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Reactivity investigations of some chosen peroxo-vanadium(V), manganese(III) and chromium(VI) compounds

MIHIR K CHAUDHURI*, SHIV K CHETTRI, GAGAN C MANDAL, PRADIP C PAUL, SATYA B PAUL and PENDYALA SRINIVAS

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

Abstract. An interpretative account of the results of reactions in aqueous medium of a highly peroxygenated vanadium(V) complex, $K[V(O_2)_3]\cdot 3H_2O$, with different organic and inorganic substrates is presented. The reactions were monitored by solution EPR spectroscopy and isolation of products at different stages of the reactions. Redox reactions between diperoxide, $K[VO(O_2)_2(H_2O)]$ and $VOSO_4$ were conducted. The results of the investigation suggest that secondary oxygen exchange-reaction occurs which not only depends on but also utilises the intermediates in the primary reaction during diperoxovanadate-dependent oxidation of $VOSO_4$.

In an interesting reaction *tris*(acetylacetonato)-manganese(III), $Mn(acac)_3$, on being reacted with a hydrogen peroxide adduct, $KF\cdot H_2O_2$, and bpy and phen afforded crystalline $[Mn(acac)_2(bpy)]$ and $[Mn(acac)_2(phen)]$, respectively. The X-ray structural analysis of $[Mn(acac)_2(phen)]$ showed that the compound crystallised in orthorhombic space group *Pbcn*. The structure consists of a pseudo-octahedral Mn(II) ion being bound to two $acac^-$ ($C_5H_5O_2^-$) and a phen ligand with the molecule lying on two-fold axis.

Reactivity profiles of two new chromium(VI) reagents viz., pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$ (PFC), and quinolinium fluorochromate $C_9H_7NH[CrO_3F]$ (QFC), have been presented. The compounds are capable of acting as both electron-transfer and oxygen-atom-transfer agents. The X-ray analysis of PFC crystals reveals that the compound crystallises in the orthorhombic space group $CmcZ_1$. The structure consists of discrete pyridinium cations and CrO_3F anions with no significant hydrogen bonding. This results in total disorder of the pyridinium cation. The tetrahedral $[CrO_3F]^-$ ion lies on a crystallographic mirror plane.

Keywords. Reactivity studies; $K[V(O_2)_3]\cdot 3H_2O$; $K[VO(O_2)_2(H_2O)]$; $Mn(acac)_3$; $C_5H_5NH[CrO_3F]$; $C_9H_7NH[CrO_3F]$; X-ray structures.

1. Introduction

On making use of the term "dioxygen" as a generic designation to an entity containing O–O linkages, irrespective of the charge on the 'O_2' species, it is noteworthy that research involving metal-dioxygen interaction has engaged the attention of a number of research groups (Chaudhuri *et al* 1989; Bhattacharjee and Chaudhuri 1992; Busch and Alcock 1994; Butler *et al* 1994; Dickman and Pope 1994; Kitajima and Moro-oka 1994; Momenteau and Reed 1994; Pecoraro *et al* 1994; Rose *et al* 1994; *Chem. Rev.* 1994). Though the approaches of different groups vary, the goal, said or implied, seems to be similar. And this is amply evident from a comprehension made in a recent

*For correspondence

thematic issue addressed to "Metal–dioxygen complexes" (*Chem Rev.* 1994). Unambiguous evidence for the presence of metal-dioxygen units ('M – O_2') in the oxidized forms of some important biological substances like hemoglobin, hemerythrin and hemocyanin, for instance has rendered the investigations related to their synthetic, structural and reactivity aspects not only very intriguing but also relevant to the understanding of their biochemical implications. Studies involving vanadium have also drawn considerable attention of contemporary researchers (Bhattacharjee *et al* 1989; Butler *et al* 1994; Ravishankar *et al* 1994; Tschirret-Guth and Butler 1994). This has been further triggered by the discovery of a new class of enzymes requiring vanadium for their activity (Vilter 1984; Butler and Walker 1993) and has led to increased interest in the coordination chemistry of the metal with biologically relevant ligands. Reactivity investigation of vanadium compounds has been the central theme of a number of studies. It is now understood that haloperoxidases act as catalysts in the *in vivo* production of a large variety of halogenated organics (Butler and Walker 1993). Noteworthy, in the context of peroxo vanadates, is that although the literature often makes reference to vanadium bromoperoxidase, there appear to be some vanadium haloperoxidases which utilise chloride as well as bromide and iodide (Soedjak and Butler 1990). Unfortunately, the exact compositions of the active oxidant and active halogenating intermediate do not seem to be known so far (Everett *et al* 1990), and this requires attention. Equally encouraging is the potential of complex peroxovanadium species as a clinical alternative of insulin for the treatment of diabetes. This area is very promising and is currently receiving a lot of attention (Schechter *et al* 1990; Shaver *et al* 1993).

