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Electronic Structure of $V_2(CO)_8(\mu\text{-}PPh_2)_2$ and $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2$ by Electron Spin Resonance Study of Their Ion Radicals

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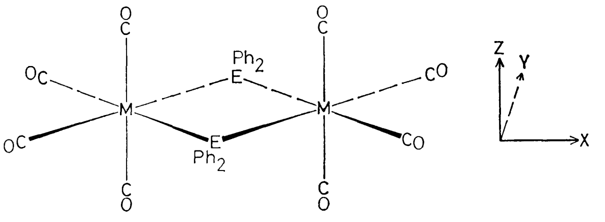
The anion radical of $V_2(CO)_8(\mu\text{-}PPh_2)_2$ and the cation radical of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2$ are generated by chemical reduction of the vanadium complex with $LiBHEt_3$ or potassium naphthalenide and by radiochemical oxidation of the manganese complex in frozen Freon mixture, respectively. Their anisotropic ESR spectra show that the V_2P_2 and the Mn_2As_2 rhomboids are planar. Their g and hyperfine splitting tensors are analyzed on the basis of a qualitative molecular orbital scheme for metal-metal bonds developed from a hypothesis that metal-ligand interactions are larger than metal-metal interactions. The odd electron orbital of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ is assigned to the metal-metal π^* MO and the odd electron density on the vanadium d AO is estimated as 0.21. The odd electron of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ is concluded to be accomodated in the metal-metal σ^* MO and odd electron densities on manganese and arsenic atoms are evaluated as $\rho(\text{Mn d})=0.25$ and $\rho(\text{As p})=0.08$ or 0.16, respectively. Order of magnitude estimates of orbital energy differences between metal-metal MO's are obtained from analyses of g tensors as $\varepsilon(\pi^*)-\varepsilon(\sigma)\simeq 0.4$ and $\varepsilon(\pi^*)-\varepsilon(\delta)\simeq 0.9$ eV for the anionic divanadium complex and $\varepsilon(\sigma^*)-\varepsilon(\delta^*)\simeq 1.1$ and $\varepsilon(\sigma^*)-\varepsilon(\pi)\simeq 1.4$ eV for the cationic dimanganese complex.

There has been considerable recent interest in electronic structures of complexes of $M_2(CO)_8(\mu\text{-}PR_2)_2$ with D_{2h} geometries where M is vanadium, chromium or manganese. Metal-metal bond lengths are shown by Vahrenkamp[1)] to be consistent with formal bond orders of 2, 1 and 0 deduced from the 18 electron rule for the vanadium, the chromium and the manganese complexes, respectively. Molecular orbital (MO) calculations by Teo, *et al.*[2)] and Shaik, *et al.*[3)] gave $\pi^2\delta^2\sigma^2\delta^{*2}$ double bond, $\pi^2\delta^2\delta^{*2}\sigma^2\pi^{*2}$ single bond and $\pi^2\delta^2\delta^{*2}\pi^{*2}\sigma^2\sigma^{*2}$ no bond configurations for metal-metal bonds of the vanadium, the chromium and the manganese complexes, respectively.



A preliminary ESR study of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ has been reported from this laboratory,[4)] and its odd electron orbital has been assigned to the b_{3u} MO with a metal-metal σ^* character and consisting mainly of the Mn $d_{x^2-y^2}$ and As p_x atomic orbitals (AO), with which calculated MO schemes[2,3)] are consistent. We have been trying to extend the study to ion radicals of bioctahedral molybdenum, which is located in the same column as chromium in the periodic table, and vanadium complexes. Meanwhile, Madach and Vahrenkamp[5)] reported that $V_2(CO)_8(\mu\text{-}PMe_2)_2$ can be reduced chemically into a stable anion radical and that its solution ESR spectrum shows hyperfine splittings due to pairs of vanadium and phosphorus nuclei. The extended Huckel MO calculation[3)] predicted that its odd electron will occupy the metal-metal π^* MO, into which the phosphorus valence shell AO's are symmetry-forbidden to mix. The phosphorus splitting in the solution ESR spectrum was thus mentioned as somewhat confusing.[5)] Since metal d AO's play dominant roles in the formation of metal-metal bond rather than metal s AO's, anisotropic spectra are more informative for the study of electronic structure of the anion radical. We report here a study of anisotropic ESR spectra of frozen solutions of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ and $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ in order to obtain quantitative informations about their electronic structures.

