Alcoholate derivatives of 3d transition metal chlorides

RAM C MEHROTRA*, K N MAHENDRA and M AGGRAWAL

Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Abstract. A brief account of the work carried out on the title compounds in our laboratories during the last few years is presented in the perspective of existing knowledge on the topic.

1. Introduction

Although alcoholate complexes of transition metal chlorides have been known (Mellor 1931) for more than a century, a few physicochemical studies on these have been carried out only during the last decade or so. In view of these alcoholate complexes being used more and more as catalysts in organic polymerization reactions and as starting materials for the synthesis of metal alkoxides, a brief review of the existing knowledge of their synthesis and physicochemical properties is presented in this article.

2. Synthetic studies

The general method employed for the synthesis of alcoholate complexes of metal chlorides is the addition of alcohols directly to the anhydrous metal chlorides. A modification of the method can be illustrated by the preparation of ethanol adducts of chlorides of nickel(II), manganese(II) and cobalt(II) by passing chlorine gas in a suspension of the powdered metal in ether and alcohol (Osthoff and West 1954). Another modification of the method is to take a suitable adduct like $CrCl_3 \cdot 3THF$ which reacts with alcohols resulting in the formation of adducts much more readily than the anhydrous chloride itself (Mahendra *et al* 1977). The more covalent metal chlorides undergo substitution, instead of simple adduct formation reactions with the formation of chloride alkoxides, which in turn form adducts, *e.g.* $TiCl_2(OC_2H_5)_2 \cdot C_2H_5OH$ (Jennings *et al* 1936). The primary alcohols generally give the most stable adducts, but the stability decreases with the chain length. Tertiary alcohols, on the other hand, give the least stable adducts which even under mild conditions tend to decompose yielding tertiary alkyl chloride and hydrolysed metal chloride. A brief description of the synthesis of alcohol adducts of chlorides of $3d^1$ to $3d^8$ metals is presented in the following paragraphs.

Scandium trichloride resembles lanthanon chlorides (Mehrotra and Batwara 1970) in forming stable tris-alcoholates with primary and secondary alcohols, but with tertiary alcohols unstable lower alcoholates, *e.g.* $ScCl_3 \cdot 1 \cdot 5Bu^tOH$ is obtained
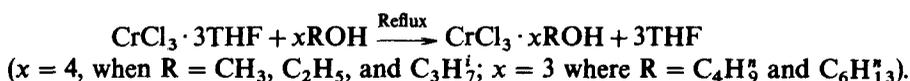
---

* To whom all correspondence should be addressed.

$ScCl_3 \cdot 3Pr^iOH$ has been shown (Mehrotra 1972) to serve as a very suitable material for the preparation of $Sc(OPr^i)_3$ by the reaction:

$$ScCl_3 \cdot 3Pr^iOH + 3NaOPr^i \xrightarrow[C_6H_6 + Pr^iOH]{} Sc(OPr^i)_3 + 3NaCl\downarrow + 3Pr^iOH$$
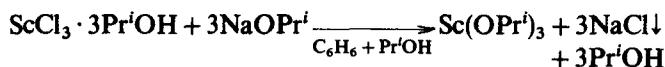
Titanium(III) chloride reacts with alcohols to give products of the type $TiCl_3 \cdot 4ROH$ (where $R = CH_3$, C_2H_5, $C_3H_7{}^i$, $C_4H_9{}^s$ etc.) (Gibbenbach and Brubeker 1968; Schlafer and Gotz 1964). Titanium tetrachloride reacts with ethanol or isopropanol to give products of the type $TiCl_2(OR)_2 \cdot ROH$ (where $R = Et$, Pr^i) (Jennings *et al* 1936). The reaction of $TiCl_4$ with Bu^nOH in the presence of sunlight yields (Hunt and Winter 1970) $TiCl_3 \cdot 3Bu^nOH$.

