

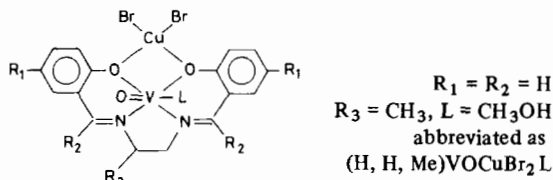
**Resonance Raman Spectrum of Dibromo [N,N'-bis-(salicylidene)propylenediaminatooxovanadium(V)] copper(I)·Methanol**

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Recently, Okawa and Kida [1] suggested that the strong electronic absorption band at  $17.9 \times 10^3 \text{ cm}^{-1}$  of dibromo [N,N'-bis(salicylidene)propylenediaminatooxovanadium(V)] copper(I)·methanol



in methanol solution may be due to the charge-transfer from the  $p\pi$ -orbital of the phenolic oxygen to the lowest vacant orbital ( $d_{xy}$ ) of the vanadium(V) atom. In the present communication, we wish to report the resonance Raman spectrum of this compound which provides direct evidence to support their assignment.

**Experimental**

The binuclear complex, (H, H, Me)VOCuBr<sub>2</sub>·CH<sub>3</sub>OH, was prepared by the method reported previously [1]. Both electronic and resonance Raman spectra of this complex were measured as KBr pellets. The electronic spectrum was recorded on a Cary Model 14 spectrophotometer. The resonance Raman spectra were measured by using a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034A photo-multiplier tube with DC amplification. Excitations at 454.5 and 514.5 nm were made by a Spectra-Physics Model 164 Argon-ion laser and that at 578.8 nm was made by a Spectra-Physics Model 365 CW dye-laser (Rhodamine 6G) pumped by the above 4W Argon-ion laser. To compare relative intensity, the internal standard (NaNO<sub>3</sub>) was mixed homogeneously with the sample in a KBr pellet. The rotating sample technique was used to avoid thermal decomposition of the complex. The infrared spectra were measured on a Beckman IR 12 infrared spectrophotometer. The spectra of the complexes were measured as KBr pellets while that of the pure ligand was obtained as a neat liquid.

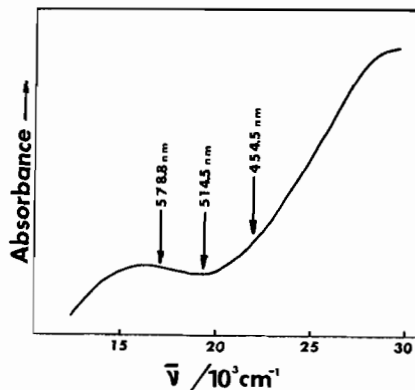


Figure 1. Electronic spectrum of (H, H, Me)VOCuBr<sub>2</sub>·CH<sub>3</sub>OH in a KBr pellet.

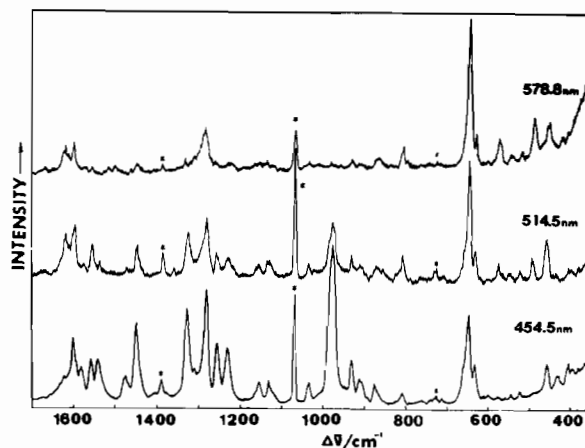


Figure 2. Resonance Raman spectra of (H, H, Me)VOCuBr<sub>2</sub>·CH<sub>3</sub>OH in a KBr pellet.

**Results and Discussion**

Figure 1 illustrates the electronic spectrum of (H, H, Me)VOCuBr<sub>2</sub>·CH<sub>3</sub>OH in a KBr pellet. Relative to the spectrum in solution [1], the bands observed in the KBr pellet are broader and flatter and the absorption maxima are shifted slightly. Even so, it is clear that the bands at  $16 \times 10^3$  and  $29 \times 10^3 \text{ cm}^{-1}$  in the solid state correspond to those observed at  $17.9 \times 10^3$  and  $27 \times 10^3 \text{ cm}^{-1}$ , respectively, in methanol solution. Figure 2 shows the resonance Raman spectra of the same compound in a KBr pellet with the laser excitations at 454.5, 514.5 and 578.8 nm. The bands marked by asterisks (1388, 1069 and  $726 \text{ cm}^{-1}$ ) are due to the internal standard, NaNO<sub>3</sub>.

