the ligand on the complex formation and the degree of formation of the different species over the whole concentration range have also been studied.

Pyrazole is an extremely weak Lewis base and is not expected to form strong coordination compounds. A number of complexes with transition metal ions have, however, been described. The solution equilibria studies have been done polarographically for the cadmium¹, lead² and silver^{3,4} complexes. The pH-metric studies of copper⁵, nickel⁵ and lead⁶ complexes have also been reported. The authors have now determined the consecutive formation constants of Cr(III) with pyrazole and methyl substituted pyrazoles in 1:1 aq. ethanol pH-metrically. The influences of substituents on the stability constants have also been studied.

Chromium nitrate (AR grade) and purified pyrazoles^{3,4} were used in the study. Nitric acid used was standardised as usual. The ligand concentration was 0.25 M. All the measurements were carried out in 1:1 (v/v) aqueous ethanol, using 0.5 M KNO_3 as the supporting electrolyte, in a precision pH-meter, equipped with glass-calomel electrode in a thermostated cell at $25 \pm 0.1^\circ\text{C}$. The metal-ligand equilibria in solution were attained within about 30 min of the mixing of the components during each titration.

The following solutions (in a total volume of 30 ml) were taken: (i) 0.005 M nitric acid + solvent, titrated against the solvent; and (ii) 0.005 M nitric acid + 0.02 M chromium nitrate + solvent, titrated against 0.25 M ligand solution prepared in the same solvent. For the conversion of the observed pH-values to the corrected pH-values, a calibration curve was prepared using the method of Van Uitert and Hass⁹. The value of the conversion factor, $\log U_H$ i.e. $\log(v \pm U_H^0)$ was

obtained as -0.125 for 50% (v/v) aqueous ethanol mixture at $25 \pm 0.1^\circ\text{C}$ and an ionic strength of 0.5 M KNO_3 .

The acid dissociation constants of the quaternized pyrazoles were determined at 25°C following the method of Musgrave and Humburg⁵. The values of pK_a for pyrazole, 3(5)-methylpyrazole, 3,5-dimethylpyrazole and 3,4,5-trimethylpyrazole were found to be 2.16, 2.62, 3.64 and 4.06 respectively. These values were found to be the same as reported earlier⁶. The slight difference in the two sets of values is due to the differences in the solvent composition and ionic strength of the media employed.

For the determination of the stability constants of chromiumpyrazole complexes, two sets of titrations (i) and (ii) reported above were carried out. At any identical point in the two titrations, the differences in $[\text{H}^+]$ gave the concentration of the quaternized pyrazoles, $[\text{HL}^+]$. The total concentration of the complexed ligands were calculated from the expression $C_L - \{[\text{L}] + [\text{HL}^+]\}$, where the concentration of the free ligand, $[\text{L}]$, was determined from $[\text{H}^+]$ and K_a of the corresponding monodentate ligand.

Now,

$$\bar{n} = \frac{\text{Conc. of the complexed ligand}}{\text{Conc. of the metal ion}}$$

$$= \frac{\sum_{n=0}^{n=N} n\beta_n[\text{L}]^n}{\sum_{n=0}^{n=N} \beta_n[\text{L}]^n} \quad \dots(1)$$

Eq. (1), after proper rearrangement, takes the form

$$\frac{\bar{n}}{(1-\bar{n})[\text{L}]} = \beta_1 + \beta_2 \frac{2-\bar{n}}{1-\bar{n}}[\text{L}] + \sum_{n=3}^{n=N} \frac{n-\bar{n}}{1-\bar{n}} \beta_n[\text{L}]^{n-1} \quad \dots(2)$$

The plot of the function $\bar{n}/(1-\bar{n})[\text{L}]$ versus $(2-\bar{n})[\text{L}]/(1-\bar{n})$ is linear, provided the third term on the right-hand side of the Eq. (2) is negligible. The intercept gives the value of β_1 and the slope that of β_2 . Similarly, the values of $\beta_1, \dots, \beta_{t-1}$ ($0 < t < N$) have been determined.