Vanadium trichloride reacts with lower alcohols (Bradley and Mehta 1962; Casey and Clark 1969) like methanol and isopropanol to give products of the type $VCl_3 \cdot 4ROH$, whereas ethanol forms 1:3 complex as $VCl_3 \cdot 3EtOH$. Vanadium tetra-chloride on the other hand (Bradley *et al* 1958) reacts with alcohols in cold benzene forming the dichloride dialkoxide alcoholates $VCl_2(OR)_2 \cdot ROH$ (where $R = Me$, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s and Am^n). Under more vigorous conditions especially with tertiary alcohols, hydrolytic side reactions occur.

The preparation of $CrCl_3 \cdot xROH$ ($x = 3$ or 4) was reported by Kandelaki (1937) and it was claimed that the adduct $CrCl_3 \cdot 4ROH \cdot R_2AlCl$ is in many cases better Zeigler-Natta catalyst (Michio *et al* 1969) than the conventional $TiCl_4 \cdot R_3Al$. In a recent study (Mahendra *et al* 1977) the purple-coloured adduct of chromium chloride with tetrahydrofuran, $CrCl_3 \cdot 3THF$ (prepared by refluxing $CrCl_3 \cdot 6H_2O$ in THF in the presence of thionyl chloride) has been found as a much more convenient starting material for the preparation of alcoholates as it is soluble in alcohols whereas anhydrous $CrCl_3$ is insoluble. Solvolytic reactions of $CrCl_3 \cdot 3THF$ in excess of alcohols under strictly anhydrous conditions lead to the formation of complexes of the type $CrCl_3 \cdot xROH$, the reactions may be depicted as follows:

$$CrCl_3 \cdot 3THF + xROH \xrightarrow{\text{Reflux}} CrCl_3 \cdot xROH + 3THF$$

($x = 4$, when $R = CH_3$, C_2H_5, and $C_3H_7^i$; $x = 3$ where $R = C_4H_9^n$ and $C_6H_{13}^n$).

As the alcoholates formed in solutions could not be crystallized, these were isolated by distilling out the excess solvent (parent alcohol), followed by drying the product under reduced pressure at a suitable temperature depending upon the boiling point of alcohol. The apparent difference in the number (4 and 3) of molecules of added alcohol for the alcoholates mentioned above may, therefore, be due to the higher temperatures employed for removal of excess alcohols in the latter alcoholates. With tertiary alcohols, hydrolytic side reactions occur in the case of $CrCl_3 \cdot 3THF$ also as reported in the case of vanadium tetrachloride.

Alcoholate derivatives with anhydrous manganese chloride have been reported with the composition $MnCl_2 \cdot xROH$ (where $x = 1-2$; $R = Me$, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, Am^n, Am^i and Hex^n) (Mehrotra and Aggrawal 1984). It was further observed that primary alcohol adducts were highly soluble in parent alcohols while solubility of adducts was lesser in secondary and much lesser in tertiary alcohols. No hydrolytic reactions could be discerned in these derivatives.

A number of alcoholates of ferric chloride have been prepared by reacting methyl,

propyl^n, propyl^i, butyl^n, butyl^i and pentyl^n alcohol with ferric chloride (Multani 1956). These can be represented by the general formula, $FeCl_3 \cdot 2ROH$, where $R = Me$, Pr^n, Pr^i, Bu^n, Bu^i and pentyl^n groups. The higher alcoholates were also prepared from diethyl and diisopropyl alcohols by alcohol interchange method. Anhydrous ferrous chloride reacts with methyl, ethyl, propyl^n, and propyl^i alcohols to give compounds which also conform to the general formula, $FeCl_2 \cdot 2ROH$ (Jain and Multani 1966). The higher alcoholates could not be prepared by alcohol interchange methods as the complexes got oxidized to the ferric state (Bradley *et al* 1958).

