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HIGHER OXIDATION STATE CHEMISTRY OF IRON, COBALT, AND NICKEL

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CONTENTS

A. INTRODUCTION

The first transition series elements scandium–manganese form compounds in oxidation states up to and including those corresponding to the group number. Their high oxidation state chemistry includes compounds of considerable importance, e.g. CrO_3–Cr^{VI} and

$KMnO_4$ $-Mn^{VII}$. In sharp contrast, the next three elements (Fe, Co, Ni) only rarely from compounds in oxidation state higher than +3 (Fe, Co) or +2 (Ni). For many years high valencies of these three elements were represented by a few poorly characterised compounds[1], and attracted little interest. The rapid growth of coordination chemistry and the recent interest in unusual oxidation states has greatly expanded our knowledge of these compounds. More recently several workers have questioned whether a number of these complexes actually contain a high oxidation state of the metal, or whether they are better described as containing cation-stabilised radical ligands. This review is concerned with the chemistry of iron (IV), – (V), – (VI), cobalt (IV), – (V), nickel (III), – (IV), and certain aspects of cobalt (III) chemistry. Compounds have been included in this review when their formal oxidation state corresponds to one of these. In a number of cases, of which that of dithiolene ligands is probably best known, the assignment of an oxidation state is very difficult[2]; doubtful cases have normally been included *. There is a paucity of thermodynamic data on these high oxidation state compounds, and hence this review is of necessity largely qualitative in approach. It is hoped that a compilation of the known data will lead to further work and rationalisation in this still neglected area.

B. IRON

The formation of a deep purple solution when water was added to the product of fusion of iron and potassium nitrate was noted by Stahl[3] as long ago as 1702. In 1841, Fremy[4] showed that the purple colour was due to potassium ferrate, K_2FeO_4. The first iron (IV) compounds were reported[5] in 1909.

Iron (IV) is best known in oxo compounds, the ferrates (IV). There are also a few halo and hydrido species stabilised by phosphorus and arsenic donor ligands, and a number of dithiolates. Iron (V) and – (VI) are restricted to ferrates (V) and – (VI), the former rare and incompletely characterised. Iron (IV) and to a much less extent iron (V) have been reported in certain biological systems.

(i) Iron (IV)

(a) Oxides and halides

Neither FeF_4 nor the FeF_6^{2-} ion have been prepared. Klemm and Huss[6] found that fluorination of a $KCl/FeCl_3$ mixture produced only the iron (III) complex, K_3FeF_6; no further studies seem to have been reported. A study of the high-pressure fluorination of $2CsCl \cdot FeCl_3$ would be interesting. The lattice energy and ΔH_f^0 of the hypothetical FeF_4 have been calculated using the Kapustinski formula[7].

Thermal decomposition of $FeO(NO_3)$ yields[8] an oxide FeO_2, which has $\mu_{eff} = 4.91$ B.M., close to the "spin-only" value for high-spin d^4 Fe^{IV}. This value may be misleading since the product may not be magnetically dilute. It has been estimated[9] that Fe_2O_3 would not be oxidised to FeO_2 by oxygen at pressure lower than 40 kbar. Impure $MFeO_3$($M = Ba, Sr$)

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* We have not attempted to arrive at any conclusions about the oxidation states or the best descriptions of the bonding in such compounds, indeed much further work is necessary before this can be done; rather, we have concentrated on bringing together the known facts on such compounds.

were originally prepared[5] by heating mixtures of $Fe(NO_3)_3$ and $M(NO_3)_2$. The barium compound prepared[10] at 680–720° by this method had the composition $BaFeO_{2.72}$. Scholder et al. reported two forms of $BaFeO_3$, an amorphous black form obtained by decomposing $BaFeO_4$ with aqueous alkali, and a dark grey crystalline form prepared by thermal decomposition of $BaFeO_4$ in oxygen[11–13]. The formation of these compounds has recently been confirmed by Russian workers[14], who report, however, that the black form has a hexagonal structure, and is not amorphous. Thermal decomposition of strontium and barium oxalato ferrates (III), and fusion of Fe_2O_3 with the metal carbonates in oxygen, leads to compounds containing both Fe^{III} and Fe^{IV}, whose compositions are highly variable[15–25]. Under appropriate conditions compositions from $MFeO_{\sim 2.5}$–$MFeO_{\sim 3.0}$ can be prepared, and the variation in properties and structures with stoichiometry has been examined. These compounds have perovskite structures[12,15,20,23], $BaFeO_3$ being very similar to α-hexagonal $BaTiO_3$. The mixed-metal $Ba(Fe_{\frac{1}{3}}Ti_{\frac{2}{3}})O_3$ has been prepared[26]; $Sr_3Fe_2O_7$, formed by heating Fe_2O_3 and $SrCO_3$ in a 1 : 3 ratio in oxygen, has a related structure, consisting of pairs of perovskite layers separated by a layer of strontium and oxide ions[21,22,27,28]. Mössbauer spectroscopy has been particularly valuable for identifying the presence of iron (IV) in these compounds[19,21–23,28].

The only alkali-metal metaferrate (IV) is Li_2FeO_3, which results from heating K_2FeO_4 with excess LiOH and extracting the excess alkali with alcohol[12]. A $Li_2FeO_3/LiFeO_2$ phase is formed by heating $LiFeO_2$ with Li_2O under pressure in oxygen[29]. Scholder et al.[12] showed that Ag_2FeO_3, and not Ag_2FeO_4 (ref. 30) is formed from $AgNO_3$ and K_2FeO_4.

Strontium and barium orthoferrates (IV), M_2FeO_4 (M = Sr, Ba), are best prepared[11,31] by heating $M_3[Fe(OH)_6]_2$ with $M(OH)_2$ in oxygen at 800–900°C. Both compounds are black powders, decomposed by mineral acids to Fe^{III} and oxygen. Since Ba_2FeO_4 has a similar X-ray powder pattern to that of Ba_2TiO_4, it may contain discrete FeO_4^{4-} ions[31,32]. Black Na_4FeO_4, formed by fusion of Na_2O with Fe_2O_3 in oxygen at 450°, is very hygroscopic, unlike the barium compounds, and disproportionates in dilute aqueous alkali.

$$3\,Na_4FeO_4 + 5\,H_2O \rightarrow Na_2FeO_4 + Fe_2O_3aq + 10\,NaOH$$

The vibrational spectra of Na_4FeO_4 and Ba_2FeO_4 have been reported (Table 1). The only representative of the third type of ferrate (IV) is Ba_3FeO_5, obtained[31] by fusion of $Ba_3[Fe(OH)_6]_2$ and $Ba(OH)_2$ in an Fe : Ba ratio of 1 : 3 at 900°C in oxygen. It is isostructural[34] with Cs_3CoCl_5 with $a = 7.323 \pm 0.004$ Å, $c = 11.752 \pm 0.008$ Å, $c/a = 1.605$. The ionic radius of Fe^{4+} has been estimated[16] as 0.58 Å.

(b) Complexes of iron (IV)

The oxidation of $[Fe(DAS)_2X_2][FeX_4]$ (DAS = *o*-phenylenebisdimethylarsine, X = Cl, Br) with nitric acid, followed by addition of the appropriate anion led to the isolation[36,36] of black *trans*-$[Fe(DAS)_2X_2]Y_2$ (Y = BF_4, ReO_4, ClO_4). The magnetic moments are consistent with a low spin d^4 octahedral configuration with a large tetragonal distortion, and Mössbauer spectra[37] indicate that the ground state is $d_{xy}^2\,d_{xz}d_{yz}$. There is a preliminary report[38] of the ion $[Fe(F\text{-}DAS)_2Cl_2]^{2+}$ {F-DAS = o-$C_6F_4(AsMe_2)_2$}. Aresta et al.[39] prepared yellow $FeH_4(PR_3)_3$ (PR_3 = $PEtPh_2$, $PBuPh_2$) by reaction of $NaBH_4$, PR_3 and $FeCl_2 \cdot 2H_2O$ in ethanol. These complexes reversibly lose hydrogen to form $FeH_2(PR_3)_3$,

TABLE 1

Vibrational spectra of tetraoxoanions (cm^{-1})

Compound	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	Ref.
Ba_2FeO_4	762	257	857	314	33
Na_4FeO_4	796	280	878	338	33
K_3FeO_4	776	265	805	335	33
K_2FeO_4	830	340	796	319	33, 88, 89
Na_2FeO_4				335, 346	74
Rb_2FeO_4	775		~ 805	325, 337	83
$BaFeO_4$	~ 790		814	282	74, 83, 89
$SrFeO_4$			800	280, 314	74
Cs_2FeO_4	771		800	310, 322, 332	83
Ba_2CoO_4	790	300	855	340	33

and are converted to Fe^{III} salts by I_2 or HCl*. On dissolving FeH_2 (dPe)$_2$ (dPe = 1, 2-bisdiphenylphosphinoethane) in perchloric acid, $[FeH_3(dPe)_2]\,ClO_4$ forms, the reaction being reversed by alkalis[40].

Iron (IV) periodato or tellurato complexes are unknown[41,42] although such ligands stabilise Mn^{IV}, Ni^{IV}, and Cu^{III}. Hulliger[43] suggested that FeP_2, $FeAs_2$, and $FeSb_2$ are d^4 systems on the basis of their magnetic properties, in contrast to FeS_2, $FeSe_2$, and $FeTe_2$, which are Fe II compounds.

A number of formally iron (IV) dithiolates are known. There have been several descriptions of the bonding in these compounds[44,45] and consensus of opinion at the present time regards the metal as being in a "normal", rather than a high oxidation state, although the subject is far from closed. The work has been comprehensively reviewed by McCleverty[45]. The dark green tris-MNT (MNT = maleonitriledithiolate dianion) complexes are among the most interesting. The effective magnetic moments of $[EPh_4]_2\,Fe(MNT)_3$ (E = P), μ_{eff} = 2.89 B.M., E = As, μ_{eff} = 3.00 B.M.)[46,47] are consistent with a low-spin d^4 system. Birchall and Greenwood[48] reported Mössbauer data which showed that in the reduction of the formally Fe^{IV}, $[Fe(MNT)_3]^{2-}$, to the $[Fe(MNT)_3]^{3-}$ ion, the added electron entered an orbital which was predominantly metallic in character, i.e. that the metal rather than the ligands was reduced. The $[Fe(MNT)_3]^{2-}$ ion is octahedral[49]. Yandell and Sutin[50] studied the kinetics and equilibria of the reactions of $[Fe(MNT)_3]^{2-}$ with a number of organic bases, which involve formal reduction of the metal. In a recent account of the structure of bis-(*N*, *N*-diethyldithiocarbamato)-*cis*-1, 2-bis(trifluoromethyl) ethylene-1, 2-dithiolate iron, Horrocks and co-workers[51] have discussed the difficulties of relating the measured C–S and C–C bond lengths in dithiolates to the bonding and oxidation state of the metal.

The isolation of iron (IV) complexes of *N*,*N*-disubstituted dithiocarbamates $[Fe(R_2NCS_2)_3]\,BF_4$ (R_2 = Me_2, Et_2, i-Pr_2, Cy_2, $-(CH_2)_4-$) has been achieved by reaction of the tris(dithiocarbamato) iron(III) complexes with BF_3 in benzene solution in the

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* Added in proof: It has been suggested that these compounds are borohydrides and hence not Fe^{IV} compounds. A.T. Hsiek, J.D. Ruddick and G. Wilkinson, *J. Chem. Soc. Dalton*, (1972) 1966.

presence of air[52]. These black complexes have magnetic moments in the range 3.15 – 3.37 B.M., and Mössbauer spectra consistent with the presence of Fe^{IV}. Tris(*N*-methyl-*N*-benzyldithiocarbamato) iron (IV) tetrafluoroborate has also been prepared and its intramolecular rearrangement studied by NMR[52A].

