Inorganica Chimica Acta, *71* (1983) 179–184

Reactions of Oxovanadium(IV) Salen and Phthalocyanine with Sulphur Compounds and Reducing Agents. Relevance to Catalytic Demetallisation

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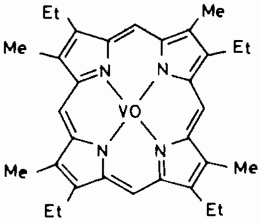
Received September 15, 1982

The nature of the vanadium compounds in some petroleum crudes is reviewed. Oxovanadium(IV) phthalocyanine and oxovanadium(IV) Schiff base complexes are proposed as models of vanadium coordination in porphyrins and asphaltenes. Reactions of these compounds with hydrogen sulphide, thiols and other organosulphur compounds, sulphur dioxide, and triethylaluminium are described. The Schiff base complex readily undergoes demetallisation, the vanadium being converted to V_2S_3. Demetallisation of the phthalocyanine (and porphyrin) complexes is more difficult. With H_2S and thiols, in the presence of nitrogen bases, the VO(phthalocyanine) was reduced with loss of terminal oxygen but without sulphur insertion. With triethylaluminium, the vanadium was reduced and the phthalocyanine ring system was attacked. The VO(phthalocyanine) catalysed the aerial oxidation of H_2S, thiols, and SO_2. The results are relevant to the problem of catalytic demetallisation.

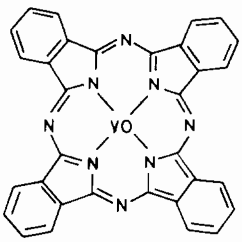
Introduction

Crude oils from some sources contain relatively high concentrations of vanadium and nickel, for example, Venezuelan Boscan whole crude, V, 1000 and Ni, 100 ppm [1]. The metals are present in the oil partly as porphyrins, *e.g.* (1), and also coordinated by N, O and S in the asphaltenes [2]. During catalytic hydrodesulphurisation (*i.e.*, hydrogenolysis of sulphur compounds usually over a Co–Mo/Al_2O_3 catalyst) [3] the vanadium compounds deposit on the catalyst and are converted to vanadium sulphides [4] which accumulate in the pores ultimately blocking access to the active components [5]. One method of overcoming the problems caused by vanadium and nickel [6] is a two-stage process; metals are removed in the first stage and the deactivated catalyst is subsequently dumped. Such deactivated catalysts could be a useful source of vanadium.

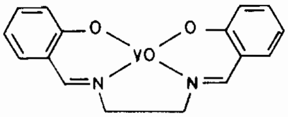
In technical operations demetallisation is associated with hydrodesulphurisation and the mechanism is not at all well understood. In a previous paper [7] we showed that the deactivating effect of vanadyl phthalocyanine (2) was the same as that of the metal-free phthalocyanine. Therefore we suggested that the primary interaction with the catalyst was *via* the organic ligand rather than vanadium. The porphyrin or phthalocyanine ring system would undergo catalytic hydrodenitrogenation prior to demetallisation [8]. One goal of research on demetallisation is to develop processes distinct from the hydrodesulphurisation process [9]. Although various methods of demetallisation have been claimed in the patent literature [10] it is apparent that rather little is known about the relevant chemistry of oxovanadium(IV) compounds [11]. The object of the work reported in this paper was to explore this chemistry. We were particularly interested in reactions which



(1) VO(Etioporphyrin)III



(2) VO(phthalocyanine)



(3) VO(salen)

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might lead to the decomposition of the vanadium complexes, having previously observed that a vanadyl Schiff base complex (3) decomposed during hds of thiophen under relatively mild conditions (350 °C, 1 atm) but that vanadyl phthalocyanine and porphyrins did not [7]. The work described in the present paper is mostly with oxovanadium(IV) phthalocyanine (2) which is structurally similar to the porphyrins, and so should serve as a model compound, and, unlike the porphyrins, is easy to prepare, and is cheap and readily available. It should be noted that, according to our earlier work [7], the Schiff base complexes [*e.g.* (3)] are less stable than the porphyrins and cannot be regarded as porphyrin model compounds. Indeed, they are better regarded as models of the non-porphyrin metal compounds in the oil.