A *bis*-ethanol adduct, $CoCl_2 \cdot 2C_2H_5OH$ was reported by Lloyd *et al* (1928) on the basis of chloride analysis. In a recent study (Singh *et al* 1980), crystalline adducts with the general formula, $CoCl_2 \cdot xROH$ have been isolated either by crystallisation or by distilling off the solvents from the clear solutions obtained by dissolving anhydrous $CoCl_2$ in different alcohols:

$$CoCl_2 + xROH \xrightarrow{\text{Reflux}} CoCl_2 \cdot xROH$$
$$\text{(excess)}$$
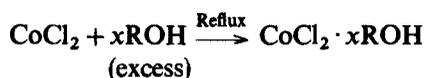
(where $R = Me$, Et, Pr^i, Bu^n, Bu^s, Bu^i; $x = 2$; and $R = Bu^t$, $x = 1$). The methanolate, ethanolate and isopropanolate adducts of $CoCl_2$ could be crystallized and were, therefore, obtained by drying the crystalline products under reduced pressure. These alcoholate derivatives are blue (except methanolate which is light pink) coloured solids. These are insoluble in common organic solvents other than in alcohols. The ethanolate adduct has also been isolated by the reaction of hydrated $CoCl_2$ with ethanol in benzene medium, removing the water azeotropically:
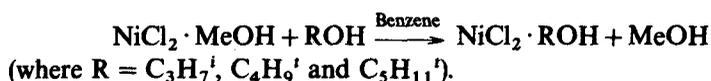
$$CoCl_2 \cdot 6H_2O + 2EtOH \xrightarrow[\text{Reflux}]{\text{Benzene}} CoCl_2 \cdot 2EtOH + 6H_2O.$$
$$\text{(excess)}$$

A number of ethanolate complexes of nickel chloride, $NiCl_2 \cdot xC_2H_5OH$ (where $x \leqslant 4$) were described by Ward (1972) at different temperatures. The *bis*-ethanol compound described by Osthoff and West (1954) could not be isolated by Ward, but he has reported thermogravimetric evidence of its existence. In a recent detailed study (Baranwal and Mehrotra 1978), a number of alcoholates of nickel chloride with different primary alcohols have been described:

$$NiCl_2 + xROH \xrightarrow{\text{Reflux}} NiCl_2 \cdot xROH$$
$$\text{(excess)}$$
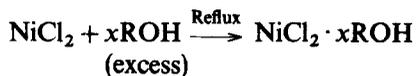
(where $R = CH_3$, C_2H_5, $C_3H_7^n$, $C_4H_9^n$, $C_6H_{13}^n$ and $C_8H_{17}^n$ and $x = 1$–4).

Anhydrous nickel chloride dissolves in primary alcohols on refluxing and from the clear green solutions thus obtained greenish yellow adducts with the formula $NiCl_2 \cdot xROH$ ($x = 2$–4) have been isolated by removal of the solvent. On drying the products further under reduced pressure (2·5 mm) at a temperature (32 to 120°C) corresponding to the boiling point of alcohol (CH_3OH to $C_8H_{17}^nOH$), yellow products corresponding in composition to $NiCl_2 \cdot ROH$ are obtained. Anhydrous nickel chloride, however, does not appear to dissolve in or react with secondary and tertiary alcohols and appears to remain unaffected when refluxed with these. Adducts with such alcohols could, however, be prepared by alcohol interchange technique which can be depicted as follows:

$$NiCl_2 \cdot MeOH + ROH \xrightarrow{\text{Benzene}} NiCl_2 \cdot ROH + MeOH$$
(where $R = C_3H_7^i$, $C_4H_9^t$ and $C_5H_{11}^t$).

The liberated methanol could be azeotropped out with benzene and the products dried under reduced pressure. These adducts are also yellow-coloured compounds but in contrast to the adducts with primary alcohols, these are insoluble in parent alcohols. This insoluble behaviour may be explained on the basis of lower polarity of secondary and tertiary alcohols compared to the primary ones and the steric hindrance to solvation by addition of further alcohol molecules to the secondary and tertiary alcohol adducts. The formation of higher alcohol adducts of the type, $NiCl_2 \cdot xROH$ (where $x > 1$) and (R = primary alkyl group) is confirmed by the exothermic reaction with change in colour from yellow to green on dissolution of mono-alcohol adducts in the primary alcohols.

3. Physicochemical studies

3.1 *Infrared spectra*

Infrared spectra of all the alcoholate complexes are almost similar. A broad and strong absorption band observed at $\sim 3080 \text{ cm}^{-1}$ in all the metal chloride complexes is assigned to ν_{OH}. In pure alcohols, this band appears at $\sim 3300 \text{ cm}^{-1}$ and the lowering can be explained to arise from the coordination of the alcohol molecule to the central metal atom (Nakamoto 1970).

