Studies on the Nature of Cobalt(III) Acetate†

Antony B. Blake, John R. Chipperfield,* Seng Lau, and David E. Webster
School of Chemistry, Hull University, Hull HU6 7RX

Cobalt(III) acetate exists as a number of species in the solid or in solution. The most important of these appear to be trinuclear oxo-centred complexes, probably the cation $[Co_3O(O_2CMe)_6(HO_2CMe)_3]^+$ and the mixed-valence complex $[Co_3O(O_2CMe)_6(HO_2CMe)_3]$. There is evidence that the hydroxo-bridged dimer $[Co_2(O_2CMe)_4(\mu\text{-}OH)_2]$ can also form. The preparation of samples containing mainly a single component is aided by careful thin layer chromatographic analysis. Extended *X*-ray absorption fine structure has been used to elucidate the structures of such amorphous samples.

When a solution of cobalt(II) acetate in acetic acid is oxidised a green solution containing cobalt(III) is formed. Many oxidants including ozone, peroxoacids, and dioxygen (when a promoter is needed) can be used, and electrolytic oxidation yields a similar result. If the solvent is removed a dark green amorphous powder is formed. This solid can have variable amounts of its total cobalt in the cobalt(III) state, and has been identified as a hydroxo-bridged cobalt(III) dimer $[Co_2(\mu\text{-}OH)_2(O_2CMe)_4]$ (**1**) with some unoxidised cobalt(II),[1,2] or as an oxo-centred trimer containing two cobalt(III) atoms and one cobalt(II) $[Co_3O(O_2CMe)_6(HO_2CMe)_3]$ (**2**).[3] No crystalline specimen has been prepared, but when pyridine (py) is added to the green powder a crystalline compound, $[Co_3O(O_2CMe)_6(py)_3]^+ \cdot O_2CMe^-$, is formed in which the cation is thought to be an oxo-centred trimer containing three cobalt(III) atoms.[4] The crystal structures of compounds containing the oxo-centred trinuclear cations $[Co_3O(O_2CMe)_5(\mu\text{-}OH)(py)_3]^+$ and $[Co_3O(O_2CMe)_3(\mu\text{-}OH)_2(py)_5]^{2+}$ (both of which contain μ-OH bridges as well as the oxo-centred trimer unit) and the binuclear hydroxo-bridged cation $[Co_2(O_2CMe)_3(\mu\text{-}OH)_2(py)_4]^+$ have been reported.[5,6]

The nature of cobalt(III) in the green solution is also not clear. Hendriks *et al.*[7] considered the cobalt(III) species in solution, whether in acetic acid or water, to be mononuclear. However, in a detailed kinetic study Jones [8,9] proposed that cobalt(III) could be present as either (**1**) or (**2**) depending upon the conditions, and also suggested that a highly unstable dimeric $[L_5Co{-}O{-}CoL_5]$ ($L = O_2CMe^-$ or HO_2CMe) was the initial product of peroxoacid oxidation of cobalt(II). Jones' conclusions were based upon kinetic measurements only, with no identification of species in solution.

In this paper we show by use of thin-layer chromatography that cobalt(III) acetate in solution can be present as various species. A partial separation of these species has been achieved, and their nature elucidated by comparison with suitable model compounds.

Experimental

Thin-layer chromatography was carried out at 0 °C on Kieselgel 60 F_{254} plates, using water–acetic acid-acetone (1:1:20) as eluant. Paper electrophoresis was carried out at 10 °C on medium flow-rate chromatographic paper, with 3 000 V applied across 66 cm and a current of about 20 mA. The paper was lightly wetted with pH 3.16 acetic acid (4 mol dm^{-3})–sodium acetate (0.1 mol dm^{-3}) buffer. Dithio-oxamide (0.5% in MeOH) was used to develop the electophoretograms when low concentrations of sample were used.

Magnetic susceptibilities were determined by the Gouy method at 18 °C.

