Electron Spin Resonance Behaviour of the $[Fe_3Pt_3(CO)_{15}]^-$ Carbonyl Cluster Anion †

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The e.s.r. spectra of the paramagnetic $[Fe_3Pt_3(CO)_{15}]^-$ monoanion have been recorded in solution and in the solid state at variable concentration and temperature. A comparison of e.s.r. and electronic diffuse-reflectance spectra with *X*-ray structural data of $[Fe_3Pt_3(CO)_{15}]^{n-}$ (n = 1 or 2) clusters suggests that the unpaired electron is mainly located in a non-degenerate molecular orbital of the triplatinum system which, under an idealized D_{3h} symmetry, may primarily be the $a_2'^*$ combination of three d_{xz} platinum orbitals. The stability of the paramagnetic cluster probably derives from the unpaired electron being localised mostly on the platinum atoms, and from the steric properties of the μ-$Fe(CO)_4$ groups which hinder spin-pairing by dimerization.

SEVERAL examples of paramagnetic metal carbonyl clusters have been reported in the literature.[1-5] Most of them have been characterized only in solution by e.s.r. spectroscopy because their lifetime is not sufficient to allow isolation in the solid state. However, when e.s.r. investigations can be substantiated with *X*-ray structural data, a more detailed picture of the bonding in metal clusters can be achieved,[6-8] and an insight into the factors affecting their stability can be reasonably expected. The isostructural paramagnetic $[Fe_3Pt_3(CO)_{15}]^-$ and diamagnetic $[Fe_3Pt_3(CO)_{15}]^{2-}$ carbonyl anions, which have been recently characterized by *X*-ray structural data,[9] provide such an opportunity.

RESULTS AND DISCUSSION

E.s.r. spectra of $[Fe_3Pt_3(CO)_{15}]^-$ have been recorded on 10^{-1}—10^{-5} mol dm^{-3} thf (tetrahydrofuran) or CH_2Cl_2 solutions prepared by dissolving preformed $[XR_4]$-$[Fe_3Pt_3(CO)_{15}]$ (where XR_4^+ is a tetrasubstituted ammonium or phosphonium cation) in the solvent.

In this range of concentration a symmetrical single resonance having a peak-to-peak linewidth of 100 G is observed at room temperature; whereas the corresponding solutions frozen at —150 °C show anisotropic resonance lines well separated into two different intensity groups, having well detectable seven-line splitting in the higher intensity group (Figure 1). The magnetic parameters are collected in the Table. A similar trend has also been observed in the solid-state spectra. Thus, undiluted polycrystalline samples of $[XR_4][Fe_3Pt_3(CO)_{15}]$ at room temperature show a very broad signal, while at low temperature the signal is split into parallel and perpendicular resonances. Under both conditions hyperfine coupling is undetectable. However, when doping a sample of $[PPh_4]_2[Fe_3Pt_3(CO)_{15}]$ with the corresponding tetraphenylphosphonium salt of $[Fe_3Pt_3(CO)_{15}]^-$ (9 : 1 molar ratio) by co-precipitation, the e.s.r. spectra show paramagnetic anisotropy of the latter even at room temperature and, furthermore, this sample cooled at —150 °C shows hyperfine coupling on both resonances. As shown in the Table, all the tensor components in the undiluted polycrystalline sample and in the 9 : 1 molar

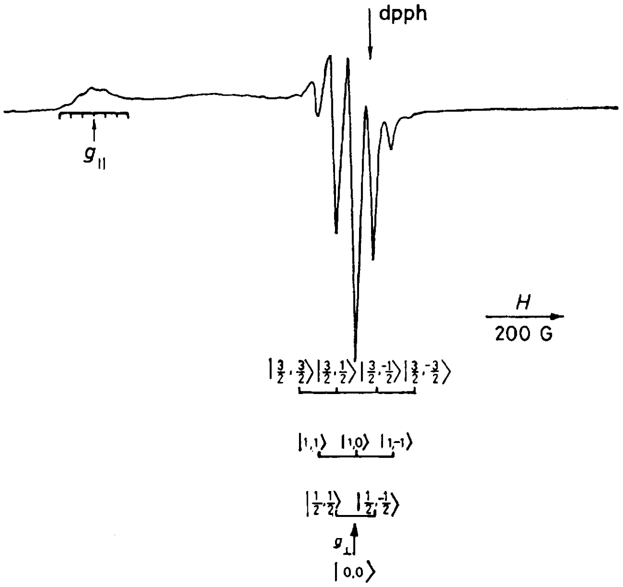

FIGURE 1 E.s.r. spectrum of $[Fe_3Pt_3(CO)_{15}]^-$ in thf frozen solution (—150 °C). Transitions have been assigned by $|I\ M_I\rangle$ values

