Paramagnetic Transition-metal Carbonyls and Cyanides. Part II.[1] An Electron Spin Resonance Study of the Radiolysis of Thallium(I) Tetracarbonylcobaltate

By **Martyn C. R. Symons** * and **Donald N. Zimmerman**, Department of Chemistry, The University, Leicester LE1 7RH

Exposure of thallium(I) tetracarbonylcobaltate to ^{60}Co γ-rays at 77 K gives a high-field resonance identified as a thallium(II) centre, together with an isotropic eight-line centre having $A \approx 500$ G and $g = 1.96$. This unusually large hyperfine coupling to ^{59}Co corresponds to *ca.* 38% spin density in the outer, 4*s*, orbital, and the low *g* value implies some 4*p* character. It is suggested that this is due to the $[Co(CO)_4]^{2-}$ anion which is probably distorted from the original tetrahedral structure. A third species, having A_{iso} (^{59}Co) = 25 G and $g_{av.} = 1.998$ is tentatively identified as $[Co(CO)_4]^{2-}$ with the unpaired electron confined to one CO ligand. At room temperature the only e.s.r. signal detected corresponds to a species having the properties expected for the peroxide $[Co(CO)_4(O_2)]$.

CONTINUING our studies of radicals derived from transition-metal carbonyls [1,2] we have turned our attention to thallium(I) tetracarbonylcobaltate, $Tl[Co(CO)_4]$. We were interested in the possibility of preparing the dianion $[Co(CO)_4]^{2-}$. This species is of particular interest since the cobalt atom already has a formal d^{10} configuration, so that the extra electron is expected to be accommodated either by ligand orbitals or by 4*s* and 4*p* orbitals on cobalt. The thallium(I) salt was selected because Tl^I is known to be a good source of electrons, and Tl^{2+} can be readily detected by e.s.r. spectroscopy.[3]

EXPERIMENTAL

Thallium(I) tetracarbonylcobaltate, prepared from octacarbonyldicobalt and thallium metal,[4] was kindly donated by Professor W. R. Robinson. The finely powdered, pale yellow, salt was exposed to ^{60}Co γ-rays either at 77 K or at room temperature in a Vickrad source at a dose rate of 1.7 Mrad h^{-1} for 0.5 h.† E.s.r. spectra were recorded with a Varian E3 spectrometer at 77 K. Samples were annealed above this temperature in the insert Dewar with continuous monitoring and recooled to 77 K as soon as significant spectral changes were observed. The sample was black immediately after exposure but slowly changed to a bright yellow colour on standing at 77 K.

RESULTS AND DISCUSSION

Irradiation at 77 K resulted in a complex e.s.r. spectrum in which three separate sets of features can be detected [(A)—(C) in Figure 1]. Feature (A), a broad asymmetric singlet in the 5 000 G region, is assigned to the high-field component ($m_F = 1 \longleftrightarrow m_F = 0$) of the doublet expected for a thallium(II) centre.[3] [Thallium has two abundant nuclei, ^{205}Tl ($I = \frac{1}{2}$, 70.48%) and ^{203}Tl ($I = \frac{1}{2}$, 29.52%), with such similar magnetic moments that separate lines are rarely resolved.] The low-field component is not detectable with an *X*-band spectrometer.

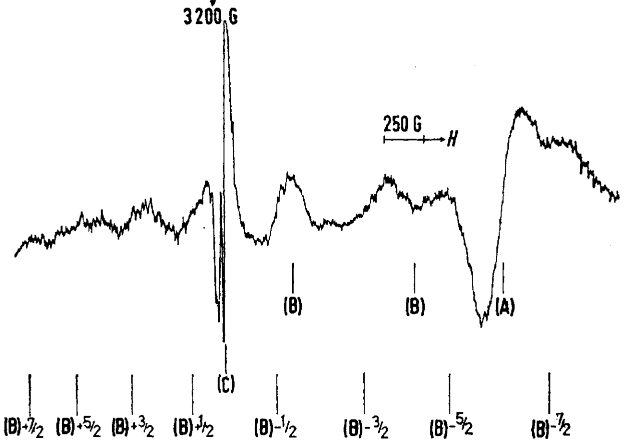

FIGURE 1 First-derivative *X*-band e.s.r. spectrum for thallium(I) tetracarbonylcobaltate after exposure to ^{60}Co γ-rays at 77 K and slight annealing, showing features assigned to species (A)—(C)

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† 1 rad = 10^{-2} J kg^{-1}, 1 G = 10^{-4} T.

