

Application of linear free energy relationship.—Swain-Scott⁷ and Edwards⁸ equations have been applied to the kinetic data and parameters like nucleophilicity and E_n values for the bases used have been computed in nitrobenzene and nitrobenzene-alcohol mixtures which help in understanding the mechanism of the process to some extent⁹. The parameters are given in Table III.

The parameters are identical in nitrobenzene and nitrobenzene-alcohol mixture demonstrating the operation of identical mechanism in both the solvent systems.

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PHYSICO-CHEMICAL STUDIES OF SOME BIVALENT METAL ION CHELATES OF N-ACETYLACETONE ORTHANILIC ACID

THE results of physico-chemical studies on the chelates of N-Acetylacetone orthanilic acid (H_2AO) with some bivalent metal ions are reported in this note.

Orthanilic acid supplied by SCHUCHAROT MUNCHEN was used. All other compounds were of BDH grade. The molecular weights, elemental analysis, magnetic susceptibility and electronic absorption spectra were determined by standard methods as reported earlier¹.

Preparation of H_2AO and its metal chelates.— H_2AO Schiff base was prepared by the method of Pfeiffer *et al.*². The metal chelates were synthesised by the method of Yamada *et al.*^{3,4} and their pyridine solvates by the method reported earlier¹.

Analysis: Found C, 51.81; H, 4.99; N, 5.47; S, 12.41. Calcd. for $C_{11}H_{13}NSO_4$. C, 51.96; H, 5.11; N, 5.51; S, 12.59%, m.p. 160°.

Results and Discussions.—Elemental analysis, molecular weight and magnetic data of the hydrated chelates are given in Table I.

The molecular weight data indicate that Fe (II), Co (II), Ni (II) and Cu (II) chelates possess the composition $[MLX_3]$ where M represents the metal ion, $X = H_2O$ or Py and $LH_2 = [C_{11}H_{13}NSO_4]$. The magnetic moment values reveal the presence of 4, 3, 2 and 1 unpaired electrons in the Fe (II), Co (II), Ni (II) and Cu (II) chelates respectively. The high magnetic moment of Co (II) chelate appears to be due to spin-orbit coupling.

The electronic absorption spectra of these chelates were studied both in dioxane and pyridine solu-

TABLE I

Elemental analyses, molecular weights and magnetic moments of the metal chelates of N-acetylacetone-orthanilic acid

| Metal chelate | Mol. wt. | Metal % | N % | H ₂ O % | μ_{eff} (B.M.) at 298° K |
|---|-------------|---------------|-------------|--------------------|---------------------------------|
| [Fe ($C_{11}H_{11}NSO_4$) X_3] | 357 (362) | 14.32 (15.46) | 3.81 (3.86) | 14.87 (14.91) | 5.48 |
| [Co ($C_{11}H_{11}NSO_4$) X_3] | 369 (365) | 16.01 (16.16) | 3.80 (3.83) | 14.71 (14.79) | 5.12 |
| [Ni ($C_{11}H_{11}NSO_4$) X_3] | 365 (364.7) | 16.80 (16.92) | 4.07 (4.11) | 14.76 (14.80) | 3.11 |
| [Cu ($C_{11}H_{11}NSO_4$) X_3] | 360 (369.5) | 17.00 (17.18) | 3.69 (3.78) | 14.51 (14.61) | 1.89 |
| [Pd ($C_{11}H_{11}NSO_4$) X] | 370 (376) | 28.07 (28.19) | 3.61 (3.72) | 4.71 (4.79) | .. |
| [Zn ($C_{11}H_{11}NSO_4$) X] | 339 (335.4) | 19.31 (19.49) | 4.10 (4.17) | 5.30 (5.36) | .. |
| [Cd ($C_{11}H_{11}NSO_4$) X] | 377 (382.4) | 29.27 (29.39) | 3.59 (3.66) | 4.59 (4.70) | .. |
| [UO ₂ ($C_{11}H_{11}NSO_4$) X] | 545 (540) | 49.90 (50.00) | 2.54 (2.59) | 3.31 (3.33) | .. |

Calculated values are given in parentheses. X refers to H_2O . Zn (II), Pd (II), Cd (II), UO₂ (II) chelates were found to be diamagnetic, as expected.

tions. The frequencies and the corresponding transitions assigned are summarised below.