3.2 *Electronic spectra*

In the case of vanadium(III) (Casey and Clark 1969), the two accessible spin-allowed *d-d* transitions for an octahedrally coordinated d^2 species are assigned as $^3T_{1g} \rightarrow {}^3T_{2g}$ (F) at lower energy (ν_1) and $^3T_{1g}$ $(F) \rightarrow {}^3T_{1g}$ (P) at higher energy (ν_2). For the chloride alcoholates of vanadium(III), ν_1 occurs in the range 14000 to 14900 cm^{-1} with a shoulder on the low frequency side. The shoulder arises from the resolution of the $^3T_{2g}$ term by low symmetry components; these are undoubtedly present, owing to the non-equivalence of the six ligands attached to the metal atom. The second band, ν_2 occurs in the range 21050–22050 cm^{-1}. The methanol complex gives rise to the highest values for both ν_1 and ν_2 and there is a general trend for both bands to move progressively to lower energies with higher alcohols. This implies that higher alcohols have slightly lower ligand field strengths than methanol. The band maxima and the extinction coefficients for the methyl, ethyl and isobutyl alcohol solutions agree closely with those originally reported by Hartmann and Schlafer (1951).

The ligand field strengths of the alcohols fall in the order $CH_3OH > C_2H_5OH > C_3H_7^n OH > C_4H_9^n OH > C_3H_7^i OH > C_4H_9^i OH > C_4H_9^s OH$. Steric hindrance of the branched alcohols probably contributes to their lowering ligand field strengths. The lower ligand field strength of the $V(C_3H_7^i OH)_4Br_2^+$ ion compared with the corresponding chloro ion is consistent with the relative positions of bromide and chloride in the spectrochemical series.

The electronic spectra of all the chromium complexes in parent alcohols are identical with their diffuse reflectance spectra and so it is evident that no immediate structural change occurs on dissolution. The spectra are strikingly similar and are in accordance

with an octahedral chromium(III) environment (Dubicki *et al* 1968). The bands around 15000 cm^{-1} (v_1) and 20500 cm^{-1} (v_2) are assigned to the $^4A_{2g} \to ^4T_{2g}$ and $^4A_{2g} \to ^4T_{1g}$ (F) transitions respectively. The first transition $^4A_{2g} \to ^4T_{2g}$ represents 10 Dq for a d^3 system in an octahedral field. The observed transitions show that the ligand field value increases as the polarity of the alcoholic group increases (in the case of primary alcohols). The interelectronic repulsion parameters in all cases are much lower than that (1030 cm^{-1}) observed for the free ion showing considerable covalent nature of the metal ligand bond in these alcoholate derivatives.

The spectra of alcoholates of manganese chloride have been recorded in concentrated solutions (Mehrotra and Aggrawal 1984) but extremely weak transitions are observed in these cases. Only a single transition ($\sim$ 29600 cm^{-1}) could be observed in case of tertiary butanol derivative while other derivatives exhibited comparatively stronger absorptions in the visible region (19000–32900 cm^{-1}). These values are indicative of tectahedral geometry in all these cases with the exception of methoxy derivative which exhibited spectra nearer to an octahedral geometry (Figgis 1976).

The spectrum of $CoCl_2 \cdot 2MeOH$ shows two well-defined bands with maxima at 18590 and 14790 cm^{-1}. The third band at 7550 cm^{-1} is observed for this compound in the near-infrared region. These bands are characteristic for Co(II) in octahedral environment of this compound and can be assigned to the following transitions:

$$7550 \text{ cm}^{-1}; \, ^4T_{1g} \to ^4T_{2g} \, (v_1),$$
$$14790 \text{ cm}^{-1}; \, ^4T_{1g} \to ^4A_{2g} \, (v_2),$$
$$18590 \text{ cm}^{-1}; \, ^4T_{1g} \to ^4T_{1g} \, (P) \, (v_3).$$

The visible spectrum of this compound is also similar to the spectra (Figgis 1976) of $Co(H_2O)_6^{2+}$ and $Co(OMe)_2$ in which also Co^{2+} ions are present in octahedral environment. With the help of these three transitions, the values of spectroscopic parameters, *e.g.* 10 Dq; interelectronic repulsion parameter (*B*) and covalency factor (*B*) have been calculated as 7600 cm^{-1}, 845 cm^{-1} and 0·87 respectively.

