ELSEVIER

Journal of Organometallic Chemistry 573 (1999) 60–66

Journal of Organo metallic Chemistry

A structural redetermination of $Co_4(CO)_{12}$: evidence for dynamic disorder and the pathway of metal atom migration in the crystalline phase[1]

Louis J. Farrugia [a],*, Dario Braga [b], Fabrizia Grepioni [b]

[a] *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK*
[b] *Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*

Received 11 March 1998

Abstract

The X-ray structure of $Co_4(CO)_{12}$ has been determined at 120 K, and redetermined at ambient temperature. At the lower temperature, the carbonyl positions for both disordered components have been resolved, affording more accurate molecular geometrical parameters. At ambient temperature four disordered orientations of the Co_4 tetrahedron are observed, which are related by rotations about one of the five fold axes of the ligand icosahedral polytope. The minor component disorder is dynamic in origin, and indicates that the Co_4 tetrahedra are rotating inside a relatively rigid ligand polytope. © 1999 Elsevier Science S.A. All rights reserved.

---

1. Introduction

The structures and dynamics, in both solution and solid phase, of the simple carbonyl clusters $M_3(CO)_{12}$ (M = Fe, Ru, Os) and $M_4(CO)_{12}$ (M = Co, Rh, Ir), have been the focus of numerous, and sometimes controversial [1] studies. In particular, they have been used as "archetypes" for discussions on the fluxional behaviour of metal carbonyls in general, as exemplified by the ligand polyhedral model [2] of Brian Johnson. These studies have tended to focus on the Group 8 metals, though the Group 9 metals pose equally interesting problems.

The determination of the crystal and molecular structure of $Co_4(CO)_{12}$ has been hampered by problems of disorder. Two-dimensional X-ray studies by Corradini and coworkers [3] established the basic C_{3v} structure, with four cobalt atoms and 12 carbonyl ligands, three of which were bridging between two cobalt atoms. The molecule lies on a crystallographic 2-fold axis in the space group *Pccn*, with the result that the cobalt tetrahedron is disordered over two sites, with one vertex in common. The set of carbonyl ligands for both half-molecules are almost superimposed, because of the effective inversion symmetry of the icosahedron they describe. Subsequent three-dimensional studies carried out at room temperature by Wei and Dahl [4] and Cotton and coworkers [5] confirmed this view. Despite some effort, Cotton and coworkers [5] were unable to 'pry apart' the two sets of carbonyl positions in $Co_4(CO)_{12}$, as they were able to do [6] for the similarly disordered $Fe_3(CO)_{12}$. This disorder has prevented the determination of accurate geometrical parameters for the molecule.

In solution $Co_4(CO)_{12}$ is highly fluxional, [7] and at low temperatures shows two signals in the ^{59}Co-NMR spectrum [8,7] and four signals in the ^{17}O-NMR spectrum [9] consistent with the solid state C_{3v} structure. Several ^{13}C-NMR studies [7] showed only three equally

---

* Corresponding author. Tel.: +44 141 3305137; fax: +44 141 3304888; e-mail: louis@chem.gla.c.uk

[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday in recognition of his outstanding contributions to organometallic and inorganic chemistry.

PII S0022-328X(98)00879-1

intense resonances, which is incompatible with the C_{3v} structure, and which led to some confusion as to the solution structure. This confusion was clarified in a study by Aime et al., [10] who showed that the fourth resonance, required by the C_{3v} structure, is present but is extremely broad. The broadness of this signal, due to the apical carbonyls, is caused by scalar coupling between ^{13}C and ^{59}Co, and by scalar relaxation of the second kind. Johnson and coworkers [11,12] have proposed that several complementary geometries are possible for the carbonyl polytopes of the clusters $M_4(CO)_{12}$ (M = Co, Rh, Ir) in solution, leading to several possible exchange mechanisms.

