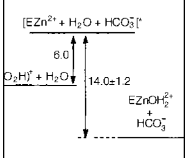


CHEMICAL SOCIETY REVIEWS

Mechanistic elucidation of small molecule – transition metal interactions by kinetic techniques

Siegfried Schindler, Colin D. Hubbard and Rudi van Eldik*

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany

This article focuses on the interaction of small molecules such as dioxygen, carbon monoxide, carbon dioxide, sulfur dioxide and nitric oxide, with transition metal centres in solution with the objective of establishing reaction mechanisms. The systems described are themselves biochemical reactions, model reactions for them, environmentally relevant reactions or are reactions that are important for industrial processes. The experimental approach is principally based on appropriately designed kinetics measurements using a variety of techniques, with considerable emphasis on the application of high pressure methods.

1 Introduction

Several small molecules such as dioxygen, carbon monoxide, carbon dioxide, sulfur dioxide and nitric oxide, play an important role in biochemical systems, in environmentally significant reactions and/or in technically important processes. The activation of these small molecules usually involves a direct or indirect interaction with the transition metal centre situated in a very specific coordination environment. It is a subject that has received considerable attention from numerous groups working on model or catalytically active systems, and many examples are given in the quoted references.[1–4]

We have prepared a progress report that covers a divergent set of reaction types and, as requested, mostly represents recent investigations from our own laboratories, with emphasis on the application of high pressure techniques. We will focus on the interactions of transition metal centres with small molecules with the purpose of developing an understanding of the detailed reaction mechanisms. In the majority of cases the transition metal centres cited will be from the first row, and are present in metalloproteins themselves, or are complexes designed to mimic the function of the metalloproteins, or can be simple aquated ions.

In order to endeavour to understand the mechanisms of the reactions involved, detailed kinetic measurements are performed as a function of temperature and pressure. Since appropriate instrumentation is not widely available, thermodynamic and kinetic measurements on reactions in solution as a function of pressure are relatively rare. The goal of equilibrium and kinetic studies at different elevated pressures is to obtain information on the overall volume change (ΔV) and volume of activation ($\Delta V^{\ddagger}$) associated with the reaction under study. This enables an analysis to be performed of the chemical events in terms of volume changes along the reaction coordinate. In the particular case of inorganic reactions the potential of this approach was noted a few decades ago.[5] The kinetic character-

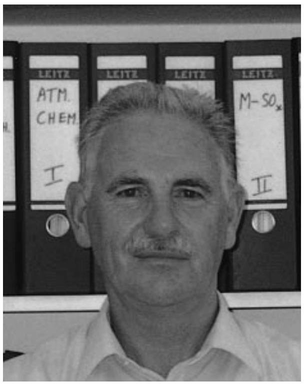
---

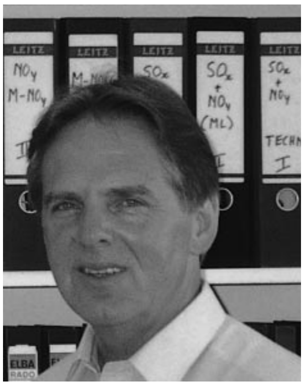
Siegfried Schindler studied Chemistry at the Technical University of Darmstadt (Germany), where he obtained his PhD under the supervision of Professor Horst Elias in 1989. He then became a research associate of Dr Carol Creutz at Brookhaven National Laboratory (Long Island, New York). He returned to Germany in 1993 and joined the group of Professor Rudi van Eldik, first at the University of Witten/Herdecke and later at the University of Erlangen-Nünberg. He completed his "Habilitation" in inorganic chemistry in 1997 and is now Privatdozent at the University of Erlangen-Nürnberg.

Colin D. Hubbard, a native of Norfolk, England, studied Chemistry at the University of Sheffield and obtained his PhD under the supervision of Professor Ralph G. Wilkins. Following post-doctoral research a MIT and Cornell (Professor G. G. Hammes), and Berkeley (Professor J. F. Kirsch), he was appointed to the faculty of chemistry at the University of New Hampshire, becoming a tenured Associate Professor in 1972 and Professor in 1979. He was a frequent research visitor to the University of Leicester (Dr J. Burgess) and to the University of Witten/Herdecke (Professor R. van Eldik). Since 1994 he has been on the staff of the Institute for Inorganic Chemistry, at the University of Erlangen-Nürnberg.

Rudi van Eldik was born in Amsterdam, but grew up in South Africa where he obtained his PhD at the Potchefstroom University in 1971. He worked as a post-doctoral fellow with Professor Gordon M. Harris (Buffalo, New York) and Professor Hartwig Kelm (Frankfurt am Main). He completed his "Habilitation" in physical chemistry at the University of Frankfurt am Main in 1982, and moved to the University of Witten/Herdecke as Professor of Inorganic Chemistry in 1987. In 1994 he accepted a call to the University of Erlangen-Nürnberg, where he is presently Professor of Inorganic and Analytical Chemistry. In 1997 the Potchefstroom University awarded him an honorary doctorate.


S. Schindler


C. D. Hubbard


R. van Eldik

isations (*i.e.* rate laws) together with the thermal and pressure activation parameters (*i.e.* $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$), together with other information lead to the postulation of reaction mechanisms.

The basic principles at issue in high pressure kinetics have been the subject of several accounts.[5–8] The equation developed for the pressure dependence of the equilibrium constant for a reaction system, can be transformed into $(\delta \ln k/\delta P)_T = -\Delta V^{\ddagger}/RT$, since within transition state theory an equilibrium is assumed between the activated complex and the reactants. Upon integration, this equation can be applied to determine the volume of activation ($\Delta V^{\ddagger}$) by plotting the natural logarithm of the rate constant k *versus* applied pressure P. If the plot is linear, and it frequently is if the pressure is < 200 MPa, then $\Delta V^{\ddagger}$ can be obtained directly from the slope of the plot. Thus a reaction is accelerated by pressure when there is a volume reduction upon reaching the transition state, *i.e.* $\Delta V^{\ddagger}$ is negative, and retarded by pressure when $\Delta V^{\ddagger}$ is positive (expansion upon reaching the transition state). These in turn are indicative, in the absence of any solvational changes, of associative and dissociative mechanisms, respectively. A reaction that is completely insensitive to pressure will yield $\Delta V^{\ddagger}$ equal to zero. In many reactions $\Delta V^{\ddagger}$ has a magnitude within the range of +30 to -30 cm^3 mol^{-1}. These values correspond to rate retardations and accelerations of about four fold at 100 MPa. The diagnostic mechanistic value of the magnitude of these values has to be carefully considered with both intrinsic and solvational contributions taken into account. Further details on the interpretation of the volume of activation are provided in the references.[5–8] A volume profile charts strictly partial molar volume changes along the reaction coordinate, as a free energy profile illustrates Gibbs free energy changes along the reaction coordinate. When actual partial molar volumes of either products and reactants are known, or when the partial molar volume of one of the latter together with the reaction volume are known, then the volume profile is on an absolute rather than a relative basis. Mechanistic conclusions based on the interpretation of volume profiles will be demonstrated in this account.

