Mixed Oxidation State Trinuclear Cobalt Complexes with Bridging Sulphito and Schiff-base Ligands. Part 1. Preparation of the Complexes $[Co^{II}(\mu-SO_3)_2(\mu-L)_2Co^{III}_2(ROH)_2]$ (L = Schiff base anion, R = alkyl) and Structure Determination of $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot2Pr^nOH$ †

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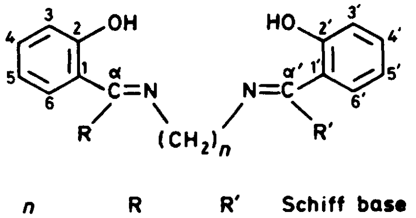
Mixed-valence complexes of the type $[Co^{II}(\mu-SO_3)_2(\mu-L)_2Co^{III}_2(H_2O)_n(ROH)_{2-n}]$ (*n* = 0, 1, or 2; R = Me or Pr^n) have been prepared and characterized, where the deprotonated Schiff-base ligands L^{2-} are either symmetrical, such as *N,N'*-ethylenebis(salicylideneiminate) (salen), *N,N'*-ethylenebis(α-methylsalicylideneiminate) (α,α'-Me_2-salen), propane-1,3-diylbis(salicylideneiminate) (salpd), and propane-1,3-diylbis(α-methylsalicylideneiminate) (α,α'-Me_2-salpd), or unsymmetrical such as propane-1,3-diyl(α-methylsalicylideneiminate)(salicylideneiminate) (α-Me-salpd). An *X*-ray structure determination of $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot2Pr^nOH$ showed the presence of bridging phenolic oxygens and sulphite ions. The mixed-valence state Co^{III} ($S = 0$)–Co^{II} ($S = \frac{3}{2}$)–Co^{III} ($S = 0$) in these trinuclear complexes has been demonstrated by cryomagnetic measurements because the effective magnetic moments (4.40—5.00) at room temperature correspond to the monomeric complex of a cobalt(II) ion in a high-spin state. Down to 77 K, no spin-exchange interaction was observed between the cobalt(III) and cobalt(II) ions. I.r. spectra and thermal gravimetric–differential thermal analysis data have been obtained and discussed with regard to the co-ordination modes of the solvent molecules water, methanol, ethanol, and propan-1-ol.

Many studies have been reported on the preparation and magnetic properties of polynuclear complexes of transition metals, especially in relation to the phenomenon of super-exchange interaction.[1–12] There are two classes of trinuclear cobalt complexes of mixed-spin states; one includes mixed-valence trinuclear complexes of the form Co^{III} ($S = 0$)–Co^{II} ($S = \frac{3}{2}$)–Co^{III} ($S = 0$)[13] and another, mixed-spin trinuclear complexes of the form Co^{II} ($S = \frac{1}{2}$)–Co^{II} ($S = \frac{3}{2}$)–Co^{II} ($S = \frac{1}{2}$).[11] The trinuclear complexes containing deprotonated Schiff-base ligands reported thus far all belong to the latter type.[11] During the examination of the reduction reactions of $[Co^{III}(sal)L]$ (Hsal = salicylaldehyde, H_2L = Schiff base)[14] with sulphur dioxide in alcohol solvents, we found some new trinuclear cobalt complexes of the former type which contained the tetradentate Schiff-base ligands summarized in Figure 1. In the present paper we report the preparation, magnetic properties, and thermal gravimetric analysis of these complexes together with an *X*-ray structure analysis of one example, $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot2Pr^nOH$.

Experimental

Preparation of Schiff-base Ligands.—The symmetrical Schiff-base ligands and their cobalt(II) complexes $[Co^{II}L]$ were prepared by the method of Hariharan and Urbach.[15]



n	R	R'	Schiff base
2	H	H	H_2salen
2	CH_3	CH_3	α,α'-Me_2-H_2salen
3	H	H	H_2salpd
3	CH_3	CH_3	α,α'-Me_2-H_2salpd
3	CH_3	H	α-Me-H_2salpd

Figure 1. Schiff-base ligands H_2L

*Preparation of the Unsymmetrical Schiff-base Propane-*1,3-*diyl*(*α-methylsalicylideneimine*)(*salicylideneimine*) (α-Me-H_2salpd).—To methanol (150 cm^3) containing propane-1,3-diamine (29.7 g, 0.40 mol) was added portionwise acetic acid (24.0 g, 0.40 mol) diluted with the same volume of methanol. The mixture was stirred vigorously for 20 min. Salicylaldehyde (48.9 g, 0.40 mol) was then added and the mixture stirred for 40 min at room temperature, whereupon *o*-hydroxyacetophenone (54.5 g, 0.40 mol) was added, followed by stirring for 10 min. After the addition of triethylamine (40.5 g, 0.40 mol) the reaction mixture was allowed to warm to 50 °C, followed by stirring for a period of 10 min at this temperature. Yellow crystals were obtained by concentrating under reduced pressure below 50 °C until precipitation started and by cooling the concentrate in a refrigerator. Crystallization of the product from methanol gave the pure crystals, m.p. 89.6—90.3 °C. Yield: 56.0 g (47.2%) (Found: C, 73.05; H, 6.90; N, 9.30. Calc. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45%).

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† {1,2;2,3-Di-μ-[propane-1,3-diylbis(α-methylsalicylideneiminato)]-*NN'*(Co^1),*N''N'''*(Co^3),*OO'*($Co^{1,2}$),*O''O'''*($Co^{2,3}$)}-1,3-bis(propan-1-ol)-[1,2;2,3-di-μ-(sulphito)-*S*($Co^{1,3}$),*O*(Co^2)]-1,2,3-tricobalt(III,II,III)–propan-1-ol (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Melting points and ^1H n.m.r. data of Schiff-base ligands

		$\delta(^1H)$/p.p.m.		
Schiff base	M.p./°C	$-CH=N-$	$-CH_2CH_2CH_2-$	$-CH_3$
α-Me-H_2salpd	89.6—90.3	8.33 (s)	3.73 (t, *J* 6), 3.61 (t, *J* 6 Hz)	2.28 (s)
α,α′-Me_2-H_2salpd	52.1—52.8		3.65 (t, *J* 6 Hz)	2.25 (s)
H_2salpd	125.0—125.8	8.32 (s)	3.64 (t, *J* 6 Hz)	

The structure of this unsymmetrical Schiff base was confirmed by comparison with melting points and ^1H n.m.r. data of related symmetrical Schiff bases as shown in Table 1.