Of the few compounds so far tested positive as potential insulin mimics some were also synthesised in this laboratory a few years ago (Basumatary *et al* 1987). As a part of our research programme we have been looking into several aspects of peroxo vanadium chemistry (Bhattacharjee *et al* 1989, 1992, 1993; Ravishankar *et al* 1994) for over a decade and have made some interesting observations. Herein we have incorporated highlights of some of the results of reactivity investigations of mainly two peroxovanadates, potassium triperoxovanadate(V) trihydrate, $K[V(O_2)_3]\cdot 3H_2O$, and potassium oxodiperoxoaquavanadate(V), $K[VO(O_2)_2(H_2O)]$.

Besides studies on peroxovanadium, this group has been for quite some time trying to gain knowledge in the area of manganese(III) chemistry (Bhattacharjee *et al* 1989, 1993). It is now well known that the metal is of no less biochemical significance than vanadium, for example. The metal has been in the recent news because of the sustained activity of several groups of researchers, being made in quest of understanding its role in various biochemical redox processes (Wieghardt 1989; Pecoraro *et al* 1994) including those related to manganese SOD (Keele *et al* 1970) manganese catalase (Kono and Fridovich 1983) and oxygen-evolving complexes (OEC) in photosystem II (Debus 1992). What is apparent from the literature is that it is rather difficult to make headway in manganese dioxygen chemistry although there has been some success in the recent years (Pecoraro *et al* 1994). In our endeavour to stabilise manganese(III) under selective ligand environments, several unsuccessful attempts were made to gain access to manganese-dioxygen species. In one such attempt $Mn(acac)_3$ [acac = acetylacetonate ($C_5H_7O_2^-$)] was allowed to interact with $KF\cdot H_2O_2$ in the presence of biochemically relevant (Creutz *et al* 1980; Smit *et al* 1980; Chiswell *et al* 1987; Reedjik 1987) ligands, bpy (2,2′-bipyridyl) and phen (1,10-phenanthroline). This involved an electron-transfer reaction between manganese(III) and H_2O_2 leading to crystalline

$[Mn(acac)_2(bpy)]$ and $[Mn(acac)_2(phen)]$, respectively. Highlights of this reactivity investigation as well as salient features of the X-ray crystal structure of $[Mn(acac)_2(phen)]$ have been discussed in this article.

While an increasing interest in the studies involving metal-dioxygen compounds has been appropriately emphasised, the importance of reactivity investigation of oxo-metal compounds, eventually leading to the development of newer reagents, cannot be underestimated. It is however necessary to note that a good reagent should be one that survives the test of time. Owing to a variety of reasons, especially the operational simplicity, reaction selectivity, and cost effectiveness, interest in the oxidation reactions involving chromium(VI) reagents seem to never diminish (Corey and Suggs 1975; Piancatelli *et al* 1982; Bhattacharjee *et al* 1982; Nonaka *et al* 1984; Bhattacharjee *et al* 1987; Banerji 1988; Bhattacharjee and Chaudhuri 1990; Moondra *et al* 1990; Agarwal *et al* 1991; Chaudhuri *et al* 1994). Our endeavour in this area has led to the development of two new chromium(VI) reagents, pyridinium fluorochromate, $(C_5H_5NH)[CrO_3F]$ (PFC), and quinolinium fluorochromate, $(C_9H_7NH)[CrO_3F]$ (QFC). Some salient features of these two reagents, their advantages and the X-ray crystal structure of PFC have been also presented in this report.

2. Reactivity profiles

2.1 *Peroxovanadates(V)*

The haloperoxidases, often referred to in the literature as vanadium bromoperoxidases, catalyse the production of a large variety of halogenated organics *in vivo* (Butler and Walker 1993). Although studies on the native enzyme are consistent with an ordered mechanism employing H_2O_2 and then halide ion (de Boer and Wever 1988), the exact nature of the active oxidant and active halogenating intermediate are unknown (Everett *et al* 1990). The vanadium centre, however, does not apeear to undergo redox cycling during turnover. Significantly, peroxovanadates are now known to be quite effective as epoxidising and hydroxylating agents (Sharpless and Michaelson 1973; Michaelson *et al* 1977; Mimoun *et al* 1983, 1986; Talsi *et al* 1991, 1993) with some of these transformations being stereoselective. Some peroxovanadate (V) systems are also capable of bringing about oxidative transformations viz., sulphides to sulphoxides/sulphones (Nakajima *et al* 1989; Ballistreri *et al* 1991), alcohols to the corresponding carbonyls (Bortolini *et al* 1985; Conte *et al* 1988), and 2,2′-bipyridine to picolinic acid (Szentivanyi and Stomberg 1983).

