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CARBIDE CLUSTERS IN THE COBALT SUBGROUP

VIII *. CRYSTALLOGRAPHIC CHARACTERIZATION OF THE ANION DICARBIDO-UNDECA-μ-CARBONYL-UNDECACARBONYL-POLYHEDRO-UNDECACOBALTATE(3—) AS ITS TRIS(BENZYLTRIMETHYLAMMONIUM) SALT **

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Summary

The new carbido-carbonyl clusters $[Co_{13}(C)_2(CO)_{24}]^{4-}$ and $[Co_{11}C_2(CO)_{22}]^{3-}$ have been obtained by pyrolysis of $Na_2[Co_6C(CO)_{15}]$. $[Co_{11}C_2(CO)_{22}]^{3-}$ has been characterized by crystallographic methods as its $[NMe_3(CH_2Ph)]^+$ salt; triclinic, a = 23.146(6), b = 21.768(5), c = 14.536(3) Å, α = 98.14(5)°, β = 103.19(5)°, γ = 111.19(5)°, Z = 4, space group $P\bar{1}$. The structure has been solved by direct methods and refined by least-squares calculations to R = 0.096 for 4595 diffraction intensities. The anion has idealized C_s-m symmetry and contains a closed polyhedron of cobalt atoms which can be described either as a tricapped cube or as a fused tetragonal antiprism/trigonal prism sharing a square-face, plus an atom in a capping position on one squareface of the trigonal prism. The latter description defines quite well the shape of the cavity containing a C_2 unit, C—C distance 1.62(5) Å. The carbonyl ligands are bonded 11 terminal and 11 edge-bridging. The Co—Co distances average

* For parts I—VII see refs. 1—7.
** Dedicated to the memory of Professor Paolo Chini.

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2.48 and 2.60 Å for bridged and unbridged edges, respectively. The Co—C(carbide) distances are in the range 1.86—2.37(3) Å.

Introduction

We have characterized a number of carbido-carbonyl clusters of cobalt and rhodium and have observed that rhodium shows a variety of cluster geometries in the range Rh_6—Rh_{15}, but that cobalt seemed to have a more limited chemistry, and the only species previously obtained were $[Co_6C(CO)_{15}]^{2-}$ [8], $[Co_6C(CO)_{14}]^-$ [6], and $[Co_8C(CO)_{18}]^{2-}$ [5]. Believing that new reaction routes had to be explored if cobalt clusters of higher nuclearity were to be obtained, we have examined the pyrolysis of smaller clusters, since increasing temperature is known to favour cluster growth.

On heating $Na_2[Co_6C(CO)_{15}]$ in diglyme at 140°C, under nitrogen, for 10—11 h, a mixture of dark-brown anions is formed, containing mainly the $[Co_{13}(C)_2(CO)_{24}]^{4-}$ anion [9] together with minor amounts of other anions and $[Co(CO)_4]^-$. Separation is achieved by evaporation to dryness in vacuo, dissolution of the mixture in methanol, and fractional precipitation of the $[NMe_3(CH_2Ph)]^+$ salts. After separation of the $[Co_{13}(C)_2(CO)_{24}]^{4-}$ anion (40—50% yield), on prolonged standing of the mother liquor or by gradual addition of water other anions are precipitated. By fractional crystallization of this mixture from methyl ethyl ketone and 2-propanol the $[Co_{11}C_2(CO)_{22}]^{3-}$ anion has been isolated in 5—10% yield. The IR spectrum in acetonitrile solution shows bands at 1973vs, 1840w, 1815mw, and 1798m cm^{-1}.

We describe here the structure of this anion, a detailed account of its synthesis and chemical characterization will be reported later, together with a complete description of $[Co_{13}(C)_2(CO)_{24}]^{4-}$.

Experimental

Crystal Data. $C_{54}H_{48}Co_{11}N_3O_{22}$, M = 1739.2, triclinic, a 23.146(6), b 21.768(5), c 14.536(3) Å, α 98.14(5)°, β 103.19(5)°, γ 111.06(5)°, U = 6449.3 Å^3, D_m = 1.76, Z = 4, D_c = 1.79 g cm^{-3}, space group $P\bar{1}$ (No. 2), $F(000)$ = 3464, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 28.31 cm^{-1}.

Intensity measurements. From a needle-like crystal a fragment with dimensions 0.08 × 0.10 × 0.35 mm was cut and mounted on a Philips PW1010 diffractometer. Diffraction intensities were measured in a half of the reciprocal lattice in the range $3 < \theta < 20°$ by the ω-scan method, scan interval 1.0°, and speed 2.4° min^{-1}. The background was measured at both sides of the reflections for a total time equal to the peak scanning time. 11 832 diffraction intensities were collected, 4595 of which $[F_o > 5\sigma(F_o)]$ were used for the structure resolution and refinement. The integrated intensities were reduced to F_0 values, the experimental correction for absorption was applied. The computations were carried out with the SHELX package of crystallographic programs [10].

