Authors: R. Bianchi, G. Gervasio and D. Marabello.

Title: An Experimental Electron Density Study of the Triclinic Phase of $Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C_4O_2H_2)$ at 120 K.

Journal: Acta Cryst. B

Supporting Information

Table 1s. Exponential radial (α's $Å^{-1}$) and electronic parameters from the multipole refinement. p1 and p2 are the population values for the first and second monopole functions, respectively. d, q, o, h indicate dipole, quadrupole, octopole and hexadecapole parameters, respectively. The α's for Co, C, O and H atoms were 3.1, 3.44, 4.50 and 2.48 $Å^{-1}$, respectively (Hehre W.J., Ditchfield R., Stewart R.F. and Pople J.A. (1970). *Journal of Chemical Physics*, **51**, 2769-2773) . The Cartesian coordinate system is defined by the matrix **R** (see below) which transforms the fractional coordinates into the orthogonal ones. The unit vectors **j** and **k** of the orthogonal system are in the plane containing approximately the γ-lactonic ring.

Atom	P1	P2	d1	d2	d3	q1	q2	q3	q4	q5
Co(1)	17.8(1)	8.90(6)	0.05(3)	0.05(3)	0.10(4)	0.42(7)	-0.59(9)	-0.13(5)	0.11(5)	0.33(6)
Co(2)	17.8(1)	8.90(6)	-0.11(4)	0.03(3)	-0.06(3)	0.33(6)	-0.63(9)	-0.14(5)	0.10(5)	0.39(7)
C(1')	2.014(9)	4.0(1)	0.08(5)	0.03(5)	-0.06(4)	-0.01(4)	-0.37(5)	-.15(4)	-0.07(4)	-0.02(5)
O(1')	2.014(9)	6.12(8)	-0.02(6)	-0.21(6)	-0.12(5)	-0.02(6)	-0.25(7)	-0.10(6)	-0.01(7)	0.02(7)
C(2')	2.014(9)	3.9(1)	-0.04(4)	0.00(5)	0.23(6)	0.01(4)	0.09(4)	0.16(5)	0.16(5)	0.01(5)
O(2')	2.014(9)	5.95(9)	0.20(6)	0.05(6)	-0.04(7)	0.01(6)	-0.05(7)	0.18(7)	0.16(7)	0.04(7)
C(3')	2.014(9)	3.8(1)	0.02(4)	-0.01(5)	0.03(6)	-0.10(4)	0.01(4)	-0.09(4)	-0.20(5)	0.20(5)
O(3')	2.014(9)	5.82(9)	-0.03(6)	-0.04(7)	-0.16(7)	0.10(6)	-0.14(6)	0.04(7)	-0.05(7)	0.25(7)
C(4)	2.014(9)	3.89(9)	0.05(3)	-0.03(4)	0.19(5)	0.00(3)	0.01(3)	0.01(4)	-0.03(5)	0.18(4)
O(4)	2.014(9)	6.04(7)	-0.02(4)	-0.05(5)	0.16(6)	0.00(5)	-0.03(5)	-0.08(5)	-0.04(6)	0.11(6)
C(5')	2.014(9)	3.9(1)	-0.08(5)	0.06(7)	0.07(8)	0.05(4)	0.29(5)	0.04(4)	0.03(4)	-0.09(4)
O(5')	2.014(9)	6.01(8)	0.03(5)	-0.04(5)	-0.04(5)	0.02(5)	-0.06(6)	-0.11(6)	0.01(6)	0.02(6)
C(6')	2.014(9)	4.0(1)	-0.02(4)	-0.09(5)	0.05(5)	0.02(4)	-0.25(4)	-0.09(4)	0.24(5)	0.11(4)
O(6')	2.014(9)	5.83(9)	0.05(5)	-0.03(5)	0.03(6)	0.03(5)	-0.24(6)	-0.05(6)	0.07(7)	0.09(6)
C(7')	2.014(9)	4.0(1)	0.02(4)	0.05(6)	0.04(6)	-0.07(4)	-0.13(4)	-0.07(4)	-0.26(5)	0.14(4)
O(7')	2.014(9)	6.0(1)	-0.04(6)	0.04(7)	0.05(8)	0.03(6)	-0.14(6)	-0.06(7)	-0.12(8)	0.01(7)
C(6)	2.014(9)	4.17(7)	0.06(3)	-0.09(3)	-0.11(4)	0.05(3)	-0.08(3)	-0.05(3)	.17(4)	0.12(4)
C(7)	2.014(9)	4.32(9)	0.00(3)	0.14(4)	0.14(6)	-0.12(4)	-0.10(3)	-0.04(4)	0.02(5)	0.18(5)
C(8)	2.014(9)	4.2(1)	0.01(3)	-0.03(5)	0.06(5)	0.02(4)	-0.01(4)	-0.08(4)	0.11(5)	0.00(5)
C(9)	2.014(9)	4.27(8)	-0.04(3)	0.01(4)	0.10(5)	-0.11(4)	-0.04(3)	-0.08(4)	0.10(4)	0.14(5)
O(6)	2.014(9)	6.01(4)	0.07(3)	-0.04(3)	-0.01(4)	0.03(4)	-0.09(4)	-0.04(4)	0.12(5)	-0.06(5)
O(7)	2.014(9)	6.12(7)	0.07(4)	-0.07(5)	0.11(7)	-0.07(5)	-0.20(5)	-0.16(6)	0.11(6)	-0.05(7)
H(8)	-	0.95(9)	0.2(1)	-0.2(2)	-0.1(2)	-	-	-	-	-
H(9)	-	0.98(7)	0.0(1)	-0.1(1)	0.0(2)	-	-	-	-	-

