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Synthetic and Paramagnetic Resonance Studies of Trigonal Vanadium Complexes

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A previous investigation[2] of tris metal complexes of the general type $[MS_6C_6R_6]^z$ has been extended to include a series of vanadium complexes of the types $[VS_6C_6R_6]^z$ ($R = CF_3$, $z = -2, -1$; $R = C_6H_5$, $z = -2, -1, 0$) and $[V(S_2C_6H_3X)_3]^{-2}$ ($X = H, CH_3$). The synthesis of these complexes is described, and their polarographic half-wave potentials and solution spin Hamiltonian parameters are determined. It is shown from paramagnetic resonance results that a previously postulated electronic configuration in which the orbital of the odd electrons appears to be predominantly localized on the ligand system occurs quite generally in complexes with $z = -2$. For the complexes with $R = C_6H_5$ it is concluded from the similarity of the spin Hamiltonian parameters that in both the $z = -2$ and 0 species the odd electron is apparently strongly localized on the ligands. Probable electronic structures of the neutral complex are considered. The e.p.r. parameters of $[V(dipy)_3]$ are shown to be very similar to those for the other vanadium complexes studied.

Introduction

In a previous paper[2] we have reported the synthesis and characterization of a series of six-coordinate complexes of the general type $[MS_6C_6R_6]^z$, in which the central metal is coordinated entirely by sulfur atoms. These complexes are similar in behavior to the planar bis complexes described earlier[3] in that they undergo facile one-electron oxidation–reduction reactions during which the coordination presumably remains intact. It was postulated[2] on the basis of the paramagnetic resonance spectra of those tris complexes for which $S = {}^1/_2$ that the orbital of the unpaired electron (possibly a_2^*) is primarily localized on the ligands.

In the complex $[VS_6C_6(CN)_6]^{-2}$, for instance, the electronic configuration was postulated to be $(a_1^*)^2(1)^1$ in D_3 symmetry in which the a_1^* orbital is an antibonding molecular orbital primarily localized on the metal, and 1 is the a_2^* molecular orbital. This configuration is in marked contrast to the configuration $(a_1^*)^1$ which has been shown by paramagnetic resonance studies of a magnetically dilute single crystal to be the ground-state configuration of tris(acetylacetonato)-titanium(III).[4] The electronic structure of $[VS_6C_6(CN)_6]^{-2}$ may be regarded, in a purely formal sense, as diamagnetic V(III) bonded to two dinegative (diamagnetic) ligands and a single radical anion. The occurrence of radical anions bonded to a central metal ion is not unique; examples have been found recently by Brown and Weissman[5] and by Eaton.[6] The complexes studied in this work, with the possible inclusion of some apparently low valent tris(α,α'-dipyridyl) metal complexes,[7] are believed to be the first substantiated examples of transition metal complexes which may be formulated as containing coordinated radical anions. This paper deals with the extension of our investigations of tris vanadium complexes. It was anticipated that a neutral complex of the type $[VS_6C_6R_6]^0$ might have the configuration $(a_1^*)^1$, which would be readily recognized by the properties of its spin Hamiltonian.[2] However, we have found that the neutral complex $[VS_6C_6(C_6H_5)_6]$, which has a doublet ground state, exhibits a paramagnetic resonance spectrum indicative of delocalization of the unpaired spin over the ligand system. Some possible interpretations of this unexpected result are given. In addition several other tris vanadium complexes are reported: $[VS_6C_6R_6]^z$ ($R = C_6H_5, CF_3, CN$, $z = -1$; $R = CF_3$, $z = -2$) and $[V(S_2C_6H_3X)_3]^{-2}$ ($X = H, CH_3$), together with the magnetic susceptibilities, conductivities, and polarographic properties. The solution spin Hamiltonian parameters are reported for the paramagnetic members of these series.

Experimental

Preparation of Compounds.—Tetraphenylarsonium tris(*cis*-1,2-dicyanoethylene-1,2-dithiolato)vanadium, $[(C_6H_5)_4As]_2[VS_6C_6(CN)_6]$, was prepared as previously described.[2] Tetraphenylarsonium hexacarbonylvanadate was prepared by metathesis in ethanol from sodium bis(diethylene glycol dimethyl ether) hexacarbonylvanadate and tetraphenylarsonium chloride. Bis(trifluoromethyl)-1,2-dithietene was obtained by the gas-phase reaction of sulfur and hexafluorobutyne-2 according to the procedure by Krespan.[8] The compound was carefully fractionated before use and the freshly distilled 96–98° fraction used in the following preparations.

