When these stable compounds were heated with certain metal acetates in organic solvents, highly colored crystalline chelates were obtained.

Compound I reacts with nickel(II) to give a deep violet complex(IV) which is soluble in organic solvents. The visible spectrum of this complex in chloroform closely resembles that of the dimethyl derivative prepared according to the method of Thompson and Busch.[1] Like biacetylbis(mercaptoethylimine)nickel(II), compound IV displays a weak absorption band at 430 mμ. Another, more intense band is exhibited at 565 mμ which is analogous to the 550 mμ band observed in the nickel(II) complex of the dimethyl derivative.

Compound II gives blue or blue-black crystalline chelates with cadmium(II) and zinc(II) which are soluble in dimethylformamide, dimethyl sulfoxide, and pyridine and give blue-violet or blue solutions. The infrared spectra of these zinc and cadmium chelates are very similar. The visible spectrum of the zinc chelate in dimethylformamide has two absorption bands at 370 and 560 mμ and the absorption bands of the cadmium chelate are observed at 360 and 540 mμ.

Compound III gives orange-red crystalline chelates with cadmium(II) and zinc(II) whose infrared spectra are very similar and which are soluble in dimethylformamide, dimethyl sulfoxide, and pyridine and give yellow or red solutions. In dimethylformamide the zinc chelate has an absorption band at 470 mμ and the cadmium chelate has one at 440 mμ.

The analyses of these metal chelates correspond to a metal:ligand ratio of 1:1.

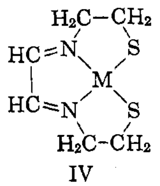
Glyoxalbis(2-mercaptoanil)cadmium(II): *Anal.* Calcd.: C, 43.93; H, 2.63; N, 7.32; S, 16.75; Cd, 29.37. Found: C, 43.98; H, 3.03; N, 7.15; S, 16.72, Cd, 28.47.

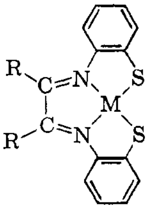
Diacetylbis(2-mercaptoanil)zinc(II): *Anal.* Calcd.: C, 52.82; H, 3.88; N, 7.70; S, 17.6. Found: C, 53.00,; H, 4.35; N, 7.65; S, 17.44.

Diacetylbis(2-mercaptoanil)cadmium(II): *Anal.* Calcd.: C, 46.78; H, 3.44; N, 6.82. Found: C, 46.88; H, 3.80; N, 6.53.

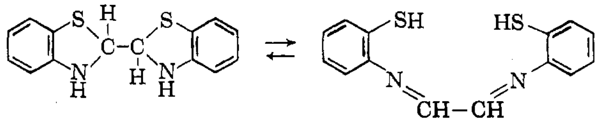
Glyoxalbis(2-mercaptoanil)zinc(II): *Anal.* Calcd.: C, 50.08; H, 3.00; N, 8.34. Found: C, 50.07; H, 3.28; N, 8.08.

Thus the structures of the chelates obtained correspond to the Schiff base complexes IV, V, and VI.


IV


V, R=H
VI, R=CH₃

The rate of formation of the colored chelate from compound II and zinc(II) or cadmium(II) in dimethylformamide solution at room temperature was followed spectrophotometrically. In the concentration range studied (2.5×10^{-4} *M* compound II and 5×10^{-2} to 1×10^{-4} *M* zinc(II)) the rate of chelate formation of compound II with zinc(II) is zero order with respect to the metal ion, but with cadmium(II) it is essentially first order (0.8) with respect to the metal ion in the concentration range 5×10^{-5} to 5×10^{-4} *M* cadmium(II) and 2.5×10^{-4} *M* compound II. Thus, although a metal complex of the same general structure is formed in both cases, the course of the reaction is seen to depend on the metal ion involved. The rate-determining step in the reaction of compound II with zinc(II) is probably the formation of the Schiff base tautomer.



On the other hand, the reaction of compound II with cadmium(II) proceeds *via* a direct attack of the thiazoline by the metal ion. These results show that the metal ion need not necessarily act as a template in the formation of chelates which are homologs of biacetylbis(mercaptoethylimine)nickel(II).