The metal atoms were located by application of the direct methods. Two independent Co_{11} polyhedra were found, they were structurally equivalent but differently oriented in the cell. After a preliminary refinement of the metal

(continued on p. 299)

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS [a, b]

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co(1)	2272(2)	7557(2)	3301(3)	19(1)	19(2)	−4(3)	34(1)	22(3)	40(2)
Co(2)	2575(2)	7624(2)	5110(3)	20(1)	20(1)	13(2)	27(1)	18(3)	42(2)
Co(3)	1865(2)	6511(2)	5317(3)	17(1)	15(2)	18(3)	34(1)	28(3)	58(3)
Co(4)	1683(2)	6335(2)	3432(3)	20(1)	15(2)	0(3)	36(1)	7(3)	40(2)
Co(5)	2653(2)	5917(2)	3679(3)	21(1)	17(2)	9(3)	28(1)	8(3)	39(2)
Co(6)	3606(2)	6965(2)	3636(3)	17(1)	19(2)	11(2)	33(1)	14(3)	38(2)
Co(7)	3517(2)	7190(2)	5332(3)	15(1)	13(1)	6(2)	26(1)	14(3)	36(2)
Co(8)	2748(2)	6110(2)	5519(3)	22(1)	17(1)	20(3)	23(1)	20(3)	50(2)
Co(9)	1665(2)	5385(2)	4152(3)	23(1)	0(2)	1(3)	27(1)	0(3)	57(3)
C(10)	2437(2)	6525(2)	2448(3)	23(1)	16(2)	−9(3)	33(1)	8(3)	36(2)
Co(11)	3449(2)	8021(2)	4236(3)	20(1)	13(2)	14(2)	31(1)	23(3)	40(2)
Co(1A)	3001(2)	866(2)	9316(3)	36(1)	33(2)	24(4)	49(2)	34(4)	70(3)
Co(2A)	2318(2)	1317(2)	10071(3)	27(1)	17(2)	20(3)	42(1)	37(3)	64(3)
Co(3A)	1277(2)	1024(2)	8797(4)	23(1)	19(2)	23(3)	49(2)	29(4)	86(3)
Co(4A)	2036(2)	732(2)	7912(3)	34(1)	9(2)	0(4)	37(1)	11(4)	61(3)
Co(5A)	2442(2)	1983(2)	7646(3)	32(1)	18(2)	20(3)	48(2)	38(4)	63(3)
Co(6A)	3546(2)	2574(2)	8980(4)	27(1)	12(2)	17(3)	48(2)	46(4)	76(3)
Co(7A)	2711(2)	2555(2)	9829(4)	39(1)	29(2)	31(4)	39(1)	28(4)	78(3)
Co(8A)	1650(2)	2192(2)	8562(4)	36(1)	40(2)	45(4)	48(1)	49(4)	100(4)
Co(9A)	1284(2)	1175(3)	7062(4)	31(1)	23(2)	9(4)	51(2)	42(4)	88(4)
C(10A)	3133(2)	1364(2)	7826(4)	37(1)	49(2)	41(3)	58(2)	52(4)	79(3)
Co(11A)	3540(2)	2040(2)	10390(3)	27(1)	24(2)	9(3)	50(2)	35(4)	68(3)

Isotropic atoms

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
C(−1)	2808(12)	7051(13)	3984(19)	2.8(6)	C(−1A)	2846(17)	1639(18)	8989(26)	6.1(10)
C(−2)	2493(14)	6603(15)	4686(22)	3.9(8)	C(−2A)	2114(18)	1643(19)	8845(28)	7.0(11)
C(1)	1758(18)	7643(20)	2349(29)	7.4(11)	C(4, 10A)	2612(36)	505(20)	7162(21)	13.0(18)
O(1)	1412(14)	7755(14)	1753(22)	9.7(9)	O(4, 10A)	2504(18)	17(15)	6553(20)	10.7(10)
C(2)	3095(15)	84.09(16)	5966(23)	4.7(8)	C(1A)	3235(22)	196(22)	8917(33)	11.0(15)

TABLE 1 (continued)