All melting points are uncorrected.

$[(C_6H_5)_4As]_2[VS_6C_6(CF_3)_6]$.—A solution of 3.4 g. of $(CF_3)_2C_2S_2$ in 10 ml. of dichloromethane was added in one portion to 2.6 g. of sodium bis(diethylene glycol dimethyl ether) hexacarbonylvanadate in 40 ml. of dichloromethane. The solution turned deep red-purple with rapid evolution of carbon monoxide.

After the gas evolution was complete the solvent was removed *in vacuo*, the product was dissolved in 100 ml. of ethanol, and the solution was filtered. The filtrate was treated with a solution of 4.2 g. of tetraphenylarsonium chloride in 200 ml. of water. The product, finely divided purple crystals, was collected on Super-Cel and washed with water, then eluted with acetone to give a clear purple solution. Isobutyl alcohol (25 ml.) was added to

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(1) Alfred P. Sloan Foundation Fellow.

(2) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964), and papers referred to therein.

(4) B. R. McGarvey, *J. Chem. Phys.*, **38**, 383 (1963).

(5) I. M. Brown and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 2528 (1963).

(6) D. R. Eaton, *Inorg. Chem.*, **3**, 1268 (1964).

(7) It has been previously suggested that certain of these complexes could have radical anions as ligands [*cf.* L. E. Orgel, *J. Chem. Soc.*, 3683 (1961)].

(8) C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

this solution, and most of the acetone was removed by heating. On slow cooling the product crystallized as shiny purple platelets. Two further recrystallizations from acetone–isobutyl alcohol gave 3.8 g. (55%) of the product, m.p. 205–206°.

Anal. Calcd.: C, 48.17; H, 2.69; F, 22.86; S, 12.86. Found: C, 48.41; H, 2.68; F, 23.68; S, 12.90.

$[(C_6H_5)_4As][VS_6C_6(CF_3)_6]$.—A solution of 1.7 g. of $(CF_3)_2C_2S_2$ in 30 ml. of dry dichloromethane was added under dry nitrogen to a solution of 1.5 g. of $[(C_6H_5)_4As][V(CO)_6]$ in 30 ml. of dry dichloromethane. Under these conditions there was slow evolution of CO gas and the solution became deep blue-purple. After the completion of gas evolution (*ca.* 3–4 hr.) the solution was filtered with exclusion of moist air. The slow addition of *n*-pentane to the filtrate caused the product to separate. It was collected and dissolved in dry carbon tetrachloride, and the resulting solution was filtered to remove a small amount of white amorphous material. Slow addition of *n*-pentane to the filtrate with agitation caused the product to crystallize as a dark purple solid; 1.7 g. (50%), m.p. 175–177°.

Anal. Calcd.: C, 38.86; H, 1.81; F, 30.73; S, 17.29. Found: C, 38.97; H, 1.68; F, 30.74; S, 16.86.

Reaction of $V(CO)_6$ and $(CF_3)_2C_2S_2$.—An attempt was made to prepare the neutral complex $[VS_6C_6(CF_3)_6]$ by the following procedure. To 2.19 g. of $V(CO)_6$ in 600 ml. of dry carbon tetrachloride a solution of 6.78 g. of $(CF_3)_2C_2S_2$ in 50 ml. of dry carbon tetrachloride was added dropwise over the course of 1 hr. A blue-purple solution was formed and carbon monoxide was rapidly evolved. Electron spin resonance experiments on this solution gave only a weak signal due to $[VS_6C_6(CF_3)_6]^{-2}$, indicating that the solution probably contained the monoanion as the principal solute species. Subsequent reduction of the solution volume and treatment with tetraphenylarsonium chloride in alcohol gave $[(C_6H_5)_4As]_2[VS_6C_6(CF_3)_6]$ as the main product. No evidence was obtained for the presence of the neutral complex in this reaction. Evidently this complex, if it is formed at all, is reduced by contaminants to the mono- or dianion. The same reaction when performed in other inert solvents such as *n*-pentane and methylcyclohexane did not yield the neutral complex in isolable amounts.