Extended X-*Ray Absorption Fine Structure* (*EXAFS*).—The EXAFS measurements at the cobalt *K* edge (7 710 eV) were performed at the S.E.R.C. Synchrotron Radiation Source, Daresbury, on Station 7.1, using a channel-cut Si(111) crystal monochromator. Samples mixed with boron nitride (mass ratio *ca.* 1:4) to give absorbance in the range 1—2 were finely powdered, pressed into 1-mm aluminium sample holders, and held in place by Mylar film. Transmission spectra between 7.3 and 8.3 keV were collected in single scans of 25—45 min, with ring energy 2 GeV and ring current 60—180 mA. Data reduction and analysis were done by use of the Daresbury Laboratory programs EXCALIB and EXBACK (background subtraction and normalisation) and EXCURVE (EXAFS data manipulation, Fourier transformation, and curve fitting by single-scattering, curved-wave theory).[10]

For curve fitting, the normalised, k^2-weighted EXAFS data were Fourier filtered to isolate contributions from shells of 0.7—4.3 Å radius. The shell radii (*R*), Debye–Waller factors (D–W), energy origin (E_0), and an imaginary potential (VPI) representing photoelectron lifetime effects were allowed to vary in the least-squares optimisation, but co-ordination numbers (*N*) were kept fixed. Atomic phase shifts were taken from the Daresbury Laboratory data base.

Preparation of Single-component Samples.—Electrolytic oxidation was carried out in a water-cooled divided flow cell (Figure 1), fitted with a platinium anode (diameter 2 cm). The cell divider was made from the anion-exchange membrane Neosepta AV-4T. The cathode was a copper gauze. Solutions were pumped through the anode compartment of the cell with a stainless-steel metering pump at 46 cm^3 h^{-1}. The sample ELS was prepared by electrolysis of a solution of cobalt(II) acetate tetrahydrate (40 g, 0.16 mol) in 50% aqueous acetic acid (150 cm^3). This was passed through the cell eight times. The cell current was limited to 1.5 A to avoid undue temperature rise. The solvent was then removed (see below). In sample ELS the ratio Co^{III}/Co^{total} was 0.89:1. The total cobalt content was determined by titration with ethylenediaminetetra-acetate; Co^{III} was determined by addition of excess of iron(II) and back titration with Ce^{4+}.

The sample OZONE was prepared by stirring cobalt(II) acetate tetrahydrate (10 g, 0.04 mol) with glacial acetic acid (80

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† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, B.M. ≈ 9.27×10^{-24} J T^{-1}.

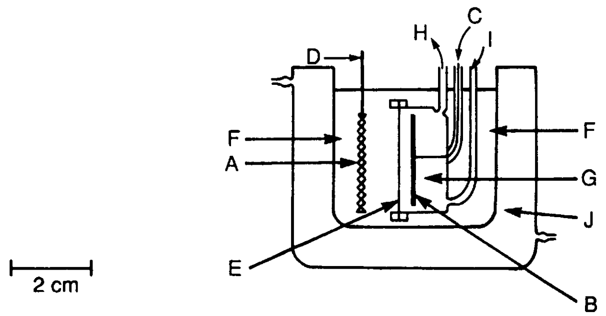

Figure 1. Flow cell used to prepare cobalt(III) acetate: A, copper gauze cathode; B, platinum anode; C, connection to anode; D, connection to cathode; E, anion-exchange-membrane cell divider; F, catholyte; G, anolyte; H, outlet from anode compartment; I, inlet to anode compartment; J, water jacket

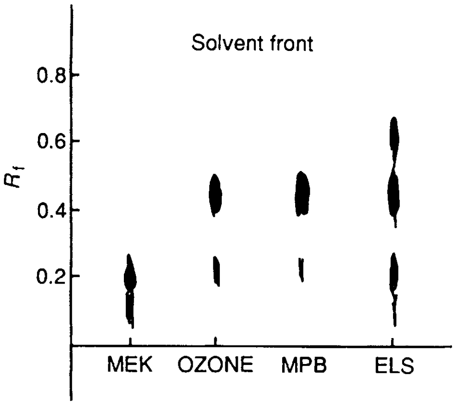

Figure 2. Thin-layer chromatograms of samples (see text) of cobalt(III) acetate. Solvent water-acetic acid-acetone (1:1:20), 0 °C

cm^3) and acetic anhydride (10 cm^3) for 5 d at room temperature while oxygen containing 2% ozone (Towers ozone apparatus GE-150) was passed through the solution at 10 cm^3 min^{-1}. The solvent was then removed (see below). In sample OZONE the ratio Co^{III}/Co^{total} was 0.86:1.

The sample MEK was prepared by stirring cobalt(II) acetate tetrahydrate (50.2 g, 0.2 mol) with glacial acetic acid (330 cm^3) at 90 °C. After all the cobalt(II) acetate had dissolved, oxygen (200 cm^3 min^{-1}) was bubbled through the solution while butan-2-one (180 cm^3) was added dropwise over 50 min. The reaction mixture was kept at 90 °C for 3 h with passage of oxygen. After cooling the solution the solvent was removed. In sample MEK the ratio Co^{III}/Co^{total} was 0.58:1.