[1] S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567 is taken as Part I.

[2] O. P. Anderson and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1972, 1020.

[3] M. C. R. Symons and J. K. Yandell, *J. Chem. Soc.* (*A*), 1971, 760.

[4] D. P. Schussler, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, 1974, **13**, 153.

The set of features (B) comprised eight very broad, almost isotropic, lines which undoubtedly stem from hyperfine coupling to ^{59}Co ($I = \frac{7}{2}$). The unusual spacing is a consequence of the non-linearity over such a wide field range. After correction using the Breit–Rabi equation [5] the hyperfine coupling was *ca.* 500 G and $g =$ *ca.* 1.96. The calculated hyperfine coupling for unit population of the 4*s* orbital on cobalt, based on the wavefunctions of Froese,[6] is 1 320 G, which gives a spin density of *ca.* 0.38 in this case. The remainder may be in a 4*p* or 3*d* orbital on cobalt, or possibly on one or more of the ligands. Unfortunately the features were too broad for any further assignment. The only simple formulation for species (B) is $[Co(CO)_4]^{2-}$, and this structure is accepted for purposes of discussion.

Spectrum (C) comprised a set of eight broad lines in the free-spin region. There was no obvious anisotropy, but the spectrum was somewhat obscured by the presence of features from species (D) [Figure 2(*a*)]. The low *A* value for ^{59}Co suggests a species having little or no spin density on cobalt, such as the peroxo-derivative [1] (which can be ruled out because of the low *g* value) or the nitroxide derivatives.[7,8] We tentatively suggest that species (C) is formed by electron addition to one carbonyl ligand.

Species (D) was the only species detectable by e.s.r. spectroscopy after irradiation at room temperature. We suggest it is the peroxo-derivative previously detected in our study of $[Co(CO)_4]$.[1] The hyperfine coupling was somewhat smaller than found before (Table), but remains quite reasonable for $[Co(CO)_4(O_2)]$ and the difference could well be an environmental effect. Only a trace amount of oxygen would be required to form the low yield of radicals detected. The signal was not removed by pumping, so the oxygen may be weakly bonded to cobalt prior to electron loss.

Structural Features.—Species (A). The calculated hyperfine coupling for this species is markedly lower than those detected for Tl^{II} in ionic environments or in aqueous solution (*ca.* 40 000 G).[3] The crystal structure of $Tl[Co(CO)_4]$ [4] establishes that each Tl^+ is surrounded by six anions, with three co-ordinating *via* a single carbonyl oxygen whilst the other three accommodate the cation in between three carbonyl groups, giving fairly short thallium–carbon and –cobalt distances. There is thus plenty of opportunity for charge delocalization on to three adjacent anions. The width (≈200 G) of the thallium(II) feature could well conceal hyperfine coupling to three ^{59}Co nuclei, and we suggest that this is the main cause for the relatively low spin density on thallium.

Species (B). If this centre is $[Co(CO)_4]^{2-}$, the most noteworthy result is the fact that the electron has no more than *ca.* 38% 4*s* character. When aquated d^{10} cations add an extra electron the outer *s* orbital is usually populated to the extent of *ca.* 90%. Clearly the carbonyl ligands are exerting a marked effect. The result is reminiscent of that for tetrahedral phosphorus compounds which, on addition of an extra electron, distort to give two nearly axial ligands and two equatorial ligands, the unpaired electron being in an *sp* hybridized orbital with *ca.* 20—30% *s* character.[9] It is tempting to suggest that a somewhat similar process is involved in the present case. A reasonable alternative would be analogous to the dissociative electron-capture process (1). The

