Preparation and Characterization of Polynuclear Cobalt(III) Complexes with Bridging Carboxylato-ligands

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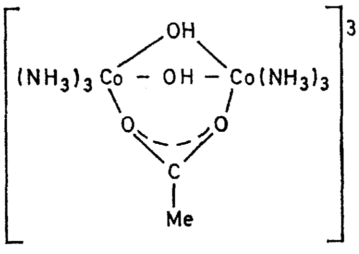
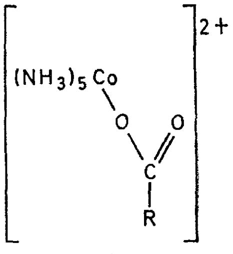
Binuclear, trinuclear, and tetranuclear cobalt(III)–ammine complexes containing a variety of organic carboxylato-ligands have been prepared from the parent complex tri-μ-hydroxo-bis[triamminecobalt(III)]$^{3+}$ and characterized A hexanuclear complex with a 9+ charge is described. Elemental analysis, u.v.–visible and i.r. spectra are reported.

SEVERAL binuclear di-μ-hydroxo-bis[triamminecobalt(III)] complexes with a carboxylato-bridging group have been described previously.[1-3] I.r. data [2] and an X-ray analysis [4] of the μ-acetato-complex indicate that the carboxylato-group is bonded as in (a). As an extension of the work this paper deals with the preparation and characterization of bi-, tri-, and tetra-nuclear cobalt(III) complexes with a variety of carboxylic acids as bridging ligands.

This type of complex is of interest for studies on electron-transfer reactions through organic structural units. Taube and Gould [5] have shown for a series of penta-amminecobalt(III) carboxylato-complexes (b) that the reduction of the Co^{III} atom with $[Cr(H_2O)_6]^{2+}$ by an inner-sphere mechanism can proceed *via* adjacent attack at one of the oxygen atoms of the carboxylate group. Scott and Sykes have shown [6] that this pathway



(a)



(b)

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[1] A. Werner, *Liebigs Ann. Chem.*, 1910, **375**, 1.

[2] H. Siebert and G. Tremmel, *Z. anorg. Chem.*, 1972, **390**, 292.

[3] K. Wieghardt, *Z. anorg. Chem.*, 1972, **391**, 142.

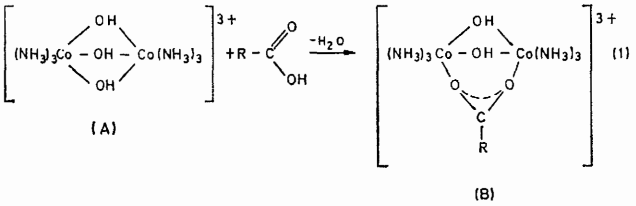
[4] B. C. Wang, W. P. Schaefer, and R. E. Marsh, unpublished work (1969) quoted from A. G. Sykes and J. A. Weil, 'Inorganic Reaction Mechanisms,' John Wiley, 1970, p. 80.

[5] H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

[6] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

is not effective when both oxygen atoms of the carboxylate group are attached to two cobalt(III) atoms because these oxygen atoms are no longer available for co-ordination with the reducing agent Cr^{2+}. This behaviour has been further substantiated in more recent work.[7] Binuclear complexes are therefore ideally suited to the study of electron-transfer reactions of this type, for if the introduction of a second functional group leads to an inner-sphere path, then the mechanism can be automatically assigned as remote attack at the second functional group. The complexes described here have been synthesised specifically for this purpose.

Synthesis of the Complexes.—These are obtained from tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate (A) which reacts in acidic aqueous solutions readily with many organic carboxylic acids:

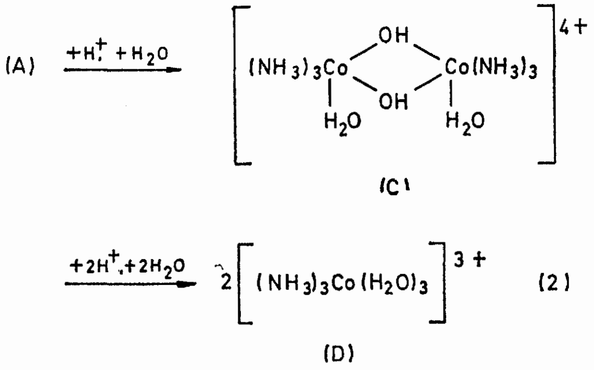


A modified method described by Siebert and Tremmel has been used.[2] To a solution of carboxylic acid (10^{-2} mol) in 0·5M perchloric acid (40 ml) at 45 °C tri-μ-hydroxo-bis-[triamminecobalt(III)] perchlorate bishydrate ($1·1 \times 10^{-2}$ mol) was added in small amounts with stirring. [The complex (A) was kept in slight excess of monocarboxylic ligand because the formation of hydroxo-bridge cleavage products (C) and (D) reduces the yield. In the case of dicarboxylic acids the ligand was taken in excess (20%) of complex (A) to avoid formation of tetranuclear complexes.] The temperature was raised to 65 °C and maintained for 10—15 min. Solid sodium perchlorate monohydrate and 10M-perchloric acid (2 ml) were added to the cooled (20 °C) and filtered solution, which was then kept at 0 °C for a few hours. Red crystals were collected and washed with absolute ethanol and ether. The yields varied according to the solubility of the free organic ligand in water and of the final product between 30—90%.

Complexes have been prepared by the above procedure where RCO_2 of complex (B) is benzoate (I), *o*-fluorobenzoate (II), *o*-chlorobenzoate (III), salicylate (IV), *o*-phthalate (V), *o*-formylbenzoate (VI), *p*-formylbenzoate (VII), *p*-cyanobenzoate (VIII), 2-pyridinecarboxylate (IX), 3-pyridinecarboxylate (X), 4-pyridinecarboxylate (XI), malonate (XII), maleate (XIII).

The reaction (1) does not appear to be affected by the varying basicity of the carboxylate groups. The μ-trifluoroacetato-complex [2] and the μ-benzoato-complex of (B) are obtained in good yields using the above method despite the different dissociation constants of the free acids (0·23 and $6·25 \times 10^{-5}$ mol l^{-1} for the latter at 25 °C [8]). It is rather the solubility of the free organic ligand in water which limits the application of the method. The insoluble terephthalic acid did not react under these conditions. However, the slightly soluble benzoic acid and the even less soluble *p*-cyanobenzoic acid and the *p*-formylbenzoic acid did react. The desired products were obtained when the free acids (10^{-2} mol) were dissolved in 200 ml of 0·5M-perchloric acid at 95 °C. Then the starting complex (A) was added ($1·1 \times 10^{-2}$ mol) and the temperature was maintained at 90 °C for 10 min. The solution was cooled to 15 °C and the unreacted free carboxylic acid was allowed to precipitate and then filtered off.

To purify the crude products two methods were applied taking into account contamination by free organic ligand and hydroxo-bridge cleavage products of the complex (A):



Recrystallization from aqueous solutions with solid sodium perchlorate and concentrated perchloric acid is sufficient to separate the desired products from inorganic impurities, since the perchlorate salts of both (C) and (D) are extremely soluble in aqueous perchlorate solution.[9] Contamination from organic ligand appeared to be insignificant when twice recrystallized from aqueous solution. However, complexes with aromatic carboxylic ligands (if they were soluble in methanol) were recrystallized once from methanol by adding small amounts of diethyl ether and finally from water with $NaClO_4$ and perchloric acid. Elemental analyses indicate no appreciable amount of free ligand.

Dicarboxylic acids react with tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate (ratio 1 : 2) to give tetranuclear complexes where four Co^{III} atoms are attached to two carboxylate groups. The identical products are formed when the binuclear complex with a free carboxylate group is reacted with (A) (ratio 1 : 1). This has been shown previously for oxalic acid and a variety of μ-hydroxo-binuclear Co^{III} complexes.[10] In the case of maleic and *o*-phthalic acid it has not been possible to

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[7] K. Wieghardt and A. G. Sykes, *J.C.S. Dalton*, submitted for publication.

