in Figure 4 requires knowledge of the ion-pair equilibrium constant. This has been measured at higher temperatures for ion pairs of $[Ru(NH_3)_6]^{3+}$ with halide ions.[17] From the temperature dependence a value of 11 M^{-1} is calculated at 4 °C and zero ionic strength. This value, however, depends on ionic strength. From the Debye–Hückel parameters obtained from spectrophotometry at 25–50 °C, we calculate that at 4 °C the fraction of ion-paired $[Ru(NH_3)_6]^{3+}$ increases from 0.45 to 0.71 as the chloride ion concentration increases from 0.25 to 0.50 M. Hence, these parameters do not predict the linear increase illustrated in Figure 4. It is likely that these data reflect a mixture of both ionic strength and specific ion effects. They do indicate that chloride ion can facilitate electron transfer between ruthenium complexes. Chloride ion participation was previously observed in the oxidation of $[Ru(NH_3)_6]^{2+}$ by $[Fe(H_2O)_6]^{3+}$.[2] A second-order rate constant of the order of 1×10^4 M^{-1} s^{-1} can be estimated for the electron-exchange reaction between the $[Ru(NH_3)_6]^{3+}$,Cl^- ion pair and $[Ru(NH_3)_6]^{2+}$. Considerable further work would be required to elucidate properly the role of counterions in this electron-transfer reaction.

A few measurements of the exchange rate were made at 25 °C by a back-extrapolation procedure. With 0.25 M $[Ru(NH_3)_6]Cl_2$ solutions a rate constant of 2.2×10^4 M^{-1} s^{-1} was obtained. From the data at 4 and 25 °C a value for ΔH^* of 5 kcal mol^{-1} can be calculated. While this is in good agreement with the results of Brown and Sutin,[5] a detailed study was not pursued because of the experimental difficulties and the composite nature of the observed rate constant.

Discussion

Proton magnetic resonance provides a direct but not entirely satisfactory means of investigating the electron-exchange reaction between $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$. A major difficulty arises from the instability of $[Ru(NH_3)_6]^{2+}$ to hydrolysis during the minutes required to acquire a spectrum (Figure 2). Because of the relative redox potentials involved, hydrolysis of a small fraction of the diamagnetic $[Ru(NH_3)_6]^{2+}$ present in excess leads to the consumption of a large fraction of the paramagnetic $[Ru(NH_3)_6]^{3+}$, which is present in low concentration. Lowering the concentration of $[Ru(NH_3)_6]^{2+}$ to reduce the rate of its hydrolysis only lengthens the time required to acquire its spectrum. Increasing the concentration of $[Ru(NH_3)_6]^{3+}$ causes an unacceptably broad resonance. Consequently, the experimental conditions under which the reaction can be studied are limited. These observations may account, however, for some of the difficulties encountered in the original work, for it is apparent that variations in the time used for experimental procedures could lead to variations in effective concentrations and results.

The rate constants found in the present work are in reasonable agreement with those reported previously by Meyer and Taube[2] and by Brown and Sutin.[5] Our absolute values are somewhat higher, reflecting both the higher ionic strength of the solutions used in these NMR studies and the presence of chloride ions in the place of trifluoroacetate or trifluoromethanesulfonate ions. Significantly, the activation enthalpy was found to be approximately 5 kcal mol^{-1}, which is in agreement with that obtained indirectly by Brown and Sutin[5] but is only half that reported by Meyer and Taube.[2]

Because of the difficulty of making reliable corrections for differences in ionic strength,[5] it is not appropriate to make detailed comparisons among the various rate constants and conditions under which the reaction has been studied. The present results serve to confirm the order-of-magnitude correctness of the previously reported rate constants, to remove the anomaly of the unreasonably large activation enthalpy originally reported, and to emphasize the desirability of examining the role of anions in these outer-sphere electron-transfer reactions by using a technique that allows studies at low ionic strengths.

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Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; Cl^-, 16887-00-6.