Preparation of [Co(α-Me-salpd)]·1.25H_2O.—To a solution containing cobalt(II) nitrate hexahydrate (14.6 g, 0.05 mol) in methanol (150 cm^3) was added triethylamine (10.1 g, 0.05 mol). Nitrogen gas was bubbled through the solution in order to remove air, and then α-Me-H_2salpd (14.8 g, 0.05 mol) was added, followed by stirring and warming over a water-bath at 40 °C for 45 min. The brown product deposited was quickly filtered off on a glass filter in an atmosphere of nitrogen gas and washed with methanol–diethyl ether (1:1) and diethyl ether. The product obtained was dried at 40 °C under reduced pressure for 90 min. Yield: 14.9 g (79.3%) (Found: C, 57.60; H, 5.65; N, 7.30. Calc.: C, 57.55; H, 5.50; N, 7.45%).

Starting Mononuclear Cobalt(III) *Complexes.*—Monomeric cobalt(III) complexes of the type [Co(L′)L] [HL′ = acetylacetone (Hacac), salicylaldehyde (Hsal), or *o*-hydroxyacetophenone (Hoap); H_2L = Schiff base] were used as the starting material for the preparation of the trinuclear cobalt complexes, and were obtained from the cobalt(II) Schiff-base complexes [$Co^{II}L$] by the methods of Podder and Biswas[16] and Fukuhara *et al.*[14]

Trinuclear Complexes.—For the preparation of the trinuclear complexes, an alcoholic solution of the complex [Co(L′)L] or a reaction mixture of [CoL] and the bidentate ligand (HL′) in alcohol was exposed to sulphur dioxide in a closed system.

[Co^{II}(μ-SO_3)$_2$(μ-salen)$_2$$Co^{III}_2$($H_2O$)$_2$]·4$H_2O$ (**1**). A mixture of [Co(sal)(salen)]·H_2O (3.0 g, 0.07 mol) and ethanol (80 cm^3) was exposed with stirring for 48 h to an atmosphere of sulphur dioxide evolved from an aqueous solution of sulphurous acid (6%) at room temperature in a closed system. Reddish brown crystals which separated were filtered off and washed with ethanol, ethanol–diethyl ether (1:1), and then diethyl ether. The complex was dried for 20 min under reduced pressure at *ca.* 50 °C. Yield: 2.4 g (98.6%) (Found: C, 39.25; H, 3.80; Co, 17.65; N, 5.75; S, 6.25. Calc.: C, 39.30; H, 4.10; Co, 18.10; N, 5.75; S, 6.55%).

[Co^{II}(μ-SO_3)$_2$(μ-salen)$_2$$Co^{III}_2$($H_2O$)($Pr^nOH$)]·$Pr^nOH$ (**2**). To propan-1-ol (80 cm^3, 97%) was added [Co(sal)(salen)]·H_2O (3.0 g, 0.007 mol) with stirring to form a green solution. When dry sulphur dioxide was bubbled through the green solution for 30 min at room temperature, reddish brown crystals started to separate. The Erlenmeyer flask containing the reaction mixture was sealed and allowed to stand for 4 d at room temperature. The reddish brown crystals were collected by filtration, washed with propan-1-ol, and air-dried at room temperature. Yield: 1.7 g (73.3%) (Found: C, 45.75; H, 5.15; Co, 17.30; N, 5.25; S, 5.95. Calc.: C, 45.30; H, 4.60; Co, 17.55; N, 5.55; S, 6.35%).

[Co^{II}(μ-SO_3)$_2$(μ-α,α′-Me_2-salen)$_2$$Co^{III}_2$($H_2O$)$_2$]·5.5$H_2O$ (**3**). This complex was obtained, in quantitative yield, when complex (**5**) (see later) was heated at 50 °C for 45 min under reduced pressure and allowed to stand for a few minutes in contact with air (Found: C, 40.55; H, 4.50; Co, 16.50; N, 5.55; S, 5.65. Calc.: C, 40.75; H, 4.85; Co, 16.70; N, 5.30; S, 6.05%).

Table 2. Atomic co-ordinates for [Co^{II}(μ-SO_3)$_2$(μ-α,α′-Me_2-salpd)$_2$-Co^{III}_2(Pr^nOH)$_2$]·2Pr^nOH with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co(1)	0.0	0.0	0.0
Co(2)	0.105 63(6)	0.096 35(8)	0.195 62(9)
S	−0.020 55(12)	0.150 98(15)	0.175 75(17)
O(1)	0.057 4(4)	−0.010 9(4)	0.166 1(5)
O(2)	0.099 3(3)	0.094 7(4)	0.033 3(4)
O(3)	−0.060 5(4)	0.122 2(6)	0.272 6(5)
O(4)	−0.022 9(4)	0.251 3(5)	0.159 7(6)
O(5)	−0.059 6(4)	0.104 6(4)	0.070 4(5)
O(6)	0.222 9(4)	0.031 2(4)	0.211 8(5)
O(7)	0.363 4(5)	0.133 8(7)	0.267 7(7)
N(1)	0.115 0(4)	0.081 2(5)	0.360 2(6)
N(2)	0.159 5(4)	0.215 8(5)	0.196 6(6)
C(1)	0.044 3(5)	−0.087 6(6)	0.238 4(7)
C(2)	0.011 9(6)	−0.170 9(7)	0.192 7(8)
C(3)	−0.007 6(7)	−0.241 2(7)	0.260 6(8)
C(4)	0.009 1(8)	−0.230 7(8)	0.380 7(10)
C(5)	0.044 5(7)	−0.152 7(7)	0.426 5(8)
C(6)	0.065 1(6)	−0.078 4(6)	0.357 2(7)
C(7)	0.105 3(5)	0.003 1(7)	0.411 8(7)
C(8)	0.145 9(7)	0.160 4(7)	0.429 1(8)
C(9)	0.108 3(7)	0.250 3(7)	0.383 5(8)
C(10)	0.148 0(7)	0.287 4(7)	0.285 6(8)
C(11)	0.207 5(5)	0.240 0(6)	0.121 9(7)
C(12)	0.221 5(5)	0.180 3(7)	0.024 8(7)
C(13)	0.293 0(6)	0.190 7(8)	−0.028 0(8)
C(14)	0.303 2(6)	0.144 0(8)	−0.125 2(9)
C(15)	0.244 7(6)	0.084 7(7)	−0.171 7(8)
C(16)	0.174 1(6)	0.069 8(7)	−0.119 7(7)
C(17)	0.164 7(5)	0.114 7(6)	−0.017 5(7)
C(18)	0.138 7(7)	−0.007 0(8)	0.535 8(8)
C(19)	0.247 1(7)	0.333 9(8)	0.126 2(9)
C(20)	0.242 6(6)	−0.046 7(7)	0.142 3(8)
C(21)	0.302 0(7)	−0.115 3(8)	0.211 8(9)
C(22)	0.267 2(9)	−0.161 0(9)	0.308 6(11)
C(23)*	0.398 1(11)	0.127 3(14)	0.379 6(15)
C(24)*	0.363 0(10)	0.058 6(14)	0.452 3(13)
C(25)*	0.391 6(14)	0.043 9(17)	0.570 1(15)

