The Reaction of Cobalt(III) β-Ketoenolates with Trifluoroacetic Acid†

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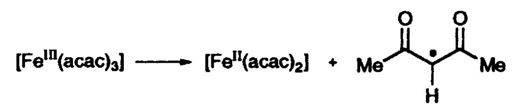
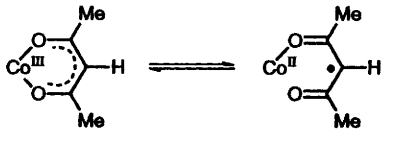
The reaction of cobalt(III) β-ketoenolates with trifluoroacetic acid (tfa) results in a ligand-to-metal electron-transfer process with the formation of radical species which have been detected and characterized by ESR spectroscopy. Depending upon the structure of the β-ketoenolate ligand, the spin delocalization varies markedly, so that the radicals can be described as cationic derivatives of cobalt(III) containing a cobalt-bonded β-ketoenolyl radical, or as cationic β-ketoenolates of cobalt(IV). The formation of these radicals was accompanied by mononuclear high-spin cobalt(II) derivatives whose ESR spectra became observable at temperatures below 50 K. Some aspects of the chemistry behind the reaction of tris(acetylacetonato)cobalt(III) with tfa are understood through UV/VIS, IR, ESR and ion spray mass spectrometry studies. On the basis of these as well as of an ESR study of the reaction of tris(3-nitropentane-2,4-dionato)cobalt(III) with oxidants such as CoF_3, $AgBF_4$, $Tl(OCOCF_3)_3$ and tetracyanoethylene, a possible route to the radicals observed is discussed.

The formation of free radicals as a consequence of an intramolecular β-ketoenolate-to-metal electron transfer was first proposed in 1962 as a key step in the destructive autoxidation of tris(acetylacetonato)iron(III) [equation (1)].[1]



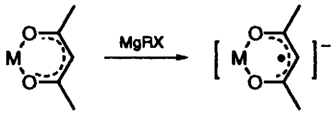
(1)

Some years later Budnik and Kochi[2] suggested that tris(acetylacetonato)cobalt(III) could undergo a reversible reductive fission and then produce cobalt(II)-bonded acetylacetonyl radicals which could be responsible for the initiation of the radical-chain cobalt-assisted epoxidation of olefins with dioxygen [equation (2)].[2] More recently, cerium(III)-co-ordinated β-ketoenolyl radicals have been proposed as intermediate species in the synthesis of alkoxycarbonylfurans by the cerium(IV) ammonium nitrate-promoted oxidative addition of 1,3-dicarbonyl compounds to vinyl acetate.[3]



(2)

Even though the behaviour of transition-metal β-ketoenolates in chemically[4,5] or electrochemically promoted[6] redox reactions has been studied extensively, no experimental evidence for the formation of free radicals as a consequence of a one-electron oxidation has been reported in the literature so far. Instead, in 1976 Kwan and Kochi[7] succeeded in detecting by ESR spectroscopy a number of radical dianions of β-diketones derived from the one-electron reduction of a number of transition-metal β-ketoenolates by organomagnesium bromides [equation (3)].[7]



(3)

During work concerning the oxidation of alkanes with dioxygen in trifluoroacetic acid (tfa), in the presence of cobalt(III) or ruthenium(III) β-ketoenolates as catalyst precursors,[8] we started some experiments aimed at throwing light on the mechanism of these reactions, and, among other things, we tried to detect by ESR spectroscopy some of the proposed radical species which could derive from the oxidation of the reacting alkane. We did not succeed in this, but discovered that the interaction of tris(β-ketoenolato)cobalt(III) complexes with tfa under a pure argon atmosphere may result in the formation of a variety of radical species as a result of a one-electron oxidation of the starting β-ketoenolato complex. The work we report here, of which preliminary results have already been communicated briefly,[9,10] is a part of a more extensive study on this unprecedented reaction.

Results and Discussion

Reaction of Tris(acetylacetonato)cobalt(III) **1** *with tfa*.—When compound **1** or a CH_2Cl_2 solution of **1** is treated with tfa at room temperature under a pure argon atmosphere, the resulting green mixture turns gradually red-brown but remains clear and organoleptically homogeneous. Monitoring these mixtures by UV/VIS spectroscopy shows that the absorbance of a band at 591 nm, due to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition of cobalt(III),[11] decreases and, after 19 h, the spectrum (500–700 nm) is similar to that shown by a tfa solution of bis(acetylacetonato)cobalt(II) (Fig. 1). Accordingly, the ESR spectrum, at 4.6 K, of the red-

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† Radical Species from Transition-metal Complexes. Part 1.
Non-SI unit employed: G = 10^{-4} T.