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Weak Curie-Type Paramagnetism of High-Nuclearity Platinum Carbonyl Clusters: Anomalous Magnetic Behavior

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Received October 24, 1985

This paper reports the magnetic behavior of large platinum carbonyl clusters: $(Bu_4N)_2[Pt_6(CO)_{12}]$ (**1**), $(Bu_4N)_2[Pt_9(CO)_{18}]$ (**2**), $(Bu_4N)_4[Pt_{19}(CO)_{22}]$ (**3**), and $(PPN)_2[Pt_{38}(CO)_{44}H_x]$ (**4**). We found these platinum clusters to be "diamagnetic" at room temperature but "weakly paramagnetic" at low temperature. The observed paramagnetism (which is an anomaly considering that these are all even-electron clusters) can be described by the simple Curie law. The Van Vleck temperature-independent paramagnetic susceptibility χ_p increases with cluster size. Such marked increase in χ_p with increasing cluster size can be attributed to the decrease in the energy gap between the occupied states and the unoccupied states as the cluster size increases. Another important result is that the effective magnetic moment, μ_{eff}, falls in the narrow range of 0.35–0.55 μ_B per cluster. From the observed magnetic moments, we calculated the μ_{eff} value per atom to be 0.1 ± 0.02 μ_B, a value very close to the corresponding value of 0.09 μ_B observed by Marzke et al. for platinum crystallites containing approximately 400 atoms. The fact that these molecular platinum clusters have magnetic properties very similar to (indeed approaching) those of the small crystallites is a strong indication that these clusters begin to enter the *quantum-size regime* where the magnetic properties are distinctly different from those of the bulk as well as those of the molecules.

Introduction

Recently there has been considerable interest in the magnetic behavior of high-nuclearity transition-metal clusters since they represent ideal models for the transition of molecular units to small particulates to bulk metal.[1,2] These molecular clusters, synthesized by chemical means,[3] have a single *size* and *shape* as opposed to

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[1] Benfield, R. E.; Edwards, P. P.; Stacy, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 525.

[2] Johnson, D. C.; Benfield, R. E.; Edwards, P. P.; Nelson, W. J. H.; Vargas, M. D. *Nature (London)* **1985**, *314*, 231.

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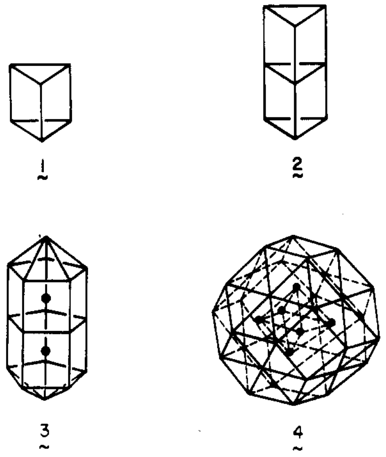
Chart I. Schematic Representation of the Idealized Molecular Architectures of **1**–**4**



a broad size distribution for clusters produced by other means.[4] The central issue of interest is the development of metallic behavior as the cluster grows in size. In other words: how many atoms must one put together in a cluster before it will behave like a metal? While there is no simple answer to this question, it is clear that it depends on which property of the metal one wishes to describe.

Two recent papers, by Benfield et al.[1] and Johnson et al.,[2] attempt to address this issue by measuring the magnetic susceptibility of high-nuclearity osmium carbonyl clusters. These authors found that small osmium clusters exhibit only temperature-independent magnetism whereas large osmium clusters may show weak Curie-type magnetism at low temperature. Johnson et al.[2] also found the temperature-independent Van Vleck paramagnetism of these clusters increases monotonically with cluster size. These studies prompted us to report here our independent study on the magnetic behavior of platinum carbonyl clusters.

Experimental Section

Four representative anionic platinum clusters, $(Bu_4N)_2[Pt_6(CO)_{12}]$ (**1**),[5] $(Bu_4N)_2[Pt_9(CO)_{18}]$ (**2**),[5] $(Bu_4N)_4[Pt_{19}(CO)_{22}]$ (**3**),[6] and $(PPN)_2[Pt_{38}(CO)_{44}H_x]$ (**4**)[7] have been synthesized by the literature methods under inert atmosphere (with Schlenk technique). Preliminary measurements on $(Bu_4N)_2[Pt_{12}(CO)_{24}]$ (**5**) and $(PPN)_2[Pt_{26}(CO)_{32}H_2]$ (**6**) have also been made. All sample manipulation were done in a Vacuum Atmospheres drybox. The samples were sealed in a quartz tube and weighed before and after the measurement. The magnetic susceptibility measurements, in the temperature range 4.2–300 K and the magnetic field range 3–12 kG, were carried out with a high-sensitivity Faraday apparatus.[8] The data were corrected for container susceptibility. The samples were checked for magnetic impurities such as Fe, Co, and Ni by atomic absorption spectroscopy. The impurity level was found to be less than 10–20 ppm by weight, if any. Furthermore, there is no field dependence of the magnetic susceptibility, indicating the absence of ferromagnetic impurities.

