195-Platinum Nuclear Magnetic Resonance Spectroscopy

MONITORING PLATINUM ELECTROPLATING BATHS

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It is well known that the performance of platinum electroplating baths can deteriorate suddenly during operation. This review suggests that 195-platinum nuclear magnetic resonance spectroscopy is a powerful technique for investigating the changes in the composition of the solution that lead to a loss in current efficiency and/or poor deposit quality and, indeed, may be used for the routine monitoring of the state of health of operational baths. This technique can also be used to gain an understanding of the complex chemistry of modern platinum electroplating baths and so assist in the continuing search for commercial baths with superior performance.

A large number of platinum electroplating baths have been described (1) but most have shortcomings in terms of deposit quality and current efficiency, especially when the objective is to deposit thick layers of platinum for engineering applications. Some of these electroplating baths occasionally suffer from sudden and catastrophic deterioration in performance. This may arise from improper use or inadequate control of the bath, but management of platinum electroplating systems would be greatly eased by a warning of the chemical changes leading to such behaviour. One reason for this behaviour could well be a change in the speciation of the platinum in solution. Recently, Johnson Matthey has started to market platinum-Q-salt (2, 3) and this solution allows the deposition of thick platinum layers ($\approx$40 μm) with good properties, and at a high current efficiency. Even this new bath must be operated within the temperature range, 90 to 100°C, and it would be desirable for it to work at a higher current density.

The problems in the design and operation of platinum electroplating baths are readily understood in terms of the inorganic chemistry of the platinum species in solution. Clearly, for a successful plating bath, the requirements are:

(a) a source of Pt(II) (or Pt(IV) although these systems are not discussed in this review) which is highly soluble

(b) when dissolved in an aqueous electrolyte, a stable Pt(II) species must be formed

(c) the Pt(II) species in solution must be easily reduced to platinum metal at a potential positive to that where hydrogen evolution occurs. The requirements (b) and (c) place stringent limitations on the extent of interactions between ligands and metal centre. They must be strong enough to prevent, for example, hydrolysis of the complex in the pH range that is normally used for plating, pH 3 to 11, but not so strong that the potential for the Pt(II)→Pt reaction is shifted negative to that for hydrogen evolution on freshly plated platinum, which is, of course, a very good catalyst for hydrogen evolution.

Pt(II) usually exists as square planar complexes and its $5d^8$ electronic configuration ensures that it behaves as a soft acid. In practice, however, its chemistry is dominated by the inertness of these square planar complexes to ligand substitution. Hence, both the stability of Pt(II) species in solution and the potential for the reduction, Pt(II)→Pt, are determined as much by kinetic as by thermodynamic considerations. For example, a recent paper reports a study of the mechanism of Pt(II) reduction in platinum-Q-salt
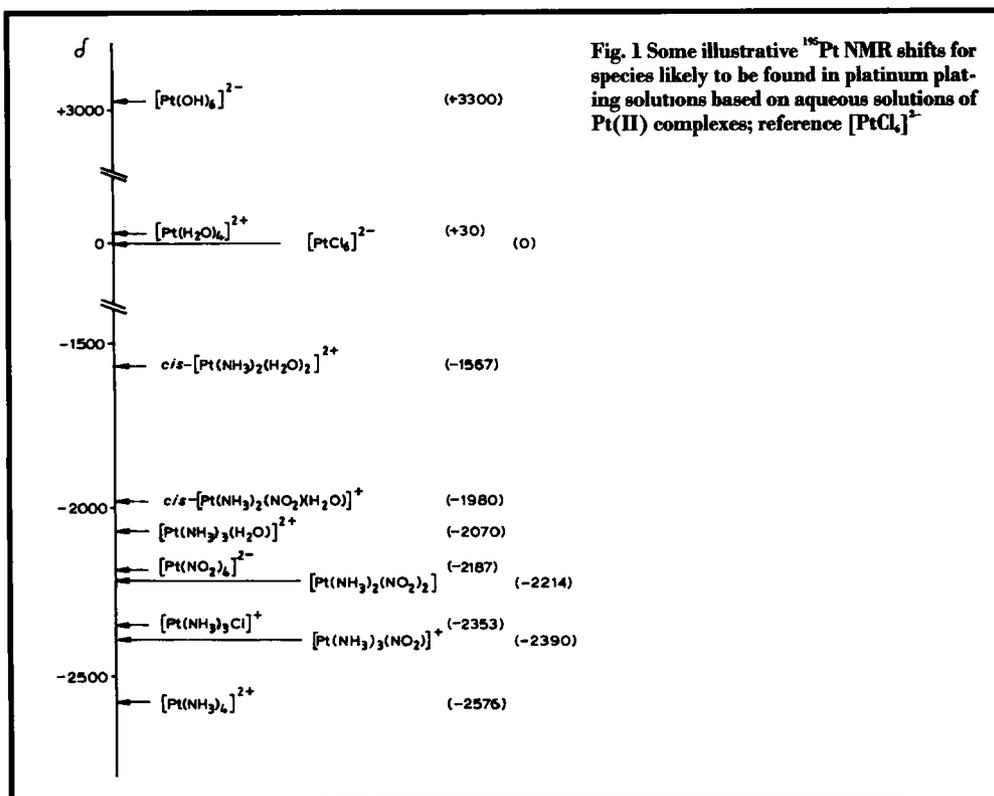
δ

