The fluoride also coprecipitates from halogen fluoride solutions with XeF$_2$ and complexes of XeF$_2$ but not with XeF$_4$.[7,8]

Recently, Avrorin et al.[9] have reported the preparation of a higher fluoride of radon, either RnF$_4$ or RnF$_6$, and a water-soluble oxide, RnO$_3$, in tracer experiments with isotope ^{222}Rn. They hydrolyzed complex mixtures of products that had been obtained by heating radon, xenon, fluorine, bromine pentafluoride, and either sodium fluoride or nickel fluoride. Part of the radon volatilized on hydrolysis and part remained in the aqueous phase, suggesting the formation of RnO$_3$. However, Avrorin et al. failed to closely examine the contents of the aqueous phase. In this note we report the results of experiments that we have carried out, using larger amounts of reagents and similar conditions, in an effort to confirm their findings.

Experimental Section

A Monel reactor (9.05-mL volume) attached to a Monel valve was loaded at room temperature with either NiF$_2$ (16.8–27.7 mmol) or NaF (39.3–42.9 mmol), cooled to –195 °C, and charged with BrF$_5$ (15.5–46.4 mmol), ^{222}Rn (49–221 μCi), xenon (0.54–0.57 mmol), and fluorine (54.7–57.1 mmol). Each mixture was heated at 250–265 °C for approximately 40 h. The excess fluorine was pumped off at –195 °C, and BrF$_5$ and uncomplexed XeF$_6$ were vacuum distilled from the reactor at 0 °C. (The XeF$_6$ product was complexes by NaF but not by NiF$_2$). Products remaining in the reactor were then hydrolyzed with 8–15 mL of 0.10 M aqueous XeO$_3$ solution at 0 °C. Radon in the hydrolysate was analyzed by measuring the γ emissions of its daughters, ^{214}Pb and ^{214}Bi, in equilibrium with their parent.[4] The hydrolysate was centrifuged and the supernate transferred to a separate container; the radon was then analyzed in each fraction. The supernate was flushed with nitrogen for 5–10 min and the residue stirred with 10 mL of either water, 0.10 M XeO$_3$ solution, or 1 M KI solution; after 4 h, the analyses were repeated.

To determine the behavior of radon in simpler mixtures, several experiments were carried out with only radon, fluorine, and NiF$_2$ or with only radon, fluorine, and NaF. Each mixture was heated at 335–350 °C for approximately 3 h, excess fluorine was pumped off at –195 °C, and the products were hydrolyzed as before.

Results and Discussion

In the experiments with quinary mixtures, we found that 70% or more of the radon initially bound as a nonvolatile fluoride was released as gas during the hydrolysis. However, the remainder was not in solution, as reported by Avrorin et al., but was trapped in undissolved solid. After the centrifugation and purge with nitrogen, less than 0.2% of the radon remained in the liquid phase. Approximately 11–29% (corrected for decay) stayed in the NiF$_2$ residue and 5–24% in the NaF residue during the course of these experiments. Stirring the solid with water, XeO$_3$ solution, or KI solution released a further amount of radon as gas but yielded no solution containing a soluble radon compound. Iodine was liberated when KI solution was added to the supernate, showing that XeO$_3$ was not removed by the purge.

In each experiment with radon, fluorine, and NiF$_2$, a complex fluoride was formed [probably (RnF$^+$)$_2$NiF$_6$$^{2-}$, a noble-gas analogue of K$_2$NiF$_6$ and Cs$_2$NiF$_6$]. The radon was found to be concentrated in the NiF$_2$ powder at the end of the fluorination. In experiments with radon, fluorine, and NaF, the radon was found to be distributed throughout the reactor, suggesting that the simple fluoride RnF$_2$ was formed. During the hydrolysis of each product, part of the radon was released as gas and part trapped in the solid, as before.