* Atom of Pr^nOH solvent molecule.

[Co^{II}(μ-SO_3)$_2$(μ-α,α′-Me_2-salen)$_2$$Co^{III}_2$($H_2O$)$_2$]·4$H_2O$·EtOH (**4**). This complex was obtained by using ethanol (99.5%) instead of methanol in a manner similar to that described (see later) for the preparation of complex (**5**). Yield for preparation on 0.05 molar scale: 3.4 g (94.7%) (Found: C, 41.90; H, 4.90; Co, 16.00; N, 5.25; S, 6.00. Calc.: C, 42.25; H, 5.05; Co, 16.35; N, 5.20; S, 5.95%).

[Co^{II}(μ-SO_3)$_2$(μ-α,α′-Me_2-salen)$_2$$Co^{III}_2$(MeOH)$_2$]·0.5$H_2O$ (**5**). To methanol (80 cm^3, 99.5%) containing *o*-hydroxyacetophenone (1.34 g, 0.010 mol) was added [Co(α,α′-Me_2-salen)] (3.5 g, 0.010 mol) with stirring for 1 h to form a green solution. When this green solution was exposed with stirring for 48 h to an atmosphere of sulphur dioxide evolved from an aqueous solution of sulphurous acid (6%) at room temperature in a closed system, reddish brown crystals separated. The product obtained was collected by filtration, washed with methanol, methanol–diethyl ether (1:1), and diethyl ether, and dried under reduced pressure for 30 min at room temperature (*ca.* 25 °C). Yield: 3.2 g (94.6%) (Found: C, 45.50; H, 4.80; Co, 17.45; N, 5.60; S, 6.35. Calc.: C, 45.70; H, 4.55; Co, 17.70; N, 5.60; S, 6.40%). This analysis was carried out on a dehydrated sample; according to the thermal analysis results, the original appears to contain 3.5H_2O.

[Co^{II}(μ-SO_3)$_2$(μ-α,α′-Me_2-salen)$_2$$Co^{III}_2$($Pr^nOH$)$_2$]·$H_2O$ (**6**).

To propan-1-ol (80 cm^3, 97%) was added [Co(oap)(α,α'-Me$_2$-salen)] (2.0 g, 0.004 mol) with stirring to form a green solution. When dry sulphur dioxide was bubbled through the green solution for 40 min at room temperature, reddish crystals started to separate. The Erlenmeyer flask containing the reaction mixture was sealed and allowed to stand for 4 d at room temperature. The reddish brown crystals were collected by filtration, washed with propan-1-ol, air-dried, and kept in a desiccator for 1 d. Yield: 2.1 g (48.6%) (Found: C, 47.55; H, 5.10; Co, 16.80; N, 5.40; S, 6.10. Calc.: C, 47.40; H, 5.10; Co, 16.60; N, 5.25; S, 6.05%).

[Co$^{\text{II}}$(μ-SO$_3$)$_2$(μ-salpd)$_2$Co$^{\text{III}}_2$(H$_2$O)(MeOH)]·6H$_2$O (**7**). A mixture of [Co(sal)(salpd)] (2.0 g, 0.0043 mol) and methanol (70 cm^3, 99.5%) was exposed with stirring to an atmosphere of sulphur dioxide evolved from an aqueous solution of sulphurous acid (6%) for 22 h at room temperature in a closed system. The reddish brown crystals were collected on a glass filter, thoroughly washed with methanol, and dried under reduced pressure for 40 min at room temperature. Yield: 1.4 g (94.1%) (Found: C, 39.75; H, 4.05; Co, 17.10; N, 5.30; S, 5.90. Calc.: C, 39.80; H, 4.75; Co, 16.75; N, 5.30; S, 6.05%).

[Co$^{\text{II}}$(μ-SO$_3$)$_2$(μ-α,α'-Me$_2$-salpd)$_2$Co$^{\text{III}}_2$(H$_2$O)(Pr^{n}OH)]·5H$_2$O (**8**). To propan-1-ol (50 cm^3, 97%) was added [Co(oap)(α,α'-Me$_2$-salpd)]·0.5H$_2$O (2.0 g, *ca.* 0.004 mol) with stirring to form a green solution. When dry sulphur dioxide was bubbled through the green solution for *ca.* 2 h, brown crystals separated which were collected by filtration, washed with propan-1-ol, and dried in a desiccator for a few days. Yield: 0.83 g (56.6%) (Found: C, 43.65; H, 5.45; Co, 15.90; N, 5.00; S, 5.20. Calc.: C, 43.80; H, 5.45; Co, 15.75; N, 5.00; S, 5.20%).

A single crystal of the trinuclear complex used for *X*-ray analysis was obtained by exposing the propan-1-ol (99.9%) solution of [Co(oap)(α,α-Me$_2$-salpd)]·0.5H$_2$O to dry sulphur dioxide which was passed over the surface for *ca.* 40 d through a glass tube (5 × 20 mm) in a closed system.