Isotropic atoms

Atom	*x*	*y*	*z*	*B* (Å^2)	Atom	*x*	*y*	*z*	*B* (Å^2)
O(2)	3368(11)	8940(11)	6501(17)	6.6(6)	O(1A)	3429(22)	−227(22)	8805(33)	13.3(12)
C(3)	1106(19)	6076(21)	5452(30)	8.2(12)	C(2A)	2526(15)	1642(16)	11295(19)	7.2(11)
O(3)	588(13)	5854(14)	5525(21)	9.5(9)	O(2A)	2612(15)	1759(16)	12138(19)	7.3(7)
C(4)	1039(17)	6571(18)	3341(26)	6.3(10)	C(3A)	530(13)	415(16)	8312(26)	7.1(11)
O(4)	609(12)	6740(13)	3277(20)	8.6(8)	O(3A)	27(13)	−34(16)	7901(26)	11.9(11)
C(5)	3246(15)	5600(16)	3940(24)	4.9(8)	C(4A)	1773(20)	−40(18)	8083(32)	10.5(15)
O(5)	3673(12)	5423(13)	4154(19)	8.3(8)	O(4A)	1575(20)	−560(18)	8291(32)	12.8(12)
C(6)	3948(22)	6693(24)	2854(35)	10.1(15)	C(5A)	2455(18)	2772(16)	7471(30)	10.3(15)
O(6)	4200(14)	6450(15)	2334(22)	9.7(9)	O(5A)	2735(18)	3330(16)	7434(30)	11.1(10)
C(7)	4062(14)	7906(15)	6176(22)	4.0(8)	C(6A)	4086(19)	2986(21)	8432(33)	11.1(16)
O(7)	4516(11)	8381(12)	6721(17)	6.7(7)	O(6A)	4417(19)	3318(21)	8033(33)	13.6(12)
C(8)	2731(16)	5413(18)	5774(26)	6.0(10)	C(7A)	2993(18)	2927(17)	11032(22)	8.6(13)
O(8)	2702(11)	4836(12)	5856(17)	6.7(6)	O(7A)	3059(18)	3239(17)	11801(22)	9.3(8)
C(9)	1252(15)	4795(16)	4624(24)	5.1(9)	C(8A)	1130(19)	2393(20)	7698(28)	11.5(16)
O(9)	976(13)	4310(14)	4917(21)	9.3(8)	O(8A)	895(19)	2727(20)	7333(28)	10.3(9)
C(10)	2660(19)	6900(20)	1575(29)	7.8(12)	C(9A)	520(16)	1058(24)	6528(32)	13.6(19)
O(10)	2815(13)	7201(14)	1014(21)	9.4(8)	O(9A)	−19(16)	882(24)	6057(32)	14.1(13)
C(11)	3990(16)	8838(18)	4792(26)	5.9(10)	C(10A)	3891(21)	1465(25)	7878(35)	11.0(15)
O(11)	4400(11)	9409(12)	5151(18)	7.5(7)	O(10A)	4328(21)	1314(25)	7888(35)	15.8(14)
C(1, 2)	2066(14)	8034(15)	4329(22)	4.2(8)	C(11A)	3969(18)	2357(20)	11599(22)	11.2(16)
O(1, 2)	1814(11)	8381(12)	4457(18)	7.0(7)	O(11A)	4238(18)	2567(20)	12436(22)	10.9(10)
C(6, 7)	4157(16)	7037(17)	4823(25)	5.3(9)	C(1, 2A)	2538(15)	551(15)	10188(23)	9.7(14)
O(6, 7)	4691(12)	7053(12)	5171(19)	7.8(7)	O(1, 2A)	2473(15)	112(15)	10610(23)	7.2(7)
C(2, 3)	1995(16)	7378(17)	5886(25)	5.3(9)	C(6, 7A)	3392(16)	3265(14)	9588(25)	6.5(10)
O(2, 3)	1821(10)	7699(11)	6443(17)	6.4(6)	O(6, 7A)	3617(16)	3869(14)	9822(25)	10.1(9)
C(7, 8)	3615(14)	6675(15)	6248(22)	3.9(8)	C(2, 3A)	1453(17)	836(17)	10019(27)	9.1(14)
O(7, 8)	4011(9)	6693(10)	6949(15)	4.8(5)	O(2, 3A)	1164(17)	484(17)	10461(27)	10.1(9)
C(3, 8)	2298(18)	6278(19)	6410(28)	6.9(11)	C(7, 8A)	2156(19)	3010(18)	9552(28)	8.9(13)
O(3, 8)	2304(10)	6261(11)	7201(16)	6.0(6)	O(7, 8A)	2150(19)	3544(18)	9856(28)	11.4(10)
C(4, 9)	1030(18)	5352(19)	3219(28)	6.9(11)	C(3, 8A)	993(20)	1719(23)	9051(33)	12.3(17)
O(4, 9)	477(13)	5067(13)	2624(20)	8.7(8)	O(3, 8A)	549(20)	1779(24)	9273(33)	13.2(12)
C(5, 9)	1979(18)	4995(19)	3421(28)	7.3(11)	C(4, 9A)	1310(17)	403(15)	6718(24)	6.9(11)
O(5, 9)	1988(12)	4486(13)	2990(19)	8.1(8)	O(4, 9A)	1130(17)	−108(15)	6110(24)	10.8(10)
C(1, 11)	2987(15)	8285(16)	3266(24)	4.9(9)	C(5, 9A)	1708(18)	1594(19)	6362(26)	6.6(11)
O(1, 11)	3096(11)	8734(11)	2816(16)	6.3(6)	O(5, 9A)	1728(18)	1835(19)	5679(26)	12.6(11)
C(6, 11)	3951(14)	7828(15)	3519(23)	4.4(8)	C(1, 11A)	3785(15)	1336(18)	10308(24)	7.8(12)
O(6, 11)	4420(10)	8209(11)	3276(17)	6.3(6)	O(1, 11A)	4227(15)	1199(18)	10657(24)	8.9(8)

