The most striking and novel feature of the structure is the directly bonded sequence W–C–O–Al; the nearly regular octahedral stereochemistry around the aluminum atom involves three such linkages through one of the carbonyls on each of three [$W(CO)_3C_5H_5$] ligands (Figure 1). This is the first reported structure in which a CO ligand directly links two metal atoms through metal–carbon and metal–oxygen bonds. The O-coordination of a terminal carbonyl on the $W(CO)_3C_5H_5$ ligand provides an interesting contrast to the uniquely coordinated bridging carbonyl in $[Fe(CO)C_5H_5COAlEt_3]_2$ recently described by Nelson, Kime, and Shriver.[5]

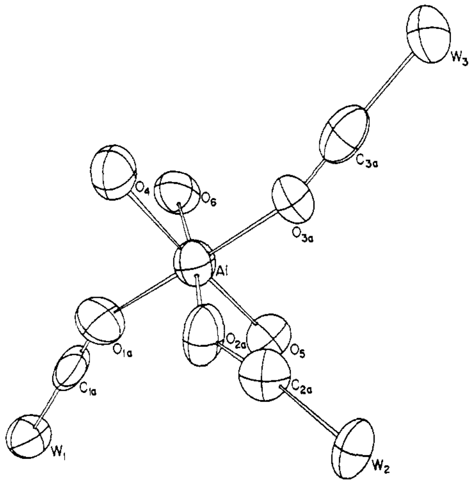

Figure 1. An ORTEP drawing of the central coordination about the aluminum atom in $Al[W(CO)_3C_4H_5]_3(C_4H_8O)_3$. THF oxygen atoms are designated O_4, O_5, and O_6. For clarity, the cyclopentadienyl groups, the terminal carbonyls, and the THF carbon atoms have been omitted.

The octahedral aluminum coordination is completed by three normal THF ligands in a mer configuration. The three [$W(CO)_3C_5H_5$] ligands display approximate mirror symmetry and are very nearly isostructural. The perpendicular distances of the three tungsten atoms to their respective π-C_5H_5 planes are identical (2.04 ± 0.01 Å) and, in each group, the cyclopentadienyl plane (with an average deviation from planarity of ±0.006 Å) is almost exactly parallel to the plane of the three carbonyl carbon atoms.

The W–C distances to the carbonyls (1.85 ± 0.02 Å) that link the tungsten atom to the central aluminum atom are systematically shorter than those to the terminal carbonyl groups (1.95 ± 0.02 Å). Conversely, the corresponding C–O distances are 1.25 ± 0.02 and 1.16 ± 0.02 Å, respectively.[15] The longer C–O bonds in the oxygen-coordinated carbonyls are presumably responsible for the unusually low carbonyl stretching frequencies observed for **1** (*vide supra*). The Al–O distances to the three carbonyls (1.827 ± 0.009 Å) are substantially shorter than those to the THF ligands (1.94 ± 0.02 Å). Thus a consistent picture of the W–C–O–Al sequence emerges, with rather tight bonding to the two metal atoms and with a somewhat extended C–O bond.

All of the W–C–O units are essentially linear (176° ± 3°) and all O–Al–O angles are orthogonal to within 3°. The Al–O–C angles, on the other hand, range from 140.4 to 162.9° and average 151°. It is probable that this spread reflects differing packing constraints at various points in the crystal.

In addition to the chromium and molybdenum analogs of **1**, we have prepared two similar series of compounds of the general formula $L_3Al[(CO)_3MC_5H_5]_3$ (M = Cr, Mo, W; L = pyridine, isoquinoline) through use of the stoichiometric quantity of L in toluene. Details of these derivatives and of the structure of **1** will be presented in forthcoming publications.[16]

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[15] One terminal CO group in the cis ligand is exceptional in that the W–C and C–O bond distances are somewhat intermediate at 1.88 ± 0.02 and 1.24 ± 0.02 Å, respectively. All nonbonded contact distances are normal for this carbonyl and no metal–oxygen interactions are indicated.

