suggestive of a hydrogen-bonding interaction (Figure 2).[8] It is apparent that a hydrogen-bonding interaction, above and below the planes defined by the phosphorus and platinum atoms, would contribute to the overall stabilization of this conformation.

Complex **2** was further characterized by its ^{1}H and ^{31}P{^{1}H} NMR spectra.[5] The ^{31}P{^{1}H} spectrum shows a singlet resonance at δ 9.7. The low-field shift of this resonance, relative to that of its free ligand, confirms the presence of a bridging diphosphine ligand.[6] The presence of inner platinum satellites, due to a three-bond platinum–phosphorus coupling constant, $^3J(\mathrm{PtP})$ = 72.4 Hz, supports the assignment of a dinuclear structure to the complex. The ^{1}H NMR spectrum also supports this assignment, with an observed PH proton resonance at δ 5.01 and a resonance appearing as a triplet of triplets, δ 2.75, due to the protons of the methylene group bridging the two phosphorus atoms. The methyl protons of the sulfide ligands generate two nonequivalent resonances, δ 2.64 and 2.94, due to the proximal methyl groups a and a′, those directed toward each other, and the distal methyl groups b and b′, those directed away from each other (Figure 1). These data suggest that the solution structure at room temperature is static with regard to the sulfide ligands and identical with the solid-state structure.

The formation of complex **2** may involve reaction of one phosphorus of the diphosphine ligand with a platinum(II) center displacing one dimethyl sulfide ligand (Scheme I). This would be followed by reaction of the "dangling" end of the diphosphine with a second platinum(II) center and loss of a dimethyl sulfide ligand. An alternative mechanism would involve coordination of the "dangling" end of the diphosphine ligand to the original platinum(II) center, forming a mononuclear chelate. This mononuclear species could react with another platinum(II) center and undergo a ligand-exchange process[9] to generate the observed product. The former mechanism (path a in Scheme I) is favored over mononuclear chelate formation (path b in Scheme I) since such chelate complexes are without precedent within disecondary diphosphine, $\mathrm{HRPCH_2PRH}$, platinum systems.

Complex **2**, a mixed bis(dimethyl sulfide) diphosphine dimer, represents a useful model for many of the intermediates invoked to rationalize dimer formation within related bis(diphosphine)-platinum(II) dimeric systems.[2a] This complex is also a likely intermediate in the formation of the complex $[\mathrm{Pt_2Cl_4}(\mu\text{-}\mathrm{H^tBuPCH_2P^tBuH})_2]$.[2b] The premise that reduced steric bulk around the phosphorus center enhances preference for occupancy of bridging coordination modes over chelating coordination modes is illustrated by the structure of complex **2**. Intramolecular hydrogen bonding in the disecondary diphosphine complex possibly plays a contributive role in the generation of this mode of diphosphine coordination.

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Supplementary Material Available: Details of the data collection and listings of final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (12 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(8) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.
(9) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.
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Large Intensity Enhancement of the Spin-Forbidden $^4A_{2g} \to {}^2E_g$ Transition in Chromium(III)–Semiquinone Complexes

The interaction of transition-metal ions with organic radicals that are directly bound to them can result in many new experimental properties that are currently being actively investigated. For instance strong ferromagnetic couplings have been observed,[1] of which perhaps the most striking example is that of $[\mathrm{Ni(CTH)(DTBSQ)}]\mathrm{PF_6}$ (CTH = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; DTBSQ = 3,5-di-*tert*-butylsemiquinone), which has a ground quartet state, as a result of the interaction between nickel(II) (S = 1) and the semiquinone (S = $^1/_2$), and no evidence, even at room temperature, of populated doublet levels.[2] In a quantitative way this corresponds to the isotropic coupling constant $J \geq 400$ cm^{-1} (throughout the paper we use the spin Hamiltonian in the form $H = JS_1S_2$), which is determined by the fact that the magnetic orbitals of the metal ion and of the radical are orthogonal to each other and are in close contact. Such high values of ferromagnetic couplings are quite unusual for pairs of metal ions,[3] and this example shows well how extremely enhanced effects can be observed when the metal ion interacts directly with a radical.

Another field where dramatic effects can be anticipated due to the coupling of metal and radical orbitals is that of optical transitions. In fact it is well-known that formally spin-forbidden transitions of single ions can acquire high intensities in pairs due to exchange effects.[4] The phenomenon has been studied with many different metal ions,[5] and particularly interesting results have been observed for chromium(III) pairs,[6,7] which are characterized by large enhancements of the $^4A_{2g} \leftrightarrow {}^2E_g$ transitions.