We conclude from this study that no higher fluoride or oxide of radon is formed in the procedure of Avrorin et al. but that,

instead, the radon is carried by solids. Other workers have also been misled by this phenomenon. In 1967, Haseltine and Moser[10] reported the oxidation of radon in aqueous solutions with hydrogen peroxide, potassium permanganate, potassium persulfate, and other reagents, but Flohr and Appelman[11] showed that the radon had not been oxidized but merely trapped in suspended solids. Gusev and Kirin[12] later confirmed Flohr and Appelman's results, using barium as a carrier.

Thus far, we have seen no evidence for the existence of radon compounds or ions in aqueous solutions. We have found that solutions of cationic radon can be prepared very readily, however, in nonaqueous solvents, such as hydrogen fluoride and halogen fluorides.[2,4]

(10) Haseltine, M. W.; Moser, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 2498.
(11) Flohr, K.; Appelman, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 3584.
(12) Gusev, Yu. K.; Kirin, I. S. *Radiokhimiya* **1971**, *13*, 916.

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New Routes to the Preparation of the Aquomolybdenum(IV) Ion by Comproportionation Reactions

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The existence of an aquomolybdenum(IV) ion was first demonstrated by Souchay and co-workers[1] in 1966. Beginning in 1975, efforts to establish the nuclearity of the aquo ion in solution produced proposals of both mononuclear[2,3] and binuclear[4–7] structures. These conclusions were based on kinetic, electrochemical and cryoscopic measurements. However, the likelihood of a trinuclear structure of the sort shown in Figure 1., e.g., [Mo$_3$(μ_3-O)(μ-O)$_3$(H$_2$O)$_9$]$^{4+}$, was suggested by the fact that merely by addition under mild conditions of certain ligands to a solution of the aquo ion crystalline products were isolated in which an Mo$_3$(μ_3-O)(μ_2-O)$_3$L$_9$ structure was found.[8–10] Direct evidence of the trinuclear character of the

(1) Souchay, P.; Cadiot, M.; Duhameaux, M. *C. R. Hebd. Seances Acad. Sci.* **1966**, *262*, 1524.
(2) Ramasami, T.; Taylor, R. S.; Sykes, A. G. *J. Am. Chem. Soc.* **1975**, *97*, 5918.
(3) Ojo, S. F.; Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 1006.
(4) Ardon, M.; Pernick. A. *J. Am. Chem. Soc.* **1973**, *95*, 6871.
(5) Ardon, M.; Bino, A.; Yahaw, G. *J. Am. Chem. Soc.* **1976**, *98*, 2338.
(6) Chalilpoyil, P.; Anson, F. C. *Inorg. Chem.* **1978**, *17*, 2418.
(7) Cramer, S. P.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2770.
(8) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.
(9) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3842.
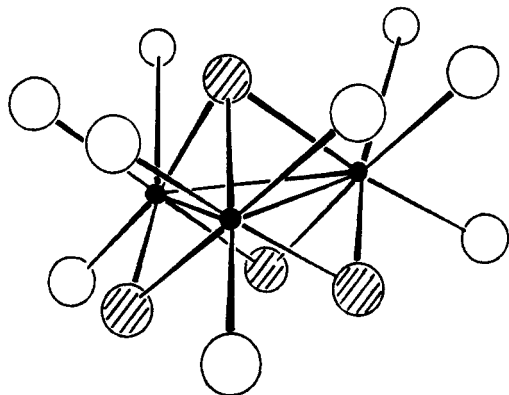(10) Schlemper, E. O.; Hussian, M. S.; Murmann, R. K. *Cryst. Struct. Commun.* **1982**, *11*, 89.

(7) Nefedov, V. D.; Toropova, M. A.; Avrorin, V. V.; Dudkin, B. N. *Radiokhimiya* **1971**, *13*, 916.
(8) Avrorin, V. V.; Nefedov, V. D.; Toropova, M. A. *Radiokhimiya* **1974**, *16*, 261.
(9) Avrorin V. V.; Krasikova, R. N.; Nefedov, V. D.; Toropova, M. A. *Radiokhimiya* **1981**, *23*, 879.

Figure 1. Idealized representation of the $[Mo_3O_4(H_2O)_9]^{4+}$ ion. The hatched and open spheres represent the oxygen atoms and water molecules, respectively.