+3000 — $[Pt(OH)_6]^{2-}$ (+3300)

Fig. 1 Some illustrative ^{195}Pt NMR shifts for species likely to be found in platinum plating solutions based on aqueous solutions of Pt(II) complexes; reference $[PtCl_4]^{2-}$

0 — $[Pt(H_2O)_4]^{2+}$ $[PtCl_4]^{2-}$ (+30)   (0)

−1500 — cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ (−1567)

−2000 — cis-$[Pt(NH_3)_2(NO_2)(H_2O)]^{+}$ (−1980)
— $[Pt(NH_3)_3(H_2O)]^{2+}$ (−2070)
— $[Pt(NO_2)_4]^{2-}$ (−2187) $[Pt(NH_3)_2(NO_2)_2]$ (−2214)
— $[Pt(NH_3)_3Cl]^{+}$ $[Pt(NH_3)_3(NO_2)]^{+}$ (−2353) (−2390)

−2500 — $[Pt(NH_3)_4]^{2+}$ (−2576)

solutions (4). $[Pt(NH_3)_4]^{2+}$ was shown to be the only species in solution but the electrochemical reduction of Pt(II) to platinum metal only occurs after the replacement of ammonia ligands by water, and the rate of this reaction is insufficient for a viable rate of plating below 90°C. Hence, it is the inertness of $[Pt(NH_3)_4]^{2+}$ to ligand substitution which is the key to both the stability of the Pt(II) in solution as well as the need to use a high temperature for electroplating. Such complex chemistry is typical of platinum plating solutions and it is also the likely cause of the sudden loss of performance in some established baths, which results in complaints by many users. The combination of the elevated temperature with an unusually high concentration of a potential ligand in solution can lead to an unwanted change in some or all of the Pt(II) species in solution. A sensitive spectroscopic method to probe for changes occurring at the platinum centre would allow the monitoring of the platinum species present in an electroplating bath and hence provide a warning of irreversible loss of Pt(II) as inactive complexes.

Such a technique is also essential to an understanding of the chemistry of platinum electroplating baths and the development of novel, improved systems. Ultraviolet-visible and nuclear magnetic resonance (NMR) spectroscopies are the most common tools available for the study of transition metal complexes in solution. The former is, however, of limited value in the study of heavy metals such as platinum because the metal centred absorptions (d-d transitions) occur at high energy, near to or in the UV region, where they are often partially obscured by ligand centred or charge transfer absorptions. As a result UV-visible spectra are essentially useless for identifying the constituents when several species are present in solution. In contrast, NMR spectroscopy is ideally suited to identifying mixtures of complexes in solution (5). The major requirements are the presence of a suitable nucleus and that the complex(es) should be diamag-