The t.l.c. results (see later) showed that by carefully controlling the conditions of preparation, and by t.l.c. monitoring, it is possible to prepare solutions containing principally a single component. The excess of solvent (mainly acetic acid) needs to be removed at low temperatures if rearrangement of complexes is to be minimised. Freeze drying was found to give the most reliable results (judged by comparing the t.l.c. of the initial solution with that of a solution of the solid redissolved in acetic acid).

Results and Discussion

Oxidation of Cobalt(II) *by Dioxygen in the Presence of a Promoter.*—Cobalt(II) acetate in acetic acid requires a promoter (usually acetaldehyde or 2-butanone) and high temperatures (80—100 °C) if dioxygen is used as oxidant. We have found that the fraction of cobalt in the +III oxidation state in cobalt(III) acetate prepared in this way is never higher than 66%, and often as low as 33%. T.l.c. analysis was used to follow the progress of such an oxidation. After reaction for 30 min the pink cobalt(II) spot was still evident, and a substantial amount of green product with R_f = 0.21 had formed. This was the major product formed even though the preparation was continued for 48 h. After 12 h the t.l.c. showed the presence of traces of two other products, one with R_f = 0.47 and one with R_f = 0.62. These additional peaks were only present during the period 12—19 h of reaction. The t.l.c. of a solution of a sample MEK prepared by this method is shown in Figure 2.

Oxidation of Cobalt(II) *by Ozone.*—Both Kochi and co-workers[2] and Ziolkowski *et al.*[3] prepared their samples of cobalt(III) acetate by ozone oxidation of cobalt(II). This oxidation is slow [5 d to oxidise 0.025 mol of cobalt(II)]. We followed the progress of this oxidation by t.l.c. analysis. The first product formed had R_f = 0.47. This complex was in contact with unreacted cobalt(II), but not until 24 h had passed was there any formation of a trace of material with R_f = 0.21. After 96 h the concentration of the compound with R_f = 0.47 had built up, but there was still unreacted cobalt(II) present. No peak with R_f = 0.62 was seen. Figure 2 shows the t.l.c. of a solution of a sample OZONE prepared in this way.

Electrochemical Oxidation of Cobalt(II).—Electrochemical oxidation of cobalt(II) was monitored by t.l.c. analysis. In order to keep the cell current as high as possible with minimum heating of the solution, the reactants were slowly pumped through the cell. After one passage through the cell (it took 3 h to pass all the solution through the cell), t.l.c. showed the presence of two components, with R_f = 0.21 and 0.47, as well as unreacted cobalt(II). On the third pass a new peak with R_f = 0.62 appeared alongside the others. Visual inspection showed that on subsequent passages through the cell the concentration of the material with R_f = 0.21 decreased until after eight passes it was not detectable, while the amounts of the compounds with R_f = 0.47 and 0.62 were increasing. After eight passes the peak with R_f = 0.62 was the major component. Figure 2 shows the t.l.c. of a solution of a sample ELS prepared in this way.

Peroxoacid Oxidation of Cobalt(II).—When a solution of cobalt(II) acetate in acetic acid is treated with 0.5 or 1.0 mole equivalent of *m*-chloroperoxobenzoic acid the pink colour changes to green immediately. T.l.c. analysis shows that the pink cobalt(II) spot (R_f = 0.1) is replaced by a green spot (R_f = 0.47) (sample MPB in Figure 2). This is the sole product and further t.l.c. after 12 h shows no change. If mole ratios of cobalt(II):oxidant of 3 or 4:1 are used, again a green spot (R_f = 0.47) is formed, but unreacted cobalt(II) is also visible. After 12 h the green spot (R_f = 0.47) has disappeared, and been replaced by a green spot at R_f = 0.21. These results fit in with Jones' suggestions[8,9] if the first species formed is the trimeric oxo-centred cation, $[Co_3O(O_2CMe)_6(HO_2CMe)_n]^+$ (**3**), R_f = 0.47 rather than dimeric (**1**). This can react with further cobalt(II) (if present) to give (**2**) (R_f = 0.21). The t.l.c. experiments are not able to detect the fleeting species $[L_5Co{-}O{-}CoL_5]$ (L = O_2CMe or HO_2CMe) suggested by Jones as the first product in this oxidation.

