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 $Na_2MoO_4 \cdot 2H_2O$ while the first scheme requires some relatively more expensive intermediate ($Mo_2(O_2CCH_3)_4$, $K_4Mo_2(SO_4)_4$) 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 $[Mo_3O_4(H_2O)_9]^{4+}$ ion.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $[Mo_3O_4(H_2O)_9]^{4+}$, 74353-85-8; $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$, 67620-45-5; $Na_4[Mo_6O_8(EDTA)_3]$, 71356-70-2; $[Mo_2(H_2O)_8]^{4+}$, 91798-52-6; Na_2MoO_4, 7631-95-0.

Contribution from the Department of Chemistry,
University of New Orleans, New Orleans, Louisiana 70148

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

Ashfaquzzaman Syed,[†] Edwin D. Stevens,* and Sandra G. Cruz

Received November 4, 1983

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*-$Pt(NH_3)_2Cl_2$ 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.

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)		

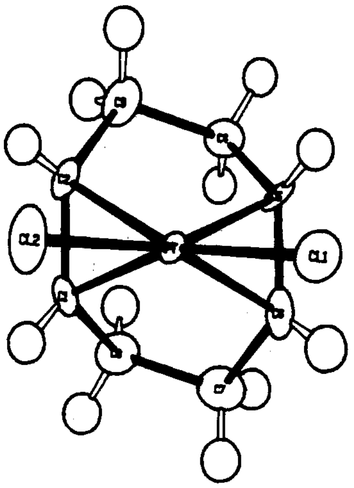

Figure 1. Structure of dichloro(cycloocta-1,5-diene)platinum(II) at 110 K showing the atom-labeling scheme. Thermal ellipsoids show 90% probability surfaces.

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

---

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

typically underestimated by a factor of 2, to cast doubt on the significance of this feature (Tables I and II).

In the structure determination at 110 K reported here, the esd's are lower by a factor of 3, and the corresponding Pt–C bond distances (2.172 (6), 2.154 (5), 2.176 (6), 2.178 (6) Å) are much closer to being equivalent. Again assuming that X-ray standard deviations given by the refinement are underestimated by a factor of 2, the possibility that the bond distances are equivalent cannot be rejected on the basis of a χ^2 test at the 0.10 significance level.[7]

An ORTEP drawing[8] of the molecule is shown in Figure 1. The important features to note in the structure of (COD)$PtCl_2$ are as follows: (i) The COD molecule is symmetrically coordinated to the Pt atom. (ii) The ethylene portions of the COD molecule are twisted to avoid eclipsing, which lowers the point group symmetry of the molecule to C_s. (iii) The coordinated C=C double bonds are lengthened (1.375 (8) and 1.387 (8) Å) by an amount comparable to that found in the isomorphous palladium complex[9] and other similar systems.[10] This is contrasted with a double-bond distance of 1.334 Å in the cyclooctatetraene molecule[11] and 1.316 and 1.320 Å bond distances for the uncoordinated double bonds in dichloro(cyclooctatetraene)palladium(II).[10c] The Pt–Cl bond distances are in the range of those observed in similar structures.[12]

Acknowledgment. This contribution is based upon work supported by the National Science Foundation (Grant CHE8311704). Funds for the purchase of an automated diffractometer were also provided in part by the National Science Foundation (Grant CHE 8208754).

Registry No. (COD)$PtCl_2$, 12080-32-9.

Supplementary Material Available: Tables of positional and thermal parameters for H atoms, bond angles involving H atoms, and anisotropic thermal parameters for non-hydrogen atoms and a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

---

(1) (a) Manojloric-Muir, L.; Muir, K. W.; Ibers, J. A. *Discuss. Faraday Soc.* **1969**. (b) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(2) (a) Rosenberg, B.; Van Camp, L.; Trosko, J. E.; Mansour, V. H. *Nature (London)* **1969**, *222*, 385. (b) Rosenberg, B. *Platinum Met. Rev.* **1971**, *15*, 42–51.

(3) Goel, A. B.; Goel, S.; van der Veer, D. *Inorg. Chim. Acta* **1982**, *65*, L205–L206.