The extreme lability of many of the reactions reported herein requires the utilisation of rapid reaction techniques, such as stopped-flow, temperature-jump and flash photolysis, as well as conventional UV–VIS spectrophotometry, and other standard methods and instrumentation. Establishment of volume profiles for unsymmetrical reactions has been an integral part of our mechanistic characterisation in many cases, an approach providing considerable insight. Other spectroscopic techniques, for example, NMR, ESR as well as X-ray structural determinations, often provide vital or supporting evidence for a particular mechanism, and complementary information. Some examples of these investigations performed in our laboratories, are summarised in this report. The nature of this review precludes a full bibliographic survey; hence the context of such studies and additional literature are best obtained from the references cited.

2 Reactions with dioxygen and carbon monoxide

The interaction of dioxygen and carbon monoxide with metal centres is usually investigated in parallel since the binding to the metal centre can involve a similar mechanism, with the difference that the subsequent reactions involving the activation of the bound small molecule frequently only occur for dioxygen. Model complexes for dioxygen carrier proteins as well as for redox active metalloenzymes have been synthesised and investigated.[2–4]

In a very simplified case it was possible to construct a volume profile for the reversible binding of dioxygen to a Co(II) macrocycle, *viz.* L = hexamethylcyclam, to produce (L)Co-O_2^{2+}, which is a Co(III)-superoxo species [eqn. (1)].[9]

$$Co^{II}(L)(H_2O)_2^{2+} + O_2 \rightleftharpoons Co^{III}(L)(H_2O)(O_2^{-})^{2+} + H_2O \qquad \textbf{(1)}$$

The kinetics of the overall reaction could be studied by flash-photolysis, since the dioxygen complex can be photo-dissociated and the subsequent reequilibration could be followed in the microsecond time range. A combination of the activation volumes for the binding and release of dioxygen results in a value of the reaction volume that is in very good agreement with that determined directly from equilibrium measurements as a function of pressure. The volume profile for the reaction is shown in Fig. 1. The small volume of activation associated with the forward reaction could be interpreted as evidence for a rate-limiting interchange of the ligands, dioxygen for water, which is followed by an intramolecular electron-transfer reaction between Co(II) and O_2 to form Co^{III}-O_2^{-}, a superoxo species. It is the latter process that accounts for the large volume reduction *en route* to the reaction products. Thus during flash-photolysis, electron transfer in the reverse direction occurs due to irradiation into the CT (charge-transfer) band. This is followed by the rapid release of dioxygen.

The mechanism of the binding of small molecules such as O_2 and CO to ferrous hemes and hemoproteins which are more complex systems, has been the focus of many investigations in recent years.[1–4] Model heme complexes were usually employed in an effort to improve the understanding of the reactions of the corresponding proteins. Two model heme systems (mono-chelated protoheme (MCPH) and protoheme dimethyl ester) and various neutral ligands were used to study the bimolecular addition to the five- coordinate ferrous model heme complexes using two different photolysis techniques.[10] The reported $\Delta V^{\ddagger}$ data correlate well with the addition rate constants. For the slower reactions, bond formation is rate determining and results in negative $\Delta V^{\ddagger}$ values, while for the faster reactions, the processes become diffusion controlled and are slowed down by increasing pressure due to the large increase in solvent (toluene) viscosity. In a subsequent study, the reaction of CO with MCPH was studied as a function of pressure in a very viscous medium.[11] The data showed that a changeover in rate-determining step occurred from one involving bond formation to a diffusion-controlled process upon increasing the pressure, *i.e* from a $\Delta V^{\ddagger}$ value of -9.6 to a value of +7.1 cm^3 mol^{-1}. These are examples of a changeover from activation control to diffusion control over reaction rates where the mechanistic diagnosis has emerged from kinetic measurements at high pressures.

In another study the binding of CO to lacunar Fe(II) complexes was studied in detail as a function of temperature and pressure in acetonitrile.[12,13] The overall reaction for the binding of CO to $[Fe^{II}(PhBzXy)](PF_6)_2$ can be summarised as in Scheme 1. The volume profile for this reaction is presented in Fig. 2. The large volume collapse associated with the forward reaction suggests that in the transition state, CO "disappears"

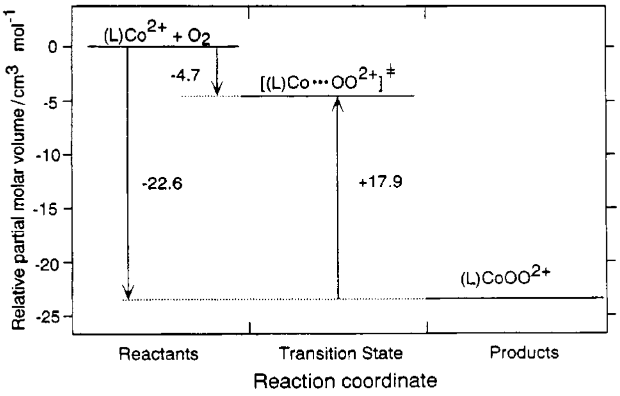
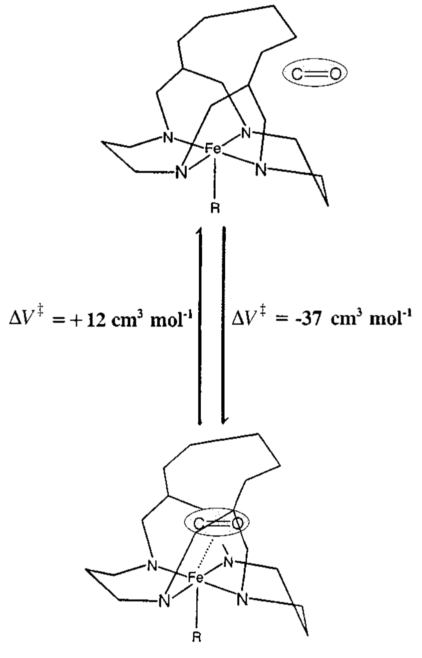