We have now found that in the octahedral complexes $\mathrm{Cr(CTH)(DTBSQ)^{2+}}$ and $\mathrm{Cr(CTH)(TCSQ)^{+}}$ (TCSQ = 3,4,5,6-tetrachlorosemiquinone) a large intensity enhancement of the $^4A_{2g} \to {}^2E_g$ transition occurs and we here wish to report its characterization.

$\mathrm{Cr(CTH)Cl_2}$ reacts with di-*tert*-butyl-*o*-benzoquinone in methanol, yielding after addition of $\mathrm{KPF_6}$, a crystalline compound of formula $[\mathrm{Cr(CTH)(DTBSQ)}]_2\mathrm{Cl(PF_6)_3}$ (I). Under the same conditions tetrachloro-*o*-benzoquinone reacts, yielding $[\mathrm{Cr(CTH)(TCCat)}]\mathrm{PF_6}$ (II; TCCat = tetrachlorocatecholato). The formulation of I and II follows from elemental analysis, IR and EPR spectroscopy, and magnetic measurements.

I is EPR silent and is characterized by an effective magnetic moment of 2.9 μ_B at room temperature. No temperature dependence of the magnetic moment was observed; therefore, it must be concluded that the coupling is strongly antiferromagnetic with a ground state S = 1 and no excited state thermally populated. Since in an exchange Hamiltonian approach the energy separation between the ground triplet state and the first excited quintet state is $2J$, the isotropic coupling constant J can be assumed to be larger than 350 cm^{-1}.

Electrochemical measurements in acetonitrile solution show that I undergoes a reversible one-electron redox process at 0.21 V vs SCE and an irreversible one at 1.3 V vs SCE. As supported by spectroscopic data and comparison with iron(III) and cobalt (III) analogues, both processes are associated with ligand-centered electron-transfer processes, i.e. catecholate–semiquinone and semiquinone–quinone.

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(1) Kahn, O.; Prins, R.; Reedijk, J.; Thompson, J. *Inorg. Chem.* **1987**, *26*, 3557.
(2) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1988**, *27*, 2831.
(3) Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.
(4) Güdel, H. U. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985.
(5) Schugar, H. J.; Rossman, G. R.; Barraclough, C. G.; Gray, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 2683.
(6) Naito, M. *J. Phys. Soc. Jpn.* **1973**, *34*, 1491.
(7) McCarthy, P. J.; Güdel, H. U. *Coord. Chem. Rev.* **1988**, *88*, 69.

0020-1669/89/1328-3089$01.50/0

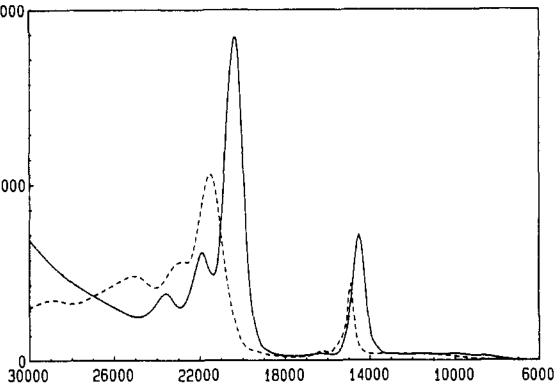

Figure 1. Electronic spectra of $[Cr(CTH)(DTBSQ)]_2Cl(PF_6)_3$ (I; - - -) and of $[Cr(CTH)(TCSQ)]^+$ (cation of III; —) in acetonitrile solution.

The cis-octahedral catecholate adduct II exhibits similar redox properties, undergoing a reversible electron-transfer process at 0.84 V vs SCE (Cr(TCCat)–Cr(TCSQ)) and an irreversible one at 2.0 V vs SCE (Cr(TCSQ)–Cr(TCQ)). In addition an irreversible process tentatively assigned to the Cr(III)/Cr(II) couple is observed at −1.92 V vs SCE.

The electronic spectrum of the acetonitrile solution of I as well as that of $Cr(CTH)(TCSQ)^+$ (III), obtained by exhaustive electrolysis of II at +0.96 V, are reported in Figure 1. They show bands at 11 500 cm^{-1} for I and 10 100 cm^{-1}, with shoulders at 8800 and 11 400 cm^{-1}, for III, which are diagnostic of semiquinone ligands and which we attributed[8] to the transition to the HOMO from the second highest occupied molecular orbital. The bands at 25 000 cm^{-1} for I and 23 500 cm^{-1} for III also compare well with the energies of the transitions seen in other semiquinone complexes and can be assigned to internal ligand transitions. The intense bands at 21 400 and 22 800 cm^{-1} for I and 20 100 and 21 800 cm^{-1} for III can be assigned to charge-transfer transitions of metal-to-ligand character because of the red shift observed when the ligand becomes more electron withdrawing.[9] The weak bands at 16 100 and 16 300 cm^{-1} for I and III, respectively, have the energies and the intensities expected for the first spin-allowed d–d transition of chromium(III) chromophores.