netic*. Suitable nuclei are those which have a nuclear sign, preferably half-integral (I = 1/2) although those with I> 1/2 can also be useful. For polyisotopic elements a reasonable natural abundance of the isotope being studied and good inherent sensitivity are advantageous. The proton (^{1}H) is the most sensitive of all nuclei used in NMR spectroscopy, but proton NMR is of limited use in the study of complexes in aqueous solution, due to the large and very broad absorption produced by the protons of the water. A further complication is that protons on electronegative elements like oxygen or nitrogen may be unobservable due to the fast chemical exchange. Platinum itself is very suitable for NMR observation and, in the systems of interest in plating baths, it is undoubtedly the nucleus of choice.
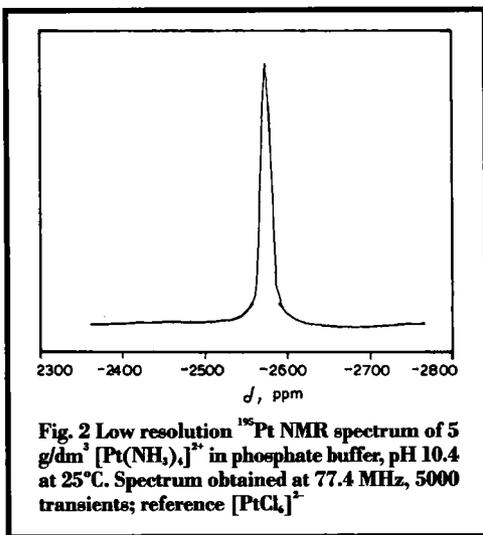
Fundamentals of ^{195}Platinum NMR

Naturally occurring platinum consists of several isotopes, one of which, ^{195}Pt, has I = 1/2 and an abundance of 33.8 per cent (6); all the other isotopes have I = 0, and do not exhibit the NMR effect. ^{195}Pt is among the more sensitive nuclei with a receptivity of 9.9×10^{-3} relative to the proton (the receptivity is the product of a number of fundamental constants, but may be taken as a guide to relative sensitivity) which when combined with an observation frequency of 21.4 MHz (in a magnetic field where protons resonate at 100 MHz) makes it easy to observe on modern Fourier Transform (FT) NMR spectrometers. Although outside the scope of this article, a great deal of ^{195}Pt NMR work has recently been performed in connection with the study of platinum anti-cancer drugs.

The ^{195}Pt NMR spectra of a large number of platinum complexes have been reported, and are collected in four review articles (6–9). It is conventional to report the NMR resonance in terms of a chemical shift (δ), in ppm, from a reference compound, rather than to specify the absolute frequency. For platinum, two references have been proposed. The [PtCl$_6$]$^{2-}$ ion in water (δ =

0) is commonly used since it is readily available and stable in solution. However, the resonance frequency is slightly temperature and concentration dependent, and large chemical shifts are produced by changing the solvent. Other workers prefer an arbitrary zero reference, Ξ, of 21.4 MHz from which the chemical shift of the complex of interest can be calculated via the field frequency lock of the spectrometer. Conversion between these two scales is $\delta([PtCl_6]^{2-}) = +4533$ ppm from Ξ. The total platinum chemical shift range is about 15,000 ppm. Theoretical interpretations of the chemical shifts have been only partially successful (6–9), but empirical predictions based upon the large available data base of ^{195}Pt shifts are valuable and reasonably reliable indicators of the species present. The shifts do not follow the formal oxidation state of the platinum ([PtF$_6$]$^{2-}$ and [PtI$_6$]$^{2-}$ lie at opposite extremes of the range), but Pt(IV) complexes usually resonate at a higher frequency than the Pt(II) analogues for similar ligand environments. Further information is often obtained from the splittings in the NMR resonance produced by spin-spin couplings to other magnetically active nuclei in the molecule. In fact, of the ligand atoms present in complexes of interest in plating baths, including chlorine, oxygen and nitrogen, only nitrogen is likely to produce coupling. The isotope, ^{15}N, is of low natural abundance and may be ignored, while ^{14}N (99.6 per cent abundant) has I = 1, which results in broad lines. In most complexes, the platinum line width v_i(the linewidth at half-height) is $\leq$ 25 Hz, but in complexes with nitrogen ligands it may be several hundred hertz. The cause of this broadening is the relaxation of the quadrupolar (I = 1) ^{14}N nuclei; this is too fast for couplings to be easily observed but not fast enough to completely decouple the nitrogen from the platinum. Hence, the line is broadened (6). In favourable cases, ^{14}N couplings may be resolved (see below). In general, the peak for a single platinum centre bonded to n equivalent atoms with spin I will be resolved into (2nI + 1) peaks with relative intensities given by the appropriate Pascal's triangle (6).

