very important in copper(II)-protein-substrate interactions.[37]

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Registry No. [Cu(L-asp)(bpy)H_2O]·$3H_2O$, 83333-56-6.

Supplementary Material Available: Listings of thermal parameters, calculated hydrogen atom positions, complete bond distances and bond angles, selected least-squares planes, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Division of Chemistry,
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EPR Spectrum of $Mn_2(CO)_9^-$ in a Single Crystal of $Mn_2(CO)_{10}$[1]

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γ-Irradiated single crystals of $Mn_2(CO)_{10}$ exhibit EPR spectra at 85 K characteristic of anisotropic interactions of a single unpaired electron with the magnetic field and with two ^{55}Mn ($I = {}^5/_2$) nuclei. The two ^{55}Mn hyperfine tensors have identical components within experimental error but are inclined at approximately 120° (or 60°) to each other. A plausible carrier is $Mn_2(CO)_9^-$, having a single carbonyl bridge and a $^2B_2$ (in C_{2v} symmetry) ground state.

Introduction

In this laboratory we recently initiated an investigation by EPR spectroscopy of transition-metal-centered free radicals trapped in single crystals.[2-6] The method provides structural information and is capable in principle of yielding an LCAO description of the semioccupied orbital (SOMO) of the species under investigation. To date[2-6] we have confined our attention to mononuclear species trapped as impurities (defects) in convenient host matrices. We hope eventually to be able to describe the SOMO in polynuclear (cluster) species, although this will be a formidable task indeed.

In two very interesting papers[7,8] Krusic and collaborators discussed the EPR spectra of various iron-cluster carbonyl radicals such as $HFe_2(CO)_8$, $Fe_3(CO)_{12}^-$, and $Fe_4(CO)_{13}^-$. Understandably, they did not attempt a description of the SOMO in these radicals with only isotropic parameters at their disposal. In related work, Peake,[9,10] Kawamura,[11] and coworkers have used anisotropic parameters derived from frozen-solution spectra to obtain a description of the SOMO in certain paramagnetic clusters. Analyses of powder spectra of such complexity are not necessarily unique, however, and their interpretation should be accepted with caution. Clearly, data are needed from single-crystal EPR studies of such species.[12] In this area, our recent success[13] at coupling a two-circle goniometer with a computer constitutes a real advance as it releases the EPR spectroscopist from his dependence on the crystallographer.

Table I. ^{55}Mn Hyperfine Interactions (G^2) and g^2 Tensors in Irradiated $Mn_2(CO)_{10}$

tensor in *lmn* axis system[a]				direction cosines[a] for principal values		
				501	1005	1180
	l	*m*	*n*			
$a_{Mn}^2 =$	870	±223	0	∓0.517	0.856	0.000
	±223	636	0	0.856	±0.517	0.000
	0	0	1180	0.000	0.000	1.000
tensor in *lmn* axis system				direction cosines for principal values		
				3.990	4.0010	3.9989
	l	*m*	*n*			
$g^2 =$	3.9940	0	0	1.000	0.000	0.000
	0	4.0010	0	0.000	1.000	0.000
	0	0	3.9989	0.000	0.000	1.000

[a] Upper signs Mn(1); lower signs Mn(2). Almost certainly, *l* is the *b* axis of the monoclinic crystal.

Our first attempt to apply this technique to a study of binuclear transition-metal free radicals is described herein.

Experimental Section

Dimanganese decacarbonyl was obtained from Strem Chemicals Inc., Newburyport, MA. Single crystals were grown by sublimation from 50 °C onto a cold finger held at room temperature. Suitable single crystals were irradiated in vacuo for several hours at 77 K in a 2000-Ci ^{60}Co γ cell and then, under liquid nitrogen, mounted on a two-circle goniometer[13] with use of isopentane as an adhesive. The goniometer was then placed in the cavity of the EPR spectrometer and the spectrum examined at 85 K for various orientations of the crystal in the magnetic field.