The formation of oxides such as Fe_2O_4 or Fe_2O_5 as intermediates in the reactions of iron salts with H_2O_2 or oxygen was suggested many years ago[53]. More recently[54] the ferryl ion FeO^{2+} has been proposed as an intermediate in the H_2O_2 oxidation of Fe^{II} salts; alternative schemes[55] involve Fe^{II} or Fe^{III} and free radicals species such as $HO_2^{\cdot}$ or $HO^{\cdot}$. Support for the ferryl ion[56] and for FeO_2H^{3+} (refs. 57, 58) have been reported. It should be remembered that the evidence for these species is indirect, their presence being inferred from the results of kinetic or tracer studies.

(c) Iron (IV) in biological systems

Ferrylmyoglobin and the product of H_2O_2 oxidation of horseradish peroxidase were early examples of biological compounds which apparently contain some higher oxidation state of iron[59,60]. The complexity of such systems has led to different interpretations of the experimental data: for example, although it is agreed that one of the oxidation products from horseradish peroxidase contains one oxidising equivalent above Fe^{III}, this has been variously interpreted as due to Fe^{IV} (refs. 59, 61, 62) to Fe^{II} or Fe^{III} complexes of oxidised ligands[63]. Considerable uncertainty still surrounds the site of the oxidising moiety in this substance[64]. A seven-coordinate Fe IV complex has been proposed in an oxidative addition model for O_2 binding to haemoglobin[65]. George[66] has discussed the estimated Fe^{IV}/Fe^{III} redox couples in some oxidase systems.

(ii) Iron (V)

Iron (V) is a very rare oxidation state, the first example K_3FeO_4 being reported[67] as recently as 1953. Impure K_3FeO_4 was obtained[68] by heating KO_x with Fe_2O_3 in a 3 : 1 K : Fe ratio in oxygen at 450°C. The black product had $\mu_{eff} = 3.67$ B.M., a reasonable value for d^3 Fe^V (spin-only value 3.87 B.M.). Scholder et al.[69] showed that a mixture of K_3FeO_4 and Na_3FeO_4 could be obtained by heating K_2FeO_4 with Na_2O at 450–600°C. Pure K_3FeO_4 is best prepared from KO_x and Fe_2O_3 in oxygen at 750–780°C with as short a reaction time as possible[70], and Rb_3FeO_4 is similarly obtained[71] from RbOH and Fe_2O_3. The sodium salt cannot be prepared similarly, but an 80% conversion of Na_3FeO_3 into Na_3FeO_4 occurs[71] on heating in oxygen at 120 atm. Only K_3FeO_4 has been studied in any detail. On heating in oxygen above 700°C, it decomposes into $KFeO_2$, whilst at 300–500°C it slowly changes[68,71] into $KFeO_2$ and KO_x. Disproportionation occurs in dilute alkali

$$6\,K_3FeO_4 + 5\,H_2O \rightarrow 4\,K_2FeO_4 + Fe_2O_3aq + 10\,KOH$$

producing Fe^{VI} and Fe^{III} in the expected 2 : 1 ratio[68]. In cold, very concentrated alkali disproportionation does not occur[70]. X-ray studies are said to show the presence of a tetrahedral FeO_4^{3-} ion[72]. The vibrational spectrum of K_3FeO_4 has been reported, but the electronic spectrum has not been studied. This is unfortunate since the FeO_4^{3-} ion is the only example of a $3d^3$ tetraoxoanion.

Kremer[57] has suggested that the FeO^{3+} ion is produced in the Fe^{3+}-catalysed decomposition of H_2O_2. Iron (V) has been suggested to occur in certain biological systems, and as with iron (IV) the data are open to various interpretations. Thus, the green oxidation product of horseradish peroxidase[59] has two oxidising equivalents above Fe^{III}, and its magnetic properties are not inconsistent[73] with the presence of Fe^{V}. However, the Mössbauer spectrum suggests that the oxidising power is associated with some part of the ligand, and is not localised on the iron[62]. (See also refs. 63, 64, 66 and references therein.)

(iii) Iron (VI)

The chemistry of Fe^{VI} is confined to the ferrates (VI). It is possible that oxide halides could be prepared, and the reactions of K_2FeO_4 with HSO_3X(X = F, Cl) and HF may be worth examination (cf. Mn, Cr). There are essentially three routes to ferrates (VI): electrolysis of a concentrated alkali solution with an iron anode[74−77], oxidation of iron (III) oxide in an alkaline melt[1], and oxidation of iron (III) in concentrated aqueous alkali[30,69,73−83]. K_2FeO_4 is best prepared[69,80,83] by oxidation of $Fe_2O_3\cdot aq$, $FeCl_3$, or $Fe(NO_3)_3$ in concentrated aqueous KOH with KClO or KBrO. Audette and Quail[83] have described the preparation of very pure (>99.5%) K, Rb and Cs salts. Cs_2FeO_4 can also be prepared[84] from Fe_2O_3 and CsO_2 in oxygen at 280°C, a reaction which apparently yields ferrates (V) with K or Rb. Metathesis in the complete absence of CO_2 yields the slightly soluble Sr and Ba salts[69,78,83,85,86]. The very soluble sodium salt has been obtained only in an impure condition by metathesis of $NaClO_4$ and K_2FeO_4 in aqueous solution, or by electrolysis[75−77]. A number of other metal ferrates (VI) have been described[1,30] but confirmation is lacking. The alkali-metal ferrates (VI) have the orthorhombic β-K_2SO_4 structure[78,83,87], although accurate dimensions of the FeO_4^{2-} ion are lacking. The effective magnetic moments are consistent with the d^2 configuration: K_2FeO_4(3.01 B.M.), Rb_2FeO_4(2.92 B.M.), Cs_2FeO_4(2.88 B.M.), $BaFeO_4$(3.15 B.M.)[83], the variation in values reported by different workers[79,84,86] being due to contamination of the samples with iron (III). The vibrational (Table 1), EPR[90,91] and Mossbauer[86,92,93] spectra have been reported. The electronic spectrum of the FeO_4^{2-} ion (Fig. 1) has been variously assigned (Table 2)[94−99].

The values of the FeO_4^{2-}/Fe^{III} redox couples in acid and alkaline solution, according to Wood[100], are respectively

$$Fe^{3+} + 4\,H_2O \rightarrow FeO_4^{2-} + 8\,H^+ + 3\,e^- \qquad E^0 = -2.2\ V$$

$$Fe(OH)_3 + 5\,OH^- \rightarrow FeO_4^{2-} + 4\,H_2O + 3\,e^- \quad E^0 = -0.72\ V$$

Latimer[101] gives the slightly different values − 1.9 V and − 0.9 V, respectively. Wood[100] also obtained ΔH_f^0 of the ferrate (VI) ion as − 115 ± 1 kcal.mole^{-1} from a study of the reaction of K_2FeO_4 with $HClO_4$ at 25°C.

On heating, K_2FeO_4 decomposes[69] into K_3FeO_4, $KFeO_2$ and oxygen, whilst $BaFeO_4$ affords $BaFeO_3$. The decomposition of the K, Ba, and Sr salts has been studied by differential thermal analysis[74]. In solution the ferrate (VI) ion decomposes[102−108]. The ferrate (VI) ion is a strong oxidising agent, although its chemistry has been little studied; only those reactions of analytical interest have been discussed in detail. Thus it oxidises arsenite[109], Cr^{III} (ref. 110), IO_3^- (ref. 111), SO_3^{2-} (ref. 108), H_2O_2 (ref. 108), I^- (ref. 78), NH_4^+ (ref. 78) and alcohols[82,112,113].

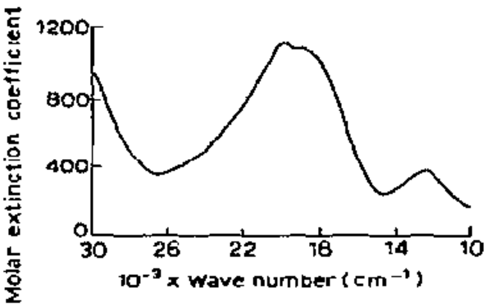


Fig. 1. Absorption spectrum of the aqueous ferrate ion, FeO_4^{2-}. (Reproduced by kind permission of The Chemical Society.)

Oxidation states higher than 6 are unknown. Russian workers[114,115] have performed some calculations on the hypothetical FeO_4. Ferrates (VIII), e.g. K_2FeO_5, were reported by Goralevitch[116] many years ago, but the claim has not been confirmed. More recently "perferrates" have appeared in accounts of the chemistry of certain steel production processes, e.g. ref. 117, but no evidence to substantiate such claims is given in the reports.

C. COBALT

The coordination chemistry of cobalt (III) is extensive, and only certain selected aspects are included here. Table 3 contains a list of previous reviews on aspects of cobalt (III) chemistry. The present paper is limited to simple cobalt (III) compounds and to coordination complexes of those ligands which stabilize nickel (III) or cobalt (IV), with the object of providing data for comparative purposes and to facilitate continuity.

Cobalt (IV) is a rare oxidation state being limited to fluoro and oxo complexes. Cobalt (V) has been reported only in cobaltates (V).

TABLE 2

Spectral assignments of the ferrate (VI) ion

Band maxima (kK)	Carrington et al.[96]*	Carrington–Symons[97]	Viste–Gray[95]	Carrington–Jørgensen[98]	De Michelis et al.[99]
12.72	$3t_2 \rightarrow 2a_1$	$t_1 \rightarrow 2_e\,(^3T_1)$	$2e \rightarrow 3t_2\,(^3T_2)$	$2e \rightarrow 3t_2$	$3T_1\,(2e \rightarrow 3t_2)$
17.80 (sh)	$t_1 \rightarrow 3t_2$				$3T_1\,(t_1 \rightarrow 2e)$
19.60	$3t_2 \rightarrow 2e$	$t_1 \rightarrow 3t_2\,(^3T_1)$	$2e \rightarrow 3t_2\,(^3T_1)$	$t_1 \rightarrow 2e$(?)	$\begin{bmatrix} 3T_1\,(t_1 \rightarrow 3t_2) \\ 3T_1\,(2t_2 \rightarrow 2e) \end{bmatrix}$
~44.3	$2t_2 \rightarrow 3t_2$				$3T_1\,(2t_2 \rightarrow 3t_2)$

* Assignment not consistent with EPR data.

(i) Cobalt (III)

(a) Halides and oxides

Brown cobalt (III) fluoride is formed[118–121] by fluorination of CoF_2 or $CoCl_2$ at 200–300°C, of cobalt oxides[122] at 150°–300°, or from $CoCl_2$ and ClF_3 (ref. 123) or BrF_3 (ref. 124). Ruff and Ascher[118] reported its reaction with a number of metals, non-metals, and simple compounds. The same workers reported that CoF_3 decomposed to CoF_2 on heating[118], but more recent work[125,126] has shown that CoF_3 is thermally stable and that the CoF_2 is formed by hydrolysis. The structure is rhombohedral[119,127], $a = 5.279$ Å, $\alpha = 56.97°$, consisting of CoF_6 octahedra with Co–F = 1.89 Å. Slightly different values for the magnetic moment have been reported – $\mu_{\mathrm{eff}} = 2.46$ B.M. (ref. 128) or 2.1 B.M. (ref. 129). The use of CoF_3 in the fluorination of organic compounds has been reviewed by Stacey and Tatlow[130].