What emerges out of the aforementioned studies is that the reactions were all conducted in organic medium and the reagents used were mainly nonperoxo-derivatives. Important among the questions that remained to be answered include the following: (i) Would the reaction profiles of such compounds in aqueous medium be similar to those one observes in organic medium, and (ii) how would a highly peroxygenated metal species react *vis-a-vis* a monoperoxo derivative? These aspects of the reaction chemistry warranted attention. Incidentally, we had at our disposal the method for the synthesis of triperoxovanadates(V) of the type, $A[V(O_2)_3]\cdot 3H_2O$ (A = Na and K) (Bhattacharjee *et al* 1989). The compounds are not only soluble in water but also appreciably stable. Considering the properties of $A[V(O_2)_3]\cdot 3H_2O$ we sought to study the reactions of the triperoxovanadate(V) complex ion with both inorganic and organic substrates especially in aqueous medium. Typically, $K[V(O_2)_3]\cdot 3H_2O$

dissolved in water was allowed to interact with SO_2. The substrate gas was bubbled through the deep blue solution at a controlled rate. The reaction took place readily with change of colour from deep blue to yellow ($pH \approx 6$), and finally to green-blue ($pH \approx 2$). While the initial reaction solution (prior to interacting with SO_2), as well as the yellow solution at $pH \approx 6$, was ESR silent, the ultimate blue-green solution at $pH \approx 2$ was ESR active. The spectrum was typical of oxovanadate(IV) with an eight-line pattern (Bhattacharjee *et al* 1989). In subsequent reaction runs, the flow of SO_2(g) was discontinued at each stage of colour change of the reaction followed by an immediate isolation of the compounds therefrom. The product isolated from the yellow solution ($pH \approx 6$) was $K[VO(O_2)_2(H_2O)]$ while that obtained from the green-blue solution ($pH \approx 2$) was $A_2[VO(SO_4)_2(H_2O)_3]H_2O$. It is thus significant that at the first stage of the reaction, it is one of the peroxide ligands that participates, in preference to the vanadium(V) centre, in the reaction. The metal centre was finally reduced, as is evident from the ESR results and the isolated product (Bhattacharjee *et al* 1989).

Unlike SO_2, carbon dioxide is a softer inorganic substrate but the study of its reactions with a peroxo-metal compound is highly relevant from the biochemical point of view. Investigation of reactions of CO_2(g) with a metal-dioxygen derivative, especially in an aqueous medium, appears to be the first of its kind to the best of our knowledge. As anticipated, the course of reaction here was quite different compared to what was observed for SO_2(g). On bubbling CO_2(g) through an aqueous solution of $K[V(O_2)_3]\cdot 3H_2O$, an immediate reaction took place as indicated by the change of colour of the reaction solution to yellow, with no further alteration of the colour even on prolonged bubbling of the substrate gas. The *p*H value of the yellow solution was 8. The solution was ESR silent. Work-up of the yellow solution afforded a yellow crystalline product which has been ascertained, by a combination of chemical and physical studies, to be $K_3(V_2O_2)_3(OH)_3]$. Evidently the compound is dimeric. The metal centers are pentavalent as evidenced by the results of magnetic susceptibility and ESR experiments. Characterisation data, including those of IR and laser Raman spectroscopy and deuteriation experiment, show that the complex $[V_2O_2(O_2)_3]^{3-}$ ion contains peroxide and $(OH)^-$ groups occurring both as terminal and bridging ligands linking two V=O centres.

Interestingly, when $K_3[V_2O_2(O_2)_3(OH)_3]$ in an aqueous suspension, was allowed to interact with SO_2(g), it dissolved immediately and the reaction proceeded further through two different stages of colour change, viz., (i) red colouration at $pH \approx 5$ and (ii) finally blue at $pH \approx 2$. The products isolated from the reaction solutions at these two stages were orange–red and blue, respectively, Both the compounds contained VO^{2+} (i.e. V(IV)). While the red product contained peroxide, the blue compound did not. An investigation of the sequence suggested that the red colouration ($pH \approx 5$) stage was an intermediate step which involved a peroxo-bridged quadrivalent vanadium intermediate. This then gave rise to the blue sulphate complex, $K_2[V_2O_2(SO_4)_3(H_2O)_4]\cdot H_2O$. The magnetic moment ($\sim 1{\cdot}73\ \mu_B$/V) and the ESR (c.f. VO^{2+}) result were in conformity with the formulation. Of the three sulphato ligands, two were chelated while the third one acted as a bridging group.