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Structure in the Electronic Spectra of Vanadyl Acetylacetonate

Sir:

A recent communication[1] of structure in the visible spectrum of some vanadyl complexes at low temperature in glassy solution prompts us to communicate some observations on structure in the low-temperature spectrum of single crystals of vanadyl acetylacetonate. Figure 1 shows that we have been able to resolve the structure in three regions in the spectrum of vanadyl acetylacetonate. In the first region, the visible, and the third region, occurring at about 25 kK., structure appears which can be interpreted as a progression of a vibrational mode of frequency about 0.7 kK. We are tempted to assign this vibrational mode to the vanadyl stretching frequency which in the ground state occurs at about 0.99 kK.[2] If our interpretation of the structure is correct, then excitation in both the 14 and 25 kK. regions must involve a considerable change in the electronic structure of the vanadyl group itself. This can be a clue to assignment of the 25 kK. band as a charge-transfer band or a vanadyl internal transition

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[1] J. Selbin, T. R. Ortolano, and J. F. Smith, *Inorg. Chem.*, **2**, 1315 (1963). (See here also the many references to vanadyl spectroscopy.)

[2] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4533 (1961).

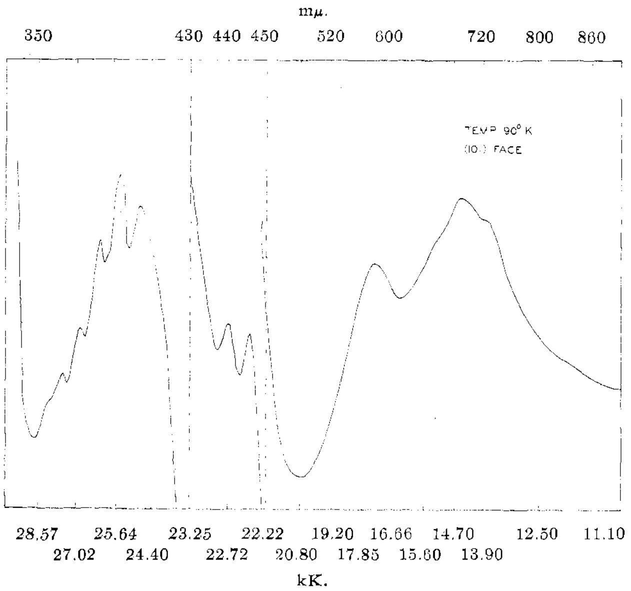

Fig. 1.—Absorption at liquid air temperature of a thin crystal of $VO(CH_3COCHCOCH_3)_2$. Sections in the far-blue and ultraviolet are arbitrarily shifted down and the segment 430–450 mμ is shown on an expanded wave length scale to show details. Note: 1 kK. = 1000 cm.$^{-1}$ = 3 × 10^{13} sec.$^{-1}$. This face contains the *b* axis; otherwise, its identification is tentative.

rather than as a transition in the acetylacetone ligand system.

The question remains whether anyone has resolved the first visible band at about 14 kK. into more electronic components. Our crystal spectra at room temperature hint at such a resolution. However, the low temperature spectrum reveals that at least part of this hinted resolution is probably just the beginning of resolution of a vibrational mode. We cannot say definitely whether more than one electronic band is seen in the 14 kK. region, although the shape of the curves in the 10–12 kK. range suggest that another band is indeed present. Further, Selbin, Ortolano, and Smith[1] report resolution of the 14 kK. band into three components. If one looks at these spectra one sees that it is possible to interpret them as vibrational structure. In fact, from Table I of Selbin, Ortolano, and Smith[1] one can calculate four possible vibrational frequencies. These average to 0.690 ± 0.100 kK. Thus, we propose that all the data as yet obtained on low-temperature spectra of vanadyl acetylacetonate in any form are consistent with there being vibrational structure, probably that of the vanadyl bond, in the 14 kK. region and the same vibrational structure in the 24 kK. region, but that there has been as yet no *unequivocal* evidence of electronic splitting in the 14 kK. region. We are attempting a better resolution of the low-energy part of the spectrum at lower temperatures in order to settle this question.