$CoF_3 \cdot 3.5H_2O$ is formed as a green powder by electrolytic oxidation of Co^{II} in 40% aqueous hydrofluoric acid[131,132]. Its structure has not been determined but from a study of its magnetic susceptibility versus temperature ($\mu = 4.47$ B.M., $\theta = 60°$), Clark et al.[133] concluded it was probably $[CoF_3(H_2O)_3]\ 0.5H_2O$ and not $[Co(H_2O)_6]\ [CoF_6] \cdot H_2O$. A compound $CoF_3 \cdot 3H_2O$, isomorphous with α-$AlF_3 \cdot 3H_2O$, has been reported[134].

An unstable dark green $CoCl_3$ was reported many years ago[135,136] but has not been substantiated by further work. A thermodynamic rationalisation of the instability of CoX_3 (X = Cl, Br, I) has been given by Nelson and Sharpe[137].

K_3CoF_6 was reported[138] to be formed by addition of KF to the solution produced on electrolytic oxidation of Co^{II} in 40% HF; attempts to repeat this work or to extend it to the preparation of the (unknown) $(NH_4)_3CoF_6$ have failed[132,140]. Blue hexafluorocobaltates (III), M_3CoF_6, are formed by fluorination of $3MCl \cdot CoCl_2$ or, preferably, $M_3Co(CN)_6$ (M = Li, Na, K, Rb, Cs)[6,139–141]. K_2NaCoF_6 and $Ba_3\ [CoF_6]_2$ were also prepared[141] but fluorination of $LaCo(CN)_6$ produced only a mixture of LaF_3 and CoF_3, presumably due to the unfavourable lattice energy of "$LaCoF_6$". Klemm et al.[140] reported the M_3CoF_6 compounds as cubic (Table 4), but Meyers and Cotton[141] have shown that only K_2NaCoF_6 is rigorously cubic, the others being distorted to varying degrees. Na_3CoF_6 has recently been reinvestigated and found to be monoclinic with a cryolite structure[142]. As expected, these compounds are decomposed by water, and form Co^{II} salts with mineral acids[140]. The systems MF_2–CoF_3 (M = Ca, Sr, Ba) have been investigated[143] and the very hygroscopic $MCoF_5$, $M_3\ [CoF_6]_2$, and $Sr_5Co_3F_{19}$ isolated. When $[Co(NH_3)_6]\ F_3$ is gently heated, $[Co(NH_3)_6]\ [CoF_6] \cdot H_2O$ is formed[151].

The Co–F stretching frequency[141,146] is in the range 475–510 cm^{-1}. The electronic spectrum[145,147,148] of the CoF_6^{3-} ion is of interest as the only example of high-spin octahedral Co^{III} known ($t_{2g}^4e_g^2$); some molecular orbital calculations have also been published[149,150].

Alkali-metal tetrafluorocobaltates (III) $MCoF_4$ (M = Li, Na, K, Rb, Cs) have only recently been described[152], although the fluorination of organic compounds by the fluorination product of $KCoF_3$ (tentatively identified as $KCoF_4$) had been reported some years ago[153]. The $MCoF_4$ compounds are produced by fluorination of $MCoF_3$ (M = Na, K) or $MCoCl_3$ (M = Li, Rb, Cs); they have magnetic moments[152] of about 3.5 B.M. There is an unconfirmed report of the $CoCl_6^{3-}$ ion in the solution produced by treatment of cobalt (III) acetate in acetic acid with chloride ions[154].

TABLE 5

Reviews on cobalt (III) chemistry

Topic	Ref.	
Comprehensive source	*Gmelin's Handbuch der Anorganische Chemie*, 8th edn., 58.B,	Verlag Chemie, Berlin, 1932, Suppl. 1964.
Binuclear complexes; formation, structure and reactions	A.G. Sykes and J.A. Weil	*Progr. Inorg. Chem.*, 13 (1970) 1.
Polynuclear complexes of cobalt (III) amines	A.W. Chester	*Advan. Chem. Ser.*, 62, (1967) 78.
Peroxy complexes	J.A. Connor and E.A.V. Ebsworth	*Advan. Inorg. Chem. Radiochem.*, 6 (1964) 279.
Peroxobridged dicobalt complexes	G.L. Goodman, H.G. Hecht and J.A. Weil	*Advan. Chem. Ser.*, 36 (1962) 90.
Kinetics and mechanisms of reactions	F. Basolo and R.G. Pearson	*Mechanisms of Inorganic Reactions*, 2nd edn., Wiley, New York, 1967, Chaps. 3, 4.
Stereoselectivity	J.H. Dunlop and R.D. Gillard	*Advan. Inorg. Chem. Radiochem.*, 9 (1966) 185.
Bipyridyl and *o*-phenanthroline complexes	W.R. McWhinnie and J.D. Millar	*Advan. Inorg. Chem. Radiochem.*, 12 (1969) 135.
Cis and *Trans* effects in cobalt (III) complexes	J.M. Pratt and R.G. Thorp	*Advan. Inorg. Chem. Radiochem.*, 12 (1969) 375.
Schiff bases and β-ketoamines	R.H. Holm, G.W. Everett, Jr., and A. Chakravorty	*Progr. Inorg. Chem.*, 7 (1966) 83.
β-Ketoenolates	J.P. Fackler, Jr.	*Progr. Inorg. Chem.*, 7 (1966) 361.
Co^{III} chemistry in aqueous perchlorate solution	G. Davies and B. Warnqvist	*Coord. Chem. Rev.*, 5 (1970) 349.
Complexes of flexible tetradentates	G.R. Brubacker, D.P. Schaefer J.H. Worrell and J.I. Legg	*Coord. Chem. Rev.*, 7 (1971) 161.
Inorganic chemistry of vitamin B_{12}	J.M. Pratt	Academic Press, London, 1972 (book).
Cyano complexes	B.M. Chadwick and A.G. Sharpe	*Advan. Inorg. Chem. Radiochem.*, 8 (1966) 84.
Bonding effects in circularly dichroic cobalt (III) complexes	L.I. Katzin and I. Eliezer	*Coord. Chem. Rev.*, 7 (1971) 331.
Carbonato complexes of cobalt (III)	C.R. Pirez Mac-coll	*Coord. Chem. Rev.*, 4 (1969) 147.

TABLE 4

Complex fluorides of cobalt and nickel

Complex	μ_{eff} (B.M.)	Structural data (A)	Ref.
Li_3CoF_6	5.2		140, 145
Na_3CoF_6	5.39	Na_3AlF_6 monoclinic, $a = 5.49, b = 5.71, c = 7.90, \beta = 90.1°$	140, 142
K_2NaCoF_6		K_2NaAlF_6 cubic, $a = 8.22$	141, 145
K_3CoF_6	5.63	K_3FeF_6 cubic, $a = 8.57$	140, 141, 145
Rb_3CoF_6	5.45	K_3FeF_6 cubic, $a = 8.90$	140
Cs_3CoF_6	5.38	K_3FeF_6 cubic, $a = 9.23$	140
$CaCoF_5$		$CaCrF_5$ monoclinic, $a = 8.92, b = 6.44, c = 7.52, \beta = 115.6°$	143
$SrCoF_5$		$SrFeF_5$ monoclinic, $a = 6.99, b = 7.23, c = 14.60, \beta = 94.7$	143
$Sr_5Co_3F_{19}$		$a = 14.24, c = 7.29$	143
$Ba_3[CoF_6]_2$	5.27	$Ba_3[FeF_6]_2$, $a = 14.63, c = 7.63$	141, 143, 145
$Sr_3[CoF_6]_2$		$Ba_3[FeF_6]_2$, $a = 13.80, c = 7.23$	143
$[Co(NH_3)_6][CoF_6] \cdot 0.5H_2O$	5.20	Cubic, $a = 9.95$	151
$Na_3Li_3Co_2F_{12}$		Cubic, $a = 12.33$	144
$Na_3Co_3F_{14}$		Tetragonal	144 A
Rb_2CoF_6	2.80	K_2PtCl_6 cubic, $a = 8.46$	246
Cs_2CoF_6	3.32	K_2PtCl_6 cubic, $a = 8.91$	140, 246
Na_3NiF_6	2.86	Na_3AlF_6 monoclinic, $a = 5.44, b = 5.67, c = 7.85, \beta = 90.1°$	140, 142
K_3NiF_6	2.54	Tetragonal, $a = 8.46, c = 8.57$	140, 142, 266
Na_2NiF_6		Cubic, $a = 7.77$	
		Hexagonal, $a = 5.63, c = 9.07$	354, 355
K_2NiF_6	Diamag.	K_2PtCl_6 cubic, $a = 8.11$	6, 351, 357
Rb_2NiF_6	Diamag.	K_2PtCl_6 cubic, $a = 8.44$	351
Cs_2NiF_6	Diamag.	K_2PtCl_6 cubic, $a = 8.94$	351

Considerable confusion surrounds the higher oxides of cobalt. Oxides of formulae Co_2O_3, $Co_2O_3 \cdot nH_2O$, $CoO(OH)$, $Co(OH)_3$, $CoO_2 \cdot nH_2O$ and Co_3O_4 have all been reported[1]. The older literature contains a number of reports of the preparation of Co_2O_3 by decomposition of cobalt (II) oxy salts on heating in air, or by dehydration of hydrated forms. More recent studies[155,156] have identified the anhydrous oxide produced as Co_3O_4. It seems reasonably certain that Co_2O_3 cannot be made by such methods. Considerable quantities of oxygen are absorbed by Co_3O_4, but no change occurs in the X-ray pattern[157]. In spite of the lack of evidence for an anhydrous Co_2O_3, this "compound" appears in numerous patents and papers dealing with catalytic systems – presumably either Co_3O_4 or some mixed-metal oxide is the actual reagent. Recently Chevenas et al.[158] have reported the preparation of Co_2O_3 by the reaction, at elevated temperature and pressure, of CoF_3 with Na_2O_2, or from $CoCrO_4$; two forms with hexagonal and corundum structures were identified.

The situation with respect to the hydrated cobalt (III) oxides is also far from clear. The formation of dark brown or black precipitates on oxidation of cobalt (II) compounds in alkaline solution has been known for many years, but only recently have structural data become available. It is practically impossible to identify the products reported in many older papers; no doubt many of these were impure due to incomplete oxidation, the presence of basic salts or absorbed alkali; nor was much attention paid to the water content. The oxidation of $Co(OH)_2$ in an alkaline suspension with molecular oxygen[159–161], $OC1^-$, OBr^-, $S_2O_8^{2-}$ (refs. 155, 162, 163) or electrolytically[162,164–166] produces "cobalt (III) hydroxide". When dried this has the formula $CoO(OH)$; there is no evidence[166] for a discrete compound $Co(OH)_3$. The product from these preparations often appears to be amorphous, but, by careful drying[160] or a suitable ageing process[167,168] $CoO(OH)$ can be obtained in a crystalline form. This α-$CoO(OH)$ has a hexagonal structure[160] with Co—$O = 1.90$ Å. A β-$CoO(OH)$ has been reported to be formed by anodic oxidation of cobalt in alkali-metal hydroxide solution[166]. When first precipitated, $CoO(OH)$ contains idefinite amounts of absorbed water[168]. On heating, $CoO(OH)$ loses both water and oxygen[161] to give Co_3O_4.