However, the visible spectra of all other alcoholate derivatives, $CoCl_2 \cdot xROH$ (where $x = 2$, R = Et, Pr^i, Bu^n, Bu^s, and Bu^i; when $x = 1$, R = Bu^t) when recorded in parent alcohols gave a band towards higher energy side in the range 14850 ± 150 cm^{-1}. The near-infrared bands for all these derivatives have been observed in the range 6325 ± 125 cm^{-1}. These transitions are characteristic for Co(II) in tetrahedral environment (Lever 1968) and can be assigned transitions as $(v_3)^4A_2 \to ^4T_1$ (P) and $v_2 \, ^4A_2 \to ^4T_1$ (F) respectively. The intense blue colour of these derivatives also supports the above view that Co^{+2} ions are also present in tetrahedral geometry in these compounds. It has been observed that the values of *B* calculated from the observed spectra for all the alcoholate derivatives of $CoCl_2$ are lower than the free ion value (1120 cm^{-1}) for Co^{2+} in $CoCl_2 \cdot 6H_2O$, indicating a higher covalent nature of the alcoholates.

The spectra of the monoalcoholate adducts of nickel exhibit three bands around 7000–8000 cm^{-1} (v_1); 12000–14000 cm^{-1} (v_2) and 21000–24000 cm^{-1} (v_3) which indicate a pseudooctahedral geometry for the complexes (Goodgame *et al* 1964; Lever *et al* 1965; Baranwal and Mehrotra 1978). The spectral behaviour of the complexes in solid phase is almost identical with that in solution. This indicates that there is no change in geometry when the complexes are taken in solution and they retain their geometry in solid state also. Various spectroscopic parameters like ligand field splitting energy (10 Dq), interelectronic repulsion parameter (*B*) and β have also been calculated

from these transitions. The 10 Dq values show that the strength of the ligand field decreases with higher alcohols, which is in agreement with the trend expected from the variation in the polarity of alcohols. The B values in all these alcoholate derivatives are below the free ion value (1040 cm^{-1}) for $NiCl_2 \cdot 6H_2O$ showing considerable covalent nature of the metal-ligand bond.

The most interesting spectral feature of these complexes is the triplet structure of the $^3A_{2g} \rightarrow \, ^3T_{1g}$ (F) band. The excited state concerned corresponds to the configuration $(t_{2g})^4 \rightarrow (e_g)^4$. The triplet structure, therefore, shows non-equivalence of $3d$ orbitals (d_{xy}, d_{yz}, d_{zx}). A rhombic symmetry of the ligand field with μ_x, μ_y and μ_z may be inferred, where μ_x, μ_y and μ_z represent the sum of the charges on the x, y and z axis respectively.

3.3 Conductivity measurements

The equivalent conductances of vanadium trichloride in various alcohols was measured (Casey and Clark 1969) at three concentrations in each case and compared with that of triethylammonium chloride in the same alcohol at comparable concentrations. Treatment of the conductivity results by the method outlined by Feltham and Hayter (1964) leads to the conclusion that the vanadium species in solution are 1:1 electrolytes.

Conductivity measurements (Mahendra et al 1977) of alcoholate complexes of $CrCl_3$ reveal them to be weak electrolytes in parent alcohols (Dubicki et al 1968).