In the solid state, the motion of the carbonyl ligands is probably quite restricted, and any fluxional exchange is likely to involve the migratory motion of the metal skeleton inside a relatively rigid ligand polytope. This has been recently demonstrated for several clusters of the type $M_3(CO)_{12}$ (M = Fe, Ru, Os) [13,14]. Four variable temperature ^{13}C MAS studies on $Co_4(CO)_{12}$ have been reported [15–18] which are surprisingly different, but all indicate a significant temperature dependence of the bandshape. In accordance with the observed disorder [3–5] in the crystal structure, it has been suggested [15,17] that the Co_4 tetrahedron is rotating inside the carbonyl polyhedral cage, about the crystallographic two-fold axis. However, on the basis of the thermal parameters of the cobalt atoms, Braga et al. [19] have proposed an alternative suggestion of libration of the Co_4 tetrahedron about the pseudo 3-fold axes. More recent work by Heaton and coworkers using ^{59}Co-NMR [18] and 2D nutation studies [20] has led to a third suggestion that a restricted re-orientation about the molecular 3-fold axis occurs, which conserves the identity of the unique apical cobalt atom.

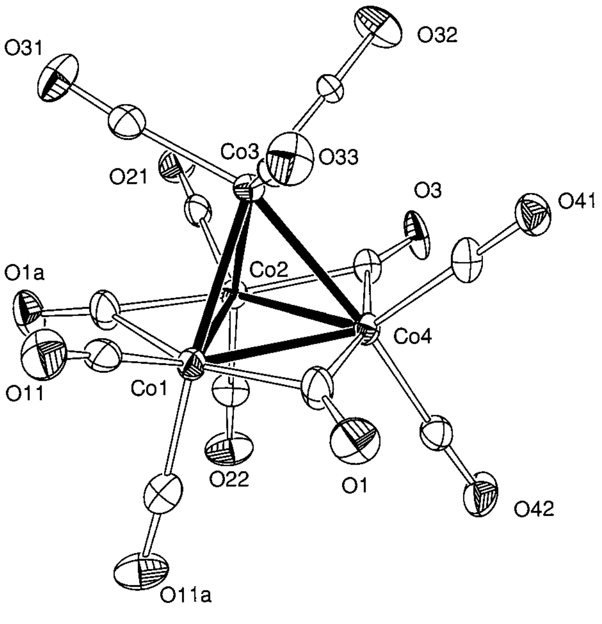

Fig. 1. Molecular structure and atomic labelling scheme for $Co_4(CO)_{12}$ at 120 K. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms have the same label as their attached oxygen atoms.

Table 1
Selected bond lengths (Å) and bond angles (°) for $Co_4(CO)_{12}$ at 120 K

Bond Lengths			
Co(1)–Co(2)	2.522(1)	Co(1)–Co(3)	2.454(1)
Co(1)–Co(4)	2.477(1)	Co(2)–Co(3)	2.529(1)
Co(2)–Co(4)	2.446(1)	Co(3)–Co(4)	2.513(1)
Co(1)–C(1)	1.940(4)	Co(1)–C(11)	1.800(4)
Co(2)–C(1)	2.016(4)	Co(2)–C(21)	1.792(10)
Co(2)–C(22)	1.799(14)	Co(3)–C(31)	1.858(14)
Co(3)–C(32)	1.826(13)	Co(3)–C(33)	1.825(12)
Co(4)–C(3)	1.928(11)	Co(4)–C(41)	1.779(10)
Co(4)–C42)	1.820(15)		
C–O (mean)	1.133(20)		
Angles			
Co(1)–C(1)–O(1)	142.8(3)	Co(4)–C(1)–O(1)	134.2(3)
Co(2)–C(1)–O(1)	133.1(4)	Co(4)–C(3)–O(3)	142.1(9)
Co(2)–C(3)–O(3)	139.2(9)	Co(1)–C(11)–O(11)	176.6(4)
Co(2)–C(21)–O(21)	176.2(11)	Co(2)–C(22)–O(22)	178.7(12)
Co(3)–C(31)–O(31)	175.7(13)	Co(3)–C(32)–O(32)	178.2(11)
Co(3)–C(33)–O(33)	179.1(11)	Co(4)–C(41)–O(41)	178.3(10)
Co(4)–C(42)–O(42)	177.7(14)		

