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THE EVALUATION OF THE ELECTRONIC TRANSITION MOMENT FOR A BAND SYSTEM OF DIATOMIC MOLECULE

It has been shown that the electronic transition moment¹ plays a very important role in the calculation of vibrational transition probabilities of diatomic molecules. The relative vibrational transition probability² $P_{v',v''}$ may be written as

$$P_{v',v''} = R_e^2(\bar{r}_{v',v''}) q_{v',v''} \quad (1)$$

where $R_e(\bar{r}_{v',v''})$ is the electronic transition moment, $\bar{r}_{v',v''}$ is the r -centroid and $q_{v',v''}$ is the Franck-Condon factor of the band in question.

The intensity in emission $I_{v',v''}$ of a band may be written as

$$I_{v',v''} = KN_{v'}E_{v',v''}^4 P_{v',v''} \quad (2)$$

in which K incorporates all the constants, $N_{v'}$ is the population of the level v' , $E_{v',v''}$ is the energy quantum of the band. Thus an array of relative $P_{v',v''}$ may be determined from $I_{v',v''}N_{v'}E_{v',v''}^4$ when the band intensities have been measured. From equations (1) and (2).

$$I_{v',v''} = KN_{v'}E_{v',v''}^4 R_e^2(\bar{r}_{v',v''}) q_{v',v''} \quad (3)$$

This equation may be used to determine the form of $R_e(\bar{r})$ for a band system.

Equation (3) may be employed to determine the relative variation of $R_e(\bar{r})$ with \bar{r} for the band system. Once a smooth curve has been obtained which shows the relative variation of $R_e(\bar{r})$ with \bar{r} , equation (1) may be employed to determine a smoothed array of $P_{v',v''}$. Values of $R_e(\bar{r}_{v',v''})$ are read from the curve at values of $\bar{r}_{v',v''}$ appropriate to each band. $R_e^2(\bar{r}_{v',v''}) q_{v',v''}$ is then a relative measure of $P_{v',v''}$ for each band. The array of $P_{v',v''}$ thereby obtained may be normalised such that $P_{00} = 1$.

In the paper of Mishra and Khanna³, the variation of $R_e(\bar{r}_{v',v''})$ with internuclear separation has been worked out by the method outlined by Nicholls⁴ and it is found that the curve shown in the figure is consistent with the relation $R_e(\bar{r}_{v',v''}) = \text{const. exp. } (0.205 r)$ over the range $1.20 \text{ \AA} < r < 1.45 \text{ \AA}$. The calculated $P_{v',v''}$ values for the bands of the A-X system of BF molecule are in fair agreement with the observed intensity distribution. Values of $P_{v',v''}$ are in good agreement with the values entered in the last column of Table I which are nothing but the product of F-C factor and r -centroid of the band. On this basis it can be inferred that vibrational transition probabilities for a band system of molecules for which $q_{00}\bar{r}_{00} \cong 1$, can be obtained without measuring the intensities of the bands. The details of this method along with the results of other band systems will be published elsewhere.

TABLE I
Data for BF (A-X) band system

| Band | $\bar{r}_{v',v''}$ (Å) | $P_{v',v''}^*$ | $P_{v',v''}$ |
|--------|------------------------|----------------|--------------|
| (0, 0) | 1957.4 | 1.000 | 0.999 |
| (0, 1) | 2001.5 | 0.271 | 0.280 |
| (0, 2) | 2068.1 | 0.023 | 0.024 |
| (1, 0) | 1911.0 | 0.227 | 0.218 |
| (1, 1) | 1962.7 | 0.577 | 0.578 |
| (1, 2) | 2016.3 | 0.481 | 0.502 |
| (1, 3) | 2071.6 | 0.022 | 0.023 |
| (2, 1) | 1917.1 | 0.330 | 0.321 |
| (2, 2) | 1968.2 | 0.198 | 0.196 |
| (2, 3) | 2021.3 | 0.539 | 0.558 |

* Data from Mishra and Khanna³.