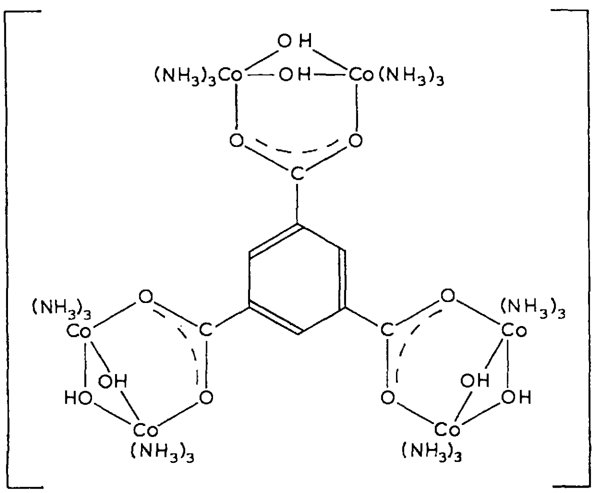
[8] The values for all dissociation constants were taken from: G. Kortüm, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solutions,' Butterworths, London, 1961.

[9] M. Linhard and H. Siebert, *Z. anorg. Chem.*, 1969, **364**, 24.

[10] K. L. Scott, K. Wieghardt, and A. G. Sykes, *Inorg. Chem.*, 1973, **12**, 655.

obtain tetranuclear complexes, whereas fumaric acid readily formed complex (XVII). It would appear that steric hindrance of the carboxylate groups seems to be the important factor for the non-formation of tetranuclear complexes. The versatility of the reaction can be demonstrated by reacting 1,3,5-benzenetricarboxylic acid with (A) (ratio 1 : 3) to form a hexanuclear complex (XIV) with a high charge of 9+.

Dicarboxylatopenta-amminecobalt(III) complexes react easily with complex (A). The products are highly unsymmetrical trinuclear complexes where the two carboxylate groups are bonded in two different fashions to three $\mathrm{Co^{III}}$ atoms. An example of this reaction is the formation of (XVI) by reaction of fumaratopenta-aminecobalt(III) perchlorate[11] with (A).

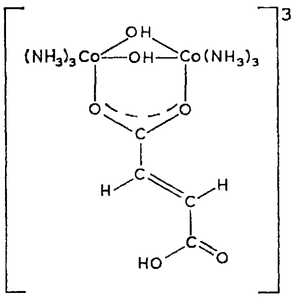


(XIV)

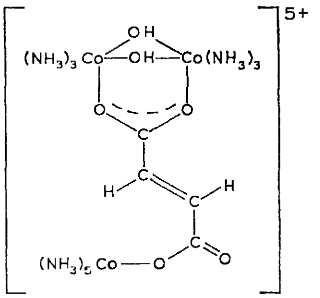
Properties of the μ-Carboxylato-complexes.—Warning. Although solid perchlorate salts of the organocobalt(III) complexes are all very stable at room temperature, decomposition with **explosion** sometimes occurs when they are heated above 60 °C.

Aqueous solutions ($0{\cdot}01\mathrm{M}$-$\mathrm{HClO_4}$) are stable at 45 °C for at least 48 h. In neutral and especially in basic solution the complexes decompose precipitating $\mathrm{Co(OH)_3}$ (aq). The perchlorate salts form well defined pink-red crystals. It would appear that complexes with unsymmetrical organic ligands tend to crystallize with varying amounts of $\mathrm{NaClO_4}$, forming double salts [*e.g.* (IXa), (Xa), (XII), (XVI), (XVII)]. The binuclear complexes with a dicarboxylic ligand crystallize more readily in their protonated forms. The unprotonated forms are very soluble and were not isolated as solids. The three isomeric μ-pyridinecarboxylato-complexes which in addition have a basic nitrogen atom were isolated in the protonated (IX)—(XI) and unprotonated (IXa)—(XIa) form respectively. Again the unprotonated forms show a much higher solubility in water, methanol, and ethanol.

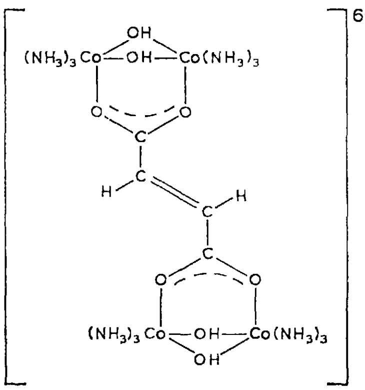
Infrared Spectra.—Details of the antisymmetric and symmetric ν(CO) stretching frequencies of the bridging carboxylate groups are listed in Table 1. Siebert and Tremmel have shown[2] that the carboxylate group is bonded to two Co atoms *via* two oxygen atoms by comparison of the easily detectable ν_{as}(CO) stretching frequency of the binuclear species (f) with the monomeric penta-amminecobalt(III) complexes (d) and the free carboxylate anions (e):