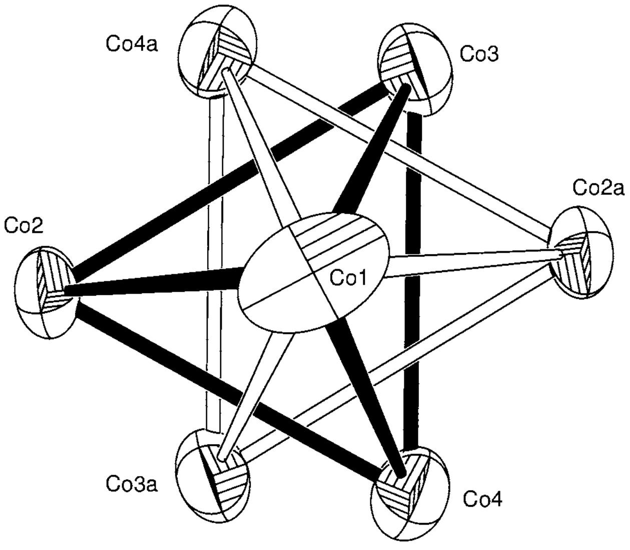

Fig. 2. View of the disordered pair of cobalt tetrahedra at 120 K. The view is along the crystallographic 2-fold axis, with thermal ellipsoids at the 50% probability level.

In this paper we report a high resolution ($\theta_{max} = 30°$) redetermination of the room temperature single crystal X-ray structure of $Co_4(CO)_{12}$ and a determination of the structure at 120 K. These studies provide more accurate molecular parameters for $Co_4(CO)_{12}$, and show unequivocally that there is dynamic disorder in the metal skeleton.

2. Results and discussion

There was no sign of a phase transition to another crystal system or space group in $Co_4(CO)_{12}$ on lowering the temperature from ambient to 120 K. The space group remains the orthorhombic centrosymmetric *Pccn*, as found in the earlier studies [3–5]. However, several improvements in our determination at 120 K, over the previous [3–5] room temperature studies, allowed more accurate molecular geometrical parameters to be obtained for this archetypal carbonyl cluster. In particular, it has proved possible to separate all the carbonyl positions for the two orientations, except those for the carbonyl atoms of CO(1) and CO(11), which were either too close together or coincident in the two orientations.

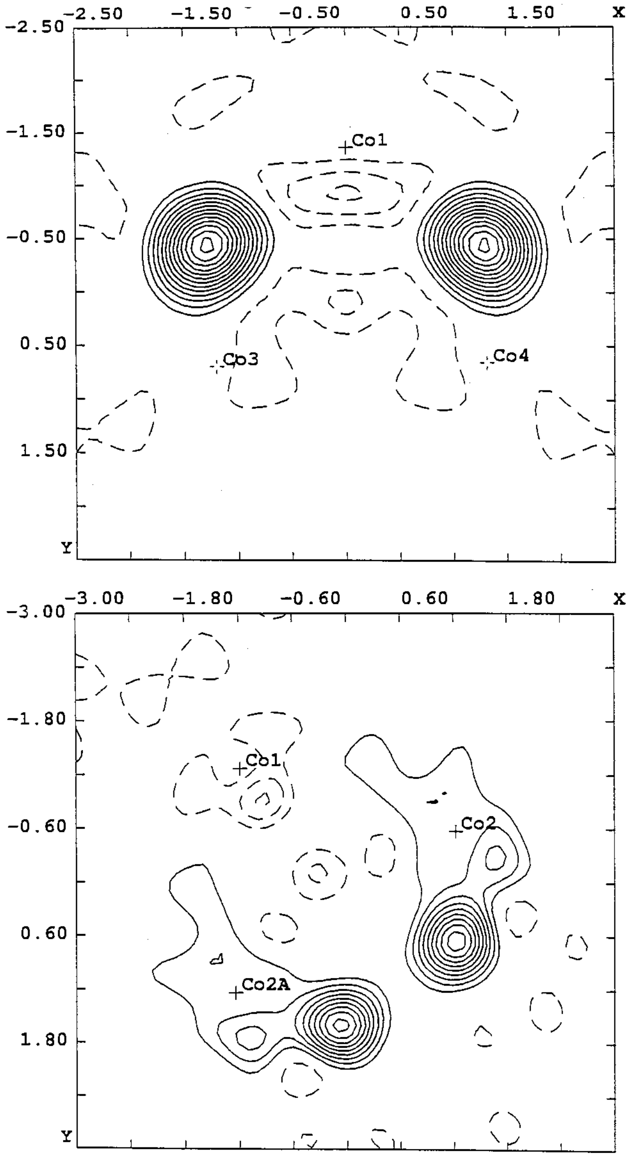

Fig. 3. Fourier map sections through the two most intense residuals (see text). Contours are drawn at the 0.25 e Å^{-3} level, positive contours are shown as solid lines, negative contours as broken lines.