Atom	o1	o2	o3	o4	o5	o6	o7
Co(1)	0.00(2)	-0.03(2)	0.03(2)	-0.01(2)	0.02(2)	-0.06(4)	0.05(3)
Co(2)	-0.04(3)	-0.02(2)	0.04(3)	-0.01(2)	0.01(2)	0.03(2)	-0.04(3)
C(1')	0.00(4)	0.01(4)	-0.03(3)	-0.09(4)	-0.09(3)	-0.07(4)	0.02(4)
O(1')	0.00(3)	0.00(3)	0.03(3)	-0.03(3)	0.01(3)	-0.01(3)	-0.05(4)
C(2')	0.04(3)	-0.06(3)	0.05(4)	-0.07(4)	0.05(4)	-0.01(4)	0.12(4)
O(2')	-0.04(3)	-0.03(4)	0.06(4)	0.05(4)	-0.07(4)	-0.08(4)	-0.14(4)
C(3')	-0.02(3)	0.02(3)	-0.04(4)	-0.02(4)	-0.04(3)	-0.11(4)	0.02(4)
O(3')	0.00(3)	0.03(3)	-0.06(4)	0.04(4)	-0.04(3)	0.03(4)	0.00(4)
C(4)	0.02(3)	-0.07(3)	0.06(4)	-0.07(3)	0.01(3)	-0.09(4)	-0.06(4)
O(4)	0.00(3)	0.01(3)	0.00(3)	-0.01(3)	0.01(3)	-0.04(3)	-0.03(3)
C(5')	-0.07(4)	0.02(4)	-0.03(3)	-0.02(4)	-0.04(3)	0.00(3)	0.00(4)
O(5')	0.06(3)	-0.01(3)	-0.01(3)	-0.02(3)	0.02(3)	0.03(3)	0.03(3)
C(6')	-0.02(3)	-0.11(3)	0.04(4)	0.05(4)	-0.02(4)	0.03(4)	-0.08(4)
O(6')	0.01(3)	-0.11(3)	0.08(3)	-0.03(4)	0.06(3)	-0.03(4)	-0.05(4)
C(7')	-0.01(3)	-0.07(3)	0.15(4)	-0.04(3)	-0.09(4)	0.03(5)	0.31(5)
O(7')	-0.09(3)	-0.02(3)	-0.02(4)	0.01(4)	0.00(3)	-0.01(4)	0.04(4)
C(6)	0.03(3)	-0.10(3)	-0.06(3)	0.02(3)	-0.04(3)	-0.13(3)	0.12(4)
C(7)	-0.01(3)	-0.07(3)	0.15(4)	-0.04(3)	-0.09(4)	0.03(5)	0.31(5)
C(8)	0.00(3)	-0.04(3)	-0.04(4)	0.02(3)	-0.01(3)	-0.04(4)	-0.08(4)
C(9)	-0.03(3)	0.06(3)	0.08(3)	-0.07(3)	0.03(3)	0.23(3)	0.08(4)
O(6)	0.00(2)	0.00(2)	-0.03(2)	-0.01(2)	0.03(2)	0.01(2)	-0.08(3)
O(7)	-0.03(3)	0.01(3)	-0.01(3)	-0.03(3)	0.05(3)	-0.03(3)	0.08(4)