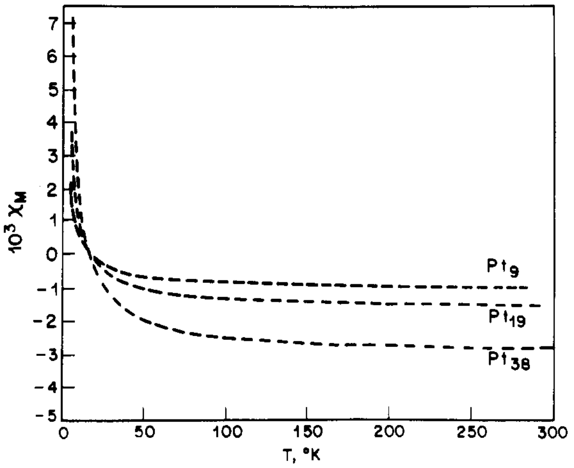


Figure 1. Temperature dependence of the molar magnetic susceptibility of Pt_9 (**2**), Pt_{19} (**3**), and Pt_{38} (**4**) clusters.

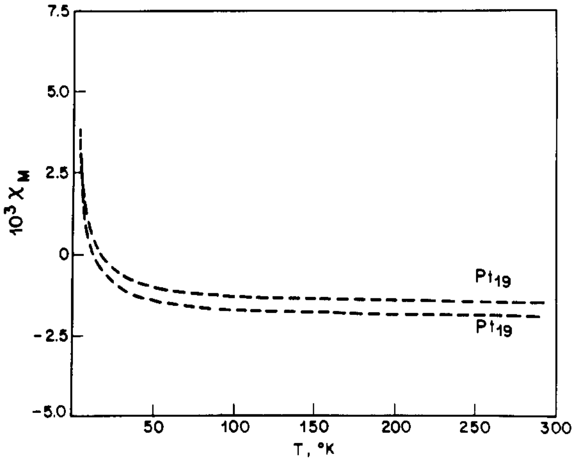


Figure 2. Comparison of the temperature dependences of the molar magnetic susceptibility of the Pt_{19} (**3**) cluster with varying levels of impurities. Atomic absorption measurements indicate no more than 0.02 and 0.004 wt % of Fe for the top and the bottom curves, respectively. These samples were prepared by carefully excluding impurities such as iron.

Table I. Magnetic Susceptibility Data for Platinum Carbonyl Clusters[a]

cluster[b]	$10^6\chi_o$[c]	$10^6\chi_d$[c]	$10^6\chi_p$[c]	10^2C_M[d]	μ_{eff}[e]
$(Bu_4N)_2[Pt_6(CO)_{12}]$ (**1**)	−822	−874	52	1.79	0.38
$(Bu_4N)_2[Pt_9(CO)_{18}]$ (**2**)	−1018	−1100	82	1.55	0.35
$(Bu_4N)_4[Pt_{19}(CO)_{22}]$ (**3**)	−1590	−2120	530	2.99	0.49
$(PPN)_2[Pt_{38}(CO)_{44}H_x]$ (**4**)	−2920	−3309	389	3.77	0.55

[a] Preliminary magnetic susceptibility measurements on $(Bu_4N)_2[Pt_{12}(CO)_{24}]$ and $(PPN)_2[Pt_{26}(CO)_{32}H_2]$ gave rise to similar results reported here. In particular, μ_{eff} values of 0.45 and ~0.67 μ_B/cluster, respectively, have been observed. [b] The temperature range (K) fitted and the relative goodness of fit (%) are as follows: **1**, 7–300, 0.49; **2**, 4–300, 0.42; **3**, 4–300, 0.17; **4**, 7–60, 0.52. [c] In units of emu/mol. [d] In units of emu K/mol. [e] In units of μ_B/cluster.

Results and Discussion

The platinum clusters were found to be "diamagnetic" at room temperature but "weakly paramagnetic" at low temperature (cf. Figure 1). The observed paramagnetism, in molar susceptibility, can be described by

$$\chi_M = \chi_o + C_M/T \qquad (1)$$

where χ_0 is the temperature-independent term and C_M/T is the simple Curie law. The temperature-independent molar susceptibility, χ_0, and the effective moment per (mole) cluster, μ_{eff} in Bohr magnetons (μ_B), calculated from C_M ($C_M = (N/3k)\mu_{eff}^2$, where N is Avogadro's number and k is Boltzmann's constant), obtained by least-squares fitting, are tabulated in Table I.

