

Acid-promoted Formation of Radical Species from Cobalt(III) β -Ketoenolates

Pietro Diversi,^a Claudia Forte,^b Mario Franceschi,^a Giovanni Ingrosso,*^a Antonio Lucherini,^a Marco Petri^a and Calogero Pinzino*^b

^a *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy*

^b *Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, via Risorgimento 35, 56126 Pisa, Italy*

The interaction of tris(β -ketoenolato)cobalt(III) complexes with protic acids results in a ligand–metal electron transfer with the formation of a variety of β -ketoenolyl radicals that can be detected by ESR spectroscopy.

The hypothesized or demonstrated occurrence of transient ligand radicals as a consequence of a ligand–metal electron transfer is ubiquitous in the inorganic and bioinorganic chemical literature.^{1,2} However, the detection of such species is often frustrated by their short lifetime.

Here, we describe what we believe is the first observation of a ligand-to-metal electron transfer in tris(β -ketoenolato)cobalt(III) complexes **1**, that takes place when a variety of such complexes interact with trifluoroacetic acid (TFA) or with a TFA–CH₂Cl₂ mixture, or, in some cases, with acetic acid. A one-electron oxidation of the β -ketoenolato ligand by cobalt(III) thus occurs with the gradual reduction of cobalt(III) to cobalt(II), as shown by UV–VIS spectroscopy, and the formation of a variety of previously unknown radicals that can

be detected and characterized by ESR spectroscopy.[†] In almost all cases well-resolved ESR spectra are obtained in the $g = 2$ region, that are unambiguously assigned to β -ketoenolyl

[†] 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. The spectrometer has been interfaced to an AT compatible PC by means of a data-acquisition system consisting of an acquisition board capable of acquiring up to 500 000 12-bit samples/s including 32-bit add to memory thus giving on-line signal averaging⁴ and a software package specially designed for ESR and ENDOR experiments.⁵ The hyperfine coupling constants and linewidths were obtained by computer simulation of the ESR spectra.

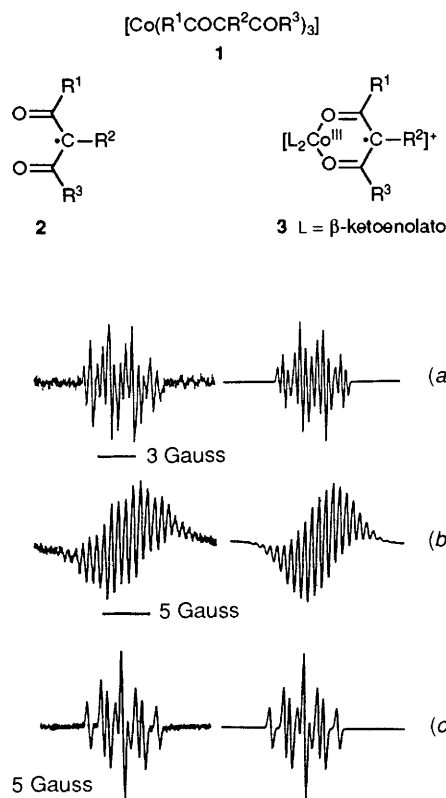


Fig. 1 Experimental (left) and computer simulated (right) first-derivative X-band ESR spectra of the radicals deriving from: (a) $\text{Co}(\text{dbm})_3$ **1** ($\text{R}^1 = \text{R}^3 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{H}$), at -30°C ; (b) $\text{Co}(\text{dbm})_3$, at -10°C ; (c) $\text{Co}(\text{tta})_3$ **1** ($\text{R}^1 = 2\text{-thienyl}$; $\text{R}^2 = \text{H}$; $\text{R}^3 = \text{CF}_3$), at -10°C

radicals; however, the lack of hyperfine splitting to the metal leaves the question whether such radicals are cobalt-free **2** or, as we are inclined to suggest, cobalt-coordinated **3**, unanswered.

