Reaction of Metal Carbonyls with Oxygen

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It is suggested that a complex previously identified as $\cdot Mn(CO)_5$ *is, in fact, the peroxo complex* $\cdot O_2Mn(CO)_5$. *The analogous cobalt complex* $\cdot O_2Co(CO)_4$ *has also been identified.*

SUBLIMATION of octacarbonyldicobalt on to a cold finger (77 K) yields a paramagnetic species, identified[1] from its e.s.r. spectrum as the tetracarbonylcobalt radical, $\cdot Co(CO)_4$, (I). We have recently become interested in radicals derived from metal carbonyls[2,3] and were attracted to the report that the pentacarbonylmanganese radical, $\cdot Mn(CO)_5$, (II) was formed[4] in the same manner as (I). In particular, it was apparent that the reported ^{55}Mn hyperfine couplings ($A_{\parallel} = 22\cdot5$ G, $A_{\perp} = 6\cdot75$ G), attributed to (II), were low compared with those of other manganese carbonyl radicals.[2,3] These couplings were also considerably lower than the ^{59}Co hyperfine couplings

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[1] H. J. Keller and H. Wawersik, *Z. Naturforsch.*, 1965, **20b**, 938.

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

[3] O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, unpublished results.

[4] E. O. Fischer, E. Offhaus, J. Muller, and D. Nothe, *Chem. Ber.*, 1972, **105**, 3027.

($A_{\parallel} = 67$ G, $A_{\perp} = 57$ G) observed for (I). Very recently (II) has been identified in solution [5] and A_{iso} (^{55}Mn) found to be 93 G.

EXPERIMENTAL

Sublimation experiments were performed in an apparatus as described by others [1,5,6] with the cold finger centred in the cavity of a Varian V4502 e.s.r. spectrometer. For oxygen-free experiments the sublimation apparatus was outgassed for a minimum of 2 h prior to the introduction of the metal carbonyl samples. Peroxo-species were readily obtained when the sublimation apparatus was evacuated for a short period (*ca.* 5 min) before introduction of the sample. Otherwise conditions were as reported by the earlier workers.[1,5] Spectra were calibrated using DPPH. $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were obtained from Strem Chemicals Incorporated, Danvers, Mass., and identical results were obtained using either the commercial or purified material.

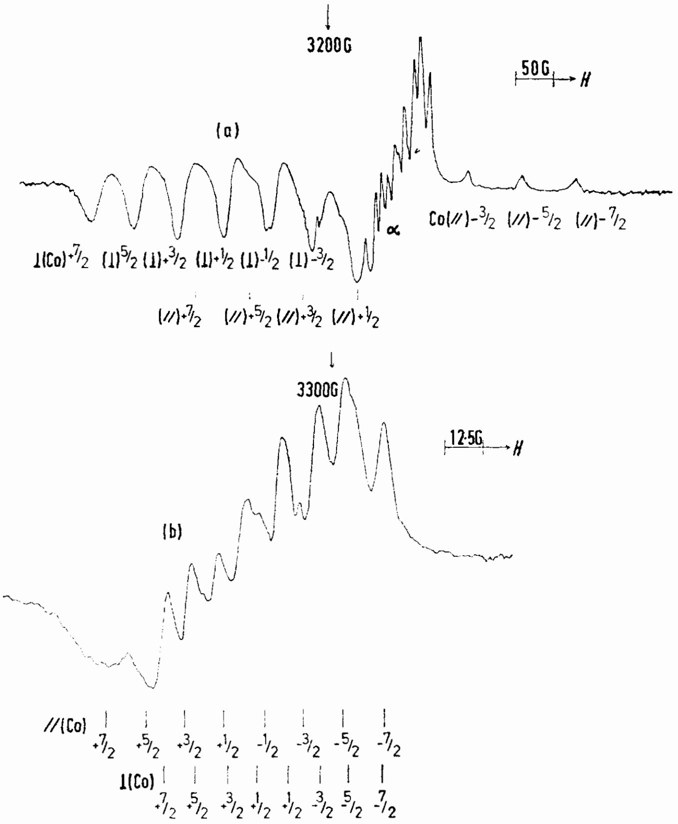

FIGURE 1 First derivative *X*-band e.s.r. spectrum for matrix isolated $\cdot Co(CO)_4$ (broad spectrum in (*a*) and $\cdot O_2Co(CO)_4$ [narrow spectrum in (*a*), shown in detail in (*b*)].