The experimental evidence that the observed temperature-dependent paramagnetism is *intrinsic* rather than extrinsic can be seen from Figure 2, where two batches of the Pt_{19} cluster (**3**) were

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[3] For reviews on transition-metal clusters see e.g.: (a) Chini, P. *Gazz. Chim. Ital* **1979**, *109*, 225. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (c) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (d) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley-Interscience: Chichester, England, 1980. (e) Benfield, R. E.; Johnson, B. F. G. *Top. Stereochem.* **1981**, *12*, 253.

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[8] See ref 13 for experimental details of magnetic susceptibility measurements.

prepared by carefully excluding impurities such as iron and measured. Atomic absorption measurements indicate approximately 0.02 and 0.004 wt % (upper limits) of Fe for the top and the bottom curves, which amount to 1 Fe/1000 Pt atoms and 1 Fe/5000 Pt atoms, respectively. Even though the impurity contents are different, the results are very similar. There is a small shift in χ_o between the two samples. Although the origin of the shift is not certain, it is suspected that the susceptibility of the compound is anisotropic, since the crystal structure is not cubic, and that the small crystallites measured are not randomly oriented. In that case the average susceptibility measured would vary from sample to sample depending upon the actual orientation of the crystallites.

Temperature-Independent Paramagnetism. If we now define the "paramagnetic molecular susceptibility," χ_p, as the difference between the observed temperature-independent molar magnetic susceptibility, χ_o, and the sum of the diamagnetic contributions of all the atoms within the cluster (including the cations), χ_d,

$$\chi_p = \chi_o - \chi_d \tag{2}$$

we find, as shown in Table I, that χ_p increases with cluster size, in analogy to the case for the osmium carbonyl clusters.[2] Such marked increase in χ_p with increasing cluster size has been attributed by Johnson et al.[2] to the decrease in the energy gap between the occupied states and the unoccupied states as the cluster size increases. In other words, since Van Vleck temperature-independent paramagnetism (TIP) for atomic or molecular systems, which has no magnetic moment in the ground state, can be described by[9a]

$$\chi = \sum|\langle f|\mu_z|i\rangle|^2/\Delta \tag{3}$$

for $\Delta >> kT$ (where $\langle f|\mu_z|i\rangle$ is the nondiagonal matrix element of the magnetic moment operator connecting the occupied states $|i\rangle$ and the unoccupied states $|f\rangle$ with an energy gap Δ between them), it is not surprising that as the cluster size increases, Δ decreases, which leads to an increase in χ_p.

Temperature-Dependent Paramagnetism (Curie Behavior). The most important result to note in our study is the discovery that the effective magnetic moment, μ_{eff}, falls in the narrow range of 0.35–0.55 μ_B per cluster. Of all the osmium carbonyl clusters reported by Benfield et al.[1] and Johnson et al.[2] (Os_3 to Os_{10}), only one cluster, $Os_{10}C(CO)_{24}H_2$, exhibits weak Curie-type paramagnetic temperature dependence (at low temperatures) with $\mu_{eff} \approx 0.62$ μ_B/cluster while others exhibit only temperature-independent magnetic susceptibility down to 1.5 K (note that $Os_{10}C(CO)_{24}I_2$, which has a more "open" structure than $Os_{10}C(CO)_{24}H_2$, has only temperature-independent magnetic susceptibility). Phenomenologically, it is clear that, depending upon the metal and the structure (geometry as well as symmetry), each metal cluster series will reach the so-called "quantum-size" regime[10] at different cluster sizes, beyond which anomalous physical behavior (such as a temperature-dependent magnetic susceptibility observed here) will be operative. Quantum-size effects[10] generally refer to size-dependent properties that result from the presence of the energy gap between the highest occupied and the lowest unoccupied energy levels. While there is no simple theoretical explanation at present for the observed temperature-dependent magnetic behavior, it is worth noting that in a single-electron picture such a moment cannot occur in an even-electron system, unless there is a degeneracy of the highest occupied level.[9b]

If an accidental degeneracy is responsible for the paramagnetism, this would need to occur for all the compounds studied by us and by others.[1,2] While this is not impossible, it seems somewhat unlikely. Nonetheless, the observed Curie behavior can be accounted for if each of the frontier orbitals is degenerate or nearly degenerate with level spacing of 1 K or less. This would probably require a cluster of certain size and shape and with high molecular symmetry. Of course left out of the discussion are the effects of *spin–orbit coupling* and of *electron–electron correlations*. The latter effects could lead to paramagnetism for even moderate values of Δ, and the magnetic moment obtained could be considerably shifted from a $g = 2$, $S = {}^1/_2$ moment by the large value of the spin–orbit coupling found in the third-row transition metals. Another possibility is that some intrinsic defects in the clusters (e.g. dangling bonds, vacancies, fluxionality, etc.) are responsible for the magnetic moment. Finally, charge transfer of metal d electrons into the vacant carbonyl π^* orbitals may create holes in the "d band" of the cluster framework, thereby giving rise to the small magnetic moment. Again, for this last picture to be viable, the cluster must reach a size and shape that is more or less "bulk-like." (In any case, this discussion is not so much meant to be explanatory as to raise possibilities for the source of the observed magnetic moments.)

