Polyacrylate Resins bearing the Transition Metal Cluster Unit $Co_3(CO)_9C$

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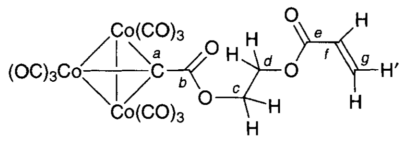
The alkylidyne tricobalt nonacarbonyl clusters $[Co_3(CO)_9\{C(CO)OCH_2CH{=}CH_2\}]$ **1** and $[Co_3(CO)_9\{C(CO)O(CH_2)_2O(CO)CH{=}CH_2\}]$ **2** are prepared; compound **2** readily undergoes polymerisation to form polyacrylate resins containing the $CCo_3(CO)_9$ unit intact, as shown by GPC/UV–VIS and IR spectroscopy.

We are particularly interested in developing routes to new monomeric precursors to polymeric materials and films containing potentially photolytically active cobalt centres. To this end we have undertaken a systematic exploration of derivatives of the $Co_3(CO)_9C$ unit containing known polymer precursor units. In this communication we report the full characterisation of the two compounds $[Co_3(CO)_9(CR)]$ [**1**, R = $(CO)OCH_2CH{=}CH_2$ and **2**, R = $(CO)OCH_2CH_2O(CO)CH{=}CH_2$], together with polymerisation and copolymerisation of **2** to produce stable films.

Several years ago Seyferth and his coworkers[1] described the formation of the acylium haloaluminate salt $[Co_3(CO)_9(CCO)][AlX_4]$ from the reaction of aluminium trihalide AlX_3 (X = Cl, Br or I) with the halomethylidyne tricobalt nonacarbonyl complex $[Co_3(CX)(CO)_9]$ (X = Cl, Br). They further reported that, on reaction with a diverse range of nucleophiles Y, this salt formed the cluster compounds $[Co_3\{CC(O)Y\}(CO)_9]$. At that time these compounds were characterised solely on the basis of the usual spectroscopic and analytical methods.

Compound **1** was prepared by the method previously reported by Seyferth and his coworkers[1] by reacting freshly prepared $[Co_3(CO)_9C(CO)][AlCl_4]$ with allyl alcohol. After separation by column chromatography on silica, very dark purple crystals suitable for X-ray diffraction analysis were grown by vacuum sublimation. Compound **2** was prepared from $[Co_3(CO)_9C(CO)]^+$ and $HOCH_2CH_2O(CO)CHCH_2$ following essentially the same procedure. This compound was characterised solely on the basis of its spectroscopic properties (Fig. 1) and its structure is totally analogous to that established for **1** (see below).

We find that compound **1** does not readily undergo polymerisation but that **2** readily forms dark purple polymeric



	δ (¹H)	δ (¹³C)
a	—	178.5
b	—	170.0
c	4.54, m, 2 H	63.5
d	4.44, m, 2 H	62.6
e	—	165.8
f	6.05, dd, 1 H, J_{cis} = 17.2, J_{trans} = 10.4 Hz	128.2
g	H: 6.38, dd, 1 H, J_{trans} = 10.4, J_{gem} = 1.6 Hz H′: 5.80, dd, 1 H, J_{cis} = 17.2, J_{gem} = 1.6 Hz	130.9
Co(*C*O)	—	199.0

NMR solvent: $CDCl_3$

FTIR (CH_2Cl_2): ν(CO)/cm⁻¹: 2109m, 2062vs, 2046vs, 1724m and 1681m; FABMS: M + 3 = 587, plus sequential loss of 9 CO ligands

