

and Ewens¹³ and supported by infrared data.¹⁴ The diverse physical properties of the two carbonyls despite possible structural similarities might be explained in terms of the vacant orbital on the center Fe of $\text{Fe}_3(\text{CO})_{12}$ which may, for example, facilitate solvation. No such orbital is available in $\text{Fe}_2(\text{CO})_9$. Despite the fact that the weak intensities of the carbonyl bridges have not been satisfactorily explained, we believe the weight of evidence supports the "staggered" 3-3-3-3 structure for $\text{Fe}_3(\text{CO})_{12}$.

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Electronic Spectra of Vanadyl Complexes at Low Temperatures

Sir:

Electronic absorption spectra of various complexes of the oxovanadium(IV) ion, VO^{2+} , have been reported for over a dozen years,¹⁻¹⁹ and several authors^{7-9,11,13,16-18} have attempted to assign some of the observed bands to theoretically predicted transitions. Ballhausen and Gray¹³ present the most elegant and detailed discussion of the electronic structure of the VO^{2+} ion in a C_{4v} symmetry environment; specifically they treat $\text{VO}(\text{H}_2\text{O})_5^{2+}$. They compare their own experimental data and that of others with calculations from a molecular orbital model. Others have used their model to assign bands observed in the visible and ultraviolet spectra of other vanadyl¹⁶⁻¹⁸

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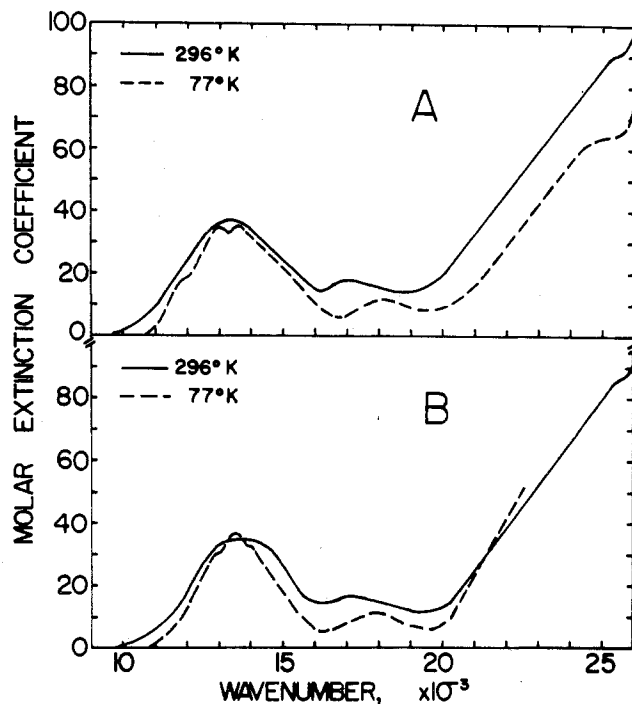


Fig. 1.—The optical absorption spectra of $\text{VO}(\text{acac})_2$ dissolved in: A, 3:7 isopropyl alcohol:isopentane; B, 2:5:5 ethanol:isopentane:ether; at 296°K. and at 77°K.

complexes and chromyl and molybdenyl²⁰ complexes.

We wish to report our results of preliminary spectral studies of complexes of oxovanadium(IV) ion at low temperatures because these results strongly suggest that while the Ballhausen and Gray¹³ model may correctly describe the $\text{VO}(\text{H}_2\text{O})_5^{2+}$ ion, the model should be modified before it is generally applied to other vanadyl species, as is currently being done.

In Fig. 1 are shown optical spectra obtained for bis-(acetylacetonato)-oxovanadium(IV), $\text{VO}(\text{acac})_2$, in two different solvent media, at both room temperature and liquid nitrogen temperature. The particular solvents (see legend to Fig. 1) were chosen because they solidify to clear glasses at low temperature.²¹ The low temperature double beam absorption cell designed and built by Smith, Smith, and McGlynn²¹ for use in Beckman DK-1 and DK-2 recording spectrophotometers was used to obtain the spectra reported here. From Fig. 1 and Table I, in which we have listed the values of the band maxima, it is seen that the broad "first band" is resolved into at least three bands at low temperature. The symmetry of $\text{VO}(\text{acac})_2$ is no higher than C_{2v} and in such a symmetry the number of crystal field (C.F.) or d-d bands expected is four¹⁷ regardless of whether a simple C.F.²² or more involved M.O. model is consulted. Therefore we propose that the four relatively low intensity bands ($\epsilon \sim 40$) occurring in the 12,000-18,000 cm^{-1} range arise from just the expected four d-d transitions. This then implies

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(22) In the crystal field model it is most readily seen that all degeneracy is removed from the five d-orbitals of the vanadium in C_{2v} , giving rise to four possible d-d transitions of the lone d-electron in V(IV).