$[(n\text{-}C_4H_9)_4N]_2[V(S_2C_6H_4)_3]$.—A suspension of 5.1 g. of 1,2-bis-(*n*-butylthio)benzene[9] in liquid ammonia was cleaved to give disodium *o*-benzenedithiolate.[10] After removal of excess sodium with ammonium chloride the ammonia was evaporated and the flask heated to 60° to remove the last traces of ammonia. Tetrahydrofuran (150 ml.) was distilled into the flask under nitrogen. Anhydrous VCl_3 (0.8 g.) was added to the mixture under nitrogen. There was no reaction on stirring the mixture for 20 min. Ethanol (150 ml.) was added, producing a dark green solution. Exposure of this solution to the air caused it first to turn brownish and then rapidly reddish purple. The solution was filtered through Super-Cel and then treated with excess *n*-butyl ammonium bromide in ethanol. The dropwise addition of water to this solution caused the product to crystallize as dark purple platelets. These were twice recrystallized from acetone–water and dried in air to give 1.2 g. (27%) of product; m.p. 201–203.5°.

Anal. Calcd.: C, 62.78; H, 8.85; N, 2.93; S, 20.11. Found: C, 62.68; H, 9.05; N, 2.95; S, 19.56.

$[(n\text{-}C_4H_9)_4N]_2[V(S_2C_6H_3\cdot CH_3)_3]$.—The procedure for this complex was exactly analogous to that for $[(n\text{-}C_4H_9)_4N]_2[V(S_2C_6H_4)_3]$, the sodium salt being prepared in liquid ammonia from toluene-3,4-dithiol and sodium. Erratic yields were obtained in this reaction and considerable care has to be exercised to ensure that the vanadium trichloride is anhydrous and that the initial reaction takes place under anerobic conditions so as to generate the $[V(S_2C_6H_3\cdot CH_3)_3]^{-3}$ anion prior to its aerial oxidation. The product is a dark red-purple microcrystalline powder, m.p. 188–190°.

Anal. Calcd.: C, 63.74; H, 9.09; N, 2.81; S, 19.27. Found: C, 64.07; H, 9.06; N, 2.74; S, 20.83.

$[(C_6H_5)_4As][VS_6C_6(CN)_6]$.—A mixture of 3.70 g. of $[(C_6H_5)_4As]_2[VS_6C_6(CN)_6]$ and 2.40 g. of $[MoS_6C_6(CF_3)_6]$ was refluxed under dry nitrogen in dry dichloromethane for 2.5 hr. The solution became intensely blue and was filtered to remove a small amount of unreacted molybdenum complex. The filtrate was treated with 400 ml. of dry carbon tetrachloride added slowly with agitation. Filtration followed by extensive washing with dry carbon tetrachloride (to remove $[(C_6H_5)_4As][MoS_6C_6(CF_3)_6]$) until the washings were very pale violet yielded the product (2.51 g., 95%) as shiny purple crystals. The material could not be purified further due to its sensitivity to moisture and reduction.

Anal. Calcd.: C, 50.58; H, 2.36; N, 9.83; S, 22.51. Found: C, 50.98; H, 2.63; N, 7.70; S, 19.02.

$[(C_2H_5)_4N][VS_6C_6(C_6H_5)_6]$.—A mixture of 120 g. of P_4S_{10} and 40 g. of benzoin was refluxed in 500 ml. of xylene for 10 hr. The solution was allowed to cool to room temperature and separated from the insoluble material by decantation. This solution was treated with the suspension of a halovanadium(III) complex[11] prepared by the reaction of 6.0 g. of anhydrous VCl_3 with 8.5 g. of tetraethylammonium bromide in 200 ml. of acetonitrile. Prior to the addition of the vanadium species the xylene solution presumably contained the thiophosphoric ester of the dithioacyloin.[12] The mixture was heated for 10 min. on a steam bath. The solution became red-brown and the vanadium species dissolved (further heating for 1 hr. caused no change.) To the hot solution was added 800 ml. of ethanol and 30 ml. of 0.1 *N* NaOH. The resultant solution was heated to boiling; the solution first became deep green and then rapidly turned very dark blue-black. Boiling was continued for 20 min. and was accompanied by separation of dark needles from the now pale green solution. Filtration of the hot solution followed by washing with hot xylene (50 ml.), hot ethanol (100 ml.), and ligroin (50 ml.) yielded the product as very dark blue shiny needles (6.5 g.). The product, although obtained in crystalline form at this point, did not analyze satisfactorily (found: C, 63.49, 63.59; H, 5.12, 5.39; N, 1.30, 1.21; S, 19.93, 20.20), but was pure enough for the preparation of $[VS_6C_6(C_6H_5)_6]$ (*vide infra*). The product was purified by Soxhlet extraction using dichloromethane, in which it is sparingly soluble ($\sim 10^{-3}$ *M*) and forms intensely blue solutions. Very dark blue crystals were isolated; m.p. >300°.