Black Co_3O_4 is formed by heating $CoO(OH)$ and many Co^{II} oxy salts in air[155,161,169,170], or by anodic oxidation of cobalt[164–166]. It is a normal spinel[171], $Co^{II}(Co_2^{III}O_4)$ (refs. 170, 171) not Co^{IV} $[Co_2^{II}O_4]$ (ref. 172), $a = 8.08$ Å (ref. 170), with a magnetic moment corresponding to 2.98 B.M./Co atom[169]. On strong heating it loses oxygen to give CoO; it absorbs water, but does not seem to give a definite hydrate[173]. There are a large number of mixed-metal oxides containing Co^{III} which will not be described. Cobaltates (III) are also known, e.g. $LiCoO_2$ (ref. 13) $NaCoO_2$ (refs. 13, 174), and $AgCoO_2$ (refs. 175, 176).

(b) Cobalt (III) in solution

Davies and Warnqvist[177] have reviewed the aqueous chemistry of cobalt (III) in perchlorate solution. In acid solution the Co^{III} aq/Co^{II} aq couple has been variously given as 1.84 V, (ref. 178), 1.93 V (ref. 179) and 1.90 V (ref. 180). In basic solution it is 0.17 V, $Co(OH)_3/Co(OH)_2$ (ref. 101). As expected from the high redox potential, $[Co(H_2O)_6]^{3+}$ is unstable and rapidly decomposes in solution[181]. The Co^{III} oxidation of organic compounds has been reviewed[182].

(c) Cobalt (III) complexes

The coverage is limited to complexes of phosphorus, arsenic and some oxygen and sulphur donor ligands.

Phosphorus and arsenic donors. The only Co^{III} complexes of monodentate P donor ligands are the intensely coloured trialkylphosphine compounds $Co(PR_3)_2X_3$ (X = Cl, Br) obtained by Jensen et al.[183,184]. Oxidation of $Co(PR_3)_2X_2$ is possible for R = Me, Et, Pr, *n*-Bu, *i*-Bu, *s*-Bu, although only the PEt_3 compounds have been obtained in pure form. They are monomeric, diamagnetic compounds, and probably have a trigonal bipyramidal structure. Diphosphine complexes have been little studied (Table 5). Hartley et al.[194] have prepared two red compounds $[Co(QP)X_2]BPh_4$ (X = Cl, Br) with the tetradentate phosphine, where QP is tris(*o*-diphenylphosphinophenyl)phosphine.

Nyholm[197] obtained *o*-phenylenebisdimethylarsine complexes over 20 years ago. Air oxidation of the cobalt (II) complex, $[Co(DAS)_2X_2]$, produced octahedral cobalt (III) cations, $[Co(DAS)_2X_2]^+$ (X = Cl, Br, I, CNS). Addition of ClO_4^- yields the green $[Co(DAS)_2X_2]ClO_4$ (X = Cl, Br) which was shown to be the *trans* isomer by IR and visible spectral studies[199,200]. Purple *cis*-$[Co(DAS)_2X_2]ClO_4$ (X = Cl, Br)[200,203] are also known, as in $[Co(DAS)_3](ClO_4)_3$ (refs. 195, 196). Baylis and Bailar[201] have shown that proton NMR spectra can be used to distinguish *cis* and *trans* isomers, and they also succeeded in preparing several new *cis* complexes by treatment of *trans*-$[Co(DAS)_2Cl_2]^+$ with AgY(Y = OAc, NO_3, $\frac{1}{2}C_2O_4$, $\frac{1}{2}CO_3$). X-ray structures have been determined for *trans*-$[Co(DAS)_2Cl_2]ClO_4$ (ref. 198) and *trans*-$[Co(DAS)_2Cl_2]Cl$ (ref. 202). Co–As = 2.334(2) Å, Co–Cl = 2.256(3) Å.

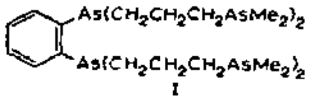
Kinetic studies on the *cis-trans* isomerisation[209,210] of $[Co(DAS)_2Cl_2]^+$ and of the reaction

$$trans\text{-}[Co(DAS)_2Cl_2]^+ + 2\,X^- \rightarrow trans\text{-}[Co(DAS)_2X_2]^+ + 2\,Cl^-$$

(X = ^{35}Cl, CNS) have been reported[211,212]. It has also been shown that $(C_6F_5)_2TlBr$ oxidises $Co(DAS)_2Br_2$ to green $[Co(DAS)_2(C_6F_5)Br]Br$, presumably the *trans* isomer[213]. $[Co(F{-}DAS)_2Cl_2]$ is much more easily oxidised[38] to the Co^{III} complex than $[Co(DAS)_2Cl_2]$ (ref. 38).

Cobalt (III) complexes of *cis*-1,2-bisdimethylarsinoethylene (*cis*-edas) are easily obtained by air oxidation of the cobalt (II) compounds[204,205], and are generally very similar to those of DAS. So far only *trans*-$[Co(cis\text{-}edas)_2X_2]^+$ and $[Co(cis\text{-}edas)_3]^{3+}$ have been obtained, although Bennett and Wild[204] have mentioned very low yields of purple complexes (not characterised) which may be the *cis* isomers.

Octahedral $[Co(TTAS)X_3]$ (TTAS = bis(*o*-dimethylarsinophenyl)-methylarsine) complexes (X = Cl, Br, I, CNS, NO_2, NO_3) are obtained by oxidation of the Co^{II} analogues or by metathesis[206]. All are diamagnetic non-electrolytes (except the NO_3 which dissociates in solution), and only one isomer of each is known. The $[Co(TTAS)_2]^{3+}$ cation can also be prepared[206]. The kinetics of the displacement of Cl^- from $[Co(TTAS)Cl_3]$ have been studied by Nanda and Tobe[214]. Two cobalt (III) complexes of the hexadentate arsine, *o*-phenylenebisdi(3-dimethylarsinopropylarsine) (SAS, I) $[Co(SAS)]X_3$ (X = ClO_4, I) have been reported in a preliminary communication[207]. Several Co^{III} hydridocomplexes stabilized by phosphines are known (Table 5).



I

TABLE 5

Cobalt (III) complexes of phosphines and arsines

Complex	Properties	Ref.
$[Co(PEt_3)_2X_3]$, X = Cl, Br	μ_{eff} = 3.03 B.M.; zero dipole moment monomeric	183, 184
$[Co(Et_2PC_2H_4PEt_2)_2X_2]$ X, X = Cl, Br, I.	Diamagnetic; 1 : 1 electrolytes	185
$[Co(Ph(H)PC_2H_4P(H)Ph)_2Br_2]$ Br	Diamagnetic	186
$[Co(Ph_2PC_2H_4PPh_2)_2H_2]ClO_4$	Diamagnetic; ν(Co–H) = 1940, 1985 cm^{-1}	187
$[Co(Ph_2PC_2H_4PPh_2)_2HX]$ X		188
$[Co(Me_2PCH_2CH_2CH_2PMe_2)_2X_2]ClO_4$X = Cl, Br, I	Diamagnetic; 1 : 1 electrolytes	208
$[Co(PR_3)_3H_3]$, R_3 = Ph_3, $PhEt_2$, Ph_2Et, $(p\text{-}RC_6H_4)_3$		189–193
$[Co(QP)X_2]BPh_4$, X = Cl, Br	Diamagnetic; octahedral	194
$[Co(DAS)_3](ClO_4)_3$	Diamagnetic	195, 196
$\{Co(DAS)_2X_2\}_2[CoX_4]$, X = Cl, Br	*Trans* cation	197
$[Co(DAS)_2X_2]X'$, X = Cl, Br, CNS, X′ = X, ClO_4	*Trans* structure; green perchlorates	195–202
$Co(DAS)_2I_3$	*Cis* isomer	203
$[Co(DAS)_2X_2]ClO_4$, X = Cl, Br	*Cis* structure; purple	200, 201, 203
$[Co(DAS)_2X]$ Y, X = OAc, CO_3, C_2O_4, $2NO_3$ Y = BF_4, PF_6	*Cis* structure	201
$[Co(F\text{-}DAS)_2Cl_2]^+$		38
$[Co(cis\text{-}edas)_2X_2]$ Y, X = Cl, Br, I, CNS Y = PF_6, X	*Trans* structure	204, 205
$[Co(cis\text{-}edas)_3](BF_4)_3$		204
$[Co(TTAS)X_3]$, X = Cl, Br, I, NCS, NO_2, NO_3	Octahedral; non-electrolytes	206
$[Co(TTAS)_2]^{3+}$		206
$[CoSAS)]X_3$, X = I, ClO_4	Diamagnetic; octahedral	207
$M[Co(Ph_2PCH_2CH_2PPh_2)_2(CN)_2]X_3$, M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}, X = halogen	The complex cation is behaving as a zwitterion bonded to MX_3 group by N atom of cyano group	181

Oxygen donors. Cobalt (III) sulphate, $Co_2(SO_4)_3 \cdot 18H_2O$ and its alums $MCo(SO_4)_2 \cdot 12H_2O$($M = Cs, Rb, K, NH_4$), are produced by oxidation of solutions of the cobalt (II) compounds with ozone, fluorine or, best, electrolytically[215–218]. The deep blue crystalline diamagnetic products decompose fairly rapidly[219–221]. This rapid decomposition appears to be due to traces of extraneous water, which promotes reduction and, by careful drying, Johnson and Sharpe[222] produced considerably more stable samples of the sulphate and of the Rb and Cs alums. Cobalt (III) selenate has been reported[218], but is in need of further characterisation. Anhydrous cobalt (III) nitrate is formed as hygroscopic green crystals[223] by reaction of CoF_3 with N_2O_5. It dissolves in water to give a green solution which rapidly turns pink (Co^{II}) evolving oxygen. The cobalt (III) is in a distorted octahedral environment produced by three bidentate nitrato groups[224]. An impure cobalt(III) acetate is formed by electrolytic oxidation of the cobalt (II) compound in glacial acetic acid containing 2% water[225]. Its structure is unknown but it may be $[Co_3O(O_2CCH_3)_6]$ $[O_2CCH_3] \cdot CH_3COOH$, similar to the Mn^{III} and Fe^{III} analogues.

Stable periodato and tellurato complexes are formed by alkaline hypochlorite oxidation of cobalt (II) salts in the presence of alkali-metal periodates or tellurates[226–233]. The former are also formed using the periodate itself as oxidant[226,228]. Lister et al.[229–231] have characterised the green diamagnetic complexes $Na_5H_2Co(IO_6)_2 \cdot 10H_2O$, $K_4H_3(IO_6)_2 \cdot 3H_2O$, $Ba_5[H_2Co(IO_6)_2]_2 \cdot 10H_2O$ and $K_3H_6Co(TeO_6)_2 \cdot 2H_2O$. The acid, $H_3[Co_4I_3O_{24}H_{12}] \cdot xH_2O$, is also known[227,228]. Cobalt (III) is stabilised by incorporation into a heteropolyanion; for example $K_7[CoP_2W_{17}O_{62}H_2] \cdot 22H_2O$ (ref. 234), $K_3H_6[CoMo_6O_{24}]$ (ref. 235) and the novel $Na_5[Co(en)(Nb_6O_{19})(H_2O)] \cdot 17H_2O$ (en = ethylenediamine[236]).