The molecular structure and atomic labelling scheme is shown in Fig. 1, and important metrical parameters are given in Table 1. All atoms, apart from CO(1) and CO(11), have site occupation factors of 0.5, as required by the crystallographic two-fold axis which passes through the cobalt atom Co(1). The molecular geometry obtained in this study is much more realistic than in the previous [3–5] studies. In particular the terminal carbonyls are all very close to linearity, with a mean Co–C–O angle of 177.5° and a range 175.7(13)–179.1(11)°. The three Co(basal)–Co(apical) distances average 2.499 Å (range 2.454(1)–2.529(1) Å), while the three Co(basal)–Co(basal) distances average 2.482 (range 2.446(1)–2.522(1) Å). The latter is thus only 0.017 Å shorter than the former, though the range is quite large. In a study on the metal–metal bond lengths in substitution derivatives of $M_4(CO)_{12}$ (M = Co, Rh, Ir) [21], the mean Co(basal)–Co(basal) distance was found to be 0.068 Å shorter than the mean Co(basal)–Co(apical) distance. In $Co_4(CO)_{12}$ itself, this difference appears to be substantially less, but this may be an artefact (see below). The two longest Co–Co distances and the shortest distance are associated with Co(2). The order of increasing Co–C distances is Co(basal)–C(terminal) < Co(apical)–C(terminal) < Co(basal)–C(bridging), with mean distances of 1.798, 1.838 and 1.963 Å, respectively. The molecular symmetry is thus C_1 but very close to C_{3v}.

It is not clear whether the minor distortions in the metal skeleton away from C_{3v} symmetry are real, or an artefact of the disorder. An investigation of the metal atom anisotropic displacement parameters (a.d.p.'s) suggests it may be the latter. Fig. 2 shows the two interlocking metal tetrahedra, viewed along the crystallographic 2-fold axis passing through Co(1). The a.d.p. of atom Co(1) displays a much more marked apparent thermal motion perpendicular to this axis than the other atoms. One possible cause of this apparent thermal motion is that the determined a.d.p. is actually subsuming a further disorder in the positions of the Co(1) atoms in the two tetrahedra, i.e. these atoms does not lie exactly on the crystallographic 2-fold axis, but are each displaced by a small distance, perhaps ca. 0.05 Å. This would imply that the bond distances in Table 1, associated with Co(1), are less reliable However, since these putative disordered positions are too close together (ca. 0.1 Å) to be refinable as separate atomic positions in the least-squares procedures, this hypothesis must remain conjectural.

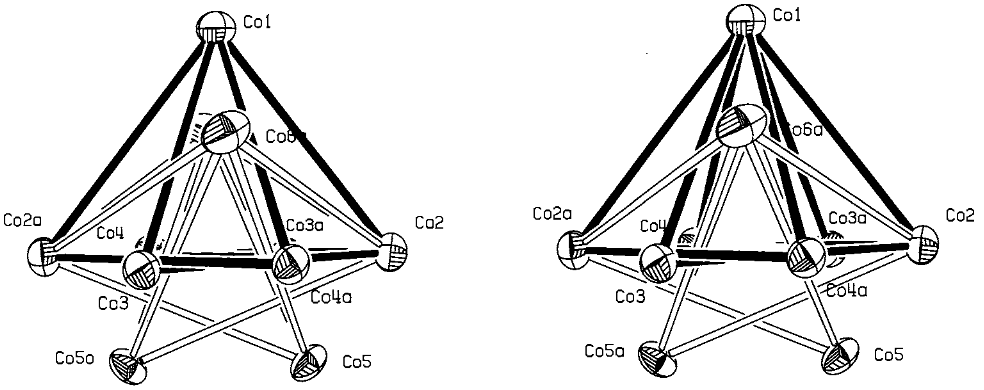

Fig. 4. Stereo view of the disordered components of the Co_4 tetrahedron at 292 K. Thermal ellipsoids are drawn at the 30% probablity level.

