similarly unresolved. $H_2CdY{\cdot}6H_6O$ has a similar spectrum to that of the cobalt complex. The contrast in the spectroscopie features suggests different structures without non-coordinated carboxyl groups in the Co(II) and Cd(II) complexes.

The Raman spectrum of $H_2ZnY{\cdot}2H_2O$ was obtained (though that of $H_2NiY{\cdot}2H_2O$ could not, because of the instability of the complex to laser radiation). In the Raman spectrum νC–O bands are at 1713, 1610 and 1578 cm^{-1} and in the νC–C region there are bands at 921, 903 and 885 cm^{-1}. This combination of a high wave number νC–O band and a νC–C band at less than 900 cm^{-1}, is that observed for acid solutions of EDTA complexes in which a free protonated carboxyl arm is present[2]. Observation of two νC–O carboxylate bands and two νC–C bands above 900 cm^{-1}, is however possibly indicative of a distorted structure in which the coordinated carboxylate groups are non equivalent. In support of this suggestion, we note that the spectra of $H_2NiY{\cdot}2H_2O$ and $H_2ZnY{\cdot}2H_2O$ are far more complex than those of the other acid complexes, not only in the 1200–1270 cm^{-1} region but also between 800–1100 cm^{-1} where νC–N and νC–C are observed. In contrast, the Raman spectrum of $H_2CdY{\cdot}6H_2O$ has no νC–O bands above 1700 cm^{-1}, nor νC–C below 900 cm^{-1} indicating, as was inferred from the IR spectrum, that in this complex there are no free carboxyl arms.

In support of formulation as a compound with two coordinated water molecules, thermo-gravimetric analysis of $H_2NiY{\cdot}2H_2O$ shows that water is lost from 150–250°C, a temperature range which is higher than that usually associated with the loss of lattice water in EDTA complexes[10]. For $H_2ZnY{\cdot}2H_2O$ the observed temperature range is from 110–160°C, indicating a lower thermal stability which may perhaps be explained on the basis of the relative stability of four coordinate zinc complexes compared with those of nickel.

EXPERIMENTAL

All the complexes were prepared by heating equimolar quantities of metal(II) carbonate and H_2EDTA in water at 90°C until the starting materials had dissolved and CO_2evolution has ceased. The diprotonated complex separated as the solution cooled. IR spectra were obtained from mulls using a Perkin-Elmer 457 spectrometer. (We note that despite the very numerous alkali disc spectra of EDTA complexes reported in the literature, marked changes in spectra occur in this medium.) Raman spectra were obtained from the powdered solids using a Coderg Ramalog spectrometer.

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Studies on iron(III) thiocyanate complexes of N,N′ ethylene bis(salicylideneimine), N,N′ bis *o*-hydroxybenzylidene *o*-phenylenediamine and N,N′ propylene bis (salicylideneimine)

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Complexes of the tetradentate Schiff bases N,N′ ethylene bis (salicylideneimine) (ensal) and N,N′ bis *o*-hydroxy benzylidene *o*-phenylenediamine (*o*-phensal) have been widely investigated[1, 2]. The chloro and the bromo complexes of iron(III) with ensal show interesting magnetic properties and these complexes are reported to be dimeric[3]. A few iron(III) cyanide complexes with Schiff bases have been reported recently[4]. We have prepared iron(III) thiocyanate complexes of ensal, *o*-phensal and N,N′ propylene bis(salicylideneimine) (pnsal) for the first time and have investigated their magnetic properties, IR spectra and electrical conductance. The pyridine adducts of the parent complexes also have been isolated and investigated.

EXPERIMENTAL

Materials employed. The Schiff bases ensal and *o*-phensal were prepared by condensing salicylaldehyde (BDH) with ethylenediamine or *o*-phenylenediamine in ethanol. The solid Schiff bases separated were filtered, washed with ethanol and finally recrystallised from benzene. $FeCl_3{\cdot}6H_2O$ and KCNS were BDH laboratory grade and AnalaR reagents respectively. Nitrobenzene was dried over P_2O_5 and distilled before use. Acetonitrile, ethanol and ether were purified by standard methods[5].