Anal. Calcd.: C, 66.12; H, 5.55; N, 1.54; S, 21.18; V, 5.61. Found: C, 65.88, 66.03; H, 5.48, 5.55; N, 1.36, 1.53; S, 21.43, 21.56; V, 5.48, 5.76. Calcd. for $[(C_2H_5)_4N][VS_4C_4(C_6H_5)_4]$: C, 64.93; H, 6.05; N, 2.10; S, 19.26; V, 7.65.

$[VS_6C_6(C_6H_5)_6]$.—Crude $[(C_2H_5)_4N][VS_6C_6(C_6H_5)_6]$ (4.0 g.) was added to a solution of 3.2 g. of iodine in 400 ml. of dichloromethane, and the mixture was shaken vigorously for 5 min. The intense violet solution was then treated with 500 ml. of ethanol, producing a red-brown solution and the separation of small platelets. These were collected, washed with ethanol until the washings were very pale violet, washed twice with 25 ml. of *n*-pentane, and dried in the air. The product (red-purple platelets, 2.95 g., 86%, m.p. 232–234°) did not analyze satisfactorily at this point. Final purification was effected by Soxhlet extraction with dichloromethane, in which the product is sparingly soluble and forms an intense violet solution. Very dark purple crystals were isolated, m.p. 250–252° dec.

Anal. Calcd.: C, 64.84; H, 3.89; S, 24.73; V, 6.55. Found: C, 64.09, 64.26; H, 3.82, 4.03; S, 24.23, 23.98; V, 6.37, 6.47. Calcd. for $[VS_4C_4(C_6H_5)_4]$: C, 62.79; H, 3.76; S, 23.94; V, 9.51.

Reduction of $[VS_6C_6(C_6H_5)_6]$.—Pure $[VS_6C_6(C_6H_5)_6]$ (1.5 g.) was suspended in 300 ml. of ethanol and treated with 30 ml. of 10% ethanolic hydrazine solution. A deep blue color developed. The solution was filtered and treated with 2.0 g. of tetraethylammonium bromide in 30 ml. of ethanol. The product imme-

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[9] R. Adams, W. Reifschneider, and A. Ferretti, *Org. Syn.*, **42**, 22 (1962).

[10] A. Ferretti, *ibid.*, **42**, 54 (1962).

[11] D. E. Scaife, Abstracts, International Conference on Coordination Chemistry, Special Publication No. 13, The Chemical Society, London, 1959, pp. 152, 153; R. S. Nyholm, *Croat. Chem. Acta*, **33**, 157 (1961).

[12] G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964).

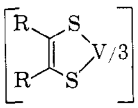
diately crystallized as blue platelets which were collected and washed with 50 ml. of absolute ethanol and 25 ml. of *n*-pentane. The product was then Soxhlet-extracted with dichloromethane to yield 1.2 g. (69%) of very dark blue crystals which were shown to be $[(C_2H_5)_4N][VS_6C_6(C_6H_5)_6]$.

Anal. Found: C, 65.97, 66.02; H, 5.53, 5.74; N, 1.51, 1.56; S, 21.01, 21.21; V, 5.54, 5.75.

Physical Measurements.—Measurements of magnetic susceptibilities, electron paramagnetic resonance, conductivities, and polarographic half-wave potentials were made as previously described.[2] E.p.r. measurements were performed on solutions prepared from analyzed complexes except for measurements of $[VS_6C_6(C_6H_5)_6]^{-2}$, which was generated in the microwave cavity by controlled potential electrolysis at −1.0 v. (*cf.* Table II), and $[V(dipy)_3]$,[13,14] which was obtained by reduction of $[V(dipy)_3]I_2$[13] with zinc amalgam[14] in pyridine solution.

Results and Discussion

Synthetic Studies.—The compounds described in this work are of the general types **1** and **2**. Those of



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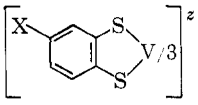

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type **1** with R = CF_3, $z = -2$; R = CF_3, CN, C_6H_5, $z = -1$; R = C_6H_5, $z = 0$ and the complexes of type **2** for which X = H, CH_3, $z = -2$ clearly represent an extension of our previous studies[2] on tris-1,2-dithiolato complexes. The composition of all of the new compounds has been firmly established by elemental analysis. The conductance data in nitromethane solution show that all of the salts are uni-univalent or bi-univalent electrolytes. In addition the existence of $[VS_6C_6(C_6H_5)_6]^{-2}$ has been established from polarographic and paramagnetic resonance studies (Tables II and III). Like the complexes described previously[2] all of these species are members of a series which are interrelated by one-electron transfer reactions. Our synthetic studies were directed primarily toward the preparation of a neutral vanadium complex of type **1** or **2** by oxidation of a mono- or dianion or by direct synthesis. Such a vanadium complex might reasonably have been expected to be paramagnetic and to have an unpaired electron in the (a_1*) orbital.