E.s.r. parameters of $[Fe_3Pt_3(CO)_{15}]^-$

Complex	θc/°C	$g_{\parallel}$	$g_{\perp}$	$g_{iso.}$	$A_{\parallel}$/G	$A_{\perp}$/G
$[PPh_4][Fe_3Pt_3(CO)_{15}]$ as undiluted powder	25	unresolved signal				
	—150	2.55	2.04			
$[NMe_3(CH_2Ph)][Fe_3Pt_3(CO)_{15}]$ diluted in $[NMe_3(CH_2Ph)]_2[Fe_3Pt_3(CO)_{15}]$(1 : 9)	25	2.57	2.03			
	—150	2.57	2.03		60	100
$[Fe_3Pt_3(CO)_{15}]^-$ in thf or CH_2Cl_2 solution	25			2.18		
	—150	2.57	2.03		60	100

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† Tricarbonyltris(μ-tetracarbonylferrio)-*triangul*-triplatinate-(1—).

ratio $[PPh_4]_2[Fe_3Pt_3(CO)_{15}]$: $[PPh_4][Fe_3Pt_3(CO)_{15}]$ doped sample are quite comparable with those observed in solution at low temperature. Therefore, interaction of the paramagnetic compound with the solvent can be ruled out, as suggested also by identical magnetic parameters in thf or dichloromethane. It may be noted that both room- and low-temperature spectra indicate an electronic situation greatly affected by the high value of the platinum spin–orbit coupling constant and that the g anisotropy ($\Delta g = g_{\parallel} - g_{\perp} = 0.51$) is comparable to that found in monomeric platinum compounds.[10]

The hyperfine splitting observed at low temperatures is clearly due to ^{195}Pt. Since ^{195}Pt has $I = \frac{1}{2}$ and occurs naturally with 33.8% abundance, while the remaining platinum isotopes have $I = 0$, the spectrum should result in a superimposed singlet, doublet, triplet, and quartet when there are respectively 0, 1, 2, and 3 ^{195}Pt nuclei in the central Pt_3 triangle. Evaluation of the relative probability of occurrence of these isotopomers[11] gives the calculated relative intensities of 0.1 : 1.1 : 4.6 : 7.8 : 4.6 : 1.1 : 0.1 for the predicted non-binomial seven-line multiplet. The apparent relative intensities determined in the perpendicular resonances found in the doped sample and in the frozen solutions at −150 °C compare well with the expected values of 0.09 : 0.95 : 4.60 : 7.80 : 4.15 : 0.85 : 0.07.

A sample of $[Fe_3Pt_3(CO)_{15}]^-$ *ca.* 40% enriched in ^{13}CO does not show hyperfine coupling of the unpaired electron with ^{13}C ($I = \frac{1}{2}$) even at −150 °C, and the linewidths of the signals are unaffected. The absence of any detectable effect on the e.s.r. spectrum of $[Fe_3Pt_3(CO)_{15}]^-$ by isotopical exchange with ^{13}CO seems to imply that interaction of the odd electron with the carbon atoms is negligible, even for the carbonyl groups directly bound to the platinum atoms. This is in keeping with the values of both parallel and perpendicular components of hyperfine ^{195}Pt coupling constants, which are nearly one third of the reported values for mononuclear platinum co-ordination compounds,[10] and suggests that the unpaired electron is delocalized in a molecular orbital primarily derived from platinum atomic orbitals.

In order to give a less qualitative account of e.s.r. measurements it is useful to consider an electronic model of $[Fe_3Pt_3(CO)_{15}]^{n-}$ ($n = 1$ or 2). As schematically shown in Figure 2, the structure of these compounds consists of an equilateral triangle of platinum atoms which is bridged on each edge by a $Fe(CO)_4$ group.[9] An oversimplified approach, albeit a useful one, could be to consider the Fe–Pt bonds as two-electron, two-centre bonds and to assume that the μ-$Fe(CO)_4$ groups behave as two-electron bridging donor ligands. Under this assumption, the $[Fe_3Pt_3(CO)_{15}]^{n-}$ anions may be reformulated as $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^{n-}$, and the dianion may be considered as a 44 valence-electron cluster, isoelectronic with $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$,[12] or with the central $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ moiety found in $[Ni_5(CO)_{12}]^{2-}$ (ref. 13) and $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, or W).[14]