Results

$V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$. When a dilute benzene solution of $V_2(CO)_8(\mu\text{-}PPh_2)_2$ is mixed with an equimolar amount of potassium naphthalenide at room temperature, a paramagnetic vanadium complex is formed immediately after the mixing. The solution exhibits an isotropic ESR spectrum split into a 15-fold multiplet of $23.4\times10^{-4}\,\text{cm}^{-1}$ due to a pair of equivalent vanadium nuclei (99.8% natural abundance, $I=7/2$) split further into triplets of $6.0\times10^{-4}\,\text{cm}^{-1}$ due to a pair of equivalent phosphorus nuclei (100%, $I=1/2$) at $g=2.019$. The spectrum is quite similar to that of $V_2(CO)_8(\mu\text{-}PMe_2)_2^{-\cdot}$[5)] and is attributed to $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$.

The same anion radical is formed gradually in 0.5—1 h when the parent complex is reacted in benzene with 2—3 equivalents of $LiBHEt_3$. This slow formation of the anion radical suggests that this radical may be generated by electron transfer from an intermediate(s) formed in a foregoing step(s) rather than by direct electron transfer from the hydroborate to the parent neutral complex. The anisotropic spectra of the anion radical in benzene solutions frozen at 77 K are obtained at X-, K-, and Q-bands (Fig. 1). These anisotropic spectra fit a rhombic spin Hamiltonian in which two vanadium nuclei are magnetically equivalent and three principal directions of the g tensor and those of the vanadium hyperfine splitting tensor are parallel to each other. This spin Hamiltonian shows that the V_2P_2 rhomboid of the anion radical is planar corresponding to a D_{2h} geometry of the anion radical, otherwise even the two vanadium nuclei can not be magnetically equivalent in the anisotropic spectra.[6)] The principal values of the g tensor are:

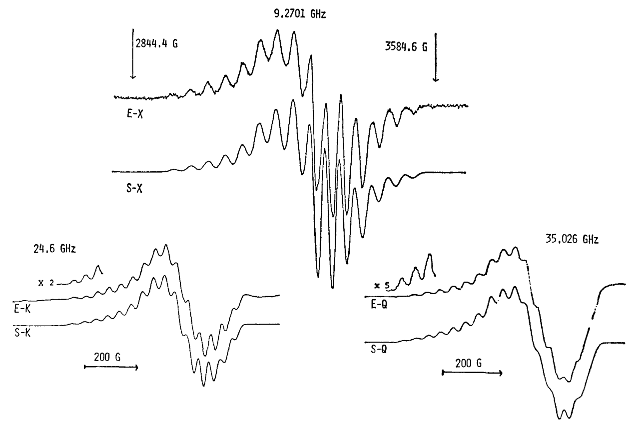


Fig. 1. Experimental (E-) and simulated (S-) ESR spectra of frozen benzene solutions of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ observed at X- (X), K- (K), and Q-bands (Q) at 77 K.

$$g_{\alpha\alpha} = 2.001,$$
$$g_{\beta\beta} = 2.018,$$
$$g_{\gamma\gamma} = 2.038,$$

and those for the vanadium splitting tensor are:

$$|A_{\alpha\alpha}(V)|/hc = |A_{\beta\beta}(V)|/hc = (15\pm2)\times10^{-4}\,\mathrm{cm}^{-1},$$
$$|A_{\gamma\gamma}(V)|/hc = 39.2\times10^{-4}\,\mathrm{cm}^{-1},$$

where α, β, and γ designate the rectangular axes for the spin Hamiltonian. It should be pointed out that the vanadium splitting tensor is axially symmetric. Hyperfine splittings due to the phosphorus nuclei are unfortunately hidden behind the line width in the anisotropic spectra.

$Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$. The analysis of the ESR spectra of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ has been reported in the preliminary report.[4] The principal values of the g tensor are:

$$g_{\alpha\alpha} = 2.031,$$
$$g_{\beta\beta} = 2.025,$$
$$g_{\gamma\gamma} = 2.001,$$

and those for the manganese and arsenic hyperfine splitting tensors are:

$$|A_{\alpha\alpha}(Mn)|/hc = |A_{\beta\beta}(Mn)|/hc \leqq 3\times10^{-4}\,\mathrm{cm}^{-1},$$
$$|A_{\gamma\gamma}(Mn)|/hc = 43.0\times10^{-4}\,\mathrm{cm}^{-1},$$
$$|A_{\alpha\alpha}(As)|/hc = 14.4\times10^{-4}\,\mathrm{cm}^{-1},$$
$$|A_{\beta\beta}(As)|/hc = 41.5\times10^{-4}\,\mathrm{cm}^{-1},$$
$$|A_{\gamma\gamma}(As)|/hc = 39.9\times10^{-4}\,\mathrm{cm}^{-1}.^{4)}$$

Discussion

Qualitative Molecular Orbital Scheme for Metal-Metal Bond. The results of molecular orbital calculations of $M_2(CO)_8(\mu\text{-}PH_2)_2$[2,3] can be reproduced qualitatively from a hypothesis that metal-ligand interactions are larger than metal-metal interactions (Fig. 2). Larger interactions are considered first and weaker ones are taken into account thereafter. The present qualitative molecular orbital scheme starts from an electronic structure for a mononuclear fragment with a pseudoctahedral geometry, then two mononuclear fragments are combined together through weak metal-metal interactions into the bioctahedral complex, $M_2(CO)_8(\mu\text{-}ER_2)_2$.

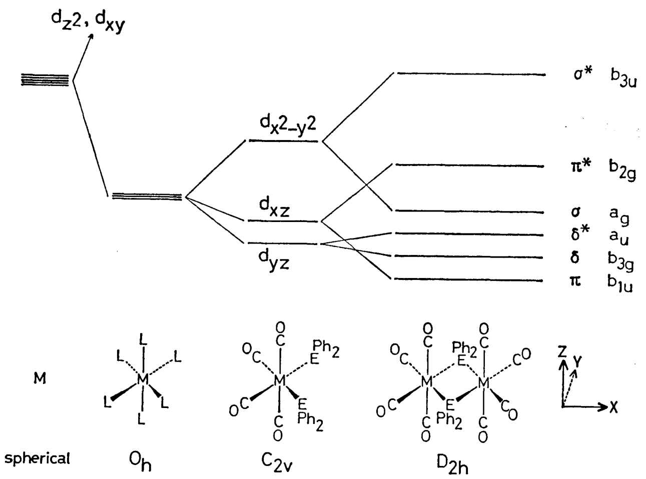


Fig. 2. Construction of qualitative metal-metal MO's for $M_2(CO)_8(\mu\text{-}EPh_2)_2$.
The σ^* MO is the odd electron orbital of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ with eleven d electrons. The π^* MO is the odd electron orbital of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ which has nine d electrons. Relative orbital energy levels of δ^* and π MO's for the divanadium anion and those between σ and δ MO's for the dimanganese cation do not have much significances.

When the mononuclear fragment is octahedral (O_h), the e_g d orbitals (d_{z^2} and d_{xy}) are located above the t_{2g} d orbitals ($d_{x^2-y^2}$, d_{xz}, and d_{yz}) in the energy diagram. When the symmetry of the fragment is lowered to the pseudoctahedral one (C_{2v}), the degeneracy of the t_{2g} orbitals is broken and the orbital energy sequence is expected to be $d_{x^2-y^2} > d_{xz} > d_{yz}$. The orbital energy of the d_{yz} is the lowest because this orbital interacts with vacant π^* MO's of three carbonyl ligands and its interaction with lone pair orbitals of the ligands is symmetry-forbidden. The $d_{x^2-y^2}$ orbital has the highest energy, since this orbital interacts with π^* MO's of only two carbonyls and with lone pair orbitals of six ligands whereas the d_{xz} orbital interacts with vacant π^* MO's of three carbonyls and lone pair orbitals of the two axial carbonyls.