The molar conductance ($\lambda_m = 170\cdot9$ ohm^{-1} cm^2 mol^{-1}) of $CoCl_2 \cdot 2MeOH$ solution in methanol (Singh et al 1980) indicates that it behaves as 1:2 electrolyte (Khan 1975) which may be represented by the formula: $[Co(MeOH)_6]^{2+} \cdot 2Cl^-$. The ethanolate derivative $CoCl_2 \cdot 2EtOH$ in ethanol solution appears to behave as 1:1 electrolyte ($\lambda_m = 47\cdot8$ ohm^{-1} cm^2 mol^{-1}) whereas the isopropanolate derivative in isopropanol appears to be weak electrolyte ($\lambda_m = 1\cdot3$ ohm^{-1} cm^2 mol^{-1}). The other alcoholate derivatives behave as non-electrolytes in parent alcohols, which may be partly due to decreasing value of dielectric constants of the solvents.

The molar conductivities of nickel chloride methanolate and ethanolate derivatives in methanol and ethanol have been found to be 145 and 122 ohm^{-1} cm^2 mol^{-1} respectively (Baranwal and Mehrotra 1978). These values correspond to the values expected for 1:2 electrolytes (Hussain and Rehman 1978) in these solvents and hence, the species in solution appears to be $[Ni(ROH)_x]^{2+} \cdot 2Cl^-$. In view of the prominent tendency of nickel to show coordination state six, the value of x in the above moieties may also be six.

3.4 Thermogravimetric studies

In the case of vanadium(IV) chloride it has been observed that on heating the dichloride diethoxide alcoholates at 158°/0·1 mm, it formed vanadium oxychloride alkoxides $V_2OCl_3(OR)_3$ (Bradley et al 1958) whereas in the case of vanadium(III) chlorides, a 1:4 complex of the type $VCl_3 \cdot 4ROH$ (R = CH_3, $C_3H_7^i$) and a 1:3 complex of the type $VCl_3 \cdot 3ROH$ (R = Et) are formed (Casey and Clark 1969).

In the case of chromium as already mentioned (Mahendra et al 1977), the apparent difference in the number (4 and 3) of molecules of adduct alcohol in the two groups of alcoholates may be due to the higher temperatures employed for removal of excess alcohols in the latter cases. In order to test this hypothesis, a thermogravimetric study of

tetramethanolate and tetraethanolate which are obtained by drying at room temperature has been carried out.

It has been observed that tetraethanolate $CrCl_3 \cdot 4EtOH$ loses one molecule of ethanol at $\sim 65°C$ forming an adduct corresponding in composition to $CrCl_3 \cdot 3EtOH$; the second and third molecules of added ethanol appear to be lost at $\sim 100°C$ and 140°C respectively. After 140°C an extensive intramolecular reaction appears to take place, resulting finally in a compound with the composition $Cr(OEt)Cl_2$ at about 200°C. An almost similar pattern of initial loss of adduct molecules followed by decomposition has been found with tetramethanolate, with the only difference that the tetramethanolate appears to be more stable to heat and the temperature required to remove the first mole of methanol is $\sim 120°C$. When the alcoholate complexes (methanolate and ethanolate) are heated at $\sim 200°C$ under atmospheric pressure for 1 hr, they appear to give a hydroxy- or oxy-product with the liberation of HCl gas which was estimated. The alcoholate complexes of ferrous chloride (Jain and Multani 1966) behave almost similar to chromium complexes (Mahendra *et al* 1977).

The thermogravimetric studies in case of manganese derivatives indicated that the products lose total alcohol molecules at about 300°C. It was observed that removal of alcohol molecules occurs at a temperature about 40–80°C higher than their respective boiling points indicating that alcohol molecules get linked someway with the metal ion (Mehrotra and Aggrawal 1984) *e.g.* in the case of $MnCl_2 \cdot 2MeOH$, the first methanol molecule was lost between 120 and 180°C while the second one is lost between 220 and 280°C after which the residue of manganese chloride only remained. Similar observations have been made in other derivatives also. These results are consistent with the studies made in the case of $MnCl_2 \cdot 2EtOH$ adduct (Osthoff and West 1954).