TABLE I
CONDUCTIVITIES AND MAGNETIC MOMENTS OF TRIS VANADIUM COMPLEXES[a]

Compound	Λ[b]	μ_{eff}, B.M.[c]
$[(C_6H_5)_4As]_2[VS_6C_6(CN)_6]$	140	1.82
$[(C_6H_5)_4As][VS_6C_6(CN)_6]$	74	∼0[e]
$[(C_6H_5)_4As]_2[VS_6C_6(CF_3)_6]$	142	1.83
$[(C_6H_5)_4As][VS_6C_6(CF_3)_6]$	56	∼0[e,f]
$[(n\text{-}C_4H_9)_4N]_2[V(S_2C_6H_3CH_3)_3]$	122	1.73
$[(C_2H_5)_4][VS_6C_6(C_6H_5)_6]$	58	∼0[e,f]
$[VS_6C_6(C_6H_5)_6]$	. . .	1.80
$[V(dipy)_3]$	. . .	1.90[d]

[a] All data obtained at ambient room temperature, 23–26°. [b] Cm.^{2} mole^{-1} ohm^{-1} in $\sim 10^{-3}$ *M* nitromethane solutions. [c] All measurements refer to solids. [d] Datum from ref. 13. [e] Small residual paramagnetism observed. [f] $\chi_{cor}^{m} \cong +300 \times 10^{-6}$.

TABLE II
POLAROGRAPHIC HALF-WAVE POTENTIALS IN ACETONITRILE SOLUTION

Couple	$E^1/_2$, v.[a]
$[VS_6C_6(C_6H_5)_6]^{-2} \rightleftharpoons [VS_6C_6(C_6H_5)_6]^- + e^-$	−0.71
$[VS_6C_6(CN)_6]^{-3} \rightleftharpoons [VS_6C_6(CN)_6]^{-2} + e^-$	−0.49
$[V(S_2C_6H_3CH_3)_3]^{-3} \rightleftharpoons [V(S_2C_6H_3CH_3)_3]^{-2} + e^-$	−0.18
$[V(S_2C_6H_4)_3]^{-3} \rightleftharpoons [V(S_2C_6H_4)_3]^{-2} + e^-$	−0.12
$[VS_6C_6(C_6H_5)_6]^- \rightleftharpoons [VS_6C_6(C_6H_5)_6]^0 + e^-$	+0.30
$[VS_6C_6(CF_3)_6]^{-2} \rightleftharpoons [VS_6C_6(CF_3)_6]^- + e^-$	+0.47
$[VS_6C_6(CN)_6]^{-2} \rightleftharpoons [VS_6C_6(CN)_6]^- + e^-$	+0.66

[a] Obtained using 0.05 *M* $[(n\text{-}C_3H_7)_4N](ClO_4)$ as supporting electrolyte and a platinum electrode; all results corrected for *IR* drop in the polarographic cell; potentials measured relative to s.c.e.; the ease of oxidation of the reduced forms decreases as the potentials become more positive.

TABLE III
ELECTRON PARAMAGNETIC RESONANCE DATA

Complex	Solvent	$\langle g \rangle$[c]	$\langle A \rangle$, gauss[e]	$\left\lvert \frac{a_2}{a_3} \right\rvert$[f]
$[VS_6C_6(C_6H_5)_6]^{-2}$ [a]	CH_3CN	1.9811	63.9 ± 0.2	1.1
$[VS_6C_6(C_6H_5)_6]$	CH_2Cl_2	1.9900	61.5 ± 0.2	0.4
$[V(S_2C_6H_3CH_3)_3]^{-2}$	CH_2Cl_2	1.9782	65.8 ± 0.3	1.4
$[V(S_2C_6H_4)_3]^{-2}$	CH_2Cl_2	1.9779	65.2 ± 0.3	1.4
$[VS_6C_6(CF_3)_6]^{-2}$	CH_2Cl_2	1.9829	62.4 ± 0.2	1.1
	CH_3CN	1.9822	62.1 ± 0.2	1.3
$[VS_6C_6(CN)_6]^{-2}$	$CHCl_3$–DMF	1.980[d]	63.3 ± 0.5	1.1
$[V(dipy)_3]$[b]	C_5H_5N	1.9830	84.0 ± 0.5	0.9

[a] Generated by electroreduction of $[VS_6C_6(C_6H_5)_6]^-$. [b] Produced by reduction of $[V(dipy)_3]I_2$ with zinc amalgam. [c] Estimated accuracy ±0.0005 unless noted otherwise. [d] ±0.001. [e] V^{51}, ∼100%, $I = {}^7/_2$. [f] ±25%.