A bonding description similar to that proposed by Dahl for the present cluster can now be reasonably used. A local right-handed co-ordinate system for each platinum atom, with the z axis directed towards the centre of the Pt_3 triangle, the x axis in the plane of the platinum atoms, and the y axis perpendicular to this plane may be chosen (see Figure 2). The nine valence platinum atomic orbitals ($6s$, $6p_x$, and $6p_z$ in character) are used for σ-bonding to the three carbonyl and the three μ-$Fe(CO)_4$ groups and their bonding combinations with suitable ligand orbitals are filled with 18 out of 44 valence electrons. The remaining 26 are then allocated in the seven bonding $[d_{z^2}(a_1')^2$, $d_{xz}(e')^4$, $d_{x^2-y^2}(a_1')^2$, $d_{yz}(a_2'')^2$, $d_{xy}(e'')^4]$ and in the lower lying six out of eight antibonding $[d_{xy}(a_1''^*)^2$, $d_{yz}(e''^*)^4$, $d_{x^2-y^2}(e'^*)^4$, $d_{xz}(a_2'^*)^2$, $d_{z^2}(e'^*)^0]$ molecular orbitals obtained from the $5d$ platinum atomic orbitals under D_{3h} symmetry. By overlap arguments the highest occupied molecular orbital would be the $a_2'^*$ antibonding combination in the xz plane. Half the occupation of this non-degenerate in-plane molecular orbital, when dealing with the 43 valence electrons of $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^-$, would be in agreement with the e.s.r. results here reported and with the structural data. *X*-Ray diffraction studies have indeed shown a significant shortening of the average Pt–Pt bond distance in going from $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^{2-}$ (2.750 Å) to $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^-$ (2.656 Å).[9] A comparable shortening of the M–M bonds has been previously ascertained in the related $[FeCo_2(CO)_9S]$–$[Co_3(CO)_9S]$ and $[CoNi_2(\eta\text{-}C_5H_5)_3(CO)_2]$–$[Ni_3(\eta\text{-}C_5H_5)_3(CO)_2]$ systems.[15]

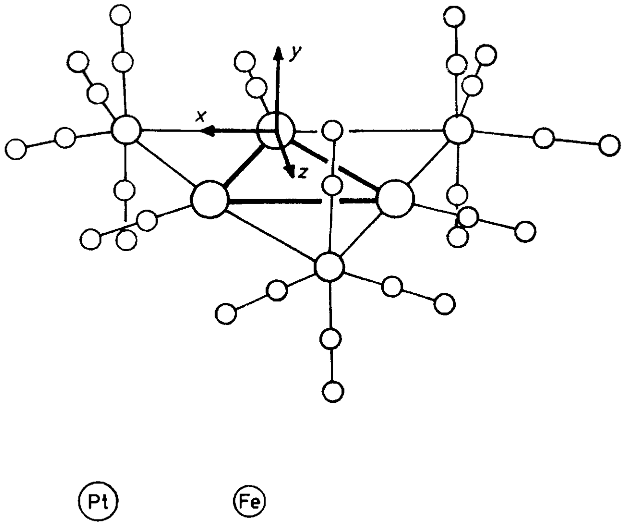

FIGURE 2 Schematic representations of the structures of $[Fe_3Pt_3(CO)_{15}]^{n-}$ ($n = 1$ or 2)

Unfortunately, the analysis of diffuse-reflectance spectra of $[Fe_3Pt_3(CO)_{15}]^{n-}$ ($n = 1$ or 2) (Figure 3) is only available for qualitative purposes, owing to the lack of detailed information on the energy levels. An absorption at 1 250 nm distinguishes the spectrum of the paramagnetic monoanion from that of the present dianion, while both compounds show a stronger absorption at 700 nm. Both the intensity and energy of these bands suggest attribution to electronic transitions between molecular orbitals deriving from the combination of platinum $5d$ orbitals. Although it is difficult to positively assign the energy differences, we tentatively suggest that the band at 1 250 nm is due to electron transfer to the $a_2'^*$ symmetry orbital, being active only in case of half-occupation.