The control reactions conducted between $[K[V(O_2)_3]\cdot 3H_2O$ and (5M) sulphuric acid solution yielded altogether different results. The reaction apparently involved two stages with the progress of addition of the acid. Thus, the deep blue solution of $K[V(O_2)_3]\cdot 3H_2O$ ($pH \approx 9$) changed its colour to yellow at $pH \approx 7{\cdot}5$ and then to red with the *p*H of the solution being 2. Here the reaction solution was ESR silent

throughout (pH $\approx$ 9 to $\approx$ 2). Evidently no reduction of the metal took place, only the bonded peroxides participated in the reaction. The yellow colouration (pH $\approx$ 7·5) was due to the formation of a transient intermediate containing V: O_2^{2-} in the ratio 1:2, but unstable. The product isolated from the red (pH $\approx$ 2) solution was extremely interesting for it was not only a monoperoxovanadate(V) species, a kind of vanadium complex not commonly encountered, but also contained coordinated sulphate. It is important to note that a sulphato coordinated peroxovanadate is unprecedented in the literature despite several earlier attempts (Chaudhuri and Islam 1985). The compound is diamagnetic, ESR inactive with its solution electrical conductance being $350\,\Omega^{-1}\,cm^2\,mol^{-1}$. The identity of the compound has been ascertained to be $K_3[VO(O_2)(SO_4)_2]$. Both peroxo and sulphato ligands are chelated to the metal centre. It is thus evident that sulphuric acid reacts with $K[V(O_2)_3]\cdot 3H_2O$ very differently from SO_2(g) or CO_2(g).

The diperoxo complex. $K[VO(O_2)_2(H_2O)]$, was easily obtained from the reaction of $K[V(O_2)_3]$ with SO_2(g), as already described. This is yet another very fundamentally important species in the domain of $V-H_2O_2$ system, because the "$VO(O_2)_2^-$" core is believed to be the active species responsible for the increase in life-span of mice with murine leukemia (Djordjevic and Wampler 1985). The complex $[VO(O_2)_2H_2O]^-$ ion is also very important as a source material for the syntheses of heteroligand oxodiperoxovanadate(V) complexes by substituting the labile aqua ligand. While diperoxovanadates(V) are potential clinical alternatives to insulin, non-peroxo vanadyl (VO^{2+}) compounds are known to be very effective hypoglycemic agents with a post-insulin receptor action (Schechter *et al* 1992).

In an interesting study, we have very recently looked into the interaction of $K[VO(O_2)_2(H_2O)]$ with $VOSO_4$ (Ravishankar *et al* 1994). The reaction was monitored by UV-Vis, EPR, and ^{51}V NMR spectroscopic studies in solution. The results revealed that an oxygen transfer, as well as an electron-transfer reaction took place between the two reactants. The vanadyl (VO^{2+}) of $VOSO_4$ was oxidised to VO_2^+ with the reduction of one of the coordinated peroxides. The oxidised VO_2^+ oligomerised, as normally happens (Crans *et al* 1990), to the cyclic tetramer as shown by ^{51}V NMR spectroscopy. The formation of the oxygen radical species. $[OV(O_2)^{2+}]$ as an intermediate is significant. This was shown by an ethanol stable EPR spectrum (1:2:2:1) quartet) recorded in the presence of dimethylpyroline-N-oxide used as a spin trap. Further, this radical triggered two secondary reactions with one of them being a dismutation process leading to a monoperoxovanadate and a non-peroxo vanadate with subsequent release of oxygen. In the other process, $[OV(O_2)^{2+}]$, in the presence of organic ligands like hydroxyl radical scavengers (viz., *tris*(hydroxyamino)methane, formate, benzoate, mannitol), singlet oxygen quenchers (e.g., imidazole, histidine) and amino acids (asparagine, aspartate), underwent an oxygen consumption reaction to form the tetramer (of VO_2^+) and QOH (Q = organic ligand) in some cases. The QOH formation might well be the result of the oxygen consumption reaction. This has been amply demonstrated by the conversion of benzoate to p-hydroxybenzoate. The detection of p-hydroxybenzoate as a product indicated the possibility of a hydroxylation reaction in the case of some ligands. The ability of peroxovanadates to support epoxidation and hydroxylation reactions is already reported (Mimoun *et al* 1983). The oxygen consumption reactions leading to the formation of both QOH and vanadate tetramers need further investigations for understanding the mechanism involved. Evaluation of the results giving an insight into the multiple reactions that occur between vanadyl and diperoxovanadate is schematically shown in figure 1.