Crystallography

Dimanganese decacarbonyl, $Mn_2(CO)_{10}$, crystallizes in the monoclinic system with space group *I*2/*a* and four molecules

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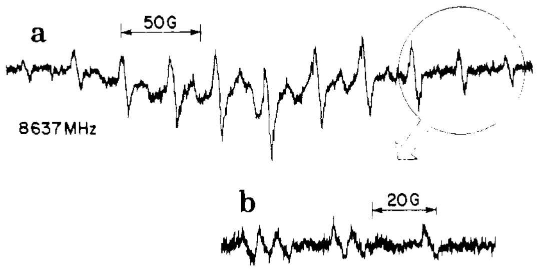


Figure 1. EPR spectrum in γ-irradiated $Mn_2(CO)_{10}$ at 90 K: (a) for H_0 parallel to the *l* axis; (b) for H_0 in the *lm* plane, 15° from *m*, showing the highest field components only.

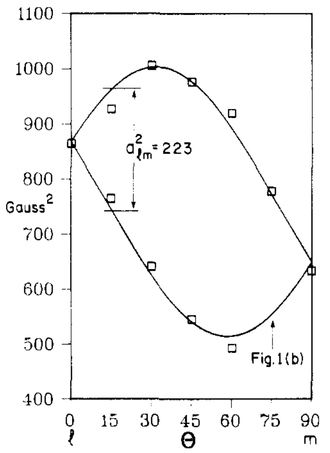


Figure 2. Variation of $\mathbf{a}_{Mn}^2$ in the *lm* plane: upper curve, Mn(1); lower curve, Mn(2). The squares are experimental points; the curve is the least-squares sinusoidal fit to them.

per unit cell.[14] The lattice consists of discrete $Mn_2(CO)_{10}$ molecules having nearly D_{4d} symmetry. All Mn–Mn bonds are parallel, lie in the *ac* plane, and are bisected by the twofold axis (*b*).

Results

It was apparent from a preliminary examination that the hyperfine structure of the spectrum was that of two ^{55}Mn nuclei ($I = 2.5$). For many orientations an 11-line manifold of equally spaced lines was observed (Figure 1a), indicating that the two Mn nuclei had equal hyperfine interactions. However, for certain orientations very much more complex spectra were observed, suggesting that the Mn nuclei were inequivalent for these orientations. The crystal structure of $Mn_2(CO)_{10}$ is such that only one "site" should be detectable. This was confirmed experimentally by the observation that the outside lines of the hyperfine manifold did not split into two components for any orientation of the crystal (Figure 1b). Location of crystal axes by the observation of spectral coalescences was, therefore, not possible. We eventually found, however, three mutually orthogonal axes (*l*, *m*, *n*) such that the two ^{55}Mn nuclei were equivalent for H_0 parallel to *l*, *m*, and *n*. Moreover, the two ^{55}Mn nuclei remained equivalent as H_0 explored the *ln* and *mn* planes but were inequivalent when H_0 lay in the *lm* plane. We therefore decided to describe the hyperfine and g tensors in the *lmn* axis system.

Figure 2 shows the variation of $\mathbf{a}_{Mn}^2$ as H_0 explores the *lm* plane. The two curves are a least-squares fit to the hyperfine data for Mn(1) and Mn(2) and (within experimental error) are superposable with a phase shift of 62°. The hyperfine interactions of Mn(1) and Mn(2) can, therefore, be expressed by a single tensor (Table I) in which the positive sign in the *lm* element corresponds to Mn(1) and the negative sign to Mn(2).

The $\mathbf{g}^2$ tensor is also shown in Table I. Here we note that $\mathbf{g}^2$ is almost isotropic and that all off-diagonal elements are zero, reflecting the absence of magnetically distinct sites.

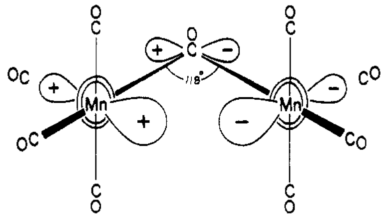
Discussion

An earlier study of a powdered sample of γ-irradiated $Mn_2(CO)_{10}$ led Symons[15] to conclude that the detected spectrum was that of $Mn_2(CO)_{10}^-$, since the hyperfine structure (as revealed by a powder spectrum) appeared to be that of two equivalent ^{55}Mn nuclei. The electron adduct $Mn_2(CO)_{10}^-$ was thought to retain the structure of the original dimer (D_{4d}), with the unpaired electron occupying a Mn–Mn antibonding (σ^*) orbital.