Identification of the Compounds which have R_f *Values of* 0.21, 0.47, *and* 0.62.—The sample MEK contained mainly the compound with R_f = 0.21. Samples prepared by this method never contained more than 66% of the cobalt in the +III oxidation state. The only compound so far proposed which has this ratio of Co^{III}/Co^{II} is (**2**). The samples OZONE (mainly the compound with R_f = 0.47) and ELS (a mixture of compounds with R_f values 0.47 and 0.62 with a trace of a compound with R_f = 0.21) each contained Co^{III}/Co^{total} ratios above 0.86:1. T.l.c. analysis of solutions of $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ and

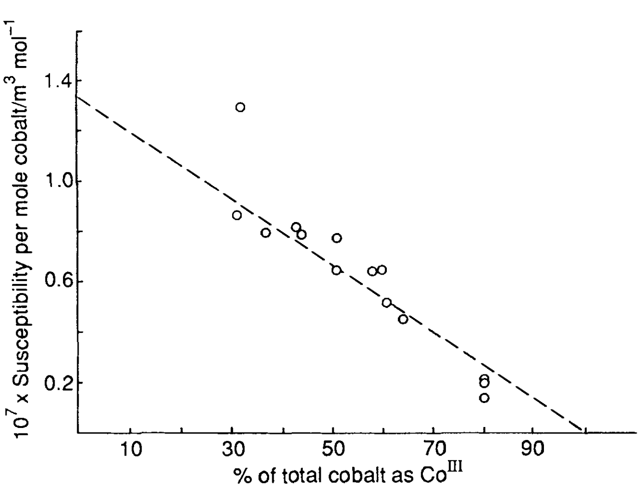

Figure 3. Plot of molar susceptibility of samples of cobalt(III) acetate against percentage of cobalt in sample present as cobalt(III) at room temperature (20 °C)

$[Fe_3O(O_2CMe)_6(H_2O)_3]Cl$ showed that these complex cations moved in a similar way to the major component of OZONE. Provisional identification is that OZONE contains mainly the oxo-centred cation (**3**) (R_f = 0.47), while ELS is a mixture of (**3**) and (**1**) (R_f = 0.62), with a small amount of (**2**).

Paper Electrophoresis of Cobalt(III) *Acetate Samples.*—Paper electrophoresis of solutions of cobalt(III) acetate showed that cations were present which moved less rapidly than pink cobalt(II). These cations moved towards the cathode at similar rates to the cations from $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ and $[Fe_3O(O_2CMe)_6(H_2O)_3]Cl$, which was taken as good evidence for the presence of cations (**3**). Most of the cobalt complexes moved very little [as expected for (**1**) and (**2**) which are both electrically neutral], whilst there was evidence for a small amount of an anionic complex, which moved very slowly towards the anode. Although some decomposition took place during the paper electrophoresis, this technique is valuable in separating charged complexes from uncharged ones.

Spectroscopy.—I.r. spectroscopy has been used to investigate the structures of oxo-centred trinuclear metal complexes.[11] The i.r. spectra of samples OZONE, MEK, and ELS were similar, and consistent with the presence of oxo-centred trinuclear complexes and bidentate acetate ligands. More detailed assignment was not possible.

N.m.r. spectroscopy was unfruitful as solutions of the cobalt acetate complexes always contained some paramagnetic cobalt(II). This broadened the peaks (spectra in CD_3OD) so much that all detail was lost for most samples. A few samples which contained the lowest concentration of cobalt(II) gave some detail, with methyl peaks in the region δ 1.9—2.5. Addition of one drop of CF_3CO_2D caused the methyl peaks to collapse to a single peak at δ 2.0, showing rapid equilibration between free and co-ordinated acetate groups.

Magnetic Susceptibility Measurements.—The magnetic susceptibility of all solid samples prepared by various methods was measured, and the molar susceptibility (calculated per mole of cobalt) plotted against the fraction of cobalt present as cobalt(III) (Figure 3). In Figure 3 is drawn the line expected if all the paramagnetism arises from cobalt(II). The majority of samples lie near to the theoretical line, within the accuracy of the cobalt analysis and the stability of the samples. We have no evidence for any paramagnetism associated with the cobalt(III) in any of the samples. This is contrary to the work of Kochi and co-workers[2] who reported a magnetic moment of 1.37 B.M. for their sample formulated as (**1**), and Ziolkowski *et al.*[3] who reported a magnetic moment of 2.1 B.M. for their sample formulated as (**2**). There is a problem if the samples change composition between analysis and the magnetic measurements, and Kochi suggests that his figures may arise, at least in part, from cobalt(II) present.