Experimental

Oxovanadium(IV) phthalocyanine, [VO(Pc)] (2) and metal-free phthalocyanine, H_2Pc, were purchased from K and K Laboratories Inc. The Schiff base compound [VO(salen)] (3) was prepared by the literature method, [Salen = N,N'-ethylene bis(salicylideneiminate)] [12].

Solvents and other liquids were dried and distilled before use.

Reactions were followed by changes in the u.v.–visible spectra of the solutions using a Unicam SP 1800 spectrophotometer or by changes in the electron spin resonance spectra using a Varian E3 Spectrometer. Infrared spectra were recorded for the compounds in KBr discs using a Perkin Elmer 683 Spectrophotometer and reactions were followed by observing changes in the i.r. spectra of the discs when they were exposed to reagents.

Solutions were prepared and reactions carried out under nitrogen and by injecting reagents from a syringe through a serum cap into a spectrophotometer cell. Concentrations of the solutions were limited by the low solubilities of the phthalocyanine and were *ca.* 10^{-4} mol l^{-1}. The [VO(salen)] solutions were more concentrated (*ca.* 10^{-2} mol l^{-1}).

Results and Discussion

The purpose of our work was to discover the circumstances in which binding of vanadium in its phthalocyanine and porphyrin complexes might be weakened. We were especially interested in (a) accessibility of the sixth coordination position (*trans* to terminal O) for binding adduct molecules, (b) reactions of the vanadium atom, especially reduction, (c) reactions of the porphyrin ring, especially those which destroyed the conjugated system. Reactions of the compounds in solution were followed by u.v.–visible and e.s.r. spectroscopy. Changes in the i.r. spectra were followed for the compounds pressed in KBr discs.

Adduct Formation

The compounds [VO(salen)] and [VO(Pc)] were dissolved in the non-coordinating solvents dichloromethane and dichloroethane and in the donor solvents trimethylamine, dimethylamine, pyridine, dimethylformamide, and dimethylsulphoxide. The positions of the crystal field transitions of [VO(salen)] [Fig. 1(a)] and the visible region bands of [VO(Pc)] respectively were the same in both types of solvent.

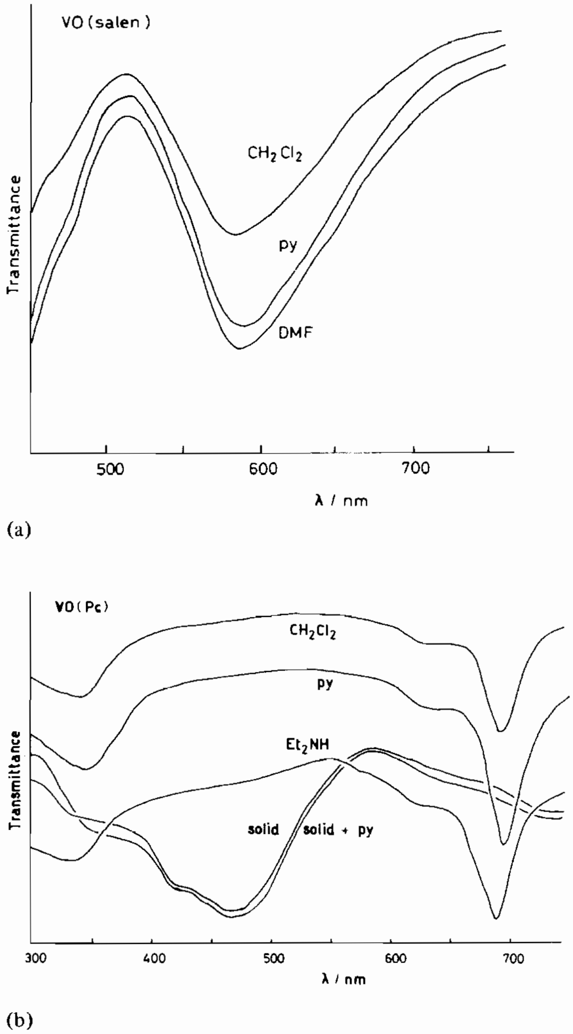
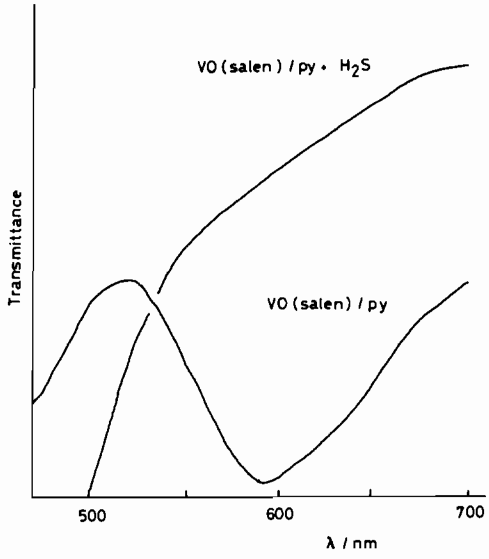


