

Platinum Group Substituted Polyoxometalate

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Various types of polyoxoanion can be formed from Group 5 and 6 elements. These polyoxoanions can be classified as either isopolyanion, $[M_mO_y]^{n-}$, or heteropolyanion, $[(X)_xM_mO_y]^{n-}$, where X can be one element or a mixture of elements.¹ With high water solubility, extensive oxidation-reduction chemistry, and a closely packed metal framework, these polyoxoanions are good potential catalysts.²

The first heteropolyanion, molybdophosphate, which exhibits the Keggin structure, was prepared by Berzelius in 1826.³ However, due to the complexity of the molecule, its structure was not determined until a century later. In 1933, by solving thirty-two x-ray powder patterns, Keggin determined the three-dimensional structure of this polyoxoanion (Figure 1).⁴ In 1953, Dawson, used x-ray diffraction to determine the structure of the polyoxoanion with the empirical formula $X_2W_{18}O_{62}^{n-}$ (Figure 2).⁵ The number of characterized polyoxoanions has increased slowly. By 1971, there were twelve different polyoxoanion structure types characterized.⁶ Since then, with the aid of x-ray diffraction and multinuclear NMR spectroscopy, the number of polyoxoanion types has increased rapidly.

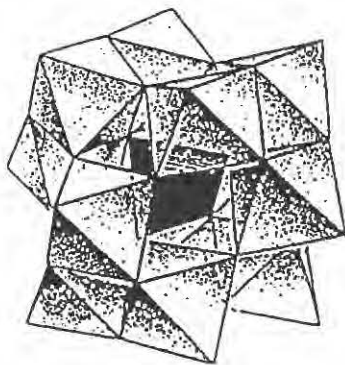


Figure 1.

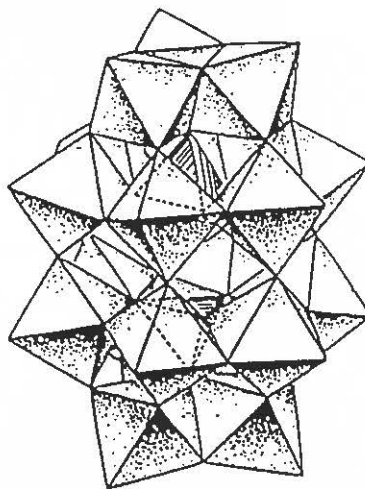


Figure 2.

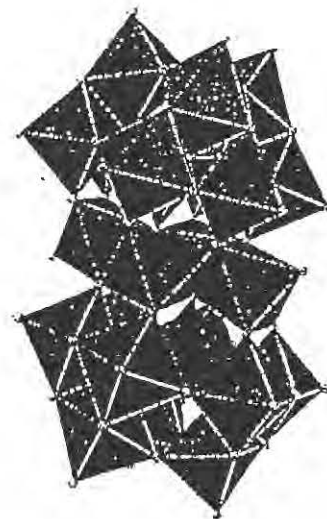
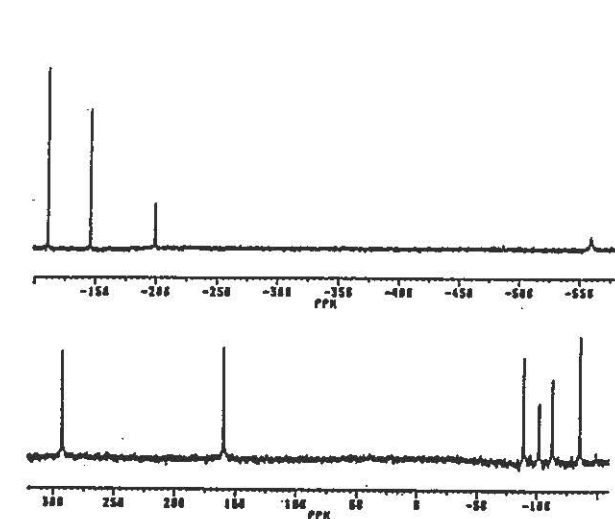


Figure 3.

