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ESR STUDY OF THE CATION RADICAL OF $Mn_2(\mu\text{-}AsPh_2)_2(CO)_8$

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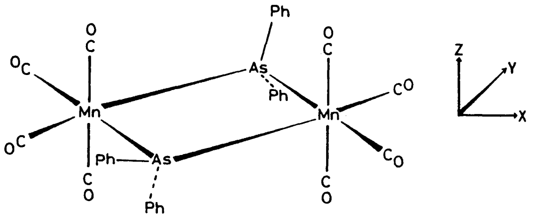
Radiochemical oxidation of $Mn_2(\mu\text{-}AsPh_2)_2(CO)_8$ in Freon mixture glass gives its cation radical, ESR spectra of which are most consistent with the odd electron orbital with σ^*_{MnMn} character and consisting mainly of Mn 3d and As 4p atomic orbitals.

A dimanganese complex, $Mn_2(\mu\text{-}AsPh_2)_2(CO)_8$,$^{1)}$ does not have a direct intermetallic bond. Molecular orbital (MO) theories describe this as that both σ_{MnMn} and σ^*_{MnMn} MO's are doubly occupied and the σ^*_{MnMn} MO has been predicted to be the highest occupied MO.$^{2)}$ This communication reports the shape of the odd electron orbital of the cation radical of the dimanganese complex deduced from its ESR spectra.



Exposure of $Mn_2(\mu\text{-}AsPh_2)_2(CO)_8$ in Freon mixture (1:1 v/v CF_2BrCF_2Br and $CFCl_3$)$^{3)}$ glass to ^{60}Co γ-ray at -196 °C gave a paramagnetic species containing pairs of magnetically equivalent Mn and As nuclei (Fig. 1). The frozen Freon mixture has been known$^{3,4)}$ to be an appropriate matrix for trapping cationic species formed from solutes upon radiolysis. The validity of this electron loss hypothesis was accomplished by an additional experiment: competitive electron release between isoquinoline and the dimanganese complex in Freon mixture upon γ-radiolysis at -196 °C showed that the intensity of ESR absorptions due to isoquinoline cation radical$^{4)}$ increases at the sacrifice of that of the signal in Fig. 1 as the concentration of isoquinoline is increased. The spectra in Fig. 1 are thus attributed to $[Mn_2(\mu\text{-}AsPh_2)_2(CO)_8]^{+\cdot}$. The microwave power dependence of the spectra showed that the shoulder absorptions with an asterisk in Fig. 1 are due to unknown paramagnetic species with shorter relaxation times than that of the cation radical.

Both X- and Q-band spectra were simulated well with a second order perturbation solution of a rhombic spin Hamiltonian$^{5)}$ with $g_\alpha = 2.031$, $g_\beta = 2.025$, $g_\gamma = 2.001$, $|A_\alpha(Mn)| \simeq |A_\beta(Mn)| \lesssim 3 \times 10^{-4}$, $|A_\gamma(Mn)| = 43.0 \times 10^{-4}$, $|A_\alpha(As)| = 14.4$

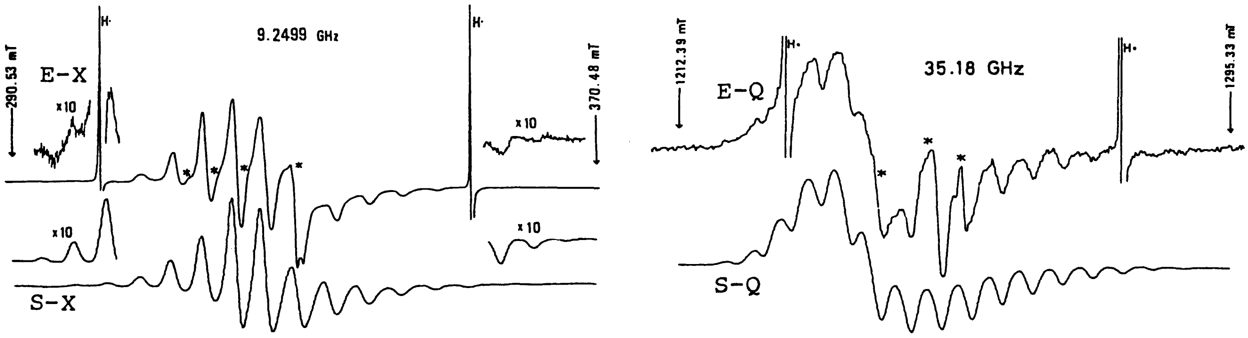


Fig. 1. Experimental (E) and simulated (S) X- (-X) and Q-band (-Q) spectra of $[Mn_2(\mu\text{-}AsPh_2)_2(CO)_8]^{+\cdot}$. Shoulders and peaks with * are due to unidentified species.