Atom	h1	h2	h3	h4	h5	h6	h7	h8	h9
Co(1)	0.04(5)	-0.02(5)	-0.03(6)	0.4(1)	-0.16(7)	0.04(6)	0.5(1)	0.16(7)	-0.20(8)
Co(2)	0.02(5)	-0.07(5)	-0.12(6)	0.4(1)	-0.23(8)	0.24(9)	0.4(1)	0.12(6)	-0.17(7)

$$R = \begin{bmatrix} 0.00426 & -0.10662 & -0.02990 \\ -0.10727 & 0.03419 & -0.04450 \\ 0.09190 & 0.04115 & -0.07203 \end{bmatrix}$$

Table 2s. The difference Δz^2_{AB} (Å^2) of the projections (see text) of the thermal displacements of bonded A and B atoms in the direction of the bond.

Pair of A and B atoms	$\lvert \Delta z^2_{AB} \rvert$
C(8)–C(9)	0.00001
C(7)–C(8)	0.00002
Co(1)–Co(2)	0.00004
Co(2)–C(5')	0.00009
C(4)–O(4)	0.00009
C(1')–O(1')	0.00031
C(3')–O(3')	0.00036
C(6)–O(6)	0.00071
Co(2)–C(6)	0.00074
C(7)–O(7)	0.00087
Co(1)–C(1')	0.00116
C(7')–O(7')	0.00129
Co(1)–C(3')	0.00134
C(6')–O(6')	0.00158
O(6)–C(7)	0.00177
Co(1)–C(6)	0.00230
C(6)–C(9)	0.00247
Co(2)–C(6')	0.00260
Co(2)–C(7')	0.00269
Co(2)–C(4)	0.00292
C(2')–O(2')	0.00295
Co(1)–C(2')	0.00308
C(5')–O(5')	0.00314
Co(1)–C(4)	0.00357