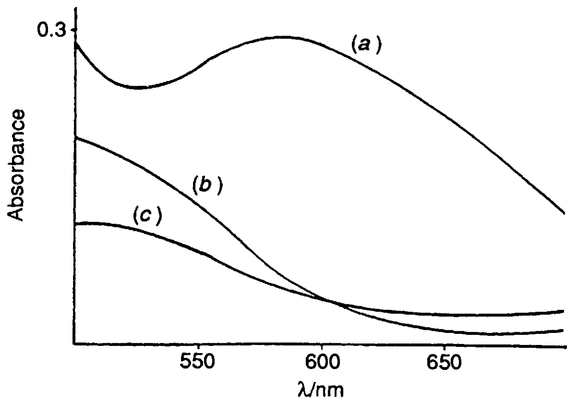
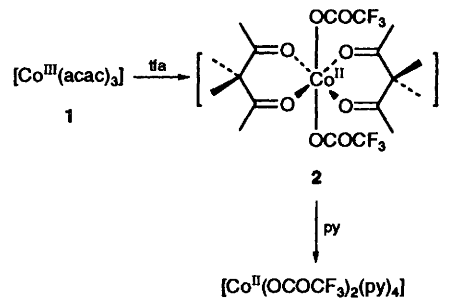


Fig. 1 Visible spectrum of a 5×10^{-2} mol dm^{-3} tfa solution of complex **1**: (*a*) immediately after the preparation of the solution; (*b*) after 19 h; (*c*) visible spectrum of a 5×10^{-2} mol dm^{-3} tfa solution of bis(acetylacetonato)cobalt(II)

brown mixture obtained by reacting **1** with tfa is attributed ($g_\perp = 4.16$, $g_\parallel = 2.30$) (Fig. 2) to a high-spin cobalt(II) complex having a distorted-octahedral geometry.[12] The numerical integrated area of the ESR pattern accounts for more than 98% of the starting cobalt centres, thus showing that at the end of the reaction practically all of these are present as cobalt(II).

Attempts to characterize fully this compound failed. However, we propose structure **2**, characterized by the presence of two easily removable cobalt-bonded acetylacetone molecules, since treatment with pyridine (py) of the oily product obtained from the reaction of **1** with tfa gives rise to pink tetrakis(pyridine)bis(trifluoroacetato)cobalt(II), at room temperature [equation (4)].[13]



(4)

While these observations show that the reduction of cobalt(III) centres occurs, questions arise as to the nature of the oxidation products as well as the role played by tfa in promoting the reaction, and, finally, the mechanism of the electron transfer. Some answers result from an ESR study of the reaction. Indeed, by carrying out the reaction between pure tfa or 1:1, 5:1 or 10:1 (v/v) CH_2Cl_2–tfa mixtures with **1** in the cavity of an ESR spectrometer, some radical species are formed at temperatures ranging from 0 to 40 °C, as indicated by the appearance of a signal whose intensity is proportional to the concentration of tfa. The mean lifetime of these radicals is around 3 min, at 0 °C, in the case of 10^{-2} mol dm^{-3} solutions of **1**. If dioxygen is allowed to interact with these mixtures, the ESR signal is quenched immediately.

Two ESR spectra having different patterns, both centred at $g_{iso} = 2.0036$, can be observed, depending upon the concentration of the cobalt complex. At concentrations of complex **1** higher than 0.5 mol dm^{-3}, the mixtures exhibit a broad one-line ($\Delta H_{pp} = 6.5$ G) spectrum, which is most probably due to the formation of aggregates as a consequence of π interactions of the radical species with neutral compounds.[14] At concentrations of complex **1** as high as 0.1 mol dm^{-3} and by bringing **1** and tfa into contact gradually, a two-line pattern is observed (whose numerical integrated area accounts for a radical concentration of *ca.* 0.5% of the total starting cobalt content) due to a 18.8 G splitting by one proton (Fig. 3), which clearly shows that a significant decrease in amplitude occurs during the acquisition. This spectrum is attributed to an acetylacetonyl radical skeleton having almost total spin delocalization on the intercarbonylic position.

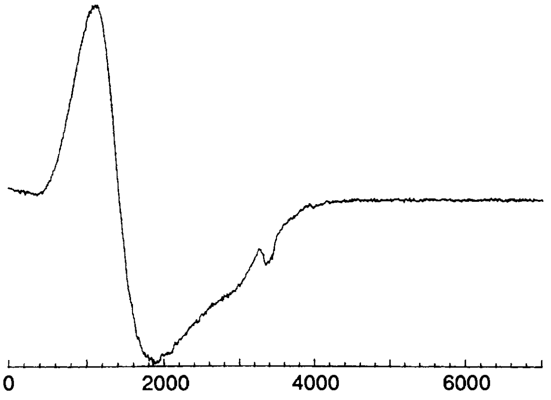


Fig. 2 The ESR spectrum (4.6 K) of a 0.1 mol dm^{-3} solution of complex **1** in tfa, kept at room temperature for 19 h