It should be emphasised that NMR is, at best, a semi-quantitative technique. Integration of peak
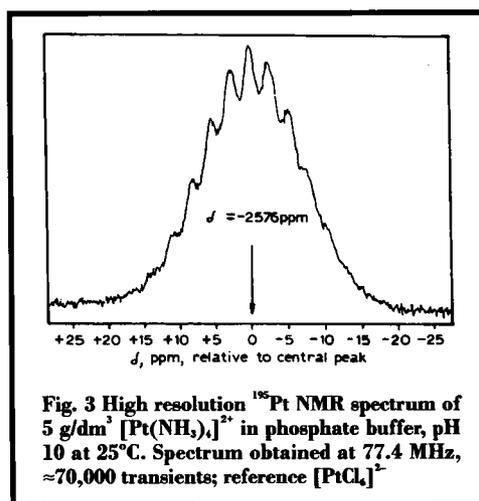
*It should be noted that paramagnetic complexes usually broaden or shift NMR resonances, and in many cases make them unobservable in practice; all Pt(II) and Pt(IV) complexes are diamagnetic.

Fig. 2 Low resolution ^{195}Pt NMR spectrum of 5 g/dm^3 [Pt(NH$_3$)$_4$]$^{2+}$ in phosphate buffer, pH 10.4 at 25°C. Spectrum obtained at 77.4 MHz, 5000 transients; reference [PtCl$_6$]$^{2-}$

areas on a single ^{195}Pt NMR spectrum is a reliable guide to the relative concentrations of the platinum species in solution. On the other hand, comparison of peak areas on different spectra in order to estimate absolute concentrations depends on exact reproduction of the spectrometer conditions, and the magnitude of the resonance can also depend on exact solution composition. Therefore, errors of ±25 per cent can occur. In the study of electroplating baths, the most convincing evidence for the decay of the solution is the appearance of new ^{195}Pt NMR peaks.

Some Practical Considerations

195-Platinum is a sensitive nucleus and, particularly in concentrated solutions such as those used in electroplating, with about 5 to 20 g/dm^3 of platinum, the NMR spectra are easily observed with modern multinuclear FT NMR spectrometers. The spectra discussed below were obtained on a Bruker AM360 operating at 77.4 MHz, but data are easily obtained on 90 MHz instruments. Spectra were obtained from aqueous solutions (0.1–001 molar for "model" compounds and for P- and Q-salt type plating baths) after the addition of 5 per cent deuterium oxide to provide the spectrometer lock and, if necessary, after adjustment of the pH, and with broad band proton decoupling. The sample is typically 2 cm^3. At the concentrations used 500 scans were ade-

quate to identify the major species and 10,000 to 30,000 scans allowed identification of minor components (in FT NMR the signal:noise ratio improves with $y^{\frac{1}{2}}$ where y = number of scans). High resolution spectra do, however, take several hours to record. For highly symmetric species such as [PtCl$_6$]$^{2-}$ slow relaxation of the platinum may require a pulse delay of approximately 0.5 seconds, but for most complexes no pulse delay is necessary. The sweep width of the instrument limits the chemical shift range that can be observed at any one time to about 1000 ppm, but since the species likely to be present are known, this is not usually a problem, and scanning two or three separate regions covers all the range of interest. However one should be aware of the possibility of "folded" resonances since, particularly at the high concentrations used in the baths, a folded resonance can appear with surprisingly convincing intensity. "Folding" is a well understood phenomenon, where a resonance outside the frequency range being studied appears in the spectrum with an erroneous chemical shift (5). It is easily detected by shifting the observed spectrometer window by a few thousand hertz, when genuine resonances have unchanged chemical shifts, but "folded" resonances appear to change their shifts. One should also be aware of the significant temperature variation in some platinum chemical shifts; in aqueous solution the proton decoupling produces considerable heating of the

