Novel Redox Systems in Hexamethylbenzene Metal Cluster Compounds of Niobium and Tantalum

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Summary The green to brown hexamethylbenzene metal cluster compounds of stoicheiometries $[(Me_6C_6)_3M_3X_6]^+$ (M = Nb and Ta; X = Cl and Br) are oxidized by a variety of oxidizing agents (*e.g.* Ce^{IV}, I_2, *N*-bromosuccinimide, and air) to give salts of brown cations of the stoicheiometries $[(Me_6C_6)_3M_3X_6]^{2+}$ (M = Nb and Ta; X = Cl and Br) isolable as their hexafluorophosphate or tetraphenylborate salts.

Fischer and Röhrscheid[1] have reported the reactions of the metal pentachlorides MCl_5 (M = Nb and Ta) with hexamethylbenzene in the presence of aluminium powder and aluminium chloride to give the green to brown salts $[(Me_6C_6)_3M_3Cl_6]Cl$ (M = Nb and Ta). This communication reports an unusual reversible oxidation of these and other closely related hexamethylbenzene metal cluster cations.

Reactions of $[(Me_6C_6)_3Nb_3Cl_6]Cl$[1] with ammonium hexanitratocerate(IV) in methanol solution gave a green-brown precipitate of stoicheiometry $[(Me_6C_6)_3Nb_3Cl_6][Ce(NO_3)_6]$. Metathesis of an aqueous solution of this precipitate with certain anions (*e.g.* PF_6^-, SCN^-, and BPh_4^-) gave green precipitates of the corresponding salts of stoicheiometry $[(Me_6C_6)_3Nb_3Cl_6]X_2$. The oxidation of $[(Me_6C_6)_3Nb_3Cl_6]^+$ to $[(Me_6C_6)_3Nb_3Cl_6]^{2+}$ can be followed by the electronic spectrum since the reduced form $[(Me_6C_6)_3Nb_3Cl_6]^+$ exhibits maxima at 419 (ϵ 44,000) and 339 nm (12,000) in several different media whereas the oxidized form $[(Me_6C_6)_3Nb_3Cl_6]^{2+}$ exhibits a maximum at 396 nm (ϵ 27,000). Other oxidizing agents suitable for the conversion of $[(Me_6C_6)_3Nb_3Cl_6]^+$ into $[(Me_6C_6)_3Nb_3Cl_6]^{2+}$ include iodine in dichloromethane solution, methanolic *N*-bromosuccinimide, chlorine in methanolic hydrochloric acid solution, and air in methanolic hydrochloric acid solution. Similarly, the tantalum derivative $[(Me_6C_6)_3Ta_3Cl_6]^+$ (λ_{max} 364 and 288 nm) can be oxidized to the cation $[(Me_6C_6)_3Ta_3Cl_6]^{2+}$ (λ_{max} 354 nm) using methanolic ammonium hexanitratocerate(IV) or methanolic *N*-bromosuccinimide. The cation $[(Me_6C_6)_3Ta_3Cl_6]^{2+}$ can be conveniently isolated as its hexafluorophosphate or thiocyanate salts. However, attempts to isolate $[(Me_6C_6)_3Ta_3Cl_6]^{2+}$ as its tetraphenylborate salt led to reduction back to $[(Me_6C_6)_3Ta_3Cl_6]^+$. The bromide salts $[(Me_6C_6)_3M_3Br_6]$ Br (M = Nb and Ta) were observed to undergo analogous oxidation reactions; however, the products were less stable.

Some exploratory electrochemical studies[2] were performed on these hexamethylbenzene metal cluster compounds in 1,2-dimethoxyethane solution using tetra-n-butylammonium perchlorate as a supporting electrolyte. An oxidation wave with $E_{\frac{1}{2}}$ −0·25 V in the polarogram of $[(Me_6C_6)_3Nb_3Cl_6]^+$ is tentatively assigned to its oxidation to $[(Me_6C_6)_3Nb_3Cl_6]^{2+}$; this process was shown to be reversible by triangular voltammetry. Controlled potential electrolysis of various $[(Me_6C_6)_3Nb_3Cl_6]^+$ salts (the tetraphenylborate was most satisfactory) at −0·1 V converted the original green-brown solution into a yellow-brown solution which is the same colour change observed upon the chemical oxidation of the system as described above. The polarogram of $[(Me_6C_6)_3Ta_3Cl_6][BPh_4]$ exhibited a reversible oxidation wave with $E_{\frac{1}{2}}$ −0·18 V which can be assigned to the oxidation of $[(Me_6C_6)_3Ta_3Cl_6]^+$ to $[(Me_6C_6)_3Ta_3Cl_6]^{2+}$; a colour change from brown to red-brown occurs during this oxidation process at a controlled potential of −0·1 V.

All of the salts of the oxidized cations of the stoicheiometry $[(Me_6C_6)_3M_3X_6]^{2+}$ were found to be diamagnetic. This indicates that these compounds must have an even number of metal atoms. The simplest possible formula for the oxidized cations consistent with their diamagnetism is the hexametallic formula $[(Me_6C_6)_6M_6X_{12}]^{4+}$. A hexametallic formulation (*i.e.* doubling of all of the trimetallic formulas given here) relates these hexamethylbenzene metal clusters of niobium and tantalum to the well-known[3] octahedral metal clusters of the type $[(M_6X_{12})Y_6]^{n-}$ (M = Nb or Ta; X and Y = Cl, Br, *etc.*; *n* = 2, 3, and 4) by substitution of the six terminal Y halide ligands with neutral hexamethylbenzene ligands acting as formal two-electron donors. The oxidations reported here would all represent the conversions of the dications $[(Me_6C_6)_6M_6X_{12}]^{2+}$ (M = Nb or Ta; X = Cl or Br) into the corresponding tetracations $[(Me_6C_6)_6M_6X_{12}]^{4+}$ and would be completely analogous to the previously reported[4] oxidations of $[(M_6Cl_{12})Cl_6]^{4-}$ (M = Nb or Ta) to $[(M_6Cl_{12})Cl_6]^{2-}$.

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