The diethyl alcoholate of ferrous chloride, $FeCl_2 \cdot 2EtOH$, when heated to 120°C loses a molecule of ethanol and the resulting compound on analysis was found to be ferrous chloride mono-alcoholate, $FeCl_2 \cdot EtOH$. When heating is continued to 200°C, ferrous hydroxy chloride is formed according to the following equation:

$$FeCl_2 \cdot 2EtOH \xrightarrow[-EtOH]{120°C} FeCl_2 \cdot EtOH \xrightarrow[-EtCl]{200°C} Fe(OH)Cl.$$
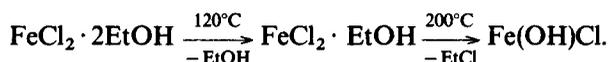
Nickel chloride tetramethanolate could be obtained (Baranwal and Mehrotra 1978) after drying the solution of $NiCl_2$ in methanol in the range 0–10°C at 20 mm pressure. It lost one molecule of methanol at 20°C/2·5 mm, giving adduct of the formula $NiCl_2 \cdot 3MeOH$. The second and third molecules of added methanol appear to be lost at $\sim 30°C$ and 45°C (2·5 mm) respectively. The mono adduct $NiCl_2MeOH$ appears to be stable upto 70°C (2·5 mm). Further loss of methanol is slow and only 0·5 molecule of methanol appears to be lost in heating the mono-alcoholate to 140–150°C (2·5 mm). Even a higher temperature ($\sim 250°C$) is required to remove the remaining methanol from the adduct. An almost similar pattern of loss of adduct molecules has been found with nickel chloride tetraethanolate (Baranwal and Mehrotra 1978).

3.5 *Magnetic moments*

The magnetic moments of the solid alcoholate complexes of vanadium(III) chloride have been measured over the range ~ 300 to $\sim 80°K$ (Casey and Clark 1969). In all cases, the magnetic moments fall with decreasing temperature in agreement with the behaviour expected for $^3T_{1g}$ ground terms. The variation with temperature is less than

that predicted for an octahedrally coordinated d^2 ion and can be explained by the presence of axial distortions in the cubic field.

Magnetic moments of alcoholate complexes of chromium at room temperature in parent alcohols lie in the range typical for chromium(III), in an octahedral environment, with the observed values of magnetic moment close to the spin only value of 3·88 BM (Mahendra *et al* 1977).

Magnetic measurements on manganese derivatives indicated moments from 5·62 to 6·09 BM, which are indicative of spin free outersphere complex formation (Carlin and Duyneveldt 1977).

Experimental values reported (Figgis and Lewis 1964) for cobalt(II) derivatives in octahedral and tetrahedral geometries lie in the ranges of 4·7–5·2 and 4·4–4·7 BM respectively. Among the alcoholate derivatives studied during the present investigations (Singh *et al* 1980), only the methanolate adduct derivative shows a magnetic moment value of 4·85 BM, which corresponds to the range typical for octahedral geometry. Magnetic moments of other alcoholate derivatives lie in the range of 4·60 ± 0·08 BM which are suggestive of Co^{2+} ions in tetrahedral environment for these derivatives. Thus these magnetic studies also support the spectral interpretations of the alcoholate derivatives of $CoCl_2$.

The magnetic moment values of nickel complexes at room temperature have been found to lie in the range 3·08–3·23 BM indicating octahedral geometry for nickel(II) (Baranwal and Mehrotra 1978). Calculations of spin-orbit coupling constants (λ) gave values in the range 155–275 cm^{-1} which are considerably lower than the free ion value of $\lambda = -324$ cm^{-1}, indicating covalent character of the metal ligand bond in these complexes.

3.6   ESR spectra

ESR spectra of only a few alcoholate complexes of transition metal halides like chromium(III), manganese(II) and nickel(II) have been carried out recently.

A chromium(III) complex of perfect octahedral symmetry is expected to show ESR signals centred around g value (Lande splitting factor) less than the free electron value (2·0023), the lowering being related to the covalent character of the metal ligand bond (Goodman and Raymor 1970). ^{53}Cr hyperfine structure and donor atom superfine splitting may also be observed. At room temperature, all the alcoholate derivatives in polycrystalline state give one signal in their spectra enabling a precise evaluation of g values. The data show that g values decrease from ethanolate to isopropanolate to normal butanolate, with the methanolate showing exceptionally low values. These values are all below the free electron values as expected. Assuming a similarity in the nature of Cr–Cl bond in all the complexes under discussion, the above data indicate a higher covalent character of the metal-ligand bond. The spectra in alcoholic solutions are generally much better defined and are almost similar to the spectra recorded for polycrystalline forms.