Preparation of ensal and o*-phensal complexes.* For the preparation of the complexes an aqueous solution of iron(III) thiocyanate was prepared by mixing 30 ml of $FeCl_3{\cdot}6H_2O$ solution (10%) with 70 ml KCNS solution (10%). The deep red iron(III) thiocyanate was extracted into an ether layer by vigorously shaking the aqueous solution with ether (75 ml). The ether layer was then separated and mixed with ensal or *o*-phensal in benzene. The ligand to metal ratio was kept as 1:1. The dark brown complexes separated instantaneously were filtered, washed with benzene several times, then with ether and dried in vacuum over P_2O_5. The pyridine adducts of the complexes were prepared by refluxing the parent complexes (3 gm) with pyridine (25 ml) for about 3 hr and evaporating the solution to 10–15 ml. On keeping the solution overnight black crystals of the adducts separated which were filtered, washed with ether to remove excess pyridine and dried. The complexes and the adducts were found to be soluble in methanol, acetone, nitrobenzene and acetonitrile and insoluble in benzene.

Preparation of pnsal complexes. Propylene diamine (1 ml) in 10 ml benzene was mixed with salicyladehyde (2.4 ml) in 25 ml benzene in a dry beaker when a yellow solution was obtained. To this ferric thiocyanate in ether was added with constant stirring. A black precipitate formed instantaneously, was filtered, washed several times with benzene to remove any excess ligand if present and then with ether and dried under vacuum over P_2O_5.

The pyridine adduct was prepared by heating pnsal complex (2 g) with pyridine (25 ml) on a waterbath for about 3 hr. The solution was concentrated to about 10 ml and ether was added when the pyridine adduct was precipitated. The brownish black compound obtained was filtered and washed several times with ether to remove excess pyridine and dried under vacuum over P_2O_5.

Physical methods and analysis. The molar conductances of the complexes in nitrobenzene and acetonitrile ($\sim 10^{-3}$ M) were determined at 25°C using a Philips Conductivity bridge GM 4249. (Cell constant 0.7511 cm^{-1}). The IR spectra of the complexes and the pure ligands were obtained on a Perkin-Elmer 221 IR spectrophotometer. The magnetic susceptibilities of the solid complexes were measured at room temperature by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant.

RESULTS AND DISCUSSION

The electrical conductance data of the complexes (Table 1) show that the parent complexes as well as the adducts are non-electrolytes in both nitrobenzene and acetonitrile. There is a slight increase in the conductance of the adducts as compared to that of the parent compounds. Even though the magnitude of the increase is not appreciable the trend is quite clear. Probably this is due to the formation of monomeric species with pyridine which makes the thiocyanate group more labile.

The effective magnetic moment values of the parent compounds indicate considerable interaction between the iron atoms as is the case with the chloro complex of ensal[6]. However, when the adduct is formed there is a marked increase in the magnetic moment and the value approaches the spin-only value expected for high spin iron(III) complexes. Thus, the magnetic behaviour of the thiocynate complexes and their pyridine adducts are quite comparable to that of the chloro complex and its adduct. It can reasonably be concluded that the parent complexes in the present case exist as dimers with considerable metal–metal interaction while the pyridine adducts are monomers.