When a pair of pseudoctahedral fragments are joined together to from a bioctahedral (D_{2h}) dimetallic complex, bonding and antibonding pairs of MO's with metal-metal σ, π, and δ symmetries are formed from the t_{2g} d orbitals through relatively weak metal-metal interactions. Among these six MO's, the σ^* MO has been calculated to have the highest orbital energy, and the π^* MO has the second highest energy.[2,3] The energies of the metal-metal MO's derived from the e_g d orbitals (d_{xy} and d_{z^2}) are far higher than those of the metal-metal MO's arising from the t_{2g} d orbitals ($d_{x^2-y^2}$, d_{xz}, and d_{yz}). This is because of the aforementioned hypothesis.

In $V_2(CO)_8(\mu\text{-}PR_2)_2$, eight "d electrons" from a pair of V(I) ions occupy the lowest four metal-metal MO's giving a double bond configuration of $\pi^2\delta^2\delta^{*2}\sigma^2$. Upon one electron reduction of this complex, the odd electron enters into the metal-metal π^* MO. The formal metal-metal bond order of the resulted anion radical is 1.5. In $Mn_2(CO)_8(\mu\text{-}AsR_2)_2$, twelve "d electrons" from a pair of Mn(I) ions occupy the six metal-metal MO's derived from the t_{2g} d orbitals, resulting in an electronic configuration of $\pi^2\delta^2\delta^{*2}\sigma^2\pi^{*2}\sigma^{*2}$ with a formal metal-metal bond order of zero. Upon one electron oxidation of this dimanganese complex, the odd electron remains in the σ^* MO. The formal metal-metal bond order of the resulted cation is 0.5.

The purposes of the present study are (i) examination of the validity of the present qualitative MO scheme in interpretations of ESR spectra, (ii) experimental estimation of the weight of d AO's in metal-metal MO's, and (iii) experimental estimation of differences between energies of metal-metal MO's.

Symmetry of Odd Electron Orbital of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$. A shift of a principal value of a g tensor, g_{xx} for example, from the free electron value of $g_e=2.0023$ has the following form:[7]

$$\Delta g_{xx} \equiv g_{xx} - g_e = 2\sum_{n}^{\neq p} \langle \psi_p | \sum_k \zeta_k l_{kx} | \psi_n \rangle \times \langle \psi_n | \sum_k l_{kx} | \psi_p \rangle / (\varepsilon_p - \varepsilon_n), \tag{1}$$

where ψ and ε are the MO and its orbital energy with the subscripts of p and n standing for the odd electron orbital and for the other MO's, respectively, l_{kx} is the x component of the orbital angular momentum of an electron on the k-th atom, and ζ_k is its one-electron spin-orbit coupling constant. The y or z principal value can be expressed by changing x in this equation into y or z.

The large anisotropy in the vanadium hyperfine splitting tensor indicates that odd electron densities on vanadium 3d AO's are large. Orbital energy differences between the odd electron orbital and MO's with dominant metal characters, which appear as the denominator in Eq. 1, are smaller than those for ligand MO's in the present MO scheme. Thus the sign of the g shift in Eq. 1 can be predicted by taking only l-s couplings in vanadium atoms into account, although the l-s coupling constant for 3d AO's of V(I) (136 cm^{-1})[8] is not distinguishably large in comparison with those for phosphorus 3p (231 cm^{-1}),[9] oxygen 2p (152 cm^{-1})[9] and carbon 2p (28 cm^{-1})[9] AO's.[10] In this approximation, all the numerators in Eq. 1 are zero or positive and signs of g shifts can be correlated directly with those of denominators in Eq. 1. A vacant ψ_n induces a negative g shift and a doubly occupied ψ_n results in a positive g shift as long as the ψ_n and the odd electron orbital share a non-zero matric element of l-s couplings in the metals.