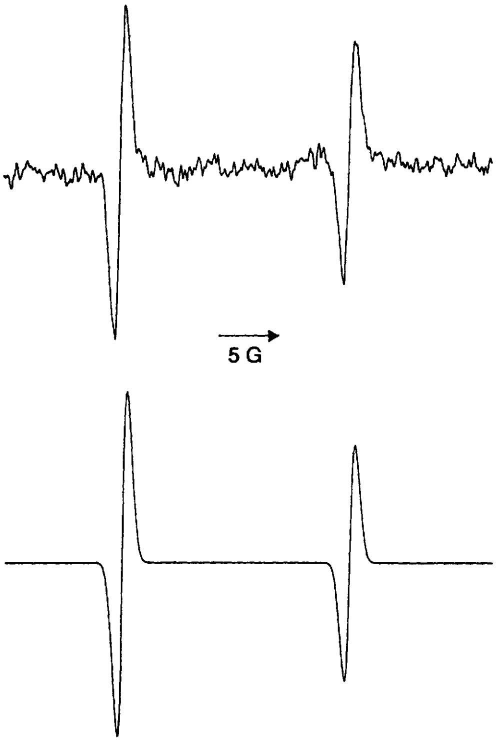
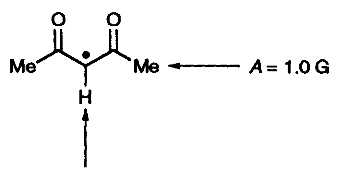
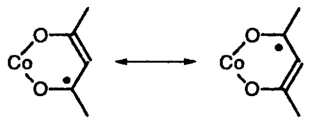


Fig. 3 Experimental (upper) and simulated (lower) first-derivative X-band ESR spectrum of the radicals derived from the reaction of complex **1** with tfa

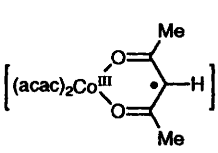
Ab initio calculations have been performed on the acetylacetonyl radicals itself.[15] Interestingly, the hyperfine coupling constants calculated at the UMP2 level are remarkably close to the values we have found for the acetylacetonyl radical (see below).



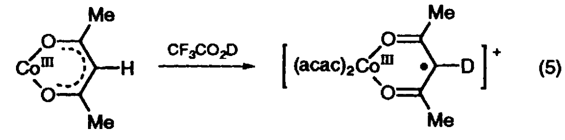
The spin-density distribution is inverted in the case of the cobalt-bonded radical dianion of acetylacetone that exhibits an ESR spectrum consisting of a septet (13 G) of doublets (2.79 G).[7] Since the doublet splitting is due to the intercarbonyl proton, the spin delocalization is higher on the oxygen-bonded carbon atoms in accordance with what can be predicted at least on the basis of the resonance canonical limiting formulae shown below.



None of the ESR spectra reported above shows hyperfine splitting by the metal. Even though this could be indicative of small, if any, bonding interactions of the radicals detected with cobalt centres, it must also be pointed out that in the ESR spectra of the cobalt-bonded radical dianion of acetylacetone no hyperfine splitting by the metal was detected.[7] It could be that, in such ligands, the oxygen atoms insulate the electronic system of the carbon skeleton from the metal orbitals to a rather large extent, as suggested for some carbon-centred radicals bonded to cobalt by a carboxylate group.[16] Therefore, since it is not so unusual that the spectra of transition metal-radical complexes show no or weak coupling to the metal,[17] in the absence of further evidence we do not discard the possibility of regarding the above-mentioned radicals as cobalt(III)-bonded species arising from a one-electron oxidation of the starting tris(acetylacetonato)cobalt(III) (see below).



When complex **1** is treated with deuteriated trifluoroacetic acid (99.5 atom% D) [equation (5)] the ESR spectrum (g_{iso} = 2.0036) (Fig. 4) of the resulting radicals shows only a well resolved deuterium triplet with a 2.88 G splitting, which is equivalent to the above 18.8 G splitting reduced by the factor $g_D/g_H = 0.1531$;[18] *vice versa*, the treatment of [Co^{III}($^2H_7$acac)$_3$] **3** (91 atom% D) with undeuteriated tfa results in the exclusive formation of the acetylacetonyl radicals undeuteriated in the intercarbonyl position [equation (6)] and thus exhibits the two-line ESR spectrum reported above (Fig. 3).



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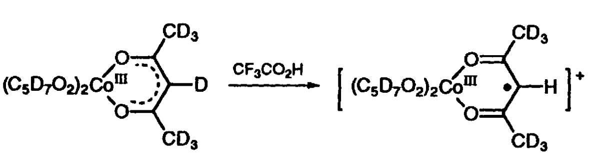
(5)



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(6)

Interestingly, these findings indicate that the electron-transfer process which gives rise to the radicals implies a very fast H/D exchange process, perhaps through a mechanism whereby the formation of the radicals observed is statistically correlated to the excess of isotopically labelled acid.