Mo^{IV} aquo ion in solution was finally provided by Murmann[11] through studies of isotopic oxygen exchange. The most recent studies[12–14] have accepted and/or provided further support for the trinuclear structure.

Previously reported preparations[1,2,4] of the $Mo^{IV}(aq)$ ion have included the comproportionation reaction of Mo^{III}, usually in the form of $MoCl_6^{3-}$, with a Mo^V or Mo^{VI} species in 2 M acid for 1–2 h at 90 °C. Before the aquo ion can be isolated in these procedures, the solution must be allowed to stand for 1–2 days to allow sufficient time for complete aquation of the trinuclear ion. To avoid this delay, we considered it worthwhile to search for alternative preparative methods by which the ion could be isolated in a shorter time period. We now report two such reactions from which the $[Mo_3O_4(H_2O)_9]^{4+}$ ion can be obtained in a pure form in significantly shorter time periods than previously required. In these reactions stoichiometric amounts of either the dinuclear $Mo^{II}(aq)$ ion or the dinuclear ion $Mo^{III}(aq)$ are reacted with sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, to produce solutions of the trinuclear $Mo^{IV}(aq)$ cation.

Experimental Section

Preparation of the $[Mo_3O_4(H_2O)_9]^{4+}$ Ion. Scheme I. An aqueous solution containing 1 mmol of $[Mo_2(H_2O)_8]^{4+}$ in 1 M trifluoromethanesulfonic acid was prepared by the method of Bowen and Taube.[15] To this solution under a N_2 atmosphere was added 0.482 g (2 mmol) of $Na_2MoO_4 \cdot 2H_2O$. After stirring for 3 h, the solution contained the deep red $Mo^{IV}(aq)$ species.

Scheme II. To a 500-mL beaker containing 20 g of zinc amalgam was added 0.75 g (3.1 mmol) of $Na_2MoO_4 \cdot 2H_2O$ dissolved in 310 mL of 1 M HCl. The mixture was stirred for 30 min at which time the solution contained the green $Mo_2^{6+}(aq)$ ion. After the Zn/Hg was removed by suction filtration, 0.38 g (1.6 mmol) of $Na_2MoO_4 \cdot 2H_2O$ in 50 mL of 1 M HCl was added to the solution. Further stirring of the mixture yields the $[Mo_3O_4(H_2O)_9]^{4+}$ ion in 45 min.

Isolation of the $[Mo_3O_4(H_2O)_9]^{4+}$ Ion. The solution obtained in Scheme II was used directly, while the solution obtained from Scheme I was diluted with an equal volume of water. The solution obtained from the preparative reaction was poured on a Dowex 50W-X2 cation-exchange column (2.5 cm × 40 cm). A red band of the $Mo^{IV}(aq)$ ion was absorbed on the column, and impurities were removed by washing the resin with a 1 M solution of p-toluenesulfonic acid. After the column was rinsed with water, the $Mo^{IV}(aq)$ ion can be eluted with a 2 M solution of virtually any strong acid, e.g., HCl, HBr, HBF$_4$, HClO$_4$, and CF$_3$SO$_3$H, in yields of 75–90%.

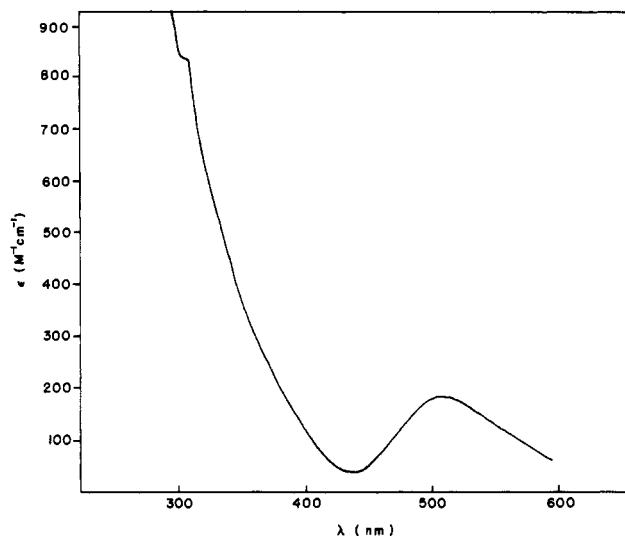(11) Murmann, R. K.; Shelton, M. E. *J. Am. Chem. Soc.* **1980**, *102*, 3984.
(12) Ghellar, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Conner, M. S.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1983**, *105*, 1527.
(13) Paffett, M. T.; Anson, F. C. *Inorg. Chem.* **1983**, *22*, 1347.
(14) Cramer, S. P.; Eidem, P. K.; Paffett, M. T.; Winkler, J. R.; Dori, Z.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 799.
(15) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287; *Inorg. Chem.* **1974**, *13*, 22435.