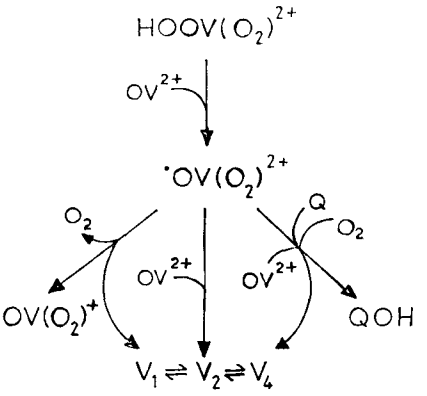

Figure 1. Multiple reactions occurring between vanadyl and diperoxovanadate.

The competing reactions of the proposed oxygen-radical intermediate of peroxovanadate with vanadyl as well as organic ligands, which produce reactive molecules, may have a vital role in the biochemical activity of these vanadium compounds.

Apart from the reactions with the chosen inorganic substrates as described above, peroxovanadium(V) compounds are known to be very efficient reagents for organic transformations. For instance, asymmetric epoxidation of allylic alcohols by *t*-BuOOH using vanadium(V) complexes with chiral hydroxamic acids (Michaelson *et al* 1977), and stereoselective epoxidation of alkenes by vanadium(V) complexes of a tridentate Schiff base and alkyl hydroperoxide (Mimoun *et al* 1986) are very significant. Incidentally, our $K[V(O_2)_3]\cdot 3H_2O$ in aqueous solution was basic with the *p*H of the solution being 11. This property led us to conjecture that the reagent might turn out to be a viable substitute for alkaline – hydrogen peroxide (H_2O_2) reagent. In order to ascertain the efficacy, reactions of $K[V(O_2)_3]\cdot 3H_2O$ separately with benzylidene acetophenone, benzonitrile, and benzil in aqueous solution were conducted (Bhattacharjee *et al* 1993). The reactions took place readily with the transformation of benzylidene acetophenone to the corresponding epoxide, benzonitrile to benzamide, and benzil to benzoic acid (cf Bayer–Villiger oxidation) in good yields. From each of the three reactions, potassium aquaoxodiperoxovanadate(V), $K[VO(O_2)_2(H_2O)]$, was isolated as the reduced product of the vanadium reagent. This implies the involvement of a common reaction pathway in the chosen cases. It is believed that $[V(O_2)_3]^-$ acted as a 1,3-dipolar reagent, $^-O\text{-}O\text{-}V(O_2)_2$, and attacked the substrate as a nucleophile which was followed by the expulsion of the reduced vanadium product, as isolated. A representative mechanism is shown in figure 2.

2.2 *Manganese(III)*

In order to understand the role of manganese binding to dioxygen in various biological systems, as well as the mechanism of water oxidation to O_2 by manganese complexes, the investigation related to the interaction of the metal with dioxygen including O_2^- and O_2^{2-} has emerged as an area of topical interest (Christou 1989; Wieghardt 1989; Debus 1992; Pecoraro *et al* 1994). Incidentally, the studies conducted so far involved mostly manganese(II) complexes and to a much lesser extent manganese(III) species which led to the formation of higher valent compounds of the metal (Coleman and Taylor 1978;

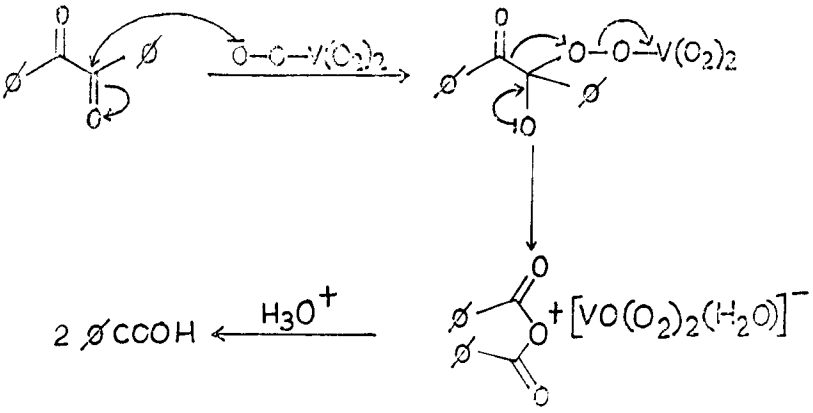

Figure 2. A representative mechanism of the transformations brought about by $[V(O_2)_3]^-$.