Fig. 1 Volume profile for the reaction of dioxygen with the Co(II)L complex, $Co^{II}(L)(H_2O)_2^{2+} + O_2 \rightleftharpoons Co^{III}(L)(H_2O)(O_2^{-})^{2+} + H_2O$, where L = hexamethyl cyclam, at 298 K

completely into the ligand pocket during partial Fe–CO bond formation, followed by a high spin to low spin transition on Fe(II) during which the metal centre moves into the ligand plane and accounts for the subsequent volume decrease.[13]

Similar kinetic techniques were applied to study the effect of pressure on the bimolecular rate constant for the reaction of sperm whale myoglobin with a series of neutral ligands in water.[10,14] It followed from the data that only the reaction with CO is characterized by a negative $\Delta V^{\ddagger}$ value, which is typical for a bond formation process. The positive $\Delta V^{\ddagger}$ values found for the other ligands were ascribed to the entry of the ligand into the protein matrix, which will be accompanied by pronounced desolvation and presumably conformational changes on the protein chain. The effect of pressure on the escape of the ligand from the protein-separated pair resulted in distinctly positive $\Delta V^{\ddagger}$ values.[10] These values are consistent with the notion of a "gate" that operates in both directions of the process.



Scheme 1

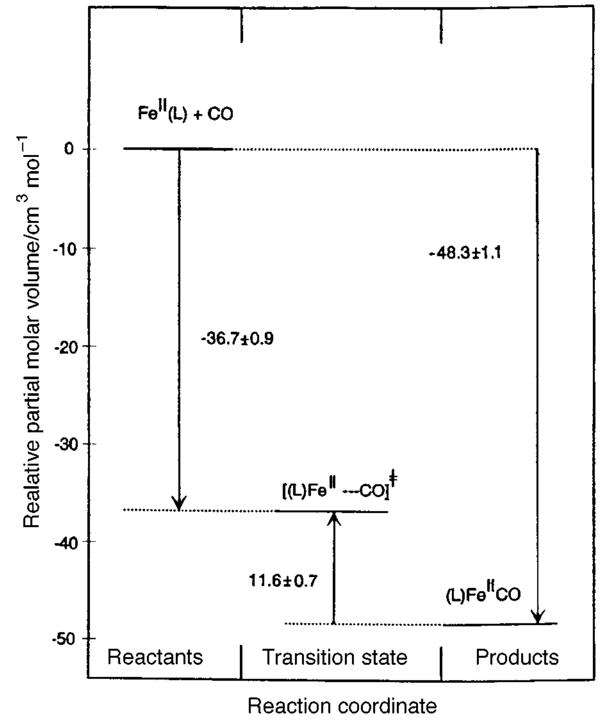


Fig. 2 Volume profile for the reaction of [Fe^{II}(PhBzXy)](PF$_6$)$_2$ with CO in acetonitrile at 298 K

The large difference in $\Delta V^{\ddagger}$ observed for the binding between O_2 and CO to deoxymyoglobin stimulated a more comprehensive study to be carried out for both systems.[14] The profiles are shown in Fig. 3. The volume profile for the binding of O_2 is characterised by a substantial increase in volume in going from the reactant to the transition state, followed by a significant volume reduction on going to the product state. The volume increase was ascribed to rate-determining movement of O_2 through the protein to the heme pocket, which may involve hydrogen bonding to the distal histidine as well as desolvation. This step is followed by rapid bond formation with the Fe(II) centre, during which a change in spin state from high to low, the movement of the Fe(II) centre into the porphyrin plane, and the associated conformational changes account for the drastic volume reduction. The overall reaction volume of −18 cm^3 mol^{-1} demonstrates the large volume reduction caused by the binding of O_2. The volume profile for the binding of CO shows a considerable volume decrease on going from the reactant to the transition state, which has been ascribed to rate-determining bond formation. The reverse bond cleavage reaction is accompanied by a volume decrease, which may be related to the different bonding mode of CO compared with O_2. This difference in bonding mode must also account for the much smaller absolute reaction volume observed in this case.

A volume profile was also generated (Fig. 4) for the binding of dioxygen to hemerythrin,[15] for which the overall reaction is given in Scheme 2. The $\Delta V^{\ddagger}$ values for the overall "on" and "off" reactions as well as the overall reaction volume are *ca.* twice the magnitudes of those for the corresponding myoglobin case. In the hemerythrin system two Fe(II) centres are oxidized to Fe(III) during which dioxygen is reduced and bound as hydroperoxide to one Fe(III) center. The $\Delta V^{\ddagger}_{on}$ value can partly

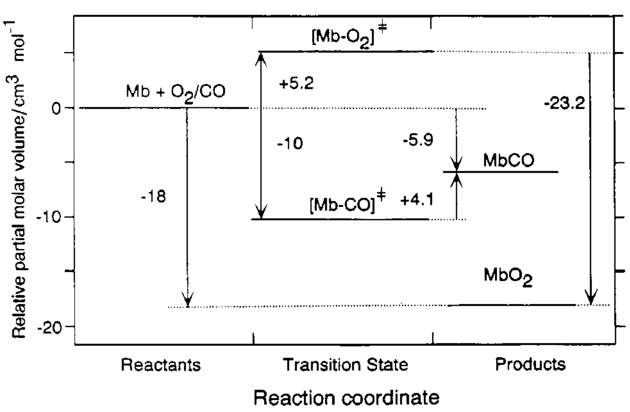


Fig. 3 Volume profile for the reactions of CO and O_2 with myoglobin at 298 K: Mb + O_2 $\rightleftharpoons$ MbO_2, Mb + CO $\rightleftharpoons$ MbCO