$\times 10^{-4}$, $|A_\beta(As)| = 41.5 \times 10^{-4}$, and $|A_\gamma(As)| = 39.9 \times 10^{-4}$ cm^{-1} (suffixes of α, β and γ denote rectangular coordinates for the spin Hamiltonian).

The relatively large Mn and As splittings indicate that the odd electron is distributed mainly over the central rhomboid. Both Mn and As splitting tensors have approximate axial symmetry. The coincidence of the principal directions of the five tensors (hyperfine splitting tensors for each of Mn and As nuclei and the g tensor) in the spin Hamiltonian indicates the planarity of the rhomboid; otherwise, even principal axes of hyperfine splitting tensors of each of Mn and As nuclei pairs should not be parallel each other.[6)]

Table 1 summarizes theoretical expectations of shifts of principal values of the g tensor from the free spin value, $g_e = 2.0023$, and of unique axes of the approximately axially symmetric Mn and As splitting tensors for each of possible odd electron orbitals. These expectations are based on a simple ligand field theory: the Mn d_{z^2} and $d_{x^2-y^2}$ atomic orbitals (AO) are used to form Mn-ligand σ bonds and stay mainly in vacant MO's, whereas the Mn $d_{x^2-y^2}$, d_{xy} and d_{yz} AO's form intermetallic σ, σ^*, π, π^*, δ, and δ^* MO's and these six MO's, except the assumed odd electron orbital, are doubly occupied. Since the odd electron orbital is mainly of metallic character (vide infra), directions of shifts of principal values

Table 1. Theoretical expectation of g-shifts and unique axes of A(Mn) and A(As).

Odd electron orbital[a)]	b_{1u} π d_{xz}	b_{2g} π^* d^*_{xz}	b_{3g} δ d_{yz}	a_u δ^* d^*_{yz}	a_g σ $d_{x^2-y^2}$	b_{3u} σ^* $d^*_{x^2-y^2}$
$g_{xx} - g_e$	< 0	< 0	> 0	> 0	> 0	> 0
$g_{yy} - g_e$	> 0	> 0	< 0	< 0	> 0	> 0
$g_{zz} - g_e$	> 0	> 0	> 0	> 0	< 0	< 0
Unique axis of A(Mn)	y	y	x	x	z	z
Unique axis of A(As)	z	y[b)]	z	y[b)]	y	x

a) σ, π, etc. designate the symmetry of the orbital with respect to the Mn-Mn axis.

b) The As 4p AO's are forbidden to mix into this MO. However, As 4d AO's can be mixed into this MO.

of the g tensor[7)] from g_e can be predicted by taking only l-s couplings around the Mn atoms into account. For example, when the odd electron is accomodated in the σ^*_{MnMn} MO (b_{3u} in D_{2h}) consisting of Mn $d_{x^2-y^2}$ AO's, shifts of g_{xx} and g_{yy} from g_e arises from excitations of an electron in MO's which are constructed mainly from Mn d_{yz} and d_{xz} AO's, respectively, into the odd electron orbital through l-s couplings: shifts of g_{xx} and g_{yy} are expected to be positive. The shift of g_{zz} from g_e arises from an excitation of the odd electron into a MO('s) containing Mn d_{xy} AO's as its major constituent: the shift is expected to be negative. The As AO that is allowed to mix into the σ^*_{MnMn} odd electron orbital is its p_x AO. Thus the unique axis of the As splitting tensor is predicted to be the x axis. Similar analyses give the expectations listed in Table 1.