Kipke *et al* 1990; Horwitz and Daily 1993; Pecoraro *et al* 1994). Interestingly, the interaction of manganese(III) species with H_2O_2 afforded in most cases manganese(IV) complexes, except possibly in one case (Gelasco and Pecoraro 1993) wherein a reversible reaction $[Mn^{II}(2\text{-OHsalpn})]_2^{2-} \rightleftharpoons [Mn^{III}(2\text{-OHsalpn})]_2$, occurred.

Our participation in the investigation of manganese chemistry provided ample evidence causing us to believe that fluoride (F^-) is a very good stabiliser for trivalent manganese (Bhattacharjee *et al* 1989, 1993). It then appeared rational to conjecture that reactions of an appropriate Mn(III) precursor with H_2O_2 in the presence of F^- and an additional ligand might lead to a higher valent heteroligand manganese–dioxygen adduct. In order to try out the strategy, $KF \cdot H_2O_2$ was used as the reagent, $Mn(acac)_3$ [acac = $C_5H_7O_2^-$] as the metal precursor, and 2,2′-bipyridyl(bpy) or 1,10-phenanthroline (phen) as the additional ligand of biochemical (Creutz *et al* 1980; Smit *et al* 1980; Chiswell *et al* 1987; Reedjik 1987) relevance. The reaction being conducted in acetonitrile medium led to the isolation of lemon yellow highly crystalline products. These have been ascertained to be manganese(II) complexes, $[Mn(acac)_2(bpy)]$ and $[Mn(acac)_2(phen)]$ (Mercati *et al* 1979). No higher valent manganese species could be isolated. Based upon the results of some studies in solution and characterisation data of the crystalline product, it is believed that in a slightly acidic medium and in the presence of peroxide (O_2^{2-}) one of the bound acetylacetonate decoordinated forming a rather unstable fluoroperoxo intermediate of the trivalent metal. The unstable intermediate might have readily undergone an internal electron-transfer between the Mn(III) centre and the peroxide ligand leading to the formation of a bivalent manganese species and oxygen. The coordinately unsaturated 'Mn(acac)$_2$', formed *in situ*, finally reacted with bpy and phen in separate reaction runs to afford hexa coordinated $[Mn(acac)_2(bpy)]$ and $[Mn(acac)_2(phen)]$ in very high yields, as obtained. The two molecular complexes are stable under normal conditions and have very favourable properties rendering them suitable as precursor probes for a variety of newer studies. Work involving these compounds are underway in this laboratory. Though these and related compounds are important from the structure and bonding points of view (Mercati *et al* 1979), X-ray structural information about them does not seem to be available to date.

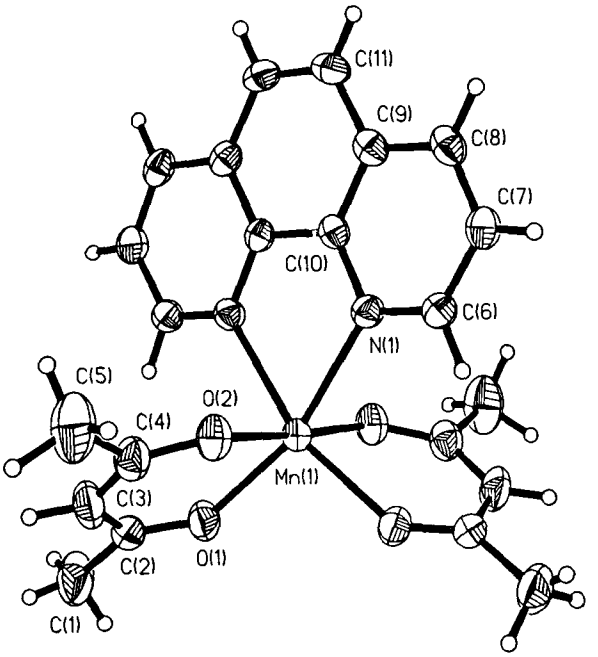

Figure 3. ORTEP view of $[Mn(acac)_2(phen)]$.