[Co$^{\text{II}}$(μ-SO$_3$)$_2$(μ-α-Me-salpd)$_2$Co$^{\text{III}}_2$(H$_2$O)$_2$]·7H$_2$O (**9**). To a methanol solution (150 cm^3) containing acetylacetone (5.3 g, 0.050 mol) were added triethylamine (5.3 g, 0.052 mol) and [Co(α-Me-salpd)]·1.25H$_2$O (19.0 g, 0.050 mol). The mixture was stirred for 24 h to form a green solution. When the filtrate of the green solution was poured into distilled water (500 cm^3), the complex [Co(acac)(α-Me-salpd)] was obtained as a green crude compound, which was dried under reduced pressure at 50 °C after washing with distilled water. Yield: 25.5 g.

The green crude complex (5.0 g) was dissolved in methanol (50 cm^3), and the filtrate of the solution exposed with stirring to an atmosphere of sulphur dioxide evolved from an aqueous solution of sulphurous acid (6%) for 4 d at room temperature in a closed system. The brown crystals formed were collected by filtration, washed with methanol, and dried in a desiccator for a week. Yield: 1.9 g (Found: C, 39.90; H, 4.60; Co, 16.00; N, 5.35; S, 6.35. Calc.: C, 39.75; H, 5.00; Co, 16.25; N, 5.15; S, 5.90%).

Infrared Spectra.—I.r. spectra of the complexes were measured with a JASCO A302 spectrophotometer on KBr discs.

Thermal Measurements.—Differential thermal analysis (d.t.a.) and thermal gravimetry (t.g.) were carried out on samples heated at a rate of 2.5 °C min^{-1} in air with a Rigaku Denki Thermoflex, standard type, differential thermal analyser. Aluminium crucibles were used, and aluminium oxide was used as reference.

Magnetic Measurements.—Magnetic susceptibilities were measured with a Shimadzu MB-2 Faraday balance in the temperature range from liquid nitrogen to room temperature. The compositions of the complexes in relation to the magnetic study (Table 6) correspond to the state after evacuation because some of their lattice water molecules are easily released *in vacuo*. The apparatus was calibrated using [Cr(NH$_3$)$_6$]Cl$_3$.

Structure Determination of [Co$^{\text{II}}$(μ-SO$_3$)$_2$(μ-α,α'-Me$_2$-salpd)$_2$-Co$^{\text{III}}_2$(Pr^{n}OH)$_2$]·2Pr^{n}OH.—*Crystal data.* C$_{50}$H$_{72}$Co$_3$N$_4$O$_{14}$S$_2$, M = 1 194.2, monoclinic, space group $P2_1/a$, a = 16.495(11),

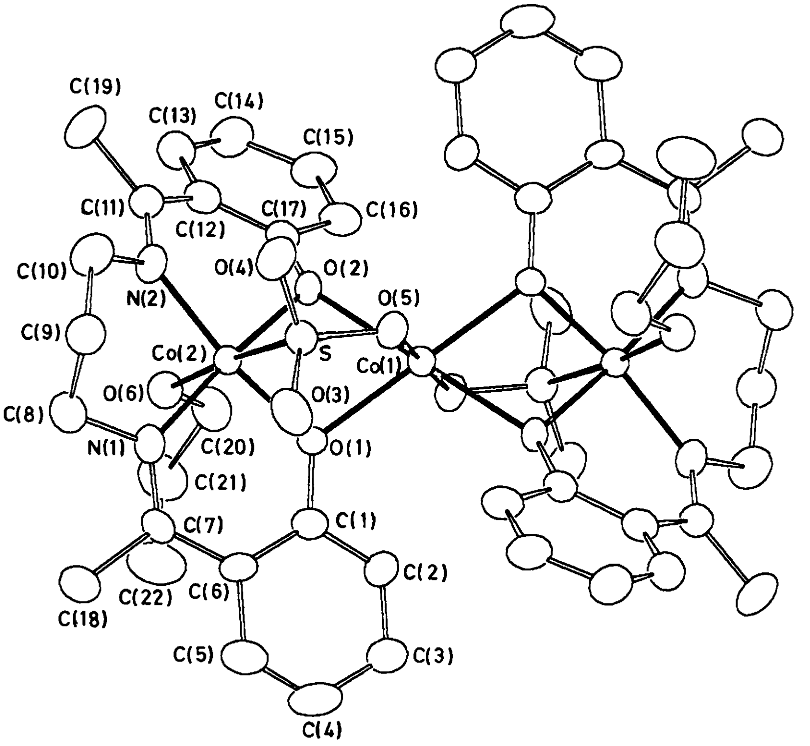

Figure 2. A perspective view of [Co$^{\text{II}}$(μ-SO$_3$)$_2$(μ-α,α'-Me$_2$-salpd)$_2$Co$^{\text{III}}_2$(Pr^{n}OH)$_2$]·2Pr^{n}OH, showing the atomic numbering scheme

$b = 14.441(6)$, $c = 11.841(6)$ Å, $\beta = 96.68(4)°$, $Z = 2$, $D_c = 1.42$ g cm^{-3}, $U = 2\,801.4(25)$ Å^3, μ(Mo-K_α) = 10.5 cm^{-1}, $F(000) = 1\,250$.

Data collection. Since the crystals easily decompose in air, the data crystal was mounted on a glass capillary and placed on a Philips PW1100 automated diffractometer. The PW1100 programs obtained 20 centred reflections, an orientation matrix, and then identified the monoclinic cell. The unit-cell dimensions were refined by least-squares analysis of the θ values of 19 reflections. Intensity data were collected using Mo-K_α radiation ($\lambda = 0.7107$ Å).

During the data collection, three standard reflections were monitored every 3 h to check the stability and orientation of the crystal. No appreciable decay was observed. Data were corrected for Lorentz-polarization effects,[17] but not for absorption. A total of 2 987 reflections [$F_o^2 \geqslant 3\sigma(F_o^2)$] were used for the subsequent structure analysis.