Fig. 3 High resolution ^{195}Pt NMR spectrum of 5 g/dm^3 [Pt(NH$_3$)$_4$]$^{2+}$ in phosphate buffer, pH 10 at 25°C. Spectrum obtained at 77.4 MHz, ≈70,000 transients; reference [PtCl$_6$]$^{2-}$
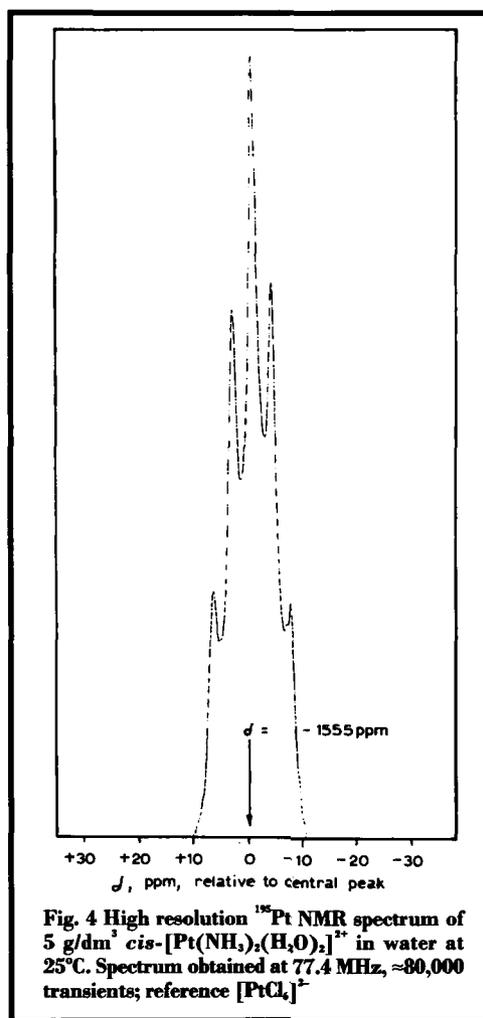
solution, and over the period of the experiment this variation may also appear as line broadening. The chemical shifts are markedly sensitive to solvent (but this is not relevant here since water was always used), concentration, the pH, and to other ions present (6–9). These effects mean that exact matching of spectra obtained under different conditions is not to be expected and agreement to within ±20 ppm, between the spectra for the bath and standards is entirely satisfactory. In view, however, of the very wide chemical shift range of platinum, these effects rarely cause any difficulties in identifying the species present.

^{195}NMR Studies of Platinum Baths

The ^{195}Pt chemical shifts of some platinum complexes which have been used in electroplating, and of related complexes which might be formed in baths under certain conditions, are shown schematically in Figure 1.

The platinum-Q-salt electroplating bath (2–4) exhibited a single broad line in the ^{195}Pt NMR spectrum at δ = –2576 ppm at 20°C, consistent with [Pt(NH$_3$)$_4$]$^{2+}$ as the only detectable platinum species (7). A typical spectrum, recorded over a period of 30 minutes, is shown in Figure 2. On heating the solution the single peak shifted progressively to lower frequency becoming δ = –2552 ppm at 95°C, the effect reversing on cooling. This equates to a temperature variation of about –0.32 ppm/°C, and shows that the tetrammine is the only species with a detectable concentration at both room temperature and the operating temperature of the bath. Confirmation of the [Pt(NH$_3$)$_4$]$^{2+}$ identity can be achieved by two routes. If the complex is prepared from ^{15}N (I = 1/2) labelled NH$_3$ then coupling to the four equivalent ^{15}N nuclei splits the ^{195}Pt resonance into a symmetrical five line pattern with appropriate intensities and coupling constant, $^1J(^{195}$Pt-^{15}N) = 287 Hz (10).

Alternatively, using very long accumulation times, careful temperature control and resolution enhancement in the data processing, it is possible to resolve the ^{14}N coupling, and this spectrum is shown in Figure 3. This spectrum, recorded overnight, shows that coupling to four equivalent ^{14}N nuclei splits the platinum reso-

Fig. 4 High resolution ^{195}Pt NMR spectrum of 5 g/dm^3 cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ in water at 25°C. Spectrum obtained at 77.4 MHz, ≈80,000 transients; reference [PtCl$_6$]$^{2-}$

nance into a nine line pattern with predicted intensities 1:4:10:16:19:16:10:4:1, and an observed coupling constant $^1J(^{195}$Pt-^{14}N) of 202 ± 5 Hz (4). This is in excellent agreement with the coupling observed in the ^{15}N labelled complex, since the couplings should be in the ratio of the magnetogyric moments of the two nitrogen nuclei (0.714) leading to a prediction for the coupling to ^{14}N of 205 Hz. Similarly, the ^{195}Pt NMR spectrum of cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ (δ = –1555 ppm) can be resolved into a five line pattern due to coupling to two equivalent ^{14}N nuclei $^1J(^{195}$Pt-^{14}N) = 244 Hz, see Figure 4.