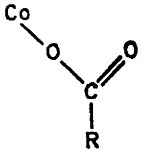
(XV)



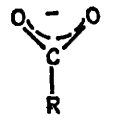
(XVI)



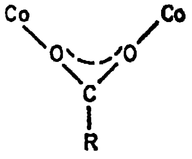
(XVII)



(d)



(e)



(f)

ν_{as}(CO): *ca.* $x + 30$ cm^{-1} x cm^{-1} *ca.* $x - 30$ cm^{-1}

The ν_{as}(CO) stretching frequency of this series of binuclear complexes is observed within the range 1530—1655 cm^{-1}. Since the immediate environment of the carboxylate group of all monocarboxylic acids in the binuclear complexes is essentially the same, the observed scattering is caused by the varying basicity of the bridging carboxylate group. In the Figure the pK_a values for the dissociation constants of the free monocarboxylic acids, taken as a measure of the basicity, are correlated with the ν_{as}(CO) stretching frequencies. (Data for the μ-formato-, μ-acetato-, and substituted μ-acetato-complexes are taken from refs. 2 and 12.)

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[11] J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1178.

[12] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 2364.

TABLE 1

Analytical [a] and i.r. [b] data for μ-carboxylato-complexes

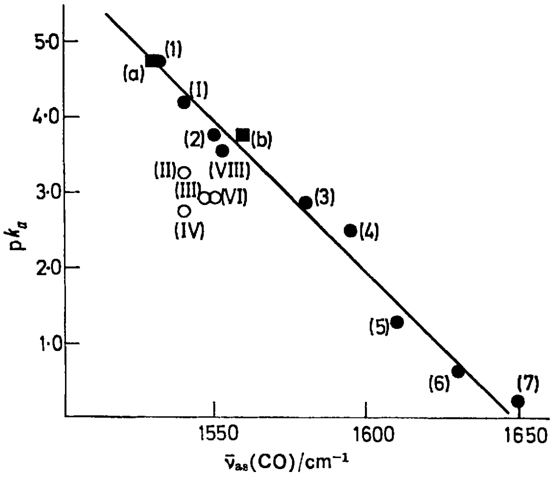
	Compound	Co	NH_3	N	C	H	Cl	Na	$\nu_{as}(CO)$	$\nu_s(CO)$
(I)	$[Co_2(NH_3)_6(OH)_2(C_7H_5O_2)](ClO_4)_3,H_2O$	16·9 (17·0)	14·6 (14·8)		12·3 (12·2)	4·2 (3·9)	15·4 (15·4)		1540	1418
(II)	$[Co_2(NH_3)_6(OH)_2(C_7H_4O_2F)](ClO_4)_3,\frac{1}{2}H_2O$	16·8 (16·8)	14·6 (14·6)		12·2 (12·0)	3·1 (3·5)			1540	1417
(III)	$[Co_2(NH_3)_6(OH)_2(C_7H_4O_2Cl)](ClO_4)_3,H_2O$			12·0 (11·6)	12·0 (11·6)	3·5 (3·5)	19·2 (19·3)		1547	1410
(IV)	$[Co_2(NH_3)_6(OH)_2(C_7H_5O_3)](ClO_4)_3,2\frac{1}{2}H_2O$	15·9 (16·0)	14·0 (13·9)		11·6 (11·5)	4·2 (4·0)	14·5 (14·5)		1540	1398
(V)	$[Co_2(NH_3)_6(OH)_2(C_8H_5O_4)](ClO_4)_3,2H_2O$	15·5 (15·6)	13·5 (13·6)		12·7 (12·8)	3·6 (3·9)	14·3 (14·2)		1550	1418
(VI)	$[Co_2(NH_3)_6(OH)_2(C_8H_5O_3)](ClO_4)_3,2H_2O$			11·3 (11·4)	13·3 (13·0)	3·9 (4·2)	14·2 (14·4)		1536	1405