Structure solution and refinement. The structure was solved by the use of MULTAN 78.[18] Refinement was carried out by the block-diagonal least-squares method. The function minimized was $\Sigma w(F_o - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$. Atomic scattering factors for the Co, S, O, N, C, and H atoms were taken from ref. 19, with anomalous dispersion corrections ($\Delta f'$) for Co and S atoms. The final R value was 0.067 [$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.101$]. The hydrogen atoms located at calculated positions (C–H, N–H = 1.0 Å) were included in the final cycles of the refinement, but their parameters were not refined. The hydrogen atoms of the un-co-ordinated propan-1-ol groups and that bonded to O(6) were not identified on the difference Fourier map. All the parameter shifts were less than 0.3σ. The maximum peak in the final difference synthesis was 1.6 e Å^{-3}.

The final atomic co-ordinates are given in Table 2. Figure 2 was drawn using ORTEP.[20] Computations were performed on the FACOM M180II-AD computer at Osaka City University, using a local version of UNICS.[21]

Results and Discussion

Formation of the Sulphito- and Phenol-oxygen-bridged Trinuclear Cobalt Mixed-valence Complexes.—The trinuclear complexes $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}L)_2Co^{III}_2(H_2O)_n(ROH)_{2-n}]$ (n = 0, 1, or 2; R = Pr^n or Me), in which a central cobalt(II) ion is bridged by sulphito ions and phenol oxygens from two $[Co^{III}(SO_3)L]^-$ complex ions, was obtained by the reaction of sulphur dioxide with [Co(L′)L] (L′ = acac, sal, or oap) in an alcoholic solvent at room temperature.

The formation of the trinuclear cobalt complexes, for example, can be represented by equations (1)—(3) (R represents a hydrogen or alkyl group). The sulphur dioxide together with water is thought to act partly as a reductant on the complex [Co(L′)L]; reaction in dehydrated alcohol produces brown products which easily decompose in contact with air. Trinuclear complexes containing the unsymmetrical ligand α-Me-salpd may be expected to form two geometrical isomers, although we could actually only obtain one compound, $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}\alpha\text{-}Me\text{-}salpd)_2Co^{III}_2(H_2O)_2]\cdot7H_2O$ (**9**).

$$\tfrac{1}{2}SO_2 + H_2O + H^+ + [Co(L')L] \longrightarrow Co^{2+} + \tfrac{1}{2}SO_4^{2-} + HL' + H_2L \quad (1)$$

$$2SO_2 + 2H_2O + 2[Co(L')L] + 2ROH \longrightarrow 2[Co(SO_3)L(ROH)]^- + 2HL' + 2H^+ \quad (2)$$

$$Co^{2+} + 2[Co(SO_3)L(ROH)]^- \longrightarrow [Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}L)_2Co^{III}_2(ROH)_2] \quad (3)$$

Table 3. Interatomic distances (Å) for $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}\alpha,\alpha'\text{-}Me_2\text{-}salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot2Pr^nOH$ with estimated standard deviations in parentheses

Co(1)–O(1)	2.103(5)	C(1)–C(6)	1.415(11)
Co(1)–O(2)	2.136(5)	C(2)–C(3)	1.357(13)
Co(1)–O(5)	2.032(6)	C(3)–C(4)	1.425(14)
Co(2)–S	2.213(2)	C(4)–C(5)	1.353(15)
Co(2)–O(1)	1.886(5)	C(5)–C(6)	1.415(13)
Co(2)–O(2)	1.913(5)	C(6)–C(7)	1.464(12)
Co(2)–O(6)	2.140(6)	C(7)–C(18)	1.514(12)
Co(2)–N(1)	1.950(7)	C(8)–C(9)	1.511(13)
Co(2)–N(2)	1.939(7)	C(9)–C(10)	1.497(14)
S–O(3)	1.449(7)	C(11)–C(12)	1.477(12)
S–O(4)	1.461(7)	C(11)–C(19)	1.503(13)
S–O(5)	1.495(5)	C(12)–C(13)	1.404(13)
O(1)–C(1)	1.323(10)	C(12)–C(17)	1.386(11)
O(2)–C(17)	1.326(9)	C(13)–C(14)	1.362(14)
O(6)–C(20)	1.453(11)	C(14)–C(15)	1.358(13)
O(7)–C(23)	1.385(18)	C(15)–C(16)	1.396(13)
N(1)–C(7)	1.302(12)	C(16)–C(17)	1.397(12)
N(1)–C(8)	1.461(11)	C(20)–C(21)	1.559(14)
N(2)–C(10)	1.504(12)	C(21)–C(22)	1.494(17)
N(2)–C(11)	1.302(11)	C(23)–C(24)	1.476(26)
C(1)–C(2)	1.399(12)	C(24)–C(25)	1.436(22)

Short contact < 3.1 Å: O(4)···O(7) ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, z) 2.91(1) Å.

Table 4. Bond angles (°) for $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}\alpha,\alpha'\text{-}Me_2\text{-}salpd)_2\text{-}Co^{III}_2(Pr^nOH)_2]\cdot2Pr^nOH$ with estimated standard deviations in parentheses

