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AN ESR STUDY OF A HYDRIDO-BRIDGED TRIMETAL CLUSTER, $Mn_3(\mu\text{-}H)_3(CO)_{12}^{-\cdot}$

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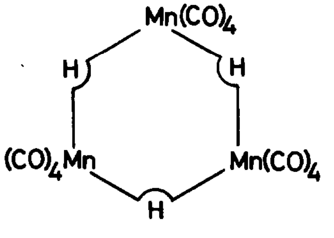
Summary

The anion radical of $Mn_3(\mu\text{-}H)_3(CO)_{12}$ has been generated in frozen 2-methyltetrahydrofuran solutions by γ-irradiation and its ESR spectra have been analyzed. The spectra are consistent with D_{3h} geometry of the anion radical. The unpaired electron is accommodated in an a_2' MO (D_{3h} point group) constructed mainly from the manganese d AO's and with bent σ^* characteristics with respect to the three Mn–Mn bonds. The spin densities on the manganese d AO's and on the hydrogen $1s$ AO are estimated as 0.21 and -0.03, respectively. The g tensor is explained using an MO diagram constructed from a model of the protonated metal–metal bond for the Mn–H–Mn bonds.

Introduction

Hydrido-bridged transition-metal clusters have attracted attention from the viewpoint of characterization of their structures and chemical bondings [1–3]. Green et al. [4] have analyzed the photoelectron spectra of this class of clusters and of closely related binary metal carbonyls and have interpreted general features in the ionization potentials of their "d-electrons".

During the course of our experimental studies of the electronic structures of transition-metal clusters [5], the frontier orbital of a hydrido-bridged cluster, $Mn_3(\mu\text{-}H)_3(CO)_{12}$ [6], was characterized by analysing the ESR spectra of its anion radical.



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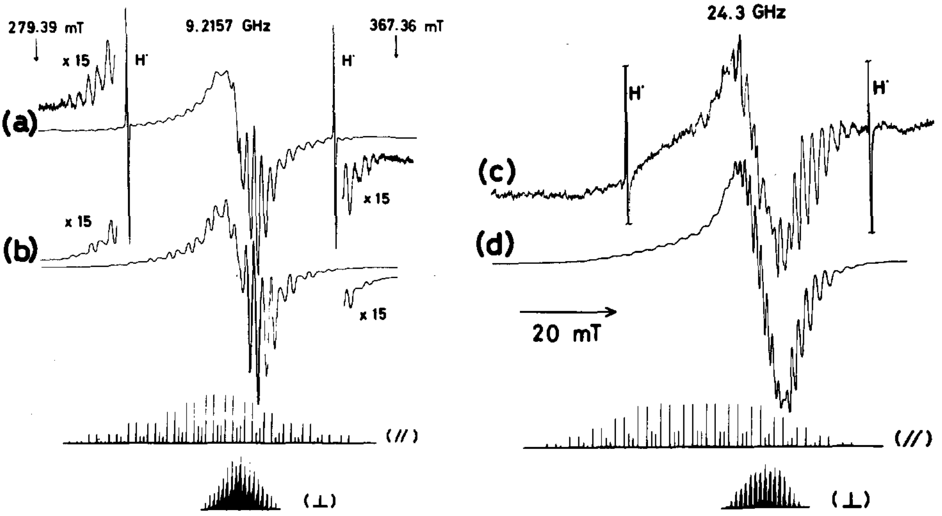

Fig. 1. *X*- (a) and *K*- (c) band ESR spectra of $Mn_3(\mu\text{-}H)_3(CO)_{12}^{-\cdot}$ in MTHF frozen solutions at 77 K and their simulations, (b) and (d), respectively. The ESR parameters are given in the text.

The present result is complementary to the photoelectron study, in the sense that the frontier orbital was directly characterized. The ESR results are interpreted using a bonding model constructed on the basis of Hückel-type molecular orbital (MO) analyses.

Results

A 2-methyltetrahydrofuran (MTHF) solution of $Mn_3(\mu\text{-}H)_3(CO)_{12}$, γ-irradiated at 77 K followed by annealing to decay radicals derived from the solvent, gave the *X*-band ESR spectrum shown in Fig. 1a at 77 K. Further annealing only caused the intensity of the whole spectrum to decrease, which is consistent with the spectrum being attributed to a single paramagnetic species. It was well reproduced on a simulation spectrum (Fig. 1b) based on an axially symmetric spin Hamiltonian, in which three manganese nuclei ($I = 5/2$, 100% natural abandance) and three protons are magnetically equivalent, respectively:

$g_{\parallel} = 2.0320 \pm 0.0005$, $g_{\perp} = 2.000 \pm 0.001$,

$A_{\parallel}(\mathrm{Mn})/hc = (-)\ (44.8 \pm 0.2) \times 10^{-4}\ \mathrm{cm}^{-1}$,

