Synthesis, Electrochemistry, and Magnetic Properties of Binuclear Cobalt Complexes containing the $Co_2(\mu\text{-}X)(\mu\text{-carboxylato})_2{}^{n+}$ Core (X = OH, Cl, or Br; *n* = 1—3). The Crystal Structures of $[Co^{II}{}_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$ and $[Co^{II}Co^{III}(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_2\cdot0.5H_2O$ (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane)†

Phalguni Chaudhuri, Jürgen Querbach, and Karl Wieghardt*
Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany
Bernhard Nuber and Johannes Weiss
Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, Federal Republic of Germany

A series of novel binuclear cobalt(II) complexes containing the μ-hydroxo-bis(μ-carboxylato)-dicobalt(II) core have been prepared where each cobalt(II) centre is capped by the tridentate macrocycle *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L, $C_9H_{21}N_3$): $[Co^{II}{}_2(\mu\text{-}RCO_2)_2L_2(\mu\text{-}OH)]PF_6$ [R = Me (**1**); ClH_2C (**2**), or Cl_2HC (**3**)]. The hydroxo bridge may be replaced by a chloro or bromo bridge: $[Co^{II}{}_2(\mu\text{-}X)(\mu\text{-}RCO_2)_2L_2]PF_6$ [X = Cl, R = Me (**4**) or ClH_2C (**5**); X = Br, R = Me (**6**)]. Air oxidation of (**1**) and (**2**) affords the mixed-valence complexes $[Co^{II}Co^{III}(\mu\text{-}RCO_2)_2(\mu\text{-}OH)L_2][PF_6]_2$ [R = Me (**7**) or ClH_2C (**8**)]. Finally, the dicobalt(III) complex $[Co^{III}{}_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_3$ (**9**) has been prepared. Cyclic voltammograms of complexes (**1**)—(**6**) in acetonitrile display a reversible and a quasi-reversible one-electron transfer process ($Co^{II}{}_2 \rightleftharpoons Co^{II}Co^{III} + e^- \rightleftharpoons Co^{III}{}_2 + e^-$). The crystal structures of (**5**) and (**7**) have been determined by *X*-ray analyses. Crystals of (**5**) are orthorhombic, space group *Pnam*, with *a* = 13.043(2), *b* = 14.824(2), *c* = 17.827(3) Å, and *Z* = 4. Crystals of (**7**) are triclinic, space group $P\bar{1}$, with *a* = 12.479(8), *b* = 16.27(1), *c* = 19.11(2)Å, α = 84.40(6), β = 74.13(6), γ = 68.60(5)°, and *Z* = 4. In (**7**) the cobalt-(II) and -(III) centres are clearly identified. From the electronic spectra and structural results it is concluded that in the mixed-valence $Co^{II}Co^{III}$ complexes the valences are localized. In the dicobalt(II) complexes weak intramolecular antiferromagnetic coupling of the two cobalt centres (d^7, high spin) has been detected from temperature-dependent susceptibility measurements in the range 98—298 K.

Binuclear carboxylate-bridged complexes of cobalt(II) are surprisingly rare[1] considering the enormous structural variety of such compounds of cobalt(III) which have been synthesized and structurally characterized since Werner's pioneering work in 1910.[2] Only two different types of μ-carboxylato bridged binuclear cobalt(II) complexes appear to be characterized by *X*-ray crystallography, namely structures (**A**)[3—9] and (**B**).[10] Structure (**A**) is quite abundant and the electronic and magnetic properties[8,9] of $Co^{II}{}_2(\mu\text{-carboxylato})_4L_2$ species have been studied in some detail; (**B**) represents a fascinating structure[10] because the two Co^{II} are bridged by a rare μ-aqua bridge which is supported in this instance by strong hydrogen bonding to two monodentate carboxylate ligands. Turpeinen *et al.*[10—14] have shown that (**B**) is a quite general structural type for divalent first-row transition metals in the presence of carboxylic acids. Thus a number of $[M_2(\mu\text{-}OH_2)(\mu\text{-}RCO_2)_2(RCO_2)_2(tmen)_2]$ complexes have been characterized (M = Co^{II} or Ni^{II}; R = Me, CH_2Cl, $CHCl_2$, or CCl_3; tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine).[10] A third structural type (**C**) containing the μ-hydroxo-bis(carboxylato)dimetal(II) core has been identified in a number of complexes of Mn^{II},[15] Fe^{II},[16] and Ni^{II}[17] when the metal centres are capped by the tridentate macrocycle *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L). A series of heterobinuclear complexes of this type including the chromium(III)cobalt(II) species has been described.[18] This core has also been identified in the active sites of a number of iron[19]- and manganese[20]-containing metalloproteins.

We report here on the syntheses, electronic and magnetic properties, and crystal structures of a novel series of cobalt(II) complexes of type (**C**). The electrochemistry of complexes (**1**)—(**9**) has been investigated and two mixed-valence cobalt (II, III) complexes (**7**) and (**8**) have been isolated. Finally, the binuclear complex (**9**) containing two cobalt(III) centres has also been prepared. The μ-hydroxo-bis(μ-carboxylato)-dicobalt(III) core has been identified previously in $[(NH_3)_3Co^{III}(\mu\text{-carboxylato})_2(\mu\text{-}OH)Co^{III}(NH_3)_3]^{3+}$ complexes by Siebert and Tremmel.[21]

Results and Discussion

Synthesis of Complexes—Cobalt(II) acetate tetrahydrate dissolved in methanol reacts with the tridentate macrocycle L (1:1) using anaerobic conditions at room temperature yielding a pink-red solution. Addition of $NaPF_6$ initiated the precipitation of red crystals of complex (**1**). Complexes (**2**) and (**3**) were prepared by the same procedure of self-assembly. It is noted that the corresponding cobalt(II) carboxylates of mono- and dichloroacetic acid must be free of chloride; the commercially available acids always contain some Cl^-. A procedure yielding pure $Co(RCO_2)_2$ (R = CH_2Cl or $CHCl_2$) as starting materials is

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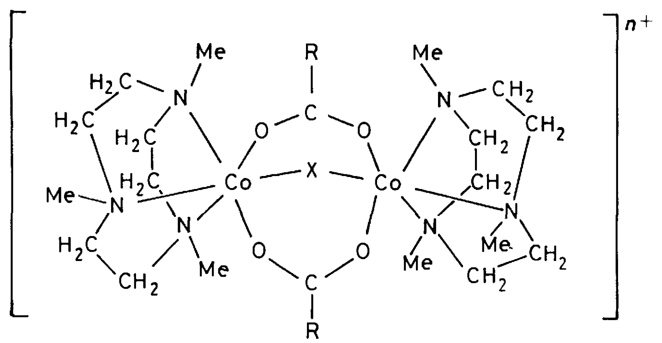
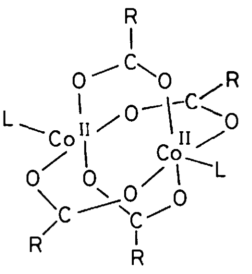
† μ-Chloro-di-μ-chloroacetato-bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)cobalt(II)] hexafluorophosphate and di-μ-acetato-μ-hydroxo-bis(1,4,7-trimethyl-1,4,7-triazacyclononane)cobalt(II)cobalt(III) diperchlorate-water (2/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