At 292 K, despite the fact that there are considerably more observed reflections in our data set than that of Cotton et al. [5], we were still unable to determine the separate carbonyl positions for each disordered component, and only averaged positions could be resolved. This averaging gives rise to six independent carbon and oxygen positions. At ambient temperature, the greater disorder (see below) and greater thermal motion leads to weaker diffracted intensities: ca. 79% of the data at 120 K have $I > 3.0\sigma(I)$, whereas only ca. 40% of the data have $I > 3.0\sigma(I)$ at 292 K.

We find that the disorder in the metal framework of $Co_4(CO)_{12}$ at 292 K is more complex than previously suspected. After refinement to convergence using the Cotton model [5], there remained two significant residuals of 3.6 and 2.4 e Å^{-3}. An examination of a Fourier map section through the most intense residual and the atoms Co(1) and the mid-points of the Co(3)–Co(4a) and Co(3a)–Co(4) vectors revealed atomic-like features (see Fig. 3, top). Similar residuals were found in the plane described by Co(1)–Co(2)–Co(2a) (see Fig. 3, bottom). Inclusion of these positions as partially occupied cobalt atoms with anisotropic thermal motion led to a satisfactorily converging refinement. The conventional R value was reduced from 0.083 to 0.054, and of course a cleaner difference map resulted. It is not possible to compare the level of residuals we observe with those from the Cotton [5] determination, since the latter were not given in the original paper. There is no trace of these secondary positions in the determination at 120 K. Moreover, analysis of a rapid data-set re-collected at ambient temperatures on the crystal specimen used for the 120 K determination, showed identical results to those reported here. The extra minor component disorder is thus reversible, and indisputably dynamic in origin.

In this new model, shown in a stereoview in Fig. 4, there are four interlocked Co_4 tetrahedra. Two tetrahedra, joined by solid lines, are at the previously observed positions [3–5] with a total population of 93%, while a second pair of tetrahedra, joined by open lines, constitute the remaining 7% of the cobalt population. The atoms pairs labelled Co(3), Co(3a) etc. are related to each other by rotation about the crystallographic 2-fold axis passing through Co(1). The atom Co(2) is a common vertex for two tetrahedra in the major and minor orientations, while atom Co(6) is a common vertex for the two minor orientations. The Co(2)–Co(6) separations of 2.258(8) and 2.262(9) Å are rather short, and probably reflect inaccuracies in the positions of these minor component metal atoms. The remaining Co–Co separations are all reasonable, Co(2)–Co(5a) = 2.523(13), Co(6)–Co(6a) = 2.547(17), Co(6)–Co(5a) = 2.553(15), Co(5a)–Co(6a) = 2.511(15) Å. The molecular structure of the minor orientation may be deduced by placing one of the minor tetrahedra inside the cage described by the observed carbonyl positions. This structure is shown in Fig. 5. There are many unrealistic

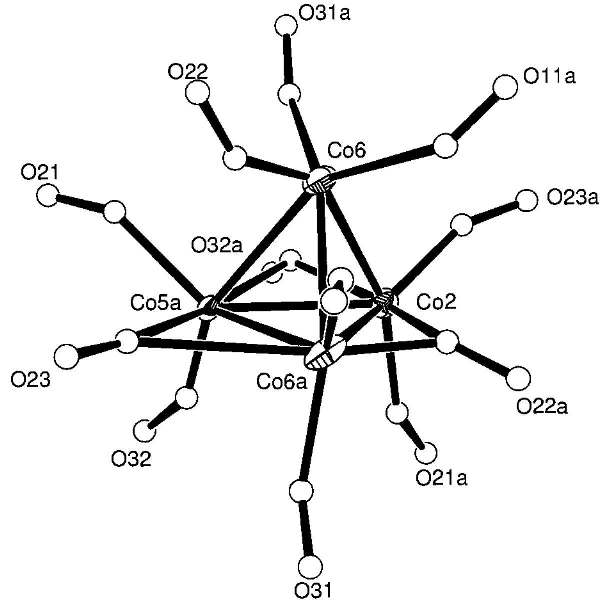

Fig. 5. The minor component Co_4 tetrahedron placed in the carbonyl polytope (see text).