The green tricyclohexylphosphine oxide complex $[CoL_2I_2]I$($L = (C_6H_{11})_3PO$) is formed[237] by iodine oxidation of $[CoL_2I_2]$.

Sulphur donors. Cobalt (II) dithiocarbamates are very readily oxidised to the Co^{III} complexes; simply mixing a $cobalt^{II}$ salt with a dithiocarbamate in aqueous solution is usually sufficient to produce the Co^{III} complex[238,239]. The structure of tris(*N*,*N*-diethyldithiocarbamato)cobalt (III) has confirmed[240] the essentially octahedral environment of the cobalt suggested on the basis of visible spectral evidence[241]. The Co—S bonds have an average length[240] of 2.258 Å. Cobalt (III) xanthate and dithioaromatic acid complexes are also known; the known complexes are listed by Coucouvanis[242]. Gray and co-workers[243] have preparaed $[Bu^n{}_4W]_3[Co(i\text{-}MNT)_3]$ (*i*-MNT = 1,1-dicyano-2,2-ethylenedithiolate) obtained as gold-green diamagnetic crystals. Dithiophosphinate complexes $Co(S_2PR_2)_3$, which are six-coordinate monomers, have been prepared by reaction of $Na_3Co(NO_2)_6$ and NaS_2PR_2($R = OEt, Me, Ph$) (ref. 244). The structure of $Co[(MeO)_2PS_2]_3$ has recently been reported[245].

The 1,2-dithiolate complexes have a much more complicated chemistry in view of their unusual electron transfer properties[45]. The diamagnetic octahedral $[Co(MNT)_3]^{3-}$ ions, isolated with large Ph_4E^+ ($E = P, As$) ions are well characterised[46,47].

(ii) Cobalt (IV)

Cobalt tetrafluoride has not been prepared, although its lattice energy and ΔH_f^0 have been calculated[7]. Golden-yellow Cs_2CoF_6 was prepared by fluorination of Cs_2CoCl_4 or $Cs_2Co(SO_4)_2$ (refs. 139, 140, 246), and Rb_2CoF_6 has recently been obtained[246]. The ıtassium salt is unknown, and the reported[6] "K_3CoF_7" has been shown[140] to be impure ,CoF_6. The hexafluorocobaltates (IV) have the K_2PtCl_6 structure[246] with Co–F = 73 (5) Å (Cs) or 1.65 (5) Å (Rb). Their magnetic moments are consistent with a $^2T_2$ ɔund state, and both salts exhibit complex ferromagnetic behaviour[240]. The diffuse :lectance spectrum of $Cs_2CoF_6^{2}$ (Fig. 2) has been assigned on the basis of a $^2T_2$ ɔund state[148,247]. Cs_2CoF_6 dissolves in anhydrous HF above 0°C with liberation of ıorine[248].

Anhydrous CoO_2 is unknown. A brown-black hydrated cobalt (IV) oxide was re-ɪrted[162,249,250] to result from oxidation of Co^{II} salts in strong alkali solution with OCl^- OBr^-, and it seems that cobalt (IV) oxide may be formed, at least partially, by electrolytic .idation[164–166]. Red-brown Ba_2CoO_4 is formed by heating Ba_2 [$Co(OH)_6$] or $Co(OH)_2$ th $Ba(OH)_2$ at 1050°C in oxygen[13,32]. It has recently been shown[251] to contain dis-:te CoO_4^{4-} ions, and has the orthorhombic β-K_2SO_4 structure (a = 7.65, b = 5.85, = 10.34 Å) with Co–O = 1.76 Å. Sr_2CoO_4 and Na_4CoO_4 are claimed[13], but no details ve been given. The tetragonal Ba_3CoO_5 (a = 7.303, c = 11.639 Å; c/a = 1.594) and Ba_2CoO_5 (a = 7.194, c = 11.497 Å; c/a = 1.598) can be prepared under different con-:ions[13, 34*].

Complex oxides containing both Co^{III} and Co^{IV} are known. Earlier work[10,252] on the stem $BaCoO_2$–$BaCoO_{3-x}$ has been confirmed and extended by Zanne et al.[253], who und six different phases at 900°C, and demonstrated that the Co^{IV} had the $t_{2g}^5e_g^0$ con-;uration. The system $La_{1-x}Sr_xCoO_{3-\lambda}$ which has unusual magnetic properties, has been ,estigated in detail[254–257]. The ionic radius of Co^{4+} is estimated[256] as 0.48 Å.

A 9-molybdocobaltate (IV) $K_6CoMo_9O_{32} \cdot 6.5H_2O$ was reported[258a] in 1907, but does ıt seem to have been further examined. Other heteropolycobaltates (IV) could probably prepared.

The magnetic properties of $CoAs_2$ and $CoSb_2$ are consistent with a d^5 configuration[43]. ɪrmally Co^{IV} is present[258] in Co(o-$C_6H_4(NH)_2$), and in some dithiolenes (Section E), .t these complexes are members of series which undergo facile electron transfer reactions.

i) Cobalt (V)

Wahl et al.[68] found that fusion of KO_x or CsO_2 with Co_3O_4 in oxygen in a 1 : 1 alkali :tal : Co ratio produced substances of approximate composition $MCoO_3$, which were lieved to be mixtures of MO_2 and $MCo^{III}Co^{IV}O_4$, rather than cobaltates (V). Further ıdies[259] on mixtures of cobalt and potassium oxides in a 1 : 3 Co : K ratio heated to .0–550°C in oxygen, resulted in the preparation of K_3CoO_4. The blue-black hygroscopic oduct exhibited unusual magnetic properties[259]. In mixed crystals with K_3PO_4 it had a ıgnetic moment corresponding to four unpaired electrons (3.2% Co concn.), which de-:ased with increasing cobalt concentration. The room temperature magnetic moment of e undiluted K_3CoO_4 was 2.1 B.M.; temperature dependence was also found. X-ray pow-ɪ patterns showed that two forms of K_3CoO_4 exist; an unstable one, isostructural with ,MO_4 (M = P, V, Mn, Fe), and a stable form into which the other transforms on standing. ıe analogous Rb and Cs compounds also have low magnetic moments (μ_{eff} 2.07, 2.33

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*Added in proof: Ruby-red crystals of Li_8CoO_6 are hexagonal and include a remarkably short Co–O listance of 1.66 Å. V.M. Jansen and R. Hoppe, *Z. Anorg. Chem.*, 398 (1973) 54.

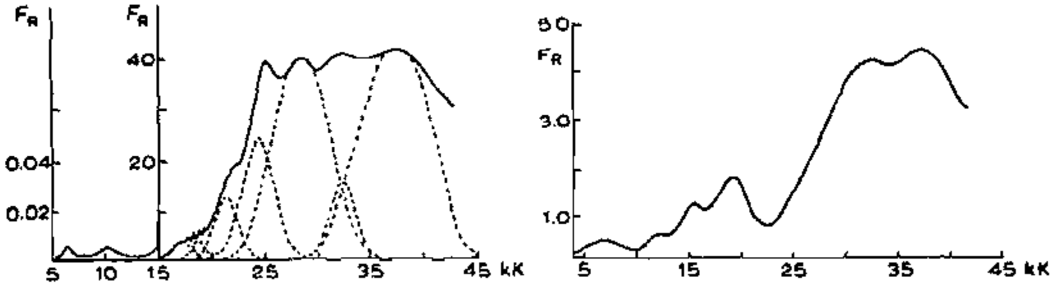


Fig. 2. (a) The diffuse reflectance spectrum[247] of caesium hexafluorocobaltate (IV), Cs_2CoF_6, in the region 5-45 kK at room temperature: observed spectrum, ———; Gaussian analysis, – – – – – –. (b) The diffuse reflectance spectrum[248] of potassium hexafluoronickelate (III), K_3NiF_6, at room temperature. (Reproduced by kind permission of the American Chemical Society.)

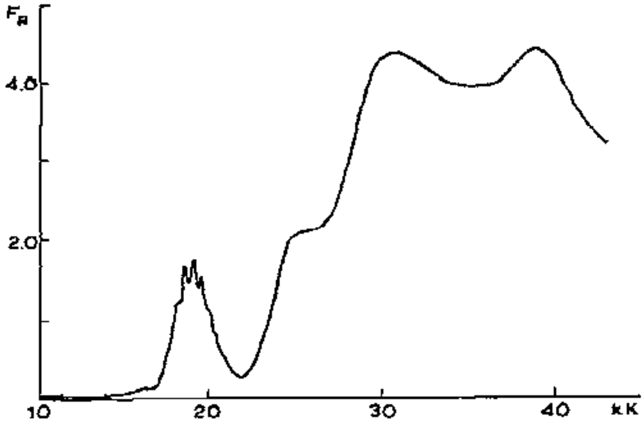


Fig. 2. (c) Diffuse reflectance spectrum[354] of the $[NiF_6]^{2-}$ ion (Na_2NiF_6). (Reproduced by kind permission of Pergamon Press.)

B.M. respectively at 293°K)[71,260]. Scholder[71] has reported that Na_2O/Co_3O_4 mixture is partially converted to Na_3CoO_4 on heating in oxygen under pressure.

D. NICKEL

The number of reported nickel (III) and nickel (IV) complexes has increased rapidly over the past ten years. More recently interest in this area has concentrated upon detailed studies of several of these complexes in an attempt to establish unequivocally the oxidation state of the metal.

(i) Nickel (III)

(a) Halides and oxides

The isolation of black NiF_3 (μ_{eff} = 2.41 B.M.) in an impure form by reaction of K_2NiF_6 with AsF_5 in liquid HF, has been reported recently[248]. There has been speculation for a number of years that the dark brown deposits which appear on nickel anodes during the electrolysis of various solutes in liquid HF (e.g. in the Simons process) may be a higher fluoride of nickel[261–263]. Stein et al.[264] have shown that similar substances are formed by dissolution of K_3NiF_6 or K_2NiF_6 in anhydrous HF. These substances have considerable oxidising power, and liberate HF and traces of F_2 on heating in vacuo, but X-ray powder patterns show the presence only of NiF_2 and KHF_2, and the identity of these products remains obscure. The "NiF_6" reported by Page[263B] probably belongs to the same class of compounds. Despite an early claim[136] for a green $NiCl_3$, it is unlikely that other nickel (III) halides could be prepared.

Violet K_3NiF_6 is formed[140,264] by fluorination of a 1 : 3 mixture of $NiSO_4$ or $NiCl_2$ and KCl; some difficulty[264,266] has been experienced in isolating samples free of contamination by Ni^{II} or Ni^{IV}, and attempts to prepare the Rb and Cs analogues seem to have failed[140]. The Na_3NiF_6 complex is also difficult to obtain pure[142]. Na_3NiF_6 has a monoclinic structure; K_3NiF_6 was reported to be cubic with the K_3FeF_6 structure[140,265] but it recently[142] been re-indexed as tetragonal. The magnetic properties of M_3NiF_6 (M = Na, K) are anomalous in that the susceptibilities do not follow the Curie–Weiss law, and their temperature-dependent magnetic moments are intermediate between the values expected for high-spin and low spin d^7 cases[140,142]. The electronic spectra are also complex[267] (Fig. 2). Allen and Warren[148,267] assigned the spectrum of K_3NiF_6 by assuming that a tetragonal Jahn–Teller distortion of the ^2E_g ground state occurs (D_{4h} symmetry). Westland et al.[268] studied the magnetic properties of K_3NiF_6 in mixed crystals with $K_{2.8}AlF_{5.8}$, and found that replacement of F^- by O^{2-} occurred with corresponding oxidation of some of the Ni^{3+} to Ni^{4+}. The Ni–F stretching frequency (ν_3) in K_3NiF_6 (580 cm^{-1}) is intermediate between the values reported for Ni^{II} and Ni^{IV} fluorocomplexes (445, 663 cm^{-1} respectively)[264]. K_3NiF_6 is thermally stable in vacuum up to 450°C, and dissolves in anhydrous HF, with disproportionation into Ni^{II} and NiF_6^{2-}. A violet $BaNiF_5$ of unknown structure is produced by fluorination of $BaNi(CN)_4$ at 300°C, and at 500°C a brown modification, also formulated $BaNiF_5$, forms[139]. Allen et al.[150], using CNDO molecular orbital calculations, have shown that a distorted structure is energetically more stable than the regular octahedral structure for the NiF_6^{3-} ion.

