

benzene molecular addition complex have been restricted to the radiofrequency region. It is our hope in the near future to extend the work to the microwave region. Work is in progress on the electron spin resonance spectra of other molecular addition complexes of DPH.

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1. Pound, R. V. and Knight, W. D. *Rev. Sci. Instr.* **21** (1950) 219.
2. Müller, E., Müller-Rodloff, I. and Bunge, W. *Ann.* **520** (1935) 244.
3. Lyons, J. A. and Watson, W. F. *J. Polymer Sci.* **18** (1955) 141.
4. Holden, A. N., Kittel, C., Merritt, F. R. and Yager, W. A. *Phys. Rev.* **77** (1950) 147.
5. Anderson, P. W. and Weiss, P. R. *Revs. Modern Phys.* **25** (1953) 269.
6. Weidner, R. T. and Whitmer, C. A. *Phys. Rev.* **91** (1953) 1279.

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Ligand Field Spectrum of Vanadium(II) Hexaquo Ions

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The absorption spectra of hexaquo ions of divalent metals in the first transition group has been one of the most common subjects for ligand field theory. Cr(II)^{1,2}, Mn(II)³, Fe(II)^{4,5}, Co(II)⁶, Ni(II)^{7,8} complexes have all been rather much studied. Only the study of vanadium(II) has been very little performed, due to the strongly reducing character of this oxidation state and the interfering colours of the probable vanadium(III) impurities. Kato⁹ photographed bands at 820, 760, 560, and 540 m μ of a solution in 3 M HCl. However, measurements on a Cary MS-11 recording spectrophotometer has not confirmed the doublet structure in the green, and it is known that the highly varying sensitivity of most photographic plates in this region may produce spurious maxima. Therefore, Ball-

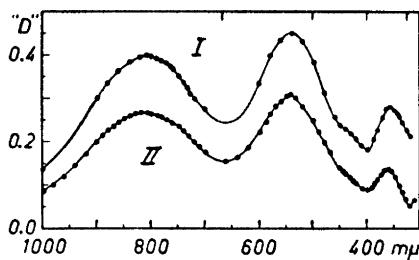


Fig. 1. Reflection spectra of vanadium(II), zinc(II) Tutton salt.

hausen and the present author concluded¹⁰ that the three spin-allowed transitions from 4A_1 to 4E_g , ${}^4I_4(F)$, and ${}^4I_4(P)$ occur at 820, 555, and 378 m μ , respectively. Similar conclusions were drawn previously by Holmes and McClure¹¹, but only published recently.

Fig. 1 gives the reflection spectra (as measured on a Beckman DU) of two samples of $(\text{NH}_4)_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ into which vanadium(II) is included isomorphically. This happens to be a method of evading the presence of vanadium(III) in the substance. The salt was also dissolved in 2 M H_2SO_4 and measured on the Cary. The band maxima (and shoulders in parentheses) occur at the wavelengths in m μ :

Sample I	Sample II	Solution
810	810	>810
(765)	(760?)	(778)
540	542	563
(430)	(434)	—
355	362	368

The solution has higher wavelengths of all its bands, compared to the solid samples. This may be caused by the presence of sulphate complexes (even though this has relatively little influence on the spectra of other divalent ions), or by partly oxidation to +3 (of which the spectral characteristics is discussed in Ref.¹² p. 79). However, another explanation may be found in the phenomenon⁸ that $\text{Ni}(\text{H}_2\text{O})_6^{++}$ has smaller wavelengths when imbedded in $(\text{NH}_4)_2[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ than in other salts or in solution. Further, the lattice constants of the zinc Tutton salt are so small that $\text{V}(\text{H}_2\text{O})_6^{++}$ may be compressed to some extent¹³.

