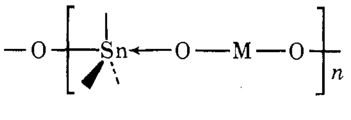
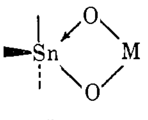
of the other trineophyltin compounds examined (probably not a solvent effect, compare the same compounds in carbon tetrachloride and acetone-d_6) and very likely due to a change in coordination number of the tin atom. The evidence in the case of the nitrate is too marginal to reach a conclusion. The large shift of the perchlorate is clear evidence of a substantial change of the methylene proton magnetic environment. This deshielding of the methylene protons may be attributed to the increased ionic character of the tin–oxygen bond.

The trineophyltin perchlorate and nitrate could have either the polymeric structure (I) ~~or~~ the monomeric structure (II). It is difficult to decide between these two. The dilute solution molecular weights (see Experimental Section) indicate clearly a monomeric structure for both.[29]


Polymer


Monomer

Trineophyltin acetate was found to have a four-coordinated tin atom (Q.S./I.S. = 1.81, infrared C=O 1660 cm.$^{-1}$, normal δCH_2). Similar "ester" carbonyl absorptions for the corresponding formate (1655 cm.$^{-1}$) and the perfluoroacetate (1720 cm.$^{-1}$), as well as normal nuclear magnetic resonance δCH_2 absorptions, indicate that here the tin atoms also have the coordination number four. The bulky neophyl groups seem to have forced the "carboxylate"–tin infrared absorptions[30–32] into the normal "ester" conformation.[35]

The above data would seem to indicate that at least two major factors operate when a change of the coordination number of tin in trialkyltin compounds is to be brought about: not only must the ligand have the proper geometry (be large enough to circumvent steric resistance) but it must also be an adequate electron donor to the tin atom. Thus, the perchlorate and nitrate groups are satisfactory bidentate ligands, fluoride would probably be a good one if it were not for its small size, while azide and carboxyl groups (both of proper size) do not coordinate to tin in this case. A qualitative order is: $ClO_4 > NO_3 > F \gg N_3 \simeq RCO_2$.

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[29] The Mössbauer and infrared spectra were obtained on the crystalline solids, the nuclear magnetic resonance spectra on solutions. In case of the trialkyltin esters[30–32] and imidazoles[33] polymers were found to exist in the crystalline state and also in solution. Increasing dilution tended to increase monomer content,[30] due probably to a shift in the coordination number of tin from five to four in case of the esters (absorption shift from 1590 and 1360 cm.$^{-1}$ RCO_2^- bidentate to 1667 cm.$^{-1}$ RC(=O)O monodentate). Infrared data indicate that trimethyltin nitrate may have the polymer configuration (I) in the crystalline state.[34]

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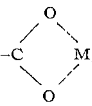
[35] The normal "ester" –C(=O)O– bonding is found in $(C_6H_5)_3MO_2CC_6H_5$ (M = Si, Ge) and $(C_6H_5)_2MO_2CC_6H_5$ (M = P, As), while the "carboxylate" bonding () is found in $(C_6H_5)_3MO_2CC_6H_5$ (M = Sn, Pb), $(C_6H_5)_2MO_2CC_6H_5$ (M = Sb, Bi), and $C_6H_5HgO_2CC_6H_5$ (all as crystalline solids). Evidently there is a sharp break in the bond character in compounds of this nature between the third and fourth row of the atomic table. W. T. Reichle, unpublished results; also see ref. 31.

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The Electron Paramagnetic Resonance Spectrum of Tetrakis-*t*-butoxyvanadium(IV)

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The electron paramagnetic resonance spectrum of tetrakis-*t*-butoxyvanadium(IV) $[V(OR)_4]$ has been measured in the temperature range of 30 to −196°. The measurements were made on pure $V(OR)_4$, 1–2% $V(OR)_4$ in $Ti(OR)_4$, and 1–2% $V(OR)_4$ in CS_2. The spectrum was essentially the same in all samples. At 30° $\langle g \rangle = 1.964$ and $\langle a \rangle = 0.0064$ cm.$^{-1}$, while at −196° in the solid, the magnetic parameters are $g_{\parallel} = 1.940$, $g_{\perp} = 1.984$, $A_{\parallel} = 0.0125$ cm.$^{-1}$, and $A_{\perp} = 0.0036$ cm.$^{-1}$. These parameters are interpreted in terms of the molecular orbital theory, and the model due to Murao is used to account for the low value of the effective spin–orbit coupling constant, 156 cm.$^{-1}$.

Numerous reports of the e.p.r. spectra and the nature of the bonding in vanadyl complexes[2–7] have been published recently. Usually, the vanadyl ion is found in a distorted octahedral environment with either five or

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[2] (a) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962); (b) D. Kivelson and S-K. Lee, *J. Chem. Phys.*, **41**, 1896 (1946).

