than its porphyrin analogue. The same consideration is also appropriate for ruthenium. Oxidation of Os(TPrPC)(CO) with *m*-CPBA in dichloromethane readily results in the generation of a dioxoosmium(VI) porphycene complex $Os(TPrPC)(O)_2$, which is as stable as its porphyrin analogue.[6] However, attempts to isolate the corresponding dioxoruthenium(VI) porphycene complex by treatment of Ru(TPrPC)(CO) with *m*-CPBA in dichloromethane have failed. Like $Os(OEP)(O)_2$,[7] $Os(TPrPC)(O)_2$ reacted with hydrazine hydrate in tetrahydrofuran under N_2 affording a dinitrogenosmium(II) porphycene complex which exhibits $\nu(N_2)$ band at 2035 cm^{-1}.

For both Os(TPrPC)(CO) and Ru(TPrPC)(CO), there appears only a single, very strong C≡O stretching band in the IR spectrum. The ν(C≡O) band of Os(TPrPC)(CO) found at 1893 cm^{-1} is very similar to that of Os(OEP)(CO)(THF) at 1897 cm^{-1} (OEP = octaethylporphyrin dianion, THF = tetrahydrofuran).[7] Ru(TPrPC)(CO) exhibits a C≡O stretching vibration at 1937 cm^{-1}, also similar to that of its porphyrin analogues.[8] The IR spectrum of $Os(TPrPC)(O)_2$ shows an intense band at 823 cm^{-1} with a shoulder at 837 cm^{-1}. The 823-cm^{-1} band, which is absent in H_2TPrPC and Os(TPrPC)(CO), can reasonably be assigned to the $\nu_{as}(OsO_2)$ stretch. For comparison, the $\nu_{as}(OsO_2)$ band of $Os(OEP)(O)_2$ appears at 825 cm^{-1}.[6a]

Figure 1 shows the UV–visible absorption spectra of Os(TPrPC)(CO), Ru(TPrPC)(CO), and $Os(TPrPC)(O)_2$ and the spectra of their octaethylporphyrin analogues[9] (inset) for comparison. The spectra of M(TPrPC)(CO) (M = Os, Ru) are typical of those of metalloporphycenes as described in the literature,[3] but the ratios of the oscillator strength of the near-UV bands to that of the visible bands are anomalously low. The spectra of the three new porphycene complexes are like those of their OEP counterparts. In the order from Os(TPrPC)(CO) to Ru(TPrPC)(CO), the bands in the visible region are significantly red shifted just as the case from Os(OEP)(CO)(Py) to Ru(OEP)(CO)(Py) (Py = pyridine). In previous studies, a similar red shift observed from Ni(TPrPC) to Cu(TPrPC) was ascribed to expansion of the porphycene macrocycle.[3f] However, in this work, the red shift of this kind could not be readily understood in this way since the Ru(II) ion should be slightly smaller than the Os(II) ion.[5] It is also evident from Figure 1 that oxidation of Os(TPrPC)(CO) to $Os(TPrPC)(O)_2$ leads to a remarkable blue shift of the near-UV bands, a large red shift of the visible bands, and appearance of a broad extra band in the visible region. This again superficially resembles the corresponding porphyrin system.

All the three new porphycene complexes give well-resolved ^1H NMR spectra. The spectral data appear in Table I, in which the data found for the related porphyrin and nickel(II) porphycene complexes are also cited for comparison. For Os(TPrPC)(CO), Ru(TPrPC)(CO), and Ni(TPrPC), the proton resonances of the porphycene ligand appear at similar positions. However, the α-CH_2 protons for the carbonyl complexes give a multiplet rather than a triplet as those in Ni(TPrPC), indicating that Os(TPrPC)(CO) and Ru(TPrPC)(CO) have a C_{2v} symmetry. Figure 2 shows the ^1H NMR spectrum of $Os(TPrPC)(O)_2$. It is apparent, from a comparison between the data of $Os(TPrPC)(O)_2$ and $Os(OEP)(O)_2$ (Table I), that $Os(TPrPC)(O)_2$ is diamagnetic. Just like the osmium porphyrin complexes, the 9,10,19,20-proton resonances (related to H_{meso} in octaethylporphyrin) and the 3,6,13,16-proton resonances (related to H_β in tetraphenylporphyrin) are significantly downfield shifted from that of the divalent metalloporphycene complexes (see Table I). The α-CH_2 protons of $Os(TPrPC)(O)_2$ appear as a triplet, consistent with a D_{2h} symmetry resulting from the embedment of a small Os(VI) ion in the center of the porphycene dianion ligand.

Conclusions

Our work demonstrated the following: (i) Porphycene can even coordinate with the relative large osmium as well as ruthenium ion to form stable complexes although it has smaller cavity than that of porphyrin. (ii) The chemistry of ruthenium and osmium porphycene complexes resembles that of their porphyrin analogues.

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Additions and Corrections

1991, Volume 30

Wei Cen, Kenneth J. Haller, and Thomas P. Fehlner*: Transition-Metal Clusters as Substituents. Synthesis, Structure, and Thermal Decomposition of $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$.

Pages 3120–3121. Additional models of higher symmetry for the structure of $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$, including refinement as a $\bar{3}$ disordered/averaged structure in space group $R\bar{3}$, have been explored. ORTEP plots of the $P\bar{1}$ ($R_1 = 0.087$, $R_2 = 0.106$) and $R\bar{3}$ ($R_1 = 0.085$, $R_2 = 0.098$) models are almost perfect superpositions of each other (including the orientations and magnitudes of the thermal ellipsoids). The diethyl ether of solvation is now modeled as a 9-position disorder, resulting in a more reasonable geometry. The highest residual electron density peaks are of similar heights and locations for the two models.

We thank Professor Richard E. Marsh for his comments and helpful suggestions concerning this problem.

Supplementary Material Available. A complete structure report for the $R\bar{3}$ model, including a textual description of the X-ray experimental procedures and tables of crystal data, fractional coordinates, thermal parameters, and interatomic distances and angles (9 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.—Thomas P. Fehlner