The IR spectra of the free ligands and their complexes are quite complex. However, it has been possible to derive some information regarding the nature of bonding between the thiocyanate group and the metal as well as the mode of attachment of the ligand to the metal from the shift in some of the important spectral bands. The broad medium intensity band present around 2800 cm^{-1} in the spectra of the free ligands assignable to the hydrogen bonded OH group disappears on complexation. This indicates the replacement of hydrogen of the OH group by metals in the complexes. A strong band observed at 2090 cm^{-1} in the spectrum of the thiocyanate complex, but not present in the free ligand spectrum can be assigned to the thiocyanate group coordinated through nitrogen[7]. For the ensal complex and its pyridine adduct the bands present at 805 cm^{-1} and 800 cm^{-1} respectively can be attributed to the C–S stretching of the nitrogen bonded thiocyanate group. These bands are at 825 and 820 cm^{-1} respectively for the *o*-phenal complexes and at 810 cm^{-1} in both the pnsal complex and its pyridine adduct.

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Table 1. Analytical and other physical data of iron(III) thiocyanate complexes

		Iron (%)		Sulphur (%)		μ_{eff}	Electrical conductance Λ_m ohm^{-1} cm^2 $mole^{-1}$		Important IR frequencies and their assignments	
Compound	Colour	Found	Cal.	Found	Cal.	B.M.	Nitrobenzene	Acetonitrile	(cm^{-1})	assignment
ensal	Yellow	—	—	—	—	—	—	—	2700bm 1525m	νOH νC=N
Fe(ensal) NCS	Dark brown	14.80	14.90	8.03	8.42	5.49	0.2	5.8	1550s 2090S 805m	νC=N νC=N νC–S
Fe(ensgl) NCS·Py	Black	12.2	12.17	6.65	7.00	5.89	1.1	10.7	1545m 2075s 800m	νC=N νC=N νC–S
o-phensal	Yellow	—	—	—	—	—	—	—	2800bm 1495m	νOH νC=N
Fe(*o*-phensal) NCS	Dark brown	13.19	13.05	7.42	7.48	5.48	0.3	7.4	1540m 2080s 825m	νC=N νC=N νC–S
Fe(*o*-phensal) NCS·Py	Black	11.13	11.02	5.99	6.31	5.97	2.1	18.8	1540s 2095s 820m	νC=N νC=N νC–S
(PnSal)	Yellow	—	—	—	—	—	—	—	2900bm 1500m	νOH νC=N
Fe(pnsal) NCS	Black	13.9	14.20	8.19	8.16	5.32	0.7	17.3	1545s 2075s 810m	νC=N νC=N νC–S
Fe(pnSal) NCS·Py	Black	11.70	11.86	6.70	6.80	6.02	0.84	24.9	1545s 2075s 810m	νC=N νC=N νC–S

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A kinetic study of the oxidation of formaldehyde by octacyanotungstate(V) ions

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The kinetics of the oxidation of formaldehyde by octacyanotungstate(V) ions in strongly alkaline medium have been investigated by a titration method. The reaction is of the first order with respect to each of $W(CN)_8^{3-}$, formaldehyde and OH^- concentrations. Product $W(CN)_8^{4-}$ ions have no retarding effect upon reaction rate. The third order rate constant is 0.306 $l^2\,mol^{-2}\,min^{-1}$ at 287.5°K with $E_a = 15.9$ kcal/mol and $\Delta S^* = -7.6$ e.u. at 298°K. A reaction mechanism is discussed.

The great number of applications in the alkaline oxidation of organic functional groups by potassium ferricyanide are well known, whilst mechanisms have been presented in a few cases. The latter compound, together with the cyano complexes of Mo(V) and W(V) exhibit approximately similar redox potentials as electron abstracting complex ions. This prompted us to investigate the oxidation kinetics of a few organic compounds by $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions in order to observe whether mechanisms parallel to those for $Fe(CN)_6^{3-}$ oxidations could be put forward.

EXPERIMENTAL

$K_4W(CN)_8\cdot 2H_2O$ and $Cs_3W(CN)_8\cdot 2H_2O$ were prepared by methods already mentioned before [1]. The latter compound was used as a primary standard for the direct weighing and preparation of solutions with a known concentration. Solutions of this compound are, however, photosensitive and were consequently stored in the dark. Stock solutions of formaldehyde were prepared from a Merck "Pro Analysi" sample and standardized by the iodimetric method. Sodium hydroxide solutions were prepared from a carbonate-free stock solution and standardized daily to check on CO_2 absorption.