O(1)–Co(1)–O(2)	70.5(2)	Co(2)–N(2)–C(11)	123.3(6)
O(1)–Co(1)–O(5)	84.8(2)	C(10)–N(2)–C(11)	115.3(7)
O(2)–Co(1)–O(5)	81.1(2)	O(1)–C(1)–C(2)	117.3(7)
S–Co(2)–O(1)	85.9(2)	O(1)–C(1)–C(6)	122.4(7)
S–Co(2)–O(2)	87.5(2)	C(2)–C(1)–C(6)	120.2(8)
S–Co(2)–O(6)	174.7(2)	C(1)–C(2)–C(3)	121.4(8)
S–Co(2)–N(1)	96.3(2)	C(2)–C(3)–C(4)	118.6(9)
S–Co(2)–N(2)	96.2(2)	C(3)–C(4)–C(5)	120.9(10)
O(1)–Co(2)–O(2)	80.2(2)	C(4)–C(5)–C(6)	121.3(9)
O(1)–Co(2)–O(6)	88.8(2)	C(1)–C(6)–C(5)	117.3(8)
O(1)–Co(2)–N(1)	93.9(3)	C(1)–C(6)–C(7)	124.0(8)
O(1)–Co(2)–N(2)	169.3(3)	C(5)–C(6)–C(7)	118.7(7)
O(2)–Co(2)–O(6)	91.6(2)	N(1)–C(7)–C(6)	124.3(7)
O(2)–Co(2)–N(1)	172.7(3)	N(1)–C(7)–C(18)	119.2(8)
O(2)–Co(2)–N(2)	89.3(3)	C(6)–C(7)–C(18)	116.4(8)
O(6)–Co(2)–N(1)	84.0(2)	N(1)–C(8)–C(9)	111.8(7)
O(6)–Co(2)–N(2)	89.0(2)	C(8)–C(9)–C(10)	112.7(8)
N(1)–Co(2)–N(2)	96.3(3)	N(2)–C(10)–C(9)	113.5(7)
Co(2)–S–O(3)	108.8(3)	N(2)–C(11)–C(12)	122.4(8)
Co(2)–S–O(4)	112.2(3)	N(2)–C(11)–C(19)	121.0(8)
Co(2)–S–O(5)	103.7(2)	C(12)–C(11)–C(19)	116.5(8)
O(3)–S–O(4)	112.3(4)	C(11)–C(12)–C(13)	120.0(8)
O(3)–S–O(5)	109.9(4)	C(11)–C(12)–C(17)	121.3(8)
O(4)–S–O(5)	109.5(4)	C(13)–C(12)–C(17)	118.7(8)
Co(1)–O(1)–Co(2)	100.3(2)	C(12)–C(13)–C(14)	121.1(8)
Co(1)–O(1)–C(1)	128.3(5)	C(13)–C(14)–C(15)	120.2(9)
Co(2)–O(1)–C(1)	129.1(5)	C(14)–C(15)–C(16)	120.5(9)
Co(1)–O(2)–Co(2)	98.3(2)	C(15)–C(16)–C(17)	119.6(8)
Co(1)–O(2)–C(17)	134.6(5)	O(2)–C(17)–C(12)	122.4(7)
Co(2)–O(2)–C(17)	120.1(4)	O(2)–C(17)–C(16)	118.1(7)
Co(1)–O(5)–S	119.6(3)	C(12)–C(17)–C(16)	119.4(8)
Co(2)–O(6)–C(20)	123.3(5)	O(6)–C(20)–C(21)	111.2(7)
Co(2)–N(1)–C(7)	124.5(6)	C(20)–C(21)–C(22)	114.3(9)
Co(2)–N(1)–C(8)	116.9(5)	O(7)–C(23)–C(24)	117.2(14)
C(7)–N(1)–C(8)	118.1(7)	C(23)–C(24)–C(25)	124.0(16)
Co(2)–N(2)–C(10)	121.4(6)		

O(2)–Co(1)–O(1) ($-x$, $-y$, $-z$)	109.5(2)
O(5)–Co(1)–O(1) ($-x$, $-y$, $-z$)	95.2(2)
O(5)–Co(1)–O(2) ($-x$, $-y$, $-z$)	98.9(2)

Structure of $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot 2Pr^nOH$.—A perspective view of the complex is shown in Figure 2. The complex is trimeric and has a crystallographic centre of inversion. The terminal cobalt(III) ions have octahedral co-ordination. The α,α'-Me_2-salpd ligand occupies the four equatorial positions, and the two apical positions are occupied by the sulphur of the bridging SO_3^{2-} anion and an oxygen of propan-1-ol. The bond lengths and angles are given in Tables 3 and 4, respectively. The molecular geometry of the complex is shown in Figure 3. The Co–N and Co–O bond lengths between cobalt and α,α'-Me_2-salpd are somewhat longer than those observed in $[Co^{III}(salen)(bzac)]$ (Hbzac = benzoylacetone).[22] On the other hand, these Co–O bonds are slightly shorter than those found in $[\{Co^{III}Et(salen)\}_2]$,[23] but the Co–N bonds are significantly longer. The Co–S bond length [2.213(2) Å] falls within the range of those so far determined for mononuclear Co^{III} complexes, in which the SO_3^{2-} anion is S-co-ordinated as a unidentate ligand. The Co–O (Pr^nOH) bond length is 2.140(6) Å which is longer than the values observed in $CoCl_2\cdot 2.5C_2H_5OH$,[25] but slightly shorter than Co^{II}–O (MeOH) [2.19(2) Å].[26] The N(1), N(2), O(1), O(2) plane and the Co–S bond make an angle of 83.3°, and the angle between the N(1), N(2), O(1), O(2) plane and Co(2)–O(6) is 86.2°. The N(2)–Co(2)–O(2) angle of 89.3(3)° is slightly larger than that [87.5(2)°] in $[Co^{III}(salphen)(dbm)]$ [H_2salphen = *o*-phenylenebis(salicylideneimine), Hdbm = dibenzoylmethane],[27] in which salphen takes the *cis*-β configuration.

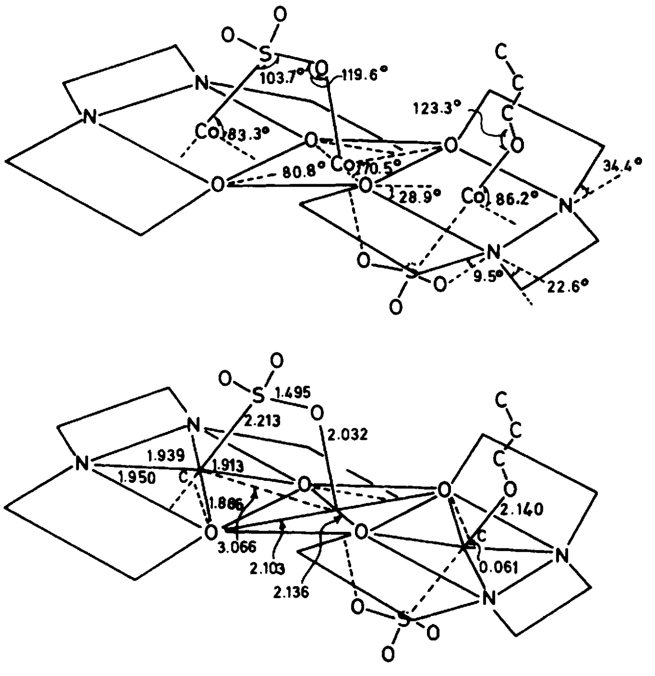

Figure 3. The molecular geometry of $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-salpd)_2Co^{III}_2(Pr^nOH)_2]\cdot 2Pr^nOH$; distances in Å

The central cobalt ion is octahedrally co-ordinated by four bridging oxygens from the α,α'-Me_2-salpd ligands and an oxygen from each of two bridging SO_3^{2-} anions. The Co–O (α,α'-Me_2-salpd) bond lengths are 2.103(5) Å, while the Co(1)–O (SO_3^{2-}) bond is 2.032(6) Å. The O(1)–Co(1)–O(2) ($-x$, $-y$, $-z$) angle of 109.5(2)° is much larger than O(1)–Co(1)–O(2) of 70.5(2)°. The angle between the O(1), O(2), O(1) ($-x$, $-y$, $-z$), O(2) ($-x$, $-y$, $-z$) plane and the Co(1)–O(5) bond is 80.8°.