The intense and sharp peaks observed at 14 850 cm^{-1} for I and 14 400 cm^{-1} for III have the energy expected for the $^4A_{2g} \rightarrow {}^2E_g$ spin-forbidden transition corresponding to a spin flip in the ground $(t_{2g})^3$ configuration,[9] but the observed molar extinction coefficients are 3 orders of magnitude higher than usual. However, the sharpness of the band, which for I has a full width at half height of 310 cm^{-1}, rules out an assignment to either charge transfer or spin-allowed d–d transitions. the band intensity was found to be practically independent of temperature in the range 22–300 K. We assign this band to the $^4A_{2g} \rightarrow {}^2E_g$ transition, which is made allowed by the strong exchange coupling between metal ion and semiquinone.

With use of C_{2v} symmetry for the molecule and the coordinate axes shown in Figure 2, the t_{2g} levels span the a_1, a_2, and b_1 representations and the ground state of chromium(III) is described as $^4B_2$. Since the HOMO of the semiquinone has b_1 symmetry,[10] the ground state for Cr(CTH)(SQ) is $^3A_2$, with an excited state $^5A_2$ that is at least 700 cm^{-1} above the ground state. The excited ^2E_g level of chromium(III) in octahedral symmetry yields $^2A_1$ and $^2B_2$ in C_{2v} symmetry, so that the excited manifold of Cr(CTH)(SQ) corresponds to $^1B_1$, $^3B_1$ and $^1A_2$, $^3A_2$, respectively. The transition between the ground $^3A_2$ and the excited $^3A_2$ states is allowed parallel to z. The mechanism by which this transition can borrow intensity is through admixing with a $^3A_2 \rightarrow {}^3A_2$ charge-transfer transition. In the formalism developed by Tanabe et al.,[11] the intensity depends on contributions of the type

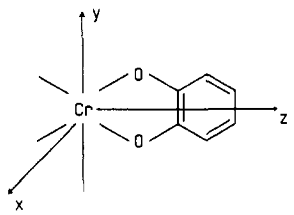

Figure 2. Reference frame used for the assignment of the state symmetry in the Cr(CTH)SQ molecule (see text).

$$\Pi_{a_i b_j} = \frac{-4\langle a_i|p|b_j\rangle\, h(a_i \rightarrow b_j)}{E(a_i \rightarrow b_j)} \tag{1}$$

where a_i and b_j are singly occupied orbitals centered on a and b respectively, $\langle a_i|p|b_j\rangle$ is the transition moment corresponding to the electron transfer from a_i to b_j, $\Delta E(a_i \rightarrow b_j)$ is the energy of this electron-transfer process, and $h(a_i \rightarrow b_j)$ is the transfer integral, which is expected to be related to the coupling between the two orbitals. The exchange coupling constant can be expected to be expressed as

$$J = \frac{1}{3}\sum_{ij}\left[\frac{4[h(a_i \rightarrow b_j)]^2}{\Delta E(a_i \rightarrow b_j)} - K_{a_i b_j b_j a_i}\right] \tag{2}$$

where K is the exchange integral, which is neglected in the following discussion.

In the present case the treatment is qualitatively very simple because there is one dominant charge-transfer integral between chromium(III) and semiquinonato, that in which one electron from the metal b_1 orbital is transferred to the HOMO of the ligand of the same symmetry: $h(b_1(Cr) \rightarrow b_1(SQ))$. It is indeed this large integral that determines the large antiferromagnetic coupling observed in the ground state, and it is the same integral that is effective in enhancing the intensity of the $^4A_{2g} \rightarrow {}^2E_g$ transition. According to eq 1 the intensity ratio of the "forbidden" transition I_f and of the allowed CT transition I_{CT} is given by

$$\frac{I_f}{I_{CT}} = \left|\frac{h(b_1(Cr) \rightarrow b_1(SQ))}{\Delta E(b_1(Cr) \rightarrow b_1(SQ))}\right|^2 \tag{3}$$

The experimentally observed ratio is 0.11 for I and 0.26 for III, which shows that the forbidden band is more intense when the charge-transfer energy is lower, as expected. The larger admixture of the CT characters in III as compared to that in I is confirmed by the fact that the forbidden band is broader in the former. The observed intensity ratios require transfer integrals of about 7000 cm^{-1}. According to eq 2 this would correspond to J values on the order of 800 cm^{-1}, in very good agreement with the observed strong antiferromagnetic coupling.