O(4, 10)	1588(15)	6155(17)	1889(24)	5.1(9)	C(6, 11A)	4213(11)	2578(15)	9966(23)	6.2(10)
O(4, 10)	1114(11)	5933(11)	1256(17)	6.5(6)	O(6, 11A)	4771(11)	2905(15)	10409(23)	9.5(8)
C(5, 10)	2584(16)	5777(17)	2199(25)	5.5(9)	C(5, 10A)	2969(16)	1731(17)	6838(24)	6.6(11)
O(5, 10)	2618(11)	5314(11)	1708(17)	6.3(6)	O(5, 10A)	3103(16)	1905(17)	6147(24)	9.2(8)
N(A)	1705(9)	−185(9)	3132(14)	8.8(6)	C(A8)	4196(10)	1263(14)	4712(22)	8.9(5)
C(A1)	1685(17)	−84(17)	4179(15)	8.8(6)	C(A9)	3875(11)	789(18)	5172(16)	8.9(5)
C(A2)	1721(17)	441(13)	2775(24)	8.8(6)	C(A10)	3266(13)	276(14)	4663(25)	8.9(5)
C(A3)	1104(12)	−801(13)	2492(22)	8.8(6)	C(B5)	3933(14)	8497(13)	291(13)	6.8(4)
C(A4)	2310(12)	−298(18)	3087(25)	8.8(6)	C(B6)	3309(13)	8376(13)	−259(21)	6.8(4)
N(B)	4412(8)	9596(8)	1736(12)	6.9(4)	C(B7)	3102(9)	8099(13)	−1260(20)	6.8(4)
C(B1)	4656(14)	9800(15)	2844(12)	6.9(4)	C(B8)	3518(14)	7942(13)	−1711(13)	6.8(4)
C(B2)	4963(11)	9945(14)	1335(21)	6.9(4)	C(B9)	4143(13)	8064(13)	−1160(21)	6.8(4)
C(B3)	3860(11)	9811(15)	1386(22)	6.9(4)	C(B10)	4350(9)	8341(13)	−159(20)	6.8(4)
C(B4)	4169(14)	8831(8)	1384(22)	6.9(4)	C(C5)	833(17)	2296(22)	3591(22)	12.2(7)
N(C)	−116(13)	2294(13)	4249(20)	14.6(10)	C(C6)	1302(16)	2866(14)	3466(27)	12.2(7)
C(C1)	−315(24)	2424(26)	5160(26)	14.6(10)	C(C7)	1546(16)	2811(15)	2681(33)	12.2(7)
C(C2)	−118(23)	2844(20)	3712(33)	14.6(10)	C(C8)	1321(17)	2185(22)	2022(22)	12.2(7)
C(C3)	−593(21)	1604(16)	3590(32)	14.6(10)	C(C9)	853(16)	1615(14)	2148(27)	12.2(7)
C(C4)	561(15)	2304(26)	4539(36)	14.6(10)	C(C10)	609(16)	1670(15)	2932(33)	12.2(7)
N(D)	−535(8)	6228(8)	9742(12)	6.8(4)	C(D5)	197(13)	7010(19)	8892(24)	11.3(7)
C(D1)	−1238(9)	5724(13)	9480(21)	6.8(4)	C(D6)	421(16)	7694(22)	9354(23)	11.3(7)
C(D2)	−92(13)	5853(14)	9888(22)	6.8(4)	C(D7)	1050(21)	8139(12)	9449(23)	11.3(7)
C(D3)	−369(15)	6753(13)	10678(16)	6.8(4)	C(D8)	1456(13)	7901(19)	9082(24)	11.3(7)
C(D4)	−444(14)	6580(14)	8922(17)	6.8(4)	C(D9)	1233(16)	7217(22)	8620(23)	11.3(7)
N(E)	3515(8)	5669(9)	−663(13)	7.8(5)	C(D10)	603(21)	6772(12)	8525(23)	11.3(7)
C(E1)	4133(12)	5666(20)	−23(21)	7.8(5)	C(E5)	2250(11)	5088(18)	−1054(18)	8.4(5)
C(E2)	3472(15)	5464(10)	−1729(14)	7.8(5)	C(E6)	1888(14)	4580(14)	−1909(22)	8.4(5)
C(E3)	3527(19)	6377(11)	−432(19)	7.8(5)	C(E7)	1285(11)	4535(13)	−2437(16)	8.4(5)
C(E4)	2930(13)	5167(14)	−466(20)	7.8(5)	C(E8)	1045(11)	4998(18)	−2112(18)	8.4(5)
N(F)	6207(14)	6483(16)	5076(23)	19.6(12)	C(E9)	1407(14)	5505(14)	−1257(22)	8.4(5)
C(F1)	6446(25)	6385(32)	4198(32)	19.6(12)	C(E10)	2009(11)	5550(13)	−728(16)	8.4(5)
C(F2)	5552(18)	5905(24)	4907(42)	19.6(12)	C(F5)	5497(19)	5472(18)	3827(24)	14.3(9)
C(F3)	6137(27)	7155(20)	5216(40)	19.6(12)	C(F6)	4941(23)	5474(18)	3212(35)	14.3(9)
C(F4)	6693(25)	6486(27)	5980(29)	19.6(12)	C(F7)	4511(15)	4896(24)	2483(30)	14.3(9)
C(A5)	2978(10)	239(14)	3693(22)	8.9(5)	C(F8)	4638(19)	4315(18)	2369(24)	14.3(9)
C(A6)	3299(11)	714(18)	3233(16)	8.9(5)	C(F9)	5195(23)	4314(18)	2984(35)	14.3(9)
C(A7)	3907(13)	1226(14)	3743(25)	8.9(5)	C(F10)	5624(15)	4892(24)	3713(30)	14.3(9)