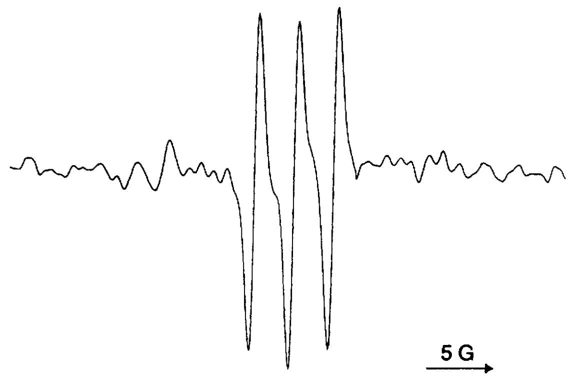
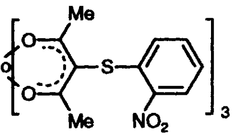


Fig. 4 Experimental first-derivative X-band ESR spectrum of the radicals derived from the reaction of complex **1** with deuteriated trifluoroacetic acid



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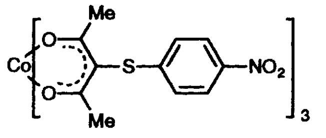


5

Radical Species from Tris[3-(2-*nitrophenylsulfanyl*)*pentane*-2,4-*dionato*]*cobalt*(III) **4**, *Tris*[3-(4-*nitrophenylsulfanyl*)*pentane*-2,4-*dionato*]*cobalt*(III) **5** *and Tris*(3-*nitropentane*-2,4-*dionato*)-*cobalt*(III) **6**.—We have found that, at least in two cases, *i.e.* the radical species arising from the reactions of complexes **4** and **5** with tfa, the ESR spectra, having g_{iso} = 2.0078 and 2.0094 respectively, show the characteristic patterns of eight hyperfine lines (ΔH_{pp} = 3 G) $A_{iso}(^{59}Co)$ = 5.2 and 5.8 G respectively, due to the interaction of the unpaired electron with one cobalt nucleus ($I = \frac{7}{2}$). As they are almost identical, only one of the spectra is reported here (Fig. 5). Integration of the ESR pattern accounts for a radical species concentration of about 0.5 and 1% of the starting cobalt content in **4** and **5**, respectively.

As an alternative plausible explanation, spin delocalization could be confined to within the skeleton of the β-ketoenolate ligand only, thereby assigning the hyperfine splitting to the hydrogen nuclei. However, while the spectrum of the radicals derived from complex **4** can be computer-simulated satisfactorily by assigning the hyperfine splittings to three magnetically non-equivalent phenyl protons, although by using an unusual[18] set of aromatic proton–electron spin coupling constants (A_H = 20.8, $A_{H'}$ = 10.6 and $A_{H''}$ = 5.3 G), the spectrum of the radicals derived from complex **5**, whose phenyl groups contain only two non-equivalent sets of protons, cannot be simulated just by electron spin–proton interactions only.

On this basis as well as on the literature reports concerning ESR studies of the oxidized forms of cobalt(III) complexes,[19] the radical species arising from **4** and **5** can be described as low-spin tris(β-ketoenolato)cobalt(IV) cationic complexes. These species are formed rapidly, even at −10 °C, by the reaction of a 1 : 1 CH_2Cl_2–tfa mixture with **4** or **5**, and are amongst the most stable radicals we have intercepted, their lifetimes being quite high (up to 4 h, depending upon solution concentration) at 20 °C.

These observations strongly support the idea of regarding all the intercepted radicals as cobalt-bonded species. Moreover, the β-ketoenolyl radicals arising from the reaction of tfa with tris(3-nitropentane-2,4-dionato)cobalt(III), [CoIII(nacac)$_3$] **6**, containing small amounts of partially nitrated complexes (see below), exhibit the same ESR and ^{14}N ENDOR (electron nuclear double resonance) spectra[9] as those shown by the radicals produced by a one-electron oxidation of complex **6** under non-protolytic conditions (Scheme 1).

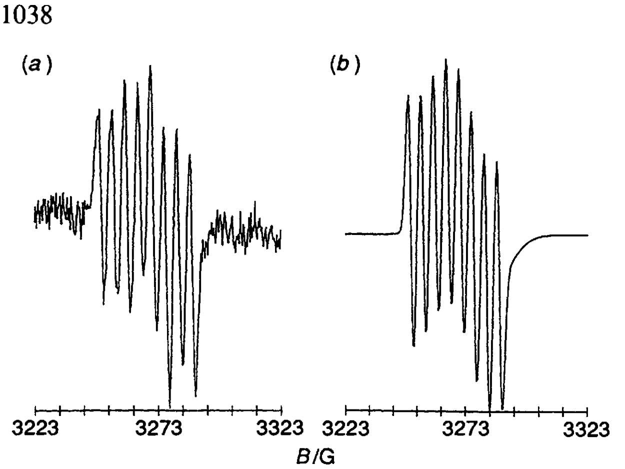
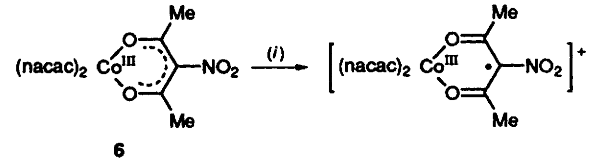