The platinum-P-salt electroplating bath was also investigated. This is prepared by dissolution

of cis-[Pt(NH$_3$)$_2$(NO$_2$)$_2$] in an ammonium phosphate buffer and the pH is usually initially adjusted to pH 9–11. During operation of the bath at 70°C, it is normal to add concentrated ammonia solution at intervals. The ^{195}Pt shifts reported (8, 10) for various [Pt(NH$_3$)$_{4-x}$(NO$_2$)$_x$]$^{(2-x)+}$ complexes are tabulated below.

	$-\delta$, ppm
[Pt(NO$_2$)$_4$]$^{2-}$	2187
[Pt(NH$_3$)$_2$(NO$_2$)$_2$]	2214
[Pt(NH$_3$)$_3$(NO$_2$)]$^+$	2390
[Pt(NH$_3$)$_4$]$^{2+}$	2567

For the freshly supplied P-salt solution, a low resolution ^{195}NMR spectrum shows a single peak with a chemical shift of –2386 ppm; this indicates that the only species in the electroplating bath is the triammine complex. It is important to the understanding of P-salt plating baths to recognise that during the preparation of the solution, the platinum source has already undergone a chemical change to give the species that are normally present in a healthy electroplating bath.

We also examined aged P-salt solution which, after extensive use in a plating shop, had become inactive. This gave a more complex spectrum characterised by resonances at –2556, –2380 and –2310 ppm in the approximate ratio 75:10:15 (obtained by integration of the ^{195}Pt spectrum). The main species can be identified as the tetrammine (–2556 ppm), with only a small proportion of the initial complex (–2380 ppm), as well as some unidentified complex (–2310 ppm) which is probably a triammine species with the fourth ligand, which is another unknown N donor. Our electrochemical studies have shown that the tetrammine does not reduce prior to hydrogen evolution at 70°C and, hence, it is not surprising that the bath is inactive (4). On refluxing a fresh P-salt solution with concentrated aqueous ammonia for 24 hours, conversion to the tetrammine was found to be 85 per cent complete. In addition, on heating the fresh P-salt solution with NaNO$_2$ for 3 hours, approximately equal amounts of tetrammine and cis-[Pt(NH$_3$)$_2$(NO$_2$)$_2$] were formed. It is clear that unwanted changes to the platinum complex in solution easily occur in the P-salt bath. We would

postulate that the P-salt bath which had exhibited catastrophic failure had been subjected to a large excess of ammonia, perhaps accompanied by a temperature excursion. The possibility of regenerating the inactive solution was also examined. The solution was heated after addition of NaNO$_2$ but, in the brief experiments, we failed to regenerate significant amounts of the [Pt(NH$_3$)$_3$(NO$_2$)]$^+$, although some dinitrodiammine complex (–2250 ppm) was produced (about 50 per cent of the platinum after 24 hours). ^{195}Pt NMR spectroscopy is certainly a very convenient way to follow the changes in the platinum species in this system.

Conclusions

It is clear that low resolution ^{195}Pt NMR spectra, which may be recorded in as little as twenty minutes, are an excellent way to identify the platinum species present in the types of solutions found in electroplating baths. It allows identification of the form of platinum present in a healthy plating bath, as well as the monitoring of changes which occur with time, pH, temperature or the addition of reagents. The spectra are also run on the bath solutions without any preparation and only a very small sample is taken. Therefore, it represents a very rapid procedure for routine monitoring of the state of health of platinum plating solutions and enables potential problems to be identified before the bath performance drops to an unacceptable level. ^{195}Pt NMR spectroscopy is, however, only a semi-quantitative technique and the most reliable evidence for changes to a plating bath is the appearance of new peaks, rather than a decline in the signal for a single species; besides the difficulty in reproducing the spectrometer conditions, the response is influenced by other constituents of the solution.

Within development programmes, it can also be useful to record high resolution spectra since the splitting pattern confirms with certainty the assignments of the structure of the platinum complex. With present instrumentation, however, such spectra usually take more than twelve hours of spectrometer time to achieve the resolution required and would not normally be considered for routine monitoring of a plating bath.