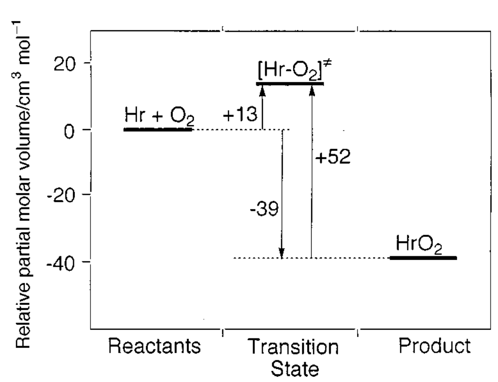


Fig. 4 Volume profile for the binding of dioxygen to hemerythrin at 298 K: Hr + O_2 $\rightleftharpoons$ HrO_2

be accounted for in terms of desolvation of oxygen during its entrance into the protein. The value is, however, such that it suggests some form of dynamic "reathing"motion of the protein that momentarily causes an opening up of a cleft and enables oxygen to enter the protein. The significant volume decrease that occurs following the formation of the transition state can be ascribed to the oxidation of the Fe centres and the reduction of O_2 to O_2^{2-}. The fact that the overall volume collapse is almost double that observed for the oxygenation of myoglobin may indicate similar structural features in oxyhemerythrin and oxymyoglobin. This would suggest that a description of the bonding mode as Fe^{III}-O_2^- or Fe^{III}-O_2H (H from histidine E7) instead of Fe^{II}-O_2, may be more appropriate for oxymyoglobin.

A suitable model for the oxygen carrier protein hemerythrin is $[Fe_2(Et\text{-}HPTB)(OBz)](BF_4)_2$, Et-HPTB = *N,N,N′,N*-tetrakis[(*N*-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane, OBz = benzoate; it can mimic the formation of a binuclear peroxo iron complex in the natural system (Scheme 3).[16] In this case it was possible to follow the irreversible uptake of dioxygen. The measured value of -12.8 cm^3 mol^{-1} for the activation volume of the reaction together with the negative value of the activation entropy, confirms the highly structured nature of the transition state.

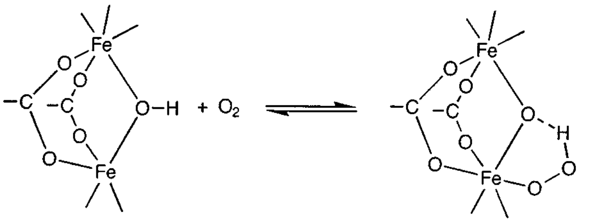
Oxidation reactions of chelated Fe(II) complexes are all markedly accelerated by pressure and accompanied by negative volumes of activation.[8] These can be ascribed to the binding of dioxygen that is accompanied by the oxidation of Fe(II) to Fe(III) and the reduction of dioxygen to superoxide and peroxide (eqns. (2) and (3)), processes that are all expected to lead to a decrease in partial molar volume.

$$Fe^{II}(L)(H_2O) + O_2 \rightleftharpoons Fe^{III}(L)(O_2^-) + H_2O \qquad (2)$$

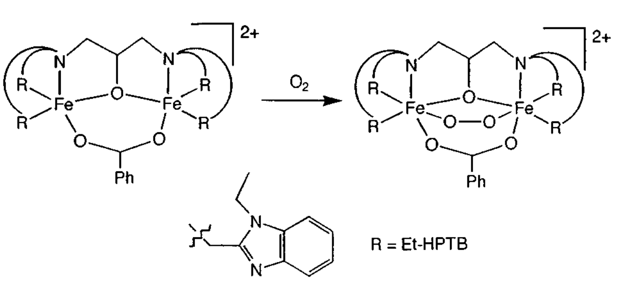
$$Fe^{II}(L)(H_2O) + Fe^{III}(L)(O_2^-) \rightarrow (L)Fe^{III}(O_2^{2-})Fe^{III}(L) + H_2O \qquad (3)$$

In a recent reinvestigation of the Fe^{II}(edta) oxidation reaction, where L = edta in eqns. (2) and (3), it was possible to resolve the different reaction steps that form part of the oxidation process, and to interpret the negative volumes of activation in a more detailed way.[17]

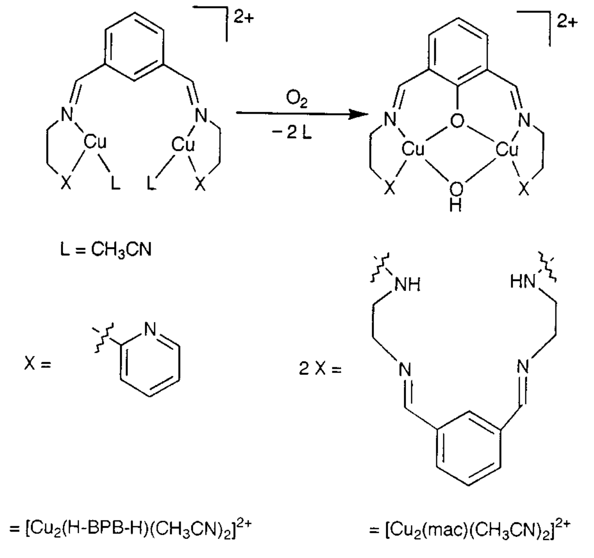
Tyrosinase, a dinuclear copper protein, is a monoxygenase which activates dioxygen for the *ortho* hydroxylation of monophenols. Efforts to model this protein functionally led to the development of a series of dinuclear copper model complexes.[4,18,19] It has been established that during the reaction of a series of dinuclear copper(I) complexes with dioxygen, intramolecular ligand hydroxylation occurs leading to phenolate bridged copper(II) complexes.[4,18,19] In a kinetic study of the reaction of dioxygen with $[Cu_2(H\text{-}BPB\text{-}H)(CH_3CN)_2](PF_6)_2$ (H-BPB-H = 1,3-bis[*N*-(2-pyridylethyl)formimidoyl]benzene), a dinuclear copper Schiff base complex in acetone, it was not possible (even at low temperatures) to observe the postulated copper peroxo intermediate complex spectroscopically (Scheme 4). However, kinetic findings provided indirect evidence for the transient existence of this complex.[18] Even though kinetic investigations were complicated because of side reactions, it was possible to extract appropriate kinetic data, and the activation parameters $\Delta H^‡ = 47 \pm 9$ kJ mol^{-1}, $\Delta S^‡ = -53 \pm 11$ J K^{-1} mol^{-1} and $\Delta V^‡ = -9.5 \pm 0.5$ cm^3 mol^{-1} were obtained. The results support a mechanism that is very similar to that proposed in our study of the reaction of $[Cu_2(mac)(CH_3CN)_2](PF_6)_2$ (mac = 3,6,9,17,20,23-hexaazatricyclo [23.3.1.1^{11,15}]triaconta-1(29),2,9,11(30),12,14,16,23,25,27-decaene) in methanol with dioxygen.[19] In a rate determining step a peroxo complex is formed as an intermediate, which then reacts in a very fast reaction to give the final product. The negative $\Delta S^‡$ and $\Delta V^‡$ values support the idea of a highly structured transition state, that is formed as a result of the presence of the highly reactive and easily oxidizable cuprous species. The negative volume of activation is a strong indication of copper–oxygen bond formation that is accompanied by electron transfer to produce the Cu(II)-O_2-Cu(II) peroxo intermediate. The formal oxidation of Cu(I) to Cu(II) and reduction of O_2 to O_2^{2-} are expected to be accompanied by a significant volume collapse, partly due to intrinsic and solvational volume changes. The activation parameters for the reaction of dioxygen with $[Cu_2(H\text{-}BPB\text{-}H)(CH_3CN)_2](PF_6)_2$ compare well with those obtained for the corresponding reaction of $[Cu_2(mac)(CH_3CN)_2](PF_6)_2$ ($\Delta H^‡ = 32 \pm 2$ kJ mol^{-1}, $\Delta S^‡ = -146 \pm 8$ J K^{-1} mol^{-1} and $\Delta V^‡ = -21 \pm 1$ cm^3 mol^{-1}). The higher values for the activation entropy and activation volume in the latter case are probably caused by larger geometrical rearrangements for the macrocyclic complex compared to those for the open complex $[Cu_2(H\text{-}BPB\text{-}H)(CH_3CN)_2](PF_6)_2$. It was assumed that the rate determining step within a whole sequence of steps must be the attack of dioxygen on the first copper(I) ion, accompanied by an electron transfer step (leading formally to a copper(II) superoxo complex). This species then reacts very quickly to produce the peroxo complex and then again in a fast reaction sequence to give the product. The negative $\Delta V^‡$ values found for the oxidation of dinuclear copper Schiff base complexes are close to the average value of -22 ± 2 cm^3 mol^{-1} reported for the oxidation of Cu(I)(phen)$_2$ by dioxygen in aqueous medium.[20] In