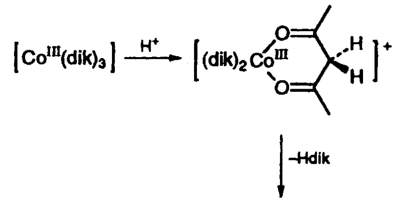
Fig. 5 Experimental (*a*) and simulated (*b*) first-derivative X-band ESR spectra of the radicals derived from the reaction of complex **4** with tfa



6

Scheme 1 (*i*) CH_2Cl_2, 20 °C; CoF_3, $Tl(OCOCF_3)_3$, $AgBF_4$ or tcne

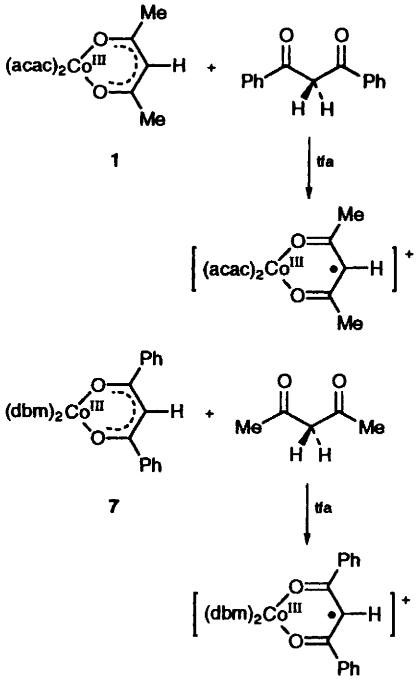
The Reaction Mechanism.—The reactions outlined in Scheme 1 mimic the oxidation pathway that could be operating in the reaction of tris(β-ketoenolato)cobalt(III) complexes with tfa, in the sense that also in this case the radicals could arise from an intermolecular ligand-to-metal electron transfer. In this connection, the role of tfa could be that of causing the formation of some cationic highly oxidant cobalt(III) centres[20] by the gradual removal of β-ketoenolate ligands (dik), as β-ketoenol (Hdik) from the cobalt(III) co-ordination sphere of the starting complexes [equation (7)].[21]



(7)

This has been substantiated by an IR and ion spray mass spectrometry (ISMS) study of the reaction of tris(acetylacetonato)cobalt(III) **1** with tfa. Thus, by following the intensity of the IR band centred at 1613 cm^{-1}, due to the enolic structure of acetylacetone,[22] it was established that almost 1.5 mol of acac is lost per mol of starting complex, in 6 h at 20 °C. On the other hand, a MS study[23] of methanolic solutions of **1** shows that, under ion spray ionization conditions,[24] the quasi-molecular ion is present if the orifice voltage is set at 30–50 V. Indeed, the spectrum shows peaks due to $[M + H]^+$ (m/z 357), $[M + NH_4]^+$ (374), $[M + Na]^+$ (379) and $[M + K]^+$ (395) adduct ions [Fig. 6(*a*)]. The daughter-ion mass spectrum of the $[M + H]^+$ adduct shows an intense peak at m/z = 257 corresponding to the $[Co(acac)_2]^+$ ion resulting from the loss of acac by the parent ion [Fig. 6(*b*)]. This process takes place even in the source as indicated by the presence of a small peak at m/z = 257 in the IS single-mass spectrum of complex **1** [Fig. 6(*a*)]. However, this phenomenon can be enhanced by increasing the orifice voltage which favours ion fragmentation, as shown clearly by the IS mass spectrum of **1** obtained at 65 V [Fig. 6(*c*)].

In order to test the hypothesis of a two-step process in which ligands are first removed from the metal by the action of acid and then oxidized by cobalt(III) cationic centres, tfa-promoted electron-transfer cross experiments were carried out on some tris(β-ketoenolato)cobalt(III) complexes in the presence of equimolar amounts of β-ketoenols different from those in the complexes themselves. These reactions [equations (8) and (9); dbm = dibenzoylmethanate] resulted unequivocally in the ESR detection of only those radicals derived from the starting cobalt-bonded β-ketoenolate (the ESR spectrum of the radicals arising from complex **7** has already been reported[9]), thus showing that the oxidation takes place on a cobalt-bonded ligand.