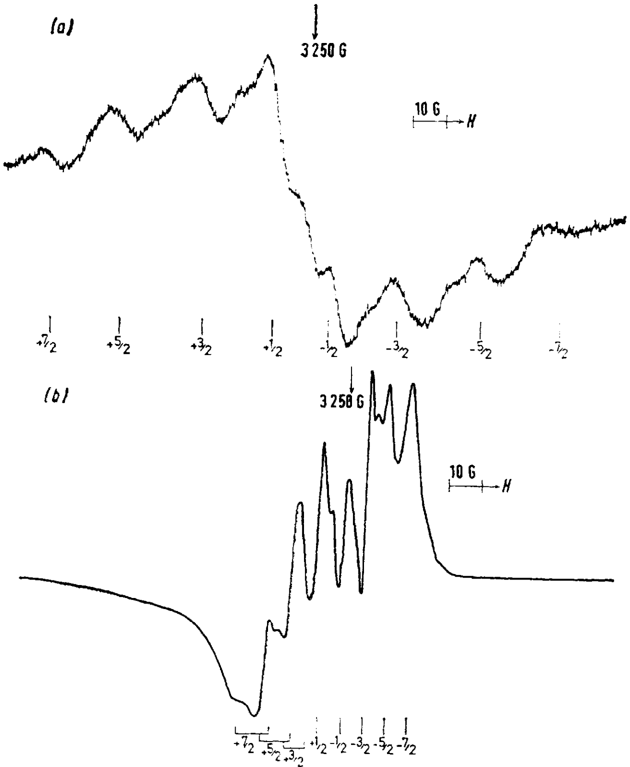

FIGURE 2 First-derivative *X*-band e.s.r. spectra for $Tl[Co(CO)_4]$ after exposure to ^{60}Co γ-rays: (*a*) at 77 K, showing features assigned to species (C); and (*b*) at room temperature, showing features assigned to species (D)

E.s.r. data for various paramagnetic centres in γ-irradiated thallium(I) tetracarbonylcobaltate

Species	Assignment	Hyperfine coupling[a]/G	g^a
(A)	Tl^{II}	7 520 ± 30	2.0 (assumed)
(B)	$[Co(CO)_4]^{2-}$	500 ± 30	1.96
(C)	*b*	25 ± 2	1.998
(D)	$[Co(CO)_4(O_2)]$	7.6 (‖), 6.1 (⊥) (±0.1)	2.004 (‖) 2.006 (⊥)
	$[Co(CO)_4(O_2]$ [c]	13.5 (‖), 10.5 (⊥) (±0.1)	2.004 (‖) 2.010 (⊥)
	d	20 (*x*), 12.5 (*y*), 12.5 (*z*) (±1.0)	2.09 (*x*) 2.012 (*y*) 2.00 (*z*) (assumed)

[a] Corrected when necessary using the Breit–Rabi equation. [b] Possibly $[Co(CO)_4]^{2-}$ with the unpaired electron on one CO ligand. [c] From ref. 1. [d] Data for [methylbis(3-salicylideneiminopropyl)amine]peroxocobalt(II) obtained from Figure 1 of ref. 11.

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[8] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Faraday II*, 1972, **68**, 1265.

[9] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

$[Co(CO)_3]^{2-}$ ion would again be expected to accommodate the unpaired electron in an *sp* hybridized orbital,[9] and

$$[Co(CO)_4]^- + e^- \longrightarrow [Co(CO)_3]^{2-} + CO \quad (1)$$

we have no way of distinguishing these species except that there seems to be no strong driving force for the loss of a carbonyl ligand. So far as we are aware these are unique species in the field of transition-metal chemistry.

Species (C). Since electron loss would give the $[Co(CO)_4]$ molecule, whose e.s.r. spectrum is typical of a d^9 system,[1] it seems probable that species (C) is also formed by electron capture. We recently detected an example of a two-stage electron-capture process in which the added electron is initially captured by a ligand prior to being transferred to the central metal atom.[10] This probably requires a distortion such as a decrease in the Co–C–O angle, and of course the ligand-acceptor orbital must be orthogonal to the metal-acceptor orbital. We consider that the small, nearly isotropic, hyperfine coupling to ^{59}Co is strong evidence for a species having low spin density on cobalt. This point is discussed further below. The hyperfine coupling to cobalt is reasonable for such a structure, which can be compared, for example, with the cobalt organic nitroxides.[7,8] The hyperfine coupling to ^{59}Co is expected to be larger than that for the nitroxides because the spin will be relatively strongly confined to carbon in the CO ligand, whereas in the RNO ligand it is more delocalized on to oxygen and the R group.