Scheme 2



Scheme 3



Scheme 4

the latter study it was concluded that the significantly negative volume of activation mainly arises from the large volume reduction associated with the formation of the intermediate $(phen)_2Cu(I)\text{-}O_2$ species.

The mononuclear copper(I) complex of the tripodal amine ligand Me_6tren (tris(2-dimethylaminoethyl)amine), reacts reversibly with oxygen at low temperatures to form superoxo and peroxo complexes according to eqns (4) and (5),[21] where L = Me_6tren and R = CH_3 or C_2H_5. The reaction could be followed by employing a low temperature stopped-flow instrument and the spectral changes that occurred during the formation of the superoxo complex (λ_{max} = 412 nm) at −90 °C are shown in Fig. 5 (absorbance *vs.* time trace is shown as an insertion). The formation of the superoxo species was predictably much faster at higher temperatures and therefore only the decomposition of the superoxo complex and the formation of the peroxo complex could be observed in the temperature range −90 to −30 °C.

$$[Cu(L)RCN]^+ + O_2 \rightleftharpoons [Cu(L)O_2]^+ + RCN \qquad (4)$$

$$[Cu(L)O_2]^+ + [Cu(L)RCN]^+ \rightleftharpoons [Cu_2(L)_2O_2]^{2+} + RCN \qquad (5)$$

3 Interaction with carbon dioxide

Early work on the binding of CO_2 by inert transition metal hydroxo complexes showed[22] that the transition state consists of a species with incipient oxygen–carbon bond formation (oxygen of the hydroxo ligand) and no breakage of the metal oxygen bond. The particular complexes employed to generate the bicarbonate species, and upon ionisation the carbonato-complex, were hydroxo complexes of $M(NH_3)_5^{3+}$ where M = Co, Rh or Ir (eqn. (6)).[22] From a study of the pressure dependence of the kinetics of both the forward and reverse reactions it could be concluded that on a volume basis the bond formation and breakage, respectively, are approximately 50% completed in the transition state.

$$M(NH_3)_5OH^{2+} + CO_2 \rightarrow M(NH_3)_5OCO_2^{+} + H^+ \qquad (6)$$

The active centre of the zinc containing metalloenzyme carbonic anhydrase (CA) is comprised of three histidine residues and one water molecule coordinated to zinc in a slightly distorted tetrahedral geometry. The reaction catalysed by CA is given in eqn. (7). Catalytic activity is integrally related to the ionisation (pK_a value *ca.* 7) of the coordinated water molecule and for human CA II the mechanism is known as the zinc hydroxide mechanism which has been described and modelled theoretically in considerable detail.[23]

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (7)$$

A simplistic expectation would be that model metal complexes designed to mimic the means of activation of CO_2 for catalysis of its hydration and of bicarbonate for the reverse dehydration reaction would possess corresponding coordinating units and geometry. It prevails that the highest catalytic activity observed, to date, for the hydration reaction, occurs when a five coordinate Zn(II) complex, ([12]aneN_4–Zn(II)-OH_2)$(ClO_4)_2$, ([12]aneN_4 = 1,4,7,10-tetraazacyclododecane)) in its deprotonated form, was employed in solution in the neutral pH region.[24] Dehydration was also accelerated by the same complex (in its +2 form). Interestingly a model zinc complex more closely resembling the zinc centre of CA, *viz.* [12]aneN_3–Zn(II),[25] is less effective catalytically. This is associated with the ability or lack thereof of the formation of a bicarbonate intermediate: the five coordinate complex of [12]aneN_4 does not allow bicarbonate chelation and it is this fact coupled with the apparently appropriate pK_a value of the coordinated water which together appear to provide the catalytic supremacy.