Oxidation of nickel (II) salts in alkaline solution produces dark-brown or black substances which contain at least part of the nickel in an oxidation state > 2. The existence of anhydrous oxides – Ni_2O_3, NiO_2 or Ni_3O_4 – is very unlikely. The reactions claimed to produce these compounds, such as heating NiO in oxygen[269], thermal decomposition[270] of $Ni(NO_3)_2$, or dehydration of the hydroxo complexes[270,271] have generally been found on repetition to give NiO or, at best, uncertain results[272–277]. The hydrated higher oxides of nickel are better established, and include $Ni_3O_2(OH)_4$, $4Ni(OH)_2 \cdot NiO(OH)$ and several forms of NiO(OH).

As in the analogous compounds of cobalt and manganese, the identification of these compounds is complicated by poor crystallinity, and by their ability to incorporate varying amounts of water and alkali-metal ions. Glemser and Einerhand[277], and Besson[162], have described a number of methods for the preparation of NiO(OH) (or $Ni_2O_3 \cdot aq$), including anodic oxidation, oxidation of nickel salts in alkaline solution with OCl^-, OBr^-, $S_2O_8^{2-}$, and hydrolysis of sodium nickelate (III). The β-NiO(OH) has the brucite structure of β-$Ni(OH)_2$, from which it can be formed by electrochemical oxidation[278–281]; $a = 2.82$, $c = 4.85$ Å. The structure of γ-NiO(OH) is more complicated being based upon the $CdCl_2$

type with an elangated cell[278,280]. Depending upon the method of preparation γ-NiO(OH) contains varying amounts of alkali-metal ions[281,282]. Other forms reported include α-NiO(OH) formed by persulphate oxidation of $K_2Ni(CN)_4$(refs. 277, 278), $Ni_3O_2(OH)_4$ (a = $Ni^{II,III}$ compound)[277, 278, 283]; and $4Ni(OH)_2 \cdot NiO(OH)$ (refs. 277, 278). (For other forms of Ni^{III} oxides, see ref. 284.) DTA and thermogravimetric data have been reported for various higher nickel oxides[285].

Several nickelates (III) are known; compounds which contain both Ni^{III} and Ni^{IV} are discussed under Ni^{IV}. Dyer et al.[286] reported that bubbling oxygen through fused NaOH or LiOH in nickel tubes produced $MNiO_2$ (M = Na, Li). $LiNiO_2$ has the α-$NaFeO_2$ structure. Bronger et al.[287] studied the system $Li_xNi_{1-x}O$ when x lay between 0 and 0.65, finding that when $x \geqslant 0.28$ the α-$NaFeO_2$ structure occurred, but below this a statistical distribution of cations in the NaCl structure was present. The variation of structure and magnetic properties with composition has been the subject of other studies[288,289]. Two forms of $NaNiO_2$ are known, a low-temperature monoclinic, and a high temperature α-$NaFeO_2$ form[286]. Distorted $Ni^{III}O_6$ octahedra are present[290]. Potassium and rubidium form products of composition $MNiO_{2.5}$, whose magnetic moments (μ = 1.67, 1.75 B.M. respectively) have been explained[291] by assuming a formulation $(M^I)_2\,(Ni^{III})_2\,(O^{2-})_3\,(O_2^{2-})$. A black substance, approximating to $Ba_2Ni_2O_5$, is formed[10,292,293] on heating $BaNiO_3$; it has μ_{eff} = 1.24 B.M. $AgNiO_2$ is formed[294] from potassium nickelate and $AgNO_3$, and rhombohedral $LaNiO_3$ is produced by heating together the oxides or carbonates[295,296]. In contrast Nd_2O_3 gives $Ni^{III} - Ni^{II}$-containing products[296].

(b) Nickel (III) complexes

Nitrogen donor ligands. Complexes of nickel (III) with NH_3 ligands have not been isolated, although Lati and Meyerstein[297] using a pulse radiolytic method, have demonstrated that $Ni^{II}(NH_3)_x$ species are oxidised by NH_2 radicals to an unstable Ni^{III} complex. Similar oxidation of glycine and ethylenediamine complexes of Ni^{II} is also possible[298]. Chlorine or bromine oxidises[299] $[Ni(en)_2X_2]$ or $[Ni(en)_3]X_2$ to the nickel (III) complexes $[Ni(en)_2X_2]X$ (X = Cl, Br), from which $[Ni(en)_2X_2]Y$ and $[Ni_2en_4Cl_3]Y_3$ (Y = ClO_4, NO_3) can be obtained. Similar propylenediamine complexes can be prepared[300]. However, attempts to oxidise nickel (II) ethylenediamine complexes with iodine produce dark complexes which are believed to be nickel (II) polyiodides rather than Ni^{III} complexes[301]. Bulk susceptibility and ESR spectroscopic studies have shown that the nickel (III) complexes fall into two groups — those with magnetic moments equivalent to one unpaired electron, and those belonging to a second group with much smaller moments (~ 0.5 – 0.85 B.M.)[302,303]. Olive-green $[NiL(NO_3)_2]ClO_4$ and $[NiLSO_4]ClO_4 \cdot \frac{1}{3}H_2SO_4$(L = meso-5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetra-aza-cyclotetradecane) are prepared by oxidation of the nickel (II) complexes in the presence of the appropriate anions[304]. Busch and co-workers[305,306] isolated Ni^{III} complexes of other macrocycles by oxidation of the nickel (II) complexes with $(NH_4)_2S_2O_8$, HNO_3 or $NOBF_4$, and Olsen and Vasilevskis[307] reported the electrolytic oxidation of cyclic amine complexes.

The blue-black compounds $KNi(Rbi)_2$ (Rbi = HNCONRCONH, R = H, alkyl) are obtained by persulphate oxidation of $K_2Ni(Rbi)_2$, and contain N-bonded ligands. $KNi(Rbi)_2$ (R = H) is isomorphous with the cobalt (III) complex[308,309]. The Ni^{II} –tetraphenyl-porphyrin complex can be electrochemically oxidised to Ni^{III}, which slowly decomposes back to the nickel (II) compound[310].

Several formally nickel (III) complexes of oxime ligands are known. From dimethylglyoxime, MeC(=NOH) Me($dmgH_2$), were obtained[311,312] black [Ni($dmgH)_2$] Br and [Ni($dmgH)_2$] (Br_3), whilst diphenylglyoxime ($dpgH_2$) produced Ni($dpgH)_2$X(X = Br, I) on addition of the halogen in an organic solvent to the nickel (II) complex[313]. However, Foust and Sonderberg[314] showed that the dpgH complexes contained Ni^{II}, the halogen *atoms* being sandwiched between the layers of planar Ni($dpgH)_2$ moieties, and apparently interacting with the phenyl rings rather than the metal. Drago and Baucom[315] have obtained what seem to be genuine Ni^{III} complexes with *syn*-2-benzolypyridineoxime, and syn-2-phenylacyl-pyridineoxime by persulphate oxidation of a mixture of the ligand and a nickel (II) salt in aqueous ammonia solution. The ESR data and the proposed bonding scheme are discussed in Section E. Nickel (III) is also reported in $[NiL_2(H_2O)_2]^{3+}$ (L = N'N'-oxydiethylenebiguanide[316]) and $[NiL_3]Cl_3$(L = N^1-chlorophenyl-N^5-isopropylbiguanide[317]).

Phosphorus and arsenic donors. Oxidation of $Ni(PEt_3)_2X_2$ with NOX (X = Cl, Br), or in the case of the bromide with Br_2 in benzene, produces very dark blue or green crystals (refs. 183, 318, 319) of $Ni(PEt_3)_2X_3$. The approximately zero dipole moments favour a trigonal bipyramidal structure with equatorial halides. X-ray studies have established the lattice parameters, but a full X-ray structure determination has so far been prevented by the instability of the complexes[320]. Similar complexes with PMe_3, PPr_3 and PBu_3 can be isolated but these are less stable and have not been prepared completely pure[183]. Bromine oxidation of $Ni(PMe_2Ph)_2Br_2$ yields the corresponding Ni^{III} complex[321], which upon recrystallisation forms $Ni(PMe_2Ph)_2Br_3 \cdot 0.5Ni(PMe_2Ph)_2Br_2 \cdot C_6H_6$. The structure of the Ni^{III} compound is trigonal bipyramidal[322]. Several nickel (II) diphosphine complexes are oxidised by bromine in an organic solvent to $NiLBr_3$ (L = $R_2PCH_2CH_2PR_2$, R = Me, Et, Ph)[185,323,324]. $[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]$ readily forms $[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]Br$, but the corresponding complex of $Ph_2PCH_2CH_2PPh_2$ is not oxidised[325].

The planar Ni^{II} complex, $[Ni(vpp)Br_2]$ (vpp = *cis*-1,2-bisdiphenylphosphinoethylene), undergoes bromine oxidation to $[Ni(vpp)Br_3]$, a pentacoordinate complex. The latter undergoes reduction on standing in air to revert to the original Ni^{II} species[325].

On heating an alcoholic solution of $Ni(DAS)_2Cl_2$ in air, in the presence of HCl, brown-yellow $Ni(DAS)_2Cl_3$ forms[326]; it was formulated as $[Ni(DAS)_2Cl_2]Cl$ as a result of conductivity studies. Metathesis with the appropriate alkali-metal salt yields the corresponding bromide and thiocyanate, whilst the ionic X group is removed by perchloric acid[326] to yield $[Ni(DAS)_2X_2]ClO_4$. Lewis et al.[199] assigned a *trans* octahedral structure to the cations on the basis of their far-IR spectra, and this has been confirmed[327,328] by an X-ray study on $[Ni(DAS)_2Cl_2]Cl$, which found Ni—As = 2.34 Å and Ni—Cl 2.425 Å. The ESR studies on these complexes are discussed in Section E. Nyholm also obtained a complex $Ni(DAS)Br_3$ by bromination of $Ni(DAS)(CO)_2$; its structure is unknown, but an octahedral polymer seems a likely possibility[329]. Reaction of $[Ni(DAS)_2Cl_2]Cl$ with NaI follows a different course[326]; the product is a black diamagnetic solid $Ni(DAS)_2I_3$, which may be a polyiodide of nickel (II).

Bennett and Wild[330] found that Ni(*cis*-edas)$_2Cl_2$ readily air-oxidised in solution to $[Ni(cis\text{-}edas)_2Cl_2]^+$, which is probably the *trans* isomer. The bromide can be prepared from the chloro complex and Et_4NBr. The *cis*-edas complexes seem to be more readily reduced than the DAS complexes.