The bond lengths about the central cobalt are significantly longer than those about the terminal cobalts, indicating that the central atom is divalent while the terminal ones are trivalent. The trimer is, therefore, a Co^{III}–Co^{II}–Co^{III} mixed-valence complex.

T.G.–D.T.A.—T.g. data for the trinuclear complexes obtained in air are given in Table 5. In the cases of compounds (**1**) and (**2**), which have $salen^{2-}$ as the deprotonated Schiff base, elimination of the lattice solvent molecules [$4H_2O$ (**1**) or Pr^nOH (**2**)] occurs at *ca.* 100—150 °C. Even after this step, the octahedral structure around the cobalt ions is considered to be retained up to *ca.* 220 °C, above which a large weight loss occurs, probably due to decomposition.

For complexes (**3**)—(**8**) (having methyl-substituted Schiff bases), the weight loss begins at a comparatively low temperature (even a little above room temperature in some cases). Then, weight losses seem to occur almost successively until the colour changes from brown to green and the total weight loss amounts to the loss of the lattice solvent molecules and a co-ordinated solvent molecule at 120—150 °C (depending on the compound).

Table 5. T.g. data of trinuclear complexes*

Complex	Release temperature of the species and decomposition temperature (°C)
(**1**)	$98 \longleftarrow -4H_2O \longrightarrow 160 \quad \xrightarrow{205}$ decomp.
(**2**)	$98 \longleftarrow -Pr^nOH(l) \longrightarrow 158 \quad \xrightarrow{190}$ decomp.
(**3**)	$28 \leftarrow -H_2O(l) \rightarrow 52 \quad 65 \leftarrow \begin{matrix} -4.5H_2O(l) \\ -H_2O(co.) \end{matrix} \rightarrow 100 \quad \xrightarrow{200}$ decomp.
(**4**)	$30 \longleftarrow -4H_2O(l), -H_2O(co.), -EtOH(l) \longrightarrow 135 \quad \xrightarrow{150}$ decomp.
(**5**)	$28 \longleftarrow -3.5H_2O(l), -MeOH(co.) \rightarrow 90 \quad \xrightarrow{170}$ decomp.
(**6**)	$25 \longleftarrow -H_2O(l) \longrightarrow 68 \longleftarrow -Pr^nOH(co.) \rightarrow 95 \quad \xrightarrow{160}$ decomp.
(**7**)	$25 \longleftarrow -6H_2O(l) \longrightarrow 103 \longleftarrow -MeOH(co.) \rightarrow 128 \longleftarrow -H_2O(l) \longrightarrow 152 \quad \xrightarrow{170}$ decomp.
(**8**)	$24 \longleftarrow -3H_2O(l) \longrightarrow 80 \longleftarrow \begin{matrix} -2H_2O(l) \\ -Pr^nOH(co.) \end{matrix} \longrightarrow 115 \longleftarrow -H_2O(co.) \longrightarrow 176 \longrightarrow$ decomp.
(**9**)	$22 \longleftarrow -6H_2O(l) \longrightarrow 80 \longleftarrow -H_2O(l), -2H_2O(co.) \rightarrow 128 \quad \xrightarrow{156}$ decomp.

* Abbreviations: l = lattice solvent molecule, co. = co-ordinated solvent molecule.

Table 6. Temperature variation (K) of molar magnetic susceptibility (c.g.s. mol^{-1}) and magnetic moment*

$[Co^{II}(\mu-SO_3)_2(\mu-salen)_2Co^{III}_2(H_2O)_2]\cdot 2H_2O$ (**1**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	250.0	275.1	303.1
$10^6\chi_M$	31 528	24 756	20 352	17 598	15 527	14 048	12 603	11 522	10 571	9 564	8 745
$\mu_{eff.}$	4.42	4.45	4.51	4.54	4.55	4.58	4.58	4.59	4.60	4.59	4.60
$[Co^{II}(\mu-SO_3)_2(\mu-salen)_2Co^{III}_2(H_2O)(Pr^nOH)]\cdot Pr^nOH$ (**2**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	250.0	275.1	302.4
$10^6\chi_M$	29 053	23 381	18 861	16 239	14 380	12 910	11 641	10 641	9 794	8 967	8 213
$\mu_{eff.}$	4.42	4.32	4.33	4.36	4.39	4.39	4.40	4.41	4.42	4.44	4.46
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salen)_2Co^{III}_2(H_2O)_2]\cdot 5.5H_2O$ (**3**)											
T	77.4	296.0									
$10^6\chi_M$	34 999	10 073									
$\mu_{eff.}$	4.65	4.88									
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salen)_2Co^{III}_2(H_2O)_2]$ (**4**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	250.0	275.1	288.1
$10^6\chi_M$	34 844	27 669	22 695	19 622	17 373	15 646	13 999	12 853	11 799	10 641	9 690
$\mu_{eff.}$	4.64	4.70	4.76	4.79	4.81	4.83	4.83	4.80	4.85	4.84	4.86
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salen)_2Co^{III}_2(MeOH)_2]$ (**5**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	250.0	275.1	302.2
$10^6\chi_M$	32 202	25 644	20 905	18 065	15 957	14 373	12 933	11 862	10 893	9 921	9 085
$\mu_{eff.}$	4.46	4.52	4.57	4.60	4.61	4.63	4.64	4.66	4.67	4.67	4.69
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salen)_2Co^{III}_2(Pr^nOH)_2]\cdot H_2O$ (**6**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	250.0	275.1	303.2
$10^6\chi_M$	34 597	27 778	22 469	19 185	17 001	15 372	13 770	12 539	11 547	10 434	9 165
$\mu_{eff.}$	4.63	4.71	4.74	4.74	4.76	4.79	4.78	4.79	4.80	4.79	4.71
$[Co^{II}(\mu-SO_3)_2(\mu-salpd)_2Co^{III}_2(H_2O)(MeOH)]\cdot 6H_2O$ (**7**)											
T	77.4	104.5	124.1	141.2	171.0	184.6	211.8	223.9	247.2	278.4	286.8
$10^6\chi_M$	37 101	27 806	23 843	21 134	17 744	16 530	14 627	13 792	12 675	11 188	10 975
$\mu_{eff.}$	4.79	4.82	4.87	4.89	4.93	4.94	4.98	4.97	5.01	4.99	5.02
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(H_2O)(Pr^nOH)]\cdot 4H_2O$ (**8**)											
T	77.4	112.4	124.8	146.2	166.7	186.6	207.9	228.6	258.6	275.1	305.1
$10^6\chi_M$	37 180	26 800	24 452	21 121	18 678	16 964	15 217	13 858	12 387	11 594	10 672
$\mu_{eff.}$	4.80	4.91	4.97	4.99	5.03	5.03	5.03	5.03	5.06	5.05	5.10
$[Co^{II}(\mu-SO_3)_2(\mu-\alpha-Me-salpd)_2Co^{III}_2(H_2O)_2]\cdot 4H_2O$ (**9**)											
T	77.4	99.8	124.8	146.2	166.7	186.6	207.9	228.6	258.6	275.1	305.1
$10^6\chi_M$	37 694	29 640	24 269	20 844	18 408	16 557	14 918	13 576	12 020	11 196	10 150
$\mu_{eff.}$	4.83	4.86	4.92	4.94	4.95	4.97	4.98	4.98	4.99	4.96	4.98