(4) The title compound crystallizes in the space group $P2_12_12_1$ with a = 6.818 (1) Å, b = 10.664 (2) Å, c = 12.423 (4) Å, Z = 4, D_{calcd} = 2.751 g cm^{-3}, and μ = 81.1 cm^{-1}. The intensities of 2265 unique reflections ($2\theta_{max}$ = 60°), were collected from a crystal of approximate dimensions 0.39 × 0.40 × 0.33 mm, on a CAD4 diffractometer in ω–2θ scan mode by using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Temperature was maintained at 110 (2) K with a cold stream of N_2 gas. A numerical absorption correction based on the measured shape of the crystal was applied (transmission factors: max = 0.172 min = 0.089). A total of 2032 reflections with $I > 3\sigma(I)$ was included in the least-squares refinement. The structure was solved by MULTAN 11/82: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 80", A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York and Louvain: York, England and Louvain, Belgium, 1980. In the refinement process by full-matrix least-squares techniques, anisotropic temperature factors were applied for all non-hydrogen atoms in the symmetric unit. Hydrogen atoms were input at their calculated positions (d_{C-H} = 0.95 Å) and used in the structure factor calculations but not refined. Final refinement included an isotropic extinction parameter, giving a total of 101 parameters. At convergence, $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.028$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.035$ where $w = 1/\sigma^2(F_o)$. The goodness of fit indicator $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$ was 1.437. A difference Fourier done at this stage did not show any significant peaks. Least-squares refinement of the structure with atomic positions inverted through a center of symmetry gave R = 0.048 and R_w = 0.062, indicating that the absolute configuration originally chosen for the structure was correct. Atomic scattering factors and anomalous dispersion corrections were taken from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. All the computations were performed on a PDP11/34 computer using the SDP system: Frenz, B. A. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, 1982.

(5) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939–2947.

(6) Eisenstein, O.; Hoffman, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148–6149; **1981**, *103*, 4308–4320.

(7) Hamilton, W. C. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1969**, *25*, 194–206.

(8) Johnson, C. K. "ORTEP", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(9) Benchekroun, L.; Herpin, P.; Julia, M.; Saussine, L. *J. Organomet. Chem.* **1977**, *128*, 275–290.

(10) (a) Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Inorg. Chem.* **1964**, 3, 1529–1535, 1535–1541. (b) Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Acta Crystallogr.* **1965**, *18*, 924–926. (c) Baenziger, N. C.; Valley Goebel, C.; Berg, T.; Doyle, J. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1340–1342.

(11) Bastiansen, O.; Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1957**, *27*, 1311.

(12) (a) Jarvis, J. A. J.; Kilbourn, B. T.; Owston, P. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 876; **1971**, *B27*, 366–372. (b) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653–2657. (c) Iball, J.; Scrimgeour, S. N. *Acta Crystallogr., Sect B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1194–1196. (d) Graves, B. J.; Hodgson, D. J.; van Kralingen, C. G.; Reedijk, J. *Inorg. Chem.* **1978**, *17*, 3007–3011.

Contribution from Chemistry Department A,
The Technical University of Denmark, 2800 Lyngby, Denmark

Micelle-Trapped Tris(benzhydroxamato)iron(III) as a Siderophore Model Compound

Ingólfur Kristjánsson, Finn H. Nielsen, and Jens Ulstrup*

Received December 12, 1983

The central coordination units of microbial siderophore iron transport compounds are chelate iron(III) complexes of hydroxamate or catecholate ligands.[1-8] In important respects the properties of "simple" (hydroxamato)- or (catecholato)iron(III) complexes can therefore be expected to represent those of the biological iron compounds. In hydroxamato siderophore complexes the iron coordination center is, however, shielded from the external aqueous medium by a "shell" constructed from the organic backbone of a multibasic aliphatic hydroxamato ligand system, the carboxylic acid constituent of which is commonly the acetyl group and which possesses on the outside a dipolar structure due to attachment of strongly polar groups at the surface. These surface properties also lead to formation of a diffuse double layer around the siderophore and in this way provide control for the access of potential reactant molecules to the iron core.

The dipolar and double-layer effects are not reproduced by simple hydroxamato complexes. On the other hand, we show in the present work that iron(III) complexes of apolar hydroxamate ligands, represented here by tris(benzhydroxamato)iron(III) (TBH), can be trapped in anionic micelles. This compound has previously been forwarded as a siderophore model compound.[4-6] It is a shortcoming of this particular compound that the acid group is aromatic, whereas those of real siderophores are acyclic and very commonly the

---

(1) Neilands, J. B. "Inorganic Biochemistry"; Eichhorn, G., Ed.; Elsevier: New York, 1973; p 167.

(2) Neilands, J. B. *Adv. Chem. Ser.* **1977**, *No. 162*, 3.

(3) Raymond, K. N, *Adv. Chem. Ser.* **1977**, *No. 162*, 33.

(4) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183.

(5) Abu-Dari, K.; Cooper, S. R.; Raymond, K. N.; *Inorg. Chem.* **1978**, *17*, 3394.

(6) Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1980**, *19*, 2034.

(7) Tufano, T. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6617.

(8) Hider, R. C.; Rahim Mohd-Nor, A.; Silver, J.; Morrison, I. E. G.; Rees, L. V. C. *J. Chem. Soc., Dalton Trans.* **1981**, 609.

0020-1669/84/1323-3674$01.50/0