Figure 2. Electronic spectrum of the $[Mo_3O_4(H_2O)_9]^{4+}$ ion in 2 M $HClO_4$.

Preparation of $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$ and $Na_4[Mo_6O_8(EDTA)_3]$. With aqueous solutions prepared according to the above procedures, both the oxalate and EDTA^{4+} complexes were prepared by the methods of Bino, Cotton, and Dori.[8,9]

Electronic Spectra. All UV–visible spectra were measured on a Cary 17D spectrometer at 25 °C. The spectrum of the $[Mo_3O_4(H_2O)_9]^{4+}$ ion in 2 M $HClO_4$, shown in Figure 2, has two peaks, one at 508 nm ($\epsilon = 191$ M^{-1} cm^{-1}) and the other at 304 nm ($\epsilon = 811$ M^{-1} cm^{-1}).

X-ray Procedures. The unit cell parameters of $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3] \cdot 4H_2O \cdot {}^1/_2H_2C_2O_4$ and $Na_4[Mo_6O_8(EDTA)_3] \cdot 14H_2O$ were obtained by use of an automated four-circle diffractometer (CAD-4) equipped with graphite-monochromated Mo $K\alpha$. The parameters were derived from a least-squares fit to the goniometer settings of 25 accurately located reflections.

Discussion

Although the stoichiometric ratios employed in the preparative reactions (1) and (2) are such as to produce molybde-

$$3Mo_2^{4+}(aq) + 6MoO_4^{2-} + 16H_3O^+ = 4[Mo_3O_4(H_2O)_9]^{4+} \quad (1)$$

$$Mo_2^{6+}(aq) + MoO_4^{2-} + 6H_2O = [Mo_3O_4(H_2O)_9]^{4+} \quad (2)$$
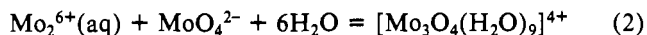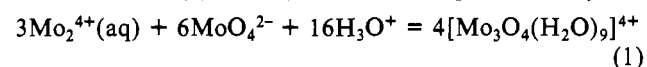
num in the IV oxidation state, it was necessary to obtain evidence that the $Mo^{IV}(aq)$ ion produced was, indeed, the $[Mo_3O_4(H_2O)_9]^{4+}$ ion. To understand the need for this, it should be recalled that by using different preparative procedures to $Mo^{III}(aq)$ ion can be obtained in mononuclear,[15] binuclear,[16] or trinuclear form.[13,17]

Such evidence was obtained in several ways. The electronic absorption spectrum of the solutions eluted from the cation-exchange columns match very well the spectra reported previously[3,13] for the $[Mo_3O_4(H_2O)_9]^{4+}$ ion. In addition, several previously reported reactions[10–12] of the $Mo^{IV}(aq)$ ion prepared by the older procedure were reproduced with use of the solutions obtained by the new methods. All of the reactions ran as reported, and the electronic spectra of the products matched those previously reported. The most conclusive evidence came from the comparison of the unit cell dimensions[8,9] of crystals of $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3] \cdot 4H_2O \cdot {}^1/_2H_2C_2O_4$ and Na_4-$[Mo_6O_8(EDTA)_3] \cdot 14H_2O$ obtained from our $Mo^{IV}(aq)$ ion to the unit cell dimensions previously reported. In both cases, the crystals from both methods were identical within experimental error. From all of these data, it is certain that we have generated the $[Mo_3O_4(H_2O)_9]^{4+}$ ion.