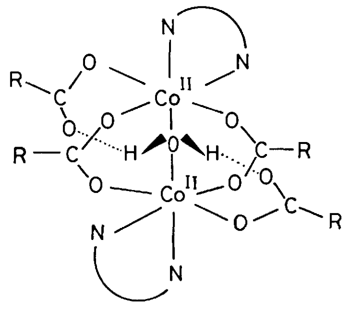


Complex	X	R	n	Oxidation state
(1)	OH	Me	1	$\mathrm{Co^{II}Co^{II}}$
(2)	OH	CH_2Cl	1	$\mathrm{Co^{II}Co^{II}}$
(3)	OH	$CHCl_2$	1	$\mathrm{Co^{II}Co^{II}}$
(4)	Cl	Me	1	$\mathrm{Co^{II}Co^{II}}$
(5)	Cl	CH_2Cl	1	$\mathrm{Co^{II}Co^{II}}$
(6)	Br	Me	1	$\mathrm{Co^{II}Co^{II}}$
(7)	OH	Me	2	$\mathrm{Co^{II}Co^{III}}$
(8)	OH	CH_2Cl	2	$\mathrm{Co^{II}Co^{III}}$
(9)	OH	Me	3	$\mathrm{Co^{III}Co^{III}}$

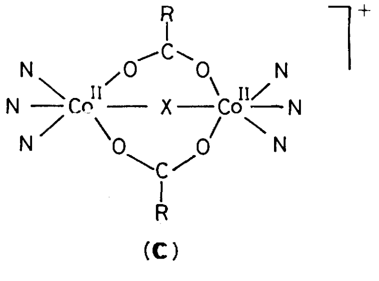
Scheme.



(**A**)



(**B**)



(**C**)

X = OH, Cl, or Br

described in the Experimental section. When the above synthesis was carried out in the presence of chloride or bromide ions and absence of water the μ-chloro and μ-bromo complexes (**4**)—(**6**) were obtained in good yields. Solutions of (**1**) and (**2**) in methanol are air-sensitive; the pink colour changes upon exposure to air to red-brown and addition of $NaPF_6$ initiates the precipitation of the mixed-valence complexes (**7**) and (**8**).

Since the electrochemical investigation of complexes (**1**)—(**3**) indicated that the binuclear cobalt(III) analogues are stable in solution, at least on the time-scale of a cyclic voltammogram (see below), we attempted the oxidation of these complexes using a variety of oxidants such as $S_2O_8^{2-}$ and H_2O_2. These experiments yielded the monomeric complex $[Co(MeCO_2)_2L]PF_6$ (**10**) as the only isolable product. From i.r. data the following structure is the most probable one.

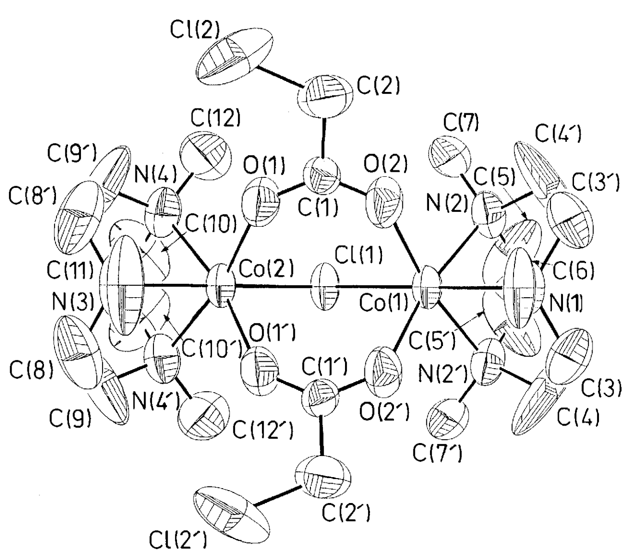
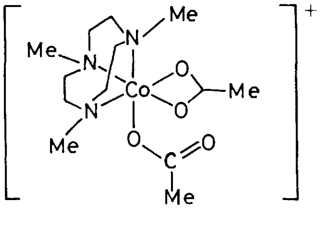


Figure 1. View of the structure of the cation in crystals of $[Co^{II}_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$, (**5**), and atom numbering scheme



(**10**)

Attempts to synthesize complex (**9**) from monomeric cobalt(III) precursor complexes, *e.g.* reactions (1) and (2), also failed. The very stable $[LCo(\mu\text{-}OH)_3CoL]^{3+}$ species formed in small quantities in addition to (**10**). Good yields of (**9**) were

$$[CoCl_3L] + 3\,Ag^+ \xrightarrow[-3AgCl]{CH_3OH} [Co(MeOH)_3L]^{3+} \qquad (1)$$

$$2[Co(MeOH)_3L]^{3+} \xrightarrow[NaO_2CMe]{H_2O} [Co_2(\mu\text{-}OH)_3L_2]^{3+}\ [\text{and } (\mathbf{10})] \qquad (2)$$

obtained when a solution of $Co(ClO_4)_2 \cdot 6H_2O$ and the ligand L (1:1) in water–glacial acetic acid (5:1) was carefully oxidized by dropwise addition of peroxyacetic acid and refluxing of this solution for 30 min. At 0 °C red-purple crystals of (**9**) precipitated within 2—3 d.

Description of the Structures of Complexes (**5**) *and* (**7**).—The structure of the monocation in crystals of $[Co^{II}_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$, (**5**), is shown in Figure 1. Atom co-ordinates are given in Table 1; selected bond distances and angles in Table 2. Two cobalt(II) centres are connected by a chloro and two symmetrical chloroacetato bridges; each Co^{II} is capped by a tridentate macrocycle L. Complexes containing the $M_2(\mu\text{-}Cl)(\mu\text{-carboxylato})_2{}^+$ core have not been characterized previously. The cation possesses a crystallographic mirror plane; atoms Co(1), Co(2), Cl(1), N(1), and N(3) lie on this plane. The site symmetry *m* is not compatible with the conformation of the co-ordinated macrocycle which forms three five-membered chelate rings $\overline{\text{Co–N–C–C–N}}$ of either (λλλ) or (δδδ) conformation. Consequently, the cation displays some

Table 1. Atom co-ordinates (× 10^4) for $[Co_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$ (**5**)