RESULTS AND DISCUSSION

Decarbonyldimanganese.—The sublimation of $Mn_2(CO)_{10}$, under conditions previously described,[1,4,6] gives no detectable e.s.r. signal *in the absence of oxygen.* However, in the presence of traces of oxygen, a spectrum similar to that originally assigned to (II) was observed. (None of our spectra displayed the weak features taken as parallel shoulders in the previous work.[4]) This result suggests that the radical is in fact the peroxo-species $O_2Mn(CO)_5$, (III). This suggestion is supported by the results using $Co_2(CO)_8$.

Octacarbonyldicobalt.—Sublimation of $Co_2(CO)_8$ in the presence of oxygen gives a species identified as $O_2Co(CO)_4$, (IV) whose e.s.r. signal is superimposed on that of (I) (Figure 1). In the absence of oxygen, the spectrum due to (I) only was obtained.

E.s.r. Spectra.—The results of the analysis of the spectrum of (IV) are given in the Table and it can be seen that the values are consistent with those obtained for a variety of other peroxo-complexes of cobalt.[7,8] There can be little doubt that the species with a large hyperfine coupling to ^{59}Co is $\cdot Co(CO)_4$ as previously concluded.[1] Since this reacts rapidly with oxygen at low temperatures, the species with the small hyperfine coupling to ^{59}Co must be the peroxo-species $(OC)_4CoO_2\cdot$. This reduction in the value of the hyperfine coupling which occurs on oxygenation of (I) is of the same order of magnitude as that previously observed for the oxygenation of other cobalt complexes.[8]

E.s.r. data for various transition metal peroxo-complexes

Radical	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/G	$A_{\perp}$/G
$(OC)_4CoO_2\cdot$ [a]	2·010$_0$	2·00$_4$	13·5	10·5
$pyCoL_1O_2\cdot$ [b,d]	2·065	2·000	16	12
$pyCoL_2O_2\cdot$ [d]	2·066	2·022	13	12
Vitamin $B_{12r}O_2\cdot$ [e] (DMF solution)	2·069	2·002	16	13
Vitamin $B_{12r}O_2\cdot$ [e] (CH_3OH glass)	2·079	2·003	18	13
$(OC)_5MnO_2\cdot$ [a]	2·007	2·003	8·5	6·3 [f]
$O_3VO_2\cdot$ [g]	2·032	2·002	6·6	3·9

[a] This work. [b] Ref. 7. [c] py = pyridine, L_1 = bisdimethylglyoximato. [d] py = pyridine, L_2 = bisdiphenylglyoximato. [e] Ref. 8. [f] These values differ from those originally reported in Ref. 4. [g] Ref. 13.

Electronic Structure of $\cdot Co(CO)_4$.—The results for this d^9 species give unambiguous information about the orbital of the unpaired electron. However, the experimental data must first be corrected for zero-field and orbital magnetic contributions. These were not considered in an earlier interpretation.[1] For the former, we have used the normal Breit–Rabi equation and for the latter, the second-order equations: [9]

$$A_{\perp}\,(\mathrm{MHz}) = A_{\mathrm{iso}} - B(1 - \tfrac{15}{4}\Delta g_{\perp})$$

and $$A_{\parallel}\,(\mathrm{MHz}) = A_{\mathrm{iso}} + 2B(1 - \tfrac{1}{4}\Delta g_{\perp}),$$

where $$\Delta g_{\perp} = g_{\perp} - g_{e}.$$

This gives, after reconverting to gauss,

$$A_{\mathrm{iso}} = -37{\cdot}4\ \mathrm{G}, \quad 2B = +107{\cdot}4\ \mathrm{G}$$

if we take $A_{\parallel}$ as positive and $A_{\perp}$ as negative. (Any other sign combinations give totally unacceptable results.) A positive sign for $2B$ is only possible for a d_{z^2} orbital which fixes the configuration as $(d\pi)^6$, $(d_{x^2-y^2})^2$,

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[5] S. A. Hallcock and A. Wojcicki, *J. Organometallic Chem.*, 1973, **54**, C27.