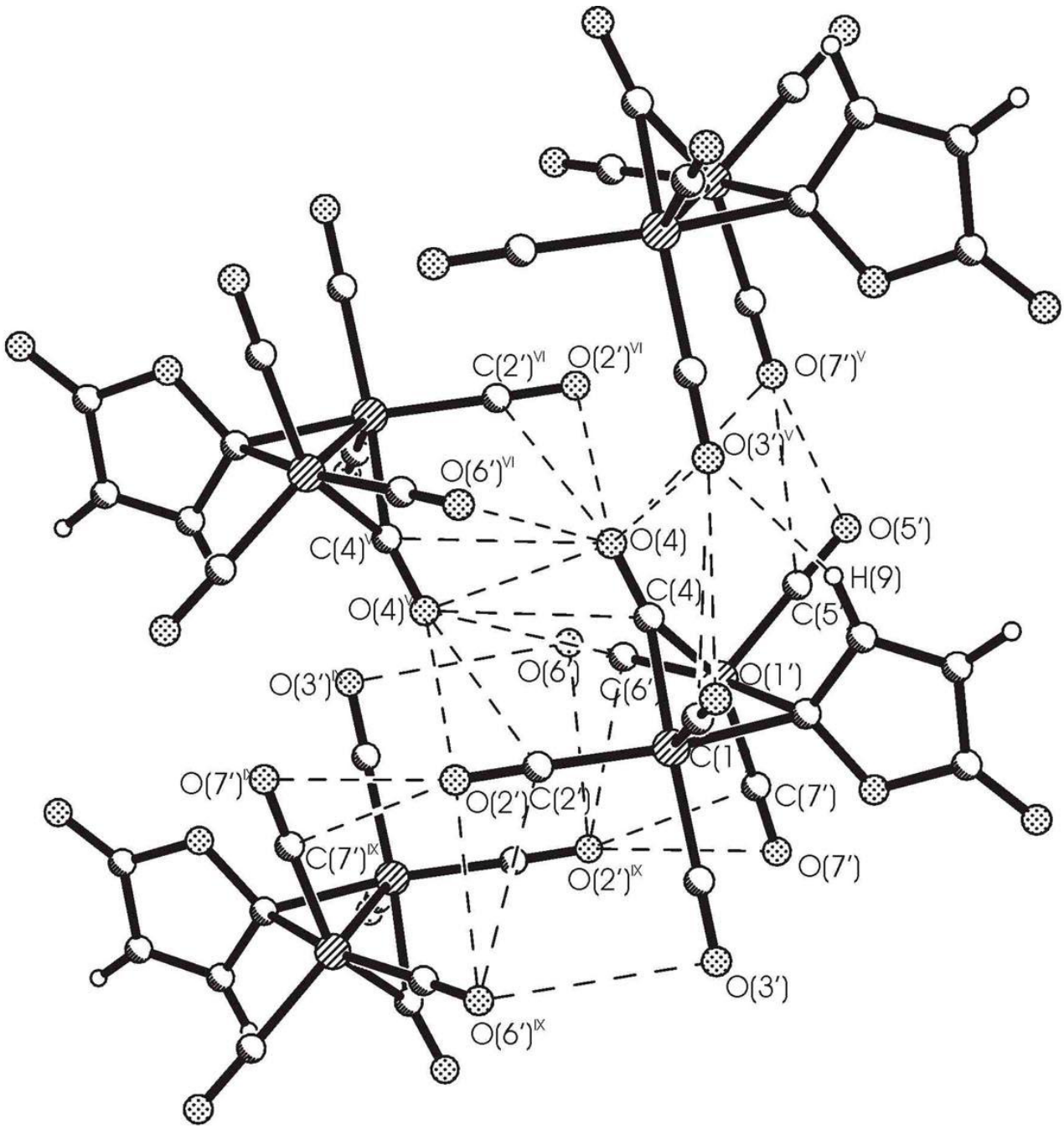

Figure 1s. View of selected intermolecular contacts in crystal packing of complex **3**.