Fig. 1. Electronic spectra of (a) [VO(salen)] and (b) [VO(Pc)] dissolved in the solvents indicated, and, for [VO(Pc)], the reflectance spectrum of the solid and the solid treated with pyridine. Note that the 600 nm peak of [VO(salen)] is assigned to a d–d transition whereas the 690 peak and 630 shoulder of [VO(Pc)] are assigned to π–π^* transitions.

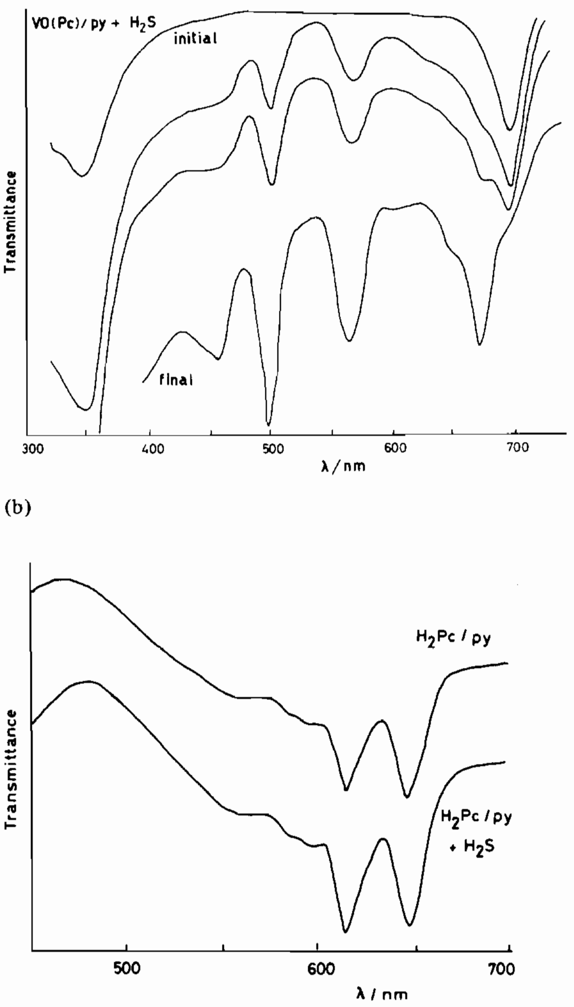
These results are in contrast with those for more flexible VO^{2+} complexes, *e.g.* the acetylacetonate [13], for which donor solvents cause appreciable shifts in the spectra. The implication is that [VO(salen)] and [VO(Pc)] have less tendency to bind an additional molecule in the sixth coordination position. One reason for this, certainly for the phthalocyanine and porphyrin complexes, is that the vanadium atom is displaced from the plane of the four nitrogen ligands towards the terminal oxide [14]. The position *trans* to the oxide is therefore rather inaccessible [15]. Addition of tetrabutylammonium hydroxide to the solutions did not affect the spectra. In view of these observations it is unlikely that oxovanadium(IV) porphyrins will bind to the catalyst surface *via* coordination of a surface atom (O or S) to vanadium.