Fig. 1 Spectroscopic properties of compound **2**

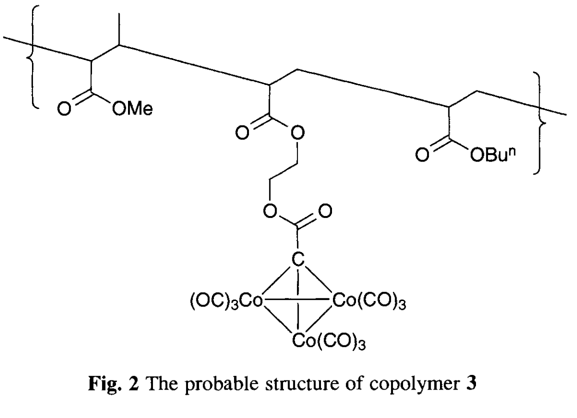


Fig. 2 The probable structure of copolymer **3**

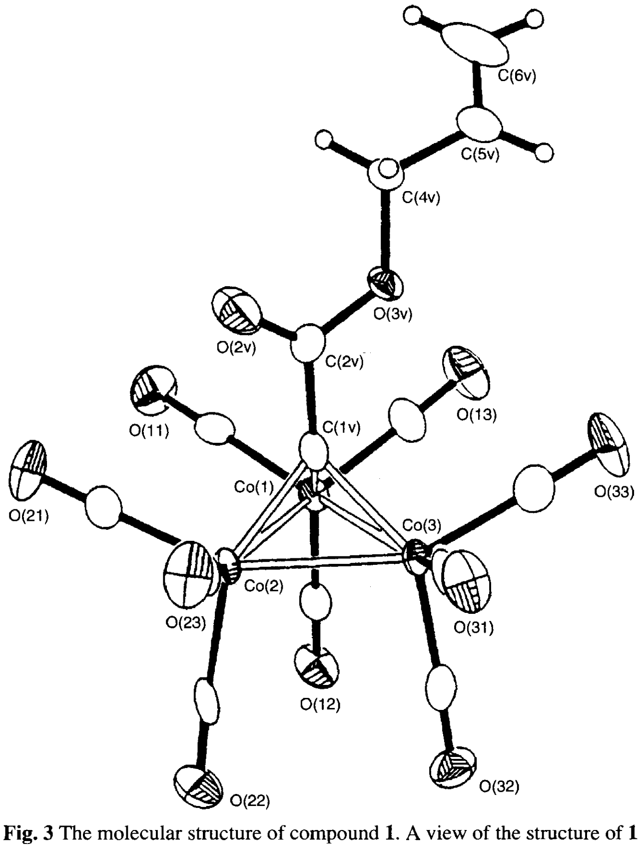
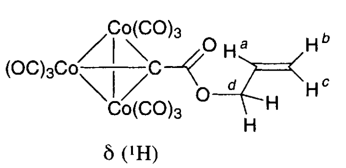


Fig. 3 The molecular structure of compound **1**. A view of the structure of **1** showing the atom numbering scheme: within each carbonyl group the C and O atoms bear the same number. Thermal ellipsoids for the non-H atoms are drawn to encompass 50% probability surfaces. Significant molecular geometry parameters are Co(1)–Co(2) 2.475(2), Co(1)–Co(3) 2.473(2), Co(2)–Co(3) 2.469(2), Co(1)–C(1v) 1.897(4), Co(2)–C(1v) 1.873(4), Co(3)–C(1v) 1.904(4), C(1v)–C(2v) 1.479(5), C(2v)–O(2v) 1.203(5), C(2v)–O(3v) 1.337(4), O(3v)–C(4v) 1.456(4), C(4v)–C(5v) 1.471(5), C(5v)–C(6v) 1.305(6) Å; Co(1)–Co(2)–Co(3) 60.03(6), Co(2)–Co(1)–Co(3) 59.86(5), Co(1)–Co(3)–Co(2) 60.11(5), Co(1)–C(1v)–C(2v) 131.0(3), Co(2)–C(1v)–C(2v) 130.3(3), Co(3)–C(1v)–C(2v) 131.7(3), C(1v)–C(2v)–O(2v) 123.8(3), O(2v)–C(2v)–O(3v) 123.1(3), C(1v)–C(2v)–O(3v) 113.0(3), C(2v)–O(3v)–C(4v) 116.3(3), O(3v)–C(4v)–C(5v) 108.4(3), C(4v)–C(5v)–C(6v) 124.7(4)°.

materials on heating on its own or in the presence of appropriate copolymerisation monomers. In contrast to the monomer **2**, these polymers are relatively air-stable. Thus, for example, free-radical-initiated solution polymerisation of **2** with mixtures of methyl methacrylate and butylacrylate produces a dark purple polymer **3**. Varying amounts of $Co_3(CO)_9C$ may be incorporated into the copolymer by changing the ratio of **2** relative to methyl methacrylate and butylacrylate. The general structure of these random co-polymers is shown in Fig. 2. These co-polymers, when drawn down with a thin film blockspreader (*ca.* 100 μm gap) produce, on evaporation of the solvent, hard integrated stable films, in which the $Co_3(CO)_9C$ units remain fully intact, apparently indefinitely, under ambient atmospheric conditions. The presence of the $Co_3(CO)_9C$ unit in both the copolymer **3** and in these films was readily confirmed by GPC-UV/VIS and IR spectroscopy [ν(CO)/cm^{-1} : 2111.3w, 2064.0vs and 2046.8 m]. GPC data shows molecular weights of **3** to be in the range 10 000–30 000.