From the average values of the two solid samples, Δ is seen to be 12 350 K ($= \text{cm}^{-1}$). The parameter of interelectronic repulsion B can be found by the same way^{7,8} as in Ni(II), viz. from the wavenumbers of all three spin-allowed bands $15B = 18\,500 + 27\,950 - 3 \times 12\,350 = 9\,400$ K, while $15B = 11\,280$ K in gaseous V^{++} . However, as pointed out by Schäfer¹³ for the isoelectronic $\text{Cr}(\text{H}_2\text{O})_6^{+++}$, the third band has undoubtedly too low wavenumber, and it is reasonable to calculate the interelectronic repulsion parameters from the positions of the two first bands alone. In this way, the comparison with isoelectronic species as Mn(IV) in MnF_6^{--} or Mo(III) in MoCl_6^{-3} is also facilitated. From this assumption, $15B$ is found $= 10\,300$ K. The ratio $\beta = 0.92$ between this value and the value for the gaseous V^{++} is comparable with $\beta = 0.93$ in $\text{Mn}(\text{H}_2\text{O})_6^{++}$ and 0.89 in $\text{Ni}(\text{H}_2\text{O})_6^{++}$, demonstrating an early position in the nephelauxetic series of central ions (while $\beta = 0.79$ for $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ and 0.76 for $\text{Fe}(\text{H}_2\text{O})_6^{+3}$).

For systematical reasons, it would be very valuable, if the spinforbidden transitions from 4T_2 to 3T_3 and 3T_4 (degenerate for pure d-electrons with the sub-shell configuration γ_5^3) could be detected. Even though water has a weak absorption range $740-790\text{ m}\mu$, it is believed that the shoulder $\sim 770\text{ m}\mu$ actually is this transition (ζ_{sd} is only 169 K in V^{++} , and correspondingly, the spin-forbidden transitions are very weak), which occurs between 700 and 650 $\text{m}\mu$ in most chromium(III) complexes. The shoulder at 430 $\text{m}\mu$ in the solid samples may be another spin-forbidden band, or it may be due to superficial oxidation to $\text{V}(\text{H}_2\text{O})_5\text{OH}^{++}$, which has an enormous absorption there¹⁴ (perhaps, it is a dimer $(\text{H}_2\text{O})_5\text{VOV}(\text{H}_2\text{O})_5^{+4}$).

It was hoped to prepare other vanadium(II) complexes by dissolving the salt in different complexing agents. Thus, a solution in concentrated aqueous ammonia exhibit bands at ~ 690 and $476\text{ m}\mu$. However, oxidation by traces of air produces a precipitate of $\text{V}(\text{OH})_3$, and the possible experiments with other ligands have not yet been successful.

Experimental. 11.7 g (0.1 mole) NH_4VO_3 was mixed with 150 ml water, and 50 ml concentrated sulphuric acid added. The red-brown solution was reduced by zinc foil (Merck p.a.) over dark blue and dark green intermediate colours (of VO^{++} and $\text{V}(\text{III})$ sulphato complexes) until a violet solution was formed. This was quickly added to strong solutions (nearly saturated) of $(\text{NH}_4)_2\text{SO}_4$ in water, and a precipitate was formed of the mixed vanadium(II) and zinc(II) Tutton salt, could be sucked dry on a Büchner funnel. The salt can be kept several months in air without oxidation.

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1. Pecsok, R. L. and Bjerrum, J. *Acta Chem. Scand.* **11** (1957) 1419.
2. Schläfer, H. L. and Skoludek, H. *Z. physik. Chem.* **11** (1957) 277.
3. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **11** (1957) 53.
4. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **8** (1954) 1502.
5. Furlani, C. *Gazz. chim. ital.* **87** (1957) 371.
6. Ballhausen, C. J. and Jørgensen, C. Klixbüll *Acta Chem. Scand.* **9** (1955) 399.
7. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **9** (1955) 1362; **10** (1956) 887.
8. Bostrup, O. and Jørgensen, C. Klixbüll *Acta Chem. Scand.* **11** (1957) 1223.
9. Kato, S. *Sci. Papers Inst. Phys. Chem. Research, Tokyo* **13** (1930) 49.
10. Ballhausen, C. J. and Jørgensen, C. Klixbüll *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1955) No. 14.
11. Holmes, O. G. and McClure, D. S. *J. Chem. Phys.* **26** (1957) 1686.
12. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **11** (1957) 73.
13. Schäfer, C. E. *International Symposium on Coordination Compounds. Suppl. Ricerca Scientifica* **28** (1958) 149.
14. Furman, S. C. and Garner, C. S. *J. Am. Chem. Soc.* **72** (1950) 1785.

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