It is apparent from the present results that Symons' conclusion[15] was an oversimplification due to the meager information available from a powder spectrum. The two ^{55}Mn hyperfine tensors have identical principal values (Table I), but the directions of their 501- and 1005-G^2 principal values are 62° (or 118°) apart in the *lm* plane (Figure 2). Evidently, the species produced by γ irradiation has lower symmetry than $Mn_2(CO)_{10}$ itself.

The principal values of the Mn hyperfine tensors in units of MHz are 62.6, 88.7, and 96.1. To a good approximation, therefore, the hyperfine tensors are axial with $a_{\parallel} = 62.6$ MHz and $a_{\perp} = 92.4$ MHz. The physically most reasonable sign choice[16] for these tensor components is $a_{\parallel} = +62.6$ MHz and $a_{\perp} = -92.4$ MHz, corresponding to occupation by the unpaired electron of a d_{z^2} orbital on each manganese nucleus. Defining a parameter P_{exptl} for d_{z^2} orbitals as $^7/_6(a_{\parallel} - a_{\perp})$ and dividing its value (181 MHz) by $g\beta\gamma_{Mn}\langle r^{-3}\rangle_{3d}$ for ^{55}Mn (622 MHz[17]) give an estimate of 0.29 for the spin population in each Mn ($3d_{z^2}$) orbital.

We therefore deduce that the SOMO for the binuclear radical consists principally of an antibonding combination of Mn $3d_{z^2}$ atomic orbitals inclined at an angle of 118° to each other. The fact that the manganese atomic orbital contributions are not parallel strongly suggests that a carbonyl bridge is present in the free radical. A structure that accommodates all of our findings is that of a $Mn_2(CO)_9^-$ molecule (I) containing a single bridging carbonyl. Such a species could arise through electron capture, followed by CO expulsion and intramolecular rearrangement.



I

A SOMO of the symmetry suggested (b_2 in C_{2v}) for $Mn_2(CO)_9^-$ is consistent with the orbital scheme predicted by Hoffmann et al. for a hypothetical doubly bridged $Re_2(CO)_{10}$ molecule.[18] Their extended Hückel calculations suggest that the lowest unoccupied molecular orbital (LUMO) in such a molecule is a σ^* orbital (b_{3u} in D_{2h} symmetry) composed principally of out-of-phase $3d_{z^2}$ hybrid orbitals on the metal atoms together with p_z orbitals on the bridging carbons. This σ^* orbital is quite remote from the filled, d-block orbitals and from higher, empty orbitals. A similar orbital scheme may

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be anticipated for a singly bridged $Mn_2(CO)_9^-$ species, with the unpaired electron occupyng a remote σ^* SOMO of appropriate symmetry (b_2 in C_{2v}). Furthermore, g shifts would be small for a species having a half-filled level well separated in energy from others. The principal g^2 values for the center in $Mn_2(CO)_{10}$ are, in fact, all very close to the free-spin value of 4.009 (Table I).

Examination of the structures of the binuclear metal carbonyls shows that bridging is favored when the metal atom possesses more than seven d electrons. Even in $Mn_2(CO)_{10}$, the equatorial C–Mn–Mn angles[14] suggest a tendency toward carbonyl bridging. One should not, therefore, be too surprised to find a single bridge in $Mn_2(CO)_9^-$, a d^7d^8 species. This molecule has only one electron less than $Fe_2(CO)_9$, which has three carbonyl bridges.

The observation of a single site for the radical in the monoclinic crystal restricts the direction of the twofold axis for $Mn_2(CO)_9^-$ to one of two possibilities. It either lies in the *ac* plane or is parallel to the twofold axis (*b*) of the crystal. The latter choice is deemed more likely since the radicals would then transform according to the symmetry of the crystal space group.

Registry No. $Mn_2(CO)_9^-$, 83510-93-4; $Mn_2(CO)_{10}$, 10170-69-1.