(8)

(9)

Therefore, on the basis of all the observations above we propose that the electron-transfer step takes place according to equation (10). Accordingly, we find that if a CH_2Cl_2-tfa

$$[Co^{III}(dik)_3] + [Co^{III}(dik)_2]^+ \longrightarrow [Co^{III}(dik)_3]^{\cdot +} + [Co^{II}(dik)_2] \quad (10)$$

solution of tris[3-(2-nitrophenylsulfanyl)pentane-2,4-dionato]-cobalt(III) **4** is cooled to 10 K as soon as detectable amounts of radicals are formed at 274 K, an ESR spectrum is obtained (Fig. 7) which can be superimposed on that of Fig. 5 and another ($g_\perp$ = 4.62, $g_\parallel$ = 2.38) attributed, as above, to a high-spin mononuclear derivative of cobalt(II) having a distorted-octahedral geometry.[12] This indicates unambiguously that the formation of radicals implies the reduction of some cobalt(III) centres to cobalt(II) derivatives. When the mixture is allowed to warm from 10 to 315 K, is kept at this temperature until the ESR signal due to the cobalt(IV) species disappears, and then cooled to 10 K, only the ESR spectrum of cobalt(II) is observed. Since the numerical integrated area of this spectrum accounts for more than 99% of the starting cobalt centres, we must conclude that the decay of the cobalt(IV) species results eventually in some thermally stable cobalt(II) species.

On the basis of the above findings, one should conclude that the more favoured is the protonation of the starting β-ketoenolate ligand, the more favoured should be the formation of radical species, *i.e.* the oxidation step. Indeed, even though rigorous quantitative kinetic data are still lacking, the presence of electron-withdrawing substituents on the β-ketoenolate ligand reflects unfavourably on the reaction: in the case of tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)cobalt(III) it is

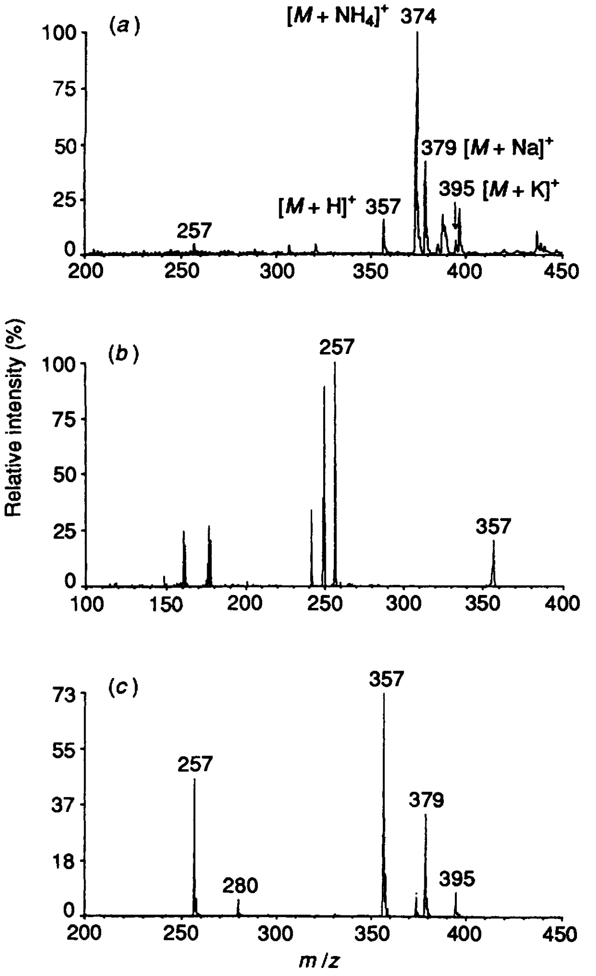


Fig. 6 (*a*) The IS mass MS spectrum of a methanolic solution of complex **1**, at 35 V; (*b*) daughter-ion spectrum of the $[M + H]^+$ adduct; (*c*) IS mass spectrum of a methanolic solution of complex **1** at 65 V

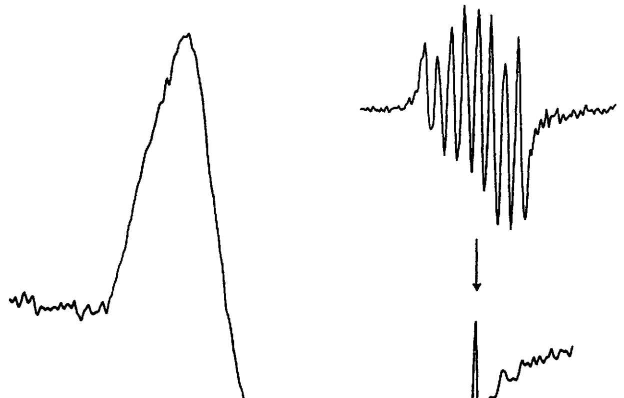


Fig. 7 First-derivative X-band ESR spectrum (10 K) of the radical species derived from the reaction of complex **4** with tfa