X-*Ray Absorption Spectra.*—EXAFS spectroscopy is a technique by which the short-range structural environment (up to *ca.* 4 Å) of a particular type of atom in a not necessarily crystalline sample can be investigated. Cobalt *K*-edge spectra were obtained as described in the Experimental section for three solid samples of cobalt(III) acetate (OZONE, ELS, and MEK) and for two 'model' compounds $[Co_3O(O_2CMe)_5(OH)(py)_3]PF_6$[5] and $K_4[Co_2(OH)_2(C_2O_4)_4]\cdot 3H_2O$.[12] The Co_3 model contains a slightly irregular triangle of cobalt atoms (Co $\cdots$ Co 2.76, 3.18, and 3.19 Å), the short edge being due to the presence of an OH bridge. Although the structure of $K_4[Co_2(OH)_2(C_2O_4)_4]$ has not been determined, the structures of a number of di-μ-hydroxo-dicobalt complexes have been reported,[13] and we assume that it is similar to that of the chromium analogue,[14] with symmetrically bridging OH groups and a Co $\cdots$ Co distance of *ca.* 2.9 Å (*i.e.* about 3% shorter than the Cr $\cdots$ Cr distance).

Initially, we attempted to fit the EXAFS spectra of OZONE and MEK (which were known to consist largely of the R_f = 0.47 and the R_f = 0.21 components respectively) by means of two alternative structural models: a trinuclear structure based on the $[Co_3O(O_2CMe)_6(HO_2CMe)_3]^+$ unit, comprising up to six shells of atoms, and a binuclear structure based on $[Co_2(O_2CMe)_4(OH)_2]$, comprising up to five shells.

Unfortunately, we found that reasonable fits could be obtained to both sets of data using either the trinuclear or the binuclear hypothetical structure. No significant improvement was obtained by using cobalt atom phases which had been optimised on the Co_3 model compound. Thus although the best fit of the OZONE data by the trinuclear structure was marginally better than that by the binuclear, and the MEK data were fitted by the binuclear structure slightly better than by the trinuclear, the differences were too small to allow definite assignment of a bi- or tri-nuclear structure to either sample.

Use of the ratio method of Stern, Sayers, and co-workers[15] gave a clearer picture. This method does not require knowledge of the phase-shift parameters, or detailed assumptions about molecular geometry. In the usual single-scattering theory, the amplitude of the EXAFS from a single shell of N identical atoms is given by equation (1), where $S_0{}^2$ and F are characteristic

$$A(k) = N\{S_0{}^2(k)F(k)\exp(-2k^2\sigma^2)\exp[-2(R-\Delta)/\lambda]\}/kR^2 \quad (1)$$

amplitude factors for the absorbing and back-scattering atoms, R is the radius of the shell, σ^2 is the mean-square variation in R due to vibration or static disorder, and Δ and λ are corrections for inelastic effects. For two components, A and B, of sufficiently similar natures, the respective values of $S_0{}^2$, F, λ, and $R - \Delta$ can be assumed to be approximately equal (phase and amplitude transferability) and equation (2) should then be true. Consequently a plot of $\ln[A_A(k)/A_B(k)]$ against k^2 should be linear

$$\ln[A_A(k)/A_B(k)] = \ln(N_A R_B{}^2/N_B R_A{}^2) - 2k^2(\sigma_A{}^2 - \sigma_B{}^2) \quad (2)$$

with intercept equal to $\ln(N_A R_B{}^2/N_B R_A{}^2)$. (Deviations from linearity at low k are to be expected as discussed below.) This provides a direct method by which the number of back-