In the present qualitative MO scheme, the odd electron of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ is accomodated in the π^* (b_{2g}, d_{xz}^*) MO. The unique axis of the axially symmetric vanadium splitting tensor should be the molecular y axis. Table 1 summerizes the shifts of the principal values of the g tensor from g_e predicted by Eq. 1 and the qualitative MO scheme in Fig. 2. For example, the shift of g_{yy} from g_e, Δg_{yy}, arises from the doubly occupied σ (a_g, $d_{x^2-y^2}$) MO and an unoccupied a_g MO consisting mainly of d_{z^2} AO's. Since metal-metal electronic interactions are assumed to be smaller than metal-ligand interactions, the σ MO contribution is expected to dominate and a positive value of Δg_{yy} is expected.

Table 1. g Shift of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ with electronic configuration of $(\pi b_{1u})^2(\delta b_{3g})^2$-$(\delta^* a_u)^2(\sigma a_g)^2(\pi^* b_{2g})^1$ based on Eq. 1

$\Delta g_{\alpha\alpha}$	l_α[a)]	ψ_n[b)]	Occptn. of ψ_n	Sign of $\Delta g_{\alpha\alpha}$
Δg_{xx}	$l_x(b_{3g})$	b_{1g}, d_{xy}	unocc.	+
Δg_{yy}	$l_y(b_{2g})$	a_g, $d_{x^2-y^2}$, σ a_g, d_{z^2}	unocc. occ.	+
Δg_{zz}	$l_z(b_{1g})$	b_{3g}, d_{yz}, δ	occ.	+

a) Component of l and its symmetry in D_{2h}. b) MO's which share non-zero matrix elements of l_α with the odd electron orbital, $\psi_p=\pi^*$. The notation of [b_{3g}, d_{yz}, δ], for exsample, indicates that ψ_n is the b_{3g} MO constructed from V d_{yz} AO's and that ψ_n is the metal-metal δ MO.

These theoretical expectations deduced from the qualitative MO scheme in Fig. 2 are consistent with the experimental results under the assignment of the spin Hamiltonian axes of α, β, and γ to the molecular axes of x, z, and y, respectively.

Odd Electron Distribution in $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$. The odd electron density on the vanadium d_{xz} AO, ρ(V xz), can be correlated with the vanadium hyperfine splitting tensor with corrections for second order effects of unquenched orbital angular momenta of electrons as follows:[11,12]

$$\left.\begin{aligned} A_{xx}(V) &= a(V) - B(V\,xz)\rho(V\,xz) \\ &\quad - (7/4)B(V\,xz)\Delta g_{xx} \\ &\quad - (3/8)B(V\,xz)(\Delta g_{yy} - \Delta g_{zz}) \\ A_{yy}(V) &= a(V) + 2B(V\,xz)\rho(V\,xz) \\ &\quad - (7/4)B(V\,xz)\Delta g_{yy} \\ &\quad - (3/8)B(V\,xz)(\Delta g_{xx} + \Delta g_{zz}) \\ A_{zz}(V) &= a(V) - B(V\,xz)\rho(V\,xz) \\ &\quad - (7/4)B(V\,xz)\Delta g_{zz} \\ &\quad + (3/8)B(V\,xz)(\Delta g_{xx} + \Delta g_{yy}) \end{aligned}\right\} \tag{2}$$

$$a(V) = Q_V(V)\rho(V\,s) + Q_I(V)\rho(V\,xz), \tag{3}$$

where $2B$(V xz) is the parallel splitting constant of a vanadium nucleus with a unit odd electron density on its d_{xz} AO and a(V) is the vanadium Fermi contact term arising from the odd electron density on the vanadium 4s AO, ρ(V s), and from the spin polarization of the inner shell s electrons which is proportional to ρ(V xz). The coefficient, $Q_V(V)$ or $Q_I(V)$, is the Fermi contact term of a vanadium nucleus with a unit odd electron density on its 4s AO or on its 3d AO. The valence orbital parameters of $Q_V(V)$ and $2B$(V xz) have been evaluated as 1390×10^{-4} and $-83.4\times10^{-4}\ cm^{-1}$, respectively.[13] The inner shell parameter, $Q_I(V)$, can be estimated as $-(100\pm20)\times10^{-4}\ cm^{-1}$ from theoretical and experimental studies on ESR of mononuclear vanadium complexes.[14]