The CA catalysed reactions themselves have been studied in intricate detail by many investigators using a wide variety of techniques, and have formed the subject of several theoretical calculations and computer simulations.[23] The application of high pressure kinetic measurements provided further mechanistic distinction than was previously available.[26] An encouraging close agreement was obtained between the reaction volume for the uncatalysed reaction obtained earlier[27] and that derived from kinetic measurements on the catalysed reaction in both directions. The first complete, detailed volume profile (see Fig. 6) for an enzyme catalysed reaction was generated. The Zn^{2+} bound hydroxy moiety subjects the carbon of CO_2 to nucleophilic attack resulting in the formation of an oxygen–carbon bond, and the results are consistent with a unidentate bonding of bicarbonate. For this process the transition state lies

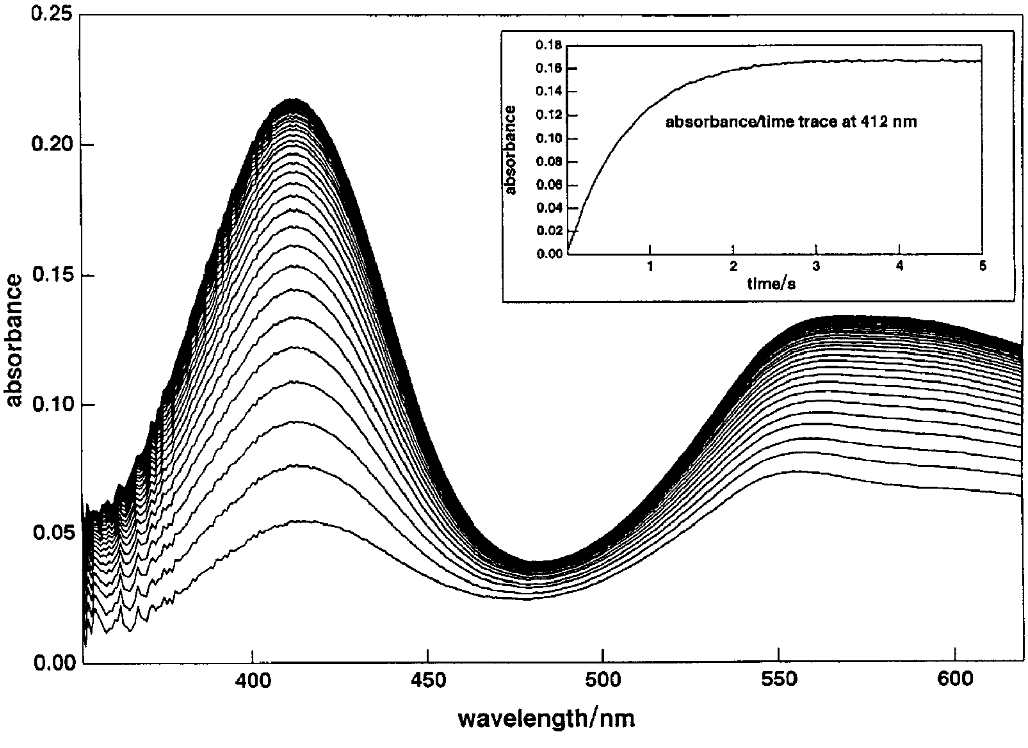


Fig. 5 Reaction of [Cu(Me_6tren)(CH_3CN)]PF_6 with dioxygen at −90 °C in dry propionitrile. The insert shows the absorbance *vs.* time trace at 412 nm.

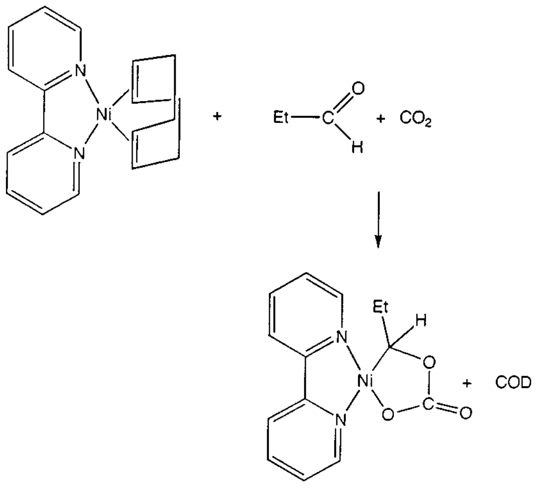
approximately halfway between the reactant and product states (see left part of volume profile). The substitution of coordinated water by bicarbonate tends more toward a limiting D mechanism (see right part of volume profile) than would be predicted on the basis of the coordination chemistry of aquated Zn^{2+}, which may result from the influence of the environment of the active centre of the enzyme.[26] Because of the complexity of this particular system, readers are kindly advised to consult the original reference for more details.

Fujita and van Eldik and others[28] have used a wide range of methods to study cobalt complexes with tetraazamacrocyclic ligands as potential catalysts for the reduction of CO_2. The interaction of the low spin $Co^{I}(HMD)^{+}$ species, HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene, with CO_2 in CH_3CN leads to a five-coordinate species, $Co^{I}(HMD)(CO_2)^{+}$, which is in equilibrium with a six-coordinate complex ion, $Co^{III}(HMD)(CO_2^{2-})(CH_3CN)^{+}$, formed through addition of CH_3CN (see eqn. (8) and (9)).

$$Co^{I}(HMD)^{+} + CO_2 \rightleftharpoons Co^{I}(HMD)(CO_2)^{+} \quad (8)$$

$$Co^{I}(HMD)(CO_2)^{+} + CH_3CN \rightleftharpoons Co^{III}(HMD)(CO_2^{2-})(CH_3CN)^{+} \quad (9)$$

Results from an XANES study together with other information provide a clear indication that in the six-coordinate complex cobalt is in the oxidation state plus three, meaning that the complex ion is $Co(III)\text{-}CO_2^{2-}$ (carboxylate). Hence the initial cobalt complex has reduced the bound CO_2. Since the six-coordinate species is yellow and the five-coordinate species is purple, the change of coordination number equilibrium can be studied readily by UV–VIS spectrophotometry; the thermodynamic parameters are $\Delta H° = -29$ kJ mol^{-1}, $\Delta S° = -113$ J mol^{-1} K^{-1} and $\Delta V° = -17.7$ cm^3 mol^{-1}. The latter two are mutually compatible and consistent with a highly ordered and compact six-coordinate complex ion. It has been proposed that a major part of the volume decrease arises from the intramolecular electron transfer process accompanied by a shortening of the $Co\text{–}CO_2$ bond (as supported by XANES and EXAFS studies) and an increase in electrostriction. Only a relatively minor contribution to the large negative reaction volume results from the intrinsic effect of CH_3CN addition.