The structure determination† of **1** (Fig. 3) shows a $Co_3(CO)_9C$ fragment similar to that observed in a large number of related derivatives with C_3 symmetry and bound symmetrically to C(1v), the first atom of the –C–C(=O)–O–CH_2–CH=CH_2 substituent chain. A search of the Cambridge Structural Database showed that the internal molecular geometry of this chain differs very little from that found in the small number of organic compounds which contain the substituent. The most striking differences affect the C(1v)–C(2v) and C(5v)=C(6v) distances of 1.479(5) and 1.305(6) Å respectively. However, these values lie close to those found in bis[(μ-chloro)(allyl acetato-*O*)trichlorotitanium(IV)].[2] The chain adopts a *trans–trans–gauche* conformation about C(2v)–O(3v) and O(3v)–C(4v); the torsion about C(4v)–C(5v) is such that C(6v) eclipses one of the methylene H atoms on C(4v). The established structure is entirely consistent with the spectroscopic data (Fig. 4).



	δ (¹H)
a	5.93–6.12, m, 1 H
b	5.26, dd, 1 H, J_{cis} = 18.8, J_{gem} = 1.27 Hz
c	5.37, dd, 1 H, J_{trans} = 10.3, J_{gem} = 1.27 Hz
d	4.77–4.81, m, 2 H

NMR solvent: $CDCl_3$

FTIR (CH_2Cl_2) ν(CO)/cm^{-1}: 2104m, 2064vs, 2046vs and 1681m; FABMS: M + 3 = 527, plus sequential loss of 9 CO ligands

Fig. 4 Spectroscopic properties of compound **1**

In this work we have been able to establish that moderately stable monomers containing the $Co_3(CO)_9C$ unit are readily accessible, and that in certain cases these easily undergo polymerisation or copolymerisation to produce stable polymeric units, which have the potential for ambient temperature film formation.

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Footnote

† *Crystal data*: $C_{14}H_5Co_3O_{11}$, M = 525.97, triclinic, space group $P\bar{1}$, a = 7.879(5), b = 8.719(6), c = 15.182(9) Å, α = 73.48(5), β = 78.87(5), γ = 67.51(5)°, U = 919.7 $Å^3$, D_c = 1.899 g cm^{-3}, Z = 2, μ = 2.730 mm^{-1}. Diffraction data were collected on a Stoe Stadi-4 four-circle diffractometer employing graphite-monochromated Mo-Kα X-radiation, ω/2θ scan mode and a learnt-profile method (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22). Due to its suspected sensitivity, a dark red crystal (lath: 0.23 × 0.15 × 0.08 mm^3) was coated in paraffin oil and quickly transferred into the cold stream of an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105) operating at 150.0(1) K. The 3054 reflections collected were corrected semi-empirically for absorption using ψ scans (transmission factors 0.619–0.760) and merged to give 2667 unique data (R_{int} 0.027). Automatic direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) identified the positions of the Co atoms and iterative cycles of least squares refinement (on F^2) and difference Fourier synthesis located the remaining non-hydrogen atoms (SHELXL-93: G. M. Sheldrick, University of Göttingen, Germany, 1993). A total of nine data, which were either ill-fitting low-angle reflections or had large negative values of F_o^2, were omitted from the analysis, leaving 2658 observations. Non-H atoms were refined anisotropically and H atoms were included in fixed, calculated positions with isotropic thermal parameters. The weighting scheme $\{w^{-1} = \sigma^2(F_o)^2 + (0.035)p^2;\ p = [(F_o^2, 0)_{max} + 2F_c^2]/3\}$ led to final convergence with $R1$, $wR2$ = 0.0258, 0.0575 respectively, S = 1.010 for 259 refined parameters and the final ΔF synthesis showed no peaks above ±0.35 $Å^{-3}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors. Issue No. 1.

References

1 D. Seyferth, G. H. Williams and C. L. Nivert, *Inorg. Chem.*, 1977, **16**, 758.
2 T. Lis, J.Utko and P. Sobota, *Acta Crystallogr., Sect. C*, 1993, **49**, 2089.