[6] H. J. Keller, *Z. Naturforsch.*, 1968, **23b**, 133.

[7] G. N. Schrauzer and C. P. Lee, *J. Amer. Chem. Soc.*, 1970, **93**, 1551.

[8] J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, 1969, **91**, 2775.

[9] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

$(d_{z^2})^1$. This in turn means that the $\cdot Co(CO)_4$ complex must have either T_d or distorted T_d symmetry since these are the only arrangements where the d_{z^2} will be the highest-energy orbital. This result is consistent with recent i.r. studies[10] in which it was concluded that *I* had C_{3v} symmetry. The magnitude of $2B$ is normal for cobalt complexes and shows that the electron is not extensively delocalised on to the ligands. In contrast, the isotropic coupling of $-37{\cdot}4$ G is low for cobalt complexes and we conclude that there is some occupancy of the outer 4*s* orbital giving a positive contribution. If we assume a normal (spin-polarisation) value of *ca.* -90 G, and a A°_{4s} value of *ca.* 132 G (estimated from the values of Froese[11]) we find that about a 4% occupancy is required to give the observed result. This is again an indication of systems having a d_{z^2} configuration.[12]

Electronic Structure of the Peroxy-species.—In a previous discussion, one of us concluded[13] that for a peroxy-species formulated as $O_3VO\dot{O}^{2-}$, the unpaired electron must be strongly confined to the two oxygen atoms despite the possibility of π-delocalisation. The same conclusion can be drawn for the species $(OC)_4CoO_2\cdot$ and $(OC)_5MnO_2\cdot$. This can be seen clearly if we ignore small corrections and calculate the approximate 4*s* and $3d_{z^2}$ populations directly from the hyperfine tensor components. This gives *ca.* (—)1·4% for the *d*-orbital population, and *ca.* (—)1·0% 4*s* for Co and (—)0·6 for Mn. These values are close to expectation for simple spin-polarisation so that delocalisation cannot be important. (There is no point in elaboration since the values used are not very accurate, and we cannot be sure that they are principal values since the *g*- and *A*-tensors need not be co-directional.)

The values for $g_{\perp}$ are smaller than are usually found for simple peroxy-radicals such as $HO_2\cdot$[14] (*ca.* 2·03). If we accept that delocalisation is trivial, this can be understood in terms of the magnitude of θ, the angle between the $Co-O_1$ and O_1-O_2 axes (Figure 2). The smaller the angle θ, the less the degeneracy of the oxygen π orbitals will be lifted and the greater will be $g_{\parallel}$. We conclude that for these carbonyls, θ is relatively large. This is in contrast with the results for a range of other cobalt peroxy-complexes which all have $g_{\parallel} \gg 2{\cdot}03$ (Table). These differences probably reflect changes in the extent to which π_x and π_y bonding can occur to oxygen.

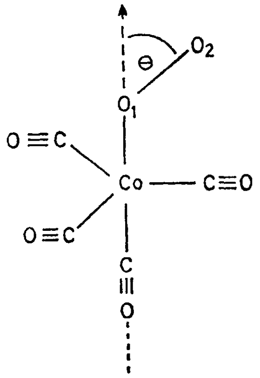

FIGURE 2 Structure of $\cdot O_2Co(CO)_4$

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[10] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.

[11] Calculated from the data of C. Vroese, *J. Chem. Phys.*, 1966, **45**, 1417.

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[13] M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1889.

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