The reaction vessel consisted of a 250 ml erlenmeyer flask previously coated with Black Japan. A mixture of accurately measured volumes of the formaldehyde and alkali solutions in the flask was previously immersed in the water bath, applying constant magnetic stirring by a submersible magnetic stirrer. A total reaction mixture of 200 ml was used in all cases. 10 ml aliquot samples were withdrawn from time to time and pipetted into a pre-cooled solution of 2 M H_2SO_4 containing a few drops of 0.1% N-phenylanthranilic acid indicator. The course of the reaction was followed by titration of the product $W(CN)_8^{4-}$ ions with a standard ceric sulphate solution. This was also checked spectrophotometrically following the decrease in the absorption maximum of $W(CN)_8^{3-}$ ions at 357 nm using a Pye Unicam S.P. 1700 spectrophotometer equipped with digital readout and automatic recording. All kinetic runs were performed in a 0.1 M KNO_3 medium.

RESULTS

A stoichiometric study with the oxidant in fourfold excess to the formaldehyde concentration, yielded the following equation:

$$HCHO + 2W(CN)_8^{3-} + 3OH^- \longrightarrow HCO_2^- + 2W(CN)_8^{4-} + 3H_2O.$$

The 2:1 ratio of reacting complex ion to formaldehyde is in agreement with many other similar reactions in both acidic and alkaline media.

Kinetic runs with the formaldehyde concentration in tenfold excess to $[W(CN)_8^{3-}]$, followed good pseudo-first order kinetics with respect to octacyanotungstate(V) concentration for more than 70% conversion of the latter. Pseudo-first order constants (k_{obs}) were determined from straight-line plots of log $[W(CN)_8^{3-}]$ against time (Table 1). The reaction was found to be of first order with respect to each of the oxidant, reductant and alkali concentrations. The addition of a 0.005 M $W(CN)_8^{4-}$ solution to an equimolar solution of $W(CN)_8^{3-}$ ions, showed no retardation of reaction rate. Third order rate constants were determined at 14.5, 19.9 and 25°C yielding values of 0.31, 0.52 and 0.84 $l^2\,mol^{-2}\,min^{-1}$ respectively. This gave an E_a value of 15.9 kcal mol^{-1} and a ΔS^* value of −7.6 e.u. at 298°K.

DISCUSSION

It is evident from the previously mentioned order relationships that the oxidation of formaldehyde by octacyanotungstate(V) closely resembles the results obtained for other oxidations of nitroparaffins, ketones and aldehydes [2, 3]. It is assumed that the formaldehyde is almost completely in its hydrated form [4], so that the alkali dependence found here must include a requisite neutralization prior to the rate determining step (2):

$$H_2C(OH)_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO^-(OH) + H_2O \qquad (1)$$

$$H_2CO^-(OH) + W(CN)_8^{3-} \xrightarrow{k_2} W(CN)_8^{4-} + H_2\dot{C}O(OH) \qquad (2)$$

$$\begin{aligned} &H_2\dot{C}O(OH) + W(CN)_8^{3-} \xrightarrow[\text{fast}]{k_3} W(CN)_8^{4-} + HCOOH + H^+ \\ &HCOOH + 2OH^- + H^+ \longrightarrow HCOO^- + 2H_2O. \end{aligned} \qquad (3)$$

If the steady state treatment is applied to the product anion in (1), the nett rate of disappearance of octacyanotungstate(V) is given by

$$\frac{-d[W(CN)_8^{3}]}{dt} = \frac{2Kk_2[H_2C(OH)_2][OH^-][W(CN)_8^{3-}]}{H_2O + \frac{k_2}{k_{-1}}[W(CN)_8^{3-}]}. \qquad (4)$$