Reactions with Hydrogen Sulphide

When H_2S was passed into solutions of [VO(salen)] and [VO(Pc)] in CH_2Cl_2 and $C_2H_4Cl_2$, the u.v.–visible spectra of the solutions did not change during *ca.* 6 h. However, when pyridine was added to solutions of the two compounds in the chlorocarbon solvents which had been saturated with H_2S the spectra did change, and also when H_2S was passed into solutions of the compounds in pyridine and amine solvents. The spectroscopic changes with pyridine as solvent are shown in Figs. 2(a) and 2(b). With [VO(salen)], after passing H_2S for *ca.* 3 h, the crystal field transitions disappeared; the solutions had become brown and slightly cloudy. The spectrum was not restored by exposure of the solution to moist air (*vide infra*). When the reaction with H_2S was carried out with solid [VO(salen)] on a large scale at *ca.* 100 °C the salen ligand sublimed and a residue of vanadium sulphide (mainly V_2S_3) remained. So H_2S converted [VO(salen)] to a vanadium sulphide and the free ligand (or its decomposition products). This result is consistent with our observation of the formation of vanadium sulphide during thiophen hds over a Co–Mo/Al_2O_3 catalyst treated with [VO(salen)] [7].



(a)



(b)

(c)

Fig. 2. Spectroscopic changes in the reaction with H_2S of pyridine solutions of (a) [VO(salen)], (b) [VO(Pc)], (c) metal-free phthalocyanine, H_2Pc.

The behaviour of [VO(Pc)] was quite different [see Fig. 2(b)]. The H_2S caused the spectrum to change with time; the intensity of the Q band at 695 nm decreased and new peaks developed at 670, 565, 500 and 460 nm. The original spectrum was restored when a drop of water was added to the solution or when it was shaken in air. So, in contrast to the changes observed with [VO(salen)], the reaction with [VO(Pc)] was reversible. The spectrum of metal-free phthalocyanine in pyridine was not affected by H_2S [see Fig. 2(c)]. Therefore the changes in the spectrum are caused by a reaction of H_2S with the vanadium.

A *possible* explanation of the spectroscopic changes is replacement of terminal oxygen by sulphur, giving a compound [VS(Pc)]; Schiff base complexes [VS(B)] have been prepared by reaction of the VO complexes with B_2S_3 [16]. They are extremely moisture sensitive and in moist air revert to the VO complexes. However, reaction of [VO(Pc)] with H_2S was accompanied by loss of the V(IV) e.s.r. signal; simple conversion of VO to VS cannot explain this since the VS compounds also contain V(IV) and are e.s.r.-active. Therefore, the reaction of [VO(Pc)] with H_2S evidently involves reduction of V(IV) presumably to a e.s.r.-inactive V(III) ($3d^2$) species. The presence of base, which is necessary for the reaction to occur, would provide for ionisation of H_2S. The reverse reaction with moist air is oxidation.

$$B + H_2S = BH^+ + HS^-$$

$$[VO(Pc)] + HS^- = [V(Pc)]^+ + HO^- + 1/2S_2{}^{2-}$$

$$BH^+ + HO^- = B + H_2O$$

$$[V(Pc)]^+ + 1/2O_2 = [VO(Pc)]$$

Sulphur was converted ultimately to sulphate (identified by i.r., *vide infra*).

The loss of terminal oxygen in the reaction of [VO(salen)] and [VO(Pc)] with H_2S was confirmed by infrared spectrophotometry. The i.r. spectra of samples of the two compounds in potassium bromide discs were measured before and after being immersed in pyridine and exposed to H_2S. The characteristic bands due to the V=O vibration [(VO(Pc)], 1005; [VO(salen)], 980 cm^{-1}] disappeared after treatment with H_2S. There was, however, no reaction (no change in the spectrum) in the absence of pyridine (or other amines). The i.r. spectrum of a disc of metal-free phthalocyanine was not affected by pyridine and H_2S. These observations confirm that, in the presence of a base, hydrogen sulphide reacts with [VO(Pc)] and [VO(salen)] with displacement of terminal oxide.