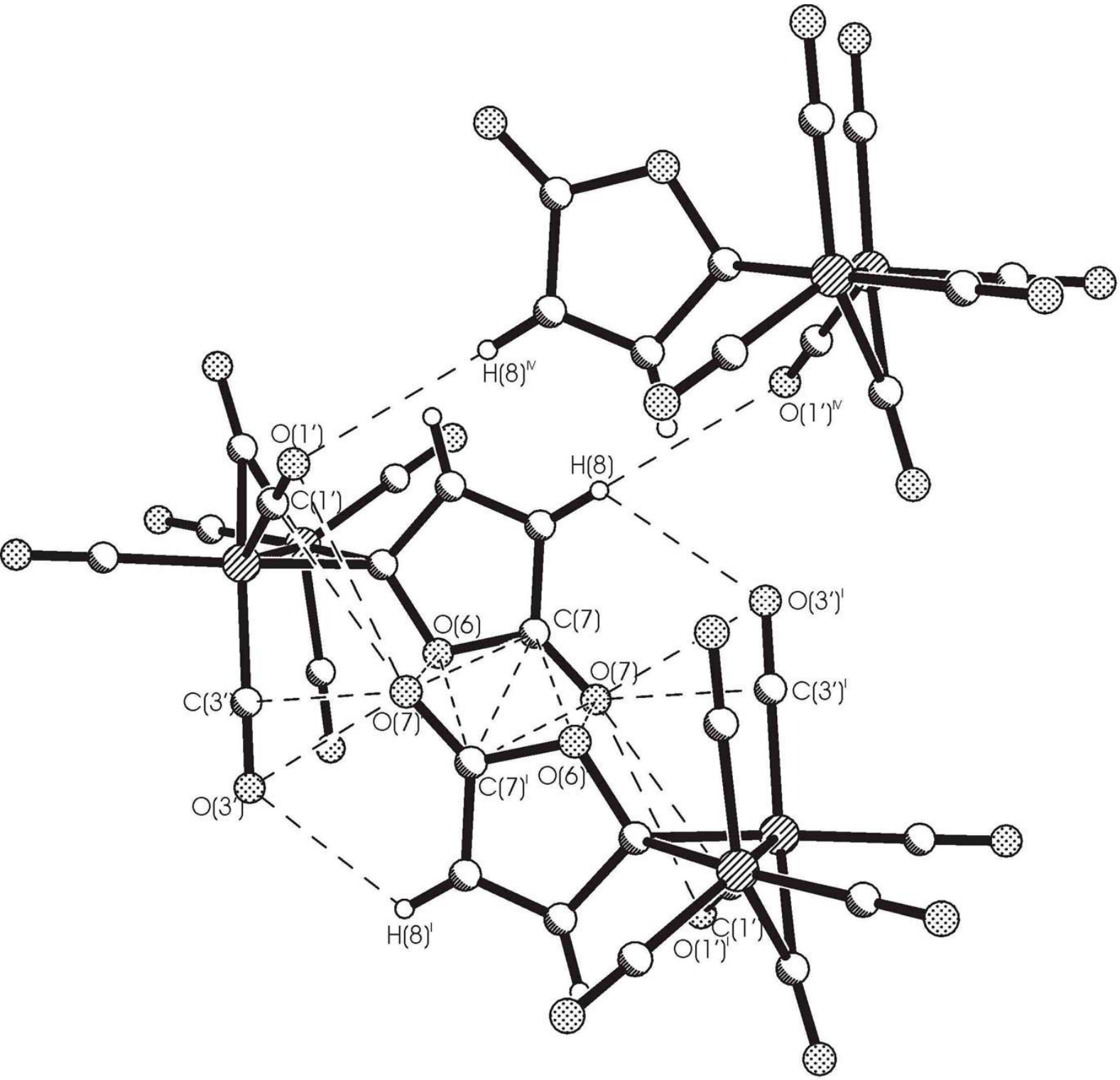

Figure 2s. View of selected intermolecular contacts in crystal packing of complex **3**.