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six ligands in the first coordination sphere. In view of the considerable interest in various transition metal ions in tetrahedral environments[8–10] and the apparent lack of e.p.r. data on tetrahedral vanadium(IV) complexes, a detailed study of the complex tetrakis-*t*-butoxyvanadium(IV) [$V(OR)_4$] was undertaken.

Three samples[11] of this material were supplied by Bradley.[12] These samples were investigated by the e.p.r. methods used previously.[13,14] The magnetic parameters are interpreted in terms of the molecular orbital theory,[15] and the model of Murao[16] is used to account for the low values of the effective spin–orbit coupling constant. The spectra obtained from the two magnetically dilute samples[11] were essentially the same, which is used as evidence to rule out the possibility of large solvent effects which might change the nature of the complex.[3,5,13]

At room temperature all of the samples were liquids, and the e.p.r. spectra of the diluted materials were quite similar to those reported by Rogers and Pake[17] for the VO^{2+} ion. Eight partially resolved hyperfine components were observed in the spectra of the pure material. The $\langle g \rangle$ and $\langle a \rangle$ values at K band and X band were identical within experimental error for all three samples. These results are given in Table I.

Table I

Magnetic Parameters for $V(OR)_4$

Liquid spectrum (30°)	
$\langle g \rangle = 1.964 \pm 0.005$	$\langle a \rangle = 0.0064 \pm 0.0002$ cm.$^{-1}$
Polycrystalline spectra (−196°)	
$g_{\parallel} = 1.940 \pm 0.005$	$A_{\parallel} = 0.0125 \pm 0.005$ cm.$^{-1}$
$g_{\perp} = 1.984 \pm 0.005$	$A_{\perp} = 0.0036 \pm 0.004$ cm.$^{-1}$

Below the freezing point (−5°), the e.p.r. spectrum of 1–2% $V(OR)_4$ in $Ti(OR)_4$ became anisotropic; below −120°, the spectrum did not change appreciably. It should be noted that above −120° the spectrum tends to be "more" isotropic, but the melting of the material at −5° precludes a determination of the Jahn–Teller barrier height. Furthermore, it is difficult to establish if it is actually a Jahn–Teller effect (vibronic) or if the effect is due to hindered rotation although the size of the molecule suggests that the latter is unlikely. The magnetic parameters were determined by the method of Sands[18] and Kneubuhl.[19] The line shape of the frozen polycrystalline material changed slightly as the sample was rotated in the magnetic field which indicated that the crystallites were not completely randomly oriented. This effect is the dominant source of the uncertainties reported in Table I.

A molecular orbital treatment was used to relate the low-temperature g and A values to the bonding parameters. The antibonding molecular orbitals are

$$|xz\rangle = \gamma|\mathrm{d}_{xz}\rangle - \gamma'|\phi_{xz}\rangle \tag{1}$$

$$|yz\rangle = \gamma|\mathrm{d}_{yz}\rangle - \gamma'|\phi_{yz}\rangle \tag{2}$$

$$|xy\rangle = \beta|\mathrm{d}_{xy}\rangle - \beta'|\phi_{xy}\rangle \tag{3}$$

$$|z^2\rangle = \delta|\mathrm{d}_{z^2}\rangle - \delta'|\phi_{z^2}\rangle \tag{4}$$

$$|x^2 - y^2\rangle = \alpha|\mathrm{d}_{x^2-y^2}\rangle - \alpha'|\phi_{x^2-y^2}\rangle \tag{5}$$

where the metal and ligand orbitals are represented in the usual way.[15] With $|x^2 - y^2\rangle$ as the ground state, the following expressions obtain[20,21]

$$g_{\parallel} = 2.0023 - [8\lambda_0'\alpha\beta/\Delta_{xy}] \times [\alpha\beta - \beta\alpha'S_1 - \alpha\beta'S_2] \tag{6}$$

$$g_{\perp} = 2.0023 - [2\lambda_0'\alpha\gamma/\Delta_{xz}] \times [\alpha\gamma - \gamma\alpha'S_1 - \alpha\gamma'S_2] \tag{7}$$

$$A_{\parallel} = P\{-\alpha^2(^4/_7 + \varkappa) - 8_0\lambda\alpha^2\beta^2/\Delta_{xy} - 6\lambda_0'\alpha^2\gamma^2/7\Delta_{xz}\} \tag{8}$$

$$A_{\perp} = P\{\alpha^2(^2/_7 - \varkappa) - 11\lambda_0'\alpha^2\gamma^2/7\Delta_{xz}\} \tag{9}$$

where S is the overlap integral and λ_0' is defined below. Since the 4p orbitals are expected to mix with the 3d orbitals which arise from the t_2 levels[8] and since the spin–orbit coupling constant for O^{2-} is 85 cm.$^{-1}$,[22] the effects of p-state admixture and ligand spin–orbit effects have been neglected. The g and A values are the magnetic parameters in the usual spin-Hamiltonian.[20] Both $A_{\parallel}$ and $A_{\perp}$ have the same sign and are assumed to be negative.[2,23]