An additional phenomenon was observed when the KBr discs containing [VO(Pc)] treated with pyridine and H_2S were exposed to air. The i.r. spectrum of the discs showed additional strong bands at 611 and 1105 cm^{-1} which we assign as ν_4 and ν_3 of the sulphate ion [17]. There was no formation of sulphate in the absence of the vanadium compound and a base. When hydrogen sulphide was passed into a solution of [VO(Pc)] (300 ppm) in pyridine or triethylamine exposed to air the intensity of the sulphate bands in a KBr disc suspended in the solution increased with time. Similar effects were observed when SO_2 was used in place of H_2S. Evidently the [VO(Pc)] is catalysing the oxidation of H_2S and SO_2 to sulphate. These reactions are being investigated in detail and will be described in a future paper. The important point for our present purpose is that H_2S effects reduction of [VO(Pc)] accompanied by loss of terminal oxygen.

Reaction with Thiophenol and Attempted Reaction with Thiophen and Tetrahydrothiophen

The spectroscopic changes observed when thiophenol was added to a solution of [VO(salen)] and [VO(Pc)] in pyridine are shown in Fig. 3. The changes were the same as observed with H_2S. The reactions were accompanied by a decrease in the intensity, and ultimate disappearance, of the VO e.s.r. signal. Thiophenol is, of course, a reducing agent (being converted to diphenyl disulphide) and will, for example, reduce molybdenum(V) and (VI) oxospecies [18]. The fact that the reactions are the same with thiophenol and H_2S confirms that they are reductions accompanied by removal of terminal oxide and not just replacement of terminal oxide by sulphide. There were *no* spectroscopic changes when thiophen and tetrahydrothiophen were used. Therefore, organosulphur compounds without a reducing function apparently do not react with [VO(Pc)] or [VO(salen)].

Reaction with Triethylaluminium

We were provoked into studying [$AlEt_3$] by a patent claim [19] for demetallisation using [$AlEt_3$].

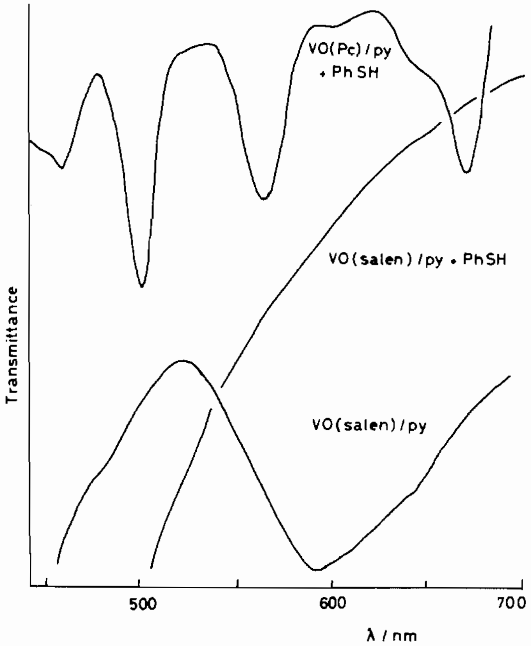


Fig. 3. Spectroscopic changes in the reaction with thiophenol of [VO(Pc)] and [VO(salen)] dissolved in pyridine.

