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EXAFS DETERMINATION OF THE COORDINATION ENVIRONMENT OF THE METAL IN THE HOMOGENEOUS ANIONIC $(NCCH_2Co(COOCH_3)(CO)_3)^-$ CARBONYLATION CATALYST

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Summary

Extended X-ray absorption fine structure (EXAFS) has been used to determine the local structure of cobalt in the complex $(NCCH_2Co(COOCH_3)(CO)_3)^- Na^+$ in alcoholic solution using the experimental phases and amplitudes derived from $NaCo(CO)_4$. The first coordination sphere consists of 3 C atoms at 1.83(2) and 2 C atoms at 2.13(2) Å, in a presumably trigonal bipyramidal arrangement.

Introduction

The known alkyl cobalt carbonyl complexes have generally been characterized only by spectroscopic techniques (viz. IR, NMR, Raman and mass spectrometry) [1–5]. The lack of X-ray structural characterization is mainly due to the instability of the products and to the difficulty of obtaining them pure and/or in suitable crystalline size. The molecular structures of only two complexes have been determined by X-ray diffraction [6].

In a previous paper two of us reported the formation of the new anionic complex $(NCCH_2Co(COOCH_3)(CO)_3)^- Na^+$ (I), and suggested a structure based on its IR, ^1H and ^{13}C NMR data and chemical behaviour [7]. Complexes such as I play an important role in the cobalt-catalyzed carbonylation of organic halides such as

ECH_2X (E = electron-withdrawing group [7]), and show other interesting catalytic properties [8]. It was considered of interest to gain further information about the structure of I in solution and we present below results of an EXAFS spectroscopy study of the local atomic arrangement around cobalt in complex I.

Experimental

Materials

Complex I was freshly prepared in MeOH solution according to ref. 7 and IR data were used to monitor formation of the anionic alkoxycarbonyl species. In view of its accepted tetrahedral cobalt coordination (Co–C 1.782 Å) [9], an alcoholic solution of $NaCo(CO)_4$ was chosen as a reference material to facilitate EXAFS phase and amplitude transfer. The freshly prepared solutions were kept overnight at −80°C under dry N_2 before the experiments described below.

X-Ray absorption measurements

The solutions were transferred under an inert atmosphere into 5 mm thick copper sample holders provided with 8 mm diameter kapton windows (thickness 25 μm). During the measurements the sample holders were kept at about −20°C by circulating a cooling fluid (CO_2 in EtOH) through the metal holder.

EXAFS spectra were recorded at LURE-CNRS on the DCI-EXAFS I spectrometer [10] (with the DCI storage ring operating at 1.56 GeV with currents of about 100 mA), using an Si (220) channel-cut monochromator. The data were recorded by means of air-filled ionization chambers as counters using 2 eV intervals over an energy range of 1 keV, up to 750 eV above the Co K-edge. Each spectrum was recorded four times.

Data handling

The data obtained are measures of the X-ray linear absorption coefficient μ in terms of the incident beam intensity I_0, the transmitted intensity I and the sample thickness x, as

$$\mu x = \ln(I_0/I) \tag{1}$$

The EXAFS modulation of the absorption coefficient above an absorption edge is given by

$$\chi(k) = \frac{\mu x(k) - \mu_B x(k) - \mu_0 x(k)}{\mu_0 x(k)} \tag{2}$$

where μ_B is background originating from pre-edge absorption processes and μ_0 the smooth atom-like contribution above the edge. The photoelectron wave-vector k is given by

$$k = \left[\frac{2m}{\hbar^2}(E_x - E_0)\right]^{1/2} \tag{3}$$

where E_x is the incident photon energy, E_0 is the photoelectron binding energy, m the electron mass, and $\hbar$ Planck's constant. For a K-edge, the simple back-scattering theory gives the relationship between the EXAFS signal $\chi(k)$ and the structural parameters [11] as the expression:

$$k\chi(k) = \Sigma_i \frac{N_i}{R_i^2} \cdot e^{-2\sigma_i^2 k^2} \cdot F_i(k) \cdot \sin[2kR_i + \Phi_i(k)] \qquad (4)$$

where R_i is the average distance separating the absorbing atom from the N_i neighbouring atoms of the ith shell, with a r.m.s. deviation σ_i (the $\exp(-2\sigma_i^2 k^2)$ Debye–Waller reflects statistical and thermal disorder); $F_i(k)$ and $\Phi_i(k)$ are the amplitude back-scattering factor and phase shift, respectively, experienced by the photoelectron and are characteristic of the selected (absorbing atom)-(back-scattering shell i) pair.