Thus we tentatively postulate that initial electron capture is followed by two alternative distortions, one being a bending of one metal–ligand bond to give a ligand-centred radical and the other a distortion from the original T_d symmetry towards a trigonal bipyramid in which the unpaired electron plays the role of an equatorial ligand.

Species (D). This species is almost certainly the peroxide $[Co(CO)_4(O_2)]$, but the smaller ^{59}Co coupling constants and smaller $g_\perp$ value compared with our previous values (Table) suggest that some environmental factors are operative. If both coupling constants are of the same sign [1] this cannot be a simple libration giving partial averaging of the g and A values, but if they are of opposite signs this would nicely accommodate the differences.

The basis of this, and our previous identification, and indeed those of many others, is the small magnitude of the metal coupling constants. However, Tovrog and Drago [11] have recently called this criterion into question. The normal representation of these dioxygen complexes is as derivatives of Co^{III} having a hyperoxide ($[O_2]^-$) ligand. Obviously this formulation is an oversimplification but, nevertheless, as we have previously demonstrated,[12] the metal hyperfine coupling constants can often be well accommodated in terms of such structures, with spin polarization of the σ-bonding electrons being responsible for the metal coupling. However, Tovrog and Drago suggest that the dioxygen adduct of [methylbis(3-salicylideneiminopropyl)amine]cobalt(II), [Co(msa)], which has an e.s.r. spectrum typical of complexes usually described as having the unpaired electron on the dioxygen ligand, is better described as a normal cobalt(II) complex with a singlet dioxygen ligand. Of the several lines of evidence advanced, perhaps the most important is the statement that the methyl isocyanide and carbon monoxide adducts have similar e.s.r. spectra. Indeed, the spectra displayed for the dioxygen and carbon monoxide adducts are remarkably similar. This requires the coincidence that the three ^{59}Co hyperfine components and the three g-tensor components be nearly identical. This is most unusual for complexes with different ligands. Although no data were extracted from these spectra, it is possible to obtain approximate values for the g and A components from the published spectrum, and these are included in the Table.

It was stated that [11] there are several reasons why the ^{59}Co coupling should be small for a normal cobalt(II) complex. We are unable to discover what these reasons are. The g-value shifts are relatively small and, after correcting for orbital paramagnetism, the coupling constants remain small with A_{iso} (^{59}Co) $= \pm 13.3$ and $2B = \pm 1.7$ G if like signs are assumed, or $A_{iso} = \mp 3.3$ and $2B = \pm 11.7$ G if unlike signs for $A_\parallel$ and $A_\perp$ are assumed. The calculated values for unit population of the 3*s*, 4*s*, and 3*d* orbitals for cobalt, based on Froese's wavefunctions,[6] are 29 539, 1 320, and 152 G respectively. Thus the maximum *s* character is *ca.* 1% and the maximum 3*d* character is *ca.* 7.7%. We consider these results to be completely incompatible with a formulation in which the unpaired electron is largely localized on cobalt. In view of the remarkable similarity in the spectra for the dioxygen and carbon monoxide complexes, it seems possible that they are both the dioxygen species. If this is incorrect, then we suggest that the unpaired electron has migrated on to the aromatic ligands. The appearance of extra splitting on the cross-over (y) features in the spectra suggests the possibility of hyperfine coupling to ^{14}N which might support this alternative.

We conclude that our spectra are properly assigned to the dioxygen complex and that this has the normal ' hyperoxide ' structure. Its formation at room temperature in the presence of oxygen implies electron loss from $[Co(CO)_4]^-$ to give $[Co(CO)_4]$, which reacts rapidly with molecular oxygen.[1] Absence of detectable concentrations of $[Co(CO)_4]$ at 77 K means that electron transfer from neighbouring Tl^+ is efficient. Alternatively, $[Co(CO)_4]^-$ may form a complex with oxygen from which an electron is more readily lost.

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