[a] Positional and anisotropic thermal parameters $\times 10^4$.

[b] The b_{ij} values are the coeffcients of: $\exp[-(h^2b_{11} + h^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$.

TABLE 2

BOND DISTANCES (Å) WITH E.S.D.'S IN PARENTHESES

	Anion I	Anion II (A)		Anion I	Anion II (A)
Co(1)—Co(2)	2.531(6)	2.503(9)	Co(1)—C(—1)	2.11(3)	1.94(4)
Co(1)—Co(4)	2.574(7)	2.554(8)	Co(2)—C(—1)	2.20(3)	2.24(4)
Co(1)—Co(10)	2.602(8)	2.587(9)	Co(4)—C(—1)	2.37(2)	2.23(3)
Co(1)—Co(11)	2.496(6)	2.492(7)	Co(5)—C(—1)	2.32(3)	2.31(4)
Co(2)—Co(3)	2.495(6)	2.483(7)	Co(6)—C(—1)	2.08(3)	2.10(4)
Co(2)—Co(4)	3.112(5)	3.039(7)	Co(7)—C(—1)	2.15(3)	2.34(4)
Co(2)—Co(7)	2.645(7)	2.622(8)	Co(10)—C(—1)	2.17(3)	2.04(4)
Co(2)—Co(11)	2.585(7)	2.587(7)	Co(11)—C(—1)	2.02(3)	2.12(4)
Co(3)—Co(4)	2.625(7)	2.597(9)	Co(2)—C(—2)	2.15(3)	2.03(4)
Co(3)—Co(8)	2.469(8)	2.475(9)	Co(3)—C(—2)	1.86(4)	1.90(4)
Co(3)—Co(9)	2.595(7)	2.591(9)	Co(4)—C(—2)	2.13(3)	2.16(4)
Co(4)—Co(5)	2.682(8)	2.661(9)	Co(5)—C(—2)	2.13(4)	2.17(4)
Co(4)—Co(9)	2.437(8)	2.459(9)	Co(7)—C(—2)	2.14(3)	2.06(3)
Co(4)—Co(10)	2.461(7)	2.458(8)	Co(8)—C(—2)	1.86(4)	1.90(5)
Co(5)—Co(6)	2.562(6)	2.572(7)	Co(9)—C(—2)	2.53(3)	2.65(4)
Co(5)—Co(7)	3.064(5)	3.070(8)	C(—1)—C(—2)	1.62(5)	1.66(6)
Co(5)—Co(8)	2.593(6)	2.624(9)	Co(1)—C(1)	1.69(4)	1.80(6)
Co(5)—Co(9)	2.467(7)	2.480(7)	Co(2)—C(2)	1.78(3)	1.71(3)
Co(5)—Co(10)	2.438(7)	2.430(9)	Co(3)—C(3)	1.74(4)	1.67(3)
Co(6)—Co(7)	2.515(7)	2.511(9)	Co(4)—C(4)	1.73(5)	1.65(4)
Co(6)—Co(10)	2.598(6)	2.622(8)	Co(5)—C(5)	1.74(4)	1.76(4)
Co(6)—Co(11)	2.521(8)	2.497(9)	Co(6)—C(6)	1.68(6)	1.69(5)
Co(7)—Co(8)	2.483(6)	2.485(7)	Co(7)—C(7)	1.69(2)	1.68(3)
Co(7)—Co(11)	2.597(7)	2.588(9)	Co(8)—C(8)	1.60(4)	1.75(5)
Co(8)—Co(9)	2.591(5)	2.610(8)	Co(9)—C(9)	1.65(4)	1.67(4)
			Co(10)—C(10)	1.68(5)	1.67(5)
Co(11)—C(11)	1.71(3)	1.71(3)	C(6)—O(6)	1.22(7)	
Co(1)—C(1,2)	1.94(4)	1.89(4)	C(7)—O(7)	1.19(3)	
Co(2)—C(1,2)	1.98(4)	1.93(4)	C(8)—O(8)	1.26(5)	
Co(1)—C(1,11)	1.85(3)	1.86(3)	C(9)—O(9)	1.21(5)	
Co(11)—C(1,11)	1.86(4)	1.81(4)	C(10)—O(10)	1.16(6)	
Co(2)—C(2,3)	1.93(4)	1.87(4)	C(11)—O(11)	1.21(4)	