Data processing was carried out on a UNIVAC 1100/20 computer, by our standard procedure [12,13] which is briefly summarized as follows:

(i). The spectral data were 'deglitched' and averaged.

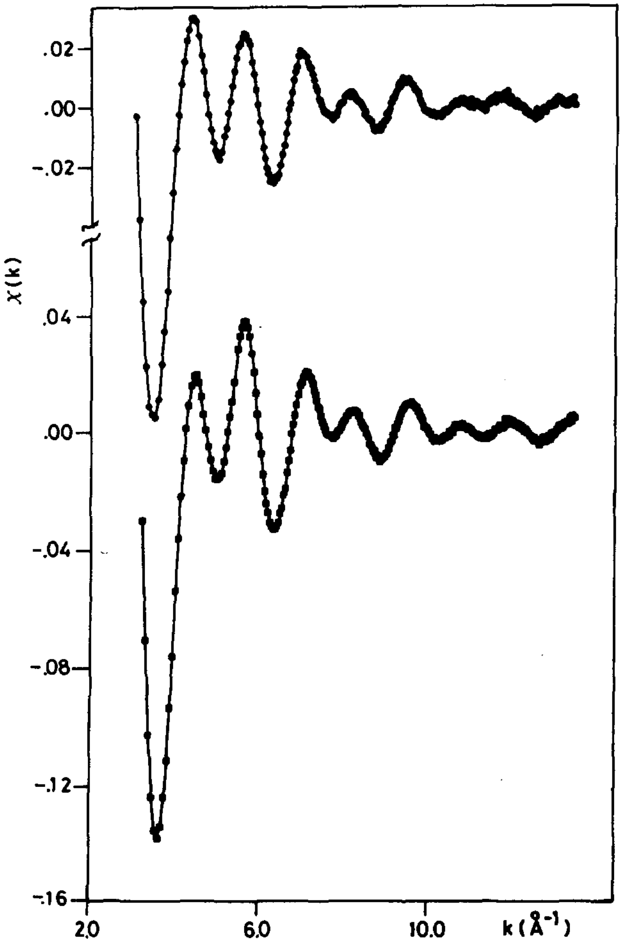

Fig. 1. EXAFS spectrum $\chi(k)$ vs. k at the Co K-edge for $(NCCH_2Co(COOCH_3)(CO)_3)^-$ Na^+ (top) and $NaCo(CO)_4$ (bottom) in alcoholic solution at $-20°C$.

(ii). μ_B was extrapolated from the pre-edge region in the form of a Victoreen fit ($\mu_B x = C\lambda^3 + D\lambda^4$) and subtracted from the experimental data. The term $\mu_0(k)$ was first expanded in a fourth-order polynomial in k and the slow residual oscillations of $\chi(k)$ were then eliminated by a multi-iterative process whose effect appears only at the very small R-values (typically $R < 1$ Å) of the modulus of the Fourier-transform. In this process E_0 was arbitrarily chosen as the inflection point of the Co K-edge in $NaCo(CO)_4$ (E_0 7722.0 eV). The reduced data so obtained in terms of eq. 2 are shown in Fig. 1 as a plot of $\chi(k)$ vs. k.

(iii). The EXAFS spectra were then Fourier-transformed from k to R-space using a Hanning window (applied to the $k_{min} + \delta k$ and $k_{max} - \delta k$ ranges, with k_{min} 3.16, k_{max} 12.55 and δk 1.1 Å^{-1}) chosen so as to minimize the loss in resolution, in accord with the instructions of Mobilio et al. [14]. For the Fourier transformation $\chi(k)$ was multiplied by k^3 in order to enhance the features of the high energy part of the EXAFS spectrum which are usually blurred by the rapid damping of $\chi(k)$. Figure 2