The isotropic vanadium splitting of $23.4\times10^{-4}\ cm^{-1}$, observed in the solution ESR spectrum, indicates that all the signs of the principal values of the vanadium splitting tensor are identical. Since the odd electron in the metal-metal π^* MO is symmetry-forbidden to delocalize onto vanadium 4s AO's, the Fermi contact term of the vanadium nuclei, $a(\mathrm{V})$, arises only from the inner shell spin polarization and should be negative due to the negative value of $Q_\mathrm{I}(\mathrm{V})$. These analyses result in the assignment of negative signs to all the principal values of the vanadium splitting tensor. By using Eq. 2, the Fermi contact term and the odd electron density on the vanadium d_{xz} AO are estimated as $a(\mathrm{V})/hc=-24.3\times10^{-4}\ \mathrm{cm}^{-1}$ and $\rho(\mathrm{V\ xz})=0.21$ respectively. Since $\rho(\mathrm{V\ s})=0$, Eq. 3 and the estimate of $\rho(\mathrm{V\ xz})=0.21$ give $a(\mathrm{V})/hc=(-16.8 - -25.2)\times10^{-4}\ \mathrm{cm}^{-1}$, which is consistent with the above estimation of $a(\mathrm{V})/hc=-24.3\times10^{-4}\ \mathrm{cm}^{-1}$ deduced from the analysis with Eq. 2. Present analyses are self-consistent. The relatively small odd electron density on the vanadium $3\mathrm{d}_{xz}$ AO implies a rather extensive π back donation from metals to carbonyl π^* MO's and/or mixing of vanadium $4\mathrm{p}_z$ AO's into the metal-metal π^* MO. Since vanadium 4p AO's are rather diffuse, the odd electron densities on these AO's do not give much influences on g and hyperfine splitting tensors.

Orbital Energy Differences. Since the odd electron orbital is the metal-metal π^* MO and the odd electron density on the vanadium d_{xz} AO is 0.21, this orbital can be expressed as follows:

$$\pi^* = \sqrt{0.21}\,\mathrm{d}_{xz}(\mathrm{V}_1) + \sqrt{0.21}\,\mathrm{d}_{xz}(\mathrm{V}_2) + \cdots, \qquad (4)$$

where the subscripts for V are numberings for the vanadium atoms. By assuming that the other MO's with dominant metal characters are localized on the metals and taking *l-s* couplings only in the metals into account, Eq. 1 correlates experimental g shifts with orbital energy differences as following:

$$\Delta g_{\beta\beta} = \Delta g_{zz} = 2\langle\pi^*|\zeta(l_{1z}+l_{2z})|\delta\rangle\langle\delta|l_{1z}+l_{2z}|\pi^*\rangle /[\varepsilon(\pi^*)-\varepsilon(\delta)] \qquad (5)$$

$$\Delta g_{\gamma\gamma} = \Delta g_{yy} = 2\langle\pi^*|\zeta(l_{1y}+l_{2y})|\sigma\rangle\langle\sigma|l_{1y}+l_{2y}|\pi^*\rangle /[\varepsilon(\pi^*)-\varepsilon(\sigma)], \qquad (6)$$