The manganese derivatives gave values of g ranging from 1·997 to 2·003 indicating a symmetrical structure around metal ion during their studies in the polycrystalline solid state at room temperature (Carlin and Duyneveldt 1977) and support the earlier discussed proposed structures.

In the case of nickel, room temperature ESR spectra of all these derivatives in the polycrystalline form show one signal from which the values of Lande splitting factor g

have been calculated (Baranwal and Mehrotra 1978). The g values lie in the range 2·03–2·44 which is expected for a nickel atom in an octahedral field.

References

Baranwal B P and Mehrotra R C 1978 *Z. Anorg. Allg. Chem.* **443** 284
Bradley D C and Mehta M L 1962 *Can. J. Chem.* **40** 1710
Bradley D C, Multani R K and Wardlow W 1958 *J. Chem. Soc.* 4647
Carlin R L and Duyneveldt A J 1977 *Magnetic properties of transition metal compounds* (Berlin: Springer-Verlag)
Casey A T and Clark R J H 1969 *Inorg. Chem.* **8** 1216
Dubicki L, Kakos G A and Winter G 1968 *Aust. J. Chem.* **21** 1461
Feltham R D and Hayter R G 1964 *J. Chem. Soc.* 4587
Figgis B N 1976 *Introduction to ligand field* (Delhi: Wiley Eastern.)
Figgis B N and Lewis J 1964 *Prog. Inorg. Chem.* **6** 37
Gibbenbach W G and Brubeker C H 1968 *Inorg. Chem.* **7** 129
Goodgame D M L, Goodgame M and Weeks M J 1964 *J. Chem. Soc.* 5194
Goodman B A and Raymor J B 1970 *Advances in inorganic chemistry and radiochemistry* (New York: Academic Press), Vol. 13, p. 135
Hunt M R and Winter G 1970 *Inorg. Nucl. Chem. Lett.* **6** 529
Hussain M S and Rehman S U 1978 *Z. Naturforsch* **33** 67
Hartman H and Schlafer H L 1951 *Z. Naturforsch.* **A6** 754
Jain B D and Multani R K 1966 *Curr. Sci.* **35** 516
Jennings J S, Wardlaw W and Way W J R 1936 *J. Chem. Soc.* 637
Kandelaki B S 1937 *Colloid. J. U.S.S.R.* **3** 483 (1938 *Chem. Abst.* **32** 6227)
Khan M M 1975 *J. Inorg. Nucl. Chem.* **37** 1621
Lever A B P, Nelson S and Shepherd T M 1965 *Inorg. Chem.* **4** 810
Lever A B P 1968 *Inorganic electronic spectroscopy* (Lausanne: Elsevier)
Lloyd J *et al* 1928 *J. Chem. Soc.* 662
Mahendra K N, Bharara P C and Mehrotra R C 1977 *Transition Met. Chem.* **2** 161
Mehrotra A 1972 Ph.D. thesis, Univ. of Rajasthan
Mehrotra R C and Agrawal M 1984 (Under communication)
Mehrotra R C and Batwara J M 1970 *Inorg. Chem.* **9** 2505
Mellor J W 1931 *A comprehensive treatise on inorganic and theoretical chemistry* (London, New York: Longman Green)
Michio *et al* 1969 *Kagyo Kagoku Zassbi* **72** 1724
Multani R K 1956 Ph.D. Thesis Univ. of London, England,
Nakamoto K 1970 *Infrared spectra of inorganic and coordination compounds* (New York: John Wiley)
Osthoff R C and West R C 1954 *J. Am. Chem. Soc.* **76** 4432
Schlafer H L and Gotz R 1964 *Z. Anorg. Allg. Chem.* 3281
Singh J V, Jain N C and Mehrotra R C 1980 *Z. Naturforsch* **356** 1555
Ward G L 1972 *Inorg. Synth.* **13** 143