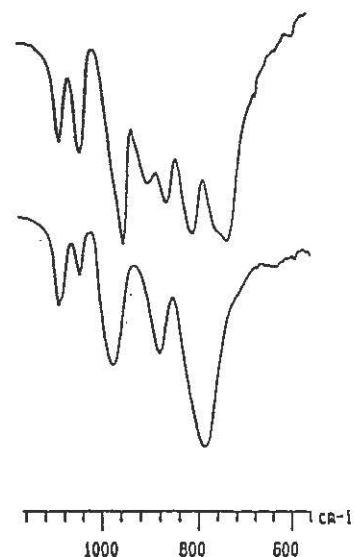
By far, the most studied polyoxoanion structure is the Keggin structure and its derivatives. Keggin polyoxoanion is characterized from the reaction of WO_4^{2-} and XO_4^{n-} . However, the reaction is very pH sensitive, different product is obtained at different pH. Transition metal substituted polyoxoanion can be synthesized from the lacunary anion. Tourne and Tourne first reported the characterization of a lacunary anion by the removal of one tungsten atom and its terminally bonded oxygen.⁷ Many transition-metal substituted Keggin polyoxometalates have been reported since 1960s.⁸ Recently, polyoxometalates substituted with Pt-group metals have been reported. Iridium, Ru, Rh, and Pd substituted polyoxoanions have been reported for both Keggin and Dawson structure.^{8a,f,9b,11} Platinum, Pd, Ru, and Rh metals substituted polyoxoanion have been reported with the sandwich type

structure (Figure 3).^{10c,d} These Pt-group substituted polyoxoanions have been analyzed by ¹⁸³W NMR and IR spectroscopy (Figure 4 and Figure 5).^{8f} Compared to the lacunary anion, the ¹⁸³W NMR of the substituted anion shows down-field shift. The down-field shift is possibly due to electron donation from the heavy metal to the tungsten. The IR spectra show a small change from the lacunary anion, which indicate the structures are similar.



¹⁸³W NMR spectra of [PW₁₁O₃₉Ru^{II}(H₂O)]²⁻ (lower) and [PW₁₁O₃₉Ru^{III}(H₂O)]⁴⁻ (upper).

Figure 4.



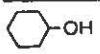
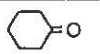
Infrared spectra of K₇[PW₁₁O₃₉] (upper) and K₇[PRu(H₂O)W₁₁O₃₉] (lower)

Figure 5.

Both the substituted Keggin and sandwich-type polyoxoanions demonstrate catalytic activities. Both types are active in the oxidation of alkanes and alkenes. Compare to Fe and Co substituted compounds with the Keggin structure, Ru and Rh substituted compounds have higher turn over numbers and higher conversion of oxidants (Table 1).¹² The Pt, Pd, and Rh substituted sandwich compounds all show similar activity in the oxidation of alkenes. However, Ru substituted sandwich compound shows a much lower activity in the same reaction conditions (Table 2).^{10c}

Table 1.

Oxidation of cyclohexane by *t*-butyl hydroperoxide catalyzed by mixed addenda heteropolyanions

Catalyst	Reaction time (h)	Yield (%) ^a		Conversion of TBHP (%)	Turnovers ^b
					
SiFeW ₁₁ O ₃₉	2	13	1	32	20
	6	15	5	70	67
SiCoW ₁₁ O ₃₉	2	23	2	21	22
SiRuW ₁₁ O ₃₉	2	11	6	75	72
SiRhW ₁₁ O ₃₉	3	11	3	78	53

Catalyst: 5 μmol, cyclohexane: 18.5 mmol, benzene (1,2-dichloroethane for Co): 20 ml, TBHP: 2 mmol, and reaction temperature 333 K

^a Based on TBHP converted; (moles of cyclohexanol or cyclohexanone)/(moles of TBHP converted).

^b Turnovers = ((moles of cyclohexanol) + 2(moles of cyclohexanone))/(moles of catalyst).

Table 2.

Oxidation of alkenes by H_2O_2 catalyzed by sandwich complexes^a

Alkene	Products (conversion mol%)			
	[Pt ₂ Zn ₃ W ₁₉ O ₆₈]	[Pd ₂ Zn ₃ W ₁₉ O ₆₈]	[Rh ₂ Zn ₃ W ₁₉ O ₆₈]	[Ru ₂ Zn ₃ W ₁₉ O ₆₈]
Cyclooctene	oxide (71)	oxide (76)	oxide (75)	oxide (17)
Cyclohexene	oxide (14) enol (1) enone (16)	oxide (38) enol (27) enone (30)	oxide (17) enol (< 0.1) enone (< 0.1)	oxide (3) enol (0.7) enone (4)
1-Octene	oxide (6.1)	oxide (4.5)	oxide (5.0)	oxide (1.6)

^a Reaction conditions: 25°C, time 24 h, [Q, M₂Zn₃W₁₉O₆₈] = 0.2 μmol, [alkene] = 0.7 mmol, [H₂O₂] = 2 mmol in 1 mL C₂H₄Cl₂.

References

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