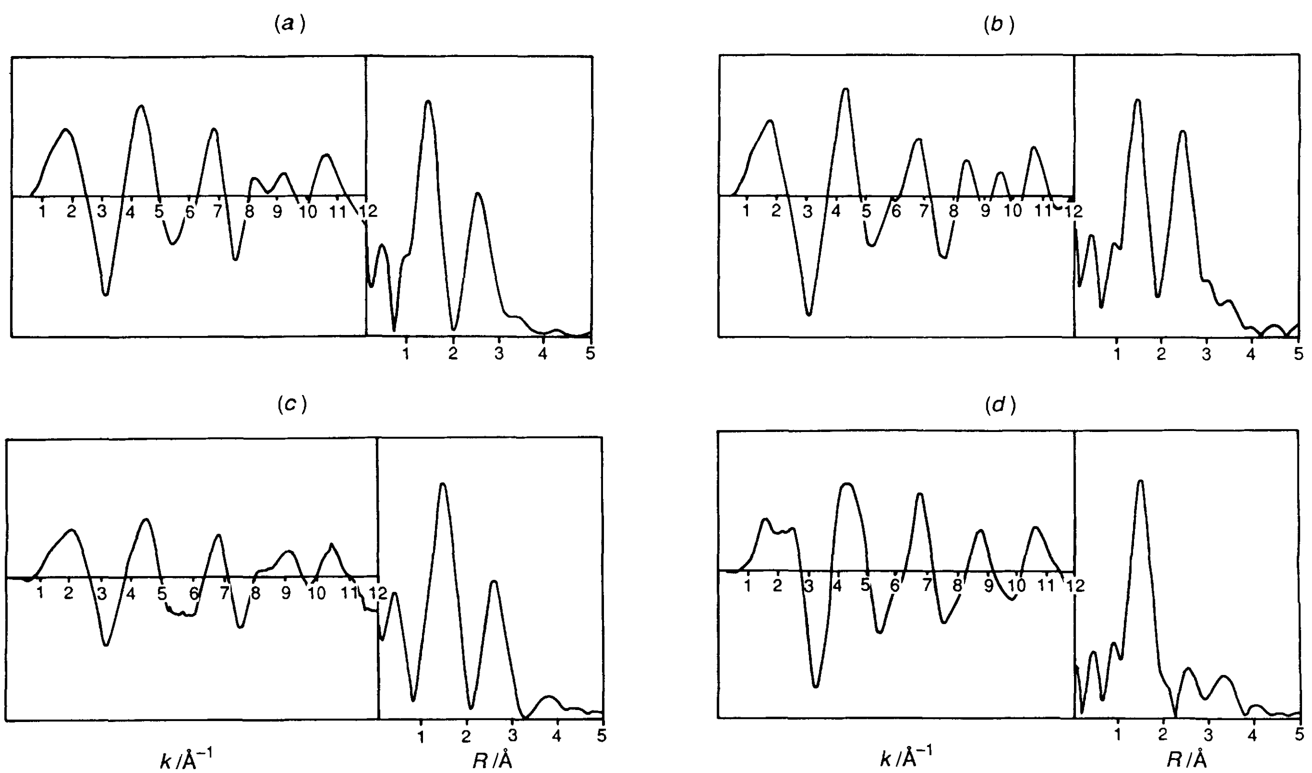

Figure 4. Left-hand diagrams: normalised k^2-weighted EXAFS spectra plotted against wave vector k/Å^{-1}. Right-hand diagrams: Fourier transforms of k^3-weighted EXAFS (k = 3.5—11.5 Å^{-1}) plotted against radial distance R/Å. Samples: (*a*) OZONE, (*b*) MEK, (*c*) $[Co_3O(O_2CMe)_5(OH)(py)_3]PF_6$, and (*d*) $K_4[Co_2(OH)_2(C_2O_4)_4]\cdot 3H_2O$

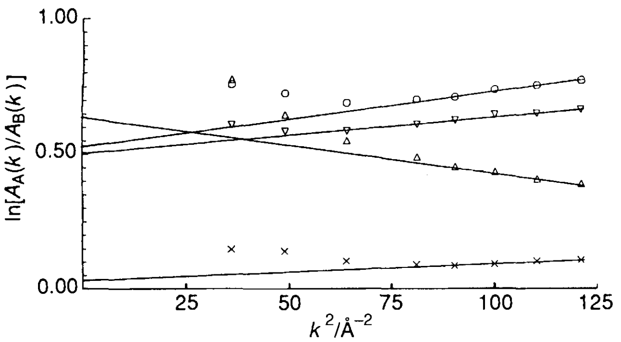

Figure 5. Plots of ln[$A_A(k)/A_B(k)$] against k^2. Upper three curves: A = OZONE (○), MEK (▽), ELS (△), B = $K_4[Co_2(OH)_2(C_2O_4)_4]\cdot 3H_2O$. Lower curve: A = OZONE, B = MEK (×)

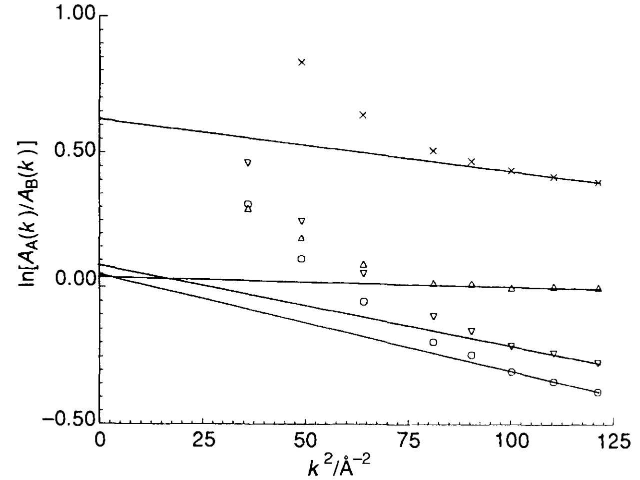

Figure 6. Plots of ln[$A_A(k)/A_B(k)$] against k^2. A = $[Co_3O(O_2CMe)_5(OH)(py)_3]PF_6$. Upper curve: B = $K_4[Co_2(OH)_2(C_2O_4)_4]\cdot 3H_2O$ (×). Lower three curves: B = OZONE (○), MEK (▽), or ELS (△)

scattering atoms in a given shell can be compared between two compounds.