The possibility of observing the phenomenon is strongly dependent on the experimental conditions adopted as well as on the structure of the β -ketoenolato ligand as a consequence of the electronic and steric effects caused by the R^1 substituents. These, indeed, influence markedly either the stability of the corresponding radicals or their ESR parameters, the spin distribution over molecular skeleton being extremely sensitive to even small structural changes, as already observed in the case of a series of dianion radicals deriving from β -diketones.³

In the case of $\text{Co}(\text{dbm})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{H}$), for instance a well resolved ESR spectrum ($g_{\text{iso}} = 2.0052$) is obtained at -30°C [Fig. 1(a)], which is consistent with a free radical exhibiting a spin delocalization confined to only one phenyl ring ($A_{\text{H}^{\text{para}}} = 1.88$; $A_{\text{H}^{\text{ortho}}} = 1.44$; $A_{\text{H}^{\text{meta}}} = 0.45$ G). At -10°C , this radical is transformed into a new one in which the spin delocalization extends over the whole ligand, as shown by its ESR spectrum centered at $g_{\text{iso}} = 2.0034$ [Fig. 1(b)].[‡] In the case of $\text{Co}(\text{tta})_3$, **1** ($\text{R}^1 = 2\text{-thienyl}$; $\text{R}^2 = \text{H}$; $\text{R}^3 = \text{CF}_3$), a spectrum centered at $g_{\text{iso}} = 2.0030$ can be observed at -10°C , which is indicative of a radical exhibiting a relatively high spin delocalization over the intercarbonylic position and the 4-carbon atom of the 2-thienyl group with similar isotropic hyperfine splittings by the corresponding protons ($A_{\text{H}} = 4.30$ G), and a lower spin delocalization over the 3- and 5-carbon atoms ($A_{\text{H}} = 3.10$ G) [Fig. 1(c)]. A radical having the same skeletal structure, but showing a different ESR pattern ($g_{\text{iso}} = 2.0075$) resulting from a different spin delocalization ($A_{\text{H}^{\text{intercarb}}} = 5.9$; $A_{\text{H}(4)} = 1.8$; $A_{\text{H}(3)} = A_{\text{H}(5)} = 1.4$ G), can be generated by interaction of $\text{Co}(\text{tta})_3$ with acetic acid, at 80°C .

[‡] As shown by computer simulation, the ESR spectrum of [Fig. 1(b)] arises from the splitting by eleven protons: two *para* protons and one intercarbonylic proton with similar coupling constants ($A_{\text{H}} = 2.29$ G), four *ortho* (*o* and *o'*) protons ($A_{\text{H}^{\text{ortho}}} = 1.53$ G), and four *meta* (*m* and *m'*) protons ($A_{\text{H}^{\text{meta}}} = 0.76$ G). If in the stable conformation of these radicals the phenyl rings were coplanar with the three-carbon skeleton, the *o* and *o'*, as well as the *m* and *m'* protons, would not be magnetically equivalent. Therefore, some magnetic or dynamic factors are operative within such radicals that are responsible for the unexpected distribution of line intensities, which is reminiscent of that observed by Kochi in the case of the dianion radical of dibenzoylmethide.³

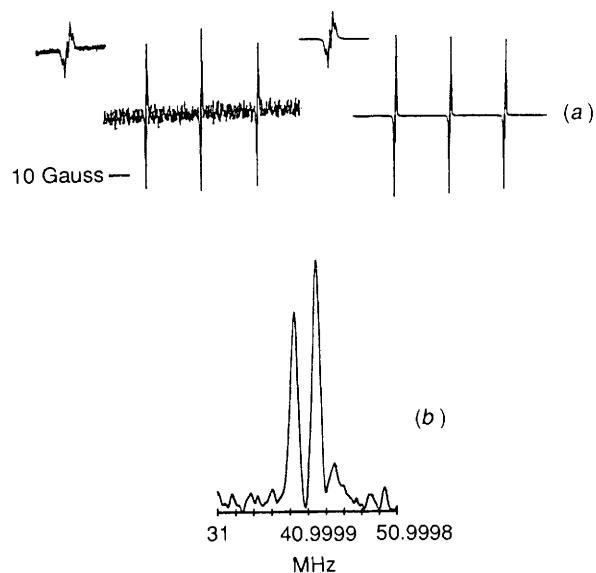


Fig. 2 Radicals deriving from $\text{Co}(\text{NO}_2\text{-acac})_3$ **1** ($\text{R}^1 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{NO}_2$): (a) experimental (left) and computer simulated (right) first-derivative X-band ESR spectra; (b) ^{14}N ENDOR spectrum