(VII)	$[Co_2(NH_3)_6(OH)_2(C_8H_5O_3)](ClO_4)_3,2H_2O$			11·7 (11·4)	13·1 (13·0)	4·0 (4·2)	14·1 (14·4)		1546	1417
(VIII)	$[Co_2(NH_3)_6(OH)_2(C_8H_4NO_2)](ClO_4)_3,2H_2O$			13·5 (13·4)	13·3 (13·1)	3·9 (3·8)	14·5 (14·5)		1552	1422
(IX)	$[Co_2(NH_3)_6(OH)_2(C_6H_5NO_2)](ClO_4)_4$	15·2 (15·2)	13·1 (13·2)		9·6 (9·3)	3·3 (3·3)	18·2 (18·3)		1596	1438
(IXa) [c]	$[Co_2(NH_3)_6(OH)_2(C_6H_4NO_2)](ClO_4)_3,NaClO_4,H_2O$			12·3 (12·1)	9·0 (8·9)	3·3 (3·2)	17·1 (17·4)		1560	1410
(X)	$[Co_2(NH_3)_6(OH)_2(C_6H_5NO_2)](ClO_4)_4,H_2O$	14·9 (14·9)	12·8 (12·9)		9·2 (9·1)	3·4 (3·4)	18·0 (17·9)		1580	1432
(Xa) [c]	$[Co_2(NH_3)_6(OH)_2(C_6H_4NO_2)](ClO_4)_3$ [d]								1550	1412
(XI)	$[Co_2(NH_3)_6(OH)_2(C_6H_5NO_2)](ClO_4)_4$	15·2 (15·2)	13·1 (13·2)		9·5 (9·3)	3·4 (3·3)	18·3 (18·3)		1586	1422
(XIa) [c]	$[Co_2(NH_3)_6(OH)_2(C_6H_4NO_2)](ClO_4)_3,2H_2O$			13·7 (13·8)	10·2 (10·2)	4·0 (3·9)	15·1 (15·0)		1548	1421
(XII)	$[Co_2(NH_3)_6(OH)_2(C_3H_3O_4)](ClO_4)_3,\frac{2}{3}NaClO_4,H_2O$	15·6 (15·6)	13·5 (13·5)		4·6 (4·8)	3·5 (3·3)	17·4 (17·2)	2·2 (2·0)	1581	1437
(XIII)	$[Co_2(NH_3)_6(OH)_2(C_4H_3O_4)](ClO_4)_3,NaClO_4,H_2O$	14·6 (14·6)	12·4 (12·7)		6·1 (5·9)	3·3 (3·1)	17·2 (17·5)	2·7 (2·8)	1558	1440
(XIV)	$[Co_6(NH_3)_{18}(OH)_6(C_9H_3O_6)](ClO_4)_9,10H_2O$	17·3 (17·3)	14·8 (15·0)		5·5 (5·3)	4·2 (4·4)	15·5 (15·6)		1550	1390
(XV)	$[Co_2(NH_3)_6(OH)_2(C_4H_3O_4)](ClO_4)_3,1\frac{1}{2}H_2O$	16·9 (17·0)	14·7 (14·7)		7·0 (6·9)	3·8 (3·8)	15·5 (15·3)		1548	1422
(XVI)	$[Co_3(NH_3)_{11}(OH)_2(C_4H_2O_4)](ClO_4)_5,\frac{1}{2}NaClO_4,2H_2O$	16·0 (16·0)	17·0 (16·9)		4·5 (4·3)	3·5 (3·7)	17·6 (17·6)	1·1 (1·0)	1546	1415
(XVII)	$[Co_4(NH_3)_{12}(OH)_4(C_4H_4O_4)](ClO_4)_6,2\frac{1}{4}NaClO_4,4H_2O$	15·1 (15·1)	13·0 (13·0)		3·2 (3·1)	3·5 (3·2)	18·5 (18·7)	3·8 (3·3)	1560	1420

[a] Theoretical figures (%) are given in parentheses. [b] Only the $\nu(CO)$ stretching frequencies of the bridging carboxylate group are given; in cm^{-1}. [c] Deprotonated forms of parent μ-pyridinecarboxylato complexes. [d] Not analytically pure.