In the Fourier transforms (*e.g.* Figure 4) of the k^3-weighted EXAFS of the five compounds studied there is a relatively well defined peak between about 2.3 and 3 Å which must contain the Co $\cdots$ Co scattering component (as well as contributions from several C and O atoms). This peak was isolated by means of a square-window function and transformed back to k space, and the resulting single-shell amplitude and phase were obtained as functions of k. Plots of ln[$A_A(k)/A_B(k)$] against k^2 were then constructed for various pairs of compounds, as shown in Figures 5 and 6.

Most of the plots are approximately linear over the range k^2 = 80—120 Å^{-2}, although they deviate considerably at lower k. This deviation can be attributed to several factors:[15] truncation effects introduced by the window function, non-transferability of amplitudes, neglect of multiple scattering (which becomes increasingly significant at low k), and the presence of C and O atoms as well as Co atoms in the shell. However, the k^3 weighting reduces the contribution from these low-Z atoms, since their scattering amplitudes fall off rapidly for $k > 5$ Å^{-1}, whereas that of Co is high over the range 6—10 Å^{-1}.[16] For the Co_3 model compound we used the average value of 3.05 Å for the cobalt-shell radius R, and for the Co_2 model a value of 2.9 Å. The intercept in Figure 6 then gives the ratio $N(Co_3 \text{ model})/N(Co_2 \text{ model})$ = 2.0:1. Since a regular Co_3 triangle has $N = 2$ and a Co_2 unit has $N = 1$ for a cobalt absorber, this result is in agreement with the known structures.

For the cobalt(III) acetate samples the cobalt-shell radii are not known. However, any value in the range 2.9—3.3 Å, when combined with the intercepts in Figures 5 and 6, leads to ratios

Table. Results of EXAFS curve fitting based on the trinuclear structure

		Sample OZONE[a]		Sample MEK[b]		
N	Atom	R/Å	D-W/Å^2	R/Å	D-W/Å^2	Assignment
1	O	1.84(2)	0.007	1.85(2)	0.005	Co-μ_3-O
4	O	1.87(2)	0.008	1.88(2)	0.020	Co-OCO
1	O	2.33(1)	0.005	2.30(1)	0.005	Co-O (terminal)
4	C	2.89(1)	0.023	2.98(1)	0.005	Co $\cdots$ CO$_2$
4	O	3.16(2)	0.000	3.19(2)	0.004	Co $\cdots$ OCO
2	Co	3.02(1)	0.004	3.01(1)	0.008	Co $\cdots$ Co

[a] E_0 = 33.7, VPI = −4.9 eV, fit index = 0.074. [b] E_0 = 39.3, VPI = −5.0 eV, fit index = 0.099. Unconstrained optimisation caused some of the Debye–Waller factors to become negative and VPI to become positive. The Debye–Waller factors were therefore given fixed positive values in the final optimisation of MEK.