Bulk Connection. Marzke et al.[11] have measured the magnetic susceptibility of platinum microcrystals with a mean diameter of 22.4 Å (containing about 400 atoms) and found that the susceptibility becomes temperature dependent near 85 K and obeys the Curie law below about 20 K. The observed low-temperature behavior corresponds to about one "unpaired electron" ($S = {}^1/_2$) per particle having spin-only paramagnetism. In other words, the effective magnetic moment is $\mu_{eff} = 2(S(S + 1))^{1/2} = 1.73$ μ_B/particle of 400 atoms. As pointed out by these authors, the observed Curie-type temperature dependence is surprising for platinum since, with 10 valence electrons, the number of electrons per particle should always be even whether there are even or odd numbers of atoms within the particle. And, according to Denton et al.,[12] the paramagnetism is *not* expected to show the Curie-type behavior that is characteristic of particles with unpaired electrons. Despite these considerations, we note that Marzke et al.'s results are fully consistent with our findings that clusters or particles containing even numbers of electrons can exhibit Curie-type temperature dependence at low temperatures in the quantum-size regime. Furthermore, if we take these observations one step further and assume that, within the quantum-size regime, a cluster (or particle) can be thought of being made up of n atoms each possessing an atomic effective magnetic moment of μ_a per (mole) atom, then $\mu_{eff}{}^2 = n\mu_a{}^2$ based on the additivity of susceptibility. Here we assume that the temperature-dependent Van Vleck paramagnetic susceptibility is also additive. We can now write

$$\mu_a = \mu_{eff}/n^{1/2} \tag{5}$$

Using eq 5, we calculate $\mu_a = 0.16$, 0.12, 0.11, and 0.09 μ_B/(mole) atom for **1**–**4**, respectively. Furthermore, our preliminary results showed that $\mu_a = 0.13$ μ_B/(mole) atom for **5** and **6**. With the exception of **1** (Pt_6), μ_a is fairly constant for the size range of n = 9–38. What is even more surprising is that $\mu_a = 1.73/400^{1/2} = 0.09$ μ_B/(mole) atom of platinum for platinum particles containing approximately 400 atoms.[11] The near-constancy of $\mu_a \approx 0.1 \pm 0.02$ μ_B/(mole) atom of platinum for such a wide size range (n = 9–400) is rather striking. *This particular correlation also establishes, for the first time, the connection between "large" platinum clusters (Pt_9–Pt_{38}) and "small" platinum particles ($Pt_{\sim 400}$) in terms of their magnetic behavior.*

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[9] (a) See, for example: Kittel, C. *Introduction to Solid State Physics*, 3rd ed.; Wiley: New York, 1968; pp 628–629 (b) It is also worth noting that the Van Vleck paramagnetic contribution transforms smoothly from temperature-independent paramagnetism (eq 3), for $\Delta >> kT$, to a Curie-type temperature-dependent paramagnetism, for $\Delta << kT$:

$$\chi = \sum|\langle f|\mu_z|i\rangle|^2/kT \tag{4}$$

Though this equation is of the usual Curie form, the mechanism of magnetization here is by *polarization* of the states of the system by the admixture of virtual excited states into the ground state, whereas with free spins the mechanism of magnetization is the *redistribution* among the spin states. It is also interesting to note that the energy gap Δ does *not* enter in the equation.[9a]

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It is perhaps also relevant to point out that one-dimensional conductors such as $Ir(CO)_3Cl_{1.1}$,[13] $K_{0.98}Ir(CO)_2Cl_{2.42}\cdot 0.2CH_3COCH_3$,[14] and $K_{0.60}Ir(CO)_2Cl_2\cdot 0.5H_2O$[14] also exhibit weak Curie-type temperature-dependent paramagnetism, giving rise to μ_{eff} values of 0.07–0.091, 0.05–0.28, and ~0.17 μ_B/(mole) iridium, respectively. The average value of 0.1 μ_B is again very close to our average μ_a value. Assuming an average μ_{eff} of 0.1 μ_B/per Ir and an average chain length of 25 Ir atoms/cluster, we obtain $\mu_{\text{eff}} \approx 25^{1/2} \times 0.1 = 0.5$ μ_B/cluster, roughly in the same size range and μ_{eff} range observed here.