| Chelate | $\nu_{\max} \text{ cm}^{-1}$ | Possible transitions |
|---------|------------------------------|---|
| | Dioxane/Pyridine | |
| Fe (II) | 11400/11900 | ${}^5T_{2g} \rightarrow {}^5E_g(D)$ |
| Co (II) | 15300/18700 | ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ |
| | 24700/29800 | ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ |
| Ni (II) | 14400/13800 | ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ |
| | 22500/22900 | ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ |
| Cu (II) | 14800/13500 | ${}^2E_g \rightarrow {}^2T_{2g}$ |
| Pd (II) | 22200/22900 | ${}^1A_{1g} \rightarrow {}^1B_{1g}$ |
| | 26800/27100 | ${}^1A_{1g} \rightarrow {}^1E_{1g}$ |
| | 30500/31200 | ${}^1A_{1g} \rightarrow {}^1A_{2u}$ |

An I.R. study of H_2AO has shown three bands at 1160 cm^{-1} , 1670 cm^{-1} and 3590 cm^{-1} which can be assigned to the presence of sulphonic acid (SO_3H), $C=N$ and enolic $-OH$ respectively. In all the metal chelates under investigation the bands at 1160 cm^{-1} and 3590 cm^{-1} could not be located which suggests their elimination due to complexation.

The presence of chelated water molecules in these compounds has been confirmed by their I.R. spectra in the region $3.1-4.0 \mu$.

These data supported by their magnetic moments confirm near octahedral structure for Fe (II), Co (II), Ni (II) and Cu (II) chelates.

The Zn (II), Pd (II), Cd (II) and UO_2 (II) also form 1 : 1 chelates and their composition can be expressed by the formula $[MLX]$, where M denotes the metal ion, $LH_2 = [C_{11}H_{13}NSO_4]$ and $X = H_2O$ or Py. The hydrated chelates and their pyridine solvates have been found to be diamagnetic. These results can be explained by assigning a tetrahedral structure for Zn (II) and Cd (II) chelates and an octahedral structure for UO_2 (II) chelate. The diamagnetic behaviour of the Pd (II) chelate indicates a square-planar stereochemistry around the central Pd (II) ion. These results are also in agreement with an earlier finding¹.

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SR ISOTOPE RATIOS OF THE ALBERT BASALT-IMPLICATIONS IN THE PETRO- GENESIS OF THE FOCAL PEAK SHIELD VOLCANO, SOUTHEAST QUEENSLAND, AUSTRALIA

In southeast Queensland and northeast New South Wales, Australia, an extinct shield volcano, named the Focal Peak Shield Volcano, exists¹. The volcanics and associated intrusives of this shield volcano are late Oligocene in age. Extrusives include, on its eastern side, the alkaline Albert Basalt and the metaluminous Mt. Gillies Rhyolite. The petrogenetic relationship between these two formations will be examined here in the light of available Sr isotope ratios. Most of the extrusives of the Albert Basalt are hawaiites, using the classification system proposed by Coombs and Wilkinson² assuming a 1-50% Fe_2O_3 content³. A few basanites, alkali olivine basalts, mugearites and even a brecciated trachyte exist.

Only limited Sr isotopic information is available for the Albert Basalt (Table I). $Sr_{87/86}$ ratios for the formation are comparable to those of continental alkali basalts and slightly higher than those normally expected for oceanic alkali basalts⁴. These data suggest that either the Albert Basalt was:

- (1) derived from mantle material with a high $Sr_{87/86}$ ratio, or
- (2) contaminated by the addition of sialic material, or
- (3) contaminated by selective diffusion of certain elements, including Sr, from continental crust into the basaltic magmas, or
- (4) selective migration of radiogenic Sr from crustal rocks into the magmas.

Major and trace element geochemistry discounts the possibility of contamination of the basaltic magmas by the addition of sialic material alone being the major causative factor. It appears that factors (3) and (4) above are the most likely causes. Isotopic contamination would probably result not only during the active transportation of the basaltic magmas to the earth's surface, but also, to a very important degree, during temporary halts of transportation within both the mantle (if isotopically heterogeneous) and, more importantly, within the continental crust. It is considered, from field and detailed geochemical studies, that the Mt. Gillies Rhyolite was derived from the Albert Basalt which includes both undersaturated and saturated representatives. Sufficient time is required to pass for the processes of strong fractionation to generate rhyolitic differentiates from basaltic parents. Consequently, the concept of halts in the transportation of magmas is important in petrogenetic discussions. In addition, it should

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