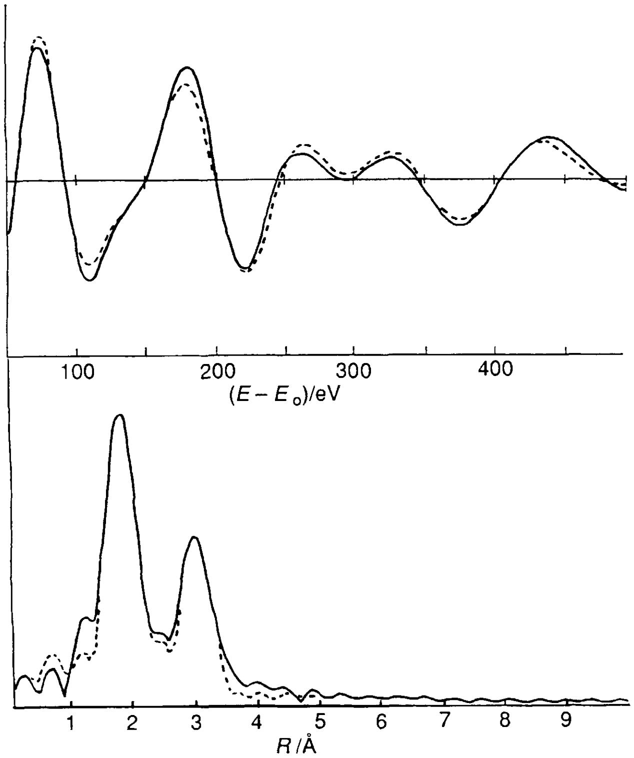

Figure 7. Optimised fit of trinuclear structure to EXAFS of sample OZONE: ——, experimental; – – –, calculated using the parameter values in the Table. Upper diagram: k^2-weighted Fourier-filtered EXAFS plotted against $(E - E_0)$/eV. Lower diagram: Fourier transform plotted against R/Å

N(Sample)/N(Co$_2$ model) 1.95 ± 0.3 and N(Sample)/N(Co$_3$ model) 1.05 ± 0.05, which clearly indicates that these samples contain Co$_3$ triangles rather than Co$_2$ pairs. Using R = 3.2 Å, the value expected for a regular Co$_3$O unit, we obtain the following values for the ratios: N(OZONE)/N(Co$_2$ model) = 1.9, N(MEK)/N(Co$_2$ model) = 1.8, N(ELS)/N(Co$_2$ model) = 2.1, N(OZONE)/N(MEK) = 1.05, N(Co$_3$ model)/N(OZONE) = 1.05, N(Co$_3$ model)/N(MEK) = 1.1, and N(Co$_3$ model)/N(ELS) = 1.0:1. In each case we estimate an uncertainty of ±10% in the value of the ratio.

The greater curvature at low k of the plots in Figure 6 may be due to the presence of two significantly different Co $\cdots$ Co distances in the Co$_3$ model compound, which would affect both the amplitude transferability and shell isolation.

Our conclusion is that all three cobalt(III) acetate samples consist predominantly of regular triangular Co$_3$ units. Hence it appears that both the R_f = 0.21 and the R_f = 0.47 components have structures based on the [Co$_3$O(O$_2$CMe)$_6$] unit, and we identify the former as the neutral, mixed-valence compound (**2**) and the latter as the fully oxidised cation (**3**).

Having established the basic geometry of these species, we used curve-fitting procedures to determine some structural details. The results of least-squares fitting of the EXAFS of samples OZONE and MEK, using a six-shell model based on a regular [Co$_3$O(O$_2$CMe)$_6$] unit, are listed in the Table and shown graphically for sample OZONE in Figure 7. (The best fit for sample MEK was slightly less satisfactory, possibly because of the presence of different oxidation states.) The interatomic distances are comparable with those in [Co$_3$O(O$_2$CMe)$_5$(OH)(py)$_3$]PF$_6$ (Co–μ_3-O 1.807, 1.816; Co–OCO 1.872—1.921; Co $\cdots$ CO$_2$ 2.808—2.872; Co $\cdots$ OCO 3.133—3.311; Co $\cdots$ Co 2.764, 3.185, and 3.188 Å).[5] Note that the Co–μ_3-O and Co $\cdots$ Co distances determined in our samples would imply that the central O atom lies out of the Co$_3$ plane by *ca.* 0.6 Å, compared with *ca.* 0.39 Å in the Co$_3$ model compound. It must be remembered, however, that these samples are not pure compounds [even OZONE, although largely compound (**3**), contains a fraction of (**2**)], and hence the structural information extracted by EXAFS analysis is of less than the usual precision.

Conclusion

The nature of cobalt(III) acetate has long been unclear, and in view of its catalytic activity in arene and alkane autoxidations[17] a deeper understanding has more than trivial interest. As the nature of cobalt(III) acetate depends markedly upon the method of preparation it is understandable that confusion has arisen in the past. Our work shows that there are a number of species containing cobalt(III) which can rapidly convert into each other. The most stable species is compound (**2**) which contains two cobalt(III) atoms and one cobalt(II) in an oxo-centred trimer. Oxidation of (**2**) gives the oxo-centred trimeric cation (**3**) where all three cobalt atoms are in the +III oxidation state. The uncharged hydroxo-bridged dimer (**1**) forms reluctantly, and is the last to form when cobalt(II) is electrolytically oxidised. In the preparation of solid cobalt(III) acetate samples it is important to avoid heating samples at any stage in solvent removal to ensure that the solids produced reflect as truly as possible the contents of the reaction mixture.

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