TABLE I

Compound	Symmetry	Solvent ^a	Temp., °K.	Absorption bands, cm. ⁻¹		
				I	II	III
VO(acac) ₂	C _{2v}	2:5:5 ethanol:isopentane:ether	296	13,790	17,000	25,970
			77	12,980	17,920	... ^b
				13,580		
				14,180		
VO(acac) ₂	C _{2v}	3:7 isopropyl alcohol:isopentane	296	13,380	16,940	25,700
			77	12,040	18,050	25,970
				12,980		
				13,600		
(NH ₄) ₃ [VOF ₅]	C _{4v}	Water	296	10,970	14,970	...
(NH ₄) ₃ [VOF ₅]	C _{4v}	1:1 water:propylene glycol	194	(8,480)	15,870	...
[(CH ₃) ₄ N] ₃ [VO(CN) ₅]	C _{4v}	1:1 water:propylene glycol		11,830		
			296	14,700	19,370	24,560
			194	(10,310)	20,660	24,810
				14,700		

^a All solvent mixtures are *by volume*. ^b Region not investigated.

that the absorption maximum observed for many vanadyl complexes in the 24,500–30,000 cm.⁻¹ region, and assigned by previous workers^{8,13,16} to the "third d-d band,"²³ might actually be the *first charge-transfer* band. We have experiments in progress to further test this hypothesis and to check out the possibility that the new bands observed at low temperature arise from vibrational fine structure.

However, there is some independent support for our hypothesis. (1) The relatively low intensity of this "third band" ($\epsilon < 100$) is in qualitative agreement with the partial forbiddance of this transition (from a filled bonding level to a half-filled nonbonding orbital). (2) It is observed^{16,17} that this "third optical band" is relatively little shifted in VO(acac)₂ spectra obtained in a whole range of solvents which markedly shift the first two optical (room temperature) bands. If the third band were the third d-d transition, it is expected¹⁶ that it would show a strong solvent effect. (3) In the vanadyl complexes (NH₄)₃[VOF₅] and [(CH₃)₄N]₃[VO(CN)₅], in which the vanadium is in a C_{4v} symmetry site, we observe at low temperature (at 194°K. in 1:1 water:propylene glycol) three optical bands at lower frequencies than the 25,000 cm.⁻¹ band, which is observed, for example, at 24,800 cm.⁻¹ in the cyano complex (see Table I). (4) Belford, Calvin, and Belford²⁴ observed the three predicted d-d bands in the very similar Cu(acac)₂ complex in the 11,300–18,800 cm.⁻¹ range and these bands were likewise found to be solvent dependent. (5) Recently²⁵ four d-d transitions were observed in the optical spectrum of bis-(3-phenylacetylacetonato)-copper at liquid nitrogen temperature and all occurred between 14,800 and 21,000 cm.⁻¹ with a familiar looking shoulder attached to an intense charge-transfer band at about 24,000 cm.⁻¹.

We plan extensive low-temperature investigations, employing organic glass and alkali halide matrices, of vanadyl and molybdenyl(V) complexes of C_{4v} and C_{2v} symmetry types. We would welcome communica-

tion from other workers who might suggest alternative explanations for our present observations.

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Stereochemistry of Ethylenediaminetetraacetato Complexes. The Chromium(III), Iron(III), and Gallium(III) Complex Acids¹

Sir:

This report on the isostructural acid complexes formed by ethylenediaminetetraacetic acid (EDTA; H₄Y) with Cr(III), Fe(III), and Ga(III) is prompted by two recent papers^{2,3} which differ materially in their characterizations of the Fe(III) acid. Stereochemical formulations from the earlier paper³ for three chelate types pertinent to this discussion are summarized as follows: (1) Fe(OH₂)Y⁻ as a sexadentate, seven-coordinate, aquo complex shown⁴ to exist in RbFe(OH₂)Y·H₂O, and considered to be the most stable anionic species; (2) the complex Fe(III) acid as a coupling of H⁺ or H₃O⁺ with the Fe(OH₂)Y⁻ specified in (1); and (3) Cr(OH₂)YH as a quinquedentate, six-coordinate, aquo complex having one free -CH₂COOH arm.

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