* θ(K) = −9.0 (**1**), −11.2 (**2**), −10.0 (**3**), −10.0 (**4**), −9.2 (**5**), −10.0 (**6**), −12.5 (**7**), −10.5 (**8**), and −7.5 (**9**); c.g.s. = 10 J T^{-2}.

Magnetic Properties.—Magnetic susceptibilities and magnetic moments of the trinuclear complexes in the temperature range 77.4—300 K are given in Table 6. The temperature dependence of the magnetic moments ($\mu_{eff.}$) is very small; the $1/\chi$ *versus* T curves are almost linear. It is proposed that there is no antiferromagnetic interaction among the three cobalt ions because the Weiss constants (θ) for these trinuclear complexes are very small ($|\theta| < 12.5$) as obtained from extrapolation of the straight lines. Their effective magnetic moments lie in the range 4.40—5.00 at room temperature, corresponding to that of the monomeric complex having a cobalt(II) ion in high-spin state.[28] Thus, from a detailed examination of the magnetic data, these trinuclear cobalt complexes are demonstrated to be in the mixed-valence state Co^{III} ($S = 0$)–Co^{II} ($S = \frac{3}{2}$)–Co^{III} ($S = 0$). This conclusion is consistent with that from the *X*-ray analysis of $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(Pr^nOH)_2]$. These trinuclear cobalt complexes may be the first examples of the mixed-valence state Co^{III} ($S = 0$)–Co^{II} ($S = \frac{3}{2}$)–Co^{III} ($S = 0$) containing Schiff-base ligands.

Infrared Spectroscopy.—I.r. bands due to skeletal and S–O (SO_3^{2-}) vibrations in the trinuclear complexes are given in Table 7. Since the bands which are considered to be related to the SO_3^{2-} groups and the phenolic oxygens of the Schiff bases assume very similar features throughout the present series of compounds, all the complexes reported here can be concluded to have the same structural characteristics, *i.e.* trinuclear structures with the SO_3^{2-} and Schiff bases both acting as bridging ligands. Thus the i.r. characteristics, especially those related to the SO_3^{2-} group, are expected to offer important information as to the i.r.-active vibration of the bridging SO_3^{2-} group which has not been elucidated so far. Strong bands at 1 132—1 170, 1 070—1 080, and 630—650 cm^{-1} are assignable to S–O vibrations. It has been reported that the free pyramidal

Table 7. I.r. data (cm^{-1}) of trinuclear cobalt complexes

Compound			$\nu_{S-O}(SO_3^{2-})$			
			$\nu_3(E)$		$\nu_1(A_1)$	$\nu_2(A_1)$
Free SO_3^{2-}	Skeletal[a]		1 010[b]		964[b]	633[b]
(1)	1 545 (1 530)	1 290	1 152	1 080	945	640
(2)	1 545 (1 530)	1 290	1 170	1 080	945	635
(3)	1 550 (1 520)	1 320	1 165	1 080	945	645
(4)	1 545 (1 520)	1 315	1 160	1 075	955	635
(5)	1 543 (1 520)	1 315	1 160	1 070	940	632
(6)	1 545 (1 520)	1 315	1 160	1 070	938	630
(7)	1 555 (1 540)	1 300	1 132	1 075	950	642
(8)	1 540 (1 535)	1 310	1 140	1 070	953	650
(9)	1 547 (1 535)	1 305	1 160	1 080	955	650

[a] Values in parentheses are the skeletal vibration for [Co^{II}L]. [b] Ref. 29.

sulphito ion (SO_3^{2-}) has bands at 1 010 [ν_3 (E)], 961 [ν_1 (A_1)], 633 [ν_2 (A_1)], and 496 [ν_4 (E)] cm^{-1}, and that co-ordination through sulphur shifts these bands to higher frequencies relative to those of the free ion.[29] Doubly degenerate vibrations due to a sulphito group co-ordinating through sulphur are anticipated to split into two bands if the symmetry is lowered by bridging co-ordination through sulphur and oxygen atoms. From these considerations it is possible to assign the bands at 1 132—1 170 and 1 070—1 080 cm^{-1} as stretching vibrations of the bridging group which should appear as doubly degenerate vibrations [ν_3 (E)] in free ions (SO_3^{2-}). I.r. bands at 1 520—1 535 cm^{-1} observed for monomeric complexes [Co^{II}L] have been assigned to skeletal vibrations. This band has been found to shift to higher frequency in polynuclear complexes having bridged phenolic oxygens.[30]

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