Even though rigorous quantitative data are still lacking, the results and observations available up to now give some indications on the influence exerted on the electron transfer by the electronic and steric features of the R^1 substituents. Indeed, the process seems to be favoured when electron-donor substituents are present, unless they introduce strong steric restrictions in which case they play an unfavourable role: in the presence of TFA, $\text{Co}(\text{acac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{Me}$ (acac = pentane-2,4-dione); $\text{R}^2 = \text{H}$), and $\text{Co}(\text{Meacac})_3$, **1** ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$), both undergo electron transfer at temperatures lower than 0°C , while in the case of $\text{Co}(\text{dpm})_3$ (dpm = tetramethylheptanedionato), **1** ($\text{R}^1 = \text{R}^3 = \text{Bu}^t$; $\text{R}^2 = \text{H}$), the complex-TFA mixture must be heated up to 40°C in order to cause the appearance of a broad one-line ($\Delta H_{\text{pp}} = 2.9$ G) ESR spectrum centered at $g_{\text{iso}} = 2.0036$. The ESR spectrum ($g_{\text{iso}} = 2.0044$) of the radicals deriving from $\text{Co}(\text{Meacac})_3$ consists of seven lines due to two magnetically equivalent methyl groups showing an isotropic hyperfine coupling constant of 11.1 G, given by the relationship $(1.62 + 18.76 \cos\theta)$, where $\theta = 5^\circ$ or $(5 \pm 120)^\circ$.⁶

The intense ESR spectrum of the radicals coming from $\text{Co}(\text{acac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{H}$), shows a two-line pattern, centered at $g_{\text{iso}} = 2.0036$, due to a 18.8 G splitting by the intercarbonylic proton, thus indicating an almost total spin delocalization on that position and an almost negligible hyperfine splitting by methylic protons. If deuterated trifluoroacetic acid (99.5 atom% D) is used in order to promote electron transfer in $\text{Co}(\text{acac})_3$, the ESR spectrum of the resulting radicals shows only a resolved deuterium triplet with a 2.88 G splitting; *vice versa*, the treatment of $\text{Co}(\text{H}_7\text{acac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{CD}_3$; $\text{R}^2 = \text{D}$) (91 atom% D), with undeuterated TFA results in the exclusive formation of the undeuterated acetylacetyl radical exhibiting the above reported two-line

pattern, centered at $g_{\text{iso}} = 2.0036$, due to a 18.8 G splitting by the intercarbonylic proton, thus indicating an almost total spin delocalization on that position and an almost negligible hyperfine splitting by methylic protons. If deuterated trifluoroacetic acid (99.5 atom% D) is used in order to promote electron transfer in $\text{Co}(\text{acac})_3$, the ESR spectrum of the resulting radicals shows only a resolved deuterium triplet with a 2.88 G splitting; *vice versa*, the treatment of $\text{Co}(\text{H}_7\text{acac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{CD}_3$; $\text{R}^2 = \text{D}$) (91 atom% D), with undeuterated TFA results in the exclusive formation of the undeuterated acetylacetyl radical exhibiting the above reported two-line

ESR spectrum. Interestingly, these data indicate that, in addition to the electron transfer, a very fast H/D exchange process occurs through a mechanism by virtue of which the formation of the observable radicals is statistically correlated to the excess of isotopically labelled acid. Quite surprisingly, no H/D exchange was observed when $\text{Co}(\text{tta})_3$ (tta = thenoyltrifluoroacetone) or $\text{Co}(\text{dbm})_3$ (dbm = dibenzoylmethanato) were treated with deuteriated TFA.

On the other hand, the presence of electron-acceptor groups in positions 1 and 3 of the propanedionate skeleton results to be unfavourable to the one-electron oxidation of the corresponding β -ketoenolato ligand, if one considers that in the case of $\text{Co}(\text{HFacac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{CF}_3$; $\text{R}^2 = \text{H}$), it was necessary to warm the complex-TFA mixture up to 110 °C for a few seconds in order to start a reaction that resulted in the appearance of a broad one-line ($\Delta H_{\text{pp}} = 3.1 \text{ G}$) ESR spectrum at $g_{\text{iso}} = 2.0036$.