References

1 M. E. Baumgärtner and Ch. J. Raub, *Platinum Metals Rev.*, 1988, **32**, (4), 188

2 P. E. Skinner, *Platinum Metals Rev.*, 1989, **33**, (3), 102

3 Johnson Matthey, *European Appl.* 358, 375; 1989

4 R. Le Penven, D. Pletcher and W. Levason, *J. Appl. Electrochem.*, 1992, **22**, 415

5 Many texts cover FT NMR spectroscopy, see J. W. Akitt, "NMR and Chemistry", 2nd Edn., Chapman and Hall, 1983; R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Longmans, 1986

6 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247

7 R. G. Kidd and R. J. Goodfellow in "NMR and the Periodic Table", eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978

8 R. J. Goodfellow in "Multinuclear NMR", ed. J. Mason, Plenum Press, New York, 1987

9 P. S. Pregosin in "Transition Metal NMR", Elsevier, Amsterdam, 1991

10 T. G. Appleton, J. R. Hall and S. F. Ralph, *Inorg. Chem.*, 1985, **24**, 4685

Dioxygen, a Versatile and Useful Oxidant

Catalytic Activation of Dioxygen by Metal Complexes

This book, which constitutes Volume 13 in the series "Catalysis by Metal Complexes", reviews the ways in which metal complexes activate molecular oxygen for the catalytic oxidation of organic compounds under mild conditions, and related oxidation reactions. It is said that this area of study is developing rapidly, but the references given are rather older on average than one would expect in support of such a claim. Research on the topic is being stimulated by potential applications in organic synthesis and by the resemblance between purely chemical processes and enzymic systems.

Transition metal dioxygen complexes are frequently involved in these oxidation reactions, and for this reason the opening chapter describes the major features of their structure, equilibria and formation kinetics. The remaining chapters describe the oxidation reactions of eleven broad classes of organic compound. Most of the metals involved are from the transition series and platinum group metals systems feature most prominently in the chapters on catalytic oxidation of saturated hydrocarbons, alkenes, alcohols and various nitrogen-, phosphorus-, and sulphur-containing organics.

Some of these reactions have potential for commercial use, although in many cases the activities and/or selectivities are not yet satisfactory. Dimeric rhodium(II)acetate, $Rh_2(OAc)_4$, is an active catalyst for hydrocarbon oxidation by molecular oxygen at atmospheric pressure and 25°C. Oxidative aromatisation of cyclohexadienes is general using this system and can be efficient, for example, 1-methoxy-1,4-cyclohexadiene gives anisole in 98 per cent yield under these conditions.

The best known example of a commercial application in this field is the catalytic oxidation of alkene derivatives, including ethylene itself, in the presence of palladium-copper systems, but the mechanism of this Wacker reaction is via the attack of water on the co-ordinated alkene, and involves no dioxygen complex. With rhodium catalysts, the reactivity of the superoxoligand is in some cases sufficient to abstract a hydrogen atom from a hydrocarbon, as is the case with a cyclooctene-rhodium-(I)-superoxo complex. The actual transfer of a co-ordinated dioxygen ligand to a co-ordinated olefin has been demonstrated for $[(diene)RhO_2]_2$ complexes, with diene = 1,5-cyclooctadiene or norbornadiene.

Complexes of rhodium and iridium catalyse the dehydrogenation of alcohols to aldehydes and ketones, producing gaseous hydrogen or transferring hydrogen to suitable acceptors like olefins. Dioxygen does not act as acceptor in these systems. An example is the dehydrogenation of isopropanol to acetone at 82.5°C in the presence of $RhCl_3.3H_2O$.

Dibenzylamine is catalytically dehydrogenated to N-benzylidene benzylamine with dioxygen in the presence of $Ru(PPh_3)_3Cl_2$ (80°C in toluene); by-products are benzaldehyde and benzonitrile. Both rhodium and iridium complexes have been used to catalyse the formation of phosphine oxides from tertiary phosphines using dioxygen; and Ru(II) in dimethylsulphoxide is an active catalyst for the oxidation of dialkylsulphides by molecular oxygen.

Overall, the book is a useful source of information on the topic of catalytic activation of dioxygen by metal complexes and related organic oxidation reactions, and in this context gives examples where platinum metals can be used for selective oxidation/dehydrogenation reactions.   D.T.T.