In making such a plot, n values less than $\sim(n-0.9)$ or greater than $\sim(n-0.1)$ have been ignored. If the highest concentration of the ligand is considered, i.e. at $\bar{n} \cong (n-0.1)$, the lower complex species are not present at sufficient concentration and the condition of linearity is satisfied. Therefore, the experimental points most appropriate for the evaluation of a

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Table 1—Acid Dissociation Constants for Pyrazoles and Its Methyl Derivatives and Their Stability with Chromium(III) Ions

Ligands	pK_a	Stability constants of chromium complexes*						Overall stability constants log β_6
		log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	
Pyrazole	2.16	2.00	1.98	1.28	2.06	0.93	1.16	9.41
3(5)-Methylpyrazole	2.62	2.08	1.25	1.71	1.68	1.62	1.68	10.00
3,5-Dimethylpyrazole	3.64	2.11	2.39	1.80	2.20	2.31	1.77	12.58
3,4,5-Trimethylpyrazole	4.06	2.30	2.87	1.83	2.32	2.66	2.40	14.38

*The estimated error in the values is $\pm 3\%$.

particular stability constant, K_n , are those with $(n - 0.9) < \bar{n} < (n + 0.1)$. The values of $\bar{n}$ obtained were found to be slightly less than 6.0. This is compatible with the formation of $[\text{Cr}(\text{Pz})_6]^{3+}$ species, where Pz denotes pyrazole and the substituted pyrazoles. Using these values of $\bar{n}$, the stability constant values of different complexes have been computed and recorded in Table 1.

In pyrazole, coordination takes place through the pyridine nitrogen atom^{10,11}. The substitution of the methyl group in the pyrazole ring increases the electron density at the pyridine nitrogen atom, thereby increasing the basicity of the ligand molecule, and rendering the complex more stable. The stabilities of the chromium complexes with pyrazoles follow the order: pyrazole < 3(5)-methylpyrazole < 3,5-dimethylpyrazole < 3,4,5-trimethylpyrazole.

The plot of log K_1 versus pK_a was linear, illustrating the graphical relation between the basicities of the ligands and their ability to undergo complexation with chromium (III) ion. The slope of 0.15 of the plot suggests that the substitutions in the pyrazole ring affect the coordinating strength of the ligands. Here metal $\rightarrow$ ligand σ -bonding is weaker than that in the corresponding proton complexes. So the slope of the linear plot is mainly influenced by strength of metal $\rightarrow$ ligand π -bonding which is more significant in the present cases. In view of the weakly basic nature of the pyrazole molecules, these ligands are not expected to form strong complexes. It is possible, however, that during complexation with transition metal ions, metal-ligand π -bonding may occur, to some extent, as has been pointed out by Crow and Westwood¹².

From the stability constant data, the values of α_j , the degree of formation of the j th complex has been calculated over the whole concentration range. A plot

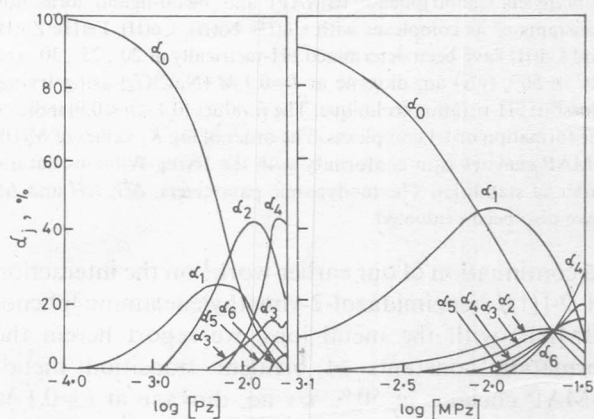


Fig. 1—Plots of α_j (in per cent) versus logarithm of ligand concentration for pyrazole (Pz) and 3(5)-methylpyrazole (MPz)

of α_j (in per cent) versus log $[L]$ for each species in the respective Cr(III)-pyrazole and -substituted pyrazole systems gives the typical families of distribution curves in the specified concentration range (Fig. 1).

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