Scheme 5

Even though it is well known that Ni(0) complexes can react with carbon dioxide, our results showed that the complex [Ni(bpy)(COD)], COD = cyclooctadiene, is unreactive towards carbon dioxide.[29] For the reaction of [Ni(bpy)(COD)] with propionaldehyde and carbon dioxide, according to Scheme 5, a thorough kinetic study clearly demonstrated that carbon dioxide does not bind to the Ni(0) center but instead reacts with the activated propionaldehyde of the product complex [Ni(bpy)(propionaldehyde)].[29]

4 Interaction with sulfur dioxide and nitric oxide

The catalytic role of metal ions and complexes in the autoxidation of sulfur and nitrogen oxides has been studied in detail because of the importance of such reactions in the treatment of gaseous effluents of coal-fired power plants and in atmospheric oxidation processes.[30,31] The application of fast kinetic and spectroscopic techniques has assisted in defining the underlying reaction mechanism. It was possible to identify and characterise the redox cycling of the catalytically active metal ions and complexes during the autoxidation of SO_x species.[32,33] A general mechanism in terms of the participating reactions based on the detailed kinetic studies referred to above is presented in eqn. (10)–(19), and illustrates the important role of redox cycling of the metal ion in such catalytic processes.

$$M^{n+} + HSO_3^{-} \rightarrow M^{(n-1)+} + SO_3^{-} + H^{+} \quad (10)$$

$$SO_3^{-} + O_2 \rightarrow SO_5^{-} \quad (11)$$

$$M^{(n-1)+} + SO_5^{-} + H^{+} \rightarrow M^{n+} + HSO_5^{-} \quad (12)$$

$$M^{(n-1)+} + HSO_5^{-} \rightarrow M^{n+} + SO_4^{-} + OH^{-} \quad (13)$$

$$M^{(n-1)+} + SO_4^{-} \rightarrow M^{n+} + SO_4^{2-} \quad (14)$$

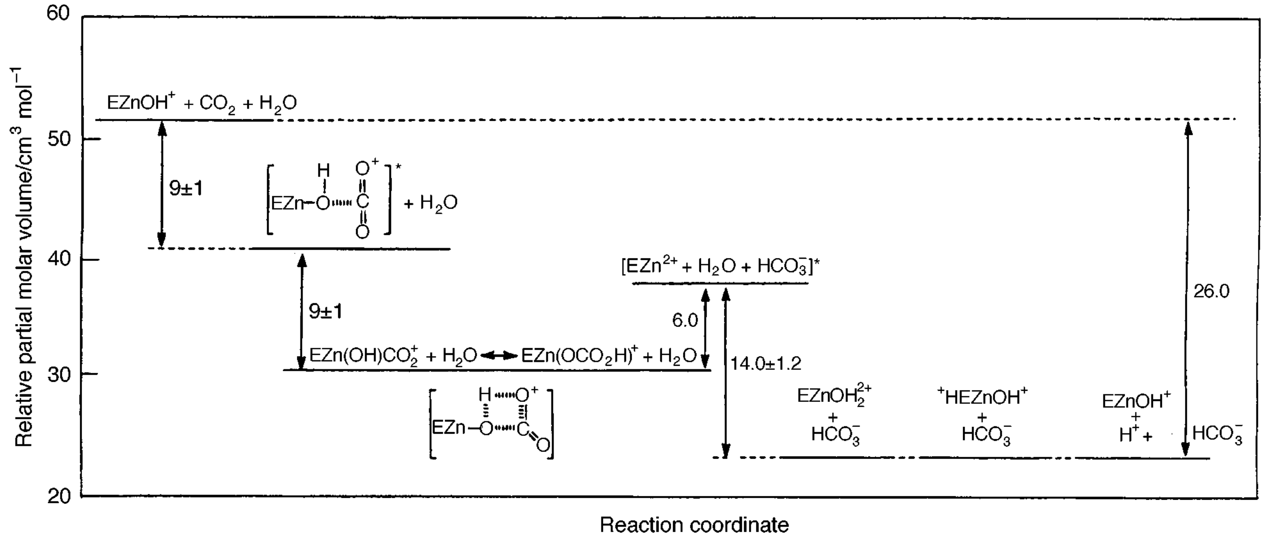


Fig. 6 Volume profile for the carbonic anhydrase catalyzed hydration of CO_2 and dehydration of HCO_3^{-} at 298 K: $CO_2 + H_2O \rightleftharpoons HCO_3^{-} + H^{+}$

$$SO_5^- + HSO_3^- \longrightarrow HSO_5^- + SO_3^- \qquad (15)$$

$$SO_5^- + HSO_3^- \longrightarrow SO_4^{2-} + SO_4^- + H^+ \qquad (16)$$

$$SO_4^- + HSO_3^- \longrightarrow SO_4^{2-} + SO_3^- + H^+ \qquad (17)$$

$$SO_5^- + SO_5^- \longrightarrow S_2O_8^{2-} + O_2 \qquad (18)$$

$$HSO_5^- + HSO_3^- + H^+ \longrightarrow 2SO_4^{2-} + 3H^+ \qquad (19)$$

Nitrogen oxides, as well as mixed sulfur–nitrogen oxides, produced during the spontaneous or metal catalysed interaction of NO/HONO/NO_2^- with SO_2/HSO_3^-/SO_3^{2-}, can interact with metal ions and complexes and affect their oxidation state. In general, Fe(II) complexes can bind NO rapidly to produce species of the type $Fe^{III}(L)NO^-$, which decompose to $Fe^{III}(L)$ and NO^-, where the latter species hydrolyses to N_2O (eqns. (20) and (21), where L = polyaminecarboxylate chelate).

$$Fe^{II}(L)(H_2O) + NO \rightleftharpoons Fe^{II}(L)NO + H_2O \qquad (20)$$

$$Fe^{II}(L)NO * Fe^{III}(L)(NO^-) \longrightarrow Fe^{III}(L) + NO^- \qquad (21)$$

Coordinated NO can interact with bisulfite to produce hydroxylaminedisulfonate (HADS), N_2O and iron(III).[34,35] Manganese(III) and iron(III) ions and complexes can affect the hydrolysis reactions of such mixed sulfur–nitrogen oxides.[36,37] For instance, HADS rapidly hydrolyses under such conditions to hydroxylaminemonosulfonate, during which the metal ions are reduced to the plus two oxidation state. In one case evidence for the redox cycling of manganese(II/III) in the presence of a sulfur–nitrogen oxide was observed.[38] The role of these reactions in atmospheric oxidation processes in water vapour or aerosols is presently unknown despite their potential importance, especially in terms of controlling the oxidation state of the catalytic metal ions.