It is conceivable that the stability of the paramagnetic carbonyl $[Fe_3Pt_3(CO)_{15}]^-$ cluster is due to a co-operative effect between high localization of the unpaired electron in this $a_2'^*$ orbital, primarily consisting of platinum d orbitals, and steric hindrance of the ligands which opposes the pairing of two paramagnetic units. The observed diamagnetism of $[Fe_4Pt_6(CO)_{22}]^{2-}$,[9] where the pairing of two hypothetical $[Fe_2Pt_3(CO)_{11}]^-$ units is favoured by the absence of a third bridging $Fe(CO)_4$ group, leads to this suggestion. Additional evidence comes also from an e.s.r. investigation of the system $[\{Pt_3(CO)_3(\mu\text{-}CO)_3\}_n]^{2-}$ ($n = 1$ or 2). Thus, when $n = 2$, we did not find evidence of the presence in solution of a dissociative equilibrium giving rise to a $[Pt_3(CO)_3(\mu\text{-}CO)_3]^-$ paramagnetic species formally corresponding to $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^-$. Moreover, we have been unable to detect this species even by the chemical oxidation '*in situ*' of $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$.

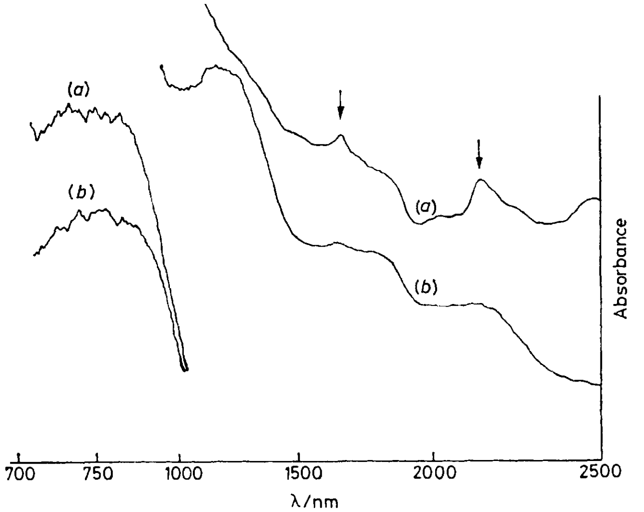

FIGURE 3 Electronic diffuse-reflectance spectra of (*a*) $[PPh_4]_2[Fe_3Pt_3(CO)_{15}]$ and (*b*) $[PPh_4][Fe_3Pt_3(CO)_{15}]$. The absorptions marked with an arrow are due to the tetraphenylphosphonium cation

EXPERIMENTAL

Tetrasubstituted ammonium or phosphonium salts of the $[Fe_3Pt_3(CO)_{15}]^-$ and $[Fe_3Pt_3(CO)_{15}]^{2-}$ anions were prepared by procedures previously reported.[9] The magnetic dilution of $[Fe_3Pt_3(CO)_{15}]^-$ into the diamagnetic $[Fe_3Pt_3(CO)_{15}]^{2-}$ parent dianion was performed by dissolving $[NMe_3(CH_2Ph)]_2[Fe_3Pt_3(CO)_{15}]$ (782 mg) and $[NMe_3(CH_2Ph)][Fe_3Pt_3(CO)_{15}]$ (66 mg) in thf (10 cm^3) following by precipitation by adding n-heptane (20 cm^3) with vigorous stirring. The ^{13}CO-enriched sample of $[PPh_4][Fe_3Pt_3(CO)_{15}]$ was obtained by the following procedure: $[PPh_4]_2[Fe_3Pt_3(CO)_{15}]$ (145 mg) in thf (5 cm^3) was stirred for 48 h in a 90% ^{13}CO atmosphere in a 30 cm^3 flask. Statistical exchange was checked by monitoring the gas phase and by recording a ^{13}C n.m.r. spectrum of the enriched $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion. The dianion was then converted into the $[Fe_3Pt_3(CO)_{15}]^-$ paramagnetic monoanion by oxidation with a slight excess of iodine in thf. The resulting brown solution was evaporated *in vacuo*, and the residue was suspended in methanol. The precipitate of $[PPh_4][Fe_3Pt_3(CO)_{15}]$ was then obtained by adding tetraphenylphosphonium chloride in excess.

E.s.r. spectra were recorded on a Varian X-band E-109 spectrometer, equipped with a Varian temperature control, and operating at 100 MHz modulation frequency.

Compounds were examined in the form of polycrystalline powders and in thf or dichloromethane solution, under strictly anaerobic conditions. Spectra were recorded at indicated temperatures, and g values were calculated by standardization with diphenylpicrylhydrazyl (dpph). Electronic diffuse-reflectance spectra on polycrystalline samples were recorded on a Beckman DK-2A spectrophotometer using a thin, flat cell filled under a nitrogen atmosphere.

The spectral analysis reported in this paper was performed by suggestion of the late Professor Paolo Chini, whose findings in the chemistry of metal carbonyl clusters will be the basis of much future developments in this area.

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