$A_{\perp}(\mathrm{Mn})/hc = (-)\ (10 \pm 3) \times 10^{-4}\ \mathrm{cm}^{-1}$,

$A_{\parallel}(\mathrm{H})/hc = (-)\ (17.6 \pm 0.2) \times 10^{-4}\ \mathrm{cm}^{-1}$,

$A_{\perp}(\mathrm{H})/hc = (-)\ (10 \pm 3) \times 10^{-4}\ \mathrm{cm}^{-1}$,

with Gaussian line-shape functions of line-widths of $\Delta H_{\mathrm{msl}\parallel} = 10$ gauss and $\Delta H_{\mathrm{msl}\perp} = 14$ gauss * for the component lines. It has often been pointed out by Morton and co-workers [7] that ESR spectra of powders or frozen solutions cannot lead to a unique analysis and that wrong conclusions may be obtained by chance if one avoids single-crystal studies. Our experience [5] has shown, however, that γ-irradiation of

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* When the angle between the molecular unique axis and the external magnetic field is θ, the line-width of the component lines is assumed to be $(\Delta H_{\mathrm{msl}\parallel}^2 \cos^2\theta + \Delta H_{\mathrm{msl}\perp}^2 \sin^2\theta)^{1/2}$ in the simulation.

single crystals of transition-metal clusters at 77 K rarely gives paramagnetic centers amenable to ESR studies. Radiolyses of frozen MTHF or Freon solutions of transition-metal clusters are more widely applicable to ESR investigations of the geometries and odd electron orbitals of ion radicals derived from diamagnetic clusters. Uncertainties in the analyses of frozen solution spectra would be excluded by comparing the *X*- and *K*- and/or *Q*-band spectra, especially when the anisotropy of the *g* tensors is appreciable.

Thus we examined the *K*-band spectrum of the same sample (Fig. 1c), which can be simulated (Fig. 1d) with the same set of *g* and hyperfine splitting tensors as that for the *X*-band spectrum with line-width parameters of $\Delta H_{\mathrm{msl}\parallel} = 14$ gauss and $\Delta H_{\mathrm{msl}\perp} = 11$ gauss. This confirms the validity of the present analysis of the spectra.

We also tried to detect paramagnetic species from the rhenium analogue, $\mathrm{Re_3(\mu\text{-}H)_3(CO)_{12}}$, by γ-irradiation of its MTHF solution, but no ESR spectrum with large splittings due to rhenium nuclei was observed.

Discussion

Assignment of the paramagnetic center and its odd electron orbital. Since it is well known that γ-irradiation of frozen MTHF solutions produces anionic species derived from solutes [8,9], the present paramagnetic center is reasonably assigned to the anion radical, $\mathrm{Mn_3(\mu\text{-}H)_3(CO)_{12}}^{-\cdot}$. The equivalence of the hyperfine splitting tensors of the three manganese nuclei and that of the three protons indicate that the anion radical retains the D_{3h} geometry of the neutral molecule [6]. Although each manganese splitting tensor and each proton splitting tensor may not have the exact co-axial symmetry, good agreement between the observed and the simulated spectra (Fig. 1) allows us to regard the anion radical as obeying an axially symmetric spin Hamiltonian within experimental errors (namely, line-widths).

The relatively large principal values together with the virtual co-axial symmetry of the splitting tensors of the three manganese nuclei are consistent with the odd electron being accommodated in an MO of which the main constituents are the manganese 3*d* AO's. The constituent from each manganese atom must be d_{xy}, $d_{x^2-y^2}$, or d_{z^2} in the local coordinate axes system shown in Fig. 2, otherwise the unique axes of the splitting tensors of the manganese nuclei and of the *g* tensor cannot be parallel to each other. The spectrum does not have any abnormally large line-widths, suggesting that the odd electron orbital is non-degenerate. Moreover, it is implied from an analysis of the proton splitting tensors (see below) that the odd

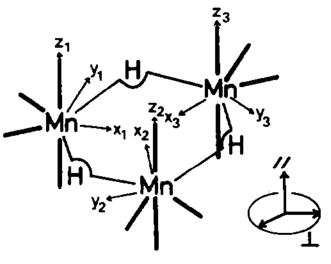

Fig. 2. Molecular geometry of $\mathrm{Mn_3(\mu\text{-}H)_3(CO)_{12}}$ and the local coordinate axes systems for each manganese atom.

electron orbital should have nodes at the positions of the hydrogen atoms. The most reasonable odd electron orbital consistent with these requirements is the out-of-phase combination of three d_{xy} AO's with equal weights (a_2' in D_{3h}).