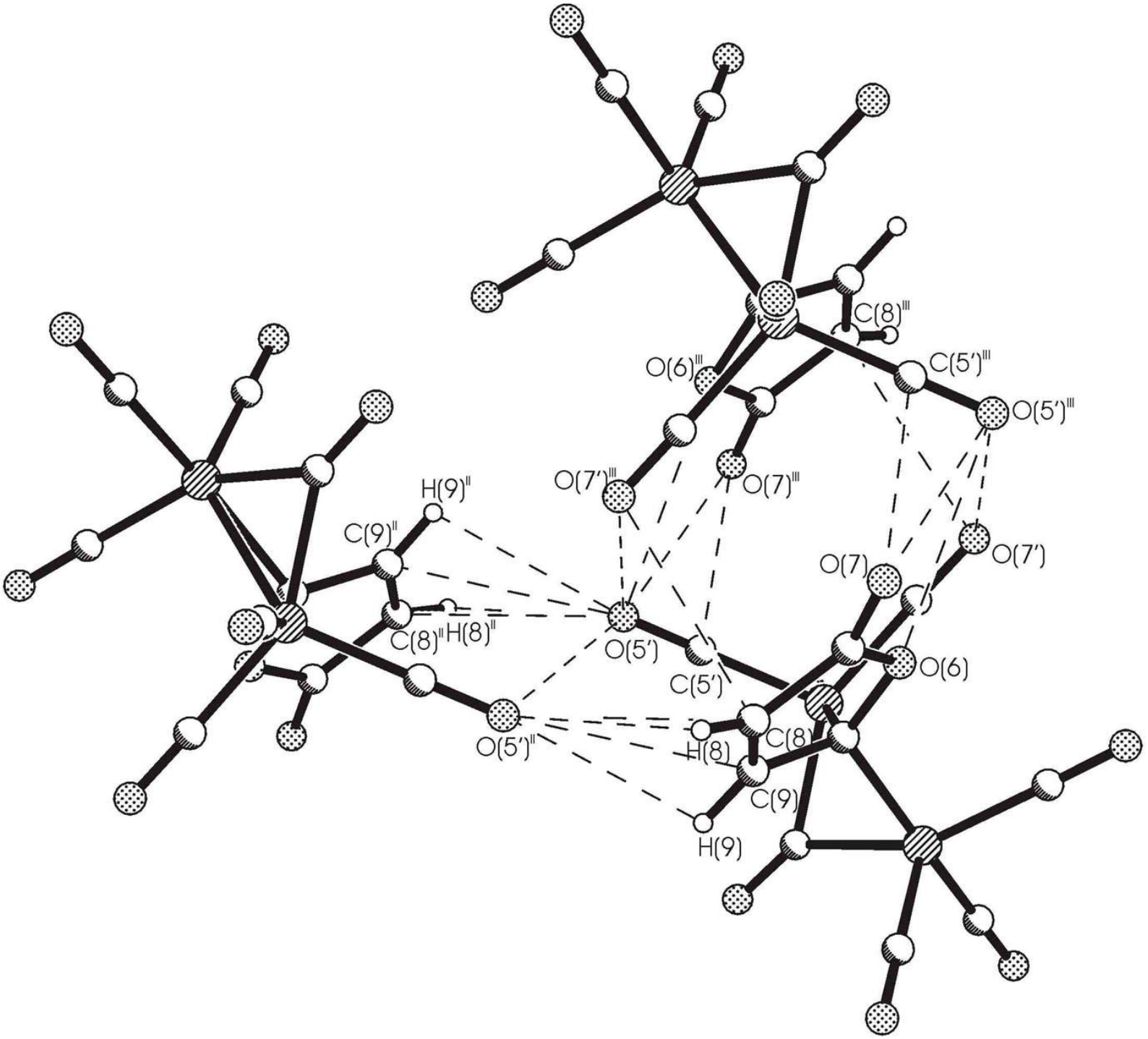

Figure 3s. View of selected intermolecular contacts in crystal packing of complex **3**.