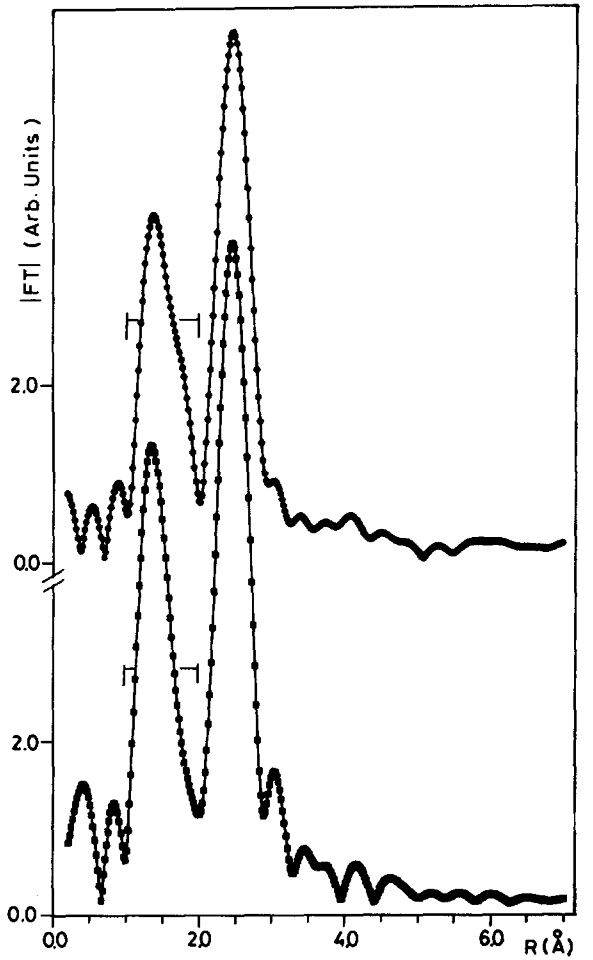

Fig. 2. Modulus of the Fourier transform of $k^3(k)$ vs. k for $(NCCH_2Co(COOCH_3)(CO)_3)^-$ Na^+ (top) and $NaCo(CO)_4$ (bottom) in alcoholic solution at −20°C.

shows the amplitude of the Fourier-transformed spectra $|FT|$ vs. R for the samples. The contribution of each shell of atoms surrounding the absorbing atom can be isolated in R-space.

(iv). The structural parameters (i.e. N_i, R_i and σ_i) can be obtained by least-squares fitting the Fourier-filtered spectra of each shell to eq. 4, provided $F_i(k)$ and $\Phi_i(k)$ are known. For this purpose a physically reasonable model was assumed for the first shell and a reference compound ($NaCo(CO)_4$) of known crystallographic structure was analyzed. The derived values of $F_i(k)$ and $\Phi_i(k)$ were transferred to the filtered Fourier-transform of the first peak of the complex, allowing a variation of E_0 (ΔE_0) in order to take into account any approximation in the transferability (the adjusted wave-vector is $k' = [k^2 + 0.262467\Delta E_0]^{1/2}$).

In our case, for the standard material the value of $\exp(-\sigma_{st}^2 k^2)$ is convoluted with the $F(k)$ function, so that the calculated parameter σ_{un} in the unknown system has a relative value only, i.e. $\Delta\sigma = \sigma_{un} - \sigma_{st}$.

Results and discussion

Two well-defined shells of atoms surrounding the absorbing Co atoms are clearly visible for the reference and (cyanomethyl)(methoxycarbonyl)-cobalt tricarbonyl species (Fig. 2). The first peak of both transforms is attributable to the Co–C pair, whereas the second peak may be ascribed to the Co–O distances. In view of the collinearity of the atoms in the cobalt carbonyl structural unit the second peak is strongly enhanced as a result of the so-called focussing effect, and its analysis cannot simply be conducted on the basis of eq. 4 [15].