Co(3)—C(2,3)	1.84(4)	1.87(4)	C(1,2)—O(1,2)	1.13(5)	
Co(3)—C(3,8)	1.91(4)	1.88(6)	C(6,7)—O(6,7)	1.21(5)	
Co(8)—C(3,8)	1.91(5)	1.86(5)	C(2,3)—O(2,3)	1.22(5)	
Co(4)—C(4,9)	2.06(4)	1.95(3)	C(7,8)—O(7,8)	1.19(4)	
Co(9)—C(4,9)	1.73(4)	1.71(4)	C(3,8)—O(3,8)	1.15(5)	
Co(4)—C(4,10)	2.17(4)	2.05(8)	C(4,9)—O(4,9)	1.24(4)	
Co(10)—C(4,10)	1.77(3)	1.79(4)	C(5,9)—O(5,9)	1.20(5)	
Co(5)—C(5,9)	1.97(4)	2.04(4)	C(1,11)—O(1,11)	1.24(5)	
Co(9)—C(5,9)	1.71(5)	1.71(4)	C(6,11)—O(6,11)	1.27(5)	
Co(5)—C(5,10)	2.09(4)	2.03(4)	C(4,10)—O(4,10)	1.15(4)	
Co(10)—C(5,10)	1.78(4)	1.77(4)	C(5,10)—O(5,10)	1.19(5)	
Co(6)—C(6,7)	1.85(4)	1.82(4)			
Co(7)—C(6,7)	1.91(3)	1.91(4)			
Co(6)—C(6,11)	1.81(3)	1.85(3)			
Co(11)—C(6,11)	1.84(4)	1.87(3)			
Co(7)—C(7,8)	1.88(4)	1.89(5)			
Co(8)—C(7,8)	1.88(3)	1.90(3)			
C(1)—O(1)	1.16(6)				
C(2)—O(2)	1.16(4)				
C(3)—O(3)	1.16(6)				
C(4)—O(4)	1.17(6)				
C(5)—O(5)	1.18(5)				

atom parameters the carbonyl groups of one anion and five out of the six independent cations were easily located. The ligands of the anion labelled A and the cation labelled F were localized with difficulty and gave trouble during the refinement. This fact was taken as an indication of disorder, but a rationalization of the observations was not possible because no image duplication was detected. In order to complete the refinement successfully some constraints were introduced in the structure model. The C—O distances in the anion A were fixed at the average values found in an earlier refinement of the unaffected anion, 1.17 and 1.19 Å for terminal and bridging groups, respectively. Each cation was divided in two rigid groups, the NC_4 tetrahedron (N—C 1.52 Å, T_d symmetry) and the phenyl ring (C—C 1.392 Å, D_{6h} symmetry). An average thermal parameter was used for each group, the hydrogen atoms were omitted. The atoms in the anions were allowed to vibrate individually, the cobalt atoms anisotropically and the light atoms isotropically. All the cations behaved well except for the previously mentioned F, but no attempts to improve the model were made.