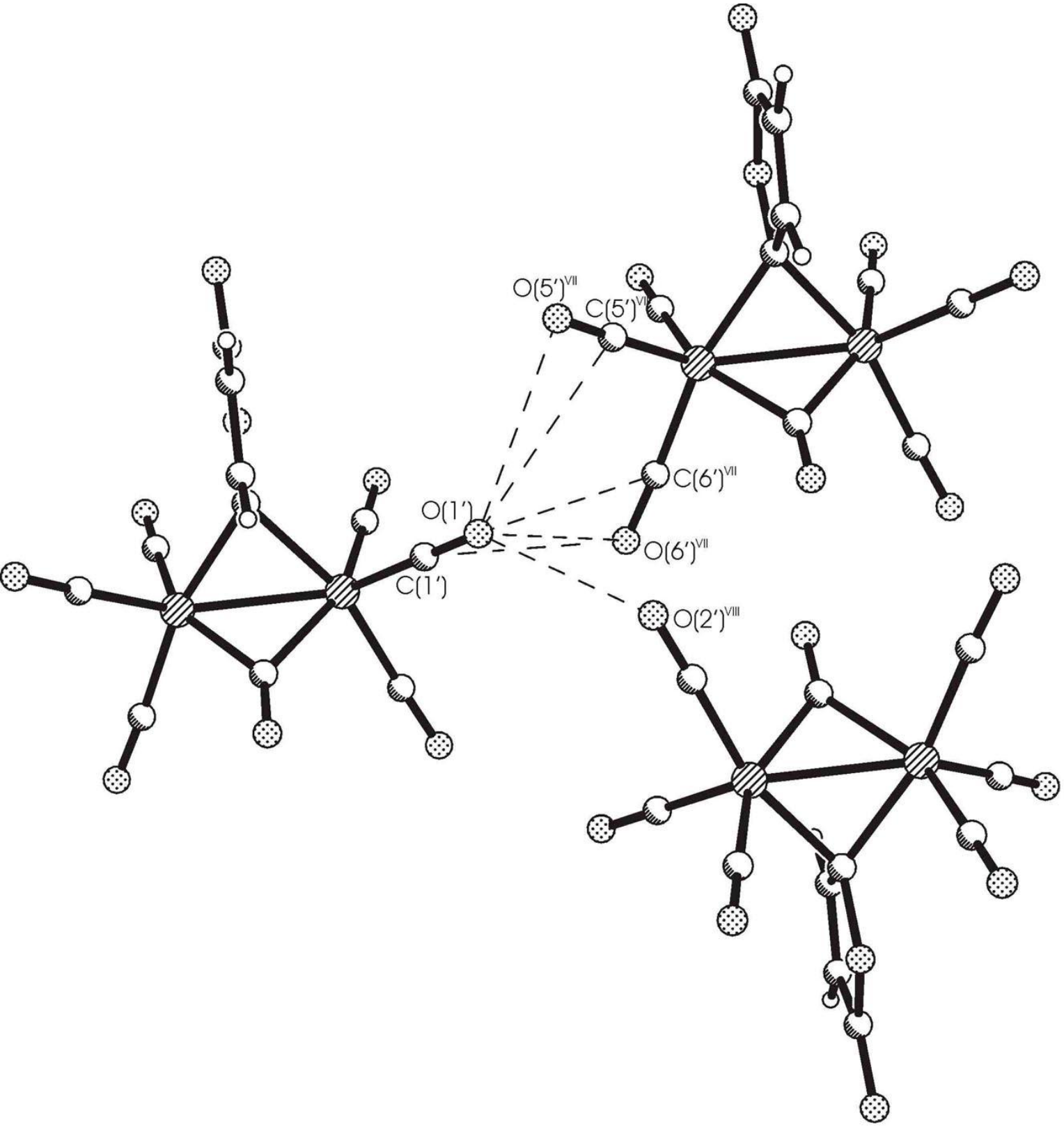

Figure 4s. View of selected intermolecular contacts in crystal packing of complex **3**.

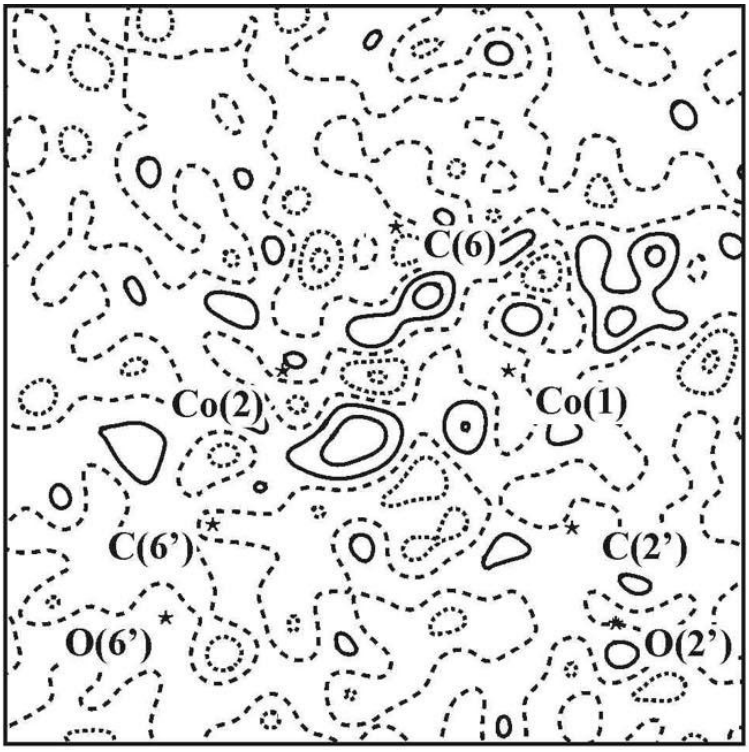

Figure 5s. Residual density in the Co(1)-Co(2)-C(6) plane. The contour interval is 0.10 eÅ^{-3}. Solid lines - positive, short dashed lines - negative, wide dashed line - zero contour.