It is also interesting to compare the observed μ_{eff} range of 0.35–0.55 μ_B/cluster reported here with the decrease in μ_{eff} per (mole) atom of silica-supported nickel particles reported by Carter and Sinfelt.[15] These authors found that as the particle size decreases from 2.6×10^4 (bulk) to 65 to 27 to 12 Å in diameter, the effective magnetic moment per nickel, obtained from the Curie–Weiss law fit to the temperature-dependent paramagnetism above the Curie temperature $\Theta(\chi = C_M/(T - \Theta))$, decreases from the bulk value 1.73 to 1.69 to 1.51 to 1.1 μ_B, respectively.

Theoretical Developments. It is clear that the explanation of the Curie-type temperature dependence of the observed paramagnetism must await further theoretical investigation. As cautioned by Johnson et al.,[2] the questions that need to be answered are, for example, whether the assumption of Boltzmann-type statistics, which is prevalent in magnetism, is indeed valid for a metal cluster reaching the quantum-size regime; or perhaps Fermi–Dirac statistics would be more appropriate? Furthermore, will the particulate metal theory[16] (which attempts to approach the problem from the bulk metal), or certain extensions of such, be able to account for the observed temperature-dependent paramagnetism of high-nuclearity metal clusters? Or perhaps should one approach the problem from small clusters via molecular orbital theory[17] or some variants of it? In the absence of a detailed theory, it is safe to say that as the cluster grows in size, the electronic levels change from discrete (as in small molecules) to quasi-continuous (as in high-nuclearity clusters) to band structure (as in bulk). The concomitant evolution of magnetic behavior changes from diamagnetism to Curie-type temperature-dependent paramagnetism to temperature-independent Pauli paramagnetism. Indeed, theoretical prediction[12,16] and experimental observation of enhanced low-temperature susceptibility have been made for particles of metals such as platinum.[11,18]

Summary. In summary, the high-nuclearity metal clusters exhibit diamagnetic behavior (χ_o in eq 2 is negative) at high temperatures since the diamagnetic contribution (χ_d) to the magnetic susceptibility outweighs the paramagnetic molecular susceptibility (χ_p in eq 2 is positive). The term χ_p increases as the cluster size increases, consistent with the decrease in energy gap between the frontier orbitals. As the cluster reaches a critical *size* and *shape* (viz., entering the so-called quantum-size regime), *intrinsic* temperature-dependent Curie-type paramagnetism at low temperatures ($\lesssim$70 K) is observed. We define the critical size and shape as the size and shape of the cluster at which the metal valence electrons (responsible for metallic bonding) are completely delocalized and can be considered collectively as a whole. The effective magnetic moment per (mole) cluster falls in the narrow range 0.35–0.67 μ_B for the size range of Pt_6–Pt_{38}. It is pointed out, for the first time, that the effective magnetic moment per (mole) atom, with the exception of Pt_6, falls within the narrow range of 0.1 ± 0.02 μ_B for Pt_9–$Pt_{\sim 400}$. The fact that these molecular platinum clusters have magnetic properties very similar to (indeed approaching) those of the small crystallites is a strong indication that these clusters begin to enter the quantum-size regime where the magnetic properties are distinctly different from that of the bulk as well as that of the molecules (viz., an anomaly). Magnetic properties of high-nuclearity metal cluster systems containing platinum as well as other metals will be subjects of future publications.

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Registry No. **1**, 72264-20-1; **2**, 61084-48-8; **3**, 72026-40-5; **5**, 61084-51-3.

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Notes

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Novel Peroxo Complexes of Zirconium Containing Organic Ligands

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In recent years there has been considerable interest in the investigation of peroxo complexes of transition metals because of their interesting coordination chemistry as well as their role in synthetic organic chemistry.[1-11] The synthesis and properties of organo peroxo complexes of thorium(IV)[12] and titanium(IV)[13] have been reported. As zirconium is also a group 4B element, it was of interest to discover whether it would form analogous peroxo complexes that contain organic moieties. The present paper describes several novel organoperoxo complexes of Zr(IV) along with their properties with respect to oxygen transfer to various substrates.

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