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ADDUCTS OF BIS (ETHYLACETOACETATO) COPPER (II) WITH NITROGEN LIGANDS

BONDING¹⁻³ of additional ligands along the axis normal to the molecular plane of planar complexes like beta-diketonates and related compounds, which involve keto-enol tautomerism, have invoked a lot of interest in recent years. Since beta-keto esters are closely related to the beta-diketones, it was thought worthwhile to extend the investigation to such chelates and this communication reports some base adducts of bis-(ethyl acetoacetato copper (II) with substituted pyridines, viz., -2, 3- and 4-methyl pyridines.

Ethanol solution of cupric chloride was reacted with ethyl acetoacetate in (1 : 2) proportion, followed by dropwise addition of ammonia with constant stirring. The green product obtained was filtered off, washed with ethanol and ether and dried in a vacuum desiccator. Metal chelate and the nitrogen ligands (in 1 : 2 ratio) were taken in minimum quantity of ethanol and refluxed for thirty minutes. On cooling the solution overnight, crystalline compounds separated out.

Metal ion in the compounds was estimated by EDTA procedure. Conductance was measured in M/1000 acetone solution using a 'Toshniwal' conductance bridge. Magnetic susceptibility was measured on the solid specimen by Gouy method. Infrared spectra were recorded in nujol mulls with Unicam SP 200 Spectrophotometer. U.V. and visible spectra were recorded using M/100 chloroform-base solution in Unicam SP 500 Spectrophotometer. The relevant analytical, conductance and magnetic susceptibility data are recorded in Table I.

Results and Discussion

The green crystalline compounds have the composition $\text{Cu}(\text{EAA})_2\text{L}_2$ where 'L' is substituted pyridine. The compounds are stable in air, have low melting points. Acetone solutions of the complexes have low molar conductance values, Λ_M being in the range of 2-4 mhos, indicating non-electrolytic nature.

Most of the absorption bands due to the free nitrogen ligands are shifted in the adducts indicating bonding to the metal, information being obtained by the "Finger Print" technique. $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the ester which occur at 1650 and 1630 cm^{-1} respectively shift to lower frequency region (1600 and 1525 cm^{-1}) on chelation and again shift to higher frequency (1620 and 1540 cm^{-1} respectively) in the nitrogen base adducts providing additional evidence for bonding of the ester and nitrogen ligand. Direct evidence could not be obtained as $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$ were beyond the range of instrument used.

An intense band appeared in the U.V. region around 260 nm ($\epsilon = 15000$) in solution spectrum of the chelate and base adducts due to the more probable $\pi \rightarrow \pi^*$ transition rather than charge transfer. In the visible region, a broad absorption band was observed around 660 nm ($\epsilon = 60$) in the chelate which was found around 650 nm ($\epsilon = 85$) in the base adducts. On coordination of the nitrogen ligands there is not much shift in the position of the absorption band though the intensity increases.

TABLE I

Analysis, M.P., Conductance and magnetic susceptibility data of bis-(ethyl acetoacetato) Copper (II) complexes

| Compounds | Colour and form | MP (°C) | Λ_M ohm ⁻¹ cm ² | μ_{eff} (B.M.) | % Metal | | % N | |
|--|-------------------|---------|---|--------------------|---------|-------|-------|-------|
| | | | | | Reqd. | Found | Reqd. | Found |
| $\text{Cu}(\text{EAA})_2(\alpha\text{-pic})_2$ | Green crystalline | 160 | 2.8 | 1.76 | 1.56 | 12.0 | 5.52 | 5.3 |
| $\text{Cu}(\text{EAA})_2(\beta\text{-pic})_2$ | do. | 180 | 3.0 | 1.74 | 12.56 | 12.1 | 5.52 | 5.25 |
| $\text{Cu}(\text{EAA})_2(\gamma\text{-pic})_2$ | do. | 175 | 4.2 | 1.78 | 12.56 | 11.9 | 5.52 | 5.32 |