In some cases of paramagnetic tricobalt clusters without hydrido-bridges [5d, 10–12], odd electron orbitals with similar symmetries (a_2' in D_{3h} and a_2 in C_{3v}) have been reported. By analogy with them, the manganese isotropic splitting constant of the present anion should have a negative sign because the manganese 4*s* AO's cannot combine with the odd electron orbital due to symmetry restrictions; the isotropic splitting arises mainly from inner-shell spin polarizations.

Odd electron distribution. Although the negative sign can be assigned to the manganese isotropic splitting constant, there still remains room for the choice of signs of $A_{\parallel}(\mathrm{Mn})$ and $A_{\perp}(\mathrm{Mn})$. If we give them opposite relative signs, a spin density of 0.3 on each manganese atom is estimated by a conventional method using the atomic parameter given by Morton and Preston [13]. A total spin density of 0.9 on the manganese atoms is too large because the odd electron delocalization onto the carbonyl ligands is anticipated to be fairly large. About 50% of the carbonyl characters have been calculated for the frontier orbitals of $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, and $Co_2(CO)_8$ from SCF-Xα calculations [14]. Indeed, relatively large ^{13}C splittings of carbonyl carbon nuclei have been observed in the ESR spectra of ^{13}C-enriched radicals: $Co_2(CO)_8{}^{-\cdot}$ [15], $HCo_2(CO)_8{}^{\cdot}$ [15], and $HFe_2(CO)_8{}^{\cdot}$ [16].

We, therefore, assign negative signs to both of the principal values: $A_{\parallel}(\mathrm{Mn}) = -44.8 \times 10^{-4}$ and $A_{\perp}(\mathrm{Mn}) = -10 \times 10^{-4}$ cm^{-1}. This sign assignment leads to a reasonable estimation of the spin densities on the manganese *d* AO's.

An appreciable displacement of $g_{\parallel}$ from the g factor of the free spin ($g_e = 2.0023$) shows that these splitting constants should be corrected for second-order effects of the unquenched orbital angular momenta of electrons around the manganese nuclei [17]:

$$A_{\parallel}(\mathrm{Mn}) = a - 2B \cdot \rho(\mathrm{Mn},xy) + (7/6)B \cdot \Delta g_{\parallel} + (1/2)B \cdot \Delta g_{\perp}$$
$$A_{\perp}(\mathrm{Mn}) = a + B \cdot \rho(\mathrm{Mn},xy) + (11/12)B \cdot \Delta g_{\perp}$$

where a is the Fermi contact term of the manganese nucleus, $\rho(\mathrm{Mn},xy)$ is the spin density on the manganese d_{xy} AO, $-2B$ is the principal splitting constant of a manganese nucleus with a unit spin density on its d_{xy} AO which is -118.6×10^{-4} cm^{-1} [13], and $\Delta g_{\parallel}$ and $\Delta g_{\perp}$ are the shifts of $g_{\parallel}$ and $g_{\perp}$ from g_e, respectively.

Using these equations, a and $\rho(\mathrm{Mn},xy)$ are estimated as -22×10^{-4} cm^{-1} and 0.21, respectively.

Proton splitting. The anisotropy of the proton splitting tensor arises from the field of the magnetic dipole of the odd electron distributed mainly on the manganese atoms. By using a point dipole approximation and by assuming the geometry of the anion to be the same as that of the parent molecule [6], the principal values of the anisotropy are estimated as -2.3×10^{-4} and $+1.1 \times 10^{-4}$ cm^{-1} for the $\parallel$ and $\perp$ directions, respectively *. Thus negative signs can be assigned to both of the observed principal values of the proton hyperfine splitting tensor. The isotropic part of the proton splitting tensor is -13×10^{-4} cm^{-1}, corresponding to a hydrogen 1*s* spin density of -0.03, which suggests that the hydrogen atoms are located on the

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* The value for the $\perp$ direction is the average of -0.7×10^{-4} and $+3.0 \times 10^{-4}$ cm^{-1} for the local x- and y-directions, respectively, where the x-direction is defined by a vector from the proton towards the center of the cluster, and the y-direction is perpendicular to both the x- and $z(\parallel)$-directions.

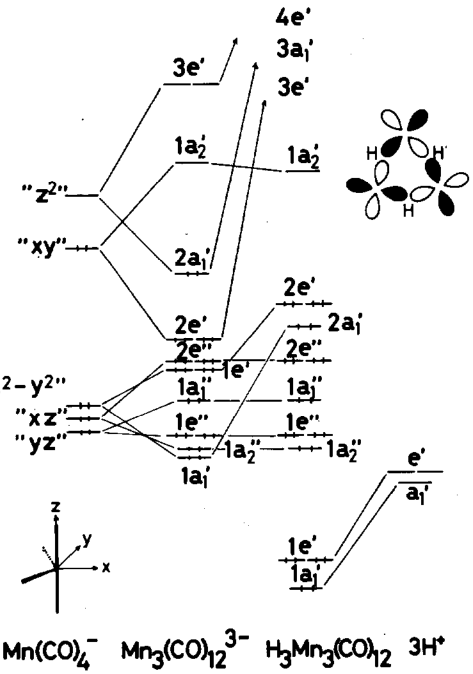

Fig. 3. A qualitative MO diagram of $Mn_3(\mu\text{-}H)_3(CO)_{12}$. The odd electron orbital of the anion radical is $1a_2'$.

nodal planes of the odd electron orbital. It should be noted that a similar estimation of the dipolar interactions of a manganese nucleus with the spin densities on the other manganese atoms resulted in no contribution greater than 0.2×10^{-4} cm^{-1} to the principal values of its splitting tensor.