Figure 1 also shows a remarkable new feature which has appeared in the low-temperature crystal spectrum, namely, two sharp bands at about 23 kK. split by about 0.35 kK. Clearly this is not the same splitting as the 0.700 kK. structure seen in the two other regions of the spectrum. Among several possibilities that come to mind are (1) components of a spin-allowed vanadyl band, (2) spin-forbidden acetylacetone-to-VO charge transfer, or (3) internal ligand bands (probably spin-forbidden $\pi \rightarrow \pi^*$ transitions), as suggested by a referee. We have no evidence to prove which assignment is correct, but make the following observations.

First, the 23 kK. transitions are much sharper than any others in the $VO(acac)_2$ spectrum. One expects the vanadyl spin-allowed bands to be broader and to include a long progression of VO stretches, as the 14 kK. and probably the 18 kK. bands do. In the case of the 18 kK. band, the total band width is sufficiently great to smear out a VO progression. However, the 23 kK. group is so sharp that we should have found it repeated within 1 kK. if a VO stretch were strongly coupled to it, whereas we see no hint of any repeat within 1.5 kK.

Because of the arguments in the previous paragraph, the suggestion that the 23 kK. bands represent spin-forbidden ligand transitions is attractive and cannot be ruled out. However, it suffers from the transition's being at somewhat lower frequency than is ordinarily expected of acetylacetonate transitions, and from the fact that apparently not all acetylacetonates have bands below 30 kK. (*cf.* Jørgensen,[3] who objects to assignment of bands in the 20–30 kK. region as acetylacetone transitions).

Arguments against the 23 kK. bands being charge transfer would be much the same as those against them being d-like vanadyl transitions. But the arguments against charge transfer are not as strong since the charge-transfer bands could be spin-forbidden (quartet–doublet) transitions which, because of the more stringent requirements for breakdown of selection rules forbidding them, are often much sharper and less strongly coupled to a long vibrational progression than are spin-allowed transitions. However, another point should be considered. If the first spin-forbidden charge transfer is at about 23 kK., and if the picture of vanadyl complexes presented by Ballhausen and Gray[4] is approximately correct, we would estimate the first spin-allowed charge transfer to be about 4 kK. lower in energy, which would place it around 19 kK., in the region of the second visible band. Such an assignment would be akin to some of the rather unorthodox suggestions made by Jørgensen,[3] who proposed assigning visible bands in $Ti(acac)_3$ and in $Mn(acac)_3$ as charge transfer (albeit metal-to-π^* electron transitions). We do not seriously propose that the 18 kK. band is a charge transfer, as (1) it is relatively weak and must be, in first approximation, forbidden, (2) it is of lower energy than we believe the first charge transfer would be, (3) the 18 kK. band has a rather more obvious assignment as a d-like vanadyl transition, and (4) the estimate given above is very crude. Nevertheless, we urge that in any serious attempts to assign all the bands, this possibility not be ruled out simply because of orthodoxy.

(3) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).

(4) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

The objections common to the 23 kK. region being d-like or charge-transfer bands could be overcome, in part, by supposing the electron to move into an orbital that is roughly *xy*. Such a transition would involve minimum changes in the vanadyl vibrations.

Finally, the origin of the splitting of the 23 kK. band into two components must be considered. The 0.35 kK. splitting seems too great to be accounted for by spin–orbit coupling. Therefore, it is likely that the two components represent two distinct orbital states and that the spin–orbit splitting is much smaller and might be resolved only at very low temperatures. An attractive explanation is that the 0.35 kK. represents splitting of an orbital which would be E in C_{4v} into two orbitals, namely B_1 and B_2, in C_{2v}. Another possibility is a splitting caused by neighboring molecule interactions in the crystal.

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Book Reviews

Valency and Molecular Structure. Edited by E. CARTMELL and G. W. A. FOWLES. Butterworths, Inc., 7235 Wisconsin Ave., Washington 14, D. C. 1961. xii + 294 pp. 14 × 22 cm. Price, $7.00.

The first edition of this book was published in 1956 and was thus one of the earliest of the many books of its type which are now available. The new edition retains the basic structure of the first edition, being divided into three parts, "Quantum Theory and Atomic Structure," "Quantum Theory of Valency," and "The Application of the Principles of Chemical Bonding."