necessary to warm the complex–TFA mixture up to 110 °C for a few seconds in order to start the reaction which then results in the appearance of a one-line ($\Delta H_{pp} = 3$ G) ESR spectrum ($g_{iso} = 2.0036$). Moreover, tris(3-nitropentane-2,4-dionato)-complex(III) does not react at all with tfa, unless, as mentioned above, it contains small amounts of (3-nitropentane-2,4-dionato)bis(pentane-2,4-dionato)cobalt(III) or bis(3-nitropentane-2,4-dionato)(pentane-2,4-dionato)cobalt(III), both these complexes being very reactive towards tfa even at 0 °C as indicated by the rapid appearance of the ESR spectrum due to the one-electron oxidation of the 3-nitropentane-2,4-dionate ligand.[9] This can easily be explained by assuming that the oxidant cobalt(III) species are produced by the protonation of pentane-2,4-dionate which is much more susceptible to electrophilic attack than 3-nitropentane-2,4-dionate.[25]

Conclusion

Cobalt(III) β-ketoenolates, as a consequence of their interaction with trifluoroacetic acid, may undergo a redox reaction which results in the formation of a number of so far unknown radicals (oxidized species) and cobalt(II) derivatives (reduced species). The radicals, according to their well resolved ESR spectra, can be described as cationic cobalt(III) complexes containing β-ketoenolyl radical in the co-ordination sphere of the metal, or as cationic cobalt(IV) β-ketoenolates, depending upon the structure of the β-ketoenolate ligand; on the other hand, the cobalt(II) derivatives are best described as mononuclear octahedral high-spin complexes. It has been demonstrated that cobalt(III) β-ketoenolates are easily protoned under very mild conditions, this being the prerequisite for the formation of cationic cobalt(III) species which can oxidize the starting tris(β-ketoenolato)cobalt(III) complex, thus giving rise to the radicals observed.

As a final comment we would like to point out that the tfa-promoted electron-transfer reaction of tris(β-ketoenolato)-cobalt(III) complexes discussed here resembles that shown below, which was discovered and studied by McKellar and West[4] several years ago.

$$[^{59}\mathrm{Co^{III}(acac)_3}] + [^{60}\mathrm{Co^{II}(acac)_2}] \longrightarrow [^{59}\mathrm{Co^{II}(acac)_2}] + [^{60}\mathrm{Co^{III}(acac)_3}]$$

Experimental

Materials.—Tris(acetylacetonato)cobalt(III) **1**,[26] $[\mathrm{Co^{III}}(^2\mathrm{H_7acac})_3]$ **3**,[26,27] tris[3-(2-nitrophenylsulfanyl)pentane-2,4-dionato]cobalt(III) **4**,[28] tris[3-(4-nitrophenylsulfanyl)pentane-2,4-dionato]cobalt(III) **5**,[29] tris(3-nitropentane-2,4-dionato)-cobalt(III) **6**,[30] tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-cobalt(III),[31] tris(dibenzolymethanato)cobalt(III) **7**[32] and perdeuterioacetylacetone (91.0 atom% D)[27] were prepared according to published procedures. Trifluoroacetic acid, deuteriated trifluoroacetic acid (99.5 atom% D), and dichloromethane were spectrophotometric grade (Aldrich) and were obtained dioxygen free by steam distillation at room temperature by using a pure argon flux and collecting the distillate into a Schlenk tube maintained at −78 °C. Cobalt(III) fluoride, thallium(III) trifluoroacetate, silver tetrafluoroborate and tetracyanoethylene (tcne) (Aldrich) were used as received and were stored under a dry argon atmosphere.