In order to evaluate the bonding parameters, the values of Δ_{xy}, Δ_{xz}, λ_0', and P must be known. In the region 7000–25,000 cm.$^{-1}$ only one broad, intense absorption band centered at 13,500 cm.$^{-1}$ with an extinction coefficient[24] of 105 cm.$^{-1}$ M^{-1} was observed at 25°. Since this complex is expected to be very nearly tetrahedral,[24] we have assigned this band as the $\mathrm{d}_{x^2-y^2} \rightarrow \mathrm{d}_{xy}, \mathrm{d}_{yz}, \mathrm{d}_{xz}$ transition. Since both λ_0 and P vary approximately[25] as $\langle r^{-3} \rangle$, the data of Kivelson and Lee[2] were used to obtain the relationship

$$\lambda_0' \approx 1.45 \times 10^4 P \tag{10}$$

By using hydrogen-like wave functions, it has been shown[25] that λ is also proportional to the fourth power of the effective nuclear charge. If it is assumed that the admixture of the 3d wave function in the bonding molecular orbitals can reduce λ_0 due to d–d screening

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effects, then, it is possible to make an estimate of λ_0' by means of the model of Murao[16] where

$$\lambda_0' = \lambda_0[1 - (a/z_0)\sum_n (2 - P_n)(\beta_n')^2]^4 \qquad (11)$$

and λ_0 is the free ion spin–orbit coupling constant[26] (250 cm.$^{-1}$), a is the d–d screening constant, P_n is the number of electrons in the nth orbital when the ion is in an ionic state, and β_n' is the coefficient of the nth linear combination of the ligand orbitals in the metal–ligand antibonding orbital.

By using eq. 8 and 9, the value of κ is found to be nearly independent of P in the range $0.001 \leq P \leq 0.02$ cm.$^{-1}$ and is calculated to be 0.63 ± 0.04. By means of an iterative procedure, in which it was assumed that $S_1 = S_2 = 0.1$ and $(\alpha')^2 = (\delta')^2$, eq. 6–11 were used to calculate the appropriate parameters. Our values of κ is considerably lower than those reported by other workers.[2b,7] Kivelson and Lee[2b] have shown that κ varies considerably in VO^{2+} complexes. Kuska and Rogers[27] have shown that κ is not necessarily constant for copper complexes. Furthermore, relatively low values of the hyperfine coupling constants in two other V(IV) complexes have recently been reported by Otherton, Locke, and McCleverty.[28]

The resulting values of λ_0' and P were 156 and 0.0108 cm.$^{-1}$, respectively. We also obtain $\alpha = 0.95$, $\beta = 0.91$, and $\gamma = 0.97$, which suggests that the bonding is moderately covalent. The value of λ_0 is reduced by about 62% owing to screening effects, and these bonding parameters are comparable to those found in various cupric and vanadyl complexes.[2,3,7,20]

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Magnetic Studies with Copper(II) Salts. VII. The Structure of Copper(II) α,ω-Dicarboxylates and Their Amine Derivatives[1,2]

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The magnetic susceptibility at temperatures between 80 and 350°K. is reported for copper(II) α,ω-dicarboxylates and their monoaniline and monopyridine derivatives of formula $Cu(O_2C(CH_2)_nCO_2)L$. Copper(II) malonate ($n = 1$) is magnetically uncomplicated; copper(II) oxalate ($n = 0$) exhibits the behavior of a linear antiferromagnet; copper(II) succinate ($n = 2$), glutarate ($n = 3$), and adipate ($n = 4$) display $\chi_M(T)$ behavior characteristic of singlet and triplet states in thermal equilibrium. With L = 0, water, and pyridine, the singlet–triplet separation is about 310–330 cm.$^{-1}$; with L = aniline the interval is reduced to about 80–100 cm.$^{-1}$. The reflectance spectra of all polymeric dicarboxylates show broad absorption at about 7000 Å. (band I), but only the succinate, glutarate, and adipate contain an additional near-ultraviolet band at 3750 Å. (band II). Band I is sensitive and band II insensitive to changes of the axially situated amine. These electronic properties are consistent with copper acetate type dimers linked in infinite nets *via* the bifunctional dicarboxylate anions only when $n = 2$, 3, and 4. Quite different structures are proposed for copper(II) malonate and copper(II) oxalate.

Introduction

The copper(II) acetate dimer is the prototype[4] of a rapidly expanding class of polynuclear molecules with metal–metal bonds.[5-10] Valence bond[11-15] and molecular orbital[16,17] methods have both been used to substantiate claims that either δ bonding[11-16] or σ bonding[17] is involved between the pairs of metal atoms. Some workers have assumed that the Cu–Cu interaction is weak,[11-15] others[16,17] that it is strong. The emergent theories have had their strengths and limitations; all have failed to provide a convincing interpretation of the observed electronic spectrum.

The possible conformations of the acetate anions are such that it can bridge copper atoms either in discrete contiguous pairs (the *syn-syn* conformation) or in infinite arrangements which involve either the *anti-anti* or *anti-syn* conformations.[18] Few examples have yet been confirmed of the acetate anion chelating simply to give a four-membered ring, although this geometry

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