The unique feature of the electronic spectra of these compounds is that of yielding an extremely intense band corresponding to the $^4A_{2g} \rightarrow {}^2E_g$ transition. This is made possible by the direct overlap of the magnetic b_1 orbitals on chromium(III) and semiquinonate, but nevertheless the interaction between them is still weak enough to allow the recognition of metal and ligand transitions. The energy separation between the ground state and the excited charge-transfer state responsible for the intensity enhancement is much smaller than in metal ion pairs, because it involves metal-to-ligand rather than metal-to-metal electron transfer.

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(8) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 1476.

(9) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(10) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907.

(11) Gondaira, K. I.; Tanabe, Y. *J. Phys. Soc. Jpn.* **1966**, *21*, 1527.

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Photochemical Grafting of Triiron Dodecacarbonyl to Silica. Formation of a Surface-Bound Anionic Trinuclear Cluster

Supported metal carbonyl clusters have attracted much attention in the preparation of catalysts containing highly dispersed metals on inorganic oxide supports.[1-4] Several transition-metal carbonyl clusters attached to oxide supports have been produced by thermally induced reactions between the cluster and surface hydroxy groups.[5-16] It has been shown that the interaction between $Fe_3(CO)_{12}$ and the hydroxy groups of silica is weak and no grafted cluster can be formed by thermal activation.[15-17] Thermal treatment between 323 and 373 K in vacuo results in complete decomposition of the physisorbed $Fe_3(CO)_{12}$.[18] Reported here is the first case of anchoring an intact triiron carbonyl cluster to the surface of silica by photochemical grafting to form the same type of anionic cluster species, $[HFe_3(CO)_{11}]^-$, resulting from a thermal reaction on alumina.[14,15]

The adsorption of $Fe_3(CO)_{12}$ onto silica was performed by dry mixing the cluster (typically 2 wt % iron metal loading) with silica (previously calcined at 450 °C under 10^{-4} Torr vacuum for 12 h) followed by thermal aging under vacuum at 313 K for 2 h.[16] Diffuse-reflectance UV-visible and FTIR analysis of the iron cluster supported on silica confirmed that the cluster is simply physisorbed.[16]

$Fe_3(CO)_{12}$ physisorbed on silica was irradiated at room temperature under an argon atmosphere with use of a Xe lamp (Ushio UXL-500D, 500 W) through a water filter (to remove infrared irradiation) and either a Toshiba O55 cutoff filter (passes light greater than 500 nm) or Toshiba L42 + C40A + B46 filter combination (passes light between 400 and 500 nm). Irradiation in this manner converted the initially dark green material to a rose color. During irradiation the UV-visible absorption spectrum was monitored. As shown in Figure 1, the absorptions at 610 and 450 nm (corresponding to $\sigma^{*\prime} \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$, respectively[19]) disappeared while an absorption at 540 nm grew in. In a similar manner the FTIR spectrum was found to change from that for the physisorbed cluster on silica to one with two strong bands at 2025 and 2002 cm^{-1}. The resulting red cluster could not be extracted from the silica surface by pure dichloromethane. However, when the rose-colored silica was stirred with a dichloromethane solution containing tetraethylammonium chloride, the silica was decolorized and the solution became red. The UV-visible absorption spectrum of the red dichloromethane solution showed an absorption maximum at 543 nm. The FTIR spectrum of the solution showed absorptions at 2002 (s), 1971 (s), and 1712 cm^{-1} (m).

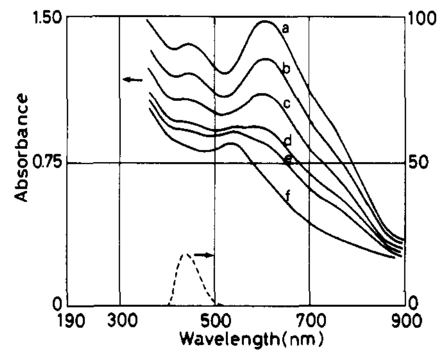

Figure 1. Light-induced UV-visible diffuse-reflectance spectral changes of $Fe_3(CO)_{12}$ physisorbed on SiO_2 versus time (hours): (a) 0; (b) 4; (c) 20; (d) 55; (e) 88; (f) 160. The transmittance curve of the filter combination used (Toshiba L42 + C40A + B46) is also shown (---).