TABLE 6

Nickel (III) and -(IV) complexes of phosphines and arsines

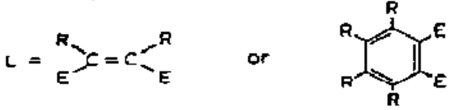
Complex	Properties	Ref.
$[Ni(PEt_3)_2X_3]$, (X = Cl, Br)	$\mu_{eff} \sim 1.7$ B.M.	183, 318–320
$[Ni(PR_3)_2X_3]$, X = Cl, Br R = Me, Pr, Bu'	Less stable than PEt_3 complexes	183
$[Ni(PMe_2Ph)_2Br_3]$	$\mu_{eff} = 2.17$ B.M., trig. bipyramid.	321, 322
$[Ni(Me_2PCH_2CH_2PMe_2)Br_3]$	$\mu_{eff} = 2.12$ B.M., non-electrolyte	323
$[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]Br$	$\mu_{eff} = 2.05$ B.M.	323
$[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]Br_3$	$\mu_{eff} = 2.02$ B.M.	323
$[Ni(Et_2PCH_2CH_2PEt_2)Br_3]$	$\mu_{eff} = 2.0$ B.M.	185
$[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$	$\mu_{eff} = 2.02$ B.M.	324
$[Ni(Ph_2PCH_2CH_2CH_2PPh_2)Br_3]$	$\mu_{eff} = 1.93$ B.M.	324
$[Ni(Ph_2PCH=CHPPh_2)Br_3]$	$\mu_{eff} = 1.91$ B.M.*	325
$[Ni(DAS)_2X_2]Y$, X = Cl, Br, CNS Y = X, ClO_4	$\mu_{eff} \sim 1.9$ B.M., oct. cations	199, 326–328
$[Ni(DAS)Br_3]$	$\mu_{eff} = 2.4$ B.M.	329
$[Ni(cis\text{-}edas)_2X_2]Y$, X = Cl, Br, Y = X, PF_6	$\mu_{eff} \sim 2.0$ B.M.	330
$[NiMeAs(CH_2CH_2CH_2AsMe_2)_2Br_3]$	$\mu_{eff} = 1.86$ B.M., non-electrolyte	332, 333
$[Ni(TTAS)Br_3]$	$\mu_{eff} = 2.5$ B.M., meridional structure	331
$[Ni(DAS)_2X_2]Y_2$, X = Cl, Br; Y = X, ClO_4	$\mu_{eff} \sim 0.7$ B.M., oct. cations	368
$[Ni(cis\text{-}edas)Cl_2](PF_6)_2$	Unstable	330

* Moment falls on exposure of compound to air, due to reduction.

Two nickel (III) bromide complexes with tridentate arsines have been reported: $NiLBr_3$, where L = TTAS (ref. 331) or $MeAs(CH_2CH_2CH_2AsMe_2)_2$ (refs. 332, 333). The reported[334] nickel (III) complexes of the quadridentate arsine tris (3-dimethylarsinopropyl)arsine, $As(CH_2CH_2CH_2AsMe_2)_3$, have been shown to be trigonal bipyramidal nickel (II) complexes[335].

Oxygen donors. The reaction of $NiCl_2$ with excess N_2O_4 yields a flocculent green powder formulated as $[NO_2^+]$ $[Ni(NO_3)_4]$, which is anomalous for a nickel (III) complex in having a magnetic moment of 4.54 B.M., i.e. high-spin Ni^{III}. On heating in vacuo[336] it evolves N_2O_5, approaching a composition $Ni(NO_3)_3$. $NiO(SO_3F)$ formed from $NiCO_3$ and $S_2O_6F_2$ also appears[337] to contain Ni^{III}.

Dithiolenes and related complexes. Ligands of type (L), where the donor atoms E can be S, NH, or O (although not all types are known), produce



complexes $[NiL_2]^-$ which are formally nickel (III) complexes of the dianionic form of the ligands[45]. As mentioned previously, this view is only one of several possibilities and the question of the best description of the bonding will be treated later (Section E).

These compounds are deeply coloured, paramagnetic (μ_{eff} corresponding to one unpaired electron) and display ESR signals in solution. Polarographic studies indicate that electron transfer reactions of these complexes occur readily to form diamagnetic $[NiL_2]$ and $[NiL_2]^{2-}$ species[338-345]. The structure of $[PPh_3Me]$ $[Ni\{S_2C_2(CN)_2\}_2]$ showed the NiS_4 grouping to be essentially planar with the anions stacked in columns, association between pairs of nickel atoms occurring through Ni · · · · S interaction. Within the anion[346] the Ni–S distance is 2.15 Å. Especially interesting is the change in bond lengths along the series $[Ni\{S_2C_2(CN)_2\}_2]^x$ when x varies between 0, – 1 and – 2. Only small changes occur in the C=C (1.33 – 1.37 Å) and Ni–S (2.00 – 2.17 Å) distances. The electronic spectra are characterised by intense absorptions in the visible and near IR regions, which are not normal "*d-d*" bands, but are due to some type of charge transfer process. The mixed ligand complex $Ni(S_2C_2(CF_3)_2)(Et_2NCS_2)$ has recently been reported[347].

Other complexes. Voltametric oxidation of nickelocene produces the unstable $Ni(\pi\text{-}C_5H_5)_2^+$ cation[348]. Replacement of the $\pi\text{-}C_5H_5$ groups by carborane moieties considerably increases the stability of the product[349,350], e.g. in $(\pi\text{-}C_5H_5)Ni(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})$ and $[Me_4N]$ $Ni(B_{10}H_{11}C_2)$.

(ii) Nickel (IV)

(a) Halides and oxides.

The red crystalline M_2NiF_6 (M = K, Rb, Cs) are prepared[6,140,265,351-353] by fluorination of $2MCl + NiCl_2$, or better, M_2NiCl_4 or $M_2Ni(CN)_4$. All three have cubic K_2PtCl_6 structures and, unlike most other 3*d* hexafluorometallates, do not exhibit polymorphism[351]. The nickel-fluorine distance[351,354] in the NiF_6^{2-} ion is 1.7 Å. Red Na_2NiF_6 is prepared[352,354] by fluorination of Na_2NiO_3 at 280°C under 120 atm, or of $2NaF \cdot NiF_2$

at 350°C and 350 atm. The product is contaminated with both Na_3NiF_6 and Na_3NiF_3. Guinier photographs show that two structural forms of Na_2NiF_6 are present—hexagonal and cubic forms[354], the latter being the only example of a Na_2MF_6 complex with the K_2PtCl_6 structure. Na_2NiF_6 is unstable, losing part of its fluorine under an argon atmosphere, and is very moisture-sensitive. There have been several reports of the electronic spectra of hexafluoronickelates (IV) (Fig. 2), agreement between different reports being generally good[148,265,352,354,355]. The IR spectra of all the alkali-metal salts have also been reported[352,356], approximate values for the NiF_6^{2-} ion being $\nu_1 \sim 560$ cm^{-1}, ν_2 520 cm^{-1}, $\nu_3 \sim 650$ cm^{-1}, $\nu_4 \sim 350$ cm^{-1}, $\nu_5 \sim 310$ cm^{-1}. Matwiyoff et al.[357] have reported ^{19}F NMR spectra for M_2NiF_6 (M = K, Rb) in anhydrous HF. Bougon[352] has obtained $(NO)_2NiF_6$, but alkaline-earth complexes have not been reported.

Black $NiO_2 \cdot aq$ has been reported to be formed by oxidation of Ni^{II} compounds in alkaline solution, but there is considerable doubt about whether a compound with sufficient oxygen content can be prepared[162,277,358]. Definite characterisation of these products has been prevented by their amorphous nature. However, it is likely that some Ni^{IV} (along with Ni^{III}) is present in the more highly oxidised preparations[162,273,281,282].

Black $BaNiO_3$ is produced by heating NiO with BaO_2 or $Ba(OH)_2$ in oxygen[292,293]. On heating it loses oxygen to give "compounds" $Ba_3Ni_3O_8$ and $Ba_2Ni_2O_5$. A very unstable sodium nickelate (IV) is reported to be present in the product of heating Na_2O_2 and NiO in oxygen at fairly low temperatures[290]. By fusion of NiO with alkali peroxides Bade et al.[291] obtained M_2NiO_3 (ref. 68) (M = Na, K, Rb), Rb_2NiO_4, Rb_3NiO_4 (?), $Cs_2NiO_{4.5}$ and Cs_3NiO_5. The magnetic moments of these complexes are somewhat anomalous and in order to fit the observed μ values to the oxidation state of the nickel, the authors proposed that in addition to oxide ions, these compounds may contain peroxide and/or superoxide groups, e.g. Rb_2NiO_3 ($\mu_{obs} = 2.1$ B.M.) could be $Rb_2Ni^{IV}O_3$ ($\mu_{calc} = 2.0$) or $Rb_6Ni_2^{III}Ni^{IV}(O^{2-})_7(O_2^{2-})$ ($\mu_{calc} = 2.1$ B.M.) and Cs_3NiO_5 ($\mu_{obs} = 2.97$ B.M.) either $Cs_3Ni^{IV}(O^{2-})_3(O_2^{-})$ ($\mu_{calc} = 2.76$ B.M.) or $Cs_6Ni^{IV}(O^{2-})_4(O_2^{2-})_3$ ($\mu_{calc} = 2.83$ B.M.)[291]. Further studies on these compounds are clearly required.

(b) Complexes

Periodato complexes $MNiIO_6 \cdot H_2O$ (M = Na, K) are formed by periodate or persulphate oxidation of nickel (II) salts in the presence of the appropriate ions[232,233,359,360]. They have magnetic moments of ~ 1 B.M. instead of the expected diamagnetism, which may be due to impurities or some decomposition. The structures of both salts have been determined from their X-ray powder patterns[361,362] with Ni—O = 2.1 Å.

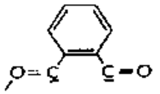
Barium[258A,363] and ammonium[363,364] 9-molybdonickelates (IV) are formed as black diamagnetic crystals by persulphate oxidation of $NiSO_4$—ammonium molybdate solutions, followed by precipitation (Ba). Similar 12-niobonickelates (IV) — $K_8Na_4NiNb_{12}O_{38} \cdot 21H_2O$ and $Na_{12}NiNb_{12}O_{38} \cdot 48-50H_2O$ (ref. 365) and a 13-vanadonickelate (IV) $K_7NiV_{13}O_{38} \cdot 18H_2O$ (ref. 366) can be isolated. $K_8Na_4NiNb_{12}O_{38} \cdot 21H_2O$ is isomorphous with the corresponding Mn^{IV} compound which has octahedral coordination about the manganese, produced by shared oxygen atoms from two Nb_6O_{19} groups[367].

Nyholm[368] found that concentrated nitric acid oxidised $[Ni(DAS)_2X_2]X$ to deep blue $[Ni(DAS)_2X_2]^{2+}$ (X = Cl, Br), which is effectively diamagnetic. $[Ni(DAS)_2Br_2]$ is similarly oxidised[213] by $(C_6F_5)_2TlBr$ to $[Ni(DAS)_2(C_6F_5)_2]Br_2$. The Ni^{II} complex of *cis*-edas

$[Ni(cis\text{-}edas)_2Cl_2]Cl$ can be oxidised to Ni^{IV} by nitric acid, but the product is considerably less stable than that of DAS, and partially decomposes on drying[330]. It has been reported[369] that $Ni(Et_2PCH_2CH_2PEt_2)Cl_2$ is oxidised to $Ni(Et_2PCH_2CH_2PEt_2)Cl_4$ by chlorine, but the magnetic moment of the product (3.36 B.M.) is unexpected.