The reaction of $V(CO)_6$ and $(CF_3)_2C_2S_2$ in inert solvents under rigorously dry conditions yielded mainly the monoanion with no direct evidence for the formation of $[VS_6C_6(CF_3)_6]$. Oxidative polarography of the monoanion showed no wave at potentials less than +1.8 v. *vs.* s.c.e. It is possible that the neutral complex, if formed, is reduced by the unreacted starting materials or by contaminants. In an attempted oxidation of $[V(S_2C_6H_4)_3]^{-2}$ in dichloromethane with two equivalents of $[MoS_6C_6(CF_3)_6]$ no vanadium complex was isolated, but reduction to $[MoS_6C_6(CF_3)_6]^-$ occurred with apparent decomposition of the vanadium complex.[15]

Examination of the half-wave potentials of these complexes (*cf.* Table II) and of those isolated previously[2,3] shows that the oxidative stability of a given

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(13) S. Herzog, *Z. anorg. allgem. Chem.*, **294**, 155 (1958).

(14) S. Herzog, *Naturwissenschaften*, **43**, 35 (1956).

(15) The $[V(S_2C_6H_3X)_3]^{-2}$ complexes did not undergo a clean polarographic oxidation, unlike the other dianions studied (*cf.* Table II). Instead, an ill-defined discontinuous wave occurred in the range +0.4 to +0.6 v.

complex depends on the nature of the ligand and for $R_2C_2S_2$-type complexes is particularly sensitive to the R substituent. For the planar complexes $[MS_4C_4R_4]^z$ with M = Ni the ease of oxidation is $C_6H_5 \gg CF_3 > CN$. This prompted us to attempt the synthesis of the complex briefly reported by Schrauzer, *et al.*,[12] (in a note appearing concurrently with this investigation) to be $[VS_4C_4(C_6H_5)_4]$. Using apparently similar reaction conditions we isolated the tris complexes $[VS_6C_6(C_6H_5)_6]^{-1,0}$ as air-stable crystalline solids. In our hands the treatment of the reaction product of benzoin and P_4S_{10} with tetraalkylammonium halovanadate(III) in basic alcoholic solution gave $[(C_2H_5)_4N][VS_6C_6(C_6H_5)_6]$ directly. The neutral tris complex $[VS_6C_6(C_6H_5)_6]$ was readily prepared by iodine oxidation of this salt. The neutral complex, however, is reduced to the monoanion with mild reducing agents, such as OH^-, which is apparently why it was obtained directly in our reactions. Reduction of $[VS_6C_6(C_6H_5)_6]$ with alcoholic hydrazine followed by precipitation as the sparingly soluble tetraethylammonium salt gave, as expected, $[(C_2H_5)_4N][VS_6C_6(C_6H_5)_6]$, which was shown to be identical with that produced in the direct synthesis. The dianion $[VS_6C_6(C_6H_5)_6]^{-2}$, whose half-wave potential is −0.71 v. *vs.* s.c.e., is very readily oxidized. This species was generated for the paramagnetic resonance studies in the microwave cavity by controlled potential electroreduction.[16a]

We have obtained no evidence for the formation of $[VS_4C_4(C_6H_5)_4]$ or its anionic forms in the reactions carried out in this work.[16b] The X-ray powder patterns of the neutral vanadium complex and $[NiS_4C_4(C_6H_5)_4]$ show the expected lack of isomorphism.