Preparation of (3-*Nitropentane*-2,4-*dionato*)*bis*(*pentane*-2,4-*dionato*)*cobalt*(III) *and Bis*(3-*nitropentane*-2,4-*dionato*)(*pentane*-2,4-*dionato*)*cobalt*(III).—Analogous to the preparation of tris(3-nitropentane-2,4-dionato)cobalt(III),[33] a mixture of $\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$ (0.72 g, 3 mmol) and acetic anhydride (20 cm^3) was stirred at 0 °C for 45 min. Tris(acetylacetonato)cobalt(III) (1.07 g, 3 mmol) was then added. The mixture was stirred for 4 h at 0 °C, for a further 1 h at room temperature and then poured at once into a beaker containing a solution of sodium acetate (12 g) in water (250 cm^3). The suspension so obtained was stirred for 1 h and then filtered. The residue was dissolved in chloroform (*ca.* 20 cm^3) and the filtrate washed with chloroform (3 × 15 cm^3). All the chloroform solutions collected were washed with a 5% aqueous sodium acetate solution (2 × 50 cm^3), then with water (1 × 100 cm^3), and, finally dried over anhydrous Na_2SO_4. The green solution was concentrated to 20 cm^3 by evaporation of the solvent under reduced pressure and then chromatographed over a column (outside diameter, 20 mm; length, 400 mm) packed with Silica Gel 60 (70–230 mesh) (Merck), using benzene–dichloromethane (1:5 v/v) as eluent. From the first band eluted, 0.58 g of green microcrystalline bis(3-nitropentane-2,4- dionato)(pentane-2,4-dionato)cobalt(III) (1.3 mmol, 43%) was obtained, m.p. (decomp.) 186–189 °C (Found: C, 40.3; H, 4.30; N, 6.40. $C_{15}H_{19}CoN_2O_{10}$ requires C, 40.35; H, 4.30; N, 6.30%). ^1H NMR (200 MHz, solvent $CDCl_3$, standard $SiMe_4$): δ 2.26 (6 H, s, 2 CH_3), 2.42 (6 H, s, 2 CH_3), 2.51 (6 H, s, 2 CH_3), 5.61 (1 H, s, 1 CH). The second band, eluted with dichloromethane–ethyl acetate (20:1 v/v) gave 0.22 g of (3-nitropentane-2,4-dionato)bis(pentane-2,4-dionato)cobalt(III) 0.55 mmol, 18%), m.p. (decomp.) 167–169 °C (Found: C, 44.8; H, 5.10; N, 3.60. $C_{15}H_{20}CoNO_8$ requires C, 44.90; H, 5.00; N, 3.50%). ^1H NMR (200 MHz, solvent $CDCl_3$, standard $SiMe_4$): δ 2.17 (6 H, s, 2 CH_3), 2.25 (6 H, s, 2 CH_3), 2.43 (6 H, s, 2 CH_3), 5.56 (2 H, s, 2 CH).

Spectroscopic and Analytical Measurements.—The ESR and ENDOR spectra were recorded on a Varian E112 spectrometer equipped with a home-built apparatus for ENDOR experiments. The temperature of the samples was controlled by a Varian E257 temperature control unit or, in the case of the spectra recorded down to 4.2 K, by an OXFORD ESR 900 cryostat. The ESR spectrometer was interfaced to an AST Premium 486/25 by means of a data-acquisition system consisting of an acquisition board capable of acquiring up to 500 000 12-bit samples per s including 32-bit add to memory thus giving on-line signal averaging[34] and a software package specially designed for ESR and ENDOR experiments.[35] The hyperfine coupling constants and linewidths were obtained by computer simulation of the ESR spectra. Proton NMR spectra were run at 200 MHz on a Varian Gemini instrument and the IR spectra were obtained with a Perkin-Elmer 983 spectrometer. Electron impact mass spectra were obtained with a VG Analytical 7070E apparatus and ion spray mass spectra with a Perkin-Elmer SCIEX API III apparatus. The UV and visible spectra were run on a Perkin-Elmer Lambda 15 spectrophotometer. Microanalyses were performed by the Laboratorio di Microanalisi dell'Istituto di Chimica Organica della Facoltà di Farmacia dell'Università di Pisa.

Reaction of Complex **1** *with tfa and Further Reaction with Pyridine: Formation of Tetrakis(pyridine)bis(trifluoroacetato)-cobalt*(II)—Complex **1** (0.25 g, 0.7 mmol) was treated with trifluoroacetic acid (5 cm^3), at room temperature under a dry argon atmosphere. After 24 h, the reaction mixture was taken to dryness by evaporation of the volatile components under reduced pressure. To the resulting reddish brown oily residue a mixture of benzene (5 cm^3) and pyridine (0.27 cm^3, 3 mmol) was added at room temperature. Within a few minutes, this caused the precipitation of a pink microcrystalline solid which was separated by filtration, washed with benzene and dried under vacuum, and identified as tatrakis-(pyridine)bis(trifluoroacetato)cobalt(II) (0.33 g, 78%).[14]

Sample Preparation for ESR or ENDOR Spectroscopy.—The reaction mixtures were prepared by placing a weighed amount of the metal complex (typically, 5 mg) into a quartz tube (external diameter, 4 mm; internal diameter, 2 mm) fitted with a quartz-Pyrex joint and a Bibby Quickfit Rotaflo Teflon tap (DISA, Milan). The tube was then attached to a vacuum line and degassed by standard vacuum/argon techniques; afterwards, it was immersed into a solid CO_2-cooled acetone bath and then charged with tfa (typically 100 μl) or a tfa solution in dichloromethane, under a pure argon atmosphere. The quartz tube was then introduced into the ESR spectrometer cavity, pre-cooled to the desired temperature, and then the reagents allowed to mix gradually. In the case of the reactions of tris-(3-nitropentane-2,4-dionato)cobalt(III) **6** with CoF_3, $Tl(O-COCF_3)_3$, $AgBF_4$ and tcne, the desired amount (typically 5 mg) of a 1:1 (molar ratio) mixture of the reactants was introduced into the ESR tube described above following the usual procedure. Afterwards, the tube was cooled to 77 K before adding dichloromethane (60–100 μl). This addition must be done as rapidly as possible in order to avoid the liquefaction of argon into the tube.

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