Atom	*x*	*y*	*z*
Co(1)	3 480(1)	5 904(1)	2 500
Co(2)	5 653(1)	4 201(1)	2 500
Cl(1)	5 393(2)	5 846(2)	2 500
O(1)	4 620(4)	3 992(4)	1 653(3)
O(2)	3 371(3)	4 982(3)	1 652(3)
C(1)	3 850(6)	4 342(5)	1 397(4)
C(2)	3 402(7)	3 977(5)	661(4)
Cl(2)	3 973(2)	3 011(2)	326(2)
N(1)	1 815(6)	6 046(5)	2 500
N(2)	3 359(5)	6 994(4)	1 709(4)
C(3)	1 582(6)	6 558(5)	3 183(5)
C(4)	2 304(6)	6 957(9)	3 569(7)
C(5)	3 626(7)	7 809(6)	2 124(5)
C(6)	1 270(8)	5 190(7)	2 500
C(7)	4 044(6)	6 941(5)	1 065(4)
N(3)	5 994(6)	2 753(5)	2 500
N(4)	6 902(4)	4 199(4)	1 711(4)
C(8)	6 570(7)	2 604(5)	3 180(5)
C(9)	7 047(9)	3 314(6)	3 538(7)
C(10)	7 809(6)	4 487(7)	2 122(5)
C(11)	5 058(8)	2 226(7)	2 500
C(12)	6 718(7)	4 791(7)	1 073(5)
P(1)	5 000	0	0
F(1)	4 602(6)	−449(8)	680(6)
F(2)	4 073(5)	556(7)	−59(5)
F(3)	4 490(10)	−601(7)	−504(8)

Table 2. Selected bond distances (Å) and angles (°) for complex (**5**)

Co(1)–Cl(1)	2.497(3)	Co(2)–Cl(1)	2.461(3)
Co(1)–N(1)	2.182(8)	Co(2)–O(1)	2.048(5)
Co(1)–O(2)	2.043(5)	Co(2)–N(4)	2.151(6)
Co(1)–N(2)	2.151(7)	Co(2)–N(3)	2.192(8)
O(1)–C(1)	1.22(1)	O(2)–C(1)	1.22(1)
C(1)–C(2)	1.54(1)	C(2)–Cl(2)	1.72(1)
Co(1) · · · Co(2)	3.795(2)		
Cl(1)–Co(1)–O(2)	92.7(1)	Cl(1)–Co(1)–N(1)	176.4(2)
O(2)–Co(1)–N(1)	89.7(2)	Cl(1)–Co(1)–N(2)	95.7(2)
O(2)–Co(1)–N(2)	90.7(2)	N(1)–Co(1)–N(2)	81.6(2)
Cl(1)–Co(1)–O(2′)	92.7(2)	O(2)–Co(1)–O(2′)	95.5(2)
N(1)–Co(1)–N(2′)	81.6(2)	N(2)–Co(1)–O(2′)	169.3(2)
Cl(1)–Co(2)–N(3)	176.2(2)	N(2)–Co(1)–N(2′)	81.9(4)
Cl(1)–Co(2)–N(4)	96.1(2)	Cl(1)–Co(2)–O(1)	93.4(2)
N(3)–Co(2)–N(4)	81.1(2)	O(1)–Co(2)–N(3)	89.1(2)
O(1)–Co(2)–O(1′)	95.0(3)	O(1)–Co(2)–N(4)	90.9(2)
N(4)–Co(2)–O(1′)	168.5(2)	Cl(1)–Co(2)–O(1′)	93.4(2)
N(4)–Co(2)–N(4′)	81.6(3)	N(3)–Co(2)–O(1′)	89.1(2)
Co(1)–Cl(1)–Co(2)	99.9(1)	Cl(1)–Co(2)–N(4′)	96.1(2)
Co(1)–O(2)–C(1)	139.2(5)	N(3)–Co(2)–N(4′)	81.1(2)
O(1)–C(1)–C(2)	118.9(7)	Co(2)–O(1)–C(1)	138.9(5)
C(1)–C(2)–Cl(2)	115.2(6)	O(1)–C(1)–O(2)	127.8(8)
		O(2)–C(1)–C(2)	113.3(7)

degree of disorder. The carbon atoms C(3)—C(5) have extraordinary large anisotropic thermal parameters. This effect is often observed in crystal structures of complexes containing co-ordinated 1,4,7-triazacyclononane ligands. The average Co–N and Co–O(acetate) bond distances at 2.16 and 2.05 Å, respectively, agree well with corresponding values in $[Co_2(\mu\text{-}OH_2)(Cl_3CCO_2)_4(tmen)_2]$[10] and $[LCr^{III}(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)Co^{II}L][ClO_4]_2\cdot0.5H_2O$;[18] they are indicative of high-spin cobalt(II) ($S = \frac{3}{2}$) in a pseudo-octahedral environment. The bridging Co–Cl bond distance of 2.48 Å is rather long as compared to terminal Co–Cl bonds in octahedral cobalt(II) complexes (2.30 Å). The Co–Cl–Co bridge is not quite symmetric: Co(1)–Cl(1) 2.497(3) and Co(2)–Cl(1) 2.461(3) Å.

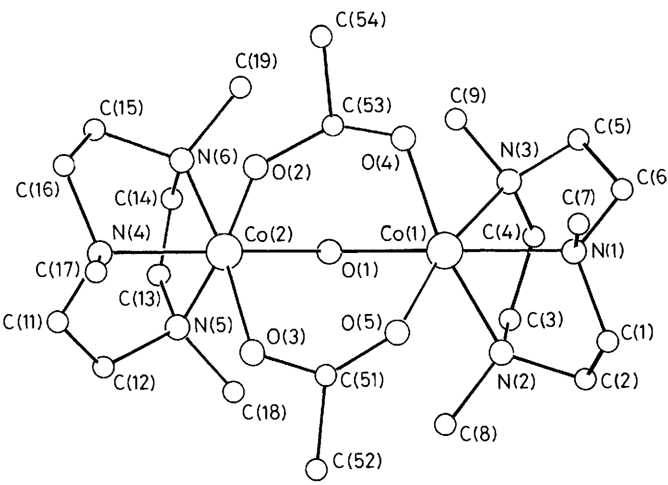


Figure 2. View of one of the two crystallographically independent dictations in crystals of $[Co^{II}Co^{III}(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_2\cdot0.5H_2O$, (**7**), and atom numbering scheme

Crystals of complex (**7**) contain the binuclear mixed-valence dication $[LCo^{II}(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)Co^{III}L]^{2+}$. Atom co-ordinates are given in Table 3, selected bond distances and angles in Table 4.

Due to the disorder of the ClO_4^- anions in (**7**) and the low *X*-ray diffraction quality of the crystals available, the structure determination is not as precise as would be desirable. Notwithstanding these obstacles we chose to present the results here because it is clearly possible to discern between the Co^{II} and Co^{III} in the dications and the determined bond distances are chemically reasonable. There are two crystallographically independent dications in the unit cell, the dimensions of which are very similar. Figure 2 shows the structure of one dication and the corresponding atom labels. In contrast to the structure of complex (**5**) the dications do not have crystallographically imposed symmetry. Inspection of the data in Table 4 reveals that the two cobalt centres in a dication are not equivalent, although each is in a pseudo-octahedral environment of a tridentate macrocycle L, a bridging OH group, and two acetato bridges. The corresponding Co–N and Co–O bond distances at Co(1) and Co(2) differ significantly. Clearly, Co(1) is in the oxidation state + II since the Co–N and Co–O distances are long [av. Co–N 2.18, Co–O(acetate) 2.06 Å] and identical to those in complex (**5**), whereas the analogous distances at Co(2) are considerably shorter [av. Co–N 2.00, Co–O(acetate) 1.91, Co–O(hydroxo) 1.90 Å]. The Co(1)–O(hydroxo) bond distance is 2.04 Å, whereas Co(2)–O(hydroxo) is 1.90 Å. Thus the Co–OH–Co unit is unsymmetrical. The differences $d[(Co^{II}–N)–(Co^{III}–N)]$ of 0.18 Å, $d[(Co^{II}–O)–(Co^{III} – O)]$(acetate) of 0.15 Å, and $d[(Co^{II}–O)–(Co^{III}–O)]$(hydroxide) of 0.13 Å are typical for differences between corresponding bonds of a high-spin cobalt(II) and a low-spin cobalt(III) centre. The valences of the metal ions in the mixed-valence dication are therefore localized (class I[22]). Localized valences have also been observed in the structure of the mixed-valence tetranuclear complex di-μ-acetato-tetrakis[μ_3-methoxo–(pentane-2,4-dionato)cobalt-(II,III)][23] where the corresponding cobalt–oxygen distances of the two cobalt(II) and two cobalt(III) centres also differ by 0.16—0.20 Å.

Electronic Spectra and Magnetic Properties of the Complexes.—These properties are summarized in Tables 5 and 6. Figure 3 shows a representative spectrum of (**1**) for all complexes containing the $Co^{II}_2(\mu\text{-}X)(\mu\text{-carboxylato})_2{}^+$ core and the spec-

Table 3. Atom co-ordinates (× 10^4) for $[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_2$ (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	3 317(2)	8 158(2)	3 572(1)	N(7)	2 304(14)	3 611(10)	1 116(9)
Co(2)	968(2)	7 416(2)	3 991(1)	N(8)	2 344(13)	2 177(9)	2 115(8)
O(1)	2 475(10)	7 374(8)	3 381(6)	N(9)	3 749(12)	1 880(10)	604(8)
O(2)	344(10)	8 686(8)	4 086(7)	C(21)	2 449(20)	3 672(15)	1 852(12)
O(3)	1 525(10)	7 242(8)	4 843(6)	C(22)	2 129(22)	3 031(16)	2 372(13)
O(4)	1 787(11)	9 239(8)	3 542(8)	C(23)	3 621(18)	1 606(14)	1 927(11)
O(5)	2 693(12)	8 048(9)	4 676(7)	C(24)	4 147(20)	1 319(15)	1 193(12)
C(51)	2 189(19)	7 580(14)	5 037(11)	C(25)	4 220(21)	2 578(16)	448(14)
C(52)	2 258(18)	7 326(13)	5 829(11)	C(26)	3 348(19)	3 480(14)	536(12)
C(53)	792(19)	9 303(14)	3 859(11)	C(27)	1 360(21)	4 453(16)	982(13)
C(54)	−183(22)	10 258(17)	3 975(13)	C(28)	1 655(18)	1 693(14)	2 651(11)
N(1)	4 167(12)	9 012(10)	3 820(8)	C(29)	4 072(19)	1 340(14)	−35(12)
N(2)	5 079(13)	7 182(11)	3 536(9)	N(10)	−1 933(12)	2 323(10)	1 896(8)
N(3)	4 215(13)	8 374(11)	2 464(8)	N(11)	−2 230(13)	3 944(9)	1 178(8)
C(1)	5 097(24)	8 447(18)	4 129(14)	N(12)	−2 071(12)	2 475(8)	474(7)
C(2)	5 742(21)	7 606(16)	3 852(13)	C(41)	−2 581(17)	3 154(12)	2 345(10)
C(3)	5 556(22)	6 930(16)	2 807(13)	C(42)	−3 113(15)	3 912(12)	1 894(9)
C(4)	5 343(22)	7 629(16)	2 254(13)	C(43)	−2 782(18)	4 068(13)	552(10)
C(5)	4 341(22)	9 215(16)	2 493(13)	C(44)	−3 100(15)	3 276(11)	479(10)
C(6)	4 626(24)	9 362(18)	3 133(14)	C(45)	−2 421(18)	1 791(13)	940(10)
C(7)	3 352(24)	9 754(18)	4 327(14)	C(46)	−2 849(15)	2 028(12)	1 704(9)
C(8)	4 990(23)	6 375(18)	3 976(14)	C(47)	−1 181(17)	1 602(13)	2 316(10)
C(9)	3 474(20)	8 427(15)	1 936(12)	C(48)	−1 755(17)	4 677(13)	1 128(10)
N(4)	−625(12)	7 449(10)	4 653(8)	C(49)	−1 436(16)	2 125(12)	−297(10)
N(5)	1 407(14)	6 107(11)	3 930(9)	Cl(1)	7 723(6)	9 385(4)	1 646(4)
N(6)	261(15)	7 534(13)	3 173(10)	O(11)	7 721(14)	8 643(11)	2 076(9)
C(11)	−498(24)	6 556(17)	4 816(15)	O(12)	6 915(28)	10 090(21)	2 009(17)
C(12)	593(23)	5 866(17)	4 549(14)	O(13)	8 804(23)	9 476(16)	1 348(13)
C(13)	1 190(24)	5 952(18)	3 250(14)	O(14)	7 114(36)	9 588(27)	1 164(23)
C(14)	766(27)	6 670(20)	2 854(16)	Cl(2)	8 729(6)	4 854(5)	3 256(4)
C(15)	−1 096(21)	7 743(16)	3 475(13)	O(21)	9 715(24)	4 444(17)	3 572(14)
C(16)	−1 508(21)	7 908(16)	4 242(12)	O(22)	7 961(40)	5 148(29)	3 809(25)
C(17)	−989(19)	7 989(14)	5 344(11)	O(23)	8 932(26)	5 485(20)	2 757(17)
C(18)	2 677(21)	5 554(16)	3 947(13)	O(24)	8 814(29)	4 212(22)	2 835(19)
C(19)	486(22)	8 229(17)	2 597(14)	Cl(3)	3 989(6)	5 803(5)	1 406(4)
Co(3)	1 807(2)	2 461(2)	1 089(1)	O(31)	4 011(18)	5 865(13)	2 133(12)
Co(4)	—1 010(2)	2 720(2)	987(1)	O(32)	4 858(21)	6 089(15)	1 005(12)
O(6)	−59(9)	2 947(7)	1 487(6)	O(33)	2 879(24)	6 244(17)	1 341(13)
O(7)	−293(10)	3 154(8)	71(6)	O(34)	4 353(23)	4 950(18)	1 234(14)
O(8)	−1(10)	1 530(7)	763(6)	Cl(4)	4 394(6)	2 542(5)	3 727(4)
O(9)	1 670(11)	2 740(9)	30(6)	O(41)	3 563(32)	3 063(24)	4 236(20)
O(10)	1 727(10)	1 223(8)	1 044(7)	O(42)	4 486(22)	3 004(16)	3 112(14)
C(55)	784(20)	3 038(13)	−242(11)	O(43)	4 025(28)	1 859(21)	3 625(17)
C(56)	1 032(16)	3 287(12)	−1 047(10)	O(44)	5 526(27)	2 144(19)	3 833(16)
C(57)	1 014(15)	1 010(11)	818(9)	O_w	6 964(22)	209(16)	3 621(14)
C(58)	1 343(17)	47(13)	630(11)				

trum of (**9**) which contains a $Co^{III}{}_2(\mu\text{-}OH)(\mu\text{-carboxylato})_2{}^{3+}$ core. The latter spectrum is very similar to those reported by Siebert and Tremmel[21] for binuclear $[(NH_3)_3Co^{III}(\mu\text{-carboxylato})_2(\mu\text{-}OH)Co^{III}(NH_3)]^{3+}$ species. It consists of one *d–d* band at 559 nm ($^1A_{1g} \longrightarrow {}^1T_{1g}$ in O_h symmetry) and a shoulder at 390 nm which is assigned to the second *d–d* transition ($^1A_{1g} \longrightarrow {}^1T_{2g}$); below 350 nm a sharp increase in absorbance is characteristic for binuclear complexes of cobalt(III) containing an OH bridge. The monomeric complex (**10**) does not exhibit this band but two *d–d* transitions in the visible region (Table 5).

The electronic spectra of complexes (**1**)—(**6**) are typical for octahedral high-spin cobalt(II). Two *d–d* transitions of moderate intensity ($\varepsilon < 30$ dm^3 mol^{-1} cm^{-1} per dimer) are observed which are assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ in the near-i.r. region and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ at higher energy. The latter bands have a complex envelope because a number of transitions to doublet excited states occur in the same region.[24] These spectra are very similar to that reported for *e.g.* $[Co(NH_3)_6]^{2+}$.[25]

Figure 4 shows the electronic spectrum of the mixed-valence complex (**7**); that of (**8**) is very similar (Table 5). Interestingly, these spectra display an absorption maximum in the near-i.r. of low intensity and a stronger band in the visible region at ≈555 nm. The former is typical for octahedral cobalt(II) and the latter is the low-energy *d–d* transition of octahedral cobalt(III). Thus in the region 450—1200 nm the spectrum of (**7**) is nearly a superposition of those of (**1**) and (**9**). This clearly indicates that the valences in (**7**) and (**8**) are localized.

The susceptibilities of powdered samples of new complexes were measured in the temperature range 98—293 K by use of the Faraday method. The results are given in Table 6. The magnetic moments per cobalt(II) centre in the binuclear compounds (**1**)—(**6**) range from 5.23 at 293 K to 4.70 at 98 K. These values are typical for octahedral high-spin cobalt(II) with a significant orbital contribution from the intrinsic orbital angular momentum in the octahedral ground state. A slight decrease of these magnetic moments with decreasing temperature may be indicative of a small intramolecular antiferromagnetic coupling of the two high-spin d^7 cobalt(II) ions. This effect is significantly stronger in binuclear μ-carboxylato cobalt(II) complexes of type (**A**)[8,9] but comparable with

Turpeinen's complex of type (**B**).[10] Interestingly, the magnetic moments of the mixed-valence compounds (**7**) and (**8**) of 4.62 and 4.89 per binuclear unit are temperature-independent in the range 98—293 K and in agreement with one high-spin cobalt(II) ion per binuclear unit. Complexes (**9**) and (**10**) are diamagnetic (low-spin Co^{III}).

Electrochemistry.—Cyclic voltammograms (c.v.s) of binuclear complexes (**1**)—(**8**) have been recorded in acetonitrile in the potential range -0.6 to $+0.6$ V *vs.* ferrocenium–ferrocene. The results are summarized in Table 6. For all complexes, except (**3**) a reversible one-electron transfer wave at cathodic potentials and one quasi-reversible one-electron transfer wave at more anodic potentials have been detected. These waves correspond to two successive one-electron oxidation processes of the binuclear species (**1**), (**2**), and (**4**)—(**6**) according to equation (3).

$$\{Co^{II}{}_2\}^+ \underset{E_{\frac{1}{2}}{}^1}{\rightleftharpoons} \{Co^{II}Co^{III}\}^{2+} \underset{E_{\frac{1}{2}}{}^2}{\rightleftharpoons} \{Co^{III}{}_2\}^{3+} \quad (3)$$

Table 4. Selected bond distances (Å) and angles (°) for one dication in crystals of complex (**7**)

Co(1)–O(1)	2.035(12)	Co(2)–O(1)	1.904(11)
Co(1)–O(4)	2.081(13)	Co(2)–O(2)	1.931(12)
Co(1)–O(5)	2.053(14)	Co(2)–O(3)	1.897(11)
Co(1)–N(1)	2.182(15)	Co(2)–N(4)	2.028(14)
Co(1)–N(2)	2.180(16)	Co(2)–N(5)	2.002(16)
Co(1)–N(3)	2.170(14)	Co(2)–N(6)	1.958(18)
O(2)–C(53)	1.304(25)	O(5)–C(51)	1.210(26)
O(3)–C(51)	1.291(25)	C(51)–C(52)	1.546(29)
O(4)–C(53)	1.195(25)	C(53)–C(54)	1.576(33)
Co(1) • • • Co(2)	3.435(4)		
O(1)–Co(1)–O(4)	88.0(7)	O(1)–Co(2)–O(2)	94.3(7)
O(1)–Co(1)–N(3)	99.9(7)	O(1)–Co(2)–N(6)	93.5(9)
O(4)–Co(1)–N(3)	92.5(8)	O(2)–Co(2)–N(6)	89.1(9)
N(1)–Co(1)–N(2)	80.6(8)	N(4)–Co(2)–N(5)	87.3(9)
O(1)–Co(1)–O(5)	91.1(7)	O(1)–Co(2)–O(3)	92.4(7)
O(4)–Co(1)–O(5)	90.7(8)	O(2)–Co(2)–O(3)	93.4(8)
O(5)–Co(1)–N(1)	86.8(7)	O(3)–Co(2)–N(4)	86.9(7)
N(1)–Co(1)–N(3)	82.3(8)	N(4)–Co(2)–N(6)	87.3(10)
O(1)–Co(1)–N(1)	178.1(14)	O(1)–Co(2)–N(4)	180.0(15)
O(4)–Co(1)–N(1)	91.1(7)	O(2)–Co(2)–N(4)	86.1(7)
O(5)–Co(1)–N(2)	93.9(8)	O(3)–Co(2)–N(5)	88.8(8)
N(2)–Co(1)–N(3)	81.3(8)	N(5)–Co(2)–N(6)	88.1(10)
O(1)–Co(1)–N(2)	100.5(8)	O(1)–Co(2)–N(5)	92.3(8)
O(4)–Co(1)–N(2)	170.2(7)	O(2)–Co(2)–N(5)	173.0(10)
O(5)–Co(1)–N(3)	168.6(6)	O(3)–Co(2)–N(6)	173.5(11)
Co(1)–O(1)–Co(2)	121.3(2)	Co(1)–O(4)–C(53)	125.8(2)
Co(2)–O(2)–C(53)	133.9(2)	Co(1)–O(5)–C(51)	131.9(2)
Co(2)–O(3)–C(51)	130.5(2)	O(3)–C(51)–C(52)	111.0(2)
O(3)–C(51)–O(5)	127.0(2)	O(5)–C(51)–C(52)	121.9(2)
O(2)–C(53)–O(4)	129.6(2)	O(2)–C(53)–C(54)	112.6(2)
O(4)–C(53)–C(54)	117.6(2)		

Bond lengths and angles for the crystallographically independent second dication are quite similar and are not tabulated.

The c.v. of (**1**) [Figure 5 (*a*)], was found to be identical with those measured for (**7**) and (**9**) which nicely corroborates the above assignment. Thus the binuclear cobalt(II) species forms the cobalt(III) analogue *via* the mixed-valence cobalt(II, III) form and *vice versa*. Figure 5(*b*) displays the c.v. of (**8**) which is again identical with that of (**2**). Substitution of the acetato bridges in (**1**) by two chloroacetato bridges as in (**8**) affects the redox potentials $E_{\frac{1}{2}}{}^1$ and $E_{\frac{1}{2}}{}^2$ only marginally [Figure 5(*b*)]. The large differences between $E_{\frac{1}{2}}{}^1$ and $E_{\frac{1}{2}}{}^2$ of 0.5 V for (**1**) and 0.425 V for (**2**) are remarkable because they indicate a substantial stabilization of the respective mixed-valence cobalt(II, III) species. According to equation (4) a comproportionation constant at 25 °C, K_C, of 3×10^8 for complexes (**1**) and (**9**) yielding (**7**), and 2×10^7 for (**2**) and its cobalt(III) form affording (**8**) may be calculated from the difference $(E_{\frac{1}{2}}{}^1 - E_{\frac{1}{2}}{}^2)$.

$$Co^{II}{}_2 + Co^{III}{}_2 \rightleftharpoons 2[Co^{II}Co^{III}] \quad (4)$$

$$K_C = \exp[(E_{\frac{1}{2}}{}^1 - E_{\frac{1}{2}}{}^2)F/RT]$$

Considering the fact that the valences in the mixed-valence forms are trapped the origin of this large stabilization remains unclear at present.

Figure 6 shows the c.v.s of complexes (**4**)—(**6**) in acetonitrile at 20 °C. These chloro- and bromo-bridged complexes exhibit also a reversible and a quasi-reversible one-electron transfer wave, respectively. In contrast to the OH-bridged compound discussed above the difference $(E_{\frac{1}{2}}{}^1 - E_{\frac{1}{2}}{}^2)$ is considerably smaller; a decrease in the order μ-OH > μ-Cl > μ-Br is observed. Consequently, the comproportionation constants for the systems of (**4**)—(**6**) are calculated to be 1.5×10^4, 2.0×10^4, and 2.5×10^3, respectively.

Experimental

The macrocycle *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L $C_9H_{21}N_3$) was prepared as described previously.[26] Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer (250—1400 nm). Temperature-dependent susceptibilities (98—298 K) of powdered samples were measured by the Faraday method (Sartorius microbalance, a Bruker research magnet B-E 1088, and B-VT-1000 automatic temperature control). Diamagnetic corrections were applied in the usual

Table 5. Electronic and i.r. spectroscopic data for the complexes

		I.r.[b]/cm^{-1}		
Complex	$\lambda_{max.}$/nm (ε dm^3 mol^{-1} cm^{-1})[a]	ν(O–H)	ν_{asym}(C–O)	ν_{sym}(C–O)
(**1**)	1 160(9); 490(23)[c]	3 600	1 603	1 410
(**2**)	1 125(10); 488(23)[c]	3 600	1 612	1 408
(**3**)	1 096(13.5); 481(18)[c]	3 600	1 679	1 381
(**4**)	1 160(9); 506(25)[c]	—	1 612	1 418
(**5**)	1 155(11); 504(21)[c]	—	1 649	1 408
(**6**)	1 000(8); 494(28)[c]	—	1 616	1 418
(**7**)	1 040(18); 560(290); 371(937)	3 580	1 605	1 410
(**8**)	1 040(18); 570(270); 394(866), 248(2.1 × 10^4)	3 600	1 630	1 380
(**9**)	559(151); 390(sh)	3 580	1 588	1 418
(**10**)	586(229); 384(176)		1 620, 1 590	1400, 1500

[a] Molar absorption coefficients are given per dimer; solvent acetonitrile. [b] Potassium bromide discs. [c] This band has a complex envelope (see text).

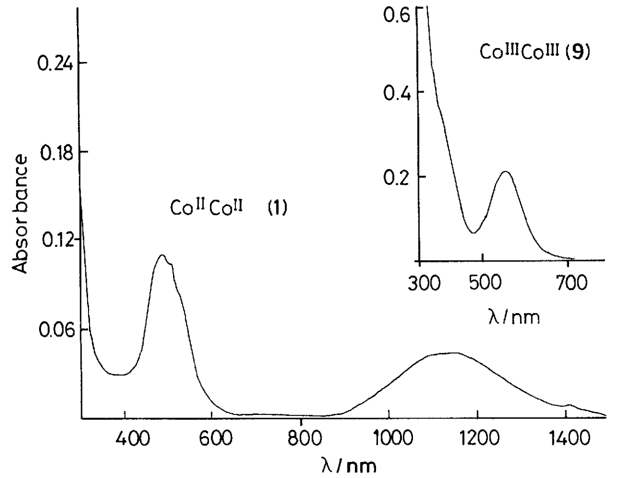


Figure 3. Electronic spectra of complex (**1**) in the visible and near-i.r. region {in MeCN; [(**1**)] = 5.1 × 10^{-3} mol dm^{-3}, 1-cm cell} and of (**9**) (inset) {in MeCN; [(**9**)] = 6.9 × 10^{-4} mol dm^{-3}; 2-cm cell}

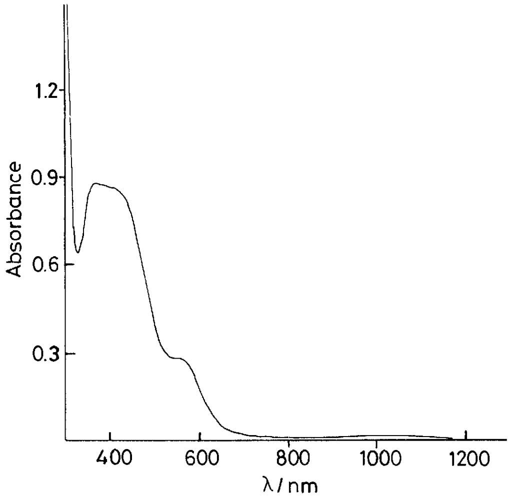


Figure 4. Electronic spectrum of the mixed-valence species (**7**) {in MeCN, [(**7**)] = 4.7 × 10^{-4} mol dm^{-3}; 2-cm cell}

Table 6. Electrochemical and magnetic data for the complexes

Complex	$E_{\frac{1}{2}}^{1a}$ (V)	$E_{\frac{1}{2}}^{2a}$ (V)	$\mu_{eff.}$
(**1**)	−0.335 (r)	+0.165 (qr)	5.13 (98—293 K)[b]
(**2**)	−0.32 (r)	+0.105 (qr)	5.04 (98—293 K)[b]
(**3**)	—	—[c]	4.70 (118 K), 4.90 (293 K)[b]
(**4**)	−0.125 (r)	+0.12 (qr)	4.94 (118 K), 5.08 (293 K)[b]
(**5**)	−0.015 (r)	+0.235 (qr)	4.99 (118 K), 5.10 (293 K)[b]
(**6**)	−0.05 (r)	+0.15 (qr)	4.89 (118 K), 5.03 (293 K)[b]
(**7**)	−0.335 (r)	+0.165 (qr)	4.62 (100—298 K)[d]
(**8**)	−0.32 (r)	+0.105 (qr)	4.89 (100—298 K)[d]
(**9**)	−0.335 (r)	+0.165 (qr)	Diamagnetic
(**10**)	—	—	Diamagnetic

[a] Potentials at scan rates 100 mV s^{-1} in acetonitrile (0.1 mol dm^{-3} $NBu^t_4PF_6$ are referenced *versus* the ferrocenium–ferrocene couple and were measured at a gold electrode; r = reversible; qr = quasi-reversible. [b] Effective magnetic moment per Co^{II}. [c] Sample decomposed in acetonitrile. [d] Effective magnetic moment per dimer.

manner with Pascal's constants. Electrochemical measurements were performed with a Princeton Applied Research model 175 programmer, 173 potentiostat, and 179 digital coulometer and a Kipp & Zonen XY recorder on acetonitrile solutions 0.1 mol

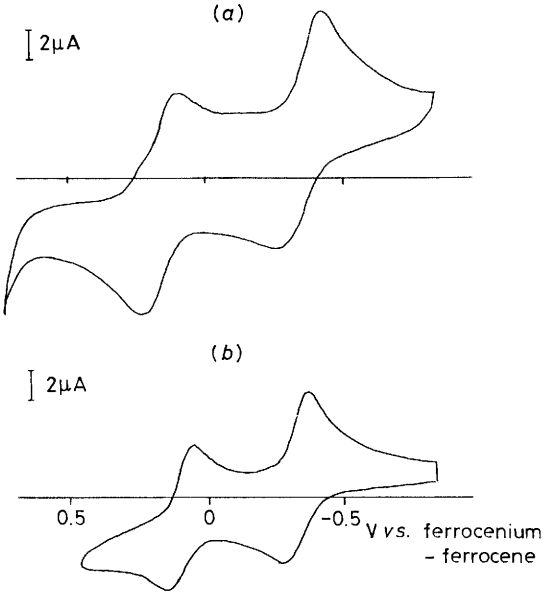


Figure 5. Cyclic voltammograms of (*a*) complex (**1**) in MeCN [c.v.s of (**7**) and (**9**) are identical] and (*b*) (**8**) in MeCN [c.v. of (**2**) is again identical]. Experimental conditions: scan rate 100 mV s^{-1}; supporting electrolyte, 0.1 mol dm^{-3} $NBu^t_4PF_6$; working electrode; Au; [complex] = 10^{-3} mol dm^{-3}; temperature 20 °C

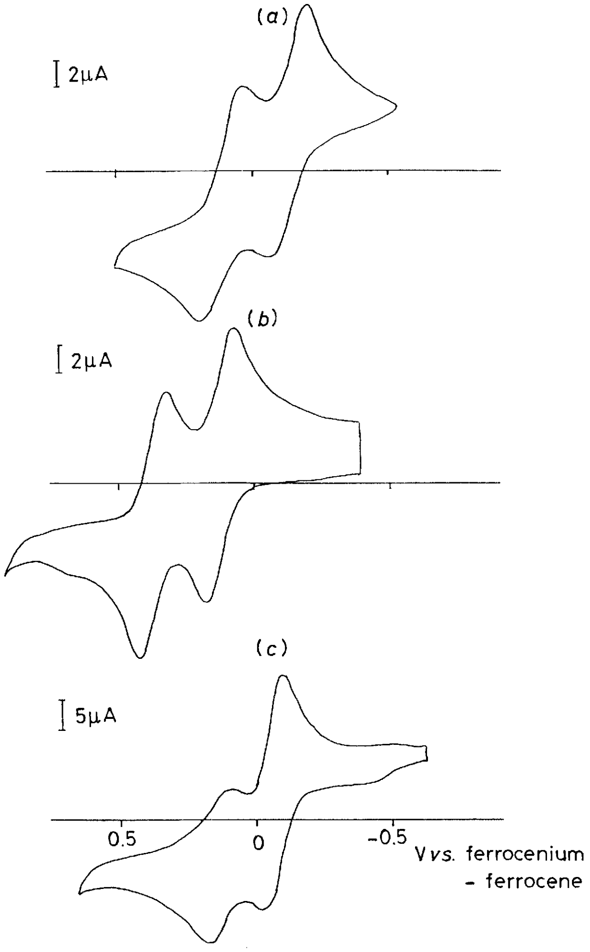


Figure 6. Cyclic voltammograms of (*a*) complex (**4**), (*b*) (**5**), and (*c*) (**6**) in MeCN. Conditions as in Figure 5

Table 7. Crystallographic data[a] for $[Co_2(\mu\text{-}ClCH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$ (**5**), and $[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_2\cdot 0.5H_2O$ (**7**)

Complex	(**5**)	(**7**)
Formula	$C_{22}H_{48}ClCo_2F_6N_6O_4P$	$C_{22}H_{50}Cl_2Co_2N_6O_{13.5}$
M	758.95	803.4
Colour	Red-purple	Red-brown
Crystal dimensions/mm	0.23 × 0.23 × 0.69	0.25 × 0.30 × 0.45
Diffractometer	Syntex R3	AED II (Siemens)
Space group	$Pnam$ (D_{2h}^{16}, no. 62)	$P\bar{1}$ (C_i^1, no. 2)
Crystal system	Orthorhombic	Triclinic
a/Å	13.043(2)	12.479(8)
b/Å	14.824(2)	16.27(1)
c/Å	17.827(3)	19.11(2)
α/°	—	84.40(6)
β/°	—	74.13(6)
γ/°	—	68.60(5)
U/Å^3	3 446.8	3 474.5
D_c/g cm^{-3}	1.46	1.54
μ(Mo-K_α)/cm^{-1}	11.0	11.2
2θ range/°	$3 < 2\theta < 65$	$3 < 2\theta < 50$
Scan method	θ—2θ	ω
Total data collected	1 991	5 745
Independent data [$I > 2.5\,\sigma(I)$]	1 897	5 604
Total variables	223	515
R^b	0.063	0.12
R'^b	0.056	0.11

[a] Details in common: $Z = 4$; Mo-K_α radiation ($\lambda = 0.710\,73$ Å). [b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ with weights $w = \sigma_F^{-2}$.

dm^{-3} in $NBu^n_4PF_6$. A standard three-electrode cell was employed with a gold working electrode, a platinum-wire auxiliary electrode, and an Ag–AgCl (saturated LiCl, C_2H_5OH) reference electrode. Potentials are *versus* the ferrocenium–ferrocene couple as internal standard.[27] Cyclic voltammograms were recorded at scan rates from 20 to 200 mV s^{-1}; the concentration of the electroactive component was ≈ 10^{-3} mol dm^{-3}.

Elemental microanalyses (C, H, and N) were performed at the Mikroanalytisches Laboratorium Beller, Göttingen, Germany. All new compounds gave satisfactory elemental analysis (C, H, N, Co, Cl, and Br).

Preparation of Complexes.—All manipulations for synthesizing binuclear cobalt(II) complexes were carried out under an argon blanketing atmosphere; the solvents were degassed prior to use.

$[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2]PF_6$ (**1**). To a solution of cobalt(II) acetate tetrahydrate (2 mmol) in methanol (10 cm^3) was added the macrocycle L (2 mmol) dissolved in methanol (5 cm^3) with stirring at room temperature. The purple colour of the solution changed to red within 10 min, after which time a solution of sodium hexafluorophosphate (1 mmol) in methanol (5 cm^3) was added. Upon reduction of the solvent volume red microcrystals precipitated which were filtered off and recrystallized from methanol or acetone (0.42 g, 28%).

$[Co_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}OH)L_2]PF_6$ (**2**) *and* $[Co_2(\mu\text{-}Cl_2HCCO_2)_2(\mu\text{-}OH)L_2]PF_6$ (**3**). Commercially available ClH_2CCO_2H and Cl_2HCCO_2H react with $CoCO_3)\cdot xH_2O$ by forming the corresponding salts $Co(ClH_2CCO_2)_2\cdot xH_2O$ and $Co(Cl_2HCCO_2)_2\cdot xH_2O$.[28] These materials were always found to be contaminated with chloride which was removed by the following procedure. The crude cobalt(II) salt (0.6 g) was dissolved in water (10 cm^3) and the chloride ions were titrated with 0.1 mol dm^{-3} $AgNO_3$. Silver chloride was then filtered off and the solvent was removed by evaporation under reduced pressure. The purified cobalt(II) acetate salts were used for the preparation of complexes (**2**) and (**3**) following the procedure described above for (**1**). Red microcrystals were obtained which were recrystallized from methanol. The yields varied between 30 and 40%.

$[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}Cl)L_2]PF_6$ (**4**). To a solution of dehydrated $Co(MeCO_2)_2$ (2 mmol) in dry methanol (50 cm^3) was added sodium chloride (0.10 g) and the macrocycle L (2 mmol). The solution was refluxed for 12 h after which time a solution of $NaPF_6$ (1 mmol) in methanol (10 cm^3) was added. Upon reduction of the solvent volume red-purple microcrystals precipitated which were filtered off and recrystallized from hot methanol (0.84 g, 55%).

$[Co_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}Cl)L_2]PF_6$ (**5**). This complex was prepared as described for (**4**). Dehydrated, purified $Co(ClH_2CCO_2)_2$ was used as starting material. Red-purple crystals (0.51 g, 31%).

$[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}Br)L_2]PF_6$ (**6**). This complex was prepared as described above for (**4**) by using dehydrated $Co(MeCO_2)_2$ and NaBr as starting materials. Red-purple crystals (0.80 g, 46%).

$[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][PF_6]_2$ (**7**). To a solution of $Co(MeCO_2)_2\cdot 4H_2O$ (2 mmol) in methanol (5 cm^3) was added a solution of L (2 mmol) dissolved in methanol (5 cm^3) in the presence of air at 20 °C. The colour of the solution turned red-brown within 5 min, after which time solid $NaPF_6$ (2 mmol) was added. Upon reduction of the solvent volume in the presence of air deep brown crystals precipitated which were filtered off and recrystallized from methanol (0.63 g, 36%). The perchlorate salt was prepared by the above procedure but $NaClO_4\cdot H_2O$ (1 g) was added instead of $NaPF_6$. Single crystals suitable for *X*-ray crystallography were grown from a methanol solution.

$[Co_2(\mu\text{-}ClH_2CCO_2)_2(\mu\text{-}OH)L_2][PF_6]_2$ (**8**). This complex was prepared as described above for (**7**) by using $Co(ClH_2CCO_2)_2\cdot xH_2O$ as starting material. Deep brown crystals were obtained which were recrystallized from an acetone–acetonitrile mixture (1:1) (0.70 g, 36%).

$[Co_2(\mu\text{-}MeCO_2)_2(\mu\text{-}OH)L_2][ClO_4]_3$ (**9**). To a solution of $Co(ClO_4)_2\cdot 6H_2O$ (4 mmol) in water–glacial acetic acid (5:1) (30 cm^3) was added the ligand L (4 mmol). Peroxyacetic acid (30%, 1.4 g) was added dropwise with stirring at 20 °C. The then brown solution was refluxed for 30 min during which time the colour changed to red-purple. The solution was cooled to 0 °C for 2—3 d. Red-purple crystals precipitated (0.42 g, 12%).

$[Co(MeCO_2)_2L]PF_6$ (**10**). If the above synthesis for complex (**9**) was carried out by using $Co(MeCO_2)_2 \cdot 4H_2O$ as starting material under otherwise identical conditions blue-violet crystals of (**10**) precipitated (1.42 g, 70%).

X-Ray Crystallography.—Crystal data and details of intensity collection for complexes (**5**) and (**7**) are summarized in Table 7. Graphite-monochromated Mo-K_α radiation was used throughout. Crystal stabilities were monitored by recording three check reflections; no deterioration was observed, respectively. The two data sets were corrected for Lorentz and polarization effects, and were also corrected for absorption (ψ scans). The structures were solved by conventional Patterson and Fourier-difference syntheses. Both structures were refined by least-squares techniques; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(I)$.[29] Neutral atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 30 and hydrogen-atom scattering factors from ref. 31. The positions of the methylene and methyl protons were calculated and included in the final refinement cycle with isotropic thermal parameters. Some special features of the crystal structure determinations of (**5**) and (**7**) are discussed below.

All non-hydrogen atoms of complex (**5**) were refined with anisotropic thermal parameters. Attempts to refine the structure in the acentric space group $Pna2_1$ failed; no convergence was obtained. Attempts to model the disorder of the methylene groups by a split-atom model failed. The disorder is borne out by physically meaningless large anisotropic thermal parameters. Crystals of (**7**) were of low *X*-ray quality, despite many efforts to grow more suitable single crystals. In order to keep the ratio of the number of observed reflections to the number of parameters reasonable, the carbon atoms, and the oxygen atoms of the ClO_4^- anions, were refined with isotropic thermal parameters only. The ClO_4^- anions are severely disordered and, consequently, the final convergence factor of $R = 0.12$ is rather poor.

Acknowledgements

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