Several formaldoxime complexes have been reported[370–373] of which the best known is the $Na_2[Ni(CH_2NO)_6]$. Dimethylglyoxime complexes of the types $M_2Ni(dmg)_3 \cdot xH_2O$ (refs. 374, 375) (M = K, Na) and $Ni(dmg)_2Br_2$ (ref. 313) have been claimed. In view of the new evidence[314] on the nature of the "Ni^{III}" analogue of the latter, this complex must be regarded as doubtful. The dark red $M_2[Ni(dmg)_3]$ complexes seem rather better established; they are diamagnetic, as expected for an octahedral $Ni^{IV}N_6$ system[374,375]. Hartkamp[376] reported that aqueous alkaline solutions of nickel (II) salts mixed with 2,6-diacetylpyridine dioxime ($dapdH_2$) were oxidised by air, and by a variety of oxidising agents—however, no complex was isolated. Subsequently Baucom and Drago[377] succeeded in isolating $Ni(dapd)_2$ as violet needles by persulphate oxidation of a mixture of $NiCl_2$ and the ligand in aqueous ammonia. The product is indefinitely stable in solution and as a solid.

A number of novel nickel (IV) species have been characterised. Bailey et al.[378] X-rayed the black diamagnetic product formed from $Ni(CO)_4$ and *o*-di-iodobenzene; which proved to be *catena*- [μ-(*o*-phthaloyl-*C*,*C*′,*O*)] -μ-iodi-iodonickel (IV), which contains I, each nickel being bonded to one ligand I through both carbons, to a second molecule of (I) through an oxygen, and to one terminal and two bridging iodides. Wilson et al.[350] reported that the Ni^{III} ion, $Ni(\pi\text{-}C_5H_5)_2^+$, can be oxidised voltametrically at −40°C to an unstable Ni^{IV} species. Replacement of the cyclopentadienyl groups by carborane derivatives produces much more stable complexes[349,350,379,390] – $[Ni(CH_{13}B_{10}N)_2]$, $[Ni(C_2H_{11}B_9)_2]$, and $Cs_2[Ni(CH_{11}B_{10})_2]$, which are believed to contain the nickel "sandwiched" between two carborane moieties, similar to those found in the cobalt complexes[381].



I

Hieber and Bruck[382] characterised the violet product formed from nickel (II) dithiobenzoate and sulphur as $[Ni(S_2CPh)_2S]_2$, containing Ni^{IV}. Extensive studies of this complex and other sulphur-rich nickel dithioacid complexes by Fackler et al.[383–386] showed that they contain planar Ni^{II} and a disulphide linkage, i.e. the sulphur has inserted into one of the Ni–S bonds. Oxidation with bromine or iodine produces similar species. However, Brinkhoff et al.[387] found that bromine oxidation of bis(*N*, *N*-di-*n*-butyldithiocarbamato nickel (II) produced $Ni(Bu_2dtc)_3Br$, a 1 : 1 electrolyte. Fackler and co-workers[388] X-rayed the product and found the nickel to be coordinated to three "normal" dithiocarbamate ligands with Ni–S = 2.26 Å. A selenium analogue $[Ni(Et_2NCSe_2)_3]Br$ (apparently the "$Ni(Et_2NCSe_2)_2Br_2$"[389] is really this complex) has been obtained[387,390]. Further studies on the dithiocarbamate complexes have confirmed the $Ni^{IV}S_6$ grouping[391,392].

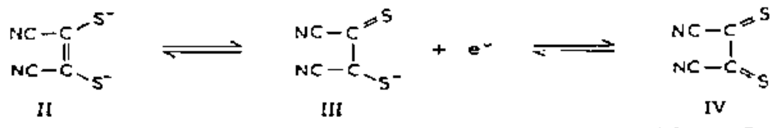
The neutral nickel dithiolates $Ni(S_2C_2R_2)$ (refs. 341, 342, 393, 394) could be described as nickel (IV) complexes of the dianions $(S_2C_2R_2)^{2-}$, although this is a somewhat naïve formulation. Similar status can be accorded to the related $[NiO_4]^-$, $[Ni(NH)_4]^0$, and $[NiN_2S_2]^0$ moieties[343–345].

E. OXIDATION STATES AND BONDING

For the majority of inorganic compounds the assignment of formal oxidation states to the various atoms is straightforward[395] and has been generally adopted as a convenient classification. However, the term oxidation state has come to mean a great deal more than just a convenient kind of chemical book-keeping; a particular oxidation state of an element has certain properties associated with it – characteristic magnetic and spectroscopic properties, an oxidising or reducing nature. All these are related to the electronic state of the element; when one says that $[Fe(DAS)_2Cl_2]^{2+}$ contains Fe^{IV}, one is stating that to a first approximation the ground state configuration of the iron is $[Ar]\,3d^4$ (although not of course going to the absurd extreme of suggesting that Fe^{4+} ions are present). As explained in the Introduction this article has been organised on the basis of formal oxidation states. In this section we take the matter further in examining the evidence in a number of cases, for the best description of the electronic state of the metal. Almost all of the work discussed has been performed upon formally nickel (III) complexes, although most of the conclusions are obviously pertinent to the chemistry of the other oxidation states covered.

Nickel (III) has the ground state electronic configuration $[Ar]\,3d^7$ and in either of the common stereochemistries (octahedral or square planar) is expected to exhibit low-spin behaviour with magnetic moments corresponding to one unpaired electron. In the past most claims for nickel (III) complexes have been supported by bulk susceptibility measurements. However, such measurements do not provide complete information about the electronic structure; in particular they do not specify where the unpaired electron resides – it could be in an orbital of predominantly metallic character, in which case the nickel (III) description is justified, or it could be localised upon the ligands, making a Ni^{II}-stabilised cation radical ligand description more realistic. Only detailed ESR spectral studies will distinguish between these possibilities.

For complexes with oxide and fluoride donors – simple and complex oxides and fluorides in heteropolyanions and periodato and tellurato complexes – the description of the bonding and electronic structure in terms of nickel (III), cobalt (IV), etc, corresponding to the formal oxidation state presents no problems. It is the complexes of conjugated bidentate sulphur ligands which have created the greatest difficulties. For example the complexes produced by reaction of metal salts with sodium maleonitriledithiolate $Na_2S_2C_2(CN)_2$ (Na_2MNT) could contain the dianion II, the dithioketone IV, or some intermediate form III – all related by addition or removal of electrons.


II III IV

For $Ni[MNT]_2^{x-}$ it is possible to prepare compounds with $x = 0, -1, -2$ by suitable chemical or polarographic oxidation or reduction. For $x = -2$, there is general agreement that a nickel (II) S_4 chromophore is present[45], but the other two complexes have been variously described[340,342,396] as $[Ni^{III}(MNT)_2^{4-}]^-$ and $[Ni^{IV}(MNT)_2^{4-}]$, or as $[Ni^{II}(MNT)_2^{3-}]^-$ and $[Ni^{II}(MNT)_2^{2-}]$. Similar complexes where the donors may be S_2N_2, O_4, $(NH)_4$, S_2O_2, or Se_4 have been described[45]. The presence of a five-membered delocalised chelate ring appears to be a required characteristic. In the formally nickel (III) complexes extensive ESR spectral studies have been performed in an attempt to locate the position(s) of the unpaired electron (see refs. 45, 343 and references therein). Although the results have been given different interpretation by different workers, there is general agreement that extensive delocalisation of the odd electron onto the ligands has occurred. It seems that both the nickel (III) and the nickel (II) radical ligand description are somewhat extreme and that one or the other may be the best description in a particular case. However, a recent preliminary account of some X-ray photoelectron spectroscopic studies on the Ni–MNT complexes has shown that the nickel binding energies change little on going from $x = 0 \rightarrow -1 \rightarrow \rightarrow -2$, and, moreover, the values are similar to those found in nickel(0) compounds[397]. This problem is clearly still open.

A further complication in this area of chemistry is the possibility that a ligand which may exhibit cation-stabilised radical behaviour in some complexes may behave as a perfectly "innocent" ligand in others. The tris-MNT complexes[46,47] of $\mathrm{Fe^{IV}}$ and Co^{III} have been less studied, although there is Mössbauer evidence which suggests that on going from $[\mathrm{Fe(MNT)_3}]^{2-}$ to $[\mathrm{Fe(MNT)_3}]^{3-}$ the added electron enters an orbital which is of predominantly metallic character[48].

In contrast to the 1,2-dithiolenes, 1,1-dithiolate and dithiocarbamate ligands behave as innocent ligands, and the assignment of $\mathrm{Fe^{IV}}$ in $[\mathrm{Fe(Et_2NCS_2)_3}]^+$ (ref. 52), or of $\mathrm{Ni^{IV}}$ in $[\mathrm{Ni(Bu_2NCS_2)_3}]\,\mathrm{Br}$ (ref. 387), seems to be acceptable on structural, spectroscopic and chemical grounds. Ligands such as the nitrogen macrocycles[304–307], biuret[309] and amines[297–303] which, being saturated, are incapable of accommodating extra electrons also seem to produce little doubt about the oxidation state of the metal. ESR evidence for d^7 $\mathrm{Ni^{III}}$ electronic states in macrocycles[307] and in ethylenediamine and propylenediamine[302,303] complexes has been reported.

The behaviour Group VB donor ligands have so far produced many fewer problems than their Group VIB analogues. Van Hecke and Horrocks[324] observed ESR signals for polycrystalline samples of $\mathrm{Ni(Ph_2PCH_2CH_2CH_2PPh_2)Br_3}$, but could not resolve the expected anisotropy, whilst Meek et al.[322] observed no ESR signal at all from $\mathrm{Ni(PPhMe_2)_2Br_3}$. There are conflicting reports for $[\mathrm{Ni(DAS)_2Cl_2}]^+$. Kreisman et al.[327] observed $^{75}\mathrm{As}$ hyperfine splitting in the ESR spectrum of this complex, which was very similar to that of the irradiated free ligand $[\mathrm{DAS}^+]$, and concluded that extensive delocalisation of the unpaired electron occurred. Manoharan and Rogers[398] disagreed with this interpretation and proposed an ^2A_g ground state with the odd electron largely in a d_z^2 orbital on the $\mathrm{Ni^{III}}$. In a further paper Gray and co-workers[328] reported the single-crystal ESR spectra of $[\mathrm{Ni(DAS)_2Cl_2}]\mathrm{ClO_4}$ in the corresponding $\mathrm{Co^{III}}$ host, and concluded that the odd electron was in a molecular orbital delocalised over the metal and the $\mathrm{As_4Cl_2}$ donors. Studies on related complexes would obviously be of great interest.

Finally, mention must be made of two stimulating papers by Drago and Baucom[315,377] in which they discuss the factors which stabilise the $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ oxime complexes, the preparations of which are described. The model proposed suggests that strong σ donor properties and a strong spherical component of the ligand field are important ligand characteristics for the stabilisation of $\mathrm{Ni^{IV}}$.

In conclusion, it is a clear that much work remains to be done in this area, both in synthesis and characterisation of new complexes, and in the detailed structural and spectroscopic reexamination of the known complexes.

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