The introduction of a variety of substituents, like $-\text{NO}_2$, $-\text{SCN}$, $-\text{Cl}$ and $-\text{Br}$ in the intercarbonylic position of the acetylacetonato ligand seems to be very favourable to the kinetics of the overall process. All these complexes, except for the bromo-derivative, generate radicals exhibiting mean lifetimes that permit their spectroscopic characterization. In particular, $\text{Co}(\text{NO}_2\text{-acac})_3$, **1** ($\text{R}^1 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{NO}_2$), gives rise easily, even in the presence of acetic acid, to relatively high concentrations of radicals that exhibit a well-resolved ESR spectrum, centered at $g_{\text{iso}} = 2.0038$ [Fig. 2(a)], showing a triplet due to splitting by nitrogen, 27.60 G, quite lower than those observed by Symons⁷ for several radical cations of nitroalkanes, and a further hyperfine splitting of each triplet line by slightly magnetically inequivalent methylic protons ($A_{\text{H}} = 0.39$ and $A_{\text{H}'} = 0.13 \text{ G}$). Owing to the relatively high kinetic stability of such radicals, which exhibit a lifetime of ca. 2 h, we succeeded in obtaining a ¹⁴N ENDOR spectrum [Fig. 2(b)], at 10 °C, which confirmed the hyperfine parameters obtained by ESR. All the other radicals we examined, even though showing quite different lifetimes, never survived for more than a few minutes.

In order to test the hypothesis of a two-step process in which ligands are first removed from the metal by action of acids and then oxidized by cobalt(III) cations, some TFA-promoted electron-transfer cross experiments were carried out on some complexes **1** in the presence of equimolar amounts of β -ketoenols different from those coming from the complexes used. All experiments unequivocally resulted in the ESR-

detection of only those radicals deriving from the starting cobalt-bonded β -ketoenolato and not from the added β -ketoenols, thus showing that the oxidation takes place on a cobalt-bonded ligand.

As mentioned above, none of all the ESR spectra examined showed hyperfine splitting by the metal. Even though this could be indicative of small, if any, bonding interactions of such radicals with the cobalt centres, it must be pointed out that also in the ESR spectra of several dianion radicals of β -ketoenolates no hyperfine splitting by the metal was detected.³ It could be that, in such ligands, oxygen atoms do insulate the electronic system of the carbon skeleton from the metal orbitals to a rather large extent, as it was suggested for some radicals bonded to cobalt centres by a carboxylate group.⁸ Therefore, in the absence of further evidence we do not discard the possibility of looking at the above-mentioned radicals as cobalt(III)-bonded species **3** arising from an intermolecular ligand-to-cobalt electron transfer. In this connection, the role of the added acid could be that of causing the formation of some cationic highly oxidant cobalt(III) centres by gradual removal of β -ketoenolato ligands from cobalt(III) coordination sphere, as it is substantiated by a preliminary IR study of the reaction of TFA with $\text{Co}(\text{acac})_3$.

Financial support for this work was provided by CNR (Rome) Progetto Finalizzato 'Materiali Speciali per Tecnologie Avanzate'.

Received, 7th April 1992; Com. 2/01852G

References

- 1 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978.
- 2 *Electron Transfer in Inorganic, Organic, and Biological Systems* eds. J. R. Bolton, N. Mataga and G. McLendon, Advances in Chemistry Series **228**, ACS, Washington, DC 1991.
- 3 C. L. Kwan and J. K. Kochi, *J. Am. Chem. Soc.*, 1976, **98**, 4903.
- 4 R. Ambrosetti and D. Ricci, *Rev. Sci. Instrum.*, 1991, **62**, 2281.
- 5 ESR-ENDOR, ICQEM-CNR (Rome, Italy), Copyright 1992.
- 6 N. M. Atherton, *Electron Spin Resonance*, Wiley, London, 1973.
- 7 D. N. Ramakrishna Rao and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 565.
- 8 M. G. Simic, M. Z. Hoffmann and N. V. Brezniak, *J. Am. Chem. Soc.*, 1977, **99**, 2166.