Electron Spin Resonance Evidence for Positive Holes Produced in Irradiated Single Crystals of Carboxylic Acids

Sir:

Although a number of esr studies have been made on irradiated single crystals of organic compounds, conclusive evidence for the positive hole has been obtained only for some sulfur-containing compounds such as thiourea derivatives, cystine hydrochloride, and dithiodiglycolic acid.[1] No conclusive evidence has been obtained for carboxylic acids, on which the most extensive work has been hitherto focused.

Recently, Iwasaki, Eda, and Toriyama found that irradiated single crystals of unsaturated carboxylic acids such as maleic acid[2] and potassium hydrogen maleate[3] give carboxyl radicals (RC(=O)O·) produced by the removal of an acidic proton, and suggested that the carboxyl radical could be formed from the positive hole by transferring H^+ to the neighboring molecule. Box, *et al.*, have also reported that a similar radical is formed in succinic acid.[1] The existence of this radical was assumed by some workers prior to our experimental evidence.[4,5]

However, the positive hole itself has never been found in irradiated carboxylic acids. Although the reason may be in the spontaneous transfer of an acidic proton from the positive hole, one may expect to find a similar carboxyl radical formed by ejection of an electron from the COO^- group if salts of the carboxylic acids are used.

An example of the latter case has been found in the present study for one of the two kinds of carboxyl radicals formed in an irradiated single crystal of potassium hydrogen fumarate (KHF) or its deuterium compound (KDF), where an unpaired electron is located in the

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(1) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, **74**, 41 (1970).

(2) M. Iwasaki, B. Eda, and K. Toriyama, *J. Amer. Chem. Soc.*, **92**, 3211 (1970).

(3) K. Toriyama and M. Iwasaki, *J. Chem. Phys.*, in press.

(4) R. N. Schwartz, M. W. Hanna, and B. L. Bales, *ibid.*, **51**, 4331 (1969).

(5) G. C. Moulton and B. Cernansky, *ibid.*, **53**, 3022 (1970).

Table I. Principal Values and Directions of the g Tensors the for Carboxyl Radicals, O_σ(I) and O_σ(II), in an Irradiated Single Crystal of Potassium Deuterium Fumarate.[a] Comparisons with X-Ray Crystallographic Data

		Principal values	Direction cosines (a^*, b, c') l	m	n	Comparisons with X-ray data
O_σ(I)	g_1	2.0033	−0.008	+0.994	+0.109	9° with bisector of O═CO(H)
	g_2	2.0074	+0.925	+0.049	−0.377	13° with normal to COO(H)
	g_3	2.0273	+0.380	−0.098	+0.920	91° with bisector of O═CO(H)
O_σ(II)	g_1	2.0023	+0.127	+0.972	−0.198	12° with bisector of O═CO$^-$
	g_2	2.0067	+0.959	−0.069	+0.274	12° with normal to COO$^-$
	g_3	2.0224	−0.252	+0.224	+0.941	99° with bisector of O═CO$^-$

[a] $K^+\ {}^-OOCCH{=}CHCOOD$.

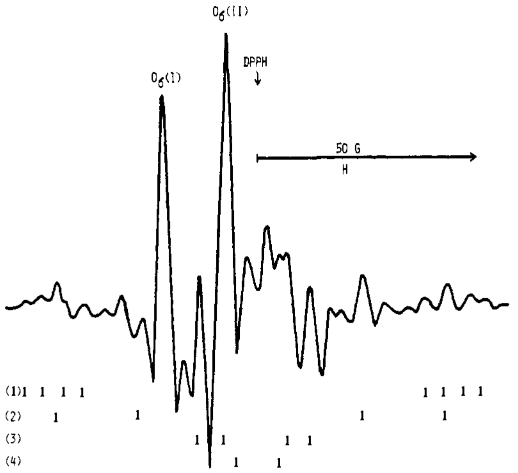

Figure 1. Esr spectrum of a single crystal of potassium hydrogen fumarate [$K^+\ {}^-OOCCH{=}CHCOOH$] irradiated at 77°K in the dark. The measurement was made with the magnetic field applied along 70° from the c' axis in the $c'a^*$ plane and with a microwave power of 1.2 mW. The strong peaks denoted by O_σ(I) and O_σ(II) are due to the carboxyl radicals, the latter being the positive hole. The other signals indicated by the stick lines are due to (1) a radical pair, (2) a hydrogen addition radical, (3) an R addition radical, and (4) a molecular anion radical.

in-plane p orbitals of the oxygen atoms of the COO$^-$ group.