The final agreement indices were $R = 0.096$ and $R' = 0.125$. A difference-Fourier map, computed after the refinement, showed the highest peaks in the vicinity of the metal atoms, not exceeding 1.6 e^- Å^{-3}. The final parameters of all the atoms are reported in Table 1 and the bond distances in Table 2. A list of observed and computed structure factors can be obtained from the authors.

Results and discussion

The crystal consists of discrete ions $[NMe_3(CH_2Ph)]^+$ and $[Co_{11}C_2(CO)_{22}]^{3-}$. In the unit cell there are two crystallographically independent but chemically equivalent anions. Due to the higher standard deviations of the bond parameters in anion II (labelled A in Table 1), the structure will be discussed with reference to anion I, but the bond parameters are not significantly different in the two anions.

The structure of the anion is depicted in Fig. 1, it has idealized C_s-m symmetry, the mirror plane being defined by Co(9), Co(10), Co(11) and contains the carbide atoms C(—1) and C(—2). The carbonyl groups are bonded 11 terminal and 11 edge-bridging, in such a way that all the cobalt atoms are bonded to three ligands. At first sight the metal atom polyhedron can be described as a tricapped cube, the capping atoms being those placed in the idealized symmetry plane; the symmetry of such a polyhedron would be C_{2v}. However, the cube edge lying between the capping atoms Co(10) and Co(11) is stretched and the symmetry is reduced to C_s. Another description of the polyhedron can be given by looking at the shape of its cavity which consists of a square antiprism and a trigonal prism sharing a face [Co(2), Co(4), Co(5), Co(7)]. Two opposite edges of this face are quite elongated [Co(2)—Co(4) and Co(5)—Co(7)] with average length 3.09 Å. The remaining atom caps a second square face of the prism.

Except for the previously mentioned elongations the Co—Co distances are normal, the edges bearing bridging ligands have average length 2.48 Å and the unbridged ones 2.60 Å. The C—C(carbide) distance, 1.62(5) Å, is longer than expected for a single bond, viz. 1.54 Å. C(—1) is contained in the antiprismatic half of the cavity with average distances from the outer and central atoms

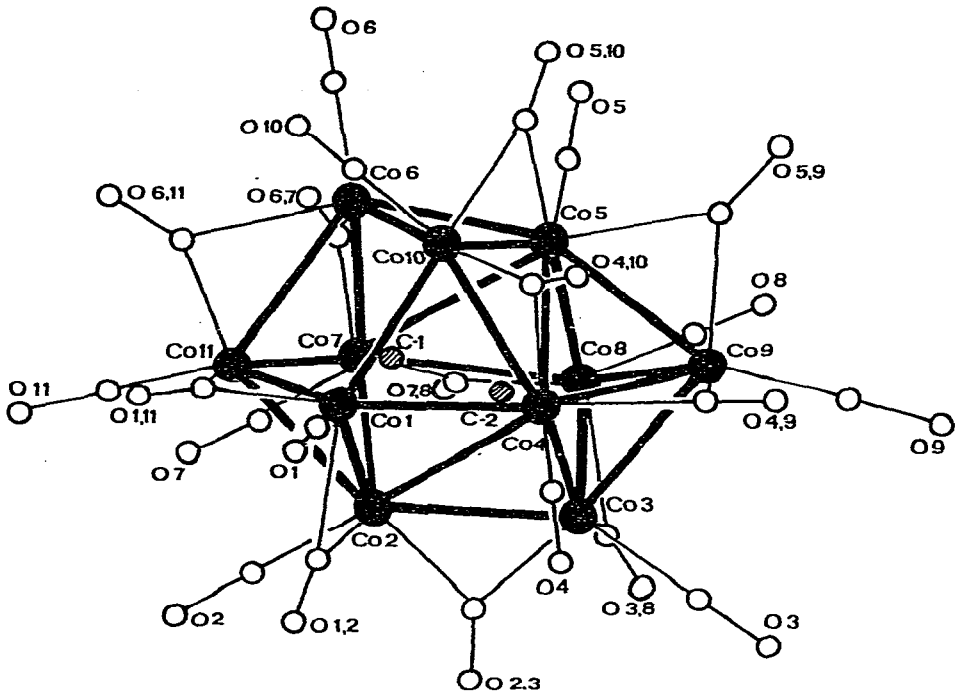

Fig. 1. Drawing of the anion $[Co_{11}C_2(CO)_{22}]^{3-}$.

(shared face) 2.10 and 2.26 Å, respectively. C(—2) is in the prismatic moiety with average distances from the atoms in the shared face 2.13 Å and from the prism-edge atoms [Co(3), Co(8)] 1.86 Å, a very short value.