where ζ is the *l-s* coupling constant of d AO's of V(I) ($136\ \mathrm{cm}^{-1}$)[8] and l_{1z} is the z component of the orbital angular momentum around the vanadium atom 1 and so on. We have neglected the contribution to Δg_{yy} from the unoccupied a_g MO consisting of vanadium d_{z^2} AO's in Eq. 6 (*vide supra*). Analyses of the g shifts with Eqs. 5 and 6 give estimates of orbital energy differences as $\varepsilon(\pi^*)-\varepsilon(\delta)\simeq0.9$ and $\varepsilon(\pi^*)-\varepsilon(\sigma)\simeq0.4$ eV. Because of approximations adopted here, these differences should be regarded as estimates of order of magnitudes. These values are in fair agreement with values of $\varepsilon(\pi^*)-\varepsilon(\delta)\simeq0.5$ and $\varepsilon(\pi^*)-\varepsilon(\sigma)\simeq0.6$ eV obtained by an extended Huckel calculation of $\mathrm{V_2(CO)_8(\mu\text{-}PH_2)_2}$.[15]

$Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$. Analyses of ESR parameters of $\mathrm{Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}}$ have led to conclusions that the odd electron occupies the metal-metal σ^* MO and that its densities on the 4s and $3\mathrm{d}_{x^2-y^2}$ AO's of the manganese atoms and the arsenic $4\mathrm{p}_x$ AO's are $\rho(\mathrm{Mn\ s})=0.004$, $\rho(\mathrm{Mn\ x^2-y^2})=0.25$ and $\rho(\mathrm{As\ x})=0.08$ or 0.16, respectively.[4] The ambiguity in the estimate of $\rho(\mathrm{As\ x})$ is due to the uncertainty of the signs of the experimental principal values of the arsenic splitting tensor.

Orbital energy differences can be estimated from g shifts by using the following equations:

$$\Delta g_{xx} = 2\langle\sigma^*|\zeta(l_{1x}+l_{2x})|\delta^*\rangle\langle\delta^*|l_{1x}+l_{2x}|\sigma^*\rangle /[\varepsilon(\sigma^*)-\varepsilon(\delta^*)] \qquad (7)$$

$$\Delta g_{yy} = 2\langle\sigma^*|\zeta(l_{1y}+l_{2y})|\pi\rangle\langle\pi|l_{1y}+l_{2y}|\sigma^*\rangle /[\varepsilon(\sigma^*)-\varepsilon(\pi)], \qquad (8)$$

where ζ is the *l-s* coupling constant of Mn(I) 3d AO's ($254\ \mathrm{cm}^{-1}$)[8] and the other notations have similar significances as in Eqs. 5 and 6. The experimental g shifts of $\Delta g_{xx}=0.029$ and $\Delta g_{yy}=0.023$ lead to order of magnitude estimates of the orbital energy differences of $\varepsilon(\sigma^*)-\varepsilon(\delta^*)\simeq1.1$ and $\varepsilon(\sigma^*)-\varepsilon(\pi)\simeq1.4$ eV. These estimates are comparable with energy differences of $\varepsilon(\sigma^*)-\varepsilon(\delta^*)\simeq1.2$ and $\varepsilon(\sigma^*)-\varepsilon(\pi)\simeq1.3$ eV calculated for $\mathrm{Mn_2(CO)_8(\mu\text{-}PH_2)_2^{+\cdot}}$ with the nonparameterized MO method by Teo and his coworkers.[2]

Concluding Remarks. Magnitudes of negative shifts of Δg_{zz} of $\mathrm{Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}}$ (-0.001) and of Δg_{xx} of $\mathrm{V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}}$ (-0.001) are far smaller than shifts of the other principal values of g tensors of both radicals. These results indicate that the energy separation between e_g and t_{2g} d orbitals in the mononuclear fragment is far larger than those among the six metal-metal MO's derived from t_{2g} d orbitals upon the formation of the dinuclear complex.