It is significant that the first peak of the $|FT|$ of I has a shoulder at high R values (not visible in the corresponding transform of the reference sample), which is indicative of a double Co–C shell. The experimental phase and amplitude of the Co–C absorber-backscatterer couple were obtained by back-transforming part of the FT of the reference compound (within the limits indicated in Fig. 2) to k-space, assuming a four-fold carbon coordination at a Co–C distance of 1.782 Å [9]. After transfer to the back-transform of the first peak of the anionic complex the structural parameters (N, R, $\Delta\sigma$) of interest and ΔE_0 were determined by least-squares fitting. It will be seen that a Co–C single-shell fit gave poor agreement between the calculated and observed data (Fig. 3, bottom) and satisfactory results were achieved by the use of a double Co–C shell model (Fig. 3, top). Table 1 summarizes the numerical data for the standard and those calculated for the complex. The estimated standard deviation of the (average) bond distances is about 0.02 Å with an accuracy for N and σ of the order of 10%. In view of the complexity of the anionic structure

TABLE 1

RESULTS OF FITTING PROCEDURE

Sample	Back-scatterer	R (Å)	N	$\Delta\sigma$ (Å)	ΔE_0
$NaCo(CO)_4$	C	1.782	4.0	–	–
I (one-shell)	C	1.81	2.4	0.0	−1.0
I (two-shells)	C	1.83	3.1	0.0	0.0
	C	2.13	2.1	0.041	0.0

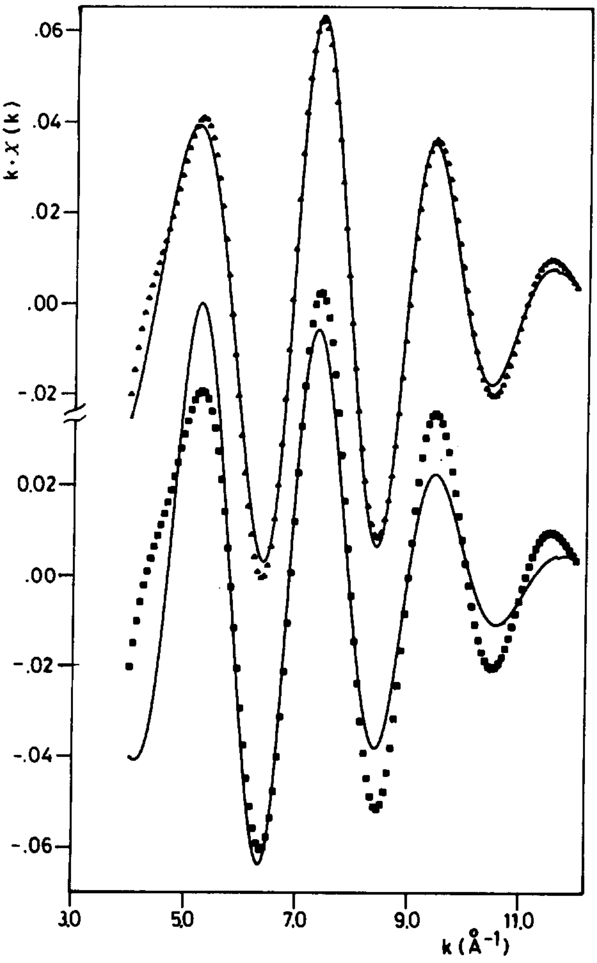

Fig. 3. Co–C two-shell (top) and one-shell (bottom) fit of the first peak of the anionic complex.

we also attempted to discriminate between the Co–C distances of the Co–C–CN and Co–$COOCH_3$ groups but without significant results; quality of the fit is not essentially improved with respect to that of Fig. 3 (top), and the difference (ΔR) in these Co–C distances (calculated by the fitting procedure) is of the order of 0.1 Å, which is not considered significant in view of the limited EXAFS data range. In this context it is recalled that the minimum observable ΔR value is given by $k_{max} = \pi/2\Delta R$ [16].

Conclusions

On the basis of the numerical results it is reasonable to suppose that the local metal environment in the anionic complex is of bipyramidal trigonal type with three (equatorial) C atoms of the carbonyl ligands at 1.83(2) Å and two longer axial Co–C bonds, with lengths of 2.13 Å (mean value).

With regard to the observed value of 0.041 Å for $\Delta\sigma$ for the twofold (presumably axial) Co–C distance, two hypotheses can be advanced:
(a) the (axial) bond lengths are indeed equal, and $\Delta\sigma$ represents effectively a variation with respect to the reference sample;
(b) the two (axial) bond lengths (mean value 2.13 Å) differ from each other by $\Delta R \approx 0.1$ Å. In this case the calculated $\Delta\sigma$ value reflects the fact that during the fitting procedure a common Co–C distance was used instead of two different ones (even though the limited EXAFS data range does not discriminate between distances with ΔR of the order of 0.1 Å).

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