Paramagnetic Resonance Results.—The following discussion and qualitative interpretation of the e.p.r. results is made in connection with our previously developed arguments,[2] to which reference should be made at this point. In Table III, we report the values of the isotropic hyperfine constant, $\langle A \rangle$, the isotropic g value, $\langle g \rangle$, and the ratio $|a_2/a_3|$. The latter quantity reflects the anisotropies in the g value and in the hyperfine interaction.[17] It is apparent, from examination of Table III, that in all the dianions the values of $\langle g \rangle$ and $\langle A \rangle$ are quite similar, although small differences outside of experimental error are apparent. The complex $[VS_6C_6(CF_3)_6]^{-2}$ was measured in two solvents to determine whether solvent effects on these parameters were important. The solvent effect was found to be negligible. The values of $|a_2/a_3|$ were also similar for the dianion, which indicates that the ratio $\Delta g/(A_\parallel - A_\perp)$ does not vary much among them. In a previous paper,[2] we determined the parameter $|A_\parallel - A_\perp|$ for the complex $[VS_6C_6(CN)_6]^{-2}$ from the spectrum of a frozen glass. The value was found to be $|A_\parallel - A_\perp| = 55 \pm 3$ gauss. This, along with the measured value of $|a_2/a_3|$, gave $|\Delta g| = 0.005 \pm 0.002$, a very small g value anisotropy. It was concluded that the orbital of the unpaired electron is primarily localized on the ligand system. Because of the similarities between the values of $\langle g \rangle$, $\langle A \rangle$, and $|a_2/a_3|$ for the dianions studied here with the values for $[VS_6C_6(CN)_6]^{-2}$, we infer that the electronic structures of all dianions are the same.

We postulated[2] that the electronic configuration of the complex $[VS_6C_6(CN)_6]^{-2}$ involves (in D_3 symmetry) an electron pair in the antibonding a_1^* orbital, which should be mainly localized on the metal, and that the unpaired electron is in a molecular orbital (possibly a_2^*) which is mainly localized on the ligand system. This orbital can be expected to be essentially nonbonding since symmetry permits admixture with the metal $4p_z$ orbital only. The complex $[VS_6C_6(C_6H_5)_6]$ contains two less valence electrons (neglecting ring substituents) than $[VS_6C_6(CN)_6]^{-2}$ and it could reasonably be expected to have the $(a_1^*)^1$ configuration. This configuration would be characterized by relatively larger values of $|\Delta g|$ and $|A_\parallel - A_\perp|^4$ than those for an l^1-type configuration. Although these quantities were not measured directly for $[VS_6C_6(C_6H_5)_6]$, $g = 1.9900$ indicates that $|\Delta g|$ is even smaller in this complex than in the dianions. If for this complex and the dianions $|A_\parallel - A_\perp|$ is approximately the same (which is suggested by the similarity of the $\langle A \rangle$ values), the smaller value of $|a_2/a_3|$ is also consistent with a smaller $|\Delta g|$.

All available evidence suggests that the unpaired electron is even less localized on the metal in $[VS_6C_6(C_6H_5)_6]$ than in the dianions. Oxidation of a complex $([VS_6C_6(C_6H_5)_6]^{-2})$ with the $(a_1^*)^2 l^1$ configuration does *not* give a species with the $(a_1^*)^1$ configuration in the only case which could be studied. This result is inconsistent with the previous ordering of molecular orbitals in the dianions,[2] *viz.*, $a_2^* > a_1^*$. We cannot offer a definite explanation of this observation, but point out two possibilities with which the available e.p.r. results are consistent but are not capable of differentiating. Removal of two electrons may invert the order of a_2^* and a_1^*, leaving the oxidized complex with the $(a_2^*)^1$ configuration. Alternatively, the configuration of the dianion might be $(a_1^*)^2(a_2^*)^2(e^*)^3$ and that of the neutral complex $(a_1^*)^2(a_2^*)^2(e^*)^1$.[19]

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(16) (a) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960); (b) after the completion of this investigation we have been informed by G. N. Schrauzer (private communication) that the complex reported by him to be $[VS_4C_4(C_6H_5)_4]$ is actually $[VS_6C_6(C_6H_5)_6]$, and that a correction will be published.

(17) According to the expressions for the paramagnetic resonance line widths of free radicals in liquids developed by Kivelson,[18] this ratio is given by

$$|a_2/a_3| = -\frac{7}{2}\Delta g H_0/(A_\parallel - A_\perp)$$

where axial symmetry is assumed for the complex. The individual quantities a_2 and a_3 are obtained by fitting the experimental line widths to a quadratic expression of the form

$$1/T_2 = (\pi\sqrt{3})^{-1}(a_1 + a_2 M_I + a_3 M_I^2)$$

where M_I is the nuclear spin quantum number of V^{51}. Δg is given by $(g_\parallel - g_\perp)$, and $1/T_2$ is the experimental line width between derivative peaks of the Lorentzian lines.

(18) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).