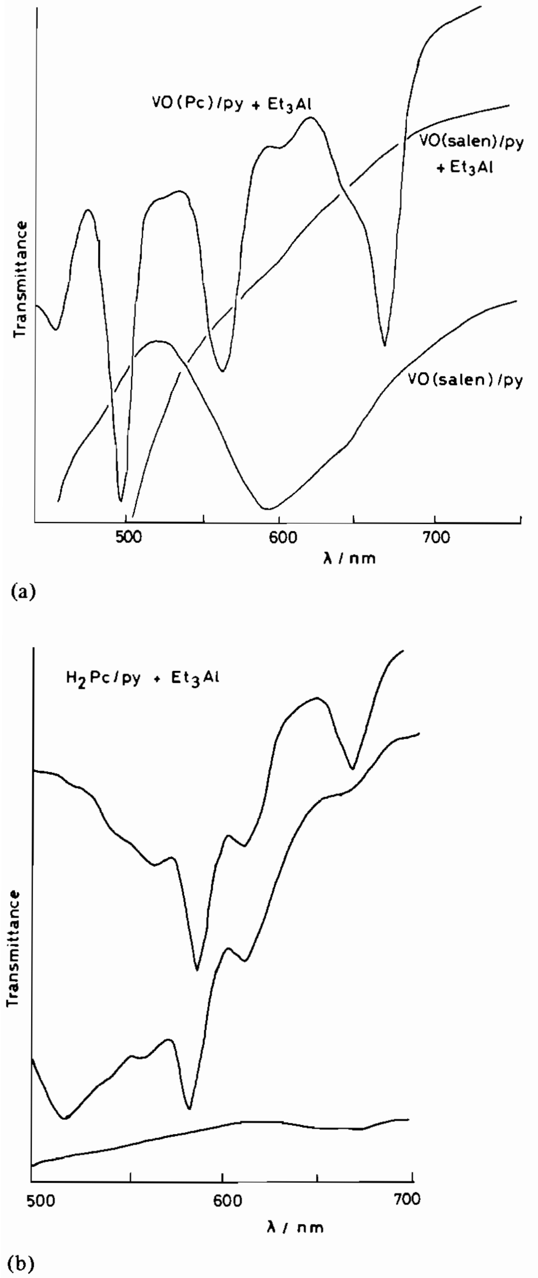


Fig. 4. Spectroscopic changes in the reaction with Et_3Al of solutions in pyridine of (a) [VO(Pc)] and [VO(salen)], (b) metal-free phthalocyanine, H_2Pc.

The [$AlEt_3$] was used as a 25% solution in hexane. When [$AlEt_3$] was added to a solution of [VO(salen)] or [VO(Pc)] in pyridine we observed changes in the u.v.–visible and e.s.r. spectra [Fig. 4(a)] which were the same as with hydrogen sulphide and thiophenol. This confirms that the reactions are reduction rather than replacement of oxide by sulphide. In the reaction of [VO(Pc)] with [$AlEt_3$] in pyridine, the new bands reached a maximum intensity after *ca.* 3 h and then decreased in intensity. After 6 h the visible region bands had disappeared. Evidently the [Et_3Al] had caused decomposition of the phthalocyanine ring system. This was confirmed when similar spectroscopic changes were observed with *metal-free* phthalocyanine [Fig. 4(b)].

Conclusions

Our main conclusions are the following. (a) The compound [VO(salen)] is much less stable with respect to demetallisation than [VO(Pc)] and with H_2S is converted to a vanadium sulphide. If we can regard the [VO(salen)] as a model of vanadium binding in the asphaltene, the implication is that asphaltenic vanadium is much more readily converted to sulphide than porphyrinic vanadium. This would be consistent with Silbernagel's description [4] of the different types of vanadium in a used catalyst, only part in the form of sulphide. (b) In the presence of pyridine and other nitrogen bases, VO(phthalocyanine) is reduced by H_2S, thiols, and SO_2. Terminal oxygen is displaced but there is no insertion of sulphur and no demetallisation and the ring system is not attacked. (c) With triethylaluminium, vanadium is reduced but the reaction proceeds further with attack on the ring system. (d) Our results suggest that under technical hydrodesulphurisation conditions vanadium in the asphaltene fraction will readily be converted to sulphide. The porphyrins will be reduced (the nitrogen base requirement being provided by nitrogenous compounds in the feedstock) but demetallised only with difficulty. We can now understand why a used catalyst contains, in addition to vanadium sulphide, vanadium prophyrin-type compounds apparently strongly bound to the catalyst surface [4].

Acknowledgement

One of us (JAV) thanks the Government of Venezuela for financial support.

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