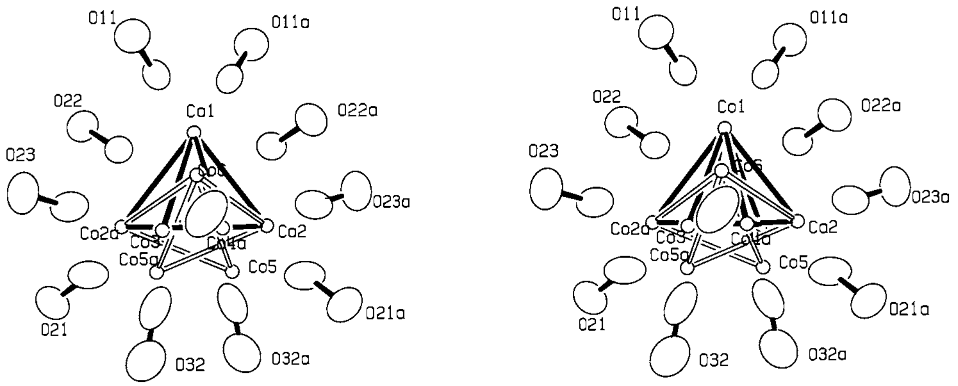

Fig. 6. Stereo view down the CO(31)–CO(31a) axis showing the disordered Co_4 tetrahedra within the carbonyl polytope at 292 K. All bonds between the carbon and cobalt atoms have been omitted for clarity.

bond lengths and bond angles, because no 'relaxation' of the carbonyl positions has been allowed. Nevertheless, it is clear that the molecule adopts the same C_{3v} structure as the major orientation.

Of particular interest is the geometrical relationship between these disordered tetrahedra. This relationship may be appreciated from Fig. 4, which shows the view down the vector-axis which lies midway between, and parallel to, the three vectors Co(3)–Co(4), Co(3a)–Co(4a) and Co(6)–Co(6a). The two major orientations are related to each other by a rotation of ca. 120° about this vector-axis, while a major orientation may be converted to a minor by a rotation of ca. 100° in the opposite sense about this same vector-axis. It is impossible to tell, from the crystallographic evidence, whether there is a dynamic interconversion between the two major orientations, because there is no change in the relative populations. However, there must be an easy pathway between one of the major orientations and at least one of the minor orientations. If the rotation follows the direction leading to the set of major-to-minor exchanges Co(3a) → Co(6), Co(4)a → Co(6a), Co(1) → Co(2a) and Co(2a) → Co(5), then the solid state ^{13}C and ^{59}Co NMR results of Heaton et al. [18,20] may be easily rationalised. The unique apical cobalt atom is Co(3)/Co(3a) in the major orientation, and Co(6) in the minor orientation (Fig. 5), thus if there is only such a restricted motion in the solid the identity of the unique apical cobalt atom is conserved.

This vector-axis relating the orientations of the Co_4 tetrahedra may be identified with one of the five-fold axes of the icosahedral carbonyl polytope. It is in fact the axis defined by the antipodal carbonyls CO(31) and CO(31a), and a stereoview directly down this axis is shown in Fig. 6. The disorder in the solid state structure therefore supports the view that there is (at least) a limited oscillation of the Co_4 tetrahedron inside a relatively rigid icosahedral carbonyl polytope. This motion about the five-fold axis of the polytope is consistent with the ligand polyhedral model [2] of Johnson, and is strikingly similar to Mann's description [1] of the low energy fluxional process in $Fe_3(CO)_{12}$ and its derivatives. In our opinion, these two approaches are alternative descriptions of the same process.