(19) Reference to the previous discussion[2] of the electronic configurations of the dianions will reveal that the $(e^*)^4$ configuration is implicit in the postulation of the $(a_1^*)^2(a_2^*)^1$ configuration. These e^* orbitals are admixtures of the local antibonding π-orbitals of the entire ligand system with the appropriate metal orbitals.

Solvent interactions and/or Jahn–Teller distortions would be expected to lift the orbital degeneracies of these configurations and reduce the orbital contributions to the g values. It should be pointed out that these configurations would be expected to lead to extremely short spin-lattice relaxation times *if* the e* orbitals were made up of a large contribution from metal d-orbitals. However, since the paramagnetic resonance results indicate that if these configurations are correct, these orbitals have very little admixture of metal orbitals, the situation might be analogous to the effect of orbital degeneracy in the benzene[20] and cyclooctatetraene[21] negative ions. In these cases the spin-lattice relaxation is only slightly enhanced in $C_6H_6^{\dot{-}}$ and not significantly in $C_8H_8^{\dot{-}}$. The principal objection to the $(e^*)^{1,3}$ configurations is that the monoanions are diamagnetic rather than having $S = 1$. However, if the e* orbitals are strongly delocalized on the ligands, electron repulsion terms may be relatively unimportant. Consequently, lower symmetry electrostatic fields from solvent interactions might remove the orbital degeneracy of e* sufficiently to yield a singlet ground state for the monoanions.

Finally, we have examined the e.p.r. spectrum of tris(dipyridyl)vanadium, $[V(dipy)_3]$.[13] This complex is known to have trigonal symmetry.[22] Its g value has been measured previously.[23] Tris(dipyridyl) complexes are generally considered to contain the metal in its lowest formal valence state consistent with the total charge on the complex; in this case the metal has been considered as V(0) (d^5).[13,14] Orgel[7] has discussed the electronic configurations of certain $[M(dipy)_3]^z$ complexes and has suggested the $(e_a^*)^4$ configuration (in our notation[2]) for $[Ti(dipy)_3]$. The $(e_a^*)^4(a_1^*)^1$ configuration for $[V(dipy)_3]$ is unlikely by the arguments already given.[2] The e.p.r. results for this complex are quite similar to those for the other vanadium complexes studied. We infer that the odd electron in $[V(dipy)_3]$ is likewise strongly delocalized on the ligand and suggest that the electronic structure may be analogous to that for $[VS_6C_6(C_6H_5)_6]$.

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The Preparation and Characterization of Compounds Containing both Hexabromorhenate(IV) and the Trirhenium Nonabromide Group[1]

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From solutions of rhenium(III) bromide in concentrated aqueous HBr, compounds with the general formula $M_2Re_4Br_{15}$ (M = quinolinium, pyridinium, or tetraethylammonium ion) have been isolated. Evidently there is oxidation of some Re(III) to Re(IV), and, by using equimolar quantities of Re_3Br_9 and $[ReBr_6]^{2-}$, the quinolinium compound can be obtained more directly. A single crystal X-ray diffraction investigation shows the presence of Re_3Br_3 groups and $ReBr_6$ groups in the quinolinium compound. The visible spectra of the $M_2Re_4Br_{15}$ compounds indicate that Re_3Br_9 and $[ReBr_6]^{2-}$ are present. From the X-ray work, the dimensions of the Re_3Br_9 group have been established and it is clear that this group is structurally homologous to the Re_3Cl_9 group which is known to occur in numerous compounds derived directly from rhenium(III) chloride and in rhenium(III) chloride itself.

Introduction

Recent studies in this[3–7] and other[8,9] laboratories have shown that compounds derived from the chloride and bromide of rhenium(III) have remarkable chemical and structural properties. The chloro compounds have been most extensively characterized, but the existence of the diverse species $Re_3Br_9L_3$, $Re_2Br_8^{2-}$, $ReBr_4^-$, and $[ReBr_4(H_2O)_2]^-$ has been briefly reported.[7,9a]

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[2] National Science Foundation Predoctoral Fellow (1962–present); Woodrow Wilson Honorary Fellow (1962–1963).

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[9a] NOTE ADDED IN PROOF.—In a preliminary communication [F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964)] the preparation of a number of derivatives of Re_3Br_9 has been described and spectroscopic evidence presented to justify their formulation as Re_3Br_9 derivatives. In another preliminary communication [J. E. Fergusson and B. R. Robinson, *Proc. Chem. Soc.*, 189 (1964)] the isolation of compounds which probably contain $[Re_3Br_{10}]^-$ and $[Re_3Br_{10}py_2]^-$ ions has been reported.