(16) Ardon, M.; Pernick. A. *Inorg. Chem.* **1974**, *13*, 2275.
(17) Richens, D.; Sykes, A. *Inorg. Chem.* **1982**, *21*, 418.

Both new methods of preparation fulfill our original goal of producing the Mo^{IV}(aq) species more quickly, but the second reaction scheme has advantages over the first one. In the second method, the reaction is run in the open and the reaction time is shorter than in the first method, which must be run under an inert atmosphere. Finally, the cost of the starting materials is a factor. The only molybdenum-containing reagent required for the second reaction scheme is Na$_2$MoO$_4$·2H$_2$O while the first scheme requires some relatively more expensive intermediate (Mo$_2$(O$_2$CCH$_3$)$_4$, K$_4$Mo$_2$(SO$_4$)$_4$) from which to form the Mo^{II}(aq) species. Therefore, the second method, described by reaction 2, provides the most practical route now available to aqueous solutions of the [Mo$_3$O$_4$-(H$_2$O)$_9$]$^{4+}$ ion.

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Reexamination of the π Bonding in Dichloro(cycloocta-1,5-diene)platinum

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In recent years, a number of cyclic and acyclic olefin complexes of metal ions with d^8 configuration have been investigated. Among these, the Pt(II) derivatives have been most widely studied.[1] Because of our interest in the electronic character of transition-metal complexes which may model catalytic intermediates and interest in complexes such as *cis*-Pt(NH$_3$)$_2$Cl$_2$ and *cis*-Pt(en)Cl$_2$, which exhibit antitumor activity,[2] an accurate determination of the structure of a complex of PtCl$_2$ and 1,5-cyclooctadiene (COD) was undertaken at low temperature. Quite recently, the metal-olefin bonding in the (COD)PtCl$_2$ complex has been reported to be unsymmetrical,[3] suggesting an activation of the coordinated ligand toward nucleophilic attack. This asymmetric complexation is not confirmed in the present study.[4]

The stability of olefin complexes of Pt(II) is explained by the Dewar-Chatt-Duncanson model.[5] The DCD model involves a synergic relation between ligand-to-metal $\pi \rightarrow \sigma$ bonding and metal-to-ligand d$\pi \leftarrow \pi^*$ electron flow. Both donation of π-electron density from the COD molecules to Pt(II) and accumulation of electron density in the COD π^* orbitals are expected to lower the π-bond order of the coordinated COD ring. As a consequence, the coordinated olefinic bond will be lengthened, as observed in the present study.

It has further been suggested that activation of coordinated olefins to nucleophilic attack may result from asymmetric complexation to the metal atom.[6] However, neither the bonding mode nor the relatively low reactivity of (COD)PtCl$_2$ would appear to indicate unsymmetrical olefin-metal bonding in the molecule. Nevertheless, in a recent room-temperature structure determination,[3] one of the two double bonds was reported to be "slipped" with respect to PtCl$_2$ (C-Pt bond distances of 2.209 (21) and 2.156 (17) Å), while the other double bond was more symmetrically coordinated (2.215 (18)

[†] On leave from Tata Iron & Steel Co., Jamshedpur, India.

Table I. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters^a

atom	x	y	z	B, Å^2
Pt	0.83888 (3)	0.09928 (2)	0.62360 (2)	0.604 (2)
Cl1	1.1176 (2)	0.1038 (2)	0.7299 (1)	1.00 (2)
Cl2	0.7315 (3)	0.2821 (2)	0.7039 (1)	1.13 (2)
C1	0.5499 (9)	0.0545 (7)	0.5608 (6)	0.90 (9)
C2	0.6427 (9)	0.1354 (6)	0.4912 (5)	0.87 (9)
C3	0.7450 (10)	0.0994 (6)	0.3872 (5)	1.12 (9)
C4	0.8728 (9)	−0.0189 (7)	0.3975 (5)	0.93 (9)
C5	0.9655 (10)	−0.0308 (6)	0.5079 (6)	0.98 (9)
C6	0.8876 (9)	−0.0993 (6)	0.5927 (5)	0.89 (8)
C7	0.6897 (10)	−0.1626 (7)	0.5912 (6)	1.09 (9)
C8	0.5255 (9)	−0.0851 (6)	0.5418 (6)	1.05 (9)

^{a} Estimated standard deviation in the least significant digit is given in parentheses. Hydrogen atom coordinates and anisotropic thermal parameters are given in the supplementary material.