3. Experimental

A sample of $Co_4(CO)_{12}$ was prepared by thermolysis of commercially available $Co_2(CO)_8$ in hexane, and recrystallised from a dichloromethane/hexane mixture. A single crystal of suitable size was attached to glass fibre using acrylic resin, and mounted on a goniometer head in a general position. The crystal was coated completely in acrylic resin to protect it from atmospheric oxidation, and this procedure proved effective in stabilising the crystal for several weeks. Data were collected in bisecting mode using graphite monochromated X-radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with an Oxford Systems Cryostream low temperature device. Details of data collection procedures and structure refinements at 292 and 120 K are given in Table 2. Precise unit cell dimensions were determined by refinement of the setting angles of high-angle reflections. Standard reflections were measured every 2 h during data collection, and an interpolated correction was applied to the reflection data where necessary. The diffractometer data were processed using the Lehman-Larsen profile fitting program PROFIT [22] and corrected for Lorentz-polarization effects. Data were corrected for absorption [23] by semi-empirical ψ-scans. All atoms were allowed anisotropic thermal motion. Refinement [24] was by full-matrix least-squares on F^2, using all the

Table 2
Experimental details for the crystallographic studies

Temperature (K)	292	120
Formula	$C_{12}Co_4O_{12}$	$C_{12}Co_4O_{12}$
Colour	black	black
M_r	571.84	571.84
Space group	*Pccn*	*Pccn*
Crystal system	Orthorhombic	Orthorhombic
a (Å)	8.9912(10)	8.865(2)
b (Å)	11.6988(10)	11.470(3)
c (Å)	17.246(2)	16.952(3)
V (Å^{-3})	1814.0(3)	1723.7(7)
θ range for cell	15.8–23.6	17.5–20.4
Z	4	4
D_{calc} (g cm^{-3})	2.094	2.204
F(000)	1104	1104
μ(Mo–K$_\alpha$) (cm^{-1})	36.53	38.46
Scan mode	$\varpi/2\theta$	$\varpi/2\theta$
ω Scan angle (°)	$0.96+0.48\tan(\theta)$	$0.83+0.48\tan(\theta)$
θ Range (°)	2.9–30.00	2.9–29.95
Crystal size (mm)	$0.5\times0.4\times0.3$	$0.5\times0.4\times0.3$
No. of data collected	6349	5896
No. of unique data	2651	2509
hkl range	$-1\rightarrow12$; $-16\rightarrow16$; $-2\rightarrow24$	$-12\rightarrow12$; $-16\rightarrow2$; $-23\rightarrow2$
R_{int}	0.029	0.044
Absorption correction method	ψ-scans	ψ-scans
Max/min transmission factors	0.262, 0.150	0.392,0.251
Standard reflections	(5 −1 4) (2 −5 −8) (4 2 4) (5 −2 6) (4 −6 0) (3 0 −12)	(2 −6 5) (−2 −6 5) (1 10 0) (−2 −4 −6) (−4 8 0) (−5 2 4)
No. of data in refinement	2651	2509
No. of refined parameters	159	213
Final R [$I>2\sigma(I)$] (all data); R_w^2 [$I>2\sigma(I)$] (all data)	0.054 (0.086); 0.133 (0.158)	0.051 (0.067); 0.111 (0.120)
Weighting parameters A,B	0.0553, 2.5465	0.0257, 7.2096
Goodness-of-fit S	1.129	1.157
Largest remaining feature in electron density map (e Å^{-3})	1.045(max) −0.46(min)	0.86 (max) −0.85 (min)
Shift/e.s.d. in last cycle (max)	0.001	0.001

$R=\Sigma(|F_o|-|F_c|)/\Sigma(F_o) wR_2=\{\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)\}^{1/2}$.

$R_{int}=\Sigma|F_o^2-F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

unique data and the weighting scheme $w=[\sigma^2(F_o)^2+(AP)^2+BP]^{-1}$ where $P=[F_o^2/3+2F_c^2/3]$. For the refinement of the 120 K data set, the anisotropic thermal parameters of atoms O21, O41, C31 and C42 were restrained using the ISOR restraint in SHELXL-97. Thermal ellipsoid plots were obtained using the program ORTEP-3 for Windows [25]. All atoms marked by an ‘a’ in Fig. 1–6 are related to their corresponding non-marked atoms by the symmetry operation 1/2-*x*, 1/2-*y*, *z*. Full tables of atomic parameters and bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation. Further information is available in electronic (CIF) format from the author on request (e-mail louis@chem.gla.ac.uk).

Acknowledgements

L.J. Farrugia thanks the EPSRC for a grant towards the purchase of a diffractometer.

References

[1] (a) B.E. Mann, J. Chem. Soc. Dalton Trans. (1997) 1457. (b) B.F.G. Johnson, J. Chem. Soc. Dalton Trans. (1997) 1473.