Both the UV-visible and FTIR absorption bands for the photochemically produced cluster on silica are the same as those for $[HFe_3(CO)_{11}]^-$ bound to the surface of alumina.[15] In addition, the UV-visible and FTIR absorption bands for the extracted red cluster are the same as those for $[HFe_3(CO)_{11}]^-[Et_4N]^+$ in solution.[15] From these results, the species formed photochemically on the surface of silica can be assigned as the hydrido cluster $[HFe_3(CO)_{11}]^-$.

The efficiency for the photochemical generation of $[HFe_3(CO)_{11}]^-$ on silica can be compared to that for the thermal reaction on alumina by comparing the UV-visible absorption intensities at 540 nm (same metal loadings). These were found to be approximately the same for a variety of irradiations in which the irradiating wavelengths were greater than 350 nm. This indicates that the photochemical process on silica is as efficient as the thermal process on alumina.

Three possibilities can be envisaged for the formation of the hydrido cluster $[HFe_3(CO)_{11}]^-$ on the surface of silica. One is nucleophilic attack of a surface hydroxy group onto the iron carbonyl cluster:

$$Fe_3(CO)_{12} + HO{-}Si{\equiv} \rightarrow [HFe_3(CO)_{11}]^-[Si{\equiv}]^+ + CO_2 \quad \text{(i)}$$

The second is nucleophilic attack by water present on the silica surface:

$$Fe_3(CO)_{12} + 2H_2O \rightarrow [HFe_3(CO)_{11}]^-[H_3O]^+ + CO_2 \quad \text{(ii)}$$

The third is a reaction with impurities such as aluminum in the silica, leading to a reaction similar to that on alumina:[14,15]

$$Fe_3(CO)_{12} + HO{-}Al{\equiv} \rightarrow [HFe_3(CO)_{11}]^-[Al{\equiv}]^+ + CO_2 \quad \text{(iii)}$$

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(1) Brenner, A. *J. Chem. Soc., Chem. Commun.* **1979**, 251.
(2) Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1976**, 26-27.
(3) Anderson, J. R.; Elmes, P. S.; Howe, R. F.; Mainwaring, D. E. *J. Catal.* **1977**, *50*, 508-518.
(4) Anderson, J. R.; Mainwaring, D. E. *J. Catal.* **1974**, *35*, 162-165.
(5) Besson, B.; Moraweck, B.; Smith, A. K.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 569-571.
(6) Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31-C34.
(7) Watson, P.; Schrader, C. L. *J. Mol. Catal.* **1980**, *9*, 129-138.
(8) Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303-307.
(9) Theolier, A.; Choplin, A.; Dornelas, L.; Basset, J. M.; Zanderighi, G.; Sourisseau, C. *Polyhedron* **1983**, *2*, 119.
(10) Dieter, T.; Gafney, H. D. *Inorg. Chem.* **1988**, *27*, 1730-1736.
(11) Scott, J. P.; Budge, J. R.; Rheingold, A. L.; Gates, B. C. *J. Am. Chem. Soc.* **1987**, *109*, 7736-7744.
(12) Choplin, A.; Huang, L.; Basset, J. M.; Mathieu, R.; Siriwardane, U.; Shore, S. G. *Organometallics* **1986**, *5*, 1547-1551.
(13) Budge, J. R.; Luecke, B. F.; Gates, B. C.; Toran, J. *J. Catal.* **1985**, *91*, 272-282.
(14) Hugues, F.; Smith, A. K.; Taarit, Y. B.; Basset, J. M.; Commereuc, D.; Chauvin, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 68-71.
(15) Hugues, F.; Basset, J. M.; Taarit, Y. B.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020-7024.
(16) Iwasawa, Y.; Yamada, M.; Ogasawara, S.; Sato, Y.; Kuroda, H. *Chem. Lett.* **1983**, 621-924.
(17) Rojas, D.; Bussiere, P.; Dalmon, J. A.; Choplin, A.; Basset, J. M.; Olivier, D. *Surf. Sci.* **1985**, *156*, 516.
(18) Psaro, R.; Ugo, R.; Gates, B. C.; Knözinger, H. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, Oxford, New York, Tokyo, 1986; pp 427-496.
(19) Tyler, D. R.; Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7888-7893.

0020-1669/89/1328-3091$01.50/0