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Electronic Absorption and Magnetic Circular Dichroism of the Linear Diaquodimercury(I) Cation

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Solution electronic absorption and magnetic circular dichroism (MCD) spectra for $[Hg_2(H_2O)_2](ClO_4)_2\cdot 1.3H_2O$ in 0.100 M $HClO_4$ are reported between 260 and 190 nm. Absorption measurements for acetonitrile solutions are also reported. An intense band and accompanying negative B_0 term observed at 4.2 μm^{-1} is assigned as ${}^1\Sigma_g^+ \rightarrow \Sigma_u^+(a^1\Sigma_u^+)$, the excited state arising from the $(3\sigma_g^+)(3\sigma_u^+)$ excited configuration $[\sigma(6s\text{–}6s) \rightarrow \sigma^*(6s\text{–}6s)]$. Two weaker bands observed at 4.68 and 4.91 μm^{-1} were assigned to transitions to the $\Pi_u(a^3\Pi_u)$ and $\Sigma_u^+(a^3\Pi_u)$ spin–orbit states of the $(3\sigma_g^+)(2\pi_u)$ excited configuration $[\sigma(6s\text{–}6s) \rightarrow \pi(6p_x,6p_y\text{–}6p_x,6p_y)]$. A negative A_1 term is observed for the band at 4.68 μm^{-1}. The bonding in the $Hg_2(H_2O)_2^{2+}$ ion is discussed in terms of orbital contributions.

Introduction

The dinuclear dimercury(I) ion, Hg_2^{2+}, is unique in its stability in aqueous acid solutions, in the absence of strongly coordinating ligands that promote disproportionation to Hg(0) and Hg(II).[1] X-ray scattering measurements on aqueous solutions of the perchlorate salt indicate two water molecules axially coordinated to give the linear $H_2O\text{–}Hg\text{–}Hg\text{–}OH_2^{2+}$ ion with two-coordination about each Hg.[2] This same ion is found in solid crystalline hydrates such as $Hg_2(NO_3)_2\cdot 2H_2O$[3] and $Hg_2(ClO_4)_2\cdot 4H_2O$.[2] The $Hg_2(H_2O)_2^{2+}$ ion is of interest because it is one of the simplest stable ions that contain a metal–metal single bond. Even so, the nature of the Hg–Hg bond in Hg(I) compounds is not well understood. For example, the bond energy is not known precisely,[4] the $\nu_{Hg\text{–}Hg}$ stretch is sensitive to the solid or solution environment,[1] and the nature of the orbitals contributing to the bond strength is not known for certain. Therefore, in order to provide a spectroscopic basis for discussion of the electronic structure of the $Hg_2(H_2O)_2^{2+}$ ion, prompted in part by our interest in electronic structure of two-coordinate complexes generally, we report some electronic absorption and magnetic circular dichroism (MCD) spectra for $Hg_2(H_2O)_2^{2+}$ in dilute acid solution. Electronic spectra of Hg_2^{2+} in the UV region have been reported previously,[5] but the measurements appear incomplete and the spectra were not assigned. Also, counterions such as NO_3^- absorb strongly in the UV region and tend to obscure the features of the Hg_2^{2+} ion. In the present study ClO_4^- served as the counterion and $HClO_4$ was used to maintain the acidity of the solutions; neither has strong absorptions in the UV region below 5.2 μm^{-1}.

Experimental Section

Mercury(I) perchlorate hydrate was purchased from Alfa-Ventron (Danvers, MA) and analyzed for water content by precipitation of Hg_2Cl_2; the hydration was found to be 3.3 water molecules/$Hg_2(ClO_4)_2$ formula unit. All aqueous spectra were obtained in 0.100 M $HClO_4$ solution to prevent hydrolysis. Absorption spectra were also obtained by dissolving the hydrated salt in Spectroquality acetonitrile.

Absorption and MCD spectra were determined with a spectrometer that allows synchronous simultaneous measurement along the same light path. The spectrometer has been described elsewhere recently.[6] MCD spectra were obtained with both a 1-T permanent magnet (sample path length 0.100 cm) and a 7-T superconducting selenoid (Oxford Instruments SM2-7, with a room-temperature bore; sample path length 1.00 cm). The spectral bandwidth was 0.5 nm throughout the wavelength range investigated, and no spectral feature was machine limited in resolution. Absorption measurements were also made on a Cary 1501. All measuremets were made at room temperature and Beer's law was found to hold for both aqueous and acetonitrile solutions.

Results and Discussion

Electronic Absorption and MCD Spectra. Figure 1 presents the electronic absorption and 7.0-T MCD spectra of $Hg_2(H_2O)_2^{2+}$ in 0.100 M $HClO_4$. Quantitative spectral data are collected in Table I. The absorption spectra consist of three intense bands, the lowest energy band (band I) being the most

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