5 Conclusions

It was our intention to provide a succinct account of the means by which the interaction of small molecules with transition metal centres occurs. At the initial level of mechanistic understanding achieved so far, the capability of monitoring UV–VIS spectral changes over a wide time range and under a variety of conditions results in an opportunity to obtain sufficient information for mechanistic proposals. Techniques other than kinetic are also vital in the establishment of mechanism.

Even though the chemistry of the reported reactions is quite different, the experimental approach and techniques employed in the mechanistic resolutions are very similar. We believe that the overall approach can be exploited for the study of the interaction of other small molecules with transition metal centres. The cited literature could be consulted for provision of a broader context, and additional background for the investigations described herein.

6 Acknowledgements

The authors gratefully acknowledge the contributions of many students and collaborators cited in the references, as well as financial support for their work from the Deutsche Forschungsgemeinschaft, Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, Volkswagen-Stiftung and Fonds der Chemischen Industrie.

7 References

1 A. M. Valentine and S. J. Lippard, *J. Chem. Soc., Dalton Trans.*, 1997, 3925.
2 L. Que, *J. Chem. Soc., Dalton Trans.*, 1997, 3933.
3 W. B. Tolman, *Acc. Chem. Res.*, 1997, **30**, 227.
4 K. D. Karlin, S. Kaderli and A. D. Zuberbühler, *Acc. Chem. Res.*, 1997, **30**, 139.
5 D. R. Stranks, *Pure Appl. Chem.*, 1974, **38**, 303.
6 S. F. Lincoln and A. E. Merbach, *Adv. Inorg. Chem.*, 1995, **42**, 1.
7 C. D. Hubbard and R. van Eldik, in *Chemistry under Extreme or Non-classical Conditions*, R. van Eldik and C. D. Hubbard (eds.), Wiley, New York, 1997, ch. 2.
8 A. Drljaca, C. D. Hubbard, R. van Eldik, T. Asano, M. V. Basilevsky and W. J. le Noble, *Chem. Rev.*, 1998, **98**, 2167.
9 M. Zhang, R. van Eldik, J. H. Espenson and A. Bakac, *Inorg. Chem.*, 1994, **33**, 130.
10 D. J. Taube, H.-D. Projahn, R. van Eldik, D. Magde and T. G. Traylor, *J. Am. Chem. Soc.*, 1990, **112**, 6880.
11 T. G. Traylor, J. Luo, J. A. Simon and P. C. Ford, *J. Am. Chem. Soc.*, 1992, **114**, 4340.
12 M. Buchalova, P. R. Warburton, R. van Eldik and D. H. Busch, *J. Am. Chem. Soc.*, 1997, **119**, 5867.
13 M. Buchalova, D. H. Busch and R. van Eldik, *Inorg. Chem.*, 1998, **37**, 1116.
14 H.-D. Projahn and R. van Eldik, *Inorg. Chem.*, 1992, **30**, 3288.
15 H.-D. Projahn, S. Schindler, R. van Eldik, D. G. Fortier, C. R. Andrew and A. G. Sykes, *Inorg. Chem.*, 1995, **34**, 5935.
16 A. L. Feig, M. Becker, S. Schindler, R. van Eldik and S. J. Lippard, *Inorg. Chem.*, 1996, **35**, 2590.
17 S. Seibig and R. van Eldik, *Inorg. Chem.*, 1997, **36**, 4115.
18 S. Ryan, H. Adams, D. E. Fenton, M. Becker and S. Schindler, *Inorg. Chem.*, 1998, **37**, 2134.
19 M. Becker, S. Schindler and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 5370.
20 S. Goldstein, G. Czapski, R. van Eldik, H. Cohen and D. Meyerstein, *J. Phys. Chem.*, 1991, **95**, 1282.
21 M. Becker, F. W. Heinemann, F. Knoch, W. Donaubauer, G. Liehr, S. Schindler, G. Golub, H. Cohen and D. Meyerstein, submitted for publication.
22 U. Spitzer, R. van Eldik and H. Kelm, *Inorg. Chem.*, 1982, **21**, 2821.
23 D. N. Silverman and S. Lindskog, *Acc. Chem. Res.*, 1988, **21**, 30, and the literature survey in ref. 26.
24 X. Zhang and R. van Eldik, *Inorg. Chem.*, 1995, **34**, 5606.
25 X. Zhang, R. van Eldik, T. Koike and E. Kimura, *Inorg. Chem.*, 1993, **32**, 5749.
26 X. Zhang, C. D. Hubbard and R. van Eldik, *J. Phys. Chem.*, 1996, **100**, 9161.
27 R. van Eldik and D. A. Palmer, *J. Solution Chem.*, 1982, **11**, 239.
28 E. Fujita and R. van Eldik, *Inorg. Chem.*, 1998, **37**, 360; and literature cited therein.
29 C. Geyer, E. Dinjus and S. Schindler, *Organometallics*, 1998, **17**, 98.
30 C. Brandt and R. van Eldik, *Chem. Rev.*, 1995, **95**, 119.
31 P. Warneck, P. Mirabel, G. A. Salmon, R. van Eldik, C. Vinkier, K. J. Wannowius and C. Zetzsch, in *Heterogeneous and Liquid-Phase Processes*, P. Warneck (ed.), Springer, Berlin, 1996, ch. 2.
32 J. Berglund, S. Fronaeus and L. I. Elding, *Inorg. Chem.*, 1993, **32**, 4527.
33 C. Brandt, I. Fabian and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 687.
34 V. Zang and R. van Eldik, *Inorg. Chem.*, 1990, **29**, 4462.
35 V. Zang, and R. van Eldik, *J. Chem. Soc., Dalton. Trans.*, 1993, 111.
36 F. F. Prinsloo, J. J. Pienaar, R. van Eldik and H. Gutberlet, *J. Chem. Soc., Dalton Trans.*, 1994, 2373.
37 V. Lepentsiotis, F. F. Prinsloo, R. van Eldik and H. Gutberlet, *J. Chem. Soc., Dalton Trans.*, 1996, 2135.
38 F. F. Prinsloo, J. J. Pienaar and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1995, 293.

Received 3rd March 1998
Accepted 19th June 1998