Qualitative MO diagram and g tensor. A qualitative MO diagram for $Mn_3(\mu\text{-}H)_3(CO)_{12}$ may be given as shown in Fig. 3 on the basis of the photoelectron study of $Re_3(\mu\text{-}H)_3(CO)_{12}$ [4] and of the orbital energy differences of $Mn_3(\mu\text{-}H)_3(CO)_{12}^{-\cdot}$ estimated from its g tensor (see below). The molecular orbitals of a $Mn(CO)_4^-$ fragment and of a D_{3h} $Mn_3(CO)_{12}^{3-}$ fragment are given by analogy with the MO's of isoelectronic $Fe(CO)_4$ and $Fe_3(CO)_{12}$ [18]. When three protons are added, three pairs of electrons in the $2e'$ and $2a_1'$ MO's in $Mn_3(CO)_{12}^{3-}$, corresponding to three Mn–Mn bonds, move formally into the $1a_1'$ and $1e'$ MO's in $Mn_3(\mu\text{-}H)_3(CO)_{12}$. The three pairs of electrons in the latter MO's correspond to three sets of three-center, two-electron Mn–H–Mn bonds [4]. The orbital energies of $3e'$ and $3a_1'$ of $Mn_3(\mu\text{-}H)_3(CO)_{12}$ should be higher than that of $1a_2'$; the $1a_2'$ MO is the odd electron orbital of $Mn_3(\mu\text{-}H)_3(CO)_{12}^{-\cdot}$.

By applying Stone's theory of the g tensor [19] and using the MO diagram in Fig. 3, $\Delta g_{\parallel}$ and $\Delta g_{\perp}$ are given as follows:

$$\Delta g_{\parallel} \doteqdot 2\zeta \left|\langle 1a_2' | \sum_i l_{\parallel}^i | 2a_1' \rangle\right|^2 / [\epsilon(1a_2') - \epsilon(2a_1')]$$

$$\Delta g_{\perp} \doteqdot \sum_n 2\zeta \left|\langle 1a_2' | \sum_i l'_{\perp} | ne'' \rangle\right|^2 / [\epsilon(1a_2') - \epsilon(ne'')]$$

where ζ is the one-electron l–s coupling constant of the manganese $3d$AO's, which is 239 cm^{-1} [20]; $l_{\parallel}^{i}$ and $l^{i}_{\perp}$ are the orbital angular momentum components in the directions of the molecular $\parallel$ and $\perp$ axes, respectively, around the ith manganese nucleus; and ϵ designates the orbital energy.

If the weight of the d AO's in $2a_1'$ is assumed to be similar to that in $1a_2'$, the energy for the excitation of an electron from $2a_1'$ to $1a_2'$ is estimated to be 3.2 eV. The equation for $\Delta g_{\perp}$ together with the diagram in Fig. 3 predicts that $\Delta g_{\perp}$ should be positive and should have magnitude similar to that of $\Delta g_{\parallel}$, contrary to the experimental $\Delta g_{\perp}$, which is slightly negative. This implies that the anion radical has a low-lying vacant e'' MO(s) with appreciable d character. The orbital energy difference between the $1a_2'$ odd electron orbital and the vacant e'' MO(s) should be similar to, or even smaller than, that between the $1a_2'$ and $2e''$ MO's. Indeed, such a vacant MO(s) would be the $\pi^{\star}$ orbitals of the carbonyls combined with the metal d_{xz} and/or d_{yz} AO's in an antibonding phase.

Experimental

The clusters $Mn_3(\mu\text{-}H)_3(CO)_{12}$ and $Re_3(\mu\text{-}H)_3(CO)_{12}$ were prepared by literature methods [21,22]. MTHF kept in contact with Na–K alloy was transferred to ESR sample tubes containing the cluster on a vacuum line. Samples were exposed to ^{60}Co γ-rays at 77 K up to 1 Mrad. The X- and K-band ESR spectrometers, equipment for annealing, and monitoring of the field sweeps and microwave frequencies have been mentioned earlier [5a,17]. The simulations are based on a matrix-diagonalization of an axially symmetric spin Hamiltonian including electron and nuclear Zeeman terms and hyperfine interactions [17].

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