The comparison of the experimental results with expectations in Table 1 reveals that the odd electron orbital is the σ_{MnMn} or σ^*_{MnMn} MO. This assignment leads to the assignment of negative sign to A_γ(Mn). The odd electron distribution on the Mn atoms can be correlated with the Mn hyperfine splitting tensor with inclusion of effects of unquenched orbital angular momenta of electrons as follows:[8)]

$$A_{xx}(\mathrm{Mn}) = Q^V(\mathrm{Mn})\rho(\mathrm{Mn}\ s) + Q^I(\mathrm{Mn})\rho(\mathrm{Mn}\ d_{x^2-y^2}) - B(\mathrm{Mn})\rho(\mathrm{Mn}\ d_{x^2-y^2}) + (7/4)B(\mathrm{Mn})(g_{xx} - g_e) - (3/8)B(\mathrm{Mn})(g_{yy} - g_e)$$

$$A_{zz}(\mathrm{Mn}) = Q^V(\mathrm{Mn})\rho(\mathrm{Mn}\ s) + Q^I(\mathrm{Mn})\rho(\mathrm{Mn}\ d_{x^2-y^2}) + 2B(\mathrm{Mn})\rho(\mathrm{Mn}\ d_{x^2-y^2}) + (7/4)B(\mathrm{Mn})(g_{zz} - g_e) + (3/8)B(\mathrm{Mn})(g_{xx} + g_{yy} - 2g_e)$$

The expression for A_{yy}(Mn) can be obtained from the equation for A_{xx}(Mn) by exchange of x and y. By using $Q^I(\mathrm{Mn}) = -75 \times 10^{-4}\ \mathrm{cm}^{-1}$ for the Mn inner shell spin polarization[9)] and valence shell parameters of Q^V(Mn) and B(Mn) in the table of Morton and Preston,[10)] we can obtain the odd electron distribution around the Mn atoms as $\rho(\mathrm{Mn}\ d_{x^2-y^2}) = 0.25$ and $\rho(\mathrm{Mn}\ s) = 0.004$.

The physically meaningful choices of signs of the principal values of the As splitting tensor are $A_\alpha(\mathrm{As}) = \pm 14.4 \times 10^{-4}$, $A_\beta(\mathrm{As}) = -41.5 \times 10^{-4}$, and $A_\gamma(\mathrm{As}) = -39.9 \times 10^{-4}\ \mathrm{cm}^{-1}$. For the choice of negative signs for all the principal values, spin densities on the As atom are deduced as $\rho(\mathrm{As}\ s) = -0.007$, $\rho(\mathrm{As}\ p_\alpha) = 0.08$, and $\rho(\mathrm{As}\ p_\beta) = -0.005$, respectively, by neglecting both the As inner shell spin polarization and effects of unquenched angular momenta of electrons[11)] and by using valence shell parameters of Q^V(As) and B(As) given by Morton and Preston.[10)] The other choice gives $\rho(\mathrm{As}\ s) = -0.005$, $\rho(\mathrm{As}\ p_\alpha) = 0.16$, and $\rho(\mathrm{As}\ p_\beta) = -0.005$. The negative spin densities on the As 4s and $4p_\beta$ AO's in both choices of signs show that the As atoms and the β axis reside on the nodal plane of the odd electron orbital: the odd electron orbital is the b_{3u} σ^*_{MnMn} MO, which has a nodal plane passing through the As nuclei and perpendicular to the central rhomboid. Thus it follows that the spin Hamiltonian axes of α and β coincide with the molecular geometrical axes of x and y, respectively.

The odd electron orbital of the present cation is most reasonably assigned to the b_{3u} MO with σ* symmetry with respect to the Mn-Mn axis and consisting mainly of the Mn $d_{x^2-y^2}$ and As p_x AO's ($\rho(\mathrm{Mn}\ d_{x^2-y^2}) = 0.25$,[12)] $\rho(\mathrm{As}\ p_x) = 0.08$ or 0.16).

This result supports the MO calculation of an isoelectronic, $Mn_2(\mu\text{-}PH_2)_2(CO)_8$, by Teo, Hall, Fenske, and Dahl$^{2a)}$ and the Walsh diagram for M_2L_{10} given by Hoffmann and his collaborators.$^{2c,2d)}$

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11) The maximum error in the estimation of the odd electron distribution around the As atom arising from the present neglect of effects of unquenched angular momenta of electrons is $[\rho(\text{As } p_\alpha)]^{1/2} \times \Delta g \times B(\text{As})/Q^V(\text{As}) \simeq 0.002$ for $\rho(\text{As } s)$ and $[\rho(\text{As } p_\alpha)]^{1/2} \times \Delta g \simeq 0.008$ for $\rho(\text{As } p_\beta)$, respectively, where Δg denotes the maximum among the shifts of the g tensor principal values from g_e.
12) More exactly, $\rho(\text{Mn } d_{x^2-y^2}) - \rho(\text{Mn } d_{z^2}) = 0.25$. However, the mixing of Mn d_{z^2} AO's into the b_{3u} σ^*_{MnMn} MO has been calculated to be minor.$^{2a)}$

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