The analyses of the hyperfine splitting tensors of arsenic and manganese nuclei of $\mathrm{Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}}$ have indicated that the metal-metal σ^* MO consists of 50% of the manganese $\mathrm{d}_{x^2-y^2}$ components and 16 or 32% of arsenic p_x components. The proposal that the Mn $\mathrm{d}_{x^2-y^2}$ orbital in the C_{2v} mononuclear fragment has the highest orbital energy among the t_{2g} d orbitals is based on this relatively large mixing between the arsenide lone pair orbitals and the manganese $\mathrm{d}_{x^2-y^2}$ orbitals. The weight of the vanadium d_{xz} AO's in the metal-metal π^* MO of $\mathrm{V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}}$ is 42% which is not very large. Since vanadium is electropositive and the carbonyl ligand is a good π accepter, most of the remaining part of the π^* MO would be carbonyl π^* MO's.

Finally, we discuss on the isotropic splitting by phosphorus nuclei resolved in the solution ESR spectrum of $\mathrm{V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}}$. The odd electron in the metal-metal π^* MO is symmetry forbidden to delocalize onto the valence shell AO'S of the phosphorus atoms. The odd electron density on the vanadium d_{xz} AO's would induce spin polarization of electrons in σ bonds between the vanadium and phosphorus atoms, which should result in negative spin densities on the phosphorus 3s AO's. The observed isotropic phosphorus splitting constant of $6.0\times10^{-4}\ \mathrm{cm}^{-1}$ corresponds to the phosphorus 3s spin density of (−)0.0014. This spin density is not an unacceptable value as induced by spin polarization. This explanation predicts that the sign of the isotropic splitting constant of the phosphorus nucleus should be negative.

Experimental

$V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$. $\mathrm{V_2(CO)_8(\mu\text{-}PPh_2)_2}$[16] (1 mg, 2 μmol) was dissolved in dry benzene (0.8 ml) in a quartz

ESR sample tube under argon. When a tetrahydrofuran solution of potassium naphthalenide (0.05 mol dm^{-3}, 50 µl, 2.5 µmol) was added to this solution, a strong ESR signal of $V_2(CO)_8(\mu\text{-}PPh_2)_2^{-\cdot}$ appeared immediately and lasted for days at room temperature. When a tetrahydrofuran solution of $LiBHEt_3$ (Aldrich Super-Hydride, 1 mol dm^{-3}, 5 µl, 5 µmol) was added to the benzene solution of the neutral divanadium complex, an ESR signal of the divanadium anion radical grew slowly in 0.5—1 h.

$Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$. $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2$[17] (*ca.* 0.4 mg) was dissolved in Freon mixture ($CFCl_3$: CF_2BrCF_2Br=1:1 volume ratio)[18] (0.7 ml) under vacuum and irradiated with 2 Mrad of ^{60}Co γ-rays at 77 K. ESR spectra of $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ were measured at low microwave powers (0.1—0.5 mW) after appropriate annealings of irradiated samples. A competitive positive hole capture between $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2$ and isoquinoline was performed by γ-irradiations of Freon mixture solutions (0.7 ml) containing $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2$ (0.05 mg, 0.06 µmol) and isoquinoline (7 µl, 0.05 µmol or 70 µl, 0.5 µmol). The irradiated sample containing the smaller amount of isoquinoline gave a superimposed ESR spectrum of signals due to $Mn_2(CO)_8(\mu\text{-}AsPh_2)_2^{+\cdot}$ and the isoquinoline cation radical,[19] and the other sample gave signals arising only from the isoquinoline cation radical.

ESR Measurements. The spectrometer and monitoring of microwave frequencies and field sweeps for measurements of X-band ESR spectra have been mentioned earlier.[11] K- and Q-band spectra were obtained on JEOL PE-2K and PE-3Q spectrometers, respectively. Q-band microwave frequencies were measured with a Shimada Rika 2A550 resonant cavity wavemeter. The K-band microwave frequency appearing in Fig. 1 is a nominal one. Field sweeps in K- and Q-band spectra were calibrated with hydrogen atom signals in irradiated samples (g=2.0022, a_H/hc=471.7×10^{-4} cm^{-1}) after higher order corrections for the hyperfine interaction.

Simulations. ESR spectra were simulated on a FACOM M200 computer with a FORTRAN program prepared according to a second order perturbation solution[20] for a rhombic spin Hamiltonian.

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