The second description of the cobalt atom polyhedron is particularly useful because it relates to the structure of $[Rh_{12}C_2(CO)_{25}]$ [4]. A comparison of the two bare polyhedra (Fig. 2) shows that they are quite similar, and that the latter can be obtained by adding another capping atom to the Co_{11} cluster. The

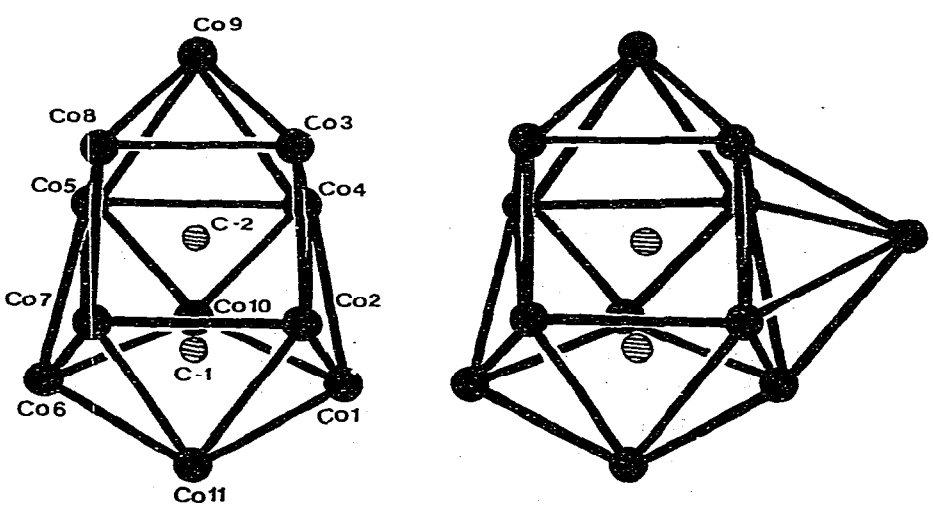

Fig. 2. The metal atom polyhedra in $[Co_{11}C_2(CO)_{22}]^{3-}$ (left) and in $[Rh_{12}C_2(CO)_{25}]$ (right).

existence of strictly comparable cavities in $[Co_{11}C_2(CO)_{22}]^{3-}$ and $[Rh_{12}C_2(CO)_{25}]$ shows that the just described ten-vertex polyhedron is the most suitable for incapsulating the C_2 interstitial unit. It is noteworthy that the already described elongation of two edges in the shared face is also present in the Rh_{12} cluster. In order to explain this characteristic feature we have calculated that the expected carbon—carbon distance in an idealized cavity with equal edges (l) is $0.708 \times l$. If the edge length is taken as 2.54 Å, the overall mean value of the Co—Co distances in the present cluster, the carbon—carbon separation would be 1.80 Å which is too long a value for an efficient bonding interaction. A 0.43 Å lengthening of two opposite edges in the central face of the composite polyhedron seems necessary in order to allow a closer carbide-carbide bonding contact. An even shorter C—C distance is possible in the bigger cavity of the Rh_{12} cluster, 1.48(2) Å.

The bond parameters of the carbonyl groups are normal, average values for Co—C and C—O interactions are 1.70, 1.19 Å for terminal groups and 1.89, 1.20 Å for the bridging ones, respectively.

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References

1 V.G. Albano, M. Sansóni, P. Chini and S. Martinengo, J. Chem. Soc. Dalton Trans., (1973) 651.
2 V.G. Albano, M. Sansoni, P. Chini, S. Martinengo and D. Strumolo, J. Chem. Soc. Dalton Trans., (1975) 305.
3 V.G. Albano, M. Sansoni, P. Chini, S. Martinengo and D. Strumolo, J. Chem. Soc. Dalton Trans., (1976) 970.
4 V.G. Albano, P. Chini, S. Martinengo, M. Sansoni and D. Strumolo, J. Chem. Soc. Dalton Trans., (1978) 459.
5 V.G. Albano, P. Chini, G. Ciani, S. Martinengo and M. Sansomi, J. Chem. Soc. Dalton Trans., (1978) 468.
6 V.G. Albano, P. Chini, G. Ciani, M. Sansoni and S. Martinengo, J. Chem. Soc. Dalton Trans., (1980) 163.
7 V.G. Albano, D. Braga and S. Martinengo, J. Chem. Soc. Dalton Trans., (1981) in the press.
8 V.G. Albano, D. Braga and S. Martinengo, to be published.
9 S. Martinengo, V.G. Albano, D. Braga, P. Chini and G. Ciani, Proc. 11th Italian Congress of Inorganic Chemistry, Arcavacata di Rende, Sept. 25—29, 1978, 4F.
10 G. Sheldrick, SHELX 75 System of Computer Programs, Cambridge, 1975.