[2] (a) R.E. Benfield, B.F.G. Johnson, J. Chem. Soc. Dalton Trans. (1978) 1554. (b) B.F.G. Johnson, Y.V. Roberts, Polyhedron 12 (1993) 977.

[3] (a) P. Corradini, J. Chem. Phys. 31 (1959) 1676. (b) P. Corradini, A. Sirigu, Ric. Sci. 36 (1966) 188.

[4] (a) C.H. Wei, L.F. Dahl, J. Am. Chem. Soc. 88 (1966) 1821. (b) C.H. Wei, Inorg. Chem. 8 (1969) 2384.

[5] F.H. Carré, F.A. Cotton, B.A. Frenz, Inorg. Chem. 15 (1976) 380.

[6] F.A. Cotton, J.M. Troup, J. Am. Chem. Soc. 96 (1974) 4155.

[7] (a) M.A. Cohen, D.R. Kidd, T.L. Brown, J. Am. Chem. Soc. 97 (1975) 4408. (b) J. Evans, B.F.G. Johnson, J. Lewis, T.W. Matheson, J. Am. Chem. Soc. 97 (1975) 1245. (c) J. Evans, B.F.G. Johnson, J. Lewis, T.W. Matheson, J.R. Norton, J. Chem. Soc. Dalton Trans. (1978) 626. (d) S. Aime, L. Milone, Prog. NMR Spectrosc. 11 (1977) 183. (e) S. Aime, L. Milone, D. Osella, A. Poli, Inorg. Chim. Acta 30 (1978) 45.

[8] (a) E.A.C. Lucken, K. Noack, D.F. Williams, J. Chem. Soc. A 148. (b) H. Haas, R.K. Sheline, J. Inorg. Nucl. Chem. 29 (1967) 693.

[9] S. Aime, D. Osella, L. Milone, G.E. Hawkes, E.W. Randall, J. Am. Chem. Soc. 103 (1981) 5920.

[10] S. Aime, R. Gobetto, D. Osella, L. Milone, G.E. Hawkes, E.W. Randall, J. Magn. Reson. 65 (1985) 308.

[11] B.F.G. Johnson, Y.V. Roberts, E. Parsini, R.E. Benfield, J. Organomet. Chem. 478 (1994) 21.

[12] Y.V. Roberts, B.F.G. Johnson, R.E. Benfield, Inorg. Chim. Acta 229 (1995) 221.

[13] D. Braga, L.J. Farrugia, A.L. Gillon, F. Grepioni, E. Tedesco, Organometallics 15 (1996) 4684.

[14] L.J. Farrugia, A.M. Senior, D. Braga, F. Grepioni, A.G. Orpen, J.G. Crossley, J. Chem. Soc. Dalton Trans. (1996) 631.

[15] B.E. Hanson, E.C. Lisic, Inorg. Chem. 25 (1986) 716.

[16] C.E. Anson, R.E. Benfield, A.W. Bott, B.F.G. Johnson, D. Braga, E.A. Marseglia, J. Chem. Soc. Chem. Commun. (1988) 889.

[17] S. Aime, M. Botta, R. Gobetto, B.E. Hanson, Inorg. Chem. 28 (1989) 1196.

[18] B.T. Heaton, J. Sabounchei, S. Kernaghan, et al., Bull. Chem. Soc. Jpn. 63 (1990) 3019.

[19] D. Braga, C.E. Anson, A. Bott, B.F.G. Johnson, E. Marseglia, J. Chem. Soc. Dalton Trans. (1990) 3517.

[20] T. Eguchi, H. Nakayama, H. Ohki, S. Takeda, N. Nakamura, S. Kernaghan, B.T. Heaton, J. Organomet. Chem. 428 (1992) 207.

[21] D. Braga, F. Grepioni, J. Organomet. Chem. 336 (1987) 9.

[22] V.A. Streltzov, V.E. Zavodnik, Sov. Phys. Crystallogr. 34 (1989) 824.

[23] A.C.T. North, D.C. Phillips, F.S. Matthews, Acta Cryst. A24 (1968) 351.

[24] SHELXL-97-A program for crystal structure refinement, G.M. Sheldrick, University of Göttingen, Göttingen, Germany, 1997. Release 97–1.

[25] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.