Table II

Distances (Å)

Pt-Cl(1)	2.315 (1)	C(8)-C(1)	1.517 (8)
Pt-Cl(2)	2.309 (1)	C(1)-H(1)	0.949 (6)
Pt-C(1)	2.172 (6)	C(2)-H(2)	0.945 (6)
Pt-C(2)	2.154 (5)	C(3)-H(3)	0.951 (6)
Pt-C(5)	2.176 (6)	C(3)-H(4)	0.960 (6)
Pt-C(6)	2.178 (6)	C(4)-H(5)	0.957 (5)
C(1)-C(2)	1.375 (8)	C(4)-H(6)	0.949 (6)
C(2)-C(3)	1.518 (8)	C(5)-H(7)	0.965 (6)
C(3)-C(4)	1.538 (8)	C(6)-H(8)	0.945 (6)
C(4)-C(5)	1.516 (8)	C(7)-H(9)	0.962 (6)
C(5)-C(6)	1.387 (8)	C(7)-H(10)	0.972 (6)
C(6)-C(7)	1.509 (8)	C(8)-H(11)	0.964 (6)
C(7)-C(8)	1.521 (9)	C(8)-H(12)	0.940 (6)

Angles (deg)

|			
Cl1-Pt-Cl2	89.78 (5)	Cl2-Pt-C6	161.0 (2)
C1-Pt-C2	37.1 (2)	Cl1-Pt-C5	93.7 (2)
C5-Pt-C6	37.2 (2)	Cl1-Pt-C6	89.8 (2)
C1-Pt-C6	82.0 (2)	Cl2-Pt-C1	93.1 (2)
C2-Pt-C5	81.7 (2)	Cl2-Pt-C2	89.0 (2)
Pt-C1-C2	70.8 (2)	C1-Pt-C5	89.0 (2)
Pt-C2-C1	72.2 (3)	C2-Pt-C6	97.7 (2)
Pt-C5-C6	71.5 (3)	C1-C2-C3	126.0 (5)
Pt-C6-C5	71.3 (3)	C2-C3-C4	113.3 (5)
Pt-C1-C8	111.8 (4)	C3-C4-C5	112.4 (4)
Pt-C2-C3	108.6 (4)	C4-C5-C6	124.9 (5)
Pt-C5-C4	112.2 (4)	C5-C6-C7	124.7 (5)
Pt-C6-C7	107.5 (4)	C6-C7-C8	114.9 (5)
Cl1-Pt-C1	162.6 (2)	C7-C8-C1	112.9 (5)
Cl1-Pt-C2	160.3 (2)	C8-C1-C2	124.6 (5)
Cl2-Pt-C5	161.7 (2)		
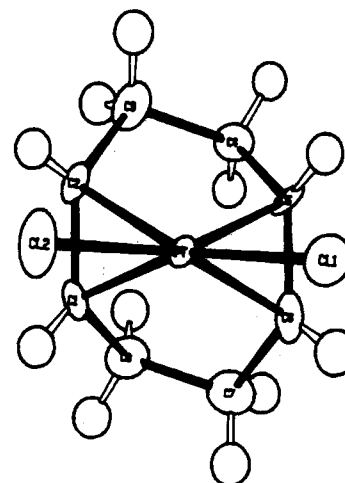
Figure 1. Structure of dichloro(cycloocta-1,5-diene)platinum(II) at 110 K showing the atom-labeling scheme. Thermal ellipsoids show 90% probability surfaces.

and 2.203 (19) Å). The estimated standard deviations are sufficiently large, especially considering that X-ray esd's are