At the 454.5 nm excitation, the compound exhibits a number of strong bands as is shown in the bottom trace of Fig. 2. It is safe to assign the strongest band at  $977 \text{ cm}^{-1}$  to the V=O stretching and all the bands between 1700 and  $1000 \text{ cm}^{-1}$  to the vibrations of the Schiff base ligand [2]. The

strong band at  $647\text{ cm}^{-1}$  with a shoulder at  $662\text{ cm}^{-1}$  is assigned to the V–O (phenolic) stretching mode. This assignment is supported by the observation that its infrared spectrum exhibits a band at  $660\text{ cm}^{-1}$  with a shoulder at  $648\text{ cm}^{-1}$ , both of which are absent in the infrared spectrum of (H, H, Me)Cu. The small splitting of this mode into two bands may be attributed to the crystal lattice effect. These frequencies are much higher than the V–O stretching frequencies of  $\text{VO}(\text{acac})_2$  ( $480\text{ cm}^{-1}$ ) [3] due to the differences in the oxidation state of the vanadium atom (+V vs. +IV) and in the nature of the oxygen atom (phenolic vs. ketonic). In fact, the antisymmetric and symmetric VOV stretching frequencies of the  $[\text{V}_2\text{O}_7]^{4-}$  ion in which the vanadium is in the +V state are  $780\text{--}680$  and  $545\text{--}500\text{ cm}^{-1}$ , respectively [4].

At the  $514.5\text{ nm}$  excitation (middle trace), the V=O stretching band at  $977\text{ cm}^{-1}$  becomes weaker together with the ligand bands between  $1700$  and  $1000\text{ cm}^{-1}$ . On the other hand, the V–O (phenolic) stretching band at  $647\text{ cm}^{-1}$  becomes stronger relative to other bands. Also, new bands emerge at  $576$  and  $490\text{ cm}^{-1}$  which correspond to the infrared bands at  $577$  and  $491\text{ cm}^{-1}$ . Since these bands are not present in the infrared spectrum of (H, H, Me)Cu, they are probably due to other  $\text{VO}_3\text{N}_2\text{L}$  skeletal modes such as the V–N and V–L stretching modes.

When the exciting frequency ( $578.8\text{ nm}$ ) approaches the absorption maximum of the lower energy electronic band at  $16 \times 10^3\text{ cm}^{-1}$ , the V=O stretching band at  $977\text{ cm}^{-1}$  is almost extinct. So are some ligand vibrations between  $1700$  and  $1000\text{ cm}^{-1}$ . On the other hand, the V–O (phenolic) stretching band at  $647\text{ cm}^{-1}$  becomes almost three times stronger than the internal standard band at  $1069$

$\text{cm}^{-1}$  (top trace). The other skeletal bands at  $576$  and  $490\text{ cm}^{-1}$  are also enhanced.

Previously, Okawa and Kida [1] assigned the lower energy electronic band of (H, H, Me) $\text{VOCuBr}_2 \cdot \text{CH}_3\text{OH}$  to the V–O (phenolic) charge-transfer transition based on the following observations: (1) the intensity of this band ( $\log \epsilon \approx 3$ ) is unusually high for a d–d transition, (2) the vanadium(V) complex of N,N'-bis(salicylidene)ethylenediamine also exhibits a strong band at  $17.9 \times 10^3\text{ cm}^{-1}$ , and (3) such bands are not observed for analogous compounds in which the VO group is replaced by other metals.

According to the theories of resonance Raman scattering, only those vibrations which are localized on a particular chromophoric group are enhanced when the energy of the exciting line approaches that of the electronic transition which originates in this chromophore (selectivity) [5, 6]. Then the dramatic changes in the resonance Raman spectrum of (H, H, Me) $\text{VOCuBr}_2 \cdot \text{CH}_3\text{OH}$  described above can only be understood if we assign the lower energy band to the V–O (phenolic) charge-transfer transition as previously suggested.

## References

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