According to X-ray crystallographic data reported by Gupta and Roy,[6] the COO$^-$ group in the KHF molecule is not coplanar with the plane of the rest of the molecule containing the COOH group, and the COO$^-$ group twists around the C–C bond with an angle of 35°. Therefore, the normals to the two COO planes in the molecule have different orientations to the crystallographic axes, making an angle of 35° with each other.

The g tensors for the carboxyl radicals determined by us[2,3] and by Box, *et al.*,[1] show that the unpaired electron occupies the antibonding orbital between the two in-plane p orbitals of the carboxyl oxygen atoms, $\psi = c_1 p_{O1} - c_2 p_{O2}$, where p_{O1} and p_{O2} represent the in-plane p orbitals of the oxygen atoms, respectively. The coefficients c_1 and c_2 seem to be affected by the inequivalence of the two oxygen atoms arising from the interaction with the rest of the molecule and with neighboring molecules, such as hydrogen bonding. However, regardless of the ratio c_1^2/c_2^2, the g_{int} axis was always found to be normal to the COO plane, resulting in the $g_{\max}$ and $g_{\min}$ axes in the COO plane. This situation together with the large g anisotropy of the carboxyl radical make it possible to determine which COO group is occupied by the unpaired electron in our radical, where the normals to the two COO planes are largely different.

The KHF or KDF crystal irradiated at 77°K in the dark gives the two kinds of carboxyl radicals, O_σ(I) and O_σ(II), the g tensors of which are quite similar in the principal values[7] but are different in the principal directions. The g tensors obtained from the KDF crystal are listed in Table I. Figure 1 indicates the spectrum of the KHF crystal, and a similar spectrum was obtained from the KDF crystal. The g_{int} axes of the two radicals make an angle of 38.7° with each other. Furthermore, it was found from a comparison with the crystallographic data that the g_{int} axes of O_σ(I) and O_σ(II) nearly coincide with the normals to the COOH and COO$^-$ groups, repectively, as shown in Table I. These results lead to the conclusion that O_σ(I) is formed by removal of the acidic proton from the COOH group and O_σ(II) by the ejection of an electron from the COO$^-$ group. The $g_{\min}$ and $g_{\max}$ axes were found to be approximately parallel and perpendicular, respectively, to the bisectors of the O═CO(H) angle for O_σ(I) and the O═CO$^-$ angle for O_σ(II). This indicates that the coefficients of the unpaired electron wave functions are nearly equal for the both radicals ($\psi = (p_{O1} - p_{O2})/\sqrt{2}$).

Finally, it is concluded that the positive hole can be trapped in the oxygen nonbonding orbital in irradiated carboxylic acid salts having no acidic proton.

Acknowledgment. We wish to thank Dr. M. P. Gupta for sending us the atomic coordinates of the potassium hydrogen fumarate crystal before publication.

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(6) M. P. Gupta and P. H. Roy, *Indian J. Phys.*, **41**, 787 (1967). The KHF crystal has triclinic symmetry with the space group of $P\bar{1}$. The two molecules in the unit cell are related by the center of symmetry, giving one-site esr spectra. Only the projection along the a axis is given in this paper so the atomic coordinates were obtained from the authors in a private communication.

(7) The principal values of the g tensors for O^σ(I) and O^σ(II) are similar to 2.0035, 2.0061, 2.0261 in maleic acid[2] and 2.003, 2.006, 2.019 in succinic acid.[1]

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Biosynthesis of the Fungal Tropolones. Stipitatic and Stipitatonic Acids

Sir:

It has been recognized for over a decade that the tropolone system of the *Penicillium stipitatum* metabolites is formed from a combination of acetate and