Significantly, the crystals of both complexes diffracted very well. The reflection profile analysis of $[Mn(acac)_2(bpy)]$, however, showed heavy twinning. The $[Mn(acac)_2(phen)]$, on the contrary behaved much better with no twinning tendency. It became evident from the data analysis that the compound crystallised in the orthorhombic space group *Pbcn*. The reflections were taken in the 2Θ range from 3 to 50°. The structure consists of a pseudo-octahedral Mn(II) ion being bound to two $acac^-$ ($C_5H_7O_2^-$) and a phen ligand with the molecule lying on two-fold axis. The ORTEP view of $[Mn(acac)_2(phen)]$ is shown in figure 3.

2.3 *Oxofluorochromates(VI)*

Study of the reactivities of Cr(VI) based oxidants has been a rewarding one for many research laboratories including ours (Bhattacharjee *et al* 1982, 1987; Bhattacharjee and Chaudhuri 1990). Oxidants with higher valent metal centres, viz. Fe, Mo, V, Os, Mn etc. (Mijs and De Jonge 1986) also appear to be promising. Most of the Cr(VI) oxidants known before 1975 lacked mildness, operational simplicity, versatility and selectivity. The search for an oxidant with such properties led to the development of a few Cr(VI) based reagents including pyridinium dichromate, PDC (Corey and Schmidt 1979), pyridinium chlorochromate, PCC (Corey and Suggs 1975; Piancatelli *et al* 1982) and pyridinium fluorochromate, PFC (Bhattacharjee *et al* 1982, 1987; Nonaka *et al* 1984; Banerji 1988; Bhattacharjee and Chaudhuri 1990; Moondra *et al* 1990; Agarwal *et al* 1991). Of all these oxidants PFC has proved to be one of the most reactive species. The reagent was introduced as an oxidising agent by this laboratory (Bhattacharjee *et al* 1982) and has been in wide use (Nonaka *et al* 1984; Bhattacharjee *et al* 1987; Banerji

1988; Bhattacharjee and Chaudhuri 1990; Moondra *et al* 1990; Agarwal *et al* 1991) since then.

PFC in CH_2Cl_2 readily oxidises primary, secondary and allylic alcohols to the corresponding carbonyls, benzoin to benzil, and anthracene and phenanthrene to anthraquinone and phenanthrene-9,10-quinone respectively. The facile oxidation of triphenylphosphine to triphenylphosphine oxide in CH_3CN provides clean evidence for an oxygen-transfer reaction (Bhattacharjee *et al* 1987).

Over the years, PFC has been serving as one of the best Cr(VI) reagents owing mainly to its favourable properties like solubility, lower acidity ($pH \approx 2{\cdot}45$), efficacy, stability and inertness towards acetonitrile. In order to throw light on the mechanism of the PFC-CH_2Cl_2 oxidation processes, the reduced chromium product, isolated after conducting the oxidation, was identified on the basis of various physico-chemical studies as $C_5H_5NH[CrO_2F]$, a chromium(IV) species, implying thereby that PFC is a 2-electron oxidant (Bhattacharjee *et al* 1987).

The favourable chemical composition of the Cr(IV) product and our interest in developing a soft synthesis for CrO_2, an extremely important compound of the metal especially used for the preparation of magnetic tapes (Rollinson 1975), prompted us to explore the possibility of obtaining CrO_2 directly from $C_5H_5NH[CrO_2F]$. The literature procedures involve very stringent methods (Swoboda *et al* 1961; Arthur and Ingraham 1964). Accordingly, pyrolysis of $C_5H_5NH[CrO_2F]$ at 200°C for 2 h afforded CrO_2 in quantitative yields. The identity of CrO_2 has been ascertained by chemical analyses, chemical determination of oxidation state of the metal, vibrational and EPR spectroscopies and magnetic susceptibility measurements.

Our continued interest in Cr(VI) reagents led to development of yet another new Cr(VI) oxidant, quinolinium fluorochromate (QFC), recently (Chaudhuri *et al* 1994). This work was initiated mainly to improve upon the solubility property of chromium reagent in non-aqueous solvents. The compound, QFC, was obtained as yellow-orange needle-shaped crystals with a relatively higher solubility in organic solvents than PFC. Interestingly, the *p*H of 0·01 M aqueous solution of QFC was found to be 3·35 indicating its more controlled acidity than PFC or PCC.