As the authors say in their preface, the first part is almost unchanged, the second part now places a greater emphasis upon molecular orbital theory, and the third part is almost entirely rewritten because of the advent of crystal field and ligand field theories and their impact upon structural aspects of modern inorganic chemistry.

It is pleasing to note that many of the inaccuracies of the first edition have been removed, *e.g.*, the identification of the real d-orbitals d_{xy}, d_{xz}, etc., with particular m_l values (see Fig. 19). On the whole, the changes in accent in part II are for the better and no new errors seem to have been introduced along with these changes. The addition of small sections on the hydrogen bond and metallic bonds is also welcomed, as brief as they are.

The reviewer's main criticisms stem from part III, where the principles are applied to structural and reaction chemistry. This part contains many errors, some printing, others of fact and/or of logic. In the first place, it seems a waste to have increased the accent on molecular orbital theory in part II when the main descriptive method of part III remains the valence bond theory.

The extensive use of the concept of hybridization has led to many passages which are either irrelevent or factually incorrect. One particularly annoying aspect is the repeated use of such phrases as " . . . the beryllium atom *uses* sp hybrid orbitals . . .," etc. (p. 184, my italics), ". . . and arsenic *uses* sp^3 orbitals to form simple tetrahedral structures . . ." (p. 171), and so on, as though such hybrids were physically measurable and their nature exactly ascertainable. The same sort of approach leads to statements such as (p. 212), "The valence-bond method predicts two possible configurations: tetrahedral and square-coplanar. In the tetrahedral arrangement, the atom uses *either* the sp^3 combinations . . *or* sd^3 hybrid orbitals . . ." (my italics). The either/or exclusion apart, there are, in addition, the tetragonal pyramid and the various asymmetric tetrahedral structures which can also be described by hybrids.

The following paragraph on p. 212 is also inconsistent with the second last paragraph on p. 209. In the latter paragraph the authors discuss sd hybridization as the "reason" for the existence of such compounds as $HgCl_2$, whereas, in the former, they claim that sp^3 hybrids must be used for tetrahedral mercury compounds because "there are no d-electrons of suitable energy available." These logical nonsequiturs are quite common in the whole of part III. As a final illustration, consider the general discussion of crystal field stabilization energy (CFSE) as a criterion for structure determination, *e.g.*, on p. 216, for d^0, d^5, and d^{10} complexes. "In each case the ligands *will* take up the tetrahedral position . . . Tetrahedral arrangements are *thus* found in $TiCl_4$, $[FeCl_4]^-$ and $[ZnX_4]^{2-}$." The authors carefully avoid $[AuCl_4]^-$, for example, and there is also XeF_4, etc., if a further example is required. Surely it is now possible to realize, and to state, that while certain approximations are useful, nonetheless there are still more factors at work than any single one of the theories is usually capable of taking into account.

In somewhat the same vein as the above, is the matter of "bonds being shorter than normal." In organic chemistry there are enough data available to even allow a statistical analysis to have been performed on bond lengths, but in inorganic chemistry, knowledge of what constitutes "normal" or "single bond" lengths is, at most, rudimentary. It is, therefore, misleading to base theoretical explanations of such shortenings on insufficient data, particularly in the matter of bonding and back donation "phenomena" (see, *e.g.*, p. 241).

Finally, the authors have included a very brief section on the "Experimental Determination of Configuration" which, one feels, could be amplified at the expense of some of the more "theoretical" ideas. This would give room for a mention of what type of information, other than vibration frequencies, comes from a study of spectroscopy. This kind of information, and a discussion of the order of accuracy to be expected, is surely something which could reasonably be expected in a book of this type.

There is much of value in this book and the authors have, indeed, succeeded in their efforts to maintain an essentially nonmathematical approach, while at the same time, they have been able to produce a relatively concise summary of the modern approach to the subject. It is a pity, therefore, that very many of the errors of the type described above have been allowed to slip past their scrutiny and to slightly mar what could otherwise have been an excellent introduction to valency and modern inorganic chemistry.