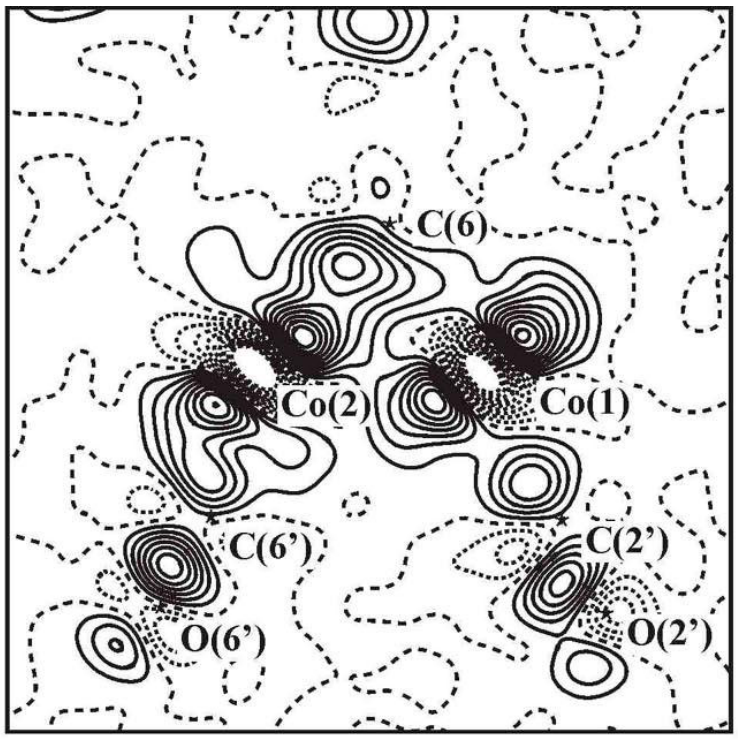

Figure 6s. Dynamic model deformation density in the Co(1)-Co(2)-C(6) plane. The contour interval is 0.10 eÅ^{-3}. Solid lines - positive, short dashed lines - negative, wide dashed line - zero contour.

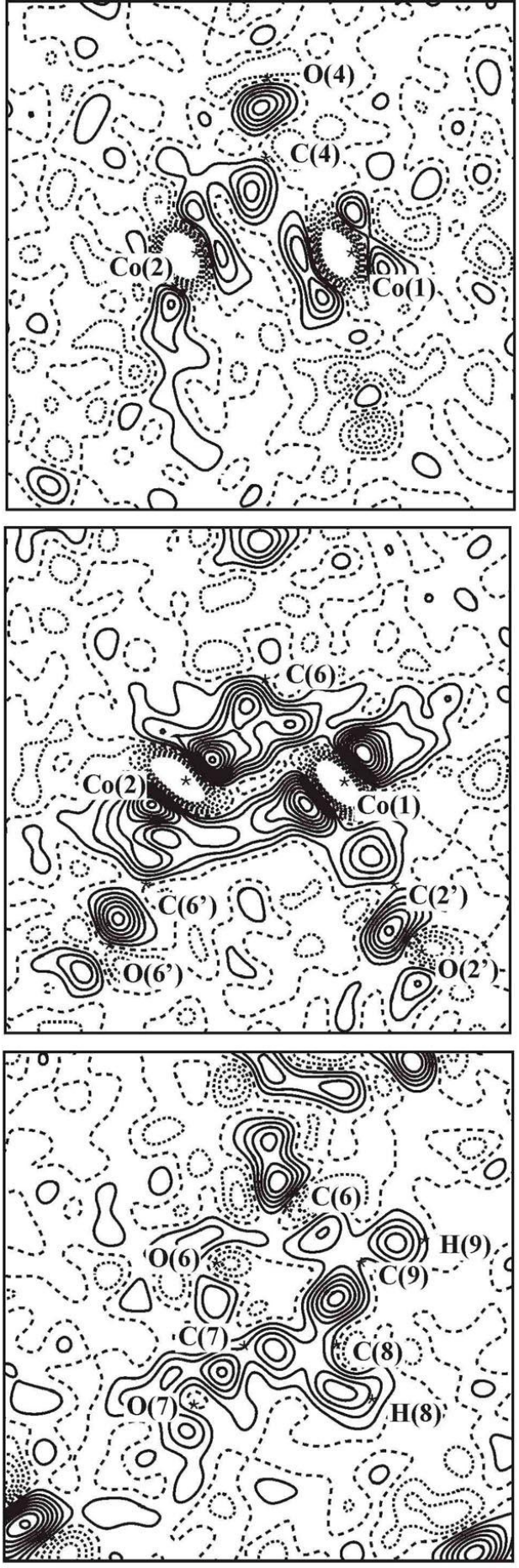

Figure 7s. Experimental deformation density in the Co(1)-Co(2)-C(4) plane (a), in the Co(1)-Co(2)-C(6) plane (b) and in the γ-lactonic plane (c). The contour interval is 0.10 eÅ^{-3}. Solid lines - positive, short dashed lines - negative, wide dashed line - zero contour.