In order to demonstrate the efficacy of the new reagent, the oxidation reactions of QFC were conducted with substrates similar to those chosen for PFC reactions as well as with some newer ones. As far as the reactions with common substrates are concerned, the reactions were identical for both the reagents with respect to the reaction times and yields of the oxidised products, The substrates included were *n*-butanol, benzylalcohol, isopropanol, cyclohexanol, benzoin, triphenylphosphine, and allylic alcohol. Significantly, the oxidation of arenes, e.g., anthracene and phenanthrene, was very facile even in CH_2Cl_2 medium. Indeed, the yields of the products were very high (anthraquinone, 72%; phenanthrene-9,10-quinone, 60%), with QFC being the reagent used under mild reaction conditions. Apart from these, QFC also oxidises diphenylsulphide to the corresponding sulphoxide in high yields. Besides, the capability of QFC to act as an oxidising agent in sensitive environments has been demonstrated by the facile oxidation of secondary hydroxyl group in an environment of isopropylidene functionality and a *bis*-trimethylsilyl ether to the corresponding ketone and quinone, respectively, at room temperature. The oxidation of citronellol to citronellal without using a buffer is one of the major advantages of QFC over its companion reagents, PFC and PCC, a result that can be attributed to be a direct consequence of its far less pronounced acidic character.

Here again, in order to comment on the oxidation process involving QFC, the reduced chromium product was isolated after each oxidation. As in the case of PFC, the reduced product was a Cr(IV) species, $C_9H_7NHCrO_2F$. Thus even under mild reaction conditions most of the Cr(VI) reagents behave as two-electron oxidants.

2.4 *Metal oxidation by Cr(VI) reagent*

In an attempt to explore further the reactivity of Cr(VI) reagents, oxidations of metals have been carried out. It is notable that oxidation of metals normally requires strong oxidising agents, viz. LTA (Debroy *et al* 1983), and until now there has been no information concerning such oxidations involving milder oxidising agents. Hence, in a so far unknown reaction, metallic copper has been oxidised to Cu(II) by PFC in CH_2Cl_2. The reactions were conducted under reflux in the presence of N-donor ligands, L(L = pyridine, 2-, 3-, or 4-methylpyridine, 2-aminopyridine or quinoline) and acetic anhydride, maintaining the molar ratio of Cu: L: PFC: $(CH_3CO)_2O$ at 1:4:1·1:2. The oxidised Cu(II) product was isolated by column chromatography. A variety of physico-chemical studies showed that the identity of the compounds was $[Cu^{II}(OOCCH_3)L]_2$.

2.5 *Crystal structure of PFC*

Though a lot of research involving Cr(VI) reagents, focussed mainly on their reactivity aspects, has been reported, the crystal structure of a halochromate reagent is yet to be published. This is relevant in the context of establishing the structure-reactivity correlation. In view of this, PFC and QFC were subjected to X-ray analysis. While the crystals of (PFC) were found to diffract well, those of QFC appeared to be unsuitable for crystallographic analysis, X-ray data for PFC crystals have been collected in the 2Θ range between 3° and 60° with Mo-K_α radiation. The compound crystallises in the ascentric orthorhombic space group $CmcZ_1$. The structure consists of discrete pyridinium cations and CrO_3F anions with no significant hydrogen bonding. This resulted in total disorder of the pyridinium cation. The tetrahedral anion $[CrO_3F]^-$ lies on a crystallographic mirror plane. The Cr–O distance in this compound is 1.622(3) Å (Cr–O for $KCrO_3Cl$ is 1·539 Å). This is in the range of 2σ for the Cr–O distance reported in the literature. The ORTEP view is shown in figure 4.

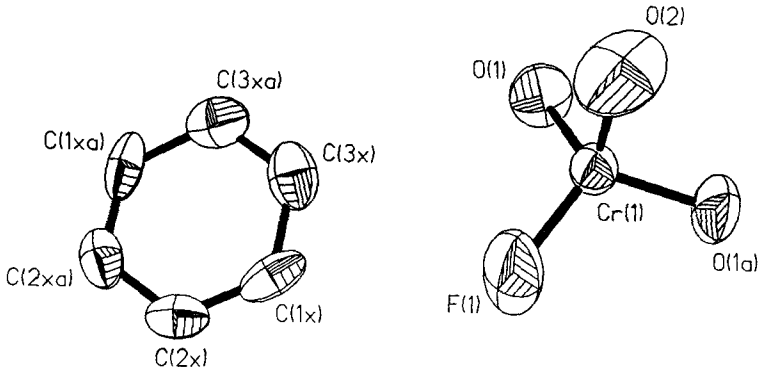

Figure 4. ORTEP view of $C_5H_5NH[CrO_3F]$ (PFC).

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