TABLE 2

U.v.-visible range spectra. Peak positions λ/nm, and absorption coefficients ($l\ mol^{-1}\ cm^{-1}$) for μ-carboxylato-complexes

	λ	ε	λ	ε	λ	$\varepsilon \times 10^{-3}$	λ	$\varepsilon \times 10^{-3}$
(I)	524	112	370sh	263	297	3·3	265sh	3·3
(II)	524	110	370sh	242	300sh	2·9	277	3·6
(III)	524	113	370sh	266	300sh	3·4	285	4·0
(IV)	524	113	370sh	256	302	7·6		
(V)	524	110	370sh	255	300	3·2	275	4·2
(VI)	524	108	370sh	258	295	4·4	257	24·0
(VII)	524	112	370sh	266	292	6·0	250sh	17·4
(VIII)	524	110	370sh	257	310sh	2·6	295	4·3
(IX)	524	111	370sh	250	300	2·8	265	10·5
(X)	524	109	370sh	250	300	2·7	260	7·9
(XI)	524	108	370sh	253	300sh	2·8	270	5·3
(XII)	524	102	370sh	250	300	2·9		
(XIII)	524	107	370sh	250	300	2·6		
(XIV)	524	326	370sh	710	299	8·5		
(XV)	524	109	370sh	255	297	2·7		
(XVI)	510	191	370sh	258	295	3·2		
(XVII)	524	224	370sh	510	296	6·4		



Plot of $\nu_{as}(CO)$ stretching frequency of the bridging carboxylate groups against pK_a values for the dissociation constants of the free acids; ■, μ-carboxylato-μ-amido-bis[tetra-ammine-cobalt(III)] complexes: (a) μ-acetato, (b) μ-formato (ref. 12)· ●, μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes (ref. 2); (1) μ-acetato, (2) μ-formato, (3) μ-chloroacetato, (4) μ-fluoroacetato, (5) μ-dichloroacetato, (6) μ-trichloroacetato, (7) μ-trifluoroacetato; ○, *ortho*-substituted μ-benzoato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes

It would appear that the $\nu_{as}(CO)$ frequencies and the pK_a values are connected by a reasonably well defined linear relationship with the exception of all *ortho*-substituted benzene carboxylic derivatives. A similar correlation has been reported for the free acids.[13] This can be rationalized if one considers that an *ortho*-substituent may influence the dissociation constant not only by a combination of inductive and resonance effects, which both directly effect the basicity of the oxygen atoms, but also by steric effects or non-bonded interactions. The latter do not effect the basicity of the carboxylate oxygen atoms. Therefore it may be concluded that the pK_a values for *ortho*-substituted benzene carboxylic acids do not reflect a true picture of the basicity of the carboxylic oxygen atoms alone.

The influence of inductive and resonance effects upon the $\nu_{as}(CO)$ stretching frequency is demonstrated in the case of the three isomeric μ-pyridinecarboxylato-complexes. The $\nu_{as}(CO)$ stretching frequencies are considerably shifted to higher wavelengths merely by protonating the basic nitrogen atom.

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[13] C. J. W. Brooks, G. Elington, and J. F. Morman, *J. Chem. Soc.*, 1961, 106.

Ultraviolet–Visible Spectra.—Details of peak positions, $\lambda_{max.}$ (nm), and absorption coefficients (here and elsewhere units l mol^{-1} cm^{-1}, and not per cobalt atom), of complexes are listed in Table 2. As a general feature of all di-μ-hydroxo-bis[triamminecobalt(III)] derivatives with a bridging carboxylate group the spectra are, within experimental error, identical ($\lambda_{max.} = 524$ nm, $\varepsilon = 109$ l mol^{-1} cm^{-1}, $\lambda_{max.}$ *ca.* 370sh nm, ε *ca.* 255 l mol^{-1} cm^{-1}) despite quite different basicities of the carboxylate ligands.[2] The presence of two hydroxo-bridges gives rise to an intense charge transfer band ($\lambda_{max.} = 300$ nm, ε *ca.* $2{\cdot}7 \times 10^3$ l mol^{-1} cm^{-1}) which in the case of aromatic carboxylate ligands is superimposed by bands in the range 300—250 nm.

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 621 and 457 spectrometers in the range 4000—250 cm^{-1} (KBr disc). Visible and u.v. spectra were measured on Unicam SP 800 (recording) and SP 500 (manual) spectrophotometers. The starting material tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate bis-hydrate